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Increased Adsorption of Sulfamethoxazole on Suspended Carbon Nanotubes by Dissolved Humic Acid

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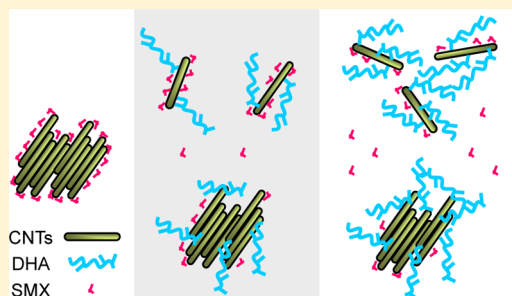
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S Supporting Information

ABSTRACT: Although dissolved organic matter (DOM) could effectively disperse carbon nanotubes (CNTs), sorption characteristics of DOM-suspended CNTs are unclear. In this study, we evaluated the relative contribution to the overall sorption from dissolved humic acid (DHA) coating (decreased sorption) and CNT dispersion (increased sorption). We observed that the sorption coefficients of sulfamethoxazole (SMX) on DHA-suspended CNTs were up to 2 orders of magnitude higher than that on aggregated CNTs. Although the mass percent of suspended CNTs were low (generally less than 1%), their contributions to SMX adsorption were up to 20%. Because DHA and SMX did not interact with each other due to their negative charges, the suspended CNTs may not be completely coated by DHA and they had considerable hydrophobic surface exposed. Importantly, this study provided the first evidence in aqueous phase of the significantly increased surface area of DHA-suspended CNTs relative to the aggregated ones based on ¹H NMR relaxometry measurements. This study emphasizes that in comparison to aggregated CNTs, the suspended ones have amply exposed surface area and thus have greater environmental impacts, such as enhancing the mobility, transport, and possibly exposure of organic contaminants.



INTRODUCTION

Carbon nanotubes (CNTs) are increasingly used as sensors, conductive composites, catalyst supports, and gas storage due to their unique properties of mechanical strength, electrical conductivity, optical activity, hydrogen storage capability, and large surface area.^{1–4} Therefore, they will be inevitably released into the environment via domestic wastewater effluent and/or during their manufacturing, application, and/or disposal, and may become a very important component of the environment.^{5–7} The coexistence of CNTs and dissolved organic matter (DOM) could widely occur in the environment because of the ubiquity of DOM and the increasing application of CNTs. The introduction of hydrophilic functional groups through DOM adsorption on CNTs decreased the hydrophobicity of CNTs⁸ and increased CNT electrostatic repulsion^{9,10} and steric hindrance.^{9,11} Thus, DOM is an effective substance to disperse CNTs.^{8,12,13} The mobility and transport of dispersed CNTs and CNT-adsorbed organic chemicals could subsequently be promoted in natural aqueous environments, potentially enhancing the spread of various organic chemicals and their environmental risk. Most studies reported decreased adsorption in the presence of DOM. For example, DOM coating decreased adsorption of phenanthrene, naphthalene, 1-naphthol, 1,3-dinitrobenzene, 1,3,5-trinitrobenzene,^{14,15} sulfapyridine and sulfamethoxazole,¹⁶ and pyrene¹⁷ on CNTs. The investigators suggested that DOM coating occupied some sorption sites for these tested compounds and

thus decreased the availability of CNTs surface in addition to making CNTs surface less hydrophobic.

A few studies, however, suggested that the dispersed nanoparticles may have higher adsorption than the aggregated ones. For example, Zhang et al. observed that sonication broke down aggregated CNTs and increased pyrene adsorption by up to 1.4 orders of magnitude.¹⁷ Increased atrazine adsorption was observed in DOM-nC₆₀ system at low DOM concentrations (2.5 to 5 mg/L), probably because of the exposed surface sites after dispersion by DOM.¹⁸ Wang et al. also proposed that the enhanced dispersion by DOM may have increased the sorption of phenanthrene, naphthalene, and 1-naphthol on CNTs, but it was offset by DOM coating to reduce the availability of surface sites.¹⁹

On the basis of the above discussion, we could notice that the key information that is missing is the adsorption of organic contaminants on the suspended CNTs. But no study directly reported the adsorption characteristics of the suspended CNTs and their potential importance for the environmental behavior and risk of organic contaminants and CNTs themselves. We thus made special efforts to identify the contribution of suspended CNTs to the overall adsorption. The primary

