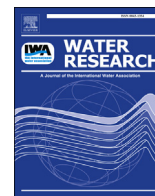




Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Distinguishable co-transport mechanisms of phenanthrene and oxytetracycline with oxidized-multiwalled carbon nanotubes through saturated soil and sediment columns: vehicle and competition effects

Jing Fang^a, Minhao Wang^{a, b}, Bing Shen^{a, b}, Luqing Zhang^b, Daohui Lin^{b, c, *}^a School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, PR China^b Department of Environmental Science, Zhejiang University, Hangzhou 310058, PR China^c Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Zhejiang University, Hangzhou 310058, PR China

ARTICLE INFO

Article history:

Received 7 August 2016

Received in revised form

3 October 2016

Accepted 1 November 2016

Available online xxx

Keywords:

Transport

Retention

Competitive sorption

Nanomaterial

Organic contaminant

ABSTRACT

To date mechanisms underlying co-transport of engineered nanomaterials (ENMs) with contaminants have not been adequately explored, which involve complex interactions among ENMs, contaminants, and soils. This study investigated co-transport behaviors of 3 oxidized-multiwalled carbon nanotubes (o-MWCNTs) with phenanthrene (PHE) and oxytetracycline (OTC) in soil and sediment columns. Sorptions and desorptions of PHE and OTC by the o-MWCNTs were examined to facilitate the discussion of co-transport mechanisms. The results showed that mobilities of PHE and OTC in the columns were significantly enhanced by the presences of o-MWCNTs in the influents; the eluted o-MWCNTs were positively correlated to the eluted total PHE but negatively correlated to the eluted total OTC; the eluted PHE was mainly in the o-MWCNTs-associated form, while it was mainly the dissolved OTC breaking through the columns. It was thus concluded that the o-MWCNTs acted as vehicles facilitating the PHE transport, while besides the vehicle effect the o-MWCNTs also competed for the adsorption sites on soil particles with OTC and thereby enhancing the OTC mobility. These findings provide new insight into the mechanisms regulating co-transport of ENMs and contaminants in porous media.

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1. Introduction

Carbon nanotubes (CNTs) are increasingly utilized in various consumer products due to their outstanding chemical and physical properties (Cha et al., 2013). Multi-walled CNTs (MWCNTs) are produced and used in much greater quantities than single-walled CNTs (Parish, 2011; Keller and Lazareva, 2014). An important environmental implication of CNTs is that they may potentially adsorb co-existing contaminants (Ji et al., 2009; Yang et al., 2006; Pan and Xing, 2008; Cho et al., 2008; Oleszczuk et al., 2009; Wu et al., 2012), and thus influence the mobility of these contaminants in porous media (Hofmann and von der Kammer, 2009; Zhang et al., 2011; Wang et al., 2012a; Fang et al., 2013; Su et al., 2016). The co-transport information is crucial for understanding environmental risks of both CNTs and the contaminants being carried.

Unfortunately, studies on the co-transport of CNTs or other engineered nanomaterials (ENMs) with contaminants are rare. The limited studies show that the presence of ENMs can either promote or restrain the mobility of contaminants in porous media (Hofmann and von der Kammer, 2009; Zhang et al., 2011; Wang et al., 2011, 2012a; Fang et al., 2011; Fang et al., 2013; Su et al., 2016; Chekli et al., 2016). Low concentration of buckminsterfullerene (nC_{60}) could significantly enhance the mobility of 2,2',5,5'-polychlorinated biphenyl (PCB) and phenanthrene (PHE) in sandy soil (Zhang et al., 2011; Wang et al., 2012a). Surfactant suspended MWCNTs were also observed to act as a carrier of PHE and enhance its mobility in silt-sandy-loam soil (Fang et al., 2013). However, it was recently observed that both the addition of MWCNTs in the porous media or in the influent significantly decreased the mobility of sulfonamide antibiotics (SAs) in a river sediment due to the limited transport of MWCNTs and their high adsorption capacity for SAs (Su et al., 2016). It is generally assumed that ENMs with high migration could act as vehicles and promote the mobility of contaminants, while ENMs with low migration would restrain the mobility of contaminants in porous media because of the strong

* Corresponding author. Department of Environmental Science, Zhejiang University, Hangzhou 310058, PR China.

E-mail address: lindaohui@zju.edu.cn (D. Lin).

adsorption effect. However, the co-transport process involves complex interactions among ENMs, contaminants, and soil particles, and much more researches are warranted to understand the law of co-transport in the environment.

Different contaminants can have different ENM-contaminant-soil interactions and co-transport behaviors with ENMs in soils. The tetracyclines (TCs) are a group of broad spectrum antibiotics used as veterinary therapeutics and growth promoters for animals, and are frequently detected in surface water, groundwater, and even drinking water (Aga, 2008). Long term exposures to low-level antibiotics in the environment have raised severe concerns of the potential toxic effect (Boxall et al., 2003; Schmitt et al., 2006). It is thus of great importance to understand the transport and fate of TCs in the environment. TCs are amphoteric and have multiple groups/moieties (phenol, amino, alcohol, and enone) that are charged and/or capable of electronic coupling. Accordingly, the adsorptive interactions of TCs with MWCNTs are different from those of hydrophobic organic compounds like polycyclic aromatic hydrocarbons. The remarkably strong adsorption of tetracycline (TC) and oxytetracycline (OTC) to MWCNTs are attributable to van der Waals forces, π - π electron-donor-acceptor interactions, and cation- π bonding with the graphitic surfaces (Ji et al., 2009; Oleszczuk et al., 2009). However, the PHE adsorption is dominated by the hydrophobic and π - π interactions with the graphitic surfaces of MWCNTs (Yang et al., 2006; Wu et al., 2012). Furthermore, significant desorption hysteresis of OTC from MWCNTs was observed, while there was no desorption hysteresis of PHE from MWCNTs (Oleszczuk et al., 2009; Yang and Xing, 2007). Therefore, the co-transport of TCs with MWCNTs in soils would be different from that of PHE, which merits to be investigated.

MWCNT surfaces are often oxidized during production to increase their stability in water or polar solvents for a wider use (Vaisman et al., 2006). Oxides can also be introduced onto MWCNTs inadvertently during purification with acids or through exposure to UV radiation, reactive radicals, and/or ozone (Wepasnick et al., 2011). Surface oxidation has been shown to dramatically influence environmental behaviors, such as aggregation, transport, and sorption of CNTs (Wu et al., 2012; Smith et al., 2009; Yang et al., 2013; Zhang et al., 2016). Therefore, the overall objective of this study was to (i) investigate co-transport behaviors of PHE and OTC with oxidized-MWCNTs (o-MWCNTs) having different degrees of surface oxidation in a soil and a sediment columns, and (ii) explore the potentially different co-transport mechanisms. Batch adsorption and desorption experiments were also conducted to understand the mechanisms controlling the mobilities of PHE and OTC in the presence of o-MWCNTs. The results are expected to increase our knowledge on environmental risks of ENMs.

2. Materials and methods

2.1. Materials

The pristine MWCNTs with purity higher than 97% and outer diameter and length respectively of about 45 nm and 5 μ m were purchased from Nanotech Port Co., Shenzhen, China. PHE and OTC were purchased from Sigma–Aldrich (St. Louis, MO, USA). Suwannee river natural organic matter (SRNOM) was purchased from the International Humic Substances Society (St. Paul, MN, USA). Elemental composition and molecular structure characteristics of SRNOM are given in Table A1 in the Supporting Information (SI). Soil samples including an agricultural soil (AS) and a lake sediment (LS) were collected from Hangzhou, Zhejiang province, China and were air dried, ground, and sequentially passed through 10 and 30 mesh Tyler sieves. The 10–30 mesh fractions were collected. Detailed characteristics of the two soil samples are described in

Table A2. The contents of fine clay particles, soil organic matter (SOM) and cation exchange capacity (CEC) of LS were much higher than those of AS.

