

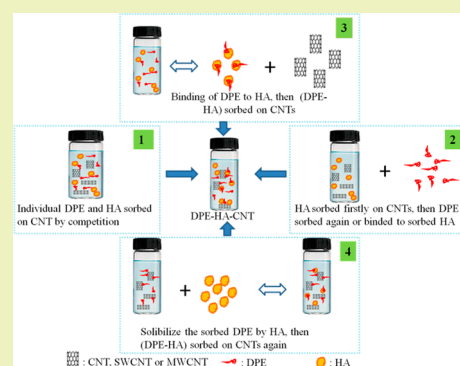
Mutual Effects of Dialkyl Phthalate Esters and Humic Acid Sorption on Carbon Nanotubes in Aqueous Environments

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S Supporting Information

ABSTRACT: Various reaction sequences of mutual sorptions of dimethyl phthalate (DMP) or diethyl phthalate (DEP) and humic acid (HA) on single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) were studied. The results indicate that the sorption of DMP and DEP on CNT decreases owing to its competition effect in the presence of HA. The competition is stronger at lower HA concentration. At higher HA concentration, weaker competition has occurred because there are steric hindrance and pore blockage of HA on CNT. The reaction sequences of DMP (or DEP) and HA sorption could affect their sorption mechanisms. The initial sorbed HA can modify the surface properties of CNT with a concomitant effect on the partial complexation of DMP (or DEP) with the sorbed HA. The Fourier transform infrared (FTIR) spectra indicate that SWCNT and MWCNT contain mainly $-\text{COO}^-$ and $-\text{COOH}$ moieties, respectively. In addition, the IR spectroscopic and thermogravimetric analyses illustrate that CNTs provide similar sorption capacity regardless of the interaction sequence of DMP (or DEP) and HA. Finally, the fluorescence quenching results indicate that DEP exhibits stronger binding to HA than that of DMP.

KEYWORDS: Dialkyl phthalate esters, Humic acid, Carbon nanotubes, Mutual sorption, Reaction sequence



INTRODUCTION

As carbon nanotubes (CNT), including single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), are produced and used at an increasing rate, more attention is paid to their potential risk because of their strong sorption capability to other toxic contaminants.^{1–3} The sorption on CNT is based on the unique arrangement of the extensive sp^2 carbon atoms in fused benzene rings.⁴ Once CNT is released into the environment, they may enter the food chains of living organisms with adverse effects.⁵ Additionally, fungi and bacteria in soil, which are involved in carbon and phosphorus biogeochemical cycles, can be adversely affected by SWCNT.⁶ Because CNT might have adverse effects on microbial communities and biogeochemical cycling of nutrients in soils, their environmental behavior is a vital issue that needs to be addressed.

Dialkyl phthalate esters (DPE), as endocrine disruption compounds, have been detected in various media including food, water, and marine ecosystems^{7,8} and are categorized as U.S. EPA priority pollutants. In our previous study, the transport behavior of DPE is affected by their strong sorption to CNT with hydrophobic and $\pi-\pi$ interactions.⁹ Furthermore, the sorption of DPE on CNT increases in the presence of Cu^{2+} ions in aqueous environments,¹⁰ indicating that the sorption behavior of CNT could be altered by other coexisting

substances in different aqueous conditions. As such, more researches should be conducted to better understand the interactions between DPE, humic acid (HA), and CNT as HA is a ubiquitous substance in our environment.

Dissolved organic matter (DOM), a common component in all natural aquatic environments, comprise hydrophobic species with some hydrophilic functionalities (e.g., carboxylic acid and phenolic groups) that exhibit a diversified water-solubility and reactivity.¹¹ Consequently, DOM plays a critical role in the biogeochemical behavior of organic or inorganic compounds and the mobility of colloidal particles by binding or sorption in aquatic environments.¹² Indeed, some studies demonstrated that the sorption of hydrophobic organic compounds onto DOM can significantly increase their aqueous solubility^{13–15} and even could enhance the transport of polycyclic aromatic hydrocarbons (PAH) in aquatic environments.¹⁶ These reactions inevitably affect the fate of chemicals in aqueous environments. Obviously, the water-solubility of organic compounds is based on their binding with DOM. Yamamoto et al. determined the sorption coefficients of endocrine disruptors including 17β -estradiol, estriol, 17α -ethynylestradiol,

Received: January 27, 2014

Revised: March 19, 2014

Published: March 25, 2014

p-nonylphenol, *p*-*tert*-octylphenol, and dibutylphthalate with various DOM such as Aldrich HA, Suwannee River HA and fulvic acid, Nordic fulvic acid, alginic acid, dextran, and tannic acid. The results show that the sorption mechanisms are closely related to the interactions of π -electrons and hydrogen bonds between the endocrine disruptors and DOM.¹⁷ In addition, Ilani et al. found that the hydrophobicity of PAH played an important role in their overall sorption on DOM, suggesting that the sorption of hydrophobic organic compounds on DOM is mostly governed by their chemical structure.¹⁸ Moreover, Kopinke et al. observed that there is a strong binding of PAH (e.g., pyrene) to DOM.¹⁹ All these results suggest that DPE may also easily interact with DOM in aquatic environments. Thus, the transport behavior of DPE in natural aqueous environments and the effect of DOM should be considered.

So far there are a number of reports on the sorption mechanisms between CNT and single organic compounds or DOM.^{2,20–23} However, the mutual sorption effects of HA and organic compounds on CNT have not been fully investigated. Wang et al. observed that HA can compete with aromatic compounds including phenanthrene, naphthalene, and 1-naphthol for the sorption sites of CNT.²⁴ Most of their work was done with both organic compounds and DOM in the system, and little is known whether the sequence of their sorption on CNT will affect their sorption behavior. Recently, Yang et al. found that the sorption on CNT is enhanced with either HA or Pb(II) being initially sorbed on CNT.¹ In order that CNT could be fully utilized for removal of DPE in our environment, it is crucial to investigate the sorption behavior of DPE on CNT in the presence of DOM and vice versa.

