Effect of Clay Minerals on Transport of Surfactants Dispersed Multi-walled Carbon Nanotubes in Porous Media

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Abstract: Clay minerals can hinder the transport of various contaminants in soil and aquifer, but how clay minerals affect the transport of nanoparticles in aquifers has not been investigated in depth. In this paper, the transport of surfactants dispersed multi-walled carbon nanotubes (MWCNTs) in well-defined quartz sand and mixtures of quartz sand and clay minerals (kaolinite and montmorillonite) with varying ionic strengths was studied. Sodium dodecyl benzenesulfonate (SDBS) and octyl-phenol-ethoxylate (TX100) MWCNT suspensions can migrate through quartz sand easily, but the presence of less than 2% w/w clay minerals in quartz sand can significantly hinder the transport of MWCNT suspensions, especially at high ion strength (0.6 mM CaCl2). The inhibition mechanism of clay minerals for surfactant-dispersed MWCNTs in porous media is the interception of MWCNTs. Kaolinite has stronger inhibition effect for MWCNTs transport than montmorillonite because more kaolinite can be retained in the quartz sand. Adsorption of surfactants by clay minerals does not affect the transport of MWCNTs significantly. This finding is important for the environmental assessment of MWCNT transport risks in soils and aquifers.

Key words: Multi-walled carbon nanotubes, clay mineral, surfactant, colloid transport, porous media

1 Introduction

The extraordinary physical and chemical properties of carbon nanotubes (CNTs) have enabled their novel and broad applications (Lee et al., 2010; De Volder et al., 2013), and this has led to environmental and health concerns (Pasquini et al., 2013). CNTs are often used as aqueous suspensions in various applications (Lu et al., 2014), and are now common surfactants used in industry and households (Matthij et al., 1999; Kume et al., 2008) are often used to disperse CNTs (Moore et al., 2003; Bouchard et al., 2012). Suspended CNTs can be released into the environment from production facilities, wastewater treatment plants, or other sources, and will eventually end up in soil and water either directly or indirectly (Nowack et al., 2007; Limbach et al., 2008). CNTs are one of the least biodegradable manmade materials (Lam et al., 2004), and are toxic to human cells and bacteria (Kang et al., 2007; Pulskamp et al., 2007). CNTs released into water and soils may eventually find their way into groundwater (Wiesner et al., 2006). Furthermore, CNTs act as strong adsorbents for organic pollutants (Pan et al., 2008; Yang et al., 2010; Wu et al., 2012) and may therefore affect the fate and mobility of these chemicals in the natural environment. CNTs facilitated transport (co-transport) of organic pollutants could lead to enhanced migration of contaminants (Hofmann et al., 2009). Therefore, the transport of CNT through natural porous media is of considerable concerns regarding potential risks to human health and organisms (Mattison et al., 2011; Petersen et al., 2011; Khan et al., 2013).

Recently, CNT transport in sand (Jaisi et al., 2008; Liu et al., 2009; Mattison et al., 2011; Tian et al., 2011;
Bouchard et al., 2012; Chowdhury et al., 2012; Tian et al., 2012a; Tian et al., 2012b; Tian et al., 2012c; Wang et al., 2012; Kasel et al., 2013a; Khan et al., 2013; O’Carroll et al., 2013) and soil (Jaisi et al., 2009; Kasel et al., 2013b; Lu et al., 2014) columns was investigated extensively, and CNT transport in undisturbed soil was also investigated recently (Kasel et al., 2013b). The transport of CNTs has been found to be sensitive to a variety of factors including the properties of CNTs, such as surface coating or functionalization (Bouchard et al., 2012; Chowdhury et al., 2012; Lu et al., 2013), diameter (O’Carroll et al., 2013), length (Jaisi et al., 2008; Wang et al., 2012) and concentration (Kasel et al., 2013a); the properties of pore water, such as solution chemistry (Jaisi et al., 2008; Jaisi and Elimelech, 2009; Bouchard et al., 2012; Tian et al., 2012a; Khan et al., 2013; Lu et al., 2014), velocity (Leconoanet et al., 2004; Liu et al., 2009), and volumetric content (Tian et al., 2011; Kasel et al., 2013b); and properties of the porous media, such as grain size (Jaisi and Elimelech, 2009; Mattison et al., 2011; Kasel et al., 2013a), surface property (Tian et al., 2012b) and composition (Liu et al., 2009; Kasel et al., 2013b; Khan et al., 2013).

