

Critical Review

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## Adsorption Mechanisms of Organic Chemicals on Carbon Nanotubes

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Carbon nanotubes (CNTs) have drawn special research attention because of their unique properties and potential applications. This review summarizes the research progress of organic chemical adsorption on CNTs, and will provide useful information for CNT application and risk assessment. Adsorption heterogeneity and hysteresis are two widely recognized features of organic chemical–CNT interactions. However, because different mechanisms may act simultaneously, mainly hydrophobic interactions,  $\pi$ – $\pi$  bonds, electrostatic interactions, and hydrogen bonds, the prediction of organic chemical adsorption on CNTs is not straightforward. The dominant adsorption mechanism is different for different types of organic chemicals (such as polar and nonpolar), thus different models may be needed to predict organic chemical–CNT interaction. Adsorption mechanisms will be better understood by investigating the effects of properties of both CNTs and organic chemicals along with environmental conditions. Another major factor affecting adsorption by CNTs is their suspendability, which also strongly affects their mobility, exposure, and risk in the environment. Therefore, organic chemical–CNT interactions as affected by CNT dispersion and suspending merit further experimental research. In addition, CNTs have potential applications in water treatment due to their adsorption characteristics. Thus column and pilot studies are needed to evaluate their performance and operational cost.

### Introduction

Carbon nanotubes (CNTs) have attracted special attention because of their unique properties, such as electrical conductivity, optical activity, and mechanical strength. This fascinating new class of materials has shown promising application in many areas since its discovery. However, CNTs are being spread quickly in the environment because of their growing use (1, 2). Several studies indicate that they are toxic to organisms and human beings (3), and their presence in the environment affects the behavior of pollutants, such as heavy metals as reviewed by Rao et al. (4). Because of their hydrophobic surfaces, strong interactions between CNTs and organic chemicals are expected. Numerous studies suggest CNTs as effective adsorbents for organic chemicals in solid-phase extraction and water treatment after compared with  $C_{18}$  (5, 6) and activated carbon (AC) (7, 8). This strong interaction also greatly alters the mobility, bioavailability, and environmental risk of organic chemicals (9, 10). In

addition, because the structures of CNTs are well defined and their surfaces are relatively uniform in contrast to AC, CNTs are considered to be a good choice to study adsorption mechanisms. Therefore, the understanding of organic chemical–CNT interactions will provide important information on assessing CNT environmental risks and in exploring their applications. Nevertheless, research in this area is still fragmentary and not complete enough for making clear conclusions. An overview of research progress on the interactions between organic chemicals and CNTs is urgently needed. Thus, in this review, we first summarize general features of organic chemical adsorption on CNTs, and then discuss adsorption mechanisms in detail by probing into how the properties of CNTs and organic molecules, coupled with environmental conditions, affect adsorption of organic chemicals by CNTs.

### General Features of Organic Chemical Adsorption on CNTs

**Heterogeneous Adsorption.** Most directly, heterogeneous adsorption indicates that organic chemical adsorption on CNTs could not be described using a single adsorption coefficient. If a single coefficient were used, significant error would occur when predicting the organic chemical–CNT interaction, and would consequently lead to a wrong conclusion regarding the environmental risk of both organic chemicals and CNTs. To date, various models have been applied to describe the adsorption of organic molecules on CNTs in aqueous phases, such as Freundlich (5, 6, 11), Langmuir (7, 8, 12, 13), BET (14), and Polanyi–Manes models (15, 16). Two reasons have been provided to explain the heterogeneous adsorption. The first is the presence of high-energy adsorption sites, such as CNT defects (17), functional groups (18), and interstitial and groove regions between CNT bundles (Figure S1 in the Supporting Information) (19). These adsorption sites commonly exist on as-grown CNTs (20), thus heterogeneous adsorption is a general feature. The second reason is condensation, such as surface and capillary condensation of gas or liquid adsorbates. Multilayer adsorption could occur when organic chemicals were adsorbed on CNT surfaces (21, 22). In this process, the first couple of layers interact with the surface, while molecules beyond the first two layers interact with each other. This process is called surface condensation. The energy of this process varies depending on the distance between the adsorbed molecules and the CNT surface, thus causing a distribution of adsorption energy. The inner pore of an open-end CNT or interstitial area in a CNT bundle forms a hollow column with both ends open. If the pore size follows the Kelvin–Laplace equation,

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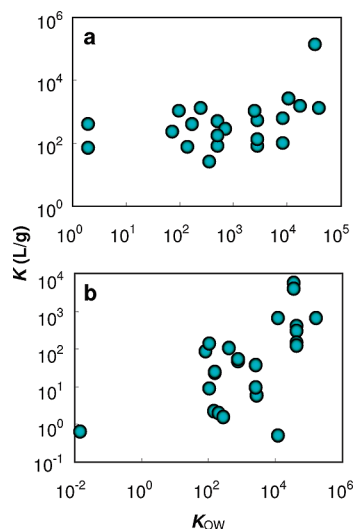
capillary condensation takes place and is responsible for load-dependent adsorption energy and heterogeneous adsorption (23, 24).