The objectives of this work are to study the sorption and competition behavior of DPE (using diethyl phthalate (DEP) and dimethyl phthalate (DMP) as the model contaminants) and HA on CNT including SWCNT and MWCNT. Our results will certainly provide a better understanding on the complex environmental behavior of DPE under the influence of HA.

EXPERIMENTAL SECTION

Materials. SWCNT with outer diameters of 1–2 nm and MWCNT with outer diameters of 10–20 nm were purchased from Shenzhen Nanotech Port (Shenzhen, Guangdong, China). Their synthesis methods and properties are displayed in the Supporting Information and Table S1, respectively. Two types of DPE, i.e., DEP and DMP, were used, and their physicochemical properties are summarized in Table S2 of the Supporting Information. HA as model DOM was purchased from Aldrich (St. Louis, MO, U.S.A.). The main characteristics are shown in the Supporting Information and also as described elsewhere.²⁵ Stock solution of HA was prepared according to our previous work.²⁶ The final HA solution was analyzed on a Shimadzu high-temperature total organic carbon (TOC) instrument (Kyoto, Japan), and a concentration of 100 mg/L was prepared. The above stock HA solution was stored in the dark at 4 °C before use. All reagents of analytical grade were used as received.

DPE Sorption. The sorption isotherms of DPE on CNT were performed on batch using 8.0 mL vials and Teflon-lined screw caps. The background solution contained 200 mg/L NaN₃ to minimize bioactivity and 0.020 M NaCl to maintain a constant ionic strength. Stock solution of DPE was made by dissolving it in methanol and was spiked into the vials using micro-syringe according to the desired DPE concentration (0.80–21 mg/L). A total of 0.2–0.5 mg of SWCNT and 0.6–2.0 mg of MWCNT were used for DMP sorption. A total of 0.2 mg of SWCNT and 0.6–2.0 mg of MWCNT were used for DEP sorption. The volume percentage of methanol in solution of each vial was kept below 0.10% (v/v) to minimize any co-solvent effect. The

head space of the vials was kept minimal. The vials were sealed and placed on a rotary shaker at 140 rpm for 3 days.⁹ After equilibration, the vials were centrifuged at 3000 rpm for 30 min. The DPE in supernatant was quantified by a Shimadzu LC20AD high-performance liquid chromatograph (HPLC) in conjunction with a SPD-20A UV detector (Kyoto, Japan) at 228 nm.²⁷ A Discovery C18 column (4.6 mm × 150 mm) was used for separation of DPE. The mobile phase was a mixture of methanol and water (4:1 v/v). The flow rate was 0.80 mL/min, and the column temperature was 35 °C. The solute losses and the difference in sorbate concentration of the blank solutions before and after the 3 day equilibration were less than 3.0% of the initial amount. Thus, the sorbed solute concentrations were determined by mass balance.

HA Sorption. The sorption isotherms of HA on CNT were done by batch using 20 mL screw cap vials. The solid to solution ratio was adjusted to about 20–80% solute uptake by CNT. The HA solution was diluted to series of initial HA concentration (3.0–80 mg/L) in the background solution. The amount of CNT was 1.0 mg for SWCNT and 8.0 mg for MWCNT. The background solution contained 200 mg/L of NaN₃ and 0.020 M NaCl. The vials containing test solutions of HA at various concentrations with the desired amounts of CNT were sealed with Teflon-screw caps and placed on a rotary shaker to mix for 3 days at room temperature (23 ± 1 °C). After mixing, the vials were centrifuged at 3000 rpm for 30 min, and the HA concentrations in the supernatants were measured on a Shimadzu UV-1800 UV–vis absorption spectrophotometer (Kyoto, Japan) at 254 nm in a 1.0 cm path-length quartz cuvette.²⁸ All samples including blanks were run in duplicate. The sorption of HA by CNT was calculated by the mass difference because their mass loss was negligible for blank samples.

DPE-HA Mutual Sorption on CNT. The mutual sorption experiments were performed using four mixing sequences of DPE, HA, and CNT: (1) DPE, HA, and CNT were prepared together [denoted as (DPE-HA-CNT)]. (2) HA and CNT were pre-equilibrated for 24 h and followed with addition of DPE [denoted as (HA-CNT)-DPE]. (3) DPE and CNT were pre-equilibrated for 24 h and followed with addition of HA [denoted as (DPE-CNT)-HA]. (4) DPE and HA were pre-equilibrated for 24 h and followed with addition of CNT [denoted as (DPE-HA)-CNT]. For the four sequence reactions, the initial concentration of DPE was 10 mg/L, and the initial concentrations of HA were 1.0–40 mg/L. In order to evaluate the effect of HA on sorption of DPE, the concentrations of DPE were 0.80–21 mg/L and HA was 10 mg/L. The amounts of SWCNT and MWCNT used for sorption of DMP and DEP were 0.2–0.5, 0.6–2.0, 0.2, and 0.6–2.0 mg, respectively. The background solution contained 200 mg/L of NaN₃ and 0.020 M NaCl. All samples including blanks were run in duplicate. All vials were shaken for 3 days at room temperature (23 ± 1 °C). After mixing, the vials were centrifuged at 3000 rpm for 30 min. The DPE concentration in the supernatant was measured by HPLC. The uptake of DPE by CNT was calculated by mass difference before and after sorption as there was no mass loss of solutes in the single and mutual sorption systems.

Characterization of CNT after Sorption of DPE. The characteristics of CNT before and after sorption of DPE were assessed by Fourier transform infrared spectroscopy (FTIR) using a Perkin-Elmer IR spectrometer (Waltham, MA, U.S.A.) and a TA Instruments Q500 thermogravimetric analyzer (TGA) (New Castle, DE, U.S.A.). In order to have sufficient samples for characterization, the amount of CNT was 30 mg per vial, and the concentrations of HA and DPE were 20 and 40 mg/L, respectively. The interaction time and conditions were the same as described in the above section. Samples were prepared as CNT, CNT-DPE, CNT-HA, (DPE-HA-CNT), (HA-CNT)-DPE, (DPE-CNT)-HA, and (DPE-HA)-CNT. After sorption, samples were washed with deionized water, centrifuged, freeze-dried, and kept at 4 °C prior to characterization. IR spectra were recorded from KBr pellets containing 5 mg solid samples and 500 mg KBr at 400–4000 cm⁻¹. TGA curves of 3.0 mg solid samples were acquired in N₂ atmosphere at a heating rate of 10 °C/min from 20 to 900 °C.

Binding Studies. A series of seven DPE-HA solutions were prepared to assess the sorption coefficients of DPE to HA. The initial

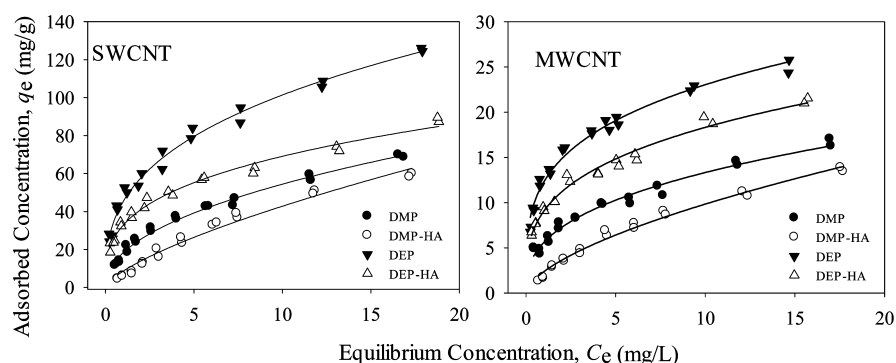


Figure 1. Sorption isotherms of DMP and DEP with or without HA on SWCNT and MWCNT. Solid lines are the Freundlich model fitting results. SWCNT is single-walled carbon nanotubes. MWCNT is multi-walled carbon nanotubes. The concentrations of DPE are 0.80–21 mg/L. Amounts of SWCNT and MWCNT used for sorption of DMP and DEP are 0.2–0.5, 0.6–2.0, 0.2, and 0.6–2.0 mg, respectively. Concentration of HA is 10 mg/L.

Table 1. Results of Freundlich Model Fits for Sorption Data of DPE by SWCNT and MWCNT^a

	CNT	K_f (mg/g)/(mg/L) ⁿ	n	r^2	K_d (L/g)	K_d/K_{hw}	K_d/SA $C_e = 0.002S_w$ (L/m ²)
HA ^a	SWCNT	115.5 ± 4.7 ^b	0.33 ± 0.01 ^b	0.985	24.69	–	–
	MWCNT	10.36 ± 0.60	0.57 ± 0.02	0.990	3.85	–	–
DMP	SWCNT	18.30 ± 0.55	0.47 ± 0.01	0.988	5.28	10.35	0.010
	MWCNT	5.61 ± 0.18	0.38 ± 0.02	0.976	1.31	2.57	0.004
DMP-HA	SWCNT	8.58 ± 0.64	0.70 ± 0.03	0.978	4.24	8.31	0.008
	MWCNT	2.38 ± 0.11	0.62 ± 0.02	0.987	0.98	1.92	0.003
DEP	SWCNT	45.28 ± 1.14	0.35 ± 0.01	0.986	40.61	26.03	0.075
	MWCNT	12.31 ± 0.23	0.27 ± 0.01	0.981	10.90	6.99	0.031
DEP-HA	SWCNT	32.77 ± 0.80	0.32 ± 0.01	0.984	29.25	18.75	0.054
	MWCNT	9.07 ± 0.20	0.31 ± 0.01	0.981	8.08	5.18	0.023

K_f : distribution coefficient. S_w : water solubility (mg/L). SA: surface area. ^a K_d values of HA are calculated at the concentration of 10 mg/L. ^bStandard errors of K_f and n .

concentration of DPE in all solutions was 20 mg/L, which was well below the aqueous solubility limit of DPE. The concentration of HA was adjusted in the range 0.0–10 mg C/L by dilution of the stock solution of HA (100 mg C/L), and this is a more realistic TOC level in the environment.¹⁷ The solutions were thoroughly mixed for 24 h in the dark at room temperature. The incubation time was selected according to a previous report.²⁹ After 24 h, the fluorescence of DPE was measured on a Hitachi F4500 spectrofluorometer (Tokyo, Japan). The excitation wavelength (λ_{ex}) was 272 nm, and the emission (λ_{em}) spectra were recorded at 300–600 nm.⁹ The slits for excitation and emission were 5 nm, and the detector voltage was 700 V. The fluorescence intensities at $\lambda_{ex}/\lambda_{em}$ of 272/340 nm without HA (F_0) and with HA (F) were measured. The Stern–Volmer plot, $F_0/F = 1 + K_{SV}[HA]$, was constructed where K_{SV} is the Stern–Volmer constant and [HA] is the concentration of HA.³⁰

Sorption Isotherm Models. The logarithmic form of the Freundlich model was used for data fitting in this work. $\log q_e = \log K_f + n \log C_e$, where q_e and C_e are the equilibrium solid (mg/g) and liquid phase (mg/L) concentration, respectively. K_f is the sorption coefficient ((mg/g)/(mg/L)ⁿ). n is often used as an indicator of isotherm nonlinearity. Sorption coefficient (K_d) of DPE and HA by CNT was calculated with the equation $K_d = q_e/C_e$.

