

ADSORPTION OF TETRACYCLINE ON SINGLE-WALLED AND MULTI-WALLED CARBON NANOTUBES AS AFFECTED BY AQUEOUS SOLUTION CHEMISTRY

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Abstract—Carbon nanotubes have shown great potential as effective adsorbents for hydrophobic organic contaminants in water treatment. The present study investigated the influence of aqueous solution chemistry on the adsorption of tetracycline to carbon nanotubes. Specifically, the effects of ionic strength (NaCl and CaCl₂) and presence of Cu²⁺ ion (7.5 mg/L) or dissolved soil or coal humic acids (50 mg/L) on adsorption of tetracycline to single-walled carbon nanotubes (SWNT), multi-walled carbon nanotubes (MWNT), and nonporous pure graphite as a model of the graphite surface were systematically estimated. The presence of humic acids suppressed tetracycline adsorption on graphite and MWNT prominently, with stronger effects observed on graphite, but only slightly affected tetracycline adsorption on SWNT. The relatively large humic acid components could not readily access the small interstitial spaces of SWNT and thus were less competitive with tetracycline adsorption. The presence of Cu²⁺ ion increased tetracycline adsorption to both SWNT and MWNT through the mechanism of cation bridging, with much larger effects observed on MWNT. This was probably because when compared with the Cu²⁺ ions complexed on the surface of SWNT, those on the surface of MWNT having larger mesoporous interstices were more accessible to the relatively bulky tetracycline molecule. Increasing the ionic strength from 10 mM to 100 mM decreased tetracycline adsorption on both SWNT and MWNT, which was attributed to electronic shielding of the negatively charged surface sites. These results show that aqueous solution chemistry is important to tetracycline adsorption on carbon nanotubes. Environ. Toxicol. Chem. 2010;29:2713–2719. © 2010 SETAC

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INTRODUCTION

Tetracycline is one of the most commonly used antibiotics in livestock production for disease treatment and growth promotion. Because most antibiotics are poorly metabolized and absorbed by the treated animal body, large fractions are excreted through urine and feces as unmodified parent compound and consequently reach aquatic and soil environments [1–4]. One of the concerns raised by environmental antibiotic residues is the antibiotic resistance propagation in microorganisms [5,6]. The removal of pharmaceutical antibiotics by conventional water and wastewater treatment technologies is generally incomplete [7]. Thus, there is an increasing demand for the development of more effective technologies to treat such emerging organic contaminants.

Carbon nanotubes have shown great promise for many nanotechnology applications, including effective adsorbents for removal of undesirable organic chemicals in water treatment [8–10]. Moreover, the rapid growth in industrial production and use of carbon nanotubes has raised serious concerns over the potential environmental impact of these materials [9,11]. For example, carbon nanotubes released to the aquatic environment might play an important role in the fate, bioavailability, exposure, and reactivity of organic contaminants due to the very strong adsorption affinity and capacity of carbon nanotubes. Thus, understanding the mechanisms and factors controlling the adsorption of organic contaminants to carbon nanotubes is a

crucial issue for both their environmental applications and environmental implications.

Previous studies on sorption of antibiotics, such as tetracyclines and sulfonamides, have mainly involved natural geosorbents, including soils, humic substances, and clay minerals [12–16]. Sorption is primarily driven by the specific mechanisms of cation exchange/bridging and surface complexation reactions (H-bonding and other polar interactions) between the multi-functionalities (amino, carboxyl, and phenol) of the antibiotic molecules and the corresponding interactive sites of the sorbents, while hydrophobic effect is only a minor driving force for sorption. A number of studies have also been performed to characterize adsorption of organic compounds on carbon nanotubes [17–20]. These studies propose a common adsorption mechanism of π - π electron coupling/stacking between the graphite surface of carbon nanotubes and the π -electrons of aromatic compounds such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated benzenes. However, reference papers on adsorption of emerging organic contaminants (antibiotics and hormones) to carbon nanotubes are still very limited [21–24]. It was recently reported that the surface of carbon nanotubes can strongly retain tetracycline because the enone structures and the protonated amino group of tetracycline strongly interact with the polarized electron-rich graphene structures of carbon nanotubes through π - π electron-donor-acceptor (EDA) interaction and cation- π bonding, respectively [21].

Aqueous solution chemistry (pH, ionic strength, and presence of heavy metal ion or dissolved humic substances) is expected to play an important role in adsorption of antibiotics to carbon nanotubes. Because antibiotics often have multifunctionalities susceptible to pH-mediated speciation reactions,

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changing pH can easily affect the adsorbate physiochemical properties (charge and hydrophobicity) and, hence, the adsorptive interactions on the carbon nanotube surface. It has been reported previously that increasing pH suppresses tetracycline adsorption on single-walled carbon nanotubes and graphite because the specific π - π EDA interaction and cation- π bonding are both impeded by dissociation of the protonated groups of tetracycline [21]. Likewise, coexisting heavy metal ions are able to complex with antibiotic functionalities, as well as the surface functional groups of carbon nanotubes, and thus impact antibiotic adsorption on carbon nanotubes. Moreover, adsorption of antibiotics on carbon nanotubes can be prominently influenced by the presence of dissolved humic substances that compete for adsorption sites.