Received: February 26, 2013

Revised: May 30, 2013

Accepted: June 6, 2013

Published: June 6, 2013

hypothesis of this study is that the dispersed CNTs have more exposed surface area, and their adsorption for other contaminants will increase greatly compared to nondispersed CNTs. The latter part of the hypothesis could be examined by comparing the sorption with or without dispersed CNTs. But the first part of the hypothesis could not be tested using traditional surface area measurement (e.g., N_2 or CO_2 sorption experiment), because the sample-drying process will greatly alter the aggregation status of CNTs. The direct measurement of surface area in aqueous phase would provide the data of accessible surface area in water. 1H NMR relaxometry provided valuable information on pore size distribution in soils,²⁰ wetting,²¹ swelling,²² and polymer adsorption on solid particles^{23,24} through water–solid interactions. A new instrument based on this technique was used to indirectly measure and compare the surface areas of suspended and aggregated CNTs in aqueous phase. An antibiotic, sulfamethoxazole (SMX), was used as the adsorbate in this study because of its negative charge at neutral pH and no interaction with DOM.^{25,26} SMX sorption behavior was investigated on three CNTs dispersed by two types of DOM. This study stresses that the sorption properties of suspended CNTs should be examined extensively because of their exposed surface area. This type of study will benefit both the application of CNTs and their risk assessment.

■ EXPERIMENTAL SECTION

Materials. CNTs used in the study were three multiwalled CNTs (purity >95%) which were hydroxylized (MH), carboxylized (MC), and graphitized (MG), respectively. They were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences. These CNTs were synthesized in the CH_4/H_2 mixture at 700 °C (MG at 2800 °C) by the chemical vapor deposition method. SMX was obtained from Bio Basic Inc. All the other chemicals were higher than analytical grade. All CNTs were characterized for their surface area (Autosorb-1C, Quantachrome) and elemental composition (MicroCube, Elementar, Germany).

Preparation of DOM. A sediment sample was collected in Dianchi Lake (N 24°48'19.22", E 102°39'52.16"), Yunnan province, China. The collected sample was freeze-dried, ground, and sieved through a 2 mm sieve. Plant residues were picked out manually. Humic acid (HA) was sequentially fractionated using traditional alkaline extraction methods.²⁷ The sequentially fractionated HA from a same soil/sediment could be compared more easily than that from different soils/sediments because the extraction from the same source excludes the interference due to different soil/sediment properties or structures. Briefly, 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ were mixed with the soil aggregates (50:1, v:w) to extract HA. After 12 h of equilibration, the mixture was centrifuged at 1000g for 10 min and the supernatant was collected. The extraction procedure was repeated successively, and the sequentially extracted solutions were collected separately. All the extractions were filtered, and HAs were precipitated with HCl. The precipitated HAs were washed using HF three times followed by distilled water until a negative test of chloride using $AgNO_3$, freeze-dried, and ground into <500 μm particles. HAs from the first extraction (HA1) and the forth extraction (HA4) were selected for use in this study. The elemental compositions of these two HAs were all analyzed on an elemental analyzer (MicroCube, Elementar, Germany) as listed in Table S1. They were dissolved in NaOH solution as

dissolved humic acid (DHA) representing DOM. The pH values of these DHA solutions were adjusted to 7 using HCl, and the solution was diluted with background solution (0.02 M NaCl and 200 mg/L NaN_3) to 250 mgC/L as a stock solution. The two DHA solutions were noted as DHA1 and DHA2 which were prepared using HA1 and HA4, respectively.