Both the aforementioned reasons indicate distributed adsorption energy of adsorption sites. Organic chemicals may occupy high-energy adsorption sites first, and then spread to sites with lower energy (25). This hypothesis indicates concentration-dependent thermodynamics and kinetics. Concentration-dependent thermodynamics has been observed in laboratory studies for organic vapors (11, 23), but has not been studied for the aqueous phase. Researchers also tried to explain prolonged adsorption/desorption kinetics by heterogeneous adsorption sites (26, 27). However, more direct evidence would be concentration-dependent kinetics, which has not been reported.

**Hysteresis.** Adsorption/desorption hysteresis was observed for small molecules (such as organic vapors of methane, ethylene, and benzene) as well as polymers (such as poly(aryleneethynylene)s) on CNTs (28). Hysteresis was presented as deviation of desorption curves from adsorption ones (29) and the absence of adsorbate in the supernatant when CNTs were repeatedly washed using organic solvents (30), buffers (31), or water (32). Real hysteresis is emphasized by conducting recovery tests, verification of equilibrium (29), or direct observation using transmission electron microscopy (TEM) and atomic force microscopy (30, 32). However, a lack of hysteresis was reported for butane (14), PAHs (9), and atrazine (15). Different hysteresis phenomena result in different opinions on CNT-related risk. For example, high adsorption capacity and reversible desorption of organic chemicals on CNTs imply the potential release of organic chemicals after intake by animals or human (9). In this case, CNTs act like pollutant collectors and thus pose high health risk. However, significant adsorption/desorption hysteresis can make CNTs pollutant sinks. This would result in decreased organic chemical mobility, bioavailability, and environmental risk (10). Therefore, proper understanding of hysteresis mechanisms is a key step toward assessing CNT-related risk and application.

Different mechanisms have been proposed to explain the hysteresis, e.g., the strong  $\pi$ - $\pi$  coupling of benzene-ring-containing chemicals with the CNT surface (30, 32) and capillary condensation (23). In addition, alteration of adsorbent structure or reorganization after adsorption has been widely accepted to explain desorption hysteresis for organic chemicals on soils/sediments (33). This explanation is applicable in organic chemical-CNT adsorption systems. For example, CNTs with adsorbed tetra-tert-butylphthalocyanine could be easily dispersed in  $\text{CHCl}_3$ , while the pure CNTs could not (30). This result indicated that the  $\pi$ - $\pi$  bonds between organic chemicals and CNTs disrupted Van der Waals interactions between CNTs and inhibited the formation of bundles. Therefore, the interference of CNT-CNT interactions by adsorption of organic chemicals results in different pathways between desorption and adsorption, which consequently induces hysteresis.

The absence of adsorption/desorption hysteresis was previously observed, which is an exception to the aforementioned mechanisms. When CNTs had few particle-particle contacts (as shown by TEM images in ref 14), CNT bundles were hardly formed and no interstitial regions were available for butane adsorption. The pore condensation accounted for less than 1% of the uptake (14). Therefore, the lack of hysteresis was explained well by the morphology of CNTs during sorption process. In another system, the  $K_{\text{HW}}$  (hexadecane-water distribution coefficient) normalized adsorption coefficients ( $K/K_{\text{HW}}$ ) of PAHs (9) were more than 1000 times lower than those of two estrogens containing phenolic groups (29). The adsorption of PAHs on CNTs may



**FIGURE 1.** Relationships between the adsorption coefficient ( $K$ ) of organic chemicals on SWCNTs (a) or MWCNTs (b) and their  $K_{\text{OW}}$ .  $K$  was calculated at the equilibrium concentration of 100  $\mu\text{g/L}$ . The database for this analysis is provided in Table S1, Supporting Information. More analysis on detailed classification of CNTs is presented in Figures S1 and S2. No explicit relationship between  $K$  and  $K_{\text{OW}}$  was observed indicating that hydrophobic interactions are not the only mechanism for the adsorption of organic chemicals on CNTs.

not be strong enough to disrupt or disassociate CNT bundles, and thus no hysteresis was observed (9).