It is quite common for organic contaminants to be present together with a complex suit of dissolved humic substances, heavy metals, and many other ionic species in contaminated water. For example, the concentration of dissolved humic substances in soil pore water can be as high as 100 mg/L [25]. Thus, to better understand the effect of aqueous solution chemistry on adsorption is imperative for exploring carbon nanomaterials as effective adsorbents for the removal of antibiotics in water treatment. However, to our knowledge, few relevant studies have been conducted thus far. In the present study, the batch technique was performed to systematically evaluate the influences of ionic strength (NaCl and CaCl₂) and presence of cosolute of heavy metal ion (Cu²⁺) or dissolved humic acids on tetracycline adsorption to both single-walled and multi-walled carbon nanotubes. Sodium and calcium are predominated cations in soil systems. Copper was selected as a representative heavy metal that is commonly present in aquatic environments.

MATERIALS AND METHODS

Materials

Tetracycline (99%, hydrate) was purchased from International Laboratory and was used as received. Chemical structure and the three acidic dissociation constants (pK_{a} s) are given in Figure 1. Soil humic acids were extracted from a soil collected from Shenyang, Liaoning Province in northeast China using standard methods [26]. Coal humic acids were purchased from Fluka with a further deashing treatment by HCl/HF using the same literature method [26]. Structural characteristics of the

two humic acids have been quantified in detail elsewhere by elemental analysis, solid-state ¹³C nuclear magnetic resonance (NMR), acid-base titration, and Zeta potential measurement [27]. In summary, the soil humic acids are mainly composed of young materials of lignin, carbohydrates and peptides, and oxidized charcoal, while the Fluka coal humic acids primarily consist of poly(methylene)-rich aliphatics with more aromatic C-O and higher negative surface charge.

Nonporous, pure graphite (Aldrich) containing 99.999% graphitized C (as provided by the manufacturer) was used as received. Single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) were purchased from the Nanotech Port Company. Based on the information provided by the manufacturer, SWNT contained >90% (by volume) of carbon nanotubes, and the content of SWNT with outer diameter <2 nm was >50%; MWNT contained >95% of carbon nanotubes, and the sizes of the outer diameter of MWNT ranged from 10 to 30 nm; the length of both carbon nanotubes was between 5 and 15 μ m. The samples of SWNT and MWNT were treated to remove amorphous carbon by heating, and trace metals by sodium hypochlorite under sonication as described elsewhere [28].

Characterization of adsorbents

Surface elemental compositions of carbon nanotubes were determined using an X-ray photoelectron spectrometer (Perkin Elmer PHI 550 ESCA/SAM). Zeta potential (ζ) of carbon nanotubes suspended in 1 mM NaCl solution was measured at different pH (equilibrated for 2 d) using a Zeta potential analyzer (Zeta PALS, Brookhaven Instruments). Surface areas and pore size distributions were characterized by N₂ adsorption/desorption on a Micromeritics ASAP 2020 (Micromeritics Instruments) apparatus at -196°C (77 K). The surface area was determined by the Brunauer-Emmett-Teller (BET) method, and the pore size distribution profile was calculated by the slit Density Function Theory (DFT).

Batch adsorption

The experiments were conducted using a batch approach developed in our previous studies [21,22]. Duplicate samples were performed for the isotherm experiments, and triplicate samples were performed for the ionic strength experiments. To prepare bulk solution of dissolved soil humic acids (DSHA) or dissolved coal humic acids (DCHA), 50 mg of humic acids were dissolved in 5 ml of 0.1 M NaOH, and then mixed with distilled water to reach an apparent concentration of 50 mg/L, corresponding to 25 mg-C/L for DSHA and 22 mg-C/L for DCHA, as measured by a total organic carbon (TOC) analyzer (TOC 5000A). The humic acid solution was adjusted to pH 6.0 with 0.1 M HCl, followed by filtration through a 0.45 μ m membrane. The obtained humic acid solution was then used to prepare an operational background solution containing 0.02 M NaCl. Single-point adsorption of the humic acids on SWNT, MWNT, and graphite was measured separately on the basis of TOC. A weighed amount of CuCl₂ was added to 0.02 M NaCl solution to prepare a background solution containing 7.5 mg/L Cu²⁺. Single-point adsorption of Cu²⁺ on SWNT and MWNT was measured separately using an atomic absorption spectrometer (Thermo Scientific Electro GF95Z). Aqueous background solutions of NaCl and CaCl₂ at concentrations of 0.01 M, 0.02 M, 0.05 M, and 0.1 M were also prepared for the ionic strength experiments.