Distinguishing the Adsorption Contributed by Suspended and Aggregated CNTs. The adsorption behavior of SMX in CNTs–DHA system was examined using a modified experimental design based on traditional batch sorption experiment, with a goal to distinguish the sorption contributed by suspended and aggregated CNTs. Briefly, 40 mL vials containing 20 mg of CNTs and 38 mL of background solution with different concentrations of DHA (0–110 mgC/L) were sonicated at maximum intensity for 90 min (AS 20500BT Ultrasonic Cleaner, Tianjin Automatic Science Instrument Co., Ltd.), and then shaken in an air-bath shaker at 25 °C for 5 d which was sufficient to reach DHA adsorption equilibrium. All the vials were centrifuged at 2000g for 20 min. The dark supernatants contained a significant fraction of suspended CNTs (up to 2.4%), and this DHA-mediated CNT suspension was stable for at least 7 d according to our preliminary study. The upper 50% of the supernatants (19 mL) were then carefully siphoned out and put into other vials. The CNTs–DHA systems were thus divided into suspended CNTs (S system) and suspended CNTs + aggregated CNTs (SA system). The adsorption difference between these two systems was the adsorption contributed by aggregated CNTs. The adsorption behaviors of SMX in both systems were studied using two batches of experiments: (a) SMX adsorption isotherms with various SMX and fixed DHA concentrations (the same suspended CNT concentration), and (b) SMX adsorption as affected by DHA concentrations (fixed SMX concentration but varied DOM and suspended CNT concentrations). According to our preliminary experiment, SMX adsorption on CNTs with sonication did not significantly suspend CNTs, and thus enhanced CNT suspending was solely attributed to DHA. Aliquots of 1 mL SMX solutions with different concentrations were added into all the glass vials (for both experiments a and b). All the vials were kept in the dark and were shaken in an air-bath shaker at 25 °C for 7 d. After equilibrated for 7 d, all the vials were centrifuged at 2000g for 20 min, and the supernatants were subjected to the quantification of suspended CNTs. The supernatants were also filtrated by 0.2 μm filters and subjected to quantification of SMX and DHA. Preliminary experiments indicated that the 0.2 μm filtration could efficiently retain the suspended CNTs but had no effect on SMX and DHA measurements when the filtrate volume was higher than 5 mL. Our previous studies also reported that no interaction between SMX and DHA was observed by dialysis equilibrium experiments and that DHA did not interfere with the quantification of SMX by HPLC.²⁶ Solution pH at equilibrium (around 7.5) was measured by a pH electrode (Leici Instruments, Shanghai, China).

Detection of SMX, DHA, and CNTs. The concentrations of SMX in the supernatants were quantified at 265 nm by high performance liquid chromatography (HPLC, Agilent Technologies 1200) equipped with a reversed-phase C8 column (5 μm , 4.6 \times 150 mm) and a UV detector. The mobile phase was 40:60 (v:v) of acetonitrile and deionized water with 0.1% acetic acid, and the flow rate was 1 mL/min. The detection limits were 0.05 mg/L. The concentrations of suspended CNTs were quantified using a UV–vis spectrometer (Shimadzu UV-2450)

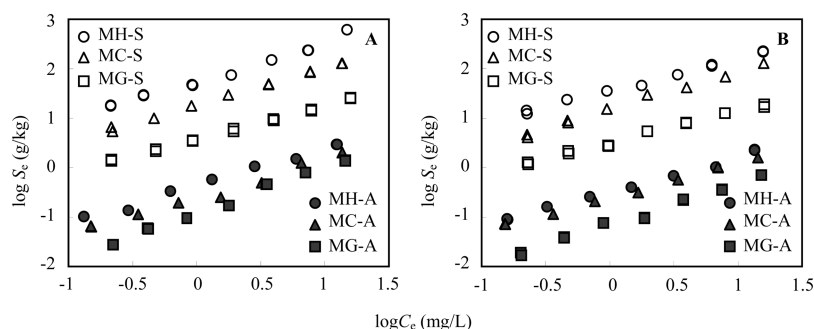


Figure 1. Adsorption isotherms of SMX on suspended and aggregated CNTs as affected by DHA1 (A) and DHA2 (B). The experiments were carried out at initial DHA concentration of 110 mgC/L. The adsorption of SMX on suspended CNTs was much higher than on aggregated CNTs due to newly exposed sorption sites. The suffixes of A and S behind MH, MC, and MG denote aggregated and suspended CNTs, respectively.

Table 1. Fitting Results of SMX Adsorption Isotherms (Figure 1) on Suspended and Aggregated CNTs Using the Freundlich Equation

	K_F [(mg/kg)/(mg/L) ^N]	N	R_{adj}^2	SEE	$\log K_d$ (L/kg) at C_e (mg/L)				
					3.56	35.6	1	10	100
SMX (DHA1-CNT-S) ^a					$\log K_d^S$				
MH	53.95 ± 2.55	0.80 ± 0.03	0.981	0.071	4.62	4.42	4.73	4.53	4.33
MC	18.12 ± 0.28	0.75 ± 0.01	0.998	0.023	4.12	3.87	4.26	4.01	3.76
MG	3.66 ± 0.06	0.67 ± 0.01	0.997	0.025	3.38	3.05	3.56	3.23	2.90
SMX (DHA1-CNT-A) ^a					$\log K_d^A$				
MH	0.43 ± 0.02	0.76 ± 0.02	0.989	0.055	2.50	2.26	2.63	2.39	2.15
MC	0.24 ± 0.01	0.77 ± 0.01	0.978	0.077	2.25	2.02	2.38	2.15	1.92
MG	0.12 ± 0.01	0.95 ± 0.02	0.992	0.054	2.05	2.00	2.08	2.03	1.98
SMX (DHA2-CNT-S) ^a					$\log K_d^S$				
MH	35.00 ± 0.79	0.65 ± 0.02	0.993	0.034	4.35	4.00	4.54	4.19	3.84
MC	14.85 ± 0.39	0.77 ± 0.02	0.994	0.039	4.04	3.81	4.17	3.94	3.71
MG	3.14 ± 0.08	0.65 ± 0.02	0.991	0.038	3.30	2.95	3.50	3.15	2.80
SMX (DHA2-CNT-A) ^a					$\log K_d^A$				
MH	0.32 ± 0.01	0.69 ± 0.02	0.991	0.045	2.33	2.02	2.51	2.20	1.89
MC	0.24 ± 0.01	0.70 ± 0.01	0.996	0.030	2.21	1.91	2.38	2.08	1.78
MG	0.07 ± 0.00	0.83 ± 0.02	0.989	0.055	1.75	1.58	1.85	1.68	1.51