**Multiple Mechanisms Acting Simultaneously.** The outer surface of individual CNTs provides evenly distributed hydrophobic sites for organic chemicals. Hydrophobic interactions were emphasized in several studies that discussed protein (31), naphthalene (22), acidic herbicides (6), and streptavidin (34) adsorption on CNTs. If hydrophobic interactions are the only mechanism for the interactions between organic chemicals and CNTs, the adsorption can be predicted using the hydrophobic parameters of organic chemicals, such as  $K_{\text{OW}}$  (octane-water distribution coefficient) or  $K_{\text{HW}}$ . If this is the case, fate modeling on the environmental behavior of organic chemicals in the presence of CNTs would be straightforward. However, this is not true for most cases. For example, Chen et al. (35) reported poor correlations between the adsorption affinity and hydrophobicity of several aromatic derivatives. Furthermore, the  $K_{\text{HW}}$  normalized adsorption coefficient varied more than 1000 times for several organic chemicals on CNTs (29). An analysis of literature data also failed to establish a general relationship between  $K_{\text{OW}}$  and adsorption coefficients (Figure 1 and Figures S2, S3, and Table S1, Supporting Information). Thus, hydrophobic interactions cannot completely explain the interaction between organic chemicals and CNTs. Other mechanisms include  $\pi$ - $\pi$  interactions (between bulk  $\pi$  systems on CNT surfaces and organic molecules with C=C double bonds or benzene rings), hydrogen bonds (because of the functional groups on CNT surfaces), and electrostatic interactions (because of the charged CNT surface) (36, 37). Different adsorption mechanisms respond to the change of environmental conditions differently, thus, the relative contribution of an individual mechanism to the overall adsorption is of major importance to predict organic chemical adsorption on CNTs. However, present studies mostly emphasize the importance of individual mechanisms, but never propose a method to quantitatively determine the relative contribution of individual mechanisms. For example, the importance of  $\pi$ - $\pi$  interactions was demonstrated by comparing the adsorption of several carefully selected organic chemicals on CNTs (38) or by comparing the adsorption

before and after a  $\pi$ - $\pi$  system was interrupted (30). However, the authors did not further discuss the quantification of  $\pi$ - $\pi$  bond contribution relative to the overall adsorption. The following method may be considered in order to reveal the relative contribution of a given mechanism:

(1) Normalization of the sorption coefficient by  $K_{\text{HW}}$  may screen out the hydrophobic effect, and thus investigators could focus on factors other than hydrophobicity (35). Although  $K_{\text{OW}}$  has been widely used to describe hydrophobicity, it has been reported to be unsuitable to normalize adsorption coefficients because of the possible interaction between -OH on octanol with organic chemicals (29). Normalization of the adsorption coefficient by  $K_{\text{HW}}$  is probably a better and more reliable method.

(2) A comparison of the adsorption of various organic chemicals on a given type of CNTs will present important information about the contribution of different adsorption mechanisms. For example, sorption comparison of a series of nonpolar chemicals with the same  $K_{\text{HW}}$  but different numbers of  $\pi$  electrons could reflect the contribution of  $\pi$ - $\pi$  interactions. Adsorption of a given organic chemical on CNTs with different extents of oxidation or functionalization should be compared with great caution because oxidation or functionalization changes not only CNT functional groups, but also surface area, surface charge, and CNT hydrophobicity.

(3) More directly, sorption experiments could be conducted in organic solvents. A comparison of the adsorption of a given chemical on CNTs from organic solvents with different polarities could directly derive the relative contribution of hydrophobic effects or other mechanisms (Figure S4). Another benefit for studying adsorption in organic solvents is to ensure reliable detection by keeping the adsorbate concentration well above the detection limit due to high solubility in organic solvents.

## Adsorption Affected by CNT Properties

**Correlation of Adsorption with CNT Physical Properties.** CNT surface areas are normally in the range of  $290 \pm 170$   $\text{m}^2/\text{g}$  (mean  $\pm$  standard error, Table SI) and are generally lower than that of ACs (39). But organic chemical adsorption on CNTs (especially on single-walled CNTs, SWCNTs) is comparable to or even higher than that on ACs (29). Thus, surface area may not be a direct parameter to predict organic chemical-CNT interactions. Su and Lu (7) attributed the higher adsorption of dissolved organic matter (DOM) on CNTs to larger average pore diameter and volume. However, in most studies, CNT porosity could not be applied to explain high adsorption. Decreased CNT diameter increases surface curvature, leading to increased number of multilayers (14), stronger adsorption (16, 40, 41), and increased separation of molecular species in a binary mixture (42). But for molecules with planar structures, adsorption increases with increased diameter because the flat surface results in better contact, such as tetracene (43) and benzene (44). The balance between these two opposite effects deserves further study. Therefore, it seems that neither CNT surface area and porosity, nor diameter alone, could be used to explain CNT adsorption characteristics completely. Adsorption that is affected by other CNT properties, such as morphology and functional groups, will be further addressed in the following sections.

**Morphology of CNTs.** The CNT that contains one layer of a rolled graphite sheet is called SWCNT, whereas several SWCNTs with different diameters concentrically nested together is called multiwalled CNT (MWCNT). The distance between the layers of MWCNTs is too small for any organic molecule to fit into (45). CNTs tend to aggregate together as bundles because of Van der Waals interactions (19). Thus, for an ideal case, the available sorption sites of CNT bundles include the surface area, the interstitial and groove areas formed between the CNTs, and the inner pores of the tubes