RESULTS AND DISCUSSION

Sorption of Individual DPE or HA. The sorption isotherms of DMP and DEP in the presence and absence of HA by SWCNT and MWCNT are presented in Figure 1. The sorption isotherms of HA on SWCNT and MWCNT are displayed in Figure S1 of the Supporting Information. The sorption data fitted well with the Freundlich model with $r^2 > 0.97$ and is depicted in Table 1. It is well known that the nonlinear isotherms indicate the heterogeneous sorption sites

of the CNT. The distribution coefficient (K_d) was calculated from the Freundlich model with an equilibrium concentration of DMP or DEP at $C_e = 0.002S_w$ and an equilibrium concentration of HA at 10 mg/g (Table 1). When the concentrations of DPE and HA increase, more sorbates could reach the surface of CNT and were then sorbed on CNT.

In aquatic environments, CNT can aggregate and form bundles along their length axis by strong van der Waals forces due to their high hydrophobicity.³¹ These bundles lead to the formation of groove, interstitial, and inner areas. The cluster structure provides heterogeneous sorption sites for HA or DPE sorption. The bundle interstitial and groove sorption sites offer much stronger force to trap sorbates.³²

The sorption of DMP and DEP on CNT follows: DEP > DMP, and SWCNT > MWCNT for DMP or DEP (Figure 1 and Table 1). The K_d/K_{hw} (hexadecane–water partition coefficient) also follows: DEP > DMP (Table 1). The sorption of DEP is two or three times of DMP, which is consistent with the hydrophobicity of DEP > DMP, indicating that DEP possesses greater dispersive force to interact with the highly polarizable graphene sheets of CNT.²⁴ Therefore, the greater K_d/K_{hw} values of DEP illustrate that the surface area of CNT and hydrophobicity of DPE play an important role on the sorbate–sorbent interaction. In addition, the π –electron-donor–acceptor (EDA) interaction has been considered as one of the predominant driving forces for the sorption of chemicals with benzene ring structure on CNT.^{9,31,33} The benzene ring on DPE can serve as an electron acceptor, while the hydroxyl groups make CNT an electron donor.³⁴ As such,

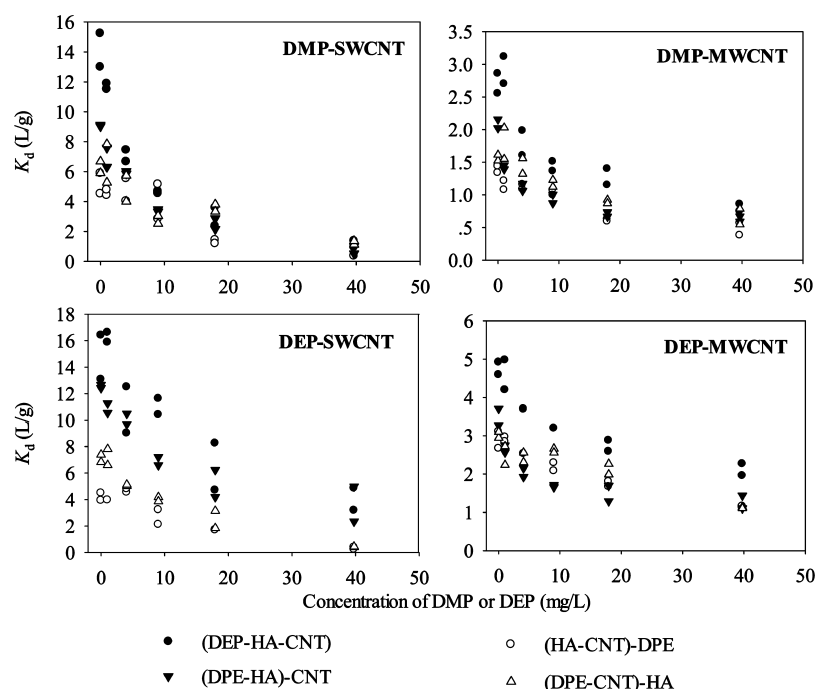


Figure 2. Sorption isotherms of DMP and DEP in the presence of HA on SWCNT and MWCNT under various addition sequences. Initial concentration of DPE is 10 mg/L. Initial concentrations of HA are 1.0, 4.0, 9.0, 18, and 40 mg/L. The concentrations of DPE are 0.80–21 mg/L. The amounts of SWCNT and MWCNT used for sorption of DMP and DEP are 0.2–0.5, 0.6–2.0, 0.2, and 0.6–2.0 mg, respectively.

the EDA interaction between DPE and CNT could increase DPE sorption on CNT.

