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Effects of Cu(II) and Ni(II) ions on adsorption of tetracycline to functionalized carbon nanotubes*

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Abstract: The environmental applications and implications of functionalized carbon nanotubes (CNTs) have received much attention. In this study, the adsorption interactions of graphitized multi-walled carbon nanotubes (G-MWCNTs) and functionalized MWCNTs, including hydroxylated MWCNTs (OH-MWCNTs), carboxylated MWCNTs (COOH-MWCNTs), and aminated MWCNTs (NH_2-MWCNTs), for tetracycline in the aqueous solution were systemically investigated, and the effects of Cu(II) and Ni(II) (two metal ions commonly present in aquatic environments) on MWCNTs-tetracycline interactions were examined. Results showed that the adsorption affinities followed an order of G-MWCNTs>OH-MWCNTs>COOH-MWCNTs>NH_2-MWCNTs, indicating that the adsorptive interactions between MWCNTs and tetracycline can be largely affected by the types and abundance of functionalities on the MWCNTs surfaces. Both Cu(II) and Ni(II) had a negligible effect on the adsorption of tetracycline to G-MWCNTs, but varied effects of the metal ions were observed for the three functionalized MWCNTs. In general, Cu(II) exhibited a more pronounced effect for the adsorption of tetracycline than Ni(II), due to the degree of complexing capability.

Key words: Carbon nanotubes (CNTs), Tetracycline, Adsorption, Complexation
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1 Introduction

The environmental applications and implications of carbon nanotubes (CNTs) have received much attention (Mauter and Elimelech, 2008; Pan and Xing, 2008; Yang and Xing, 2010). CNTs are often chemically functionalized by covalent attachment of functional groups (e.g., –COOH, –OH, and –NH_2) on the π-conjugated skeleton to explore novel structures and surface properties for wider usage (Saito *et al.*, 2002; Sun *et al.*, 2002; Balasubramanian and Burghard, 2005; Tasis *et al.*, 2006; Karousis and Tagmatarchis, 2010). Previous studies have demonstrated that functionalized CNTs can exhibit different adsorption affinities for monoaromatics, such as chlorinated benzenes and phenols, because the introduction of the surface functionalities not only alters the surface hydrophobicity of the CNTs, but also allows non-hydrophobic interactions between CNTs and organic molecules (Chen *et al.*, 2008; Wang *et al.*, 2012). However, so far, previous studies have been focused mainly on contaminants with simple structures, and very limited research has been conducted to systemically evaluate the adsorption of relatively complex organic contaminants to functionalized CNTs.

In aquatic environments, organic contaminants often coexist with heavy metal ions, such as Cu(II) and Ni(II), which are listed as high priority contaminants in the CERCLA Priority List of Hazardous

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Substances (ATSDR, 2013). In our previous study, we found that Cu(II) could serve as a bridging agent between certain organic molecules and the surface functionalities of CNTs, and the bridging effect can significantly enhance the adsorption of chlorinated phenols and 1-naphthylamine (Wang *et al.*, 2012). Note that metal ions may affect the adsorption of organic compounds via various mechanisms and the dominant mechanisms controlling the effect of metal ions of different types may differ significantly for different contaminants.

The main objective of this study was to systematically investigate the adsorption properties of tetracycline onto functionalized multi-walled CNTs (MWCNTs), and to understand the effects of metal ions on the functionalized MWCNTs-tetracycline interactions. Tetracycline is a commonly used antibiotic in livestock production for disease treatment and growth promotion (Halling-Sørensen *et al.*, 1998; Hirsch *et al.*, 1999; Luo *et al.*, 2011), and the amphoteric molecule has multiple ionizable groups/moieties (e.g., phenol, amino, and enone) which are capable of polar interactions at environmentally relevant pH values (Ji *et al.*, 2010a; 2010b; Li *et al.*, 2010; Sun *et al.*, 2010; Zhang *et al.*, 2011; Zhao *et al.*, 2011; Gao *et al.*, 2012). Functionalized MWCNTs, including hydroxylated MWCNTs (OH-MWCNTs), carboxylated MWCNTs (COOH-MWCNTs), and aminated MWCNTs (NH_2-MWCNTs), were used, and graphitized MWCNTs (G-MWCNTs) were included as additional adsorbents for assessing the roles of the graphene structure in adsorption. Moreover, Cu(II) and Ni(II) ions, two metal ions commonly existing in aquatic environments, with different complexation abilities with tetracycline were selected as the model metal ions. The predominant adsorption mechanisms of tetracycline on the functionalized MWCNTs were analyzed, and the mechanisms controlling the effects of Cu(II) and Ni(II) on the adsorption of tetracycline were discussed to better understand the underlying adsorption mechanisms.

2 Materials and methods

2.1 Materials

Tetracycline (99%, hydrate) was purchased from Sigma-Aldrich and was used as received. The chemical structure and the three acidic dissociation constants (pK_a) of tetracycline are given in Fig. 1. Analytical-grade $CuCl_2$ and $NiCl_2$ were purchased from VICTOR Co. (Tianjin, China).

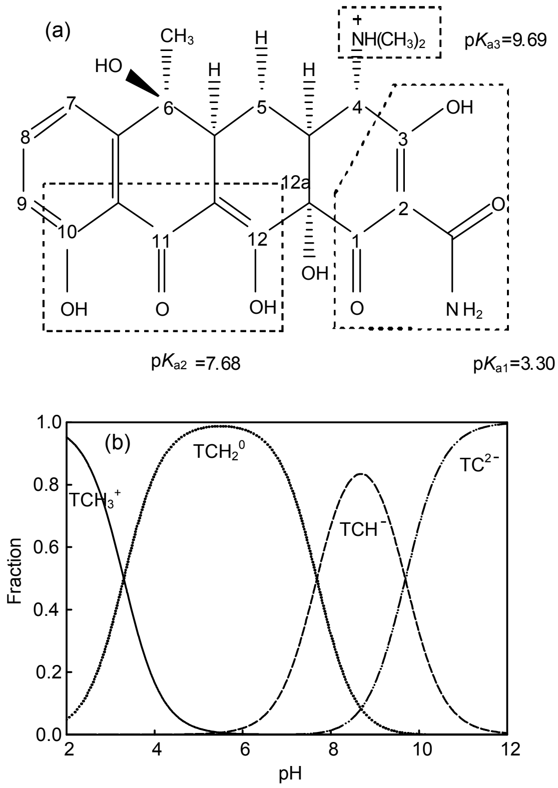

Fig. 1 Chemical structure of tetracycline (a) and pH-dependent speciation of tetracycline (TC) (b)

The framed regions represent the structure moieties mainly existed associated with the three acidic dissociation constants

Functionalized and graphitized MWCNTs were purchased from Chengdu Organic Chemicals Co. Ltd. (China). Based on the information provided by the manufacturer, G-MWCNTs was obtained by treating high-purity MWCNTs in an inert gas at 2800 °C for 20 h; OH-MWCNTs and COOH-MWCNTs were obtained by oxidizing high-purity MWCNTs with $KMnO_4$ in H_2SO_4 solutions at different acid concentrations and temperature; NH_2-MWCNTs were obtained by first covalently amidating COOH-MWCNTs with ammonium hydroxide and then decarboxylating the product at high temperature. G-MWCNTs contained more than 99.9% (in weight) MWCNTs and less than 0.1% impurities (mainly ash); OH-MWCNTs, COOH-MWCNTs, and NH_2-MWCNTs contained more than 95% MWCNTs and less than 5% impurities. The outer diameters of the MWCNTs ranged from 8 to 15 nm, and the average length was approximately 50 μm.

The Brunauer-Emmett-Teller (BET) specific surface area of the MWCNTs was determined by multipoint N_2 adsorption-desorption using a Micromeritics ASAP2010 accelerated surface area and porosimetry system (Micromeritics Co., USA). The Boehm titration method was used to determine the concentrations of the surface acidic and basic functional groups of the MWCNTs, and the pH drift method was used to determine the point of zero charge (pH_{pzc}). Selected physicochemical properties of the MWCNTs are summarized in Table 1. Ultraviolet (UV) spectra analysis was performed with a UV-Vis spectrophotometer (Shimadzu Scientific Instruments UV-2401).

2.2 Batch adsorption experiments

The experiments were conducted using a batch approach developed in our previous studies (Chen W., *et al.*, 2007; Wang *et al.*, 2008; Ji *et al.*, 2009). Prior to initiating an adsorption experiment, 10 mg MWCNTs were transferred to a 40 ml amber glass vial and pre-wetted for 24 h with a certain volume of electrolyte solution containing 0.02 mol/L NaCl. Subsequently, a predetermined amount of stock solution of tetracycline was added. The vial was then filled with the electrolyte solution to leave minimal head space, covered with aluminum foil, and mixed end-over-end at room temperature for 7 d (the time required to reach adsorption equilibrium was predetermined). After equilibrium was reached, the samples were left undisturbed on a flat surface for more than 24 h to allow complete settling of the MWCNTs, and the supernatants were withdrawn to analyze the concentrations of tetracycline. To account for the losses from processes other than adsorption (i.e., adsorption to glass vials and other possible interactions in solution), calibration curves were conducted separately from controls receiving the same treatment as the adsorption samples but without MWCNTs. Calibration curves included at least ten standards over the test concentration range. Based on the obtained calibration curves, the adsorbed mass of compounds were calculated by subtracting the mass in aqueous solution from the mass added. Each adsorption data point was run in duplicate.

In the experiments involving Cu(II) and Ni(II), an aqueous stock solution of Cu(II) and Ni(II) was added to the vial immediately before adding the stock solution of tetracycline, to give a final concentration of 0.1 mmol/L for Cu(II) and Ni(II). The concentrations of Cu(II)/Ni(II) and tetracycline used in the present study were selected to represent contamination cases under which relatively high concentrations of Cu(II), Ni(II) and/or tetracycline can be present.

2.3 Analytical methods

Tetracycline in the aqueous phase was analyzed by reverse-phase high performance liquid chromatography with a UV detector at 360 nm using a 4.6 mm×150 mm SunFire-C18 column (Waters); the mobile phase was a mixture of oxalic acid-acetonitrile (85:15, in volume) at a flow rate of 1 ml/min. Except for the peak of tetracycline, no other peaks were detected in the chromatograms, indicating no potential degraded or transformed products of tetracycline.

3 Results and discussion

3.1 Characterization of MWCNTs

The surface elemental compositions, BET specific surface area, data of surface acid, and base groups of G-MWCNTs, OH-MWCNTs, COOH-MWCNTs, and NH_2-MWCNTs are given in Table 1. The results show that the surface oxygen contents of both G-MWCNTs and NH_2-MWCNTs were very low (1.8%), whereas

Table 1 Selected physicochemical properties of MWCNTs

MWCNT	Content (%)			Amount (μmol/g)				pH_{pzc}	BET specific surface area (m^2/g)
	C	O	N	Lactone	–OH	–COOH	Basic groups		
G-MWCNTs	98.2	1.8		28.1	9.4		61.9	5.2	146
OH-MWCNTs	94.1	5.9		31.9	86.3	159.4	43.1	3.3	160
COOH-MWCNTs	97.0	3.0		28.1	3.8	103.1	41.3	3.5	185
NH_2-MWCNTs	97.7	1.8	0.5				136.9	9.8	155

OH-MWCNTs and COOH-MWCNTs contained a greater amount of surface oxygen (5.9% and 3.0%, respectively). Upon the ammonium hydroxide treatment, the NH_2-MWCNTs contained 0.5% of surface nitrogen. The Boehm titration results are also consistent with the amount of surface functionalities. G-MWCNTs contained only small amounts of lactone (28.1 μmol/g) and –OH (9.4 μmol/g). OH-MWCNTs contained the greatest amounts of surface O-functionalities, with high concentrations of –OH (86.3 μmol/g) and –COOH (159.4 μmol/g). COOH-MWCNTs contained much smaller amounts of O-functionalities than OH-MWCNTs, mainly in the form of –COOH (103.1 μmol/g). The Boehm titration results also indicated that a significant amount of amino groups were introduced to the surface of NH_2-MWCNTs, whereas the surface acid groups of NH_2-MWCNTs were negligible. The pH_{pzc} values of G-MWCNTs, OH-MWCNTs, COOH-MWCNTs, and NH_2-MWCNTs (determined using the pH-drift method) were 5.2, 3.3, 3.5, and 9.8, respectively, indicating that the surfaces of these four MWCNTs could possess different net charges under common environmental conditions.

3.2 Adsorption on G-MWCNTs and functionalized MWCNTs

Adsorption isotherms of tetracycline on the four MWCNTs are shown in Fig. 2, and adsorption isotherms of tetracycline in the absence and presence of Cu(II) or Ni(II) are shown in Fig. 3. The adsorption data were fitted to the Freundlich sorption model: $q=K_\mathrm{F}C_\mathrm{W}^n$, where q (mmol/kg) and C_W (mmol/L) are the solid-phase and aqueous-phase concentrations at adsorption equilibrium, respectively, K_F ($\mathrm{mmol}^{1-n}\mathrm{L}^n$/kg) is the Freundlich affinity coefficient, and n (unitless) is the Freundlich linearity index. The model fitting parameters are summarized in Table 2. In general, the Freundlich model fits the adsorption data reasonably, and for all MWCNTs, adsorption of tetracycline is highly nonlinear. Moreover, the fitted Freundlich linearity index values of tetracycline become even smaller in the presence of Cu(II) or Ni(II), indicating a highly heterogeneous distribution of the adsorption sites for tetracycline. To better compare the adsorption affinities of tetracycline on the four MWCNTs, the BET surface area normalized adsorption isotherms of tetracycline are plotted in Fig. 2. The adsorption affinities followed the order G-MWCNTs>OH-MWCNTs>COOH-MWCNTs>NH_2-MWCNTs. This trend correlated poorly with the hydrophobicity, O/N-content, or with the density of acidic/base groups of the MWCNTs.

The tetracycline molecule can interact with the functionalized MWCNTs via several mechanisms, including van der Waals forces, π-π electron donor and acceptor (EDA) interactions (between the conjugated enone structures of tetracycline and the MWCNTs graphene surfaces), and cation-π bonding interactions (between the protonated C4 dimethyl ammonium group of tetracycline and the MWCNTs graphene surfaces) (Ji *et al.*, 2009; 2010a; 2010b). The large differences in adsorption affinities of tetracycline observed between G-MWCNTs and the three functionalized MWCNTs were probably caused by differences in surface properties among the MWCNTs, in particular the types and abundance of the surface functional groups on the MWCNTs. For G-MWCNTs, the adsorption was the strongest,

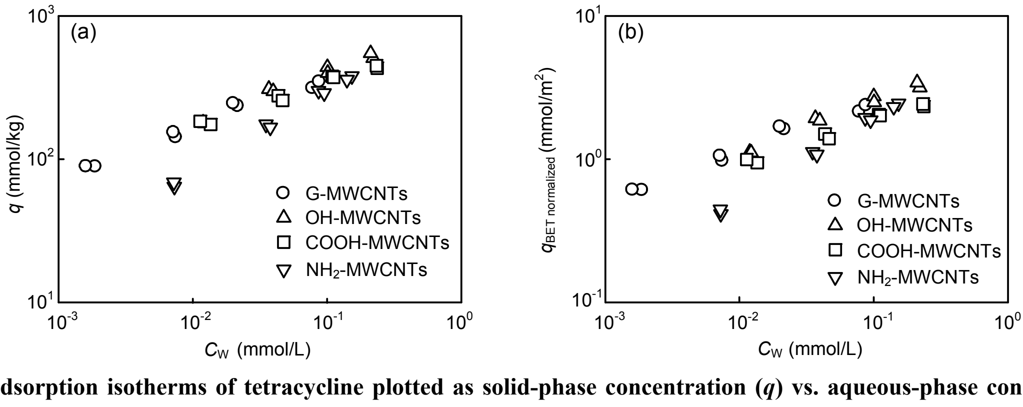

Fig. 2 Adsorption isotherms of tetracycline plotted as solid-phase concentration (q) vs. aqueous-phase concentration (C_W) at adsorption equilibrium with different MWCNTs

(a) q on unit mass basis; (b) q on unit surface area basis

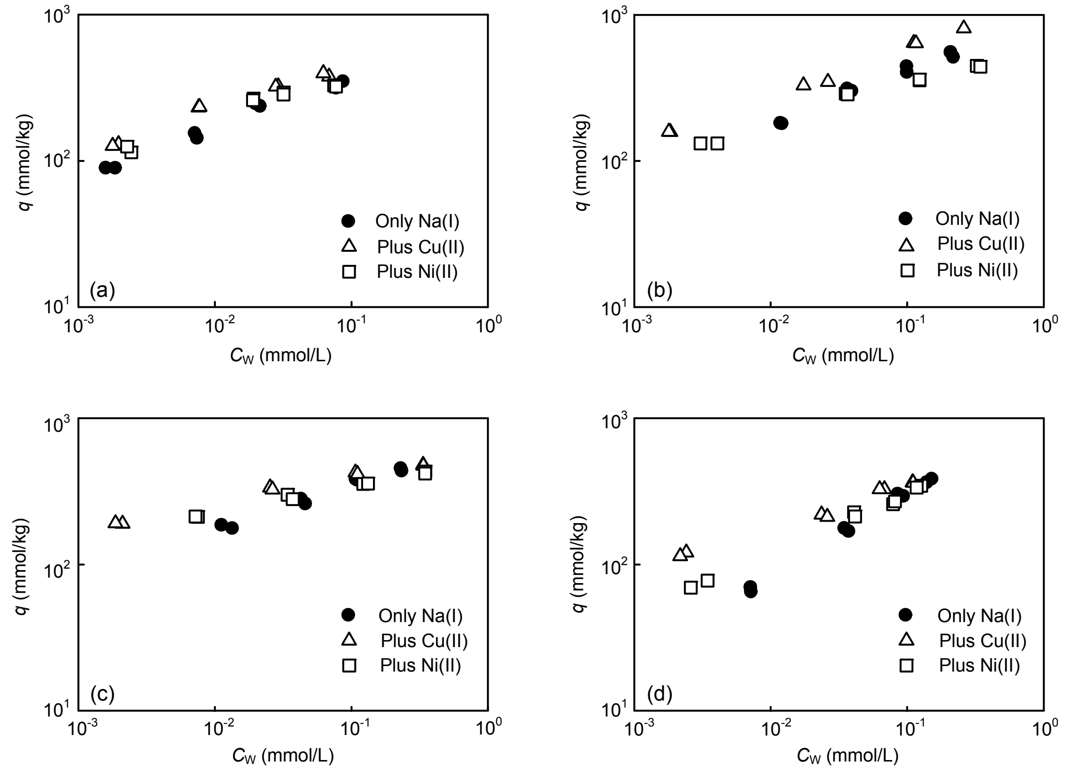

Fig. 3 Adsorption isotherms of tetracycline plotted as adsorbed concentration (q) vs. aqueous-phase concentration (C_W) in electrolyte solution containing 0.02 mol/L NaCl only, and in the presence of Cu(II) or Ni(II) (initially at 0.1 mmol/L)

(a) G-MWCNTs; (b) OH-MWCNTs; (c) COOH-MWCNTs; (d) NH_2-MWCNTs

Table 2 Summary of Freundlich model coefficients (K_F and n) obtained from tetracycline adsorption results

Adsorbent	Metal	pH	K_F (mmol^{1-n}L^n/kg)	n	R^2	lgK_d
G-MWCNTs	Na	6.0–6.5	750±70	0.32±0.03	0.9716	3.59–4.74
	Plus Cu	4.4–5.3	840±70	0.28±0.02	0.9738	3.74–4.85
	Plus Ni	4.7–5.5	660±80	0.25±0.03	0.9351	3.61–4.75
OH-MWCNTs	Na	5.2–5.4	910±60	0.35±0.03	0.9764	3.36–4.18
	Plus Cu	4.1–4.4	1290±50	0.34±0.01	0.9949	3.49–4.95
	Plus Ni	4.7–5.1	590±20	0.24±0.02	0.9800	3.14–4.63
COOH-MWCNTs	Na	5.4–5.8	700±30	0.30±0.02	0.9790	3.26–4.21
	Plus Cu	4.3–4.6	590±20	0.17±0.01	0.9805	3.15–4.95
	Plus Ni	4.7–5.2	510±10	0.18±0.01	0.9911	3.08–4.47
NH_2-MWCNTs	Na	5.8–6.2	1090±70	0.56±0.03	0.9937	3.40–3.98
	Plus Cu	4.3–5.0	740±50	0.31±0.02	0.9838	3.51–4.72
	Plus Ni	5.0–6.0	790±60	0.41±0.03	0.9879	3.44–4.42

R: correlation coefficient; $K_d=q/C_W$

which was probably because the graphene surfaces of G-MWCNTs possess an original honeycomb structure (Tasis *et al.*, 2006), and thus π-π EDA interactions and cation-π bonding interactions with it were more pronounced. For OH-MWCNTs and COOH-MWCNTs, both of them have relatively high contents of surface O-functionalities. The –OH and –COOH groups on these two MWCNTs can be partially dissociated (as indicated by the much lower pH_{pzc} values than that of G-MWCNTs), making the two MWCNTs surfaces more negatively charged. Consequently, the electrostatic attractions between the protonated C4 dimethyl ammonium group of tetracycline and the negatively charged MWCNTs surfaces may enhance tetracycline adsorption. As seen from Fig. 2, the electrostatic attraction may also explain the slightly higher adsorption affinities of OH-MWCNTs compared with COOH-MWCNTs, because OH-MWCNTs contain a greater amount of surface O-functionalities and have a lower pH_{pzc} value. However, the fact that adsorption affinities of OH-MWCNTs and COOH-MWCNTs were still much weaker than those of G-MWCNTs indicates that the electronic attraction force was not strong enough to compensate for the disruption of the honeycomb-lattice structures of MWCNTs caused by the covalence of surface O-functionalities. Within the test concentration ranges of tetracycline, the adsorption to NH_2-MWCNTs was the weakest, especially at relatively low concentrations. For example, at an equilibrium tetracycline concentration of 7 μmol/L (3.1 mg/L), the adsorption affinity of tetracycline on NH_2-MWCNTs is more than two times weaker than on G-MWCNTs. This weakened sorption affinity was probably caused by two factors. First, the existence of N-functionalities on the surface of NH_2-MWCNTs could disrupt the band-to-band transitions of π electrons, so accordingly, the π-electron conjugating potential becomes much weaker (Tasis *et al.*, 2006). Second, electrostatic repulsion between the positively charged surface sites on NH_2-MWCNTs and the positively charged C4 dimethyl ammonium group of tetracycline could act as a suppressive factor inhibiting tetracycline adsorption.

Note that very different adsorption patterns to the same four MWCNTs were observed for 1,1,2,2-tetrachloroethane in our recent studies (Chen *et al.*, 2014). The adsorption affinities followed the order G-MWCNTs/NH_2-MWCNTs>COOH-MWCNTs>OH-MWCNTs, which is consistent with the surface hydrophobicity of the MWCNTs. This observation suggested that the hydrophobic effect seems to play the dominant role in the adsorption of 1,1,2,2-tetrachloroethane related hydrophobic organic contaminants on both G-MWCNTs and functionalized MWