



Interactions of ^{14}C -labeled multi-walled carbon nanotubes with soil minerals in water

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ABSTRACT

Carbon nanotubes are often modified to be stable in the aqueous phase by adding extensive hydrophilic surface functional groups. The stability of such CNTs in water with soil or sediment is one critical factor controlling their environmental fate. We conducted a series of experiments to quantitatively assess the association between water dispersed multi-walled carbon nanotubes (MWCNTs) and three soil minerals (kaolinite, smectite, or shale) in aqueous solution under different sodium concentrations. ^{14}C -labeling was used in these experiments to unambiguously quantify MWCNTs. The results showed that increasing ionic strength strongly promoted the removal of MWCNTs from aqueous phase. The removal tendency is inversely correlated with the soil minerals' surface potential and directly correlated with their hydrophobicity. This removal can be interpreted by the extended Derjaguin–Landau–Verwey–Overbeek (EDLVO) theory especially for kaolinite and smectite. Shale, which contains large and insoluble organic materials, sorbed MWCNTs the most strongly.

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1. Introduction

Carbon nanotubes (CNTs) are one of the most popular classes of nanoparticles as a result of their exceptional properties. A CNT is a micrometer-scale graphene sheet rolled into a cylinder with a nanoscale diameter (Mauter and Elimelech, 2008). There are two main types of carbon nanotubes: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), depending upon the number of graphene layers. CNTs show extraordinary mechanical, electrical, and thermal properties because of their C–C covalent bonding and seamless hexagonal network architecture, which make them widely researched for commercial applications (Tomanek et al., 2008). Some potential CNT applications like drug delivery vessels, reinforced composites (Baughman et al., 2002; Petersen et al., 2011c), biomedical applications (Shen et al., 2009; Zhang et al., 2009), and environmental applications (Mauter and Elimelech, 2008) require a stable and homogeneous dispersion of CNTs in polar mediums such as water or polymeric resins (Vaisman et al., 2006). For these applications, CNTs are often shortened and functionalized with carboxyl, hydroxyl and/or carbonyl surface functional groups to make them

more hydrophilic and stable in water (Park et al., 2006), which is supposed to increase their mobility in the environment and influences their potential environmental impacts (Petersen et al., 2011c). Thus, the need to better understand the environmental fate of such modified CNTs is evident.

Stability of CNTs in natural water systems containing soil or sediment is one important aspect of their environmental fate. The extent to which CNTs are removed from water is influenced by the colloidal characteristics of CNTs such as the surface charge (Kennedy et al., 2008; Saleh et al., 2008; Smith et al., 2009a,b). Oxygen containing groups, especially carboxyl groups, make the CNT surface more hydrophilic and also change the surface charge (Smith et al., 2009b). Due to electrostatic repulsion, hydrophilic CNTs can be stabilized as described by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (Chen et al., 2009, 2004; Jaisi et al., 2008; Saleh et al., 2008; Sano et al., 2001; Smith et al., 2009a). Thus, the presence of common cations in the environment such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} can decrease their stability (e.g., induce aggregation) by suppressing electrostatic repulsion between the CNTs.

Most previous studies have investigated the stability of CNTs in water without a solid phase (Holbrook et al., 2010; Lin et al., 2010; Lin and Xing, 2008; Schwyzer et al., 2011), whereas in natural ecosystems the interaction between CNTs and soil or sediment particles contributes to their fate. Soil or sediment particles such as

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peat, one common type of soil organic matter, can sorb MWCNTs with the presence of sodium cations (Zhang et al., 2011a). Higher concentrations of kaolin were found to improve MWCNT removal from water (Holbrook et al., 2010). However, these phenomena have thus far rarely been studied in large part as a result of analytical method limitations for CNT quantification (Petersen and Henry, 2012; Petersen et al., 2012; Zhang et al., 2011a). An earlier study on the sorption of functionalized MWCNTs by soils revealed a linear sorption pattern, but the contribution of different soil components are still unclear (Petersen et al., 2011a). Clay minerals are a major building block of natural soils, and play an important role in the removal of various organic or inorganic pollutants via adsorption onto their large surface areas (Delle Site, 2001). The capacity for clays to remove CNTs in the natural environment has not yet been fully investigated. A previous study indicated that clay minerals can destabilize surfactant-dispersed MWCNT by two mechanisms: (1) removal of surfactants by clay minerals from solution and MWCNT surfaces and (2) bridging between clay mineral and MWCNT by surfactants (Han et al., 2008). Nonetheless, a quantitative study of the colloidal interactions between soil minerals and CNTs is needed to further elucidate the fundamental mechanisms of the environmental behaviors of CNTs.