The IR spectrum indicates that HA contains O-containing functionalities, e.g., $-\text{COOH}$ and $-\text{OH}$, as depicted in Figure S2 of the Supporting Information. These O-containing functionalities can readily form H-bonding with polar functional groups on the graphene surfaces of CNT. However, this interaction could be very weak if the oxygen content of CNT is low. Thus, the $\pi-\pi$ interaction is an important mechanism that governs the sorption of both π -EDA to graphene surfaces.^{20,26} The $\pi-\pi$ interaction could largely drive the sorption of DOM containing aromatic functionalities on CNT.²² Aldrich HA contains 45.1% of aromatic carbon, inferring that the $\pi-\pi$ interaction greatly enhances the sorption of HA on the graphene surfaces of CNT. In addition, the surface and macropores of CNT offer key sorption sites for HA due to its large molecular size in comparison with small molecular compounds (i.e., DPE). DOM contains a mixture of low molecular weight compounds and is a chemically heterogeneous macromolecule.¹⁸ The K_d values for HA are consistent with the surface area of CNT. In essence, the surface area is a key factor to determine the sorption capability of CNT, while the $\pi-\pi$ interaction and hydrophobic attraction would be the joint principal driving forces for HA and CNT interactions.

Effect of HA on Sorption of DPE. The K_d values for DPE on SWCNT or MWCNT decrease in the presence of HA, indicating that HA directly competes with DPE for the sorption sites of SWCNT and MWCNT (Figure 1 and Table 1). Figure 2 displays the sorption isotherms of DMP and DEP in the presence of HA on SWCNT and MWCNT under various addition sequences. DMP or DEP shows strong competition with HA for the sorption on CNT when the concentration of HA is low. However, the competition decreases with an increase in HA.

DMP, DEP, and HA would preferentially occupy the limited high-energy sorption sites (i.e., bundle interstitial and groove) on the CNT. The surface of CNT could offer more accessible sorption sites for DMP or DEP at low HA concentration owing to the large spaces between the HA-sorbed molecules that allow the DMP or DEP molecules to pass through to reach the CNT. By contrast, when the concentration of HA increases, the K_d values of DMP and DEP decrease gradually, inferring their weaker competition with HA. This can be explained by the fact that because HA has initially occupied the high-energy sorption sites, DMP or DEP is left to occupy the remaining low-energy sorption sites of CNT. Similarly Xing and Pignatello found that the natural aromatic acids could suppress the sorption of 1,3-dichlorobenzene or 2,4-dichlorophenol from water to soils, and the competition took place in the soil organic matter phase. The suppression of sorption decreased exponentially with increasing aromatic acid concentration as would be expected for direct competition for sites.³⁵ Yang et al. also illustrated that the surface-dominated sorption mechanism played a critical role in the competition system.³³ In fact, HA is a complex mixture of a heterogeneous natural continuum of high to low molecular weight species exhibiting various sorption capacity.¹² Most of DOMs are relatively low molecular weight (less than 2000 Da)³⁶ but are still much larger than DMP or DEP. In the previous studies, HA could retard the CNT aggregation rate and even make CNT forming a stable suspension in water.^{22,37} But CNT suspension mostly is based on the successive sonication. In this study, CNTs were not sonicated and tended to settle down when vials quiescently settled. In this case, HA may not increase the available surface area for sorption of DPE. Hence, the increased available sorption sites of CNT is limited. In addition, the number of sorption sites and spatial area occupied by a HA molecule on CNT surface should be higher and larger than that of one DMP or DEP molecule. Therefore,

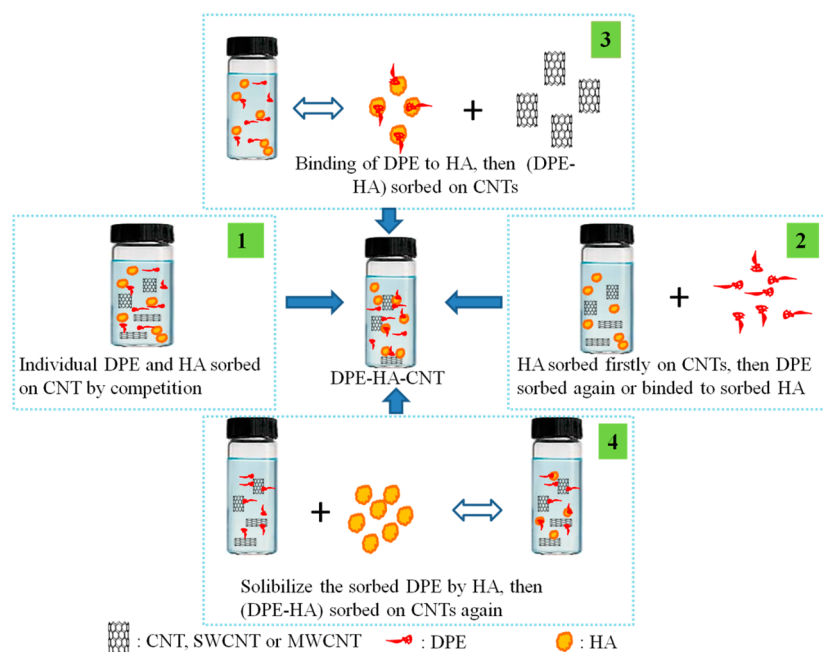


Figure 3. Schematic diagram of HA and DPE on the surface of CNT in different reaction sequences: (1) (DPE-HA-CNT), (2) (HA-CNT)-DPE, (3) (DPE-CNT)-HA, and (4) (DPE-HA)-CNT.

the initial sorption of HA would reduce further sorption of DMP or DEP.

In comparison with MWCNT, SWCNT has more sorption sites attributing to its larger surface area (Table S1, Supporting Information). This property will lead to the weaker competition of HA with DPE molecules as HA would have relatively smaller steric restriction to prevent DMP and DEP molecules from approaching CNT. A previous study also elucidated that surface sorption of PAH by CNT was a dominant mechanism instead of pore filling.³³ During the competition, either HA or DPE first approached CNT and then was sorbed. A schematic model for the sorption mechanisms is shown in Figure 3. K_d values decrease with an increase in HA concentration. But the changes in the K_d values are smaller at relatively high HA concentration. The differences and similarities among DPE sorption in the ternary systems indicate different sorption mechanisms.

