



Transport of multi-walled carbon nanotubes stabilized by carboxymethyl cellulose and starch in saturated porous media: Influences of electrolyte, clay and humic acid

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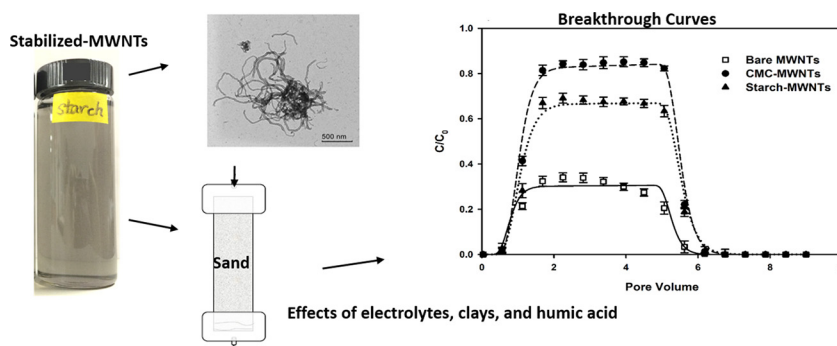
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HIGHLIGHTS

- Polysaccharide stabilizers greatly enhance mobility of MWNTs in porous medium
- CMC- or starch-stabilized MWNTs exhibit high transportability at high electrolytes
- Depending on the clay types, clay may facilitate or inhibit MWNTs transport in sand
- LHA enhances transport of bare MWNTs, but has less effect on stabilized MWNTs
- Classic transport model with filtration well models transport of stabilized MWNTs

GRAPHIC ABSTRACT



ARTICLE INFO

Article history:

Received 31 January 2017

Received in revised form 27 April 2017

Accepted 28 April 2017

Available online xxxx

Editor: D. Barcelo

Keywords:

Nanomaterials

Nanoparticles

Fate and transport

Stabilized nanoparticles

Clay particles

Carbon nanotubes

ABSTRACT

This study investigated the transport behaviors of carboxymethyl cellulose (CMC) and starch stabilized multi-walled carbon nanotubes (MWNTs) through a saturated quartz sand column in the presence of electrolytes, model clays, and natural organic matter (humic acid) through column breakthrough experiments and model simulations. Both stabilizers, CMC and starch, greatly enhanced the breakthrough of MWNTs, with a full breakthrough plateau (C/C_0) ranging from 0.69 to 0.90 at ionic strength from 0.3 to 10 mM. Between the two stabilizers, CMC was more effective in resisting particle deposition, and thus CMC-stabilized MWNTs were more transportable through the medium. While non-stabilized MWNTs were much less transportable and were vulnerable to electrolyte effects (especially Ca^{2+}), the stabilized counterparts were much more resistant to the coagulation effects of electrolytes. The presence of colloidal clay particles showed contrasting effects on the transport of bare and stabilized MWNTs. The full breakthrough C/C_0 of bare MWNTs was suppressed by kaolinite and montmorillonite particles from 0.33 to <0.15 with 5 mg/L clay, indicating that the presence of both clays enhanced the aggregation and deposition of MWNTs. However, kaolinite particles facilitated the transport of stabilized-MWNTs, while montmorillonite weakened the breakthrough of stabilized MWNTs. Humic acid had less effect on the mobility of stabilized-MWNTs than that of bare MWNTs. The advection-dispersion transport model incorporated with the filtration theory was able to simulate the breakthrough curves and quantitatively interpret the particle deposition. The results can facilitate our understanding of fate and transport of stabilized carbon nanotubes in the environment.

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1. Introduction

Carbon nanotubes (CNTs) are one of the most attractive engineered nanomaterials (ENMs) and have been used in numerous commercial products, due to their unique size- and structure-dependent electronic, optical, chemical, physical and mechanical properties (Gohardani et al., 2014; Zhu, 2017). However, the wide spread uses of carbon-based materials (e.g., CNTs, C₆₀, C₇₀) and the lack of proper regulations on their handling and disposal have resulted in their potential release into soil and sediment, and contamination of groundwater, river, and reservoirs (Gottschalk et al., 2009; Nowack and Bucheli, 2007; Troester et al., 2016). In order to determine the potential human and biological exposure to CNTs, an understanding of the transport characteristics of CNTs in the subsurface is therefore needed.

Over the last decade or so, the application of ENMs for groundwater remediation and site clean-up have also attracted growing interest (Bianco et al., 2016; He et al., 2010; Mackenzie et al., 2016). To prevent particle aggregation, CNTs are often modified by stabilizers, thus facilitating delivery of CNTs into the subsurface. Therefore, the study of the transport behaviors of stabilized or modified CNTs in the subsurface environment is also important to facilitate effective applications of engineered CNTs for in situ site remediation.