^a“S” and “A” refer to suspended and aggregated CNTs systems, respectively.

at 800 nm according to the method in the references (Figure S1).^{8,12,17} The absorbance at 800 nm was controlled in the range from 0.05 to 0.8 for accurate measurement. The preliminary experiment showed that the effect of DHA on absorbance at 800 nm of suspended CNTs was lower than 3%. DHA concentrations were also analyzed based on the absorbance at 254 nm.^{8,28} The CNTs morphologies were examined using transmission electron microscopy (TEM, JEM-2100). All CNTs samples used for TEM tests were prepared by air-drying a drop of solution containing suspended CNTs or CNTs aggregates onto a copper TEM grid. The accelerating voltage was 200 kV.

¹H NMR Relaxation Measurement of the Aggregated and Suspended CNTs in Aqueous Phase. Previous studies have suggested that monitoring the change of proton spin–spin relaxation time (T_2 , ms) provides important information on the mobility of protons. In the fast exchange limit, a single relaxation rate constant, R_2 is equal to $1/T_2$. The following equation is generally used in processing relaxation data:²⁴

$$R_{2sp} = k\psi(R_{2b}/R_2^0 - 1) \quad (1)$$

where R_{2sp} (ms^{-1}) stands for specific relaxation rate constant and could be calculated as $R_{2av}/R_2^0 - 1$. R_{2av} (ms^{-1}) is the average relaxation rate constant and could be directly measured.

R_{2b} (ms^{-1}) is the NMR relaxation time of liquid (H_2O in this study) on the particle surface. R_2^0 (ms^{-1}) is NMR relaxation time of the free or bulk liquid. ψ is the particle volume to liquid volume ratio, and k is the concentration of solvent bound at the particle surface per unit concentration of particles.

This equation could be reorganized as follows:²⁹

$$R_{2av} = k\psi(R_{2b} - R_2^0) + R_2^0 = \psi SL\rho(R_{2b} - R_2^0) + R_2^0 \quad (2)$$

Thus,

$$S = (R_{2av} - R_{2b})/(\psi K_a) \quad (3)$$

In the above equations, S (m^2/g) is the total surface area per unit weight, L (m) is the surface layer thickness of liquid, and ρ (g/m^3) is bulk particle density. K_a is defined as $L \cdot \rho \cdot (R_{2b} - R_2^0)$.

The ratio of surface area between suspended and aggregated CNTs could be obtained:

$$S_S/S_A = \frac{(R_{2av}^S - R_{2b})(1 - w_S)w_A}{(R_{2av}^A - R_{2b})(1 - w_A)w_S} \cdot \frac{K_a^A}{K_a^S} \quad (4)$$

where w (%) is the weight fraction of solid particles to liquid. The subscripts of S and A indicate suspended and aggregated CNTs, respectively. The detailed derivation of the above equations and the comparison of surface area measured using