To initiate the adsorption experiments, a 40-ml amber vial with polytetrafluoroethylene-lined screw cap received a

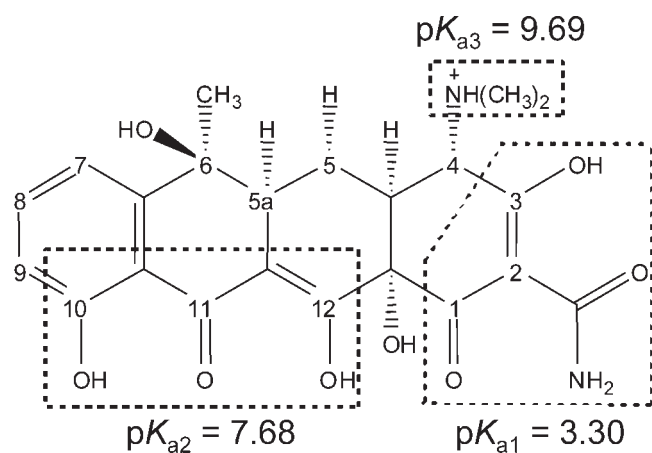


Fig. 1. Chemical structure of tetracycline. The regions framed by dashed lines represent the structural moieties associated with the three acidic dissociation constants pK_{a1} , pK_{a2} , and pK_{a3} adopted from Tolls [4].

weighed amount of adsorbent (30 mg of graphite and 10 mg of carbon nanotubes), followed by aqueous stock solution of tetracycline and a full volume of background solution. The pH of background solution was preadjusted by considering the acid/base-buffering ability of the adsorbent. The samples were covered with aluminum foil to avoid possible photodegradation of tetracycline [29] and mixed end-over-end at room temperature for 3 d. The time was sufficient to reach apparent adsorption equilibrium (no further uptake) based on the adsorption kinetics determined in our previous study [30]. Two replicates were used to characterize adsorption isotherms, and three replicates were used in the ionic strength experiments.

After centrifugation at 2,000 rpm for 10 min, tetracycline in the aqueous phase was analyzed directly by high-performance liquid chromatography (HPLC) with an ultraviolet detector using a 4.6×150 mm SB-C18 column (Agilent). Isocratic elution was performed under the following conditions: 0.01 M oxalic acid–acetonitrile–methanol (80:16:4, v:v:v) with a wavelength of 360 nm. To account for possible solute loss from processes other than adsorbent sorption (sorption to glassware and septum), calibration curves were obtained separately from controls receiving the same treatment as the adsorption samples but no adsorbent. Calibration curves included at least 14 standards over the tested concentration ranges. Based on the obtained calibration curves, the adsorbed mass of tetracycline was calculated by subtracting mass in the aqueous phase from mass added. It should be pointed out that no peaks were detected in the HPLC spectra for possible degraded or transformed products of tetracycline. The sample pH was measured at the end of batch experiments and was 5.0 ± 0.2 .

RESULTS AND DISCUSSION

Characterization of adsorbents

The information of surface elemental compositions and BET surface areas of the adsorbents is summarized in Table 1. The adsorbents are predominantly graphitized C (>91%, dry weight based) on the surfaces; however, a relatively high content of O-containing groups still exist on the surfaces of carbon nanotubes (7.25% for SWNT and 8.34% for MWNT). The pore size distribution profiles (Fig. 2) demonstrate that MWNT contains larger portions of mesopore volumes than SWNT. The Zeta potential (ζ) of SWNT and MWNT as a function of pH is presented in Figure 3. The two carbon nanotubes show similar ζ -pH relationships and are both negatively charged under the tested pH conditions, resulting from dissociation of the acidic surface functional groups. Graphite is expected to have no net surface charge due to the absence of dissociable functionalities.

Table 1. Surface elemental compositions (dry-wt based) and surface areas of single-walled carbon nanotubes (SWNT), multi-walled carbon nanotubes (MWNT), and graphite^a

| Adsorbent | Surface elemental composition ^b | | | Surface area (m ² /g) ^c |
|-----------------------|--|------|-----|---|
| | C% | O% | N% | |
| Graphite | 99.17 | 0.83 | BDL | 4.5 |
| SWNT | 91.18 | 7.25 | BDL | 419.2 |
| SWNT/Cu ²⁺ | ND | ND | ND | 474.4 |
| MWNT | 90.49 | 8.34 | BDL | 130.8 |
| MWNT/Cu ²⁺ | ND | ND | ND | 117.6 |

^a BDL = below detectable level; ND = not determined.

^b Determined by X-ray photoelectron spectroscopy (XPS).

^c Determined by N₂ adsorption using the Brunauer–Emmett–Teller (BET) method.