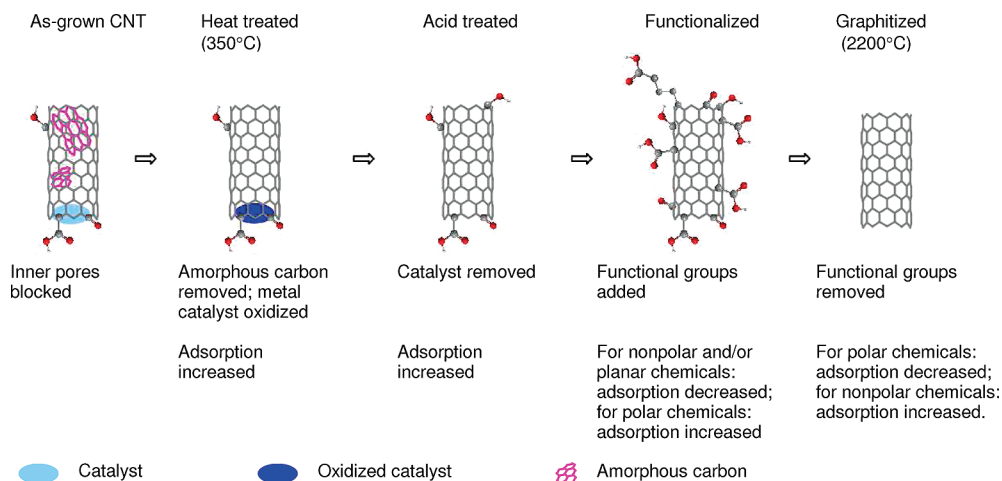
(Figure S1). External surface and groove areas are generally available for adsorption, but the interstitial and inner pores are not. For example, the external surface of SWCNT is the main area for naphthalene adsorption, but the inner pore sites are not due to the dimensional restrictions (22). On the other hand, molecules as big as enzymes were reported to enter the inner pores of CNTs with diameter 3–5 nm (46). The presence of amorphous carbon, functional groups, and metal catalysts could block the inner pores (16). The blocked inner pores can be opened up by acid treatment using HCl to eliminate metal catalysts located at the end of the CNTs (47), or using  $\text{H}_2\text{O}_2$  (21), nitric acid (22), base (48), or heat treatment (563 K in ref 43) to remove the amorphous carbon. The reason for the unavailable interstitial sites is that no bundle was formed (14) or that the organic molecules are too large to fit into this area (45). Thus, the availability of sites for organic chemical adsorption on CNTs is highly dependent on CNT properties as well as their aggregation. Liu et al. (49) observed higher sorption of organic dyes on CNTs in water than in ethanol. However, they mostly discussed the different ionic states of the dyes in different solvents. As the authors presented in their TEM results, most of the dye-functionalized CNT showed debundled structure. Hence, the change of CNT aggregation could be another key factor for organic chemical adsorption.

Another character of CNT morphology is related to the angle between the graphite plane and the tube axis, which determines the chirality of CNTs: zigzag, armchair, and chiral structures. The C-C bonds in graphite are all the same, but C-C bonds in CNTs are different by length and orientation to the tube axis (44). Thus both adsorption energy and the distance between organic chemicals and CNT surfaces could differ between zigzag and armchair tubes of a same curvature (diameter). However, no experiments have been conducted for organic chemical sorption on CNTs with different chiralities.

**Functional Groups of CNTs.** CNTs possibly contain functional groups such as -OH, -C=O, and -COOH depending on the synthetic procedure and purification process. Functional groups can also be intentionally added by oxidation (22) or removed by heat treatment (such as 2200 °C in ref 50). In a well controlled experiment, 3.3–14% surface oxides could be sequentially incorporated on CNTs using nitric acid (39). Ago et al. (51) quantified surface functional groups of acid-oxidized CNT using X-ray photoelectron spectroscopy, and presented that 5, 2, and 7% of the carbon atoms were -C-O-, -C=O, and -COO-, respectively. The air-oxidized CNTs showed higher -C-O- (9%), but lower -COO- (3%) content.

Functionalization of CNTs is aimed for easy processing, but at the same time, their adsorption properties with organic chemicals can be altered greatly. Functional groups can change the wettability of CNT surfaces, and consequently make CNT more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar compounds (13, 50, 52). On the other hand, functional groups may increase diffusional resistance (47) and reduce the accessibility and affinity of CNT surfaces for organic chemicals (39, 53). An overall view of the effect of CNT functional groups on organic molecule adsorption is summarized in Figure 2.

In previous studies, hydrogen bonds (H-bond) have been discussed extensively to understand organic chemical sorption on ACs (54). However, several studies reported that increased oxygen-containing functional groups on ACs decreased the adsorption of chemicals which can form H-bonds (55). These opposite results call for further research on the H-bond mechanism. In addition, water molecules could also form H-bonds with functional groups on ACs, which will either compete with organic chemicals for adsorption sites (54) or form a three-dimensional cluster



**FIGURE 2. Adsorption properties as affected by CNT functional groups.** This figure shows the general trend for the changes of CNT adsorption properties after different treatments. The surfaces of raw CNTs are hydrophobic as demonstrated by the strong preference for adsorption of hydrocarbons (such as hexane, benzene, and cyclohexane) over alcohols (such as ethanol, 2-propanol). Functionalization will lead to increased oxygen content, decreased surface area, and reduced adsorption of nonpolar hydrocarbons due to reduced hydrophobicity, and so do planar chemicals due to insufficient contact between CNT and the chemical. Graphitization will eliminate functional groups, and decrease the adsorption of polar chemicals, but will increase the adsorption of nonpolar and/or planar hydrocarbons.

and block the sorption sites nearby (56). Thus, the H-bond formation between water and AC functional groups could effectively decrease the sorption of organic chemicals. Therefore, the relative H-bond strength of water-ACs to organic chemicals-ACs determines the extent for adsorption of organic chemicals.