As a common component of natural soil (Valsangkar, 2011; Sun et al., 2014), clay minerals (Itami et al., 2005; Egemose et al., 2009) may either hinder the migration of nanoparticles in soil by blocking the pores (Dikinya et al., 2008), increasing the attachment of nanoparticles to porous media by its surface charge heterogeneity (Schroth et al., 1996; Kim et al., 2012), or clay minerals may enhance the transport of nanoparticles by acting as an anionic support material (Schrick et al., 2004; Cai et al., 2014). Soil samples with significant clay contents used in previous studies (Jaisi and Elimelech, 2009; Kasel et al., 2013b) suggest that clay content might be a predominant factor hindering the transport of CNTs through these soils, but the effects of clay minerals on CNT transport in porous media were not investigated in detail.

As the first attempt to address this issue, this paper investigates two types of widely used surfactants, an anion surfactant, dodecylbenzenesulfonic acid, sodium salt (SDBS), and a nonionic surfactant, octyl-phenol-ethoxylate (TX100), both used to disperse MWCNTs. The MWCNT suspensions transport through columns filled with quartz sand and clay minerals (kaolinite or montmorillonite)-quartz sand mixtures for different ionic strengths. The concentrations of MWCNTs and surfactants in the effluents, and the distribution of clay minerals and attached MWCNTs in the columns were characterized to investigate the effects of clay minerals on the transport of MWCNTs. Possible mechanisms by which clay particles (both montmorillonite and kaolinite) affected the transport behaviors of MWCNTs were proposed and evaluated. The results of this study will be essential for environmental risk assessments of MWCNTs.

### 2 Material and Methods

#### 2.1 Preparation and characterization of MWCNT suspensions

MWCNTs with an average outer diameter of 28 nm and length of 1–2 μm were purchased from Shenzhen Nanotech Co., China. They were synthesized from a CH4/H2 mixture at 700°C using a chemical vapor deposition method, and purified by a mixed HNO3 and H2SO4 solution to remove the catalyst and amorphous carbon. Their surface area was 86 m2/g determined using a multipoint Brunauer-Emmett-Teller (BET) method (Lin et al., 2008). SDBS and TX100 (Purity >98%) were purchased from Aladdin Reagent Co. (Shanghai, China).

For the preparation of MWCNT suspensions, 10 mg MWCNTs were added into 200 mL 40 mg/L surfactant solutions, sonicated (KBS-150, Kunshan Ultrasonic Instrument Co., China) at 150 W and 50 percent time interval for 1 h. After sonication, samples were centrifuged (TGL-16M, Xiangyi Centrifuge Co., China) at 7000 rpm for 70 min. The upper 75–80% of supernatants were then carefully decanted and stored as stock suspensions. These suspensions were labeled as SDBS-MWCNT and TX100-MWCNT, respectively. The suspended MWCNT concentrations were measured using a UV-visible spectrophotometer (UV-Vis, Shimadsu UV2500) at 300 nm. This method has been shown to be reliable in previous studies (Hyung et al., 2007). The suspended MWCNTs in the stock solutions were 22.0 and 16.3 mg/L for SDBS-MWCNT and TX100-MWCNT, respectively. Transmission electron microscopy (TEM, H-7500, Hitachi, Japan) observation showed that the suspended MWCNTs were present primarily as individual tubes (Fig. 1) and were stable for more than 6 months. MWCNT hydrodynamic diameters (Dh) and zeta potentials in aqueous suspensions were measured using dynamic light scattering with a ZetaSizer Nano ZS90 (Malvern Instruments, Worcestershire, UK). Zeta potentials of the suspensions were calculated by the electrophoretic mobility of charged particles using Smoluchowski equation (Fig. 2). Key properties of the MWCNT suspensions were listed in Table 1.

#### 2.2 Porous media

Quartz sand was purchased from Tianjin Nankai Chemical Co. (China). The quartz sand was sieved and the particles between 0.105 mm and 0.5 mm (average diameter 276 μm) were collected and treated for 2 h with...
65% nitric acid to remove metal oxides, then with 10% peroxide to eliminate organic material (Mattison et al., 2011). The quartz sand was repeatedly rinsed with de-ionized water following both acid and peroxide treatments until a neutral pH was achieved in the rinsing water.