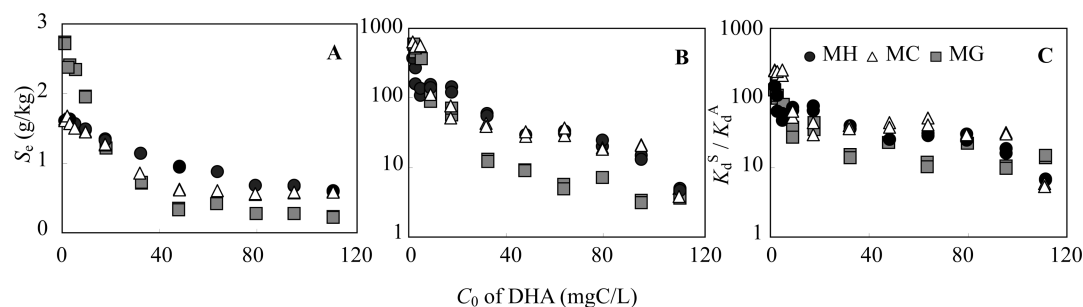


Figure 2. SMX adsorption on aggregated (A) and suspended CNTs (B) as a function of aqueous DHA concentrations. The adsorption coefficients of SMX on aggregated and suspended CNTs were noted as K_d^A and K_d^S , respectively. The comparison of these two coefficients is illustrated as K_d^S / K_d^A (C). The experiments were carried out at initial SMX concentration of 5 mg/L. S_e is the solid-phase concentration. This figure presents the results for DHA1, and the results for DHA2 are provided as Figure S5. K_d^S was 1–2 orders of magnitude higher than K_d^A .

this method and the traditional Brunauer–Emmett–Teller method are presented in the Supporting Information.

The experiment was conducted in 100 MHz NMR tubes with an outer diameter of 5 mm using an Acron area analyzer (XiGo nanotools). DHA-mediated CNT suspension was obtained as described above. The supernatants were filtered, and the filtrates were used as blank samples. The unfiltered supernatant (containing DHA and CNTs) represent suspended CNTs. The filtered supernatants were mixed by hand with aggregated CNTs and then quickly measured representing aggregated CNTs. The parameters for the measurement were as follows: Carr–Purcell–Meiboom–Gill sequence with 275 echo cycles and $\tau = 0.5$ ms, averaging four scans with a recycle delay of 2200 ms. The ratios between the surface areas of suspended and aggregated CNTs were obtained at different DHA concentrations according to eq 4. Each sample had 10 replicate measurements.

RESULTS AND DISCUSSION

Enhanced SMX Adsorption on Suspended CNTs. SMX adsorption isotherms on suspended and aggregated CNTs were obtained in the presence of DHA (Figure 1). These isotherms were well fitted using the Freundlich model, and the fitting results are presented in Table 1. The single-point K_d values were calculated for a better comparison in this study and with literature results. The first observation is that for the same type of CNTs, adsorption of SMX on suspended CNTs (K_d^S) was 1–2 orders of magnitude higher than that on aggregated CNTs (K_d^A) depending on SMX concentration. Our previous study has reported SMX adsorption on CNTs without DOM.²⁵ It could be easily compared that K_d^S values were up to 1.7 orders of magnitude higher (e.g., for MH and DHA1 combination) than the adsorption coefficients of the original CNTs at SMX concentration range of 1–100 mg/L (MH, 2.73–2.84 L/kg). It could also be compared that the K_d^S values for the MH–DHA1 combination were higher than the adsorption coefficients of single-walled CNTs and activated carbon at SMX concentration of 3.56 to 35.6 mg/L.³⁰ Therefore, DHA-suspended CNTs had much higher SMX adsorption than aggregated CNTs.

The K_d^A values (Table 1) were nearly 1 order of magnitude lower than the original CNTs (MH, 2.73–2.84 L/kg).²⁵ This significantly reduced SMX adsorption was observed for all three CNTs by two DHAs (Figures 2 and S7–S9), probably resulting from micropore blockage and direct competition by DHA adsorption on CNTs (on polar functional groups and hydrophobic surface) as discussed in the literature.^{14–16,19,31} The highest SMX adsorption reduction was observed on MG

with the highest hydrophobicity among the three types of CNTs. In addition, the higher hydrophobic DHA2 showed the higher inhibition for SMX adsorption than DHA1. DHA2 is more hydrophobic than DHA1 as suggested by (N+O)/C (Table S1). This result may provide further evidence that SMX adsorption on CNTs was mostly controlled by hydrophobic effect, consistent with our previous results.²⁵

Previous studies have also indicated that the theoretical surface area of CNTs is much higher than the measured values, probably because of their aggregation.^{32,33} Thus, the availability of adsorption sites in aggregated CNTs was low, which was the reason why the adsorption of organic chemicals on CNTs was generally lower than activated carbon.³¹ It was expected that if the surface area in aggregated CNTs could be efficiently exposed, a great potential of CNTs to be used as sorbents to remove organic chemicals would be exhibited. To effectively suspend CNTs may enable very efficient application in adsorption-related engineering activities.