Similar arguments apply for organic chemical sorption on CNTs. Although H-bonds are reported unlikely to be a primary interaction mechanism (36, 37), benzene ring on CNT surface may act as H-bond donor and form H-bonds with oxygen-containing functional groups on organic chemicals (57). In addition, H-bonds may play an important role for ionic chemical adsorption on oxidized CNTs. Clearly, further study is required to systematically evaluate H-bonds in organic chemical-CNT interactions. During CNT surface functionalization, purification, or exposure to oxidizing agents after release to the environment, CNTs will eventually be oxidized (39). Therefore, a better understanding of toxicology and adsorption properties of oxidized CNTs is important for CNT environmental risk assessment.

### Adsorption Mechanisms of Different types of Organic Chemicals on CNTs

**Molecular Morphology.** Molecular size and shape determine the availability of different adsorption sites on CNTs. The discussion of the relative size between organic molecules and CNTs applies here, too. Specifically for organic chemicals, larger molecules have higher adsorption energies, and thus larger differences in molecular size result in better separation in a system with mixed chemicals (42). Linear hydrocarbons (42) and planar chemicals (49), especially linear planar chemicals (such as tetracene in ref 58), have a better contact with the CNT surface than other chemicals, and hence show stronger adsorption on CNTs.

The bottleneck for the rate of organic chemical diffusion is also dependent on molecular size. An example is given by slow diffusion of water and ethanol as compared to that of n-hexane (26). Sorption of n-hexane on CNTs reached equilibrium in 20–30 min, while water and ethanol took more than 10 h. This phenomenon may be partially explained by the higher hydrophobicity of hexane as the authors presented. However, their data could be reevaluated because the much higher sorption capacity (more than 10 times higher) for water and ethanol may indicate different avail-

ability of adsorption sites for chemicals with different sizes. For smaller molecules (water and ethanol), the diffusion into inner sites of CNTs can be the rate-limiting process, and could result in extremely low diffusivities. However, bigger molecules (hexane) have a much faster sorption rate because contribution of hexane adsorption in the inner pores is very low.

Molecules, especially the larger ones, can twist themselves so that they match with the curvature surface, thus forming stable complexes with the CNTs (59–61). This molecular reorganization is possible because the adsorption energy can compensate the steric energy required for conformational changes of organic chemicals (29). Wang et al. (30) reported lower decomposition temperature for tetra-tert-butylphthalocyanines after adsorption on CNTs, which is a result of the increased internal energy. A similar result was also reported for L-phenylalanine sorption on CNTs (52), however, the authors attributed the reduced decomposition temperature to the catalysis of CNTs. The geometrical configurations of both chemicals and CNTs affect their interactions. It is reasonable to expect a significant effect of the geometrical configurations of both chemicals and CNTs on their interactions because the surface curvature of CNTs is comparable to the dimensions of organic molecules. However, few studies have yet focused on conformational rearrangement of organic chemicals on CNTs.

**Functional Groups of Organic Chemicals.** Each carbon atom in a CNT has a  $\pi$  electron orbit perpendicular to CNT surface (62). Therefore, organic molecules containing  $\pi$  electrons can form  $\pi$ - $\pi$  bonds with CNTs, such as organic molecules with C=C double bonds or benzene rings, which has been confirmed by experimental data (36, 37, 63), molecular dynamic simulations (64–66), Raman band (58), Fourier transform infrared spectra (43), and nuclear magnetic resonance spectra (28). The most widely recognized influence of organic chemical functional groups on organic chemical-CNT interactions is on the electron-donor-acceptor (EDA)  $\pi$ - $\pi$  interaction, i.e., the strength of  $\pi$ - $\pi$  bond is greatly dependent on the functional groups attached to the benzene-rings for organic chemicals (37). Because CNTs could be viewed as either electron-donors or acceptors, adsorption of either electron-acceptors (such as nitroaromatics in ref 35) or electron-donors (such as phenols in ref 53) on CNTs is expected to be stronger as compared to unsubstituted

aromatic hydrocarbons. In addition, the tendency of a molecule to accept or donate electrons also determines the strength of the  $\pi$ - $\pi$  bond, as in the case with strong charge donors over weak charge donors (such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone over benzene in ref 65). The introduction of carboxylic groups to CNTs made CNTs electron acceptors. Thus increased adsorption of electron donors (such as phenanthrene in ref 43 and BTEX in ref 67), and decreased adsorption of electron acceptors (such as chlorophenol in ref 68) were observed.

