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Deposition and transport of functionalized carbon nanotubes in water-saturated sand columns

Yuan Tian¹, Bin Gao^{1}, Yu Wang¹, Verónica L. Morales², Rafael Muñoz-Carpena¹,
Qingguo Huang³, and Liuyan Yang⁴*

*1. Department of Agricultural and Biological Engineering, University of Florida,
Gainesville, FL 32611-0570*

2. SIMBIOS Centre, University of Abertay, Dundee, DDI U.K.

3. Department of Crop and Soil Sciences, University of Georgia, Griffin, GA 30223

*4. State Key Laboratory of Pollution Control and Resource Reuse, School of the
Environment, Nanjing University, Nanjing 210093, China*

* Corresponding Author, Phone: (352) 392-1864 ext. 285, email: bg55@ufl.edu

Abstract

Knowledge of the fate and transport of functionalized carbon nanotubes (CNTs) in porous media is crucial to understand their environmental impacts. In this study, laboratory column and modeling experiments were conducted to mechanistically compare the retention and transport of two types of functionalized CNTs (i.e., single-walled nanotubes and multi-walled nanotubes) in acid-cleaned, baked, and natural sand under unfavorable conditions. The CNTs were highly mobile in the acid-cleaned sand columns but showed little transport in the both natural and baked sand columns. In addition, the retention of the CNTs in the both baked and natural sand was strong and almost irreversible even after reverse, high-velocity, or surfactant flow flushing. Both experimental and modeling results showed that pH is one of the factors dominating CNT retention and transport in natural and baked sand. Retention of the functionalized CNTs in the natural and baked sand columns reduced dramatically when the system pH increased. Our results suggest that the retention and transport of the functionalized CNTs in natural sand porous media were mainly controlled by strong surface deposition through the electrostatic and/or hydrogen-bonding attractions between surface function groups of the CNTs and metal oxyhydroxide impurities on the sand surfaces.

Keywords: Transport, mobilization, surface charge heterogeneity, SWNT, MWNT

1. Introduction

Advances in nanotechnology make it possible to develop many new and exciting materials to benefit society. Large-scale production of engineered nanomaterials (ENMs), however, will inevitably result in their release into the environment and compromise the ecosystem and public health [1-5]. Carbon nanotubes (CNTs) are one of the most commonly used ENMs, which have attracted much research attention recently. CNTs can be categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). SWNTs are one-layered graphitic cylinders having diameters on the order of a few nanometers. MWNTs comprise of 2 to 30 concentric cylinders having outer diameters often between 10-50 nm. Due to their special mechanical, electrical, optical, and thermal properties, CNTs have been widely applied in a broad range of commercial and industrial applications [6]. Concerns about the environmental impact and risk assessment of CNTs have surfaced with the discovery of broader applications. Many studies have shown toxic effects of CNTs to various aquatic and mammalian organisms [7-10]. It is therefore important to improve current understanding of the transport, behavior, and fate of CNTs in the environment.

In many applications, CNT surfaces are often functionally engineered in order to increase their stability and optimize their performance [11]. Because functionalized CNTs are more stable in solution, when released into soils and groundwater, they are likely to experience higher mobility, which increases the risk for fresh water contamination and aquatic organism toxicity. In addition, several studies have also demonstrated that functionalized CNTs have high affinity for soil and groundwater contaminants, including heavy metals and recalcitrant organic pollutants [12-15].

Transport of CNTs in soils is consequently suspected to affect the fate of other contaminants thought to have very limited mobility in soils. Such, facilitated transport of reactive contaminants in soils by colloids and nanoparticles is a well-known phenomenon that has been observed in several circumstances [16-18].

Despite the environmental importance, only a limited amount of studies have been conducted to examine the transport of CNTs in porous media [1, 19-25]. In most of these studies, laboratory columns packed with acid-cleaned sand or glass beads (i.e., clean columns) are used as model porous media to explore the governing mechanisms of CNT transport. Results obtained from the model systems suggested that surface properties of the CNTs play an important role in controlling their retention and transport in porous media. It was found that CNTs coated with natural organic matter (NOM), a natural and ubiquitous substance in terrestrial and aquatic environments, have much higher mobility in saturated porous media than uncoated CNTs [21]. Recent studies have also shown that CNTs coated with anionic surfactant are highly mobile in both saturated and unsaturated porous media [1, 22, 23]. The transport of functionalized CNTs in model porous media has also been investigated and showed only slightly lower transport compared to NOM- or surfactant-coated CNTs under similar experimental conditions [19, 20]. In natural sandy soils, however, the mobility of functionalized CNTs reduced substantially [26]; suggesting that surface properties of the porous media are also important to CNT transport. Taken together, evidence up to now strongly suggests that surface deposition (interaction) is an important mechanism of CNT retention in porous media, but a mechanistic understanding of this effect is lacking.