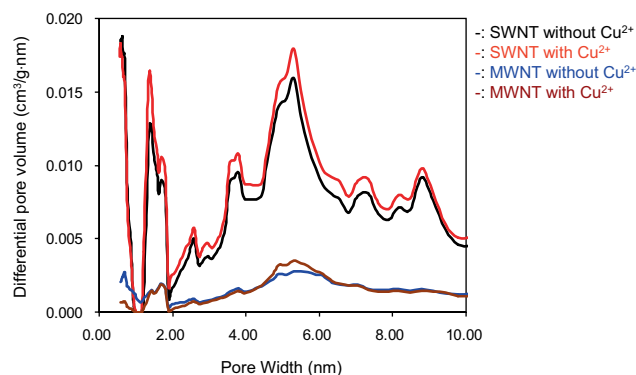


Fig. 2. Pore size distributions of single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) with and without the presence of Cu²⁺ ion.

Adsorption

Adsorption isotherms. Adsorption isotherms of tetracycline on SWNT, MWNT, and graphite are presented in Figure 4. The adsorption data are fitted to the Freundlich model, $q = K_F C_e^n$, by nonlinear regression (weighed on $1/q$), where q (mmol/kg) and C_e (μ mol/L) are the adsorbed concentration and aqueous concentration, respectively, at adsorption equilibrium; K_F (mmol¹⁻ⁿ Lⁿ/kg) is the Freundlich affinity coefficient; n (unitless) is the Freundlich linearity index. The fitting parameters are summarized in Table 2, along with the upper and lower boundary values of the adsorption distribution coefficient (K_d) measured within the examined concentration ranges. The Freundlich model fits the adsorption data reasonably except for the graphite-only condition. For all adsorption data, the linearity index (n) is much smaller than 1, reflecting the high adsorption nonlinearity. Adsorption of tetracycline on the three carbonaceous adsorbents is very strong. Within the examined concentration ranges, the K_d is in the order of 10^4 to 10^6 L/kg for SWNT, 10^3 to 10^5 L/kg for MWNT, and 10^3 to 10^5 L/kg for graphite. Mechanisms of strong interactions (van der Waals forces, π - π EDA interactions and cation- π bonding) with the graphite surface have been proposed to account for the high adsorption affinity of tetracycline on carbon nanotubes and graphite [21]. The graphite

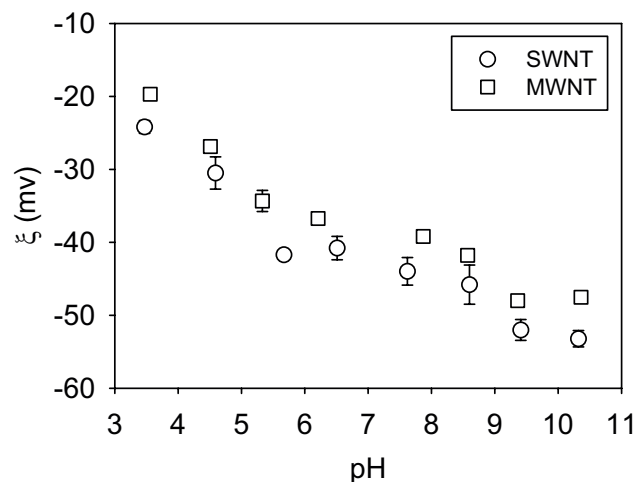


Fig. 3. Zeta potential (ζ) of single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes (MWNT) as a function of pH. Each data point was based on three (MWNT) or four (SWNT) replicate samples. Bidirectional error bars represent standard deviations.