Therefore, quantification of EDA strength could provide a valuable parameter to predicting organic chemical-CNT interactions. Zhao et al. (65) used a charge transfer parameter, specifically, the total Mulliken charge number on several molecules, to quantitatively describe the ability of a certain molecule to donate or withdraw electrons. Sone et al. (69) proposed that aromatic compounds with a smaller gap between the highest occupied molecular orbital energy and the lowest unoccupied molecular orbital will have a higher affinity toward CNTs. Both methods seem to be promising to predict the strength of organic chemical-CNT interactions. However, no information is available on how well these theories could explain experimental data. Additional laboratory experiments should be conducted.

Functional groups also greatly determine organic chemical polarity. Because the predominant mechanisms are different for polar and nonpolar chemicals, predictions of their adsorption on CNTs require different models. For example, for polar organic chemicals, the adsorption tends to increase with increased CNT oxygen content because of the enhanced H-bond or EDA interaction. However, for nonpolar chemicals, the adsorption may decrease with increased CNT oxygen content because of the depressed hydrophobic interaction (Figure S4). These opposite trends have not been examined extensively in literature, but could be very important for CNT applications. For example, if CNTs are to be used in water treatment, chemical-specific modification may be needed to improve treatment performance. For the same reason, chemical-specific models may also be needed to predict organic chemical-CNT interactions. The present data are too limited for further discussion on predictive models.

### Adsorption Affected by Environmental Conditions

Environmental conditions have not been widely studied for their impact on organic chemical-CNT interactions. However, a limited number of studies in this area have demonstrated their importance.

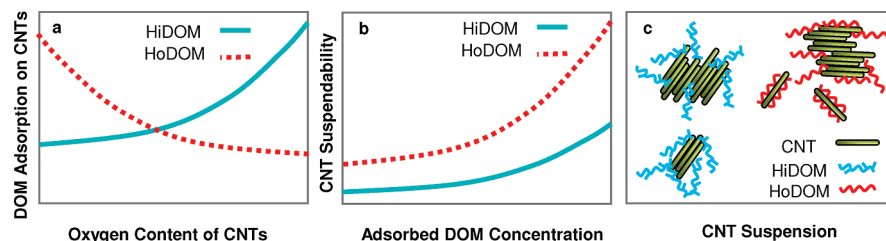
**pH and Ionic Strength.** For ionizable organic chemicals, the variation in pH can result in a change in chemical speciation, consequently altering their adsorption characteristics. Increased pH generally leads to increased ionization, solubility, and hydrophilicity, and thus decreased adsorption of natural organic matter (8, 70), resorcinol (53), and herbicides (6, 71) on CNTs. This type of trend is more obvious for functionalized CNTs compared with graphitized ones, which was attributed to the enhanced formation of water clusters or reduced H-bond formation when CNT carboxylic groups were ionized at elevated pHs (50). On the other hand, increased adsorption with increased pH was also observed and was attributed to enhanced EDA interactions (3, 37). The apparent pH influence on organic chemical adsorption depends on how the increase in attractive forces (e.g., EDA) counteracts the increase of repulsive forces (e.g., charge repulsion) and/or the decline of certain attractive interactions (e.g., H-bond formation and hydrophobic interaction). Valuable data may also be derived by comparing solution pH, the  $pK_a$  of the organic chemical, and the  $pH_{pzc}$  (point of zero charge) of CNTs. Low adsorption would be expected at  $pH > pK_a$  and  $pH_{pzc}$  because both adsorbent and adsorbate are negatively charged and electrostatic repulsion may be

one of the dominant mechanisms. On the other hand, the organic chemical would show high adsorption under conditions with  $pH_{pzc} > pH > pK_a$  because of their electrostatic attraction with CNTs.