Montmorillonite and kaolinite with mean particle sizes of about 2 μm were purchased from Fluka Co. (Germany). They were washed with de-ionized water until the conductivity of 1% W/W solutions was <4 μS/cm, freeze dried, and ground for subsequent use. The zeta potentials of montmorillonite and kaolinite were also measured by ZetaSizer Nano ZS90 (Malvern Instruments, Worcestershire, UK) (Fig. 3).

Clay mineral (kaolinite or montmorillonite)-quartz sand mixtures were made by adding 2.0 g clay minerals to 100 g quartz sand, and mixing in a mortar gently to obtain a uniform mixture. Before filling into columns, the mixtures were rinsed with de-ionized water to prevent separation of clay minerals and quartz sand, and labeled as Kaoli-Quartz and Mont-Quartz, respectively, or Clay-Quartz for both of them.

### 2.3 MWCNTs transport in porous media

The MWCNT transport experiments were conducted in glass columns with an inner diameter of 2.4 cm and a...
length of 12 cm. Cleaned quartz sand, Kaoli-Quartz and Mont-Quartz were used as porous media. All columns were wet-packed in 1.0 cm segments while the columns were vibrated to minimize layering or air entrapment, and each segment was tapped prior to adding subsequent segments. The height of quartz sand was kept constant at 10 cm in all column experiments. The porosities of all the columns were calculated by the weight differences of water saturated columns and dry columns and was listed in Table 2. In the transport experiments, the packed columns were first equilibrated with 10 pore volumes of 0.6 mM CaCl₂ solution or de-ionized water using a peristaltic pump (model HL-2B, Shanghai Huxi Analysis Instrument Co. China), until no absorbance at 220–800 nm wavelength in UV/visible spectrophotometer could be detected in the effluent, then 5.0–6.0 porous volume of MWCNT suspensions with or without 0.6 mM CaCl₂ were fed continuously to the bottoms of columns followed by 2 pore volumes of de-ionized water with or without 0.6 mM CaCl₂. All column experiments were performed at a pore water velocity of 6.63±0.6 m/d. This speed is to represent fluid velocities in coarse aquifer sediments, forced-gradient conditions, or engineered filtration systems (Harter et al., 1999).

The effluent was collected manually at 5 min intervals and the MWCNT concentrations were measured by UV-visible spectrophotometer (Shimadzu 2500, Japan) at 300 nm. Concentrations of SDBS and TX100 were also measured by UV-vis at wavelength of 223 nm after the effluents were centrifuged and filtrated by 0.2 μm Teflon filters.

After the transport experiments, the quartz sand in each column was pushed out by a plastic pestle and each 1 cm section was collected in different vials. The deposition of MWCNTs on the surface of quartz sand was observed by scanning electron microscope (SEM, Hitachi S-4800, Japan). The deposited clay minerals in each quartz sand section was washed off by de-ionized water in a 140 mesh sieve, dried and weighed. The MWCNTs on quartz sand and clay minerals were separated by soaking the quartz sand and clay minerals in 5 ml 490 mg/L SDBS solution, sonicated by a ultrasonic cleaner (Ningbo Xinzhi Co, China) for 10 minutes, centrifuged at 4000 rpm for 10 minutes, and the supernatant was collected for subsequent measurement. This process was repeated 3 times and all the supernatant was mixed and the MWCNT concentrations were measured by UV-vis at 300 nm.

3 Results and Discussion

3.1 Characterization of MWCNTs

Most of the surfactant dispersed MWCNTs are single tubes in suspension, and their diameter (20–40 nm) and length (1–2 μm) are consistent with that stated by the supplier (Fig. 1). The pristine or sonicated MWCNTs without surfactants only have slightly negative surface charge in de-ionized water (Han et al. 2008), but the presence of surfactants altered the MWCNT zeta potentials significantly. The Point of Zero Charge (PZCs) of water and surfactant suspended MWCNTs in the presence of 0.6 mM CaCl₂ were 3.5 (TX100-MWCNTs), and <2 (SDBS-MWCNTs) (Fig. 2). The presence of 0.6 mM CaCl₂ depressed the surface charge of TX100-MWCNTs and SDBS-MWCNTs drastically. For instance, the zeta potential of TX100-MWCNTs changed from about −40 mV to −20 mV at pH 7, and that of SDBS-MWCNTs changed from −58 mV to −21 mV. This decrease of surface charge has a strong influence on the transport ability of MWCNTs in porous media, which will be discussed later.