For different CNTs, MH showed the highest adsorption for DHA (Figures S5 and S6, probably because of its largest surface area and more –OH functional groups), while MG was suspended more easily than the other two CNTs (Figure S4, highest suspended amount at the same DHA concentration). Thus, using adsorption capacity of DHA to evaluate CNTs suspension would be misleading. The chemical properties and physical conformation of the adsorbed DHA molecules may play an important role in suspending CNTs as well as their sorption properties, which deserves extended studies. Yang et al. proposed that the adsorbed surfactants formed hemimicelles on CNT surface and favored naphthalene partitioning.³⁴ However, this conformational organization may not contribute greatly to SMX adsorption on suspended CNTs because, if it is the case, SMX adsorption increase should be more distinct at higher DHA loading on suspended CNTs. On the contrary, SMX adsorption increase was less significant at higher DHA loading on CNTs (as discussed in the following section). Thus, the increased SMX adsorption on suspended CNTs should be primarily resulted from the exposed CNT surface.

SMX Adsorption on Suspended and Aggregated CNTs as Affected by Total DHA Concentration. With the increase of DHA concentration, CNT suspension was increased up to 10 mg/L (Figure S4), suggesting the significant role that DHA played in suspending CNTs. Knowing that K_d^S values were up to 2 orders of magnitude higher than K_d^A values, SMX adsorption on both suspended and aggregated CNTs decreased significantly with increasing DHA concentration in solution (Figure 2). It is interesting to note that SMX

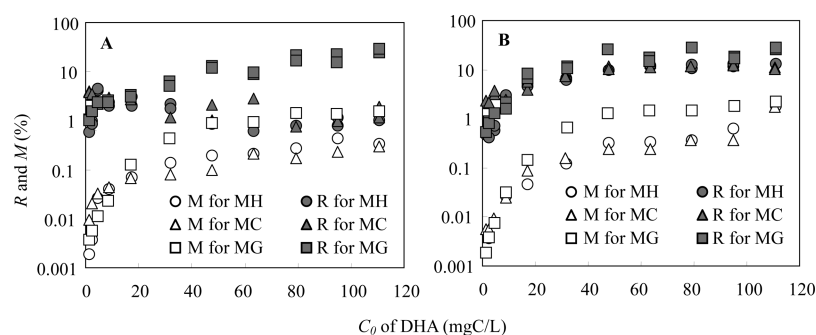


Figure 3. Adsorption contribution of suspended CNTs to the overall SMX adsorption (R , gray solid symbols) and the mass ratio of suspended CNTs to the overall CNTs (M , open symbols) as affected by DHA1 (A) and DHA2 (B). Although the mass ratio of suspended CNTs to total CNTs was low, the contribution of suspended CNTs to overall adsorption of SMX was not negligible.