In the (DPE-HA-CNT) system, DPE and HA compete for sorption sites of CNT simultaneously. DPE molecules could more easily occupy the sorption sites as they are smaller, especially under low HA concentration where DPE encounter relatively smaller steric hindrance. This is why the K_d values are higher than the other three mixing systems of DPE, HA, and CNT, inferring that there is less free DPE in the (DPE-HA-CNT) aquatic environments.

In the aqueous phase, hydrophobic compounds could be attached to HA,^{19,38,39} and this can affect the sorption of DPE to CNT. In the (HA-CNT)-DPE system, HA is initially sorbed on the CNT surfaces, and then DMP or DEP is added. There is a strong complexation of DPE with HA, resulting in DPE sorption. A similar observation has been reported for PAH in the (HA-MWCNT) system. The initial coating of HA on MWCNT did not suppress the sorption of PAH on MWCNT. The sorbed HA molecules on MWCNT could create new sorption sites for hydrophobic compounds.²¹ In the (DPE-HA)-CNT system, DPE is pre-equilibrated with HA to form complexes with subsequent sorption on CNT. In the case of (DPE-CNT)-HA, HA is added to a suspension of DPE-CNT.

The complexation of HA in solution with the sorbed DPE is also possible.

It is obvious that the competition of DPE with HA could decrease with an increase in HA concentration based on the DPE and HA sorption sequences. It is possible that the concentration of HA is not high enough to form complexes with all DPE molecules so that some free DPE molecules are left to sorb on the CNT surfaces. However, when the concentration of HA increases, more DPE are bound with HA, making the free DPE (if existing in the solution) much harder to reach the surface of CNT and thus weaken the competition. Another interesting observation is that K_d values tend to be more or less the same under high HA concentrations, illustrating that both soluble HA in the solution and surface-sorbed HA could govern the transportation behavior of organic contaminants. Regardless of the addition sequences of DPE and HA to CNT, the final equilibration might tend to be uniform among the free sorbate and HA, complex of sorbate and HA, and surface-sorbed sorbate and HA.

FTIR and TGA. Figure 4 and Figure S3 of the Supporting Information show the FTIR spectra of CNT, CNT-DPE, CNT-HA, (DPE-HA-CNT), (HA-CNT)-DPE, (DPE-CNT)-HA, and (DPE-HA)-CNT. A significant absorption at about 1720 cm^{-1} (ester $\text{C}=\text{O}$ or $-\text{COOH}$) and $1600\text{--}1550\text{ cm}^{-1}$ (aromatic $\text{C}=\text{C}$ and carboxyl $\text{C}=\text{O}$)^{40,41} and peak shift of CNT were observed in comparison to the free CNT. Terkhi et al. reported the shift of the frequency band ($-\text{COO}^-$) from 1612 to 1590 cm^{-1} of pure Fluka HA with Hg^{2+} .⁴² In our study, the peak shift from about 1530 to 1590 cm^{-1} indicates that DPE and HA have already attached to the surface of CNT. The absorption intensity of the $-\text{CH}_2$ band at $2800\text{--}3000\text{ cm}^{-1}$ (C-H stretching of alkyl structure) shows no obvious differences. The bands at $1260\text{--}1200$ and $1070\text{--}1030\text{ cm}^{-1}$ are attributed to the stretch vibration of the carboxylic acid functional group ($-\text{COOH}$) and asymmetric stretch of carbohydrates ($-\text{COO}^-$), respectively.⁴⁰ Tanaka reported that

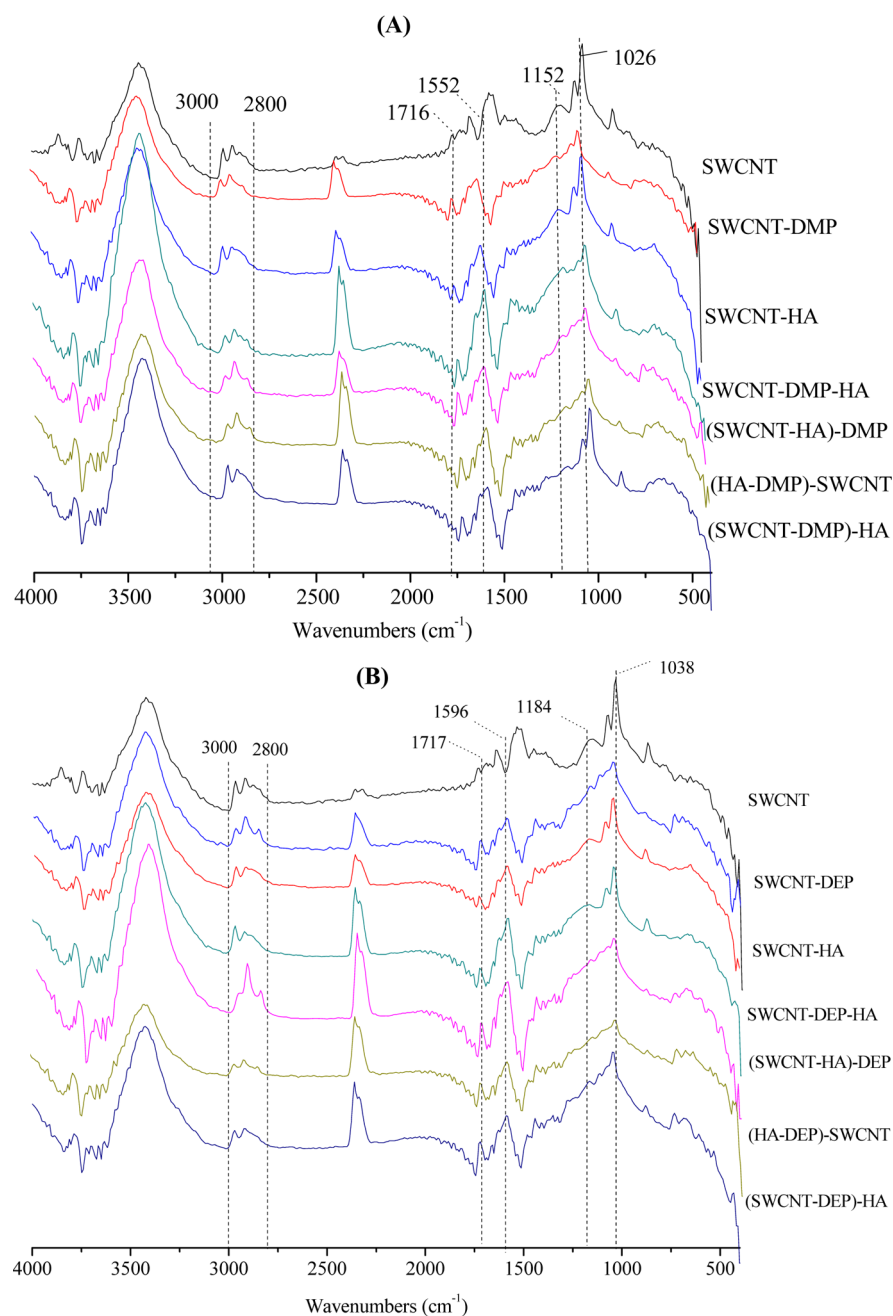


Figure 4. FTIR spectra of SWCNT, DPE-SWCNT, HA-SWCNT, (DPE-HA-SWCNT), (HA-SWCNT)-DPE, (DPE-HA)-SWCNT, and (DPE-SWCNT)-HA, where DPE is (A) DMP and (B) DEP.

the OH deformation and C–O stretching of COOH are evidenced by the weak absorption in the region of 1200–1300 cm^{-1} ,⁴³ indicating that the different active sites of SWCNT and MWCNT are due to the strong absorption at about 1030 and 1200 cm^{-1} , respectively, which may affect their sorption behavior.

Carboxyl behavior is dependent on the local structural environment within the macromolecules, i.e., the energies of the asymmetric stretching vibrations of the COO^- are sensitive to the structure environment of COOH.⁴⁴ Indeed, it may cause the differences in the spectral features. The changes of SWCNT IR spectrum are smaller than that of MWCNT at less than 1200 cm^{-1} . HA, DPE, and SWCNT mainly contain COO^- in aquatic environments, whereas MWCNT contains COOH (Figure 5 and Figure S3, Supporting Information). Therefore,

there is no obvious difference the in SWCNT IR spectrum under different combinations. By contrast, the sorption of DPE and HA can cause more significant changes in the IR spectrum of MWCNT. For example, the absorption peak of MWCNT is shifted from about 1200 to 1030 cm^{-1} before and after sorption of DPE and HA. Similar broad peaks were observed at 1200–1030 cm^{-1} for DPE-MWCNT and (HA-MWCNT)-DPE systems, indicating that the sequence of HA and DPE sorption on CNT could affect the surface properties of CNT. In the (HA-MWCNT)-DPE system, the IR spectrum of MWCNT initially sorbed with HA, and then DPE is similar to that of DPE-MWCNT. The IR spectra of HA-MWCNT, (DPE-HA-MWCNT), (DPE-HA)-MWCNT, and (DPE-MWCNT)-HA systems display mainly the characteristics of HA. In general, these spectral features suggest that the sorption capacities of

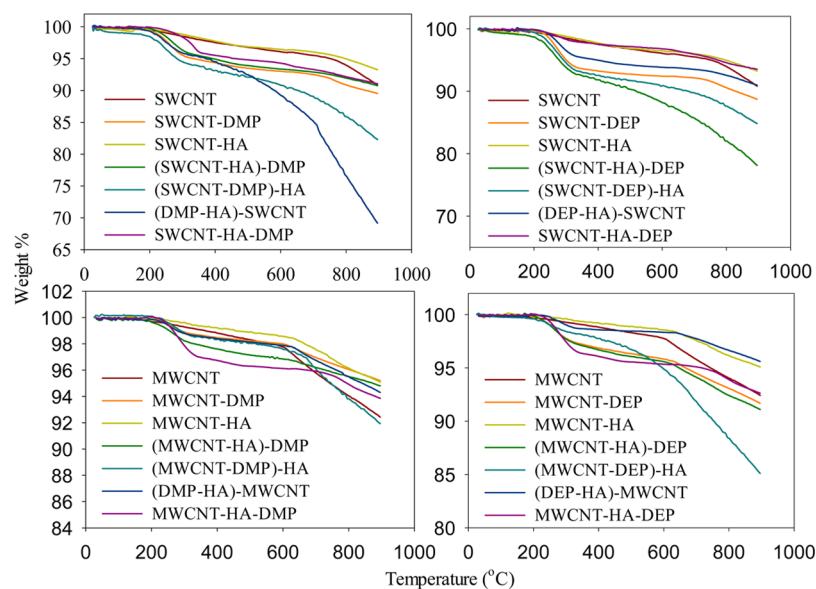


Figure 5. Thermograms of CNT, CNT-DPE, CNT-HA, CNT-HA-DPE, (CNT-HA)-DPE, (HA-DPE)-CNT, and (CNT-DPE)-HA, where DPE is DMP and DEP and CNT is SWCNT and MWCNT, respectively.

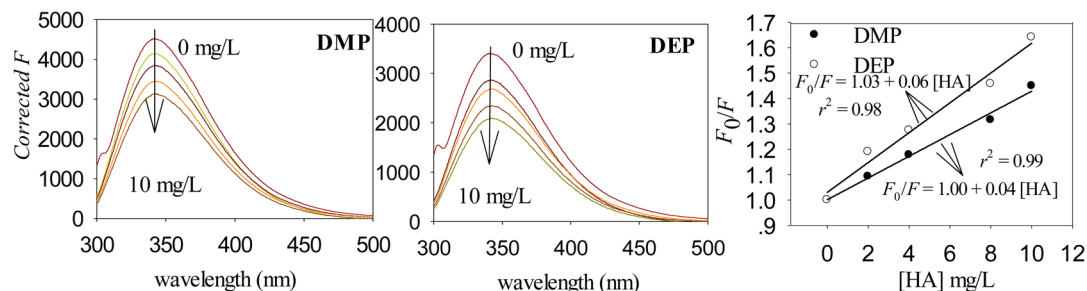


Figure 6. Fluorescence emission spectra of DMP and DEP (20 mg/L) with various concentrations of HA (0.0–10 mg C/L). Right panel displays the Stern–Volmer plots of DMP and DEP.

CNT are similar in different interaction systems. All these results vindicate that the sorption mechanisms of DPE and HA on CNT are related to their mixing sequences.

The thermal properties of both SWCNT and MWCNT after sorption of HA and DMP/DEP are evaluated by TGA and are depicted in Figure 5. The slow weight loss for CNT and HA-CNT until about 700 °C is attributed to the decomposition of impurities and HA. The weight loss below 220 °C for CNT with sorbed DMP or DEP is assigned to the evaporation of DMP/DEP by heat. The curves then become relatively constant with a small weight loss until 700 °C. It has been reported that there is a rapid weight loss of both raw MWCNT and MWCNT-poly(acrylic acid) at 550–680 °C owing due to the decomposition of MWCNT.⁴⁵ The weight loss of MWCNT in the range 350–500 °C can be attributed to the elimination of its hydroxyl groups.⁴⁶ However, these phenomena are not very obvious for our sorption systems, suggesting that the decomposition of CNT is very complicated, and it is difficult to observe the individual decomposition steps. Anyway, the similar weight loss of each sorption system indicates that the sorption capacities CNT for HA, DMP, and DEP are close.

DPE-HA Interaction. The fluorescence emission of DPE is quenched by HA. Figure 6 displays the fluorescence quenching of DPE by various concentrations of HA. The Stern–Volmer plots for DMP and DEP are displayed in the right panel of Figure 6. The plots of F_0/F versus $[HA]$ yield straight lines with

the y -intercepts close to 1 (1.00 ± 0.002 for DMP, 1.03 ± 0.006 for DEP). The K_{SV} values for DMP and DEP are 4×10^4 and 6×10^4 L/kg, respectively, suggesting that DEP has a higher affinity with HA than that of DMP. These results are more consistent with the hydrophobicity of DEP (octanol–water partition coefficient (K_{OW}), $\log K_{OW} = 2.39$) than that of DMP ($\log K_{OW} = 1.53$). Figure S4 of the Supporting Information displays the relationship between the adsorption coefficient of DPE to organic carbon (K_{SV}) and K_{OW} by plotting $\log K_{SV}$ against $\log K_{OW}$. The $\log K_{SV}$ of DPE increases linearly with $\log K_{OW}$, which is in good agreement, considering that the binding of DPE to HA is a partitioning process driven mainly by the hydrophobicity of DPE.¹⁷ Similar linear relationships between hydrophobic compounds (naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, and benzo[*a*]pyrene) and HA have been reported in the literature.⁴⁷ It has been found that the partition coefficients of atrazine to 16 different humic materials from soil, peat, and coal are mainly governed by the hydrophobic interaction between atrazine and humic acid.²⁹ It is anticipated that the sorption of DPE to humic acid will also determine their hydrophobicity and different sources of humic acid will possess different hydrophobicities.

CONCLUSIONS

The sorption of DPE and HA on CNT depends on the surface area of CNT and hydrophobicity of DPE. CNT of greater

surface area will certainly affect the transport behavior of organic carbon in the environment. Our results demonstrate that HA suppressed the DPE sorption by CNT. This effect increases with an increase in HA concentration owing to the steric hindrance from surface coverage and pore blockage. The IR and TGA data validate that the reaction sequences of DPE, HA, and CNT do not present very obvious differences in their competitive sorption under ambient conditions, suggesting that sorbate, sorbent, and DOM tend to reach equilibrium in aqueous environments. In addition, the binding of DEP and HA to CNT is stronger than that of DMP. This work provides a better understanding of the sorption behavior of DPE and HA to CNT and is thus of paramount importance to the use of CNT for environmental pollution cleanup.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis methods and characteristics of SWCNT and MWCNT. Physical-chemical properties of DMP and DEP. Sorption isotherms of HA on CNTs. FTIR spectrum of HA and MWCNT in various interaction systems. Relationship between the adsorption coefficient of DPE to organic carbon (K_{SV}) and their octanol–water partition coefficient (K_{OW}). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported in part by grants from the International Joint Key Project from the Chinese Ministry of Science and Technology (2010DFB23160), International Joint Key Project from the National Natural Science Foundation of China (40920134003), National Natural Science Foundation of China (41103060, 41273092, and 41273131), National Outstanding Youth Research Foundation of China (40925010), and Overseas, Hong Kong, and Macau Young Scholars Collaborative Research Fund (41328005).

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