Physical straining has been suggested as an important process driving retention and transport of CNTs in saturated porous media; particularly under favorable conditions [19, 26]. Straining refers to the trapping of particles, such as colloids or nanoparticles, in pores that are too small to allow their passage. This process is believed to occur when the ratio of the particle and collector grain diameters falls below a critical value [27-29]. Under unfavorable conditions, however, there is a debate on whether straining should be considered as one of the governing mechanisms of particle retention in porous media [30, 31]. Previous studies of CNT transport in saturated porous media also had split opinions on the importance of the straining mechanism. On one hand, some studies suggested that physical straining plays an important role in retention and transport of functionalized CNTs, particularly CNTs with a large aspect ratio and their aggregates, in both model and natural porous media [19, 26]. On the other hand, straining was considered insignificant in several studies of the retention and transport of humic acid coated, surfactant coated, and functionalized CNTs in model porous media [20-23]. Additional investigations are thus needed to examine the governing mechanisms of CNT transport in porous media.

The overarching goal of this study was to determine the governing retention mechanisms of two types of functionalized CNTs (SWNTs and MWNTs) in natural porous media. We hypothesized that the retention of functionalized CNTs in natural sand are mainly controlled by surface deposition through interactions between the functional groups of the CNTs and surface impurities (metal oxyhydroxides) of the natural sand. To test this hypothesis, retention and transport of functionalized SWNTs and MWNTs were examined in laboratory columns packed with natural, baked, and acid-cleaned sand under different conditions. Our specific objectives were to: (1) compare the retention and

transport of the CNTs in laboratory column packed with natural, acid-cleaned, and baked sand, (2) determine the effect of perturbations in flow direction, flow rate, and surfactant concentration on remobilization of initially retained CNTs in natural and baked sand, and (3) examine the retention and transport of the CNTs in natural and baked sand under different pH conditions.

2. Materials and Methods

2.1. Functionalized of CNTs

Carboxyl functionalized SWNTs (Cheap Tubes Inc., Brattleboro, VT) were used as received from the manufacturer. Functionalized MWNTs were synthesized using a chemical vapor deposition (CVD) method with nickel and magnesium catalysts and acid oxidized using a 3 to 1 ratio of sulfuric and nitric acids to add hydroxyl and carboxyl functional groups on its surface. To prepare the suspensions for experimentation, 16 mg CNTs were suspended in 1000 ml deionized (DI) water, followed by 30 min of ultrasonication (Misonix S3000). A fresh CNT stock was used for each transport experiment and the experimental time was controlled to be within 4 hours. The pH of the CNT suspensions in DI water was around 5.6. Stability experiments confirmed that two CNT suspensions were stable at least for 24 hours after the sonication (Fig. S1, Supporting Information). The electrophoretic mobility (EPM) and hydrodynamic diameter of the SWNT and MWNT were determined using a ZetaPlus (Brookhaven Instrument Co., Holtsville, NY). Smoluchowski's model was used to estimate the zeta potential of the functionalized CNTs. Because Smoluchowski's model is rigorously valid only for spherical particles, this estimation may overestimate the actual zeta-potential by

up to 20% [21]. The point of zero charge (PZC) of the CNTs was determined using the mass titration method [32]. A brief description of the mass titration method can be found in the Supporting Information.

2.2. Porous media

Natural silica sand porous media were obtained from Standard Sand & Silica Co. (Davenport, FL) and were carefully sieved into a size range of 0.5 - 0.6 mm to ensure uniformity. The sand was washed sequentially by tap water and DI water, oven dried at 70 °C, and used in this study as natural sand. to determine the organic matter on the surface of sand. Part of the washed natural sand was baked in a furnace at 550 °C to remove surface organic matters and used as baked sand [23]. Another batch of the sand was cleaned with 10% nitrate acid (i.e., acid-cleaned sand) to remove surface impurities using the procedures reported by Tian et al. [22]. The organic carbon (OC) content of the sand was determined using the Walkley-Black chromic acid digestion method [33]. There were about 0.08% of OC on the natural sand, but no detectable OC on the baked or acid-cleaned sand. The zeta potential of the natural, baked, and acid-cleaned sand was determined according to the procedure of Johnson et al. [34]. Their PZC were determined using the mass titration method (Supporting Information). Scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS) was employed to examine the presence of metal elements on all of the sand surfaces. The EDS has a penetration depth of about 100 nm at the surface of the samples. Additionally, metal element concentrations of the natural sand were determined by inductively coupled

plasma with atomic emission spectrometry (ICP-AES), after digestion with concentrated HNO₃ and HCl, as per the EPA protocol 200.7.

2.3. Packed sand column preparation

The sand was wet-packed (i.e., saturated) uniformly into an acrylic column measuring 2.5 cm in diameter and 16.7 cm in height. Membranes with 50 µm pores (Spectra/Mesh, Spectrum Laboratories, Inc.) were used at the column inlet and outlet to distribute the flow and to maintain the capillary pressure. The membranes were in immediate contact with the porous media and sealed by rubber O-rings. To pack each saturated sand column, a small amount of sand was poured gently into 8 ml of DI water standing at the bottom of the column until the sand surface was 0.5 to 1 cm below the water level. A polypropylene stir-rod was used to stir the sand in the column. Approximately 8 mL DI water was then added to the column and the sides of the column were gently tapped a uniform number of times. This procedure was repeated several times until the column was packed to a height of 15 cm. The porosity of the natural and acid-cleaned sand columns was approximately 0.40.

2.4. CNT transport in natural, baked, and acid-cleaned sand columns

A peristaltic pump (Masterflex L/S, Cole Parmer Instrument in Vernon Hills, IL) was connected to the inlet at the top of the sand column to regulate the flow. DI water was first pumped through the column for approximately 2 hr. at velocity of 1.0 cm/min to wash the column and ensure no background interferences in the effluent for CNT

measurements. DI water was used in this work to make the experimental condition be ‘unfavorable for deposition’. This approach has been demonstrated to be an effective way to explore alternative (non-DLVO) retention mechanisms of fine particles in porous media [28, 35]. A pulse of prepared CNT suspension of either MWNTs or SWNTs in the same chemical conditions was then introduced into the column, followed by CNT-free DI water to flush out unretained CNTs at the same flow velocity. The suspension pulse volumes were about 15 pore volumes (PVs) for natural sand columns, and 2 PVs for acid-cleaned sand columns. Effluent samples were collected from the bottom outlet of the column using a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography in Houston, TX). CNT concentrations were determined by measuring the total absorption of light at wavelengths of 255 nm with UV-Vis Spectrophotometer (Evolution 60, Thermo Scientific). The absorbance spectra and calibration curves of the two CNTs can be found in the supporting information (Fig. S2). Bromide (NaBr, 40 ppm) was also applied to the column as a conservative tracer.

2.5. Distribution of retained CNT in natural and baked sand columns

The deposition profiles of retained CNTs in the natural and baked sand columns were analyzed at the end of the transport experiments by dividing the columns post-transport experiments into nine layers of equivalent mass of sand along the depth gradient. Each sand layer was placed into a vial and washed with 25 mL DI water by shaking the mixture by hand. The supernatant was carefully transferred into a new vial to determine the resuspended CNT concentration. An additional 25 mL of DI water was subsequently added to the sand and the vial was ultrasonicated for 30 min. The second supernatant was

carefully transferred into a vial to determine the CNT concentration. The residual sand was oven dried at 75 °C to determine the presence of CNTs on its surfaces. A fresh batch of natural sand was used in the experiment following the same procedure as the control.

2.6. Mobilization of retained CNTs in natural and baked sand columns

For some of the natural sand and the baked sand columns, after the CNT injection and DI water flushing, the effect of flow direction, flow rate, and surfactant concentration on mobilization of retained CNTs was investigated. The flow direction experiment was initiated by switching downward DI water flow to upward at the same velocity (1.0 cm/min) for four PVs. The effect of flow rate on CNT mobilization was tested by increasing the flow velocity to 2.0 cm/min (downward) for four PVs. Sodium Dodecylbenzenesulphonate (SDBS), an anionic surfactant, was used in the experiment as the mobilization agent in this study because it is commonly used to disperse CNTs in water [22]. The SDBS (1% by weight) solution was applied to the natural sand column for four PVs at flow velocity of 1.0 cm/min to mobilize previously retained CNTs. Effluent samples from the mobilization experiment were collected in the same fashion stated previously, by fraction collector and CNT concentrations were determined with the spectrophotometer.

2.7. Effect of pH on CNT transport in natural and baked sand columns

To test the effect of solution pH on CNT transport in the natural and baked sand

columns, 0.1 mol/L NaOH solution was used to adjust the pH of the experimental solutions (CNT suspensions and DI water) to either 8.0 or 10. A fresh sand column was first flushed with the high pH working solution at a flow velocity of 1.0 cm/min until the effluent pH reached the same value. The inflow was then switched to the CNT suspension at the same pH and flow velocity for about 2 PVs. The column was then flushed again with the working solution for about 2 PVs at the same conditions. Effluent samples were collected to determine CNT breakthrough concentrations.

2.8. Modeling

A transport model based on the colloid filtration theory was used to simulate the retention and transport of the CNTs in the sand columns. The governing equation can be written as [36]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - kC \quad (1)$$

where C is the concentration, D is the hydrodynamic dispersion coefficient, v is the average linear water velocity, z is the travel distance in the direction of flow, and k is the clean-bed filtration rate constant. This equation can be solved analytically with a zero initial concentrations, a pulse-input boundary condition, and a zero-concentration-gradient condition at the outlet boundary [37]. The Levenberg-Marquardt algorithm was used to estimate the value of the model parameters to minimize the sum-of-the-squared differences between model-calculated and measured breakthrough concentrations [38, 39]. This model optimization method was first applied to bromide breakthrough data to

estimate D. Triplicated bromide tracer experiments were conducted and the best-fit D was 0.062 cm²/min (R²=1.00).

3. Results and Discussion

3.1. Surface characteristics

Measurements of the EPMs (Table 1) indicated that the two functionalized CNTs were negatively charged under all experimental conditions used in this study, which are consistent with the results reported in the literature [19, 20]. MWNTs had slightly lower EPMs than the SWNTs, probably because of the presence of both hydroxyl and carboxyl functional groups on their surfaces. The ionization of functional groups (i.e., deprotonation of hydroxyl and carboxyl groups) introduces strong negative charges and electrostatic repulsion between functionalized CNTs, and consequently enhances their stability in suspension. The estimated zeta potentials of the two functional CNTs under all experimental conditions were below -30 mV (Table 1), indicating good stability. The Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to estimate the interaction energies (Supporting Information). The DLVO theory was developed for interactions between spherical particles and homogeneous surfaces; therefore, the calculations can be only used as exploratory estimations here. The estimated DLVO energy profiles between the CNT particles in solution confirmed that the experimental conditions were unfavorable for CNT aggregating (Fig. S3a-b, Supporting Information). This is consistent with the results of the stability experiments (Fig. S1, Supporting Information). Mass titration curves (Fig. S4, Supporting Information) indicated that the PZC of the two CNTs were similar with values lower than 3, confirming both SWNT and

MWNT were negatively charged for all the tested conditions.

The surfaces of the natural, baked, and the acid-cleaned sand were also determined to be negatively charged under all experimental conditions tested (Table 1). Both the EPM and zeta potential of the baked and natural sand was slightly higher than the acid-cleaned sand, probably due to presence of positively charged impurities on the baked and natural sand surfaces. Without considerations of surface charge heterogeneity, the DLVO energy estimations indicated that the experimental conditions were unfavorable for attachment (i.e., traditional DLVO deposition) of the CNTs onto either the acid-cleaned, baked, or the natural sand (Fig. S2c-h, Supporting Information). The PZC values of the three types of sand were similar to each other with values close to 3, which agree with reported values of silica/quartz PZC in the literature [40]. The similarities of EPM, zeta potential, and PZC among natural, baked, and acid-cleaned sand grains suggested the dominance of the silica on the sand surfaces.

SEM-EDS analyses confirmed the dominance of silica signature on natural, baked, and acid-cleaned sand surfaces (Fig. 1). While no impurities were identified on the acid-cleaned sand surface, the SEM-EDS spectrum did show the presence of metallic impurities (i.e., Fe, Al, and Ni) on both natural and baked sand surfaces (Fig. 1). ICP-AES analyses corroborated the SEM-EDS results and showed relatively high levels of Fe (167.4 mg/kg) and Al (1086.6 mg/kg), and a very low level of Ni (0.7 mg/kg) on the natural sand. The identification of these elements agrees with the previously reported aluminum and iron oxyhydroxides on natural sand surfaces [41]. Because metal oxyhydroxides are positively charged under most practical circumstances, their presence introduces charge heterogeneity on the natural and the baked sand surfaces; a

physicochemical factor that will likely affect the transport of functional CNTs. As pointed out by Johnson et al [30], surface charge heterogeneity is likely a primary factor controlling deposition and transport of nanoparticles in porous media.

3.2. Retention in the acid-cleaned sand columns

Both the SWNTs and the MWNTs showed high mobility in the saturated columns packed with acid-cleaned sand (Fig. 2a). This is consistent with interaction energy calculations from the DLVO theory. SWNTs and MWNTs in their respective experiments were detected in the effluent about one PV after the pulse was applied. The breakthrough response for both CNT suspensions quickly increased and plateaued with additional input of CNTs. The breakthrough concentrations of the two CNTs quickly returned back to zero when the column influent was switched to CNT-free DI water. The plateau of the normalized breakthrough curves (C/C_0) for both SWNTs and MWNTs approached unity (i.e., $C/C_0 = 0.96$ and 1.00 , respectively), and the general shape of the breakthrough curves resembled that of bromide (Fig. 2). The resemblance of BTCs to the conservative tracer confirms low CNT retention in the acid-cleaned sand columns, and lack of interaction with the porous media surfaces. Mass balance calculations showed that only 3% and 1% of the SWNTs and MWNTs were retained, respectively in the acid-washed sand columns. Simulations of the transport model matched well the breakthrough data of CNTs in acid-cleaned sand columns ($R^2 > 0.97$) (Table 2). The best-fit, clean-bed filtration coefficients (k) of the SWNTs and MWNTs in the acid-cleaned sand columns were 0.0036 and 0.0012 min^{-1} , respectively. The Damkohler number for SWNT and MWNT deposition ($Da = \frac{kL}{v}$, where L is the column length and v is flow velocity) were

0.059 and 0.020, respectively. The magnitude of the Da number indicates that the time scale was much longer for retention than for advection through the columns. These results confirmed that experimental conditions where acid-washed sand is used as the porous medium do not favor for CNT retention. The high mobility of functionalized CNTs in laboratory columns packed with acid-cleaned sand was also observed in other studies under similar experimental conditions [19, 20].

3.3. *Retention in the natural and baked sand columns*

The breakthrough responses of the CNTs in the natural and the baked sand columns were similar and were much lower than that in the acid-cleaned sand columns (Fig. 2). This is inconsistent with interaction energy calculations from the DLVO theory, suggesting the strong retention of CNTs in the columns may not be controlled by the traditional DLVO deposition. Although the CNTs were applied to both the natural sand and the bake sand columns for an extended period of time, the normalized breakthrough concentrations reached the plateau stage quickly and remained at low peak C/C_0 concentration of 0.02-0.12. The recovery rates of SWNTs and MWNTs was 2.1% and 8.6% for natural sand columns, and 9.5% and 12% for the baked sand columns (Table 2), indicating that CNT mobility is significantly lower in chemically heterogeneous sand (i.e., natural and baked sand) than in oxyhydroxides-free sand columns (i.e., acid-cleaned). The transport model described almost all transport data well but performed weakly for MWNT transport in the natural sand column ($R^2 = 0.60$) (Table 2). The best-fit k values of the SWNTs and MWNTs in the natural and baked sand columns were 0.13-0.24 min^{-1} , which are two orders higher than that in acid-cleaned sand columns (Table 2). The

Damkohler numbers for the SWNTs and MWNTs in the natural and the baked sand columns were 2.1-3.9 (Table 2), indicating the time scale of retention was comparable to that of the advection process.

The enhanced retention of the two CNTs in the natural and the baked sand columns can be attributed to the surface deposition mechanism because all types of sand (i.e., natural, baked, and acid-cleaned) were similar in most the physicochemical properties, except in the surface characteristics. While the acid-cleaned sand has relatively homogeneous surfaces, surfaces of both natural and baked sand contain metal oxyhydroxides, which introduce surface charge heterogeneities. The CNTs are covered with negatively charged functional groups (of carboxyl dominance for SWNTs and a combination of carboxyl and hydroxyl for MWNTs), and they thus can attach strongly to the metal oxyhydroxides on natural or baked sand surfaces through electrostatic and/or hydrogen-bonding interactions [21]. Previous studies have demonstrated the strong interactions between metal oxyhydroxides and hydrophilic surface functional groups, especially carboxyl and hydroxyl groups [42-44].

The results also suggested that physical straining might not be considered as a dominant retention mechanism for CNT transport in the natural sand columns under the tested experimental conditions. This is consistent with previous transport studies of surfactant-dispersed SWNTs, NOM-coated SWNTs, and functionalized MWNT in clean porous media [20-23]. In a recent study, Tian et al. [22] did not observe any straining of surfactant-dispersed SWNTs in water-saturated columns packed with acid-cleaned quartz sand with different grain-size distributions and assumed that CNT might orient parallel to the streamlines in flow to avoid the pore straining in porous media.

3.4. Distribution of retained CNTs in natural and baked sand columns

Measurements of the retained CNTs in the natural and the baked sand columns confirmed their strong deposition on the sand grain surfaces. When the sand was excavated from the column, its color was much darker than the original natural sand, especially near the column inlet. Supernatant samples obtained after washing the sand with DI water were transparent and appeared to be the same as the control solution (Fig. 3a). The CNT concentrations in the supernatants were zero as measured by the UV-Vis spectrophotometer at 255 nm, confirming that CNTs in the porous media were not retained through physical straining. Subsequent sonication of the sand layers successfully detached a fraction of the retained CNTs from the sand; particularly from the layers closer to the inlet (Fig. 3b). Although we were not able to determine the CNT concentration of the sonicated supernatants by spectrophotometry because the sonication step generated additional sand colloids, the light absorption of all samples at 255 nm was higher than that of the control. Sonication could detach retained CNTs from the sand surface; however, the color of the sonicated sand was still darker than the original sand (Fig. 3c). This result further confirmed the strong interaction between the functionalized CNTs and the metal oxyhydroxides on sand surfaces.

3.5. Mobilization of retained CNTs in natural and baked sand columns

The concentration of CNTs in the effluent after the reverse, high-velocity, or SDBS

flushing was below detection limit; suggesting that none of the tested physical and chemical transients can effectively remobilize the retained CNTs in the natural sand or the baked sand columns. If pore straining was one of the dominant mechanisms of CNT retention in the columns, change in flow direction would likely result in the release of the retained CNTs from pore throats of the porous media [45, 46]. On the other side, the lack of mobilization of CNTs from either increases in flow velocity or addition of SDBS suggest that interactions between the grain and CNT surfaces are controlled by relatively strong attraction forces, such as electrostatic and/or hydrogen-bonding attractions. This result is consistent with the hypothesis that the retention of the functionalized CNTs in the sand is mainly controlled by surface deposition through interactions between the functional groups and metal oxyhydroxides.

3.6. *pH effect*

When higher pH was used, the breakthrough of the two types CNTs in both the natural sand and the baked sand columns increased (Fig. 4). For the functionalized SWNT in natural sand, the normalized peak breakthrough concentrations were 0.24 and 0.74 when the column pH values were at 8.0 and 10, respectively (see breakthrough curves in Fig. 4a). Similarly, the normalized peak breakthrough concentrations for the functionalized MWNT were 0.23 and 0.78 with pH of 8.0 and 10.0, respectively (see breakthrough curves in Fig. 4b). The recovery rates of the SWNTs and MWNTs from the natural sand columns also increased dramatically when the transport conditions were alkaline. Approximately 22% and 78% of the SWNT and 23% and 71% of the MWNT were recovered from the natural sand columns at pH of 8.0 and 10, respectively.

Similarly about 23% and 75% of the SWNT and 24% and 75% of the MWNT were recovered from the baked sand columns at pH of 8.0 and 10, respectively. The transport model described all the pH experiment very well with R^2 higher than 0.97 (Table 2). The best-fit k values of the SWNTs and MWNTs in the natural and the baked sand columns at two pH values ranged from 0.22 to 0.78 min^{-1} (Table 2). The Damkohler numbers for the SWNTs and MWNTs in the natural sand and the baked sand columns were 0.21-1.5 (Table 2), suggesting the time scale of retention was comparable to that of the advection process.

Both experimental and modeling results revealed that pH played an important role in enhancing the transport of functionalized CNTs in sand porous media. This result concurs with the hypothesis that deposition of functionalized CNTs onto the natural sand surfaces is driven by electrostatic and/or hydrogen-bonding attractions between the functional groups and metal oxyhydroxides. Characterization of the natural and the baked sand indicated that the surface charge heterogeneity is mainly introduced by the Fe, Al, and Ni oxyhydroxides. Metal oxyhydroxide impurities on the sandy medium act as favorable deposition sites that are positively charged at pH 5.6 (DI water) and promote deposition of negatively charged CNTs. Previous studies have shown that the points of the zero charge of the metal oxyhydroxides identified in our sand fall between 6.1 and 11.3 (Table S1, Supporting Information) [40, 47, 48]. When the system pH increased from 5.6 to 8.0 or 10, it reduced or reversed the positive charge of the metal oxyhydroxides and diminished the surface charge heterogeneity. The higher the system pH is, the less positive the surface charge of the metal oxyhydroxides will be. As a result, transport of the functionalized CNTs in the sand columns increased with the pH increments.

4. Conclusions

This study demonstrates the importance of chemical surface interactions between the nanoparticles and the porous media, which strongly control transport. Our results suggest that surface charge heterogeneity, is a key factor that controls the transport behavior of nanoparticles moving through porous media. Although it is commonly believed that the nanoparticle filtration efficiency of sandy soils is low, our study presents evidence that functionalized ENMs have limited mobility in natural sandy porous media that are rich in metal oxyhydroxides. Surface functionalization is a routine step in the preparation of nanoparticle suspensions to improve their performance, but may render additional benefits for the prevention of uncontrolled dispersal of nano-litter in the environment as nanoparticles encounter chemically heterogeneous soil environments and become chemically immobilized. Findings from this study also suggest that natural sand may be used as an efficient filter to remove functionalized ENMs from wastewater.

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Tables

Table 1. Surface characteristics of the functionalized CNTs and the porous media

	Size (mm)	Effective hydro- dynamic diameter (nm)	Point of zero charge	Electrophoretic mobility ($\times 10^{-8} \text{ m}^2/(\text{Vs})$)			Zeta-potential (mV)		
				pH=5.6	pH=8	pH=10	pH=5.6	pH=8	pH=10
SWNT	-	152.7	2.9	-2.71	-2.69	-2.75	-34.6	-36.4	-37.2
MWNT	-	179.8	2.4	-2.99	-2.82	-2.89	-38.2	-38.2	-39.1
Acid-cleaned sand	0.5 - 0.6	-	2.9	-1.43	-3.04	-3.34	-19.4	-41.1	-45.2
baked sand	0.5 - 0.6	-	3.1	-1.13	-2.61	-2.87	-15.3	-35.4	-38.8
Natural sand	0.5 - 0.6	-	3.1	-1.11	-2.46	-2.69	-15.1	-33.3	-36.4

Table 2. Summary of experimental conditions and model results of CNT transport in the sand columns.

	pH	Mass recovery	Deposition rate, k (min^{-1})	Damkohler number, Da	R^2
<u>SWNT transport in</u>					
Acid-cleaned sand	5.6	0.97	0.0036	0.059	0.99
Baked sand	5.6	0.095	0.14	2.3	0.97
Natural sand	5.6	0.021	0.24	3.9	0.83
Baked sand	8.0	0.23	0.088	1.5	0.98
Natural sand	8.0	0.23	0.088	1.5	0.97
Baked sand	10	0.75	0.017	0.27	1
Natural sand	10	0.71	0.018	0.30	0.97
<u>MWNT transport in</u>					
Acid-cleaned sand	5.6	0.99	0.0012	0.02	0.97
Baked sand	5.6	0.12	0.13	2.1	0.97
Natural sand	5.6	0.086	0.15	2.5	0.6
Baked sand	8.0	0.24	0.084	1.4	0.99
Natural sand	8.0	0.22	0.091	1.5	0.98
Baked sand	10	0.75	0.013	0.21	0.99
Natural sand	10	0.78	0.015	0.25	0.99

Figure Captions

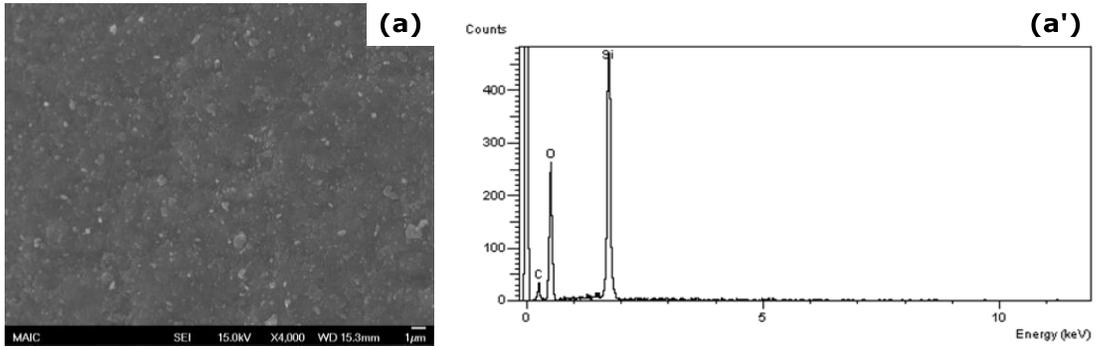
Fig. 1. SEM images (a, b and c) and corresponding EDS spectra (a', b' and c') of acid-cleaned sand, baked sand, and the natural sand at 4000X, respectively. EDS spectra were recorded at the same locations showed in the SEM image.

Fig. 2. Transport of CNTs in water-saturated columns in DI water system packed with (a) acid-cleaned sand, (b) baked sand and (c) natural sand.

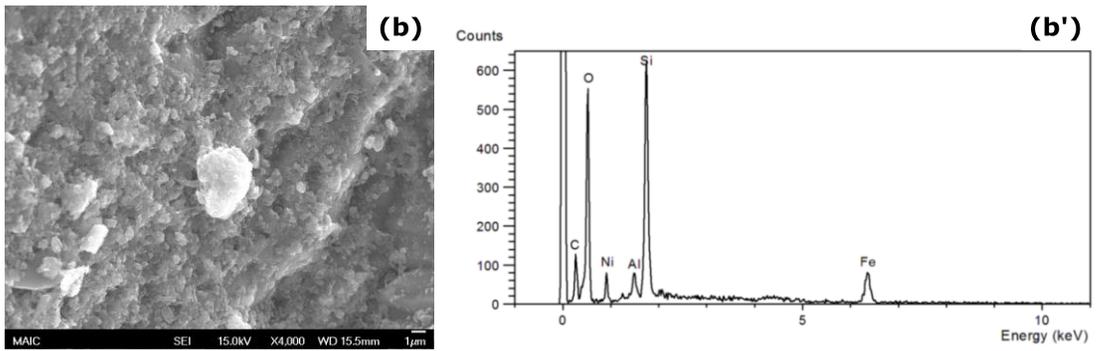
Fig. 3. Distribution of retained CNTs in the natural sand column: (a) supernatants from different layers after DI water washing; (b) supernatants from different layers after ultrasonication; (c) sand from different layers dried after ultrasonication. The vials on the right end are controls without CNTs. Only images of MWNT experiment are shown in the Fig. because the results were identical for SWNTs and MWNTs.

Fig. 4. Transport of CNTs in water-saturated columns packed with baked and natural sand at different pH conditions: (a) functionalized SWNTs in baked sand; (b) functionalized MWNTs in baked sand; (c) functionalized SWNTs in natural sand; (d) functionalized MWNTs in natural sand.

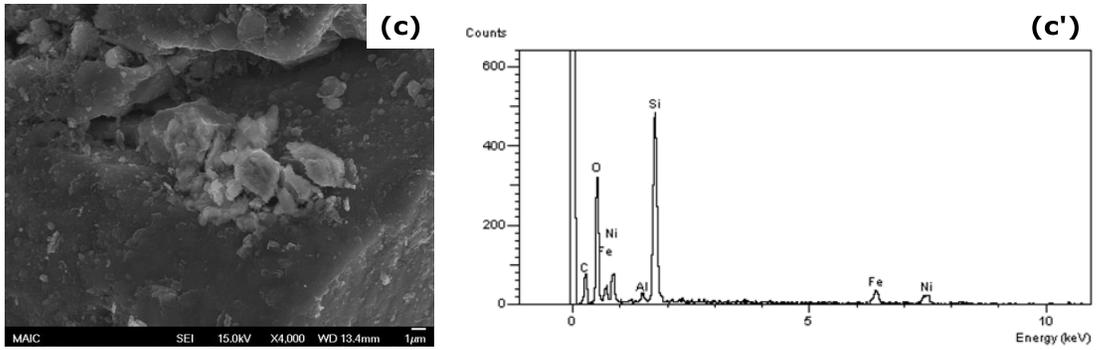
Fig. 1



Acid-cleaned sand



Baked sand



Natural Sand

Fig. 2

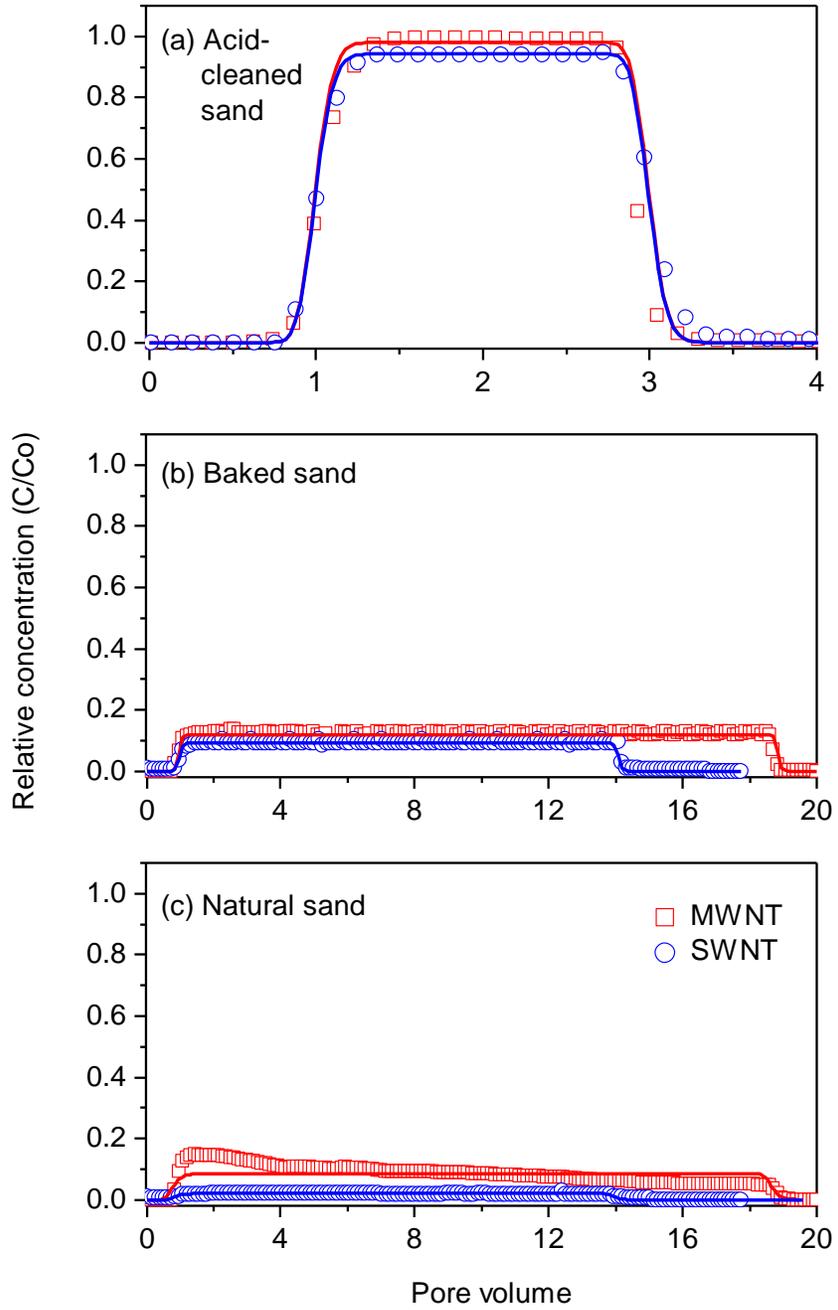


Fig. 3

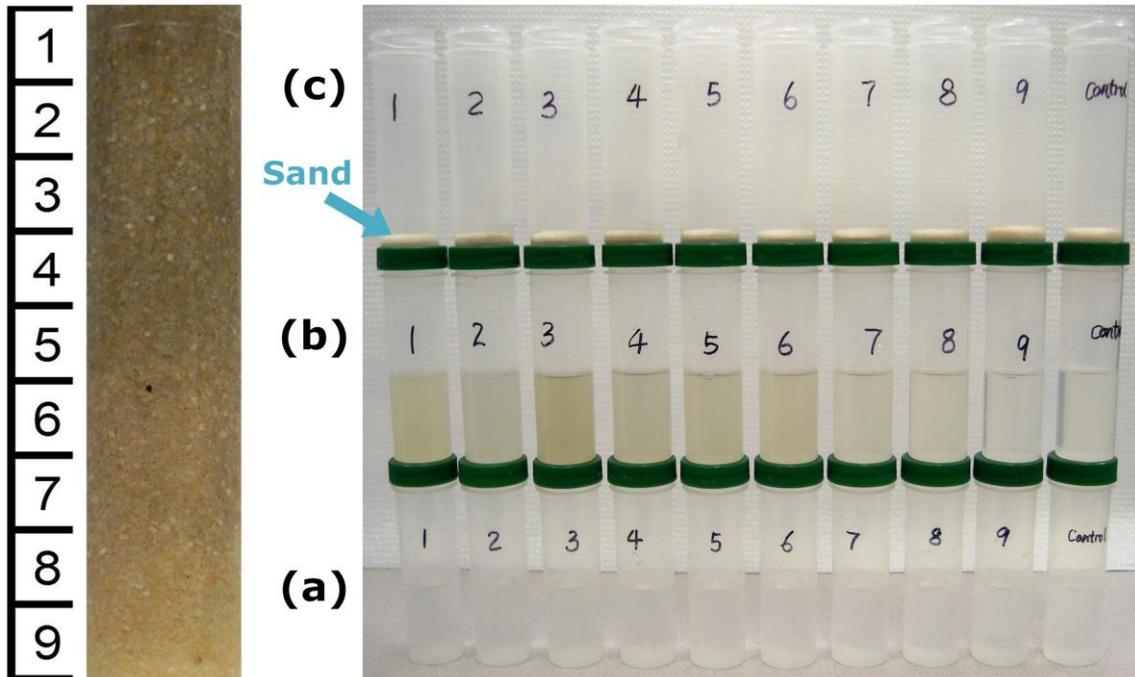


Fig. 4