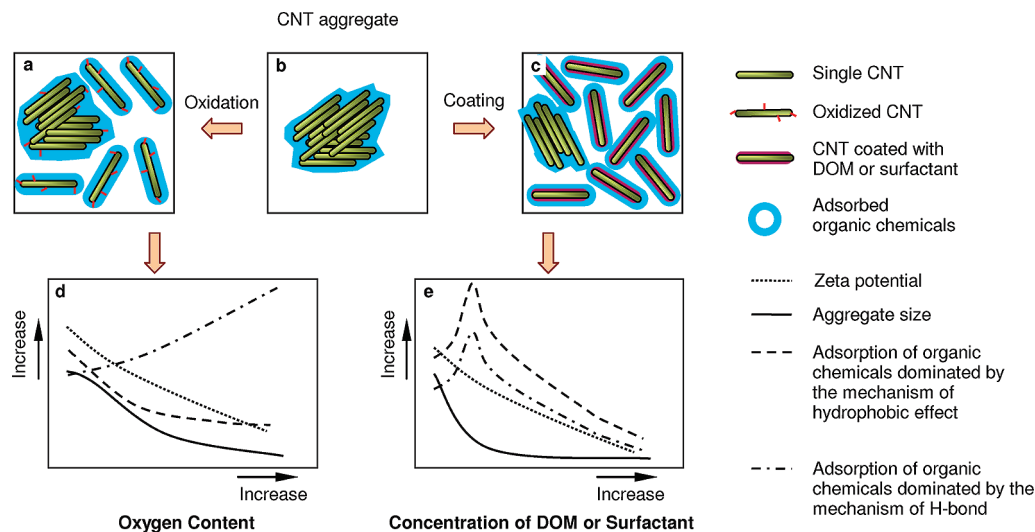
The presence of metal ions can bridge DOM and functional groups on CNTs, compress the double layer, neutralize negative charges of DOM, and thus weaken the repulsion between DOM molecules, and between DOM and CNTs (8, 70, 72). However, several questions remain unanswered. It is still unknown how the adsorption of metal ions alters the aggregation of CNT bundles, which consequently changes CNT adsorption with organic chemicals. Also, adsorption of mixed pollutants (including metals and organic chemicals) has not been widely investigated. The adsorption that is affected by the presence of another organic chemical could be understood from the competition between organic chemicals (73). But the presence of both metals and organic chemicals is a more complicated situation. Studies on wood charcoal adsorption properties have shown that coadsorption of copper ions decreased organic chemical sorption because of the formation of hydration shell (74). However, coadsorption of silver ions increased organic chemical sorption owing to the declined hydrophilicity of the local region around adsorbed silver ions, and thus reduced competitive sorption of water. Similar study on CNTs could provide useful information on organic chemical sorption mechanisms. Although significant effects of ionic strength on CNT adsorption characteristics has not been observed (43, 63), further research is needed, which will facilitate the prediction of organic chemical sorption on CNTs in a real environment.

**Dispersion of CNTs by Surfactants or DOM.** Both surfactants (60, 75, 76) and DOM (7, 77, 78) have been reported to suspend CNTs significantly. Different dispersion mechanisms have been proposed, such as CNT solubilization inside surfactant columnar micelles (79), surfactant or DOM monolayer coatings on CNT surfaces (80), and "unzipping" of CNT bundles (81). Among all these mechanisms, surface coating of surfactants or DOM on CNTs is a key process. Although aromatic carbon content was observed to be proportional to DOM adsorption on CNTs, the amount of stable CNT suspension in aqueous phase did not follow a simple linear relationship with the adsorbed DOM concentration (72). The ability of a certain DOM to suspend CNTs is highly dependent on DOM properties. For example, hydrophobic DOM fraction may suspend CNTs more efficiently than hydrophilic DOM fraction simply because of better contact of the hydrophobic fraction with the CNT surface (Figure 3). This speculation could be easily tested and may serve as a useful theory for effectively dispersing and suspending CNTs.

Organic chemical-CNT interactions could be remarkably altered after CNT suspension. On one hand, the presence of surfactants or DOM could enhance the solubility of organic chemicals, and decrease their adsorption. On the other hand, surfactants or DOM can disperse CNT bundles and make more adsorption sites available for adsorbates, thus increasing the adsorption (82). The net impact depends on the balance of these two opposite factors as summarized in Figure 4. Enhanced adsorption of phenanthrene (21), benzene, toluene, and n-undecane (82) on CNTs after being dispersed by surfactants was observed. The authors concluded that organic chemicals were able to interact more strongly with CNT surfaces in the presence of surfactants than without surfactants because of CNT dispersion by surfactants. Very few studies focused on CNT adsorption properties after being suspended by DOM. Although a humic acid (HA) had much lower sorption for phenanthrene, naphthalene, and  $\alpha$ -naphthol than CNTs, the HA-coated CNTs did not show distinct changes in sorption of these compounds relative to the original CNTs, probably due to the newly exposed sites



**FIGURE 3.** CNT suspension as affected by DOM adsorption. HiDOM (solid line) stands for hydrophilic DOM fraction and HoDOM (dotted line) stands for hydrophobic fraction. Adsorption of HoDOM decreases with increased CNT oxygen content because of the decreased hydrophobicity of CNTs after oxidation. For the same reason, HiDOM follows the opposite trend (a). HoDOM suspends CNTs more efficiently than HiDOM (b) because a better contact between CNT and HoDOM is expected (c).



**FIGURE 4.** Schematic diagram for dispersion of CNTs and their properties. The CNT aggregates can be dispersed after oxidation (a) or after coating with DOM or surfactants (c). Aggregate sizes (solid line) and zeta potentials (dotted line) decrease with increasing oxygen content (d) or DOM/surfactant concentration (e). For the adsorption of organic chemicals on CNTs dominated by hydrophobic effects, the oxidation of CNTs results in a decrease of adsorption because of the increased hydrophilicity of CNT surface. As they are further oxidized, the CNTs are dispersed and more adsorption sites are available, which may result in a slow rate of adsorption reduction (dashed line in panel d). However, for the adsorption of organic chemicals on CNTs dominated by H-bonds, adsorption would proportionally increase with oxygen content (dashed/dotted line in panel d). The adsorption of organic chemicals on CNTs may increase dramatically with the concentration of DOM or surfactant because of DOM fractionation and CNT dispersion (dashed and dashed/dotted lines in panel e). Further increase of DOM or surfactants concentration in solution increases the solubility of organic chemicals strikingly, thus the apparent adsorption would decrease.

from enhanced dispersion as a result of the HA coating (83). Chen et al. (63) observed decreased adsorption of CNTs in the presence of DOM in the aqueous phase. However, no CNT suspension was involved in their study. Future studies need to consider the complexity of organic chemical behavior in an organic chemical–DOM–CNT three-phase system including fractionation of DOM upon adsorption on CNTs, nonideal interactions between organic chemicals and DOM, and disaggregation of CNT bundles.