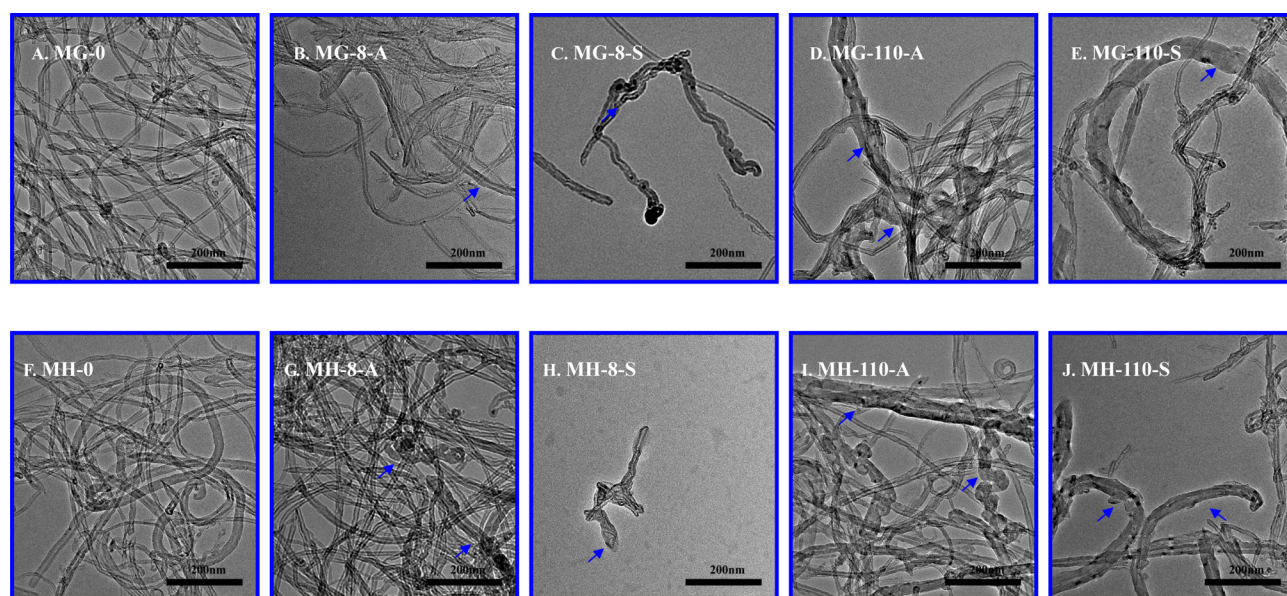


Figure 4. TEM images of CNTs in the background solution without DHA (A, F) and with initial DHA concentrations of 8 mgC/L (B, C, G, H) and 110 mgC/L (D, E, I, J). Hydroxylized multiwalled carbon nanotubes and graphitized multiwalled carbon nanotubes were abbreviated as MH and MG, respectively. “A” and “S” stand for aggregated and suspended CNTs, respectively. Arrowheads indicate the surface of CNTs coated by DHA. The diameter of CNTs increased with increasing DHA concentration due to the coverage of DHA. The single CNTs were easily found for the suspended CNTs samples, but in the aggregated CNTs system, most of the CNTs tended to aggregate together.

adsorption decrease was more significant for suspended CNTs than aggregated CNTs, as suggested by decreased K_d^S/K_d^A ratios with increasing DHA concentrations (Figure 2C). After dispersion, more CNT surface area was exposed to interact with DHA, which consequently resulted in a more decrease of SMX adsorption on suspended CNTs.

The adsorption contribution (R) of suspended CNTs to the overall SMX adsorption and the mass ratio (M) of suspended CNTs to the overall CNTs were calculated and compared (Figure 3). It is important to notice that although the M values were very low (generally less than 1%), the contribution of suspended CNTs to the overall adsorption of SMX was not negligible. For example, at the environmentally relevant DOM concentration (around 20 mgC/L), the K_d^S values were at least 50 times higher than K_d^A . The 0.1% suspended CNTs accounted for up to 10% of the adsorbed SMX, suggesting very high SMX sorption by the suspended CNTs.

Previous studies have indicated that CNT suspension was resulted from complete coating of CNTs by surfactants or DOM.³⁵ Given that SMX does not interact with either DHA in aqueous phase (as showed using dialysis equilibrium system²⁶)

or DHA coated on CNTs (as indicated by nearly 100% inhibition of SMX adsorption on MG by DHA2, Figures S8 and S9), the very high adsorption of SMX on suspended CNTs suggests that the suspended CNTs were not completely covered by DHA. The branches of DHA molecules could greatly enhance the steric repulsion between CNTs, which promoted suspending CNTs without complete coverage.

Enhanced Surface Area of Suspended CNTs. Transmission electron microscopy (TEM) is used to provide direct evidence of CNT morphology because of its easy operation and accessibility. Our TEM observation showed the surface wrapping of CNTs by DHA as suggested by the increased CNT diameter with the increasing DHA concentrations (such as Figure 4C,E). This phenomenon resulted in the increased inhibitive adsorption of SMX with increasing DHA concentrations. In addition, significantly different physical organizations of aggregated and suspended CNTs were observed. For example, single CNTs were easily observed from suspended CNTs samples (panels C, E and H, J of Figure 4). But for aggregated CNTs, most of them were cross-linked and aggregated together (panels B, D and G, I of Figure 4). This

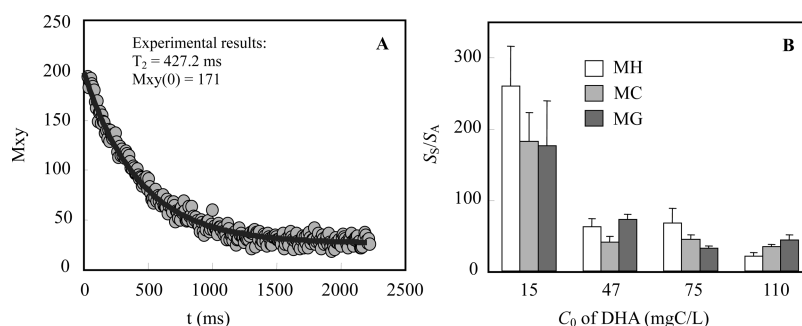


Figure 5. Measurements of CNTs surface area using an Acron Area analyzer. Panel A presents the measurements of MH aggregated at $[DHA] = 15$ mgC/L. M_{xy} refers to transversal magnetization. Panel B shows the S_s/S_A values which were obtained through eq 4. The averages and standard errors of 10 replications are indicated by the bars.

observation provides the evidence for much higher exposed surface area of the suspended CNTs over aggregated CNTs. However, their exposed surface area could not be quantitatively compared, because the microscope-based method focuses on a very small detecting area and thus the observed surface property is fragmental.³⁶ In addition, the dispersed CNTs may be rebundled during the drying process for the TEM measurement (such as in Figure 4E) as discussed by Gotovac et al.³³ Therefore, the surface areas of aggregated and suspended CNTs were evaluated in aqueous phase using a XIGO surface area analyzer.