3.2 Effects of clay minerals on the transport of MWCNTs

3.2.1 In de-ionized water

In de-ionized water, both SDBS-MWCNT and TX100-MWCNT can migrate through quartz sand easily; the relative effluent concentration can reach over 0.95 after 2 pore volumes (Fig. 4). But when montmorillonite or kaolinite are present in the quartz sand, the effluent concentration was significantly decreased. Kaolinite can
decrease the effluent MWCNT concentration more than montmorillonite for both SDBS-MWCNT and TX100-MWCNT.

3.2.2 In 0.6 mM CaCl₂ solution

With the presence of 0.6 mM CaCl₂, the maximum effluent concentrations of SDBS-MWCNT and TX100-MWCNT in quartz sand were only slightly less than that without 0.6 mM CaCl₂, but they can hardly migrate through Mont-Quartz and Kaoli-Quartz (Fig. 5). The effects of montmorillonite and kaolinite on the retention of MWCNT in the columns were drastically enhanced by the presence of 0.6 mM CaCl₂.

3.3 Clay minerals effects on the transport of surfactants

The BTCs of SDBS and TX100 in quartz sand and clay-quartz are shown in Fig. 6 (in de-ionized water) and Fig. 7 (in 0.6 mM CaCl₂). The transport of SDBS and TX100 was also inhibited by the presence of clay minerals in distinct ways.

In the absence of CaCl₂, almost all SDBS could migrate through both quartz sand and Mont-Quartz, but slightly delayed in Kaoli-Quartz (Fig. 6a), TX100 could migrate through quartz sand but was drastically inhibited in the Kaoli-Quartz and Mont-Quartz columns. This differences of BTCs of SDBS and TX100 may be attributed to the different adsorption of SDBS and TX100 on montmorillonite and kaolinite.

In the presence of CaCl₂, most SDBS was adsorbed when transported through Kaoli-Quartz, while only a small fraction of SDBS was adsorbed when transported through Mont-Quartz. This difference may result from the precipitation mechanisms. DBS can be precipitated by Ca²⁺ (Yang et al., 2007). Since montmorillonite can deplete Ca²⁺ in solution by cation exchange adsorption, it may prevent the precipitation of Ca(DBS)₂. The transport of TX100 in Kaoli-Quartz did not show distinct changes with the presence of CaCl₂, because TX100 is a non-ionic surfactant.

By comparing Fig. 4 and Fig. 6, we discovered the strong inhibition of MWCNT transport by kaolinite was not achieved by the depletion of surfactants in MWCNT suspensions. By comparing Fig. 5 and Fig. 7, it was found that the total removal of MWCNTs from the effluent by Mont-Quartz or Kaoli-Quartz was also not achieved by
surfactant depletion. In general, due to the different filtration mechanism, surfactants showed different transport behaviors as compared to MWCNTs, and the adsorption of surfactants by clay minerals did not affect the transport of MWCNTs significantly, this will be discussed in the following sections in detail.

3.4 Mechanisms by which clay minerals affect the transport of MWCNTs

According to the deep bed filtration theory (Yao et al., 1971), there are 3 filtration mechanisms for colloid particles in porous media: interception, sedimentation and diffusion.

3.4.1 Interception

Interception happens if a suspended particle following a streamline of the flow may come in contact with the collector (porous media particles) by virtue of its own size (Yao et al., 1971). The lengths of MWCNTs used are 1–2 μm in this study. MWCNTs can easily flow through the pore throats in between quartz sand (average particle size 276 μm), but when montmorillonite or kaolinite with particle sizes of about 2 μm was mixed in the sand, MWCNTs could be easily intercepted by clay mineral particles. This was confirmed by the SEM topography images (Fig. 8). Similarly, the pore throat blocking effects of kaolinite and montmorillonite in porous media have already observed in previous studies (Khilar et al., 1984; Mays et al., 2007).

The differences of MWCNT transport abilities in Clay-Quartz with or without 0.6 mM CaCl₂ can be explained by the drastic decrease of zeta potentials of both clay minerals and both MWCNTs with the presence of 0.6 mM CaCl₂ (Fig. 2 and Fig. 3). This decrease of zeta potential reduced the surface repulsion between MWCNTs and clay minerals, and enhanced the interception efficiency (Jaisi et al., 2008).