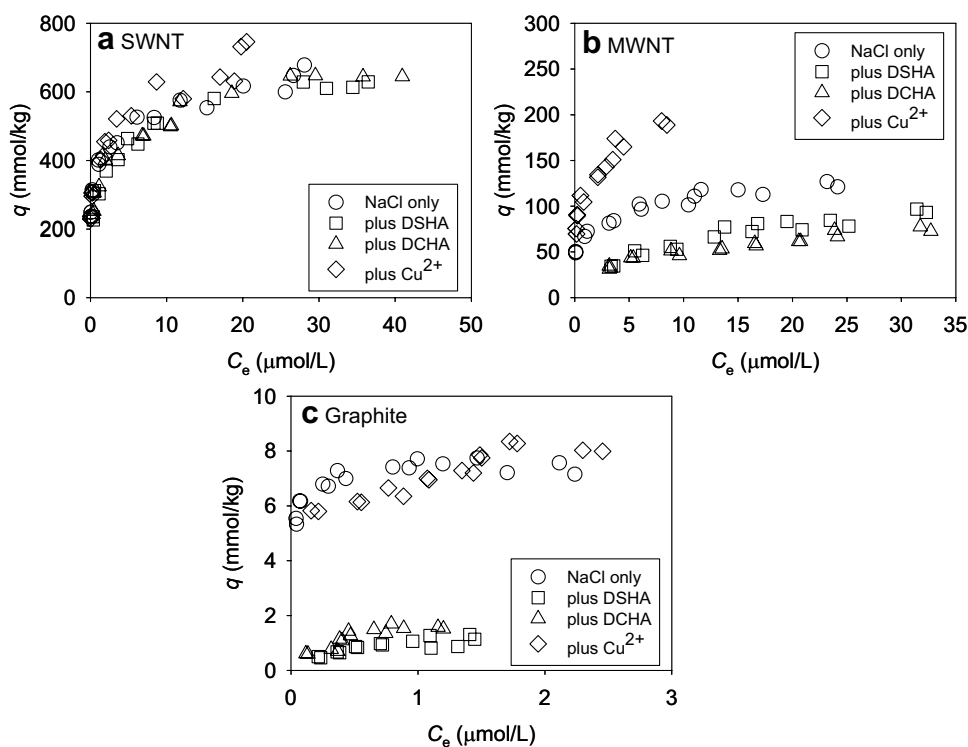


Fig. 4. Adsorption isotherms plotted as adsorbed concentration (q) versus aqueous-phase concentration (C_e) at equilibrium pH of approximately 5.0 under different aqueous solution chemistry conditions: in 0.02 M NaCl only, in the presence of dissolved soil humic acids (DSHA) (initially at 50 mg/L) in 0.02 M NaCl, in the presence of dissolved coal humic acids (DCHA) (initially at 50 mg/L) in 0.02 M NaCl, and in the presence of Cu^{2+} ion (initially at 7.5 mg/L) in 0.02 M NaCl. (a) Single-walled carbon nanotubes (SWNT). (b) Multi-walled carbon nanotubes (MWNT). (c) Graphite.

surface has a very high van der Waals index, and the tetracycline molecule has a planar geometry, giving rise to strong van der Waals forces in adsorption on carbonaceous adsorbents. Due to the strong electron-withdrawing ability of the ketone group, the enone structures of tetracycline (Fig. 1) are considered π -electron-acceptors and may interact strongly with the polarized electron-rich regions (π -electron-donor) on the graphite surface of carbonaceous adsorbents through π - π EDA interactions. Additionally, the protonated amino group of tetracycline may facilitate cation- π bonding with π -electrons on the graphite surface of carbon nanotubes and graphite.

Effect of dissolved humic acids. It is evident from Figure 4 that the presence of DSHA or DCHA decreases tetracycline adsorption on graphite and MWNT markedly, up to about

90 and 50%, respectively. Nonetheless, tetracycline adsorption on SWNT is not much affected by the presence of dissolved humic acids. Despite the structural differences, DSHA and DCHA have similar effects on tetracycline adsorption. Under the tested pH conditions (5.0 ± 0.2), humic acid molecules are negatively charged due to the dissociation of carboxyl groups, and thus may invoke repulsive electrostatic interactions with the same negatively charged carbon nanotube surface. However, the various structural components in humic acids are expected to interact strongly with the graphite surface through van der Waals forces and other specific mechanisms such as π - π electron coupling and H-bonding. As a result, the two dissolved humic acids show high adsorption affinity to the carbonaceous adsorbents, consequently causing competitive effect on tetra-

Table 2. Freundlich model parameters K_F and $n \pm$ standard deviation and adsorption distribution coefficient (K_d) for adsorption isotherms of tetracycline on single-walled carbon nanotubes (SWNT), multi-walled carbon nanotubes (MWNT), and graphite under different aqueous solution chemistry conditions^a

| Adsorbent/conditions ^b | K_F ($\text{mmol}^{1-n} \text{L}^n \text{kg}^{-1}$) | n | R^2 | K_d (L/kg) ^c |
|-----------------------------------|---|-------------------|-------|--------------------------------------|
| SWNT/NaCl only | $1,150 \pm 40$ | 0.162 ± 0.006 | 0.985 | 10^4 – 10^6 |
| SWNT/DSHA | $1,290 \pm 70$ | 0.21 ± 0.01 | 0.973 | 10^4 – 10^5 |
| SWNT/DCHA | $1,300 \pm 60$ | 0.202 ± 0.009 | 0.977 | 10^4 – 10^5 |
| SWNT/ Cu^{2+} | $1,420 \pm 70$ | 0.186 ± 0.008 | 0.977 | 10^4 – 10^6 |
| MWNT/NaCl only | 240 ± 10 | 0.174 ± 0.008 | 0.976 | 10^3 – 10^5 |
| MWNT/DSHA | 410 ± 50 | 0.43 ± 0.03 | 0.946 | 10^3 – 10^4 |
| MWNT/DCHA | 230 ± 20 | 0.34 ± 0.02 | 0.953 | 10^3 – 10^4 |
| MWNT/ Cu^{2+} | 560 ± 50 | 0.23 ± 0.01 | 0.966 | 10^4 – 10^5 |
| Graphite/NaCl only | 12.2 ± 0.8 | 0.074 ± 0.009 | 0.843 | 10^3 – 10^5 |
| Graphite/DSHA | 16 ± 8 | 0.40 ± 0.07 | 0.761 | 10^2 – 10^3 |
| Graphite/DCHA | 40 ± 20 | 0.46 ± 0.07 | 0.809 | 10^3 – 10^3 |
| Graphite/ Cu^{2+} | 20 ± 3 | 0.15 ± 0.02 | 0.839 | 10^3 – 10^4 |

^a DSHA = dissolved soil humic acids at an initial concentration of 50 mg/L; DCHA = dissolved coal humic acids at an initial concentration of 50 mg/L; Cu^{2+} = Cu^{2+} at an initial concentration of 7.5 mg/L.

^b In background solution of 0.02 M NaCl with presence of additional solute (if applied) as noted.

^c Reported as upper and lower boundary values within the examined concentration ranges.

cycline adsorption. The K_d on SWNT, MWNT, and graphite measured from single-point adsorption is $1,500 \pm 200$ L/kg (standard deviation based on four replicates), $1,100 \pm 200$ L/kg, and 120 ± 20 L/kg for DSHA, and $2,000 \pm 100$ L/kg, 900 ± 300 L/kg, and 64 ± 5 L/kg for DCHA, respectively. Consistent results were reported in a previous study [31] that coadsorption of humic acids suppresses adsorption of aromatic compounds on multi-walled carbon nanotubes, and the suppressive effects negatively correlate with adsorbent surface area and microporosity.

One may argue that the suppressed tetracycline adsorption on MWNT and graphite is due to competitive complexation of tetracycline with the free dissolved humic acids in aqueous solutions. This seems reasonable, considering that humic substances bind the tetracycline molecule very strongly through a variety of specific mechanisms, including ligand exchange and complexation reactions such as H-bonding [13,27]. However, this hypothesis can be ruled out by comparing the sorption ratios of tetracycline on the carbonaceous adsorbents versus on the dissolved humic acids as single sorbents. Graphite exhibits the strongest humic acid-suppressed adsorption of tetracycline, and thus is used as an example for the comparison. According to our previous study [27], the K_d for tetracycline sorption to the solid-state humic acids (surrogates for the dissolved form) is in the order of 10^3 L/kg, which is up to two orders of magnitude lower than the K_d for tetracycline adsorption on graphite (Table 2). The difference in magnitudes would be even larger for the carbon nanotubes. Moreover, the difference in adsorption ratio between the two sorbents would become even larger after taking into account the sorbent amount applied (on a mass basis, 30 mg of graphite and maximum 2 mg of dissolved humic acids without abatement from adsorption to graphite). Therefore, compared with adsorbed humic acids, the competitive effect caused by dissolved humic acids on tetracycline adsorption to the carbonaceous adsorbents is considered negligible.

The discrepancies of suppressed tetracycline adsorption between the three carbonaceous adsorbents can be well explained by the accessibility of adsorption sites for humic acids regulated by adsorbent porosity. The entire surface area of nonporous graphite should be available to all sized humic acid components. The available adsorption sites of carbon nanotube bundles mainly include the external surface and the interstitial and groove spaces between individual carbon nanotubes. However, a large portion of the surface area (especially that associated with micropores) of carbon nanotubes is expectedly inaccessible to the large-sized humic acid molecules due to size exclusion. The pore size distribution information (Fig. 2) indicates that MWNT is less microporous than SWNT. Hence, the percentage of surface area available for humic acid adsorption is higher on MWNT than on SWNT. A better illustration of the proposed mechanism can be obtained by comparing surface area-normalized adsorption of humic acids between the three adsorbents. Based on the single-point data, the normalized adsorption of the two humic acids is ordered as follows: graphite \gg MWNT $>$ SWNT, which is in accordance with the observed suppressive effects on tetracycline adsorption. It is also interesting to note that the presence of DSHA or DCHA decreases the nonlinearity of tetracycline adsorption on the three adsorbents (reflected by the enhanced Freundlich n values, Table 2) in the same order as the suppressive effects on adsorption affinity. To take graphite as an example, the Freundlich n value is increased remarkably from 0.074 to 0.40 by coadsorption of DSHA. Humic acid adsorption on the carbonaceous adsorbents blocks certain surface sites and/or narrows the

adsorbent pore size distribution by occupying the large pores. As a result, the heterogeneity of adsorption sites is lessened and, in turn, adsorption becomes more linear.