For CNTs, the K_a in eq 3 is not available yet. Thus, this study avoided the discussion on the exact absolute values of CNT surface area in aqueous phase. As presented in eq 4, if the value of K_a^A/K_a^S could be obtained, the comparison of S_s and S_A is straightforward. The central question becomes if the relaxation rate constant of the bound water (R_{2b}) is comparable for suspended and aggregated CNTs. We assume that K_a^A and K_a^S are similar based on the following two points: (1) The DHA solution did not show significantly different relaxation time compared to bulk water, suggesting that the mobility of water molecules were not greatly decreased after binding with DHA. (2) In a previous study on the coating of polymer on completely dispersed particles (fixed S), increased polymer concentration did not change the slope of R_{2sp} vs ψ (Figure 3 in reference 24) in comparison to bare particles. According to eqs 1 and 2, the slope was SK_a/R_2^0 . The constant S and R_2^0 resulted in constant K_a , which suggested that the introduction of polymer in the dispersion system did not alter the apparent K_a . Therefore, although extended study is needed for K_a comparison, here it is reasonable to consider that K_a^A equals K_a^S , and the following results could be discussed.

The relaxation times (T_{2av}) and thus relaxation rate constants (R_{2av}) were obtained through the measurement as presented in Figure 5A. The mass ratios were calculated based on the experimental design and UV-vis detection of the suspended CNT concentrations. The data collected at lower DHA concentrations were not stable, and thus the results were only presented for DHA concentrations higher than 15 mgC/L. The surface area of the suspended CNTs was 20 to 250 times higher than that of the aggregated CNTs. We expect that the surface area measured in water is more relevant to that measured by N_2/CO_2 (in dry state) regarding CNT sorption properties in aqueous phase. Thus, this measurement provides direct support for our earlier statement that suspended CNTs exposed more sites for SMX adsorption. In addition, the ratios decreased with increasing DHA concentration (Figure 5B), supporting the discussion related to Figure 2C that increased

DHA coating inhibited SMX adsorption and decreased the adsorption difference between aggregated and suspended CNTs.

The above application of surface area measurement in aqueous phase provided the key evidence of the in situ properties of CNTs. This evidence is more reliable than the characterization method involved sample drying. Zhang et al. unexpectedly obtained decreased surface area of CNTs after sonication (breaking CNT sizes from 40 to 500 μm down to 0.6–60 μm). The authors proposed that the newly formed amorphous carbon could block some of the pores during the drying procedure.¹⁷ Knowing the importance of surface area regarding CNT suspending and transport, Zhou et al. compared the surface area-based concentrations in aqueous phase, but they used the surface areas based on N_2 -adsorption measurements.¹³ We expect that the surface areas measured in aqueous phase will also present more useful and relevant information for the data interpretations in the two above-mentioned studies.

Although the apparent SMX adsorption was decreased in DHA–CNTs system, the exposed surface area of the suspended CNTs enabled their sorption 2 orders of magnitude higher than the aggregated ones. Combining our data with the literature results mentioned in the Introduction section, we summarize that the apparent adsorption of organic chemicals in CNT suspending-involved system was balanced between the newly exposed sorption sites and the occupation of sorption sites by the coated DOM. This study emphasizes that the sorption of SMX (most likely many other organic contaminants) on the suspended CNTs is high because of the newly exposed surface area, and that they will have much stronger impact on the environmental behavior of various contaminants. This hypothesis deserves detailed investigations in the near future.

■ ASSOCIATED CONTENT

Supporting Information

Nine figures, two tables, and some discussions are presented in Supporting Information. 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

The authors thank the five anonymous reviewers for their valuable comments. This research was supported by the National Scientific Foundation of China (41222025, 41273138), Program for New Century Excellent Talents in University, Chinese Ministry of Education, Recruitment Program of Highly-Qualified Scholars in Yunnan (2010CI109), a Research Fund for Senior Visiting Scholar at State Key Laboratory of Pollution Control and Resource Reuse (PCRRF11032), and USDA-AFRI Hatch Program (MAS 00978).

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