2.2. Preparation and characterization of o-MWCNT suspensions

The o-MWCNTs were prepared and characterized in our previous study (Zhang et al., 2016). Briefly, the pristine MWCNTs were ultrasonically treated with a concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ solution (3/1, v/v) at room temperature for 1, 4, and 8 h, and the resultant o-MWCNTs were accordingly named as o-MWCNTs1, o-MWCNTs4, and o-MWCNTs8, respectively. Twenty mg of the o-MWCNTs were dispersed into 100 mL of ultrapure water via bath sonication (100 W, 40 kHz, 25 °C, 2 h). The supernatants containing stabilized o-MWCNTs after the centrifugation (3500g, 30 min) were collected and used as the stock o-MWCNT suspensions, in which the concentration of o-MWCNTs remained constant within several months. The characteristics of o-MWCNTs and o-MWCNT suspensions are summarized in the SI (Fig. A1 and Table A3). The oxygen content and specific surface area of o-MWCNTs increased from 5.22% to 7.25% and from 53.2 to 76.0 $\text{m}^2 \text{g}^{-1}$, respectively, when the oxidation time increased from 1 to 8 h, and the zeta potential of o-MWCNTs suspensions decreased from -39.8 mV to -51.3 mV.

2.3. Adsorption and desorption experiments

Adsorption kinetics was monitored in a batch experiment (Li et al., 2014; Lin et al., 2012; Lin and Xing, 2008), which was conducted with 1 mg of the o-MWCNTs and 40 mL of 0.2 mg L^{-1} PHE or 8 mL of 10 mg L^{-1} OTC. The background sorptive solution contained 0.01 mol L^{-1} NaCl and 100 mg L^{-1} NaNO_3 (as a biocide) in ultrapure water. The mixtures were shaken on a rotary shaker (150 rpm) for 0.25, 0.5, 1, 3, 6, 12, 24, 48, 72, 96, and 144 h at room temperature. At the selected time points, the mixtures were centrifuged (3500g, 20 min) and the mass of adsorbed PHE or OTC was calculated as the mass decrease in the aqueous phase. The same sorptive system was used to obtain the adsorption-desorption isotherms, with the initial concentrations ranged from 0.01 to 0.80 mg L^{-1} and 0.50–25 mg L^{-1} and the equilibration time fixed at 72 and 96 h for PHE and OTC, respectively. There were two parallel vials for each time point in the kinetic experiments and each concentration point in the isotherm experiments, including blanks that contained no o-MWCNTs. The mass losses of sorbates in the experiments were less than 4%, and thus the adsorbed sorbate concentrations by the o-MWCNTs were directly calculated by the mass balances. The aqueous concentrations of PHE and OTC were determined by a Fluorescence spectrophotometer (Shimadzu, RF-5301PC; excitation: 250 nm, emission: 366 nm) and UV spectrophotometer (Shimadzu, UV-2450; at 360 nm), respectively.

To investigate the effect of SRNOM on the adsorption of PHE and OTC by the o-MWCNTs, 10 mg L^{-1} SRNOM were added in the background sorptive solution and adsorption isotherms were obtained by the same batch equilibration technique. In order to eliminate the influence of SRNOM on the measurement of PHE and OTC, concentrations of PHE and OTC were analyzed by high-performance liquid chromatography (HPLC) with a UV detector using SB-18 column (Agilent, USA) at 247 nm and 360 nm, respectively. The mobile phase was 90:10 methanol:water (v/v) for PHE and 22:78 methanol: phosphoric acid (0.02 M) (v/v) for OTC.

Desorption experiments were conducted immediately following the adsorption procedures. A half of each sorptive solution after the adsorption equilibration and centrifugation (3500g, 20 min) was displaced by the equivalent volume of the sorbate-free background solution. The resultant mixtures were shaken for another 72 and 96 h for PHE and OTC, respectively, and the residual sorbates

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