3.4.2 Sedimentation and diffusion

Sedimentation refers to the change of trajectory which is due to the influence of the gravitational force. Diffusion refers to the Brownian movement of the particle. Because the addition of clay minerals neither changed the density of MWCNTs nor changed their particle sizes or the flow field, both clay minerals cannot enhance the filtration of MWCNTs by sedimentation and diffusion.
3.4.3 Clay minerals effects on the collision efficiency

When MWCNT particles contact with the porous media, only a portion of them successfully adhere to the porous media. Collision efficiency is the ratio of the colloid particles successfully adhered to the filter media divided by the number of collisions which occur between suspended particles and the porous media (Yao et al., 1971). Collision efficiency mainly reflects the chemistry of the system.

The impact of clay minerals on the collision efficiency of MWCNT could be twofold: (i) competitive adsorption of the surfactant with MWCNTs, and thus reducing the repulsive forces between MWCNTs and porous media; (ii) adsorb the surfactant, and retain the surfactant dispersed MWCNTs by bridging effect of the surfactant. In the following we discuss these two mechanisms in detail.

3.4.3.1 Adsorption of surfactant.

The amount of MWCNTs or single-walled carbon nanotubes suspended increases with the surfactant concentration in the suspension (Wang et al., 2004; Han et al., 2008). The destabilization of colloids in filtration is similar to destabilization in coagulation (Yao et al., 1971), thus higher effluent concentration of surfactants should accompanied by higher MWCNT concentration. In all the experiments, the effluent concentrations of SDBS-MWCNT and TX100-MWCNT in Mont-Quartz were larger than in Kaoli-Quartz, but the concentrations of SDBS in effluent of Mont-Quartz are about the same or only slightly higher (Fig. 6a and Fig. 7a) than that in Kaoli-Quartz, and the concentration of TX100 in Mont-Quartz are much lower than that in Kaoli-Quartz, this is contrary to the aforementioned mechanism. This implies the adsorption of surfactants by clay minerals does not affect the collision efficiency significantly.

3.4.3.2 Retain MWCNTs by bridging effect of the surfactant

Our previous studies have shown that cationic surfactant suspended MWCNTs can adhere to the surface of kaolinite, but SDBS-MWCNT or TX100-MWCNT do not adhere to the surface of kaolinite or montmorillonite particles (Han et al. 2008), so they are not likely to be retained by the bridging effect.

3.5 The relationship of clay mineral content and the concentration of attached MWCNTs.

Clay minerals in all the columns is evenly distributed,
while all the concentration of attached MWCNTs has a decreasing tendency from the bottom (the inlet) to the top of all the columns (Fig. 9). The evenly distributed clay minerals indicate the mixed clay minerals were not remobilized significantly during the MWCNT transport test. The decreasing tendency from the inlet to the outlet is in accordance with colloid filtration theory and was confirmed by a previous study (Kasel et al., 2013a). No significant relationship was found between the concentration of attached MWCNTs and the content of clay minerals.

3.6 Effect of clay type and total content on MWCNTs retention

Since both clay minerals mainly affect the transport of MWCNTs by interception, the different transport abilities of both MWCNT suspensions in Clay-Quartz should mainly result from the different interception abilities of Kaoli-Quartz and Mont-Quartz. The particle sizes of kaolinite and montmorillonite are about the same. Thus the main difference of kaolinite and montmorillonite in retaining the MWCNTs may come from their amounts in the columns, since only 488–548 mg of montmorillonite was present in the studied columns, while 924–1066 mg of kaolinite was kept in the columns studied (Table 1).

4 Conclusions

The presence of clay minerals in porous media can significantly affect the transport of MWCNTs by interception due to the small particle sizes and favorable surface chemistry of clay minerals. The interception effects of clay minerals are in proportion to their contents in the porous media. The surface charges of clay minerals can also influence MWCNT transport. In 0.6 mM CaCl$_2$ solution, the interception effects of clay minerals were drastically enhanced because the surface potential of both clay minerals and MWCNTs were decreased. The adsorption of surfactants by clay minerals did not affect the transport of MWCNTs. As a common constituent of natural soils and aquifers, clay minerals can significantly hinder the flow through of surfactant suspended MWCNTs, which is an important finding for the environmental assessment of MWCNT transport risks in soils and aquifers.

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References


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