Effect of Cu^{2+} ion. The effect of Cu^{2+} ion on tetracycline adsorption to the three adsorbents is also shown in Figure 4. In the presence of Cu^{2+} , adsorption to MWNT is doubled; however, adsorption increases only slightly on SWNT and keeps nearly constant on graphite with the presence of Cu^{2+} ion. Recently, it has also been reported that phenol adsorption on N-doped carbon nanotubes is facilitated by preadsorption of Cd^{2+} ion, which is attributed to the alleviated repulsive interaction between phenol and the adsorbent surface due to Cd^{2+} complexation with the surface O-containing groups [32]. In contrast, heavy metal-induced suppressive effects have been shown for adsorption of organic compounds on black carbon (wood-made charcoal and crop residue-burning ash) [33,34]. For example, the presence of Cu^{2+} ion at 50 mg/L decreases adsorption of both polar (2,4-dichlorophenol) and nonpolar compounds (1,2-dichlorobenzene and naphthalene) on highly microporous wood-made charcoals up to 30 to 60%, as measured by changes in K_d [33]. It is proposed that Cu^{2+} complexation with the surface functional groups forms hydration shells of dense water to directly compete with the organics for adsorption surface area.

It is well recognized that coadsorption of multivalent metal ions (Cu^{2+} , Al^{3+} , and Fe^{3+}) can increase tetracycline sorption to humic substances and mineral surfaces considerably through cation bridging between the metal ion and tetracycline and sorbent ligand groups [35,36]. Under the tested pH conditions (5.0 ± 0.2), tetracycline is predominated by the zwitterions which contain deprotonated hydroxyl group and amide group to enable Cu^{2+} ion coordination; in parallel, the surface acidic functional groups (carboxyl and hydroxyl) of carbon nanotubes can strongly bind Cu^{2+} ions through ligand-exchange reactions. Hence, ternary complexes are expected to form between Cu^{2+} ions and tetracycline and carbon nanotube functional groups, resulting in Cu^{2+} -enhanced tetracycline adsorption on the carbon nanotubes. In agreement with the cation bridging mechanism, the presence of Cu^{2+} ion causes negligible effect of tetracycline adsorption on graphite because it is free of surface complexing functionality. Additionally, similar to the two dissolved humic acids, the presence of Cu^{2+} ion also decreases the nonlinearity of tetracycline adsorption on the three adsorbents, but in much less degrees (see the Freundlich n values in Table 2). This is probably because the distribution of adsorption sites for tetracycline becomes less heterogeneous when tetracycline and/or carbon nanotube functional groups coordinate Cu^{2+} ions.

However, the stronger Cu^{2+} -enhanced tetracycline adsorption observed on MWNT than on SWNT cannot be explained by the cation bridging mechanism alone. Notably, the binding affinity of Cu^{2+} to SWNT is higher than that to MWNT; the measured K_d of Cu^{2+} is $3,900 \pm 300$ L/kg (based on single-point adsorption data with five replicates) for SWNT and $1,570 \pm 80$ L/kg for MWNT. Additionally, the differences in surface area (up to 10%) and pore size distribution between the pristine carbon nanotubes and the Cu^{2+} -complexed carbon nanotubes are too small to cause any noticeable effect on tetracycline adsorption. It is proposed that the stronger degree of Cu^{2+} -enhanced adsorption on MWNT is due to the larger mesoporous interstices of MWNT (see pore size distribution data in Fig. 2); therefore, the Cu^{2+} ions complexed on the surface of MWNT are more accessible to the relatively bulky tetracycline molecules. More research is needed to verify the