Dispersed CNTs are stable in various solvents, such as in water, toluene, and chloroform (84, 85). Thus dispersed CNTs and CNT-adsorbed organic chemicals can readily move in environmental media, which would subsequently facilitate the spread of various organic chemicals and thus increase their environmental risk, as expected from CNT's high adsorption capacity. However, previous studies have rarely focused on CNT dispersion in relation to their adsorption with organic chemicals. One of the major reasons could be the difficulty in separating free dissolved organic chemicals from suspended CNTs. Because environmental risks of both CNTs and organic chemicals could be accurately assessed only if free dissolved organic chemicals could be separated and analyzed, proper separation methods need to be developed to study adsorption properties of suspended CNTs. Filtration (72, 78) and/or dialysis systems (86) may be applicable for separation purposes in future studies.

### Adsorption of Organic Chemicals by CNTs in Comparison with ACs

CNTs, especially SWCNTs, have shown to be more efficient adsorbents than ACs and other adsorbents (Table SIII), with higher adsorption capacity (7, 13, 87), shorter equilibrium time (13, 50, 87), higher adsorption energy (88), and easier and more efficient regeneration (7, 8). As presented in Figure S5, SWCNTs generally have higher adsorption coefficients than ACs. For the above reasons, SWCNTs have the potential to be adsorbents for air purification and water treatment. Some studies reported low adsorption capacities of CNTs depending on their properties (27, 89). However, these authors speculate that an important part of CNT surfaces does not participate in adsorption processes (89), and adsorption capacity could be enhanced after proper treatment and processing, e.g., end-opening and functionalization. The unit price for ACs is currently much cheaper than that for SWCNTs, and thus they are widely used in air and water treatment. For the purpose of application in water treatment, numerous experiments have been conducted in column and pilot scales to evaluate ACs performance and operational cost (e.g., ref 90). However, such experiments are not available for CNTs. It should be emphasized that CNTs can be regenerated, maintaining high adsorption efficiency. Thus, they last longer than ACs do. Therefore, the

operational expense for CNTs in water treatment could be lower if they are properly regenerated. However, accurate estimate of these benefits and operational performance warrant investigations.

## Perspectives

Various mechanisms may simultaneously control organic chemical adsorption on CNTs. Each adsorption mechanism may be affected differently by environmental conditions. For example, when H-bonds are the predominant mechanism, increased oxygen-containing functional groups on CNTs would increase the sorption. However, for sorption controlled by hydrophobic interactions, the increased functional groups would decrease the accessibility and affinity of CNTs for organic chemicals. Therefore, it is of great importance to obtain the relative contribution of different mechanisms to the overall sorption in the future. Comparisons between sorption results with or without a given mechanism may clarify the contribution and importance of individual mechanisms. For instance, sorption experiments conducted in aqueous phase complicate the discussion of sorption mechanisms because of the overwhelming hydrophobic effect. Analysis of sorption results obtained from sorption experiments in organic solvents with various polarities may help understand the contribution of hydrophobic effect.

Nearly half of the current studies are theoretical simulations. Theoretical simulations often use vacuum conditions, not as they would behave in the real environment. Therefore, the results from the simulations may hardly be applicable in environmental conditions. More laboratory studies are required to systematically investigate the sorption of organic chemicals with different functional groups, hydrophobicity, and ability to donate or withdraw electrons (e.g., total Mulliken charge number). Also, very limited studies reported the effect of water chemistry on organic chemical sorption on CNTs. Extensive work is needed to examine the pH-, ionic strength-, and DOM-dependent sorption. Special concern should be directed to investigating CNT aggregation in different water chemistry conditions, and the resulting influence on sorption properties.

As more and more CNTs enter the environment during CNT production, application, and disposal, environmental risk posed by CNTs will be controlled by their transport, exposure, and interaction with other pollutants. A better understanding of organic chemical-CNT interaction mechanisms and subsequent environmental behavior of both organic chemicals and CNTs will provide a fundamental basis for the prediction of CNT risk. In addition, being aware of CNT environmental risk helps to develop guidelines for safe design and application of CNTs. Numerous studies have recommended CNTs as alternative adsorbents in water treatment over ACs after batch adsorption experiments, but further work should investigate the performance and operational cost of CNTs in column and pilot scales.

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## Supporting Information Available

Three tables and five figures. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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