We in this study examined the stability of MWCNTs in aqueous solutions containing three minerals (kaolinite, smectite, and shale) under varying sodium concentrations. In this system composed by both an aqueous and solid phase, the mechanisms of MWCNTs removal were 1) settling due to aggregation and 2) favorable interactions between solid phases and MWCNTs or MWCNTs aggregates, which is termed as “sorption” hereafter. These two processes occur concurrently and cannot be separated experimentally. Our assumption is that these processes are additive, so that quantity of MWCNTs sorbed to the solid phase can be determined by comparing results from systems with and without solids present. According to previous studies, van der Waals and electrostatic forces are likely to play roles in determining the stability of MWCNTs (Chen et al., 2009). Thus, the extended DLVO theory (EDLVO) was applied to interpret the interactions. The EDLVO theory incorporates the acid-base force in addition to van der Waals and electrostatic forces to describe the effects of hydrophobic and hydrophilic interactions, and has been proven to yield more precise predictions of many colloidal systems than the traditional DLVO simulation (Bostrom et al., 2006; Hoek and Agarwal, 2006; Zhang et al., 2011b). The overall goal of this study was to provide insights into the fundamental mechanisms governing the aqueous stability of MWCNTs with the presence of solid phase, and to quantitatively estimate their interactions, thereby contributing towards a scientific understanding of the environmental fate of MWCNTs.

2. Materials and methods

2.1. ^{14}C labeled MWCNT

Radioactive MWCNTs were synthesized using modified chemical vapor deposition (CVD) with mixtures of ^{14}C -labeled and regular methane gas as the carbon source. This synthesis method has been thoroughly described previously (Petersen et al., 2008a,b). To remove metal catalyst impurities, MWCNTs were bath sonicated with concentrated hydrochloric acid (11.1 mol/L) for 1 h. These nanotubes were then bath sonicated in an acid mixture of concentrated sulfuric (14.8 mol/L) and nitric (15.6 mol/L) acids by a 3:1 (V:V) ratio for 2 h to make them more stable in water by imparting additional oxygen-containing functional groups (Petersen et al., 2009a; Petersen et al., 2010). These surface-modified MWCNTs have a specific radioactivity of 0.1 mCi/g determined by liquid scintillation counting after biological oxidation (OX 500; R. J. Harvey Instrument Co. Tappan, NY). The BET MWCNT surface area is 111 m^2/g (Zhang et al., 2011a), which is comparable to previous results with purified but not acid-treated MWCNTs synthesized by the same technique (Petersen et al., 2009b). Thermal gravimetric analysis (TGA) revealed that these acid-treated carbon nanotubes were (99.7 \pm 0.2)% pure with respect to metal catalyst impurities and indicated an absence of amorphous carbon (Petersen et al., 2010); it was

previously shown using TGA that ultrasonication for 6 h only slightly increased the percentage of oxygen and did not produce detectable quantities of amorphous carbon (Zhang et al., 2011a). Diameters of these MWCNTs were previously measured with SEM to range predominately from 30 to 70 nm (Petersen et al., 2008a,b).

To prepare a stable stock suspension, MWCNTs (100 mg) were dispersed in 1 L of de-ionized water (>18 M Ω) by ultrasonication (200 W; Cole-Parmer CV33, IL) for 2 h, and then left at room temperature for 6 h. The stable portion was collected as the stock solution. The average length of MWCNTs was (353 \pm 452) nm (n = 836; uncertainties always represent standard deviations) measured using an FEI Inspect F50 FEG scanning electron microscope (SEM) operating at an accelerating voltage of 15.00 kV. According to x-ray photoelectron spectroscopy (XPS), the percentage of carbon atoms associated with oxygenated functional groups and total oxygen percentage were both approximately 7.4% for the acid-treated MWCNTs (Zhang et al., 2011a).

2.2. Soil minerals: kaolinite, smectite and shale

Clay minerals are generally composed of two building blocks, silicon tetrahedron ($\text{Si}_2\text{O}_5^{2-}$) and aluminum octahedron ($\text{Al}(\text{OH})_6^{3-}$), and are particles with sizes of less than 1 or 2 μm (Guggenheim and Martin, 1995). Kaolinite, a common clay material in most soils (Cooper, 2009), was obtained from Washington County, Georgia and was sieved and purified. Kaolinite belongs to the 1:1 clay minerals which contain one tetrahedral and one octahedral sheet per clay layer.

Smectite was obtained from Sigma–Aldrich (CAS number of 1318-93-0). This product is a calcium montmorillonite that has been treated by hydrochloric acid. Smectite is a typical 2:1 clay mineral which contains two silicon sheets with one aluminum layer in between (Cooper, 2009), and has a permanent layer charge resulting from isomorphous substitution. The surface area was (240 \pm 15) m^2/g and thus larger than that of kaolinite ((16.2 \pm 0.7) m^2/g) (n = 3 for both clays).