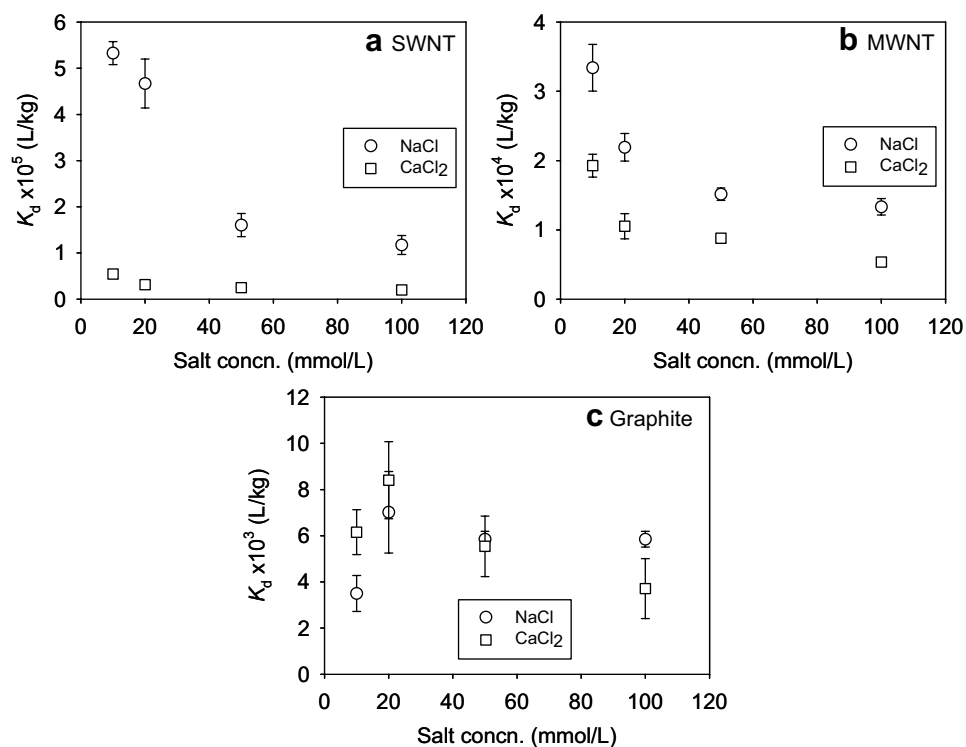


Fig. 5. Effect of ionic strength (NaCl, CaCl₂) on distribution coefficient (K_d) for single-point adsorption at equilibrium pH of approximately 5.0. (a) Single-walled carbon nanotubes (SWNT). (b) Multi-walled carbon nanotubes (MWNT). (c) Graphite. Tetracycline was spiked at 0.10 mmol/L for SWNT, 0.027 mmol/L for MWNT, and 0.0059 mmol/L for graphite. Error bars represent standard deviations from triplicate samples.

underlying mechanisms for the different Cu²⁺ effects on tetracycline adsorption between SWNT and MWNT.

Effect of ionic strength. Figure 5 displays the effect of ionic strength (NaCl, CaCl₂) on tetracycline adsorption on the three carbonaceous adsorbents. Several trends are evident for SWNT and MWNT. First, tetracycline adsorption decreases with the ionic strength (up to 4.5 times, as measured by changes in K_d). Second, given the same ionic strength, tetracycline adsorption is stronger with NaCl than with CaCl₂. Third, the above-mentioned effects are more pronounced on SWNT than on MWNT. An increase in ionic strength would interfere with the electrostatic interactions between the cationized amino group of tetracycline zwitterions (predominated under the tested pH conditions) and the deprotonated carboxyl groups of carbon nanotubes, due to electronic screening of the surface charge sites by the added cation (Na⁺ and Ca²⁺). On the other hand, no clear trend of ionic strength effects is observed for graphite because it has no net surface charge. In previous studies [16,37], a similar mechanism that Na⁺ or Ca²⁺ ions compete for negatively charged sites has been proposed to explain the ionic strength effects observed on sorption of antibiotics (dodecylpyridinium, sulfachloropyridazine, tylosin, and oxytetracycline) to minerals and soils. In contrast with tetracycline, much smaller and inconsistent ionic strength effects have been shown for adsorption of nonionic/anionic compounds such as naphthalene and sulfamethoxazole on carbon nanotubes [22,38]. The results are understandable because the mechanism of attractive electrostatic forces is not applicable for the adsorption of these compounds. Compared with the monovalent Na⁺ ion, the bivalent Ca²⁺ ion causes larger electronic screening effect and, hence, greater suppressed tetracycline adsorption on carbon nanotubes. The cation bridging mechanism proposed for the Cu²⁺-enhanced adsorption is negligible for Ca²⁺, because of its much lower complexing ability than Cu²⁺. The stronger

ionic strength effects observed on SWNT than on MWNT can be attributed to the higher surface charge of SWNT at the tested pH (see the Zeta potential results presented in Fig. 3). However, when compared with other adsorptive interactions (van der Waals forces, π - π EDA and cation- π bonding), the electrostatic forces should be considered only a minor cause for tetracycline adsorption on carbon nanotubes. This is corroborated by the fact that, after normalization to adsorbent surface area, SWNT exhibits even slightly lower adsorption than charge-free graphite as shown in our previous study [21].

CONCLUSION

Previous studies show that carbon nanotubes are promising special adsorbents for the removal of pharmaceutical antibiotics, including tetracycline from water. The present study indicates that aqueous solution chemistry (dissolved humic acids, Cu²⁺ ion, and ionic strength) plays an important role in tetracycline adsorption on carbon nanotubes. The dissolved humic acids (50 mg/L) inhibit tetracycline adsorption on MWNT prominently, but only slightly affect tetracycline adsorption on SWNT; the difference could be attributed to the accessibility of adsorption sites for humic acids regulated by adsorbent porosity. Compared with SWNT, tetracycline adsorption on MWNT is more significantly enhanced by the presence of Cu²⁺. The larger mesoporous interstices of MWNT could make the Cu²⁺ ions complexed on the surface more accessible to the relatively bulky tetracycline molecule. Increasing the ionic strength from 0.01 M to 0.1 M (NaCl or CaCl₂) consistently decreased tetracycline adsorption on SWNT and MWNT, due to electronic shielding of the negatively charged surface sites by the added cation.

In addition to the potential application of carbon nanotubes as special adsorbents in water treatment, the present study

implies that the accidental or incidental release of carbon nanotubes to the environment could greatly affect the bioavailability and toxicity of pharmaceutical antibiotics that exhibit strong adsorption affinity. More research is needed to further understand the impact of aqueous solution chemistry on antibiotic adsorption to carbon nanotubes to advance both potential applications and environmental implications of these materials.

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