In the aquatic environment, the transport of ENMs will be affected by water matrix conditions, such as inorganic ions, natural organic matter (NOM), and suspended clay minerals. Researchers have studied effects of humic acid (HA) and ionic strength on the transport of CNTs, and observed that the aggregation and deposition of CNTs on porous media is favored at elevated electrolyte concentrations, and in particular, in the presence of multivalent cations, while HA impedes the aggregation and deposition of the CNTs (Jaisi et al., 2008; Li and Huang, 2010; Zhang et al., 2017; Zhao et al., 2016). In addition, the surface charge heterogeneity on clay mineral surfaces is considered to play an important role in colloid transport (Abdel-Fattah et al., 2013; Cai et al., 2014; Han et al., 2008; Syngouna and Chrysikopoulos, 2016). Colloidal clay particles are natural inorganic colloids and can interact with other colloids. Moreover, clay particles may transport in the subsurface. Consequently, clay particles may promote or inhibit the transport of engineered nanoparticles in porous media depending on the physicochemical property and charge heterogeneity. Cai et al. (2014) studied transport of TiO₂ particles in the presence of bentonite and kaolinite colloids, and found that in NaCl solutions, both types of the clay particles facilitated TiO₂ transport; however, in CaCl₂ solutions, the presence of bentonite facilitated TiO₂ transport while kaolinite inhibited. They attributed the inhibiting effect to the formation of large TiO₂-kaolinite clusters in CaCl₂ solutions. Han et al. (2008) studied the influence of kaolinite and montmorillonite on the stability of surfactants-facilitated multi-walled carbon nanotubes (MWNTs), and found that both clay minerals did not change the stability of MWNTs modified with dodecylbenzenesulfonic acid sodium salt (SDBS), however, both clays greatly diminished the stability of MWNTs suspended by cetyltrimethylammonium bromide (CTAB) due to the competitive adsorption of surfactants on the clay surface.

Modifications of CNTs through surface coatings can increase their stability and deliverability in porous media (Jaisi et al., 2008; Jaisi and Elimelech, 2009; Liang et al., 2016; Liu et al., 2009). For example, acid treatments have been generally practiced to graft acidic functional groups on CNTs surfaces (Mattison et al., 2011; Wang et al., 2012). Surface coatings such as surfactants, polymers (e.g., polyethyleneimine and dendrimers), and NOMs (e.g., HA) can enhance stability of the dispersions (Liang et al., 2016; Shen et al., 2009; Tian et al., 2012).

CMC and starch are modified polysaccharides, which are among the most effective and “green” surface modifiers. Both CMC and starch can effectively stabilize nanoparticles and facilitate transport of nanoparticles in contaminated soil (Gong et al., 2014; Han et al., 2017). Previously, we studied the aggregation behaviors and mechanisms of CMC and starch modified MWNTs in aqueous suspensions based on the

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Liu et al., 2016a). However, information on transport of stabilized-MWNTs in porous media remains lacking. Such transport data are important because the particles in porous media will interact with the media (collectors) and are subject to the filtration effects. As modified CNTs are more stable, they are likely to be more mobile in soil and groundwater, which would result in a greater exposure to aquatic organisms and human than bare or non-stabilized CNTs. For instance, NOM- or surfactant-coated CNTs have been shown to be more transportable than their bare counterparts in porous media under similar experimental conditions (Tian et al., 2012). However, few studies are available on transport of surface modified CNTs by long-chain polymers (e.g., CMC and starch), and no information is available on the effects of natural clay particles on the transport of polysaccharide stabilized MWNTs.

The objectives of this work were to investigate the transport behaviors of CMC- and starch-stabilized MWNTs in a model quartz sand, and to understand the roles of electrolytes, clay particles, and NOM on the retention of MWNTs by examining the breakthrough behaviors under a series of column transport conditions. Model simulation was carried out to interpret the experimental transport data and quantitatively analyze the particle deposition based on the filtration theory. Taken together the experimental and model simulation results, the underlying mechanisms were elucidated.

2. Materials and methods

2.1. Preparation of MWNTs suspensions

MWNTs (carbon content > 99%) were purchased from TCI America (Portland, OR) with diameters of 10–20 nm and lengths of 5–15 μm according to the manufacturer. To prepare non-stabilized (bare) MWNTs suspension, 25 mg of the materials was dispersed into 250 mL deionized water (DI water, 18.2 MΩ·cm, Millipore Inc., MA), and then the mixture was sonicated (70 W, 42 kHz) in a bath sonicator (BRANSONIC 1510R) for 2 h. The effective acoustic power delivered to the suspension was calculated to be 27 W according to the calorimetric method (Section S1 in Supplementary Material (SM)) (Taurozzi et al., 2011). The MWNTs suspension was stored at 4 °C in dark for use. The total organic carbon (TOC) of MWNTs stock solution was determined on a Tekmar Dohrmann Pheonix 8000 UV-Persulfate TOC analyzer (Mason, OH), and all the concentrations of MWNTs in this study were expressed as TOC.

CMC (MW = 90,000 in the sodium form) and a potato starch (hydrolyzed for electrophoresis) were purchased from Acros Organics (Morris Plains, NJ), and a working solution of 1.0 wt% was prepared for each of the stabilizers. CMC and starch suspended MWNTs suspensions were then prepared separately following the same procedure used for preparing the bare MWNTs suspension, except that either the CMC solution or the starch solution was used. The mixture was also sonicated for 2 h. The stabilized MWNTs concentrations were measured as TOC in the mixture subtracting the contributions from CMC or starch.

2.2. Preparation of MWNTs suspensions with electrolytes, clay minerals, and humic acid

Electrolyte solutions (1 and 10 mM of NaCl and 0.1 and 0.5 mM of CaCl₂) were prepared in DI water and stirred to obtain complete dissolution. Kaolinite and montmorillonite are two typical clay minerals in soil (Han et al., 2008). Kaolinites are found in most weathering zones and soil profiles, whereas montmorillonites, which are chemically more complex than kaolinites, are common in the lower parts of weathering profiles (Foley, 1999). Kaolinite (J.T. Baker Avantor Performance Materials, Center Valley, PA) and montmorillonite (Acros Organics, Morris Plains, NJ) were chosen as model clay particles in this study. Separate stock suspensions for each of the clay minerals (100 mg/L each) were prepared by suspending the two types of

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