Lachine shale was collected from the Paxton Quarry west of Alpena, MI. The shale was crushed and sieved, and has been thoroughly characterized in previous studies (Huang and Weber, 1997; Huang et al., 1997). Shale contains diagenetically old organic material such as kerogen, one type of organic matter with a large molecular weight (>1000 D), relatively low O/H ratio and high H/C ratio (Huang and Weber, 1997; Huang et al., 1997). The organic carbon content of this shale is 8.27% (Huang and Weber, 1997). The surface area of this material ((6.60 \pm 0.15) m^2/g (n = 3)) is similar to that of kaolinite. The weight loss of the dry shale after heating at 600 $^\circ\text{C}$ overnight was (13.8 \pm 4.9)% (n = 3).

To remove the extra salts associated with clay particles as well as simplify the types of cations bonded with the clay particles, potassium saturated clay was prepared by soaking all three clay minerals in 0.1 mol/L KCl four times for 12 h each time, then extensively washing by de-ionized water until no Cl^- was eluted by an AgNO_3 test of the filtered solution (Charles et al., 2006). The organic carbon present in the smectite particles was minimum, indicated by a weight loss of (4.9 \pm 0.6)% (n = 3) after heating at 600 $^\circ\text{C}$. The weight loss of kaolinite under the same conditions was larger (12.9 \pm 5.7)% (n = 3), probably due to the loss of CO_2 from carbonates. The clay and shale samples were also analyzed by scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) (FEI Inspect F FEG-SEM equipped with EDAX). Images and surface element compositions are shown in Figs. S1 and S2, and Table S6 summarizes the EDS results.

2.3. Quantification and characterization

The concentrations of MWCNTs were determined based on their radioactivity. A 3-mL aliquot of each sample was mixed with 3 mL of scintillation cocktail (Insta-Gel Plus, PerkinElmer, MA), and the radioactivity was measured with a Beckman LS 5801 liquid scintillation counter (Brea, CA). The detection limit for this method was 0.04 mg/L, determined by mixing 3 mL of de-ionized water with 3 mL of scintillation cocktail (n = 6), measuring their radioactivity, and defining the detection limit as three times the standard deviation; lower detection limits can be achieved using larger volumes of solution. The electrophoretic mobility was determined from duplicate samples per condition using a Malvern Zetasizer Nano ZS instrument operating at 25 $^\circ\text{C}$.

The contact angles of the three types of mineral particles were measured by flattening them as thin layers on 5 cm \times 5 cm clean glass cover slips (Kuna et al., 2009; Voitchofsky et al., 2010). The glass cover slips were immersed in 2% (v/v) nitric acid solution for 30 min and then rinsed vigorously with 90% (v/v) ethanol (VWR Histology reagent alcohol 95%). A 2-mL aliquot of each clay suspension (approximately 1 g/L concentration) was dropped on the cover slip, which was then spun at 100 g for 5 min on a spin coater device (WS-400E, Laurel Technologies Corporation, US). A thin layer of the mineral particles was achieved after air drying for 5 to 10 min. Equilibrium contact angles (θ_L) of the clay layers were measured on a Model 250 Ramé-hart goniometer at ambient conditions. Three types of suspensions were prepared for each mineral for this test using three different probe solvents (de-ionized water, glycerol, and formamide) which surface tension properties were summarized in Table S1.

2.4. Association of MWCNTs with solid phase in different aqueous systems

The stability of MWCNTs in aqueous phase with or without solid phase was investigated using a bottle-point technique as described previously (Zhang et al.,

2011a). Ten initial concentrations of MWCNTs were selected from 0.1 mg/L to 16 mg/L. In each treatment, 10-mL of MWCNT suspension was added to a 150-mL flask with 50 mg of kaolinite, smectite, or shale; experiments were also conducted with 10 mg of shale. The contents were mixed and set still for 7 d when the aqueous concentrations of MWCNTs reached a quasi-equilibrium as indicated in a previous study (Zhang et al., 2011a). Each treatment was sampled and centrifuged at 3500 g for 1 min to remove suspended soil minerals, conditions shown in a preliminary test for effectively removal of the mineral particles. Without the centrifugation step, some fraction of the soil minerals remained in suspension, thus the centrifugation step was necessary to quantify the nanotubes remaining in aqueous phase. The radioactivity in 3 mL of solution was then measured to quantify the MWCNT concentration. Each experiment was repeated three times with each condition to confirm the reproducibility of the results. Control treatments without solid phase were also tested using the same method with sodium concentrations of 0, 0.4, 4, and 40 mmol/L to characterize MWCNT removal in the absence of the solid phase. The removal of MWCNT from water during the 7 d period and the centrifugation step in systems without a solid phase will be referred to hereafter as “settling.”

The total mass of MWCNTs that had distributed into solid phase in each treatment, M_s (mg), was obtained by mass balance using Eq. (1)

$$M_s = (C_0 - C_e) \times V \quad (1)$$

where C_0 and C_e are the initial and final aqueous concentrations of MWCNTs (mg/L), respectively, and V is the sample volume (0.010 L). For the control treatments, M_s represents the mass of nanotubes that have settled out of solution, while in clay treatments, M_s also includes the association between soil minerals and MWCNTs. The solid phase MWCNT concentration (q_s) is defined as

$$q_s = \frac{M_s}{D} \quad (2)$$

where D is the dosage of soil minerals (0.050 g).

A linear model was used to quantify the relationship between q_s and C_e . The linear parameter, a , was calculated as

$$q_s = aC_e \quad (3)$$

Parameter a demonstrates the tendency of MWCNTs to be removed from the aqueous phase. Control treatments gave a_1 which shows the settling of aggregated MWCNTs caused by sodium, while the treatments with solid phase gave a_2 which includes both settling and sorption of MWCNTs under different sodium concentrations. A new parameter, Δa , was calculated as

$$\Delta a = a_2 - a_1 \quad (4)$$

and indicates the contribution of sorption to the solid phase.

The influence of dissolved material from all three soil minerals on MWCNT stability was also investigated as described in the [Supplementary Material](#), because dissolved organic matter from peat was shown in our previous study to substantially reduce MWCNT settling (Zhang et al., 2011a).

Homogeneity of slope tests were performed using SAS 9.2 to test the differences of the values of a between: 1) different sodium concentrations; 2) different soil minerals; 3) with or without soil minerals, i.e., a_2 and a_1 ; and 4) with or without extractable materials from soil minerals. The null hypothesis for each test was that each pair of slopes were the same, and the p -values of this assumption were calculated accordingly. Statistically significant values were determined using $\alpha = 0.05$.

2.5. Interaction energy calculation by the EDLVO theory

The EDLVO theory was used to estimate the MWCNT-clay particle interaction energy by considering the non-retarded van der Waals (vdW) attraction, electrical double layer (EDL) repulsion, and Lewis acid–base (AB) interaction (Boström et al., 2006; Hoek and Agarwal, 2006). The mathematical expressions for the van der Waals and electrostatic forces vary with the geometry of the interacting entities. Because the mineral particles are at least 1.5–2 μm in one dimension while the length of MWCNTs is in the range of a few hundred nanometers and diameters were measured to typically range between 30 and 70 nm, the clay-MWCNT interaction was approximated as a particle-plate geometry. Definitions and determinations of all other parameters are provided in [supplementary material sections S2 and S3 and Tables S2 through S4](#).

3. Results and discussions

3.1. Settling and sorption of MWCNT with different soil minerals: model analysis

[Fig. 1](#) illustrates the overall removal of MWCNTs in the presence of kaolinite (part a), smectite (part b), or shale (part c) or without a solid phase (part d). A linear regression model was proposed to

describe the pattern of MWCNTs distributed between the aqueous and solid phases (see [Table 1](#)). The final concentrations of MWCNTs ranged from 0.05 mg/L to 10 mg/L. Within this range, the linear model fits sorption data equally well as the Freundlich model or Langmuir model, models that typically yield more robust fits of sorption behaviors. Moreover, previous studies showed nearly linear sorption pattern of MWCNTs by peat or three different types of soils (Petersen et al., 2011a; Zhang et al., 2011a).

A larger value of a indicates a higher tendency of MWCNTs to be removed from the aqueous phase by settling or sorption. The value of a increased significantly (as shown in [Table S9](#)) with increasing sodium concentration for all three minerals, demonstrating the effect of sodium cations to promote MWCNT removal from the aqueous phase, while MWCNTs tended to remain suspended without the addition of sodium ions.

When the sodium concentration reached a certain level, MWCNTs were almost completely eliminated from solution (less than 10% remaining in the aqueous phase). Above this threshold, there were not significantly different changes in a by increasing the sodium concentration (see [Table S9](#)). The threshold sodium concentrations were 4 mmol/L and 40 mmol/L for kaolinite and smectite, respectively. When the dose of shale was 50 mg, MWCNTs were almost entirely eliminated from the aqueous phase regardless of the sodium concentration, indicating the strong association tendency between MWCNTs and shale. To more carefully investigate the effects of varying sodium concentrations, the shale dose was reduced from 50 mg to 10 mg. For a shale dose of 10 mg, the threshold value of sodium concentration for nearly complete removal was 4 mmol/L.

The effects of the three types of soil minerals at the same sodium concentration (4 mmol/L) and mineral dosage (50 mg) were also directly compared in [Fig. 1](#) part e. Similar to the results shown in [Fig. 1](#) parts a, b, and c, smectite demonstrated the lowest tendency to associate with MWCNTs, while the MWCNTs were almost eliminated from the aqueous phase with the presence of kaolinite or shale. However, there was no statistical difference in the MWCNT stability among the different soil minerals without added sodium or at a sodium concentration of 40 mmol/L, because the MWCNTs were either highly stable or almost entirely removed from the aqueous phase, respectively.

The important effect of cation concentration on MWCNT removal from the aqueous phase differs to some extent from our previous study with peat (Zhang et al., 2011a). Peat released substantial concentrations of dissolved organic matter to water, which helped the MWCNTs remain in solution and mitigated the effects of the sodium cations to a certain extent (Zhang et al., 2011a). There was no statistically significant difference with or without dissolved components of the three minerals except for kaolinite at 0.4 mol/L sodium ions (see [Supplementary Material](#) for more information).

3.2. EDLVO modeling and mechanisms influencing MWCNTs stability

One of the important processes influencing the stability of MWCNTs is electrostatic interactions. Given that both minerals and MWCNTs have negative charges under almost all of the conditions tested (see [Table 3](#)), the electrostatic interaction between them was repulsive. Van der Waal's forces, which universally exists between two interacting materials, also play an important role in the interaction between MWCNTs and soil minerals or between individual MWCNTs. Furthermore, to account for the effects of hydrophobic and hydrophilic interactions, Lewis acid–base (AB) interactions were also included in the EDLVO theory in addition to van der Waal's and electrostatic forces. This model was applied to calculate

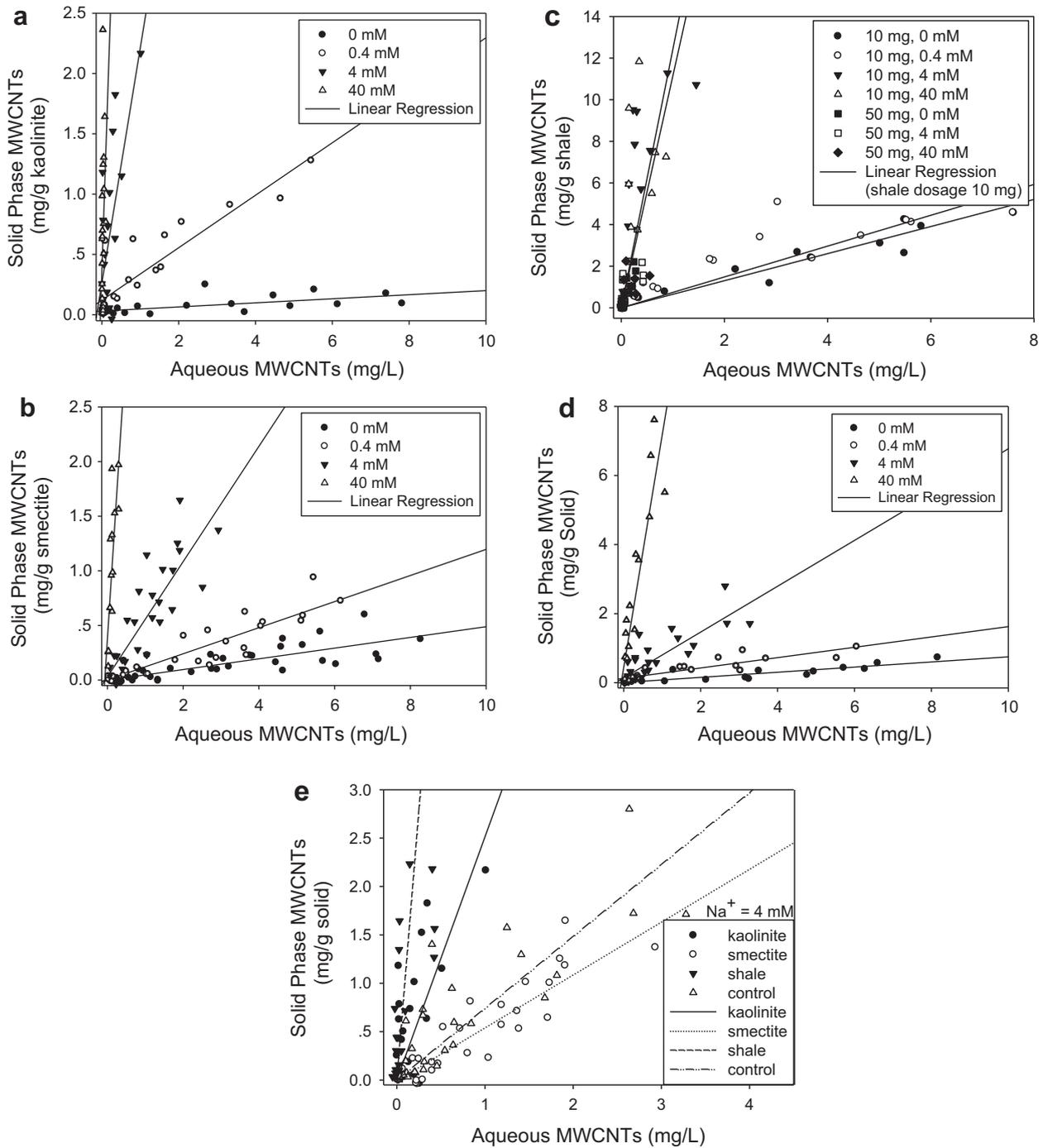


Fig. 1. Sorption of MWCNTs by clay minerals under sodium concentrations of 0, 0.4, 4, and 40 mmol/L: a) kaolinite; b) smectite; and c) shale. In a) and b), the dose of clay particles is 50 mg/10 ml, while in c) the dose is either 50 mg/10 ml or 10 mg/10 ml. d) A control treatment without clay minerals. e) Sorption of MWCNTs under sodium concentrations of 4 mmol/L by three type of clay particles (50 mg/10 ml). Uncertainty analysis of the plots is provided by the standard errors of the fitted linear model in Table 1.

Table 1

Parameters obtained by data fitting to the equation $q_t = aC_{aq}$.

Sodium conc. (mmol/L)	Kaolinite		Smectite		Shale	
	<i>a</i> (mg/g clay)	<i>R</i> ²	<i>a</i> (mg/g clay)	<i>R</i> ²	<i>a</i> (mg/g clay)	<i>R</i> ²
0	0.035 (0.008) ^a	0.17	0.049 (0.004)	0.665	0.651 (0.044)	0.816
0.4	0.225 (0.022)	0.75	0.120 (0.007)	0.809	0.741 (0.007)	0.556
4	2.514 (0.370)	0.39	0.546 (0.037)	0.729	11.146 (1.875)	0.063
40	16.705 (3.474)	0.01	7.3858 (0.816)	0.490	12.424 (2.756)	0.232

^a Values in parentheses are standard error. The number of samples tested ranged from 20 to 30. The dose of clay particles for kaolinite and smectite was 50 mg, while for shale is 10 mg.

the interaction energies under different sodium concentrations in our study. The energy potentials with respect to interaction distances are shown in Fig. 2.

As shown in Fig. 2 part a–c, there were energy barriers separating two minima of potential energy between MWCNTs and clay particles under each condition except for the treatment with kaolinite and 40-mmol/L sodium concentration. The positive energy barrier indicates that the association of MWCNTs with clay particles is thermodynamically unfavorable. The height of the energy barrier indicates the potential energy between clay particles and MWCNTs, which must

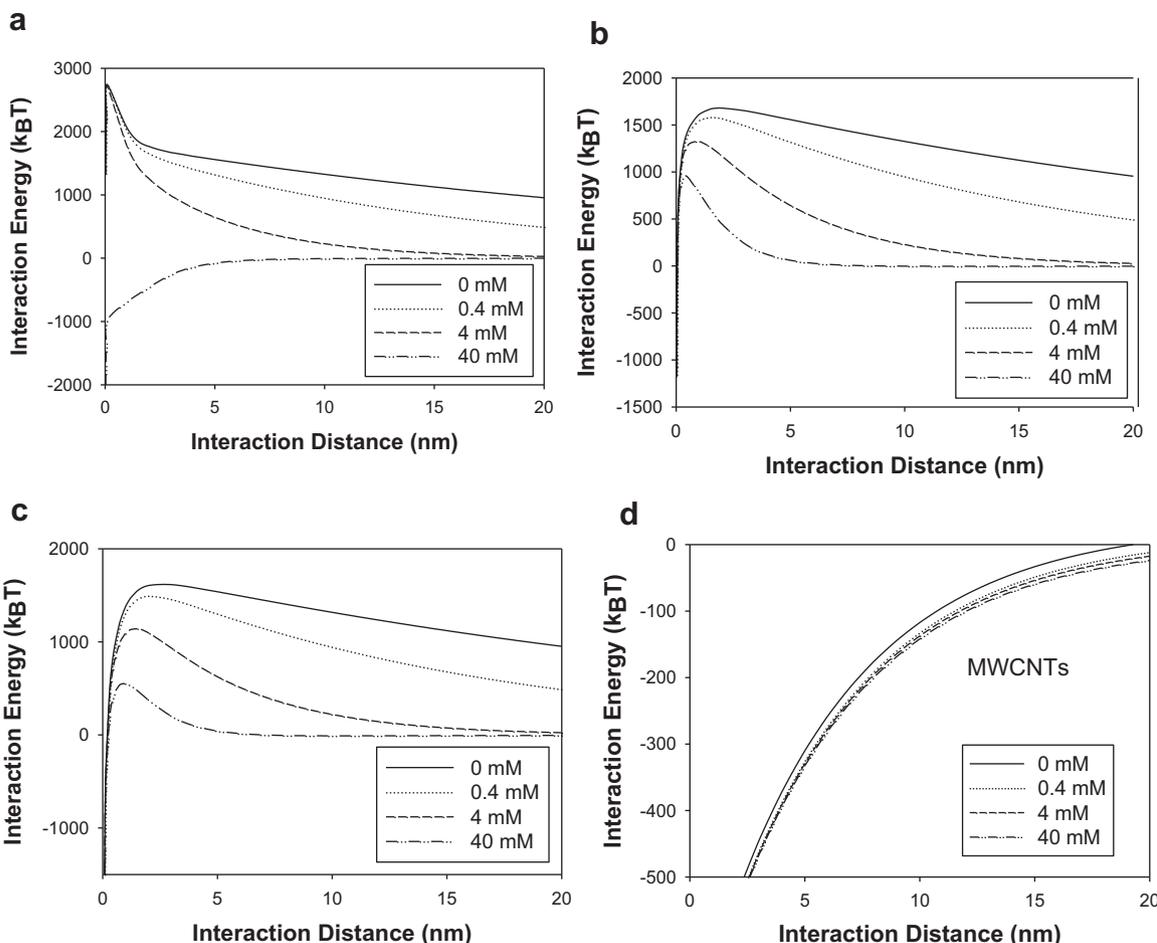


Fig. 2. Interaction energies between MWCNT and a) kaolinite; b) smectite; c) shale; and d) another MWCNT under different ionic strengths using the EDLVO model.

be overcome for the association process to occur and thus the height of the energy barrier may strongly influence the fate of MWCNTs. The values of the energy barrier decreased with increasing sodium concentrations due to decreased electric double layer repulsion. In other words, increasing ionic strength raised the likelihood of MWCNT associations with the mineral particles and decreased the stability of MWCNTs in the aqueous phase. According to the calculation, the interaction energies between these acid-treated MWCNTs were always negative when the sodium concentration were 0, 0.4, 4, and 40 mmol/L (see Fig. 2d). This result indicates a favorable association between MWCNTs, and explains the strong settling tendency of the MWCNTs due to aggregation.

To correlate the tendency of MWCNTs to enter the solid phase with the thermodynamics from the EDLVO theory, the common log of the linear model parameter, a , was plotted with the values of the energy barrier, as shown in Fig. 3. Clearly, $\log a$ was inversely correlated with the energy barrier value for each mineral. According to Fig. 3, there was a linear trend between the $\log a$ and the energy barrier. If we fit $\log a$ to the energy barrier of both clay minerals together (excluding shale), the correlation factor, R , which indicates the strength of that relationship was 0.98. This result shows the ability of the EDLVO theory to predict the trend of the association of MWCNTs with solid phase under different conditions for kaolinite and smectite. The major interaction forces between the clay particles and MWCNTs can be well summarized by the acid-base interaction, the electrostatic force, and van der Waals force. However, the pattern of shale which contains organic matters, differed from those of the other two inorganic minerals. This suggests that when

organic matter is present as for shale, additional non-DLVO forces such as entropy-driven or steric interactions may exist, which are needed to accurately reflect the complex interactions occurring.

3.3. Contribution of mineral particles

Values for the parameter indicating only sorption, Δa , are listed in Table 2. When the sodium concentration was 0 mmol/L, the

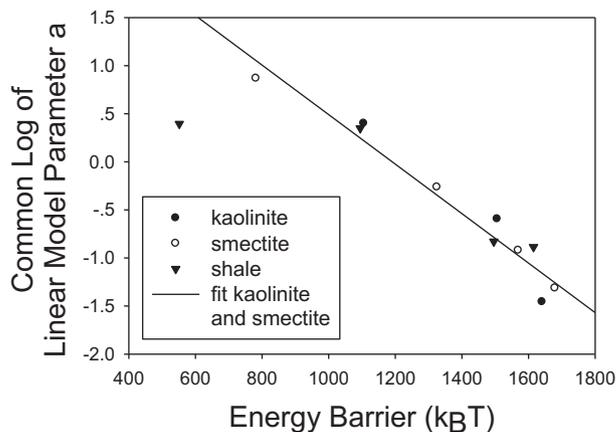


Fig. 3. The relationship between the Langmuir model parameter, a , and the energy barrier calculated by the EDLVO theory. The linear fit line is for kaolinite and smectite only.

Table 2
The contribution of clay particles indicated by the difference of model parameter, Δa .

Sodium conc. (mmol/L)	Kaolinite	Smectite	Shale (10 mg)
	Δa (mg/g clay)	Δa (mg/g clay)	Δa (mg/g clay)
0	-0.041 ^b (0.001) ^a	-0.027 ^b (0.001)	0.575 ^b (0.005)
0.4	0.0705 ^b (0.038)	-0.065 ^b (0.023)	0.556 ^b (0.086)
4	1.771 ^b (0.432)	-0.197 (0.098)	10.404 ^b (1.936)
40	9.251 (4.134)	-0.068 (1.476)	4.970 ^b (3.416)

^a Values in parentheses are standard errors calculated using Gauss error propagation. The number of samples tested ranged from 20 to 30. The dose of clay particles for kaolinite and smectite was 50 mg, while for shale it was 10 mg.

^b Values are significantly different from zero ($\alpha = 0.05$), tested by comparing the a values with and without solid phase.

effect of kaolinite or smectite on the stability of MWCNTs was not pronounced, which differs from the effects of shale. The net effect of smectite across the range of sodium concentrations, was to stabilize MWCNTs in aqueous phase, while those of kaolinite and shale were to promote the removal of MWCNTs.

The increasing of affinity towards MWCNTs in the order of smectite, kaolinite, and shale under the same sodium concentration can be explained by the surface charge and hydrophobicity of different soil minerals. This trend corresponds to the increase of hydrophobicity indicated by the contact angles (see Table S2). Compared to smectite, kaolinite is less charged demonstrated by the absolute value of the electrophoretic mobility of kaolinite being less than that of smectite for each sodium concentration (see Table 3). The negative charge on the clay surface can repulse the negatively charged MWCNTs, and consequently prevent them from coming into contact. Therefore, the more negatively charged smectite renders the MWCNTs more stable than the less negatively charged kaolinite. Interestingly, shale has a higher electrostatic potential than kaolinite and smectite as evidenced by its electrophoretic mobility, but more association affinity with MWCNTs. This is probably due to the organic content of shale that can strongly sorb MWCNTs, which dominates MWCNT-shale interactions. Our previous study also demonstrated that the diagenetically young soil organic matter, peat, sorbed MWCNTs when sodium ions were present (Zhang et al., 2011a). The high affinity between MWCNTs and shale is thus probably ascribed to the sorption ability of soil organic matter.

3.4. Environmental implications

Minerals like clay are extensively distributed on the earth surface as important components of soils and sediments. Therefore, understanding the interactions between MWCNTs and such minerals is of significance in predicting the fate of MWCNTs in environment matrices. For clay particles without organic matter, surface charge is critical in these interactions. Therefore environmental conditions that can change the surface charges such as ionic strength can also influence the effect of clay particles on MWCNTs. In sea water and hard water, MWCNTs will likely be removed from the aqueous phase by settling or association with soil or sediment particles, whereas in fresh water with low cation concentrations, MWCNTs are more likely to remain in the aqueous phase. A much more favorable association between the shale and MWCNTs was

Table 3
Electrophoretic mobility values of clay particles and MWCNTs ($\mu\text{m cm/Vs}$).

Sodium conc. (mM)	Kaolinite	Smectite	Shale	MWCNTs
0	-2.17 (0.03) ^a	-2.78 (0.29)	-3.18 (0.57)	-1.51 (0.02)
0.4	-1.32 (0.02)	-2.14 (0.06)	-3.60 (0.73)	-1.10 (0.08)
4	-0.52 (0.02)	-1.18 (0.01)	-3.69 (0.61)	-0.95 (0.14)
40	0.01 (0.37)	-0.65 (0.08)	-3.11 (1.29)	-0.94 (0.06)

^a Values in parentheses are standard errors ($n = 2$).

observed in comparison to inorganic minerals. The relative effects of these minerals also depend on their concentrations in soils and sediments, which is an interesting topic for further researches.

We also demonstrated the capability of the EDLVO theory to describe the interaction between MWCNTs and soil minerals. The calculated energy barrier based on the EDLVO theory was well correlated with the tendency of MWCNT association with solid phase (the parameter a) and accurately described the behavior of clay particles under different sodium concentrations, regardless of the clay type. Thus, the EDLVO theory may serve as a powerful tool to quantitatively study the stability of MWCNTs in the environment. However, approximations were also adopted in the EDLVO calculation (summarized in Supplementary Material S2). The effect of these approximations is left for future investigations.

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Appendix. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envpol.2012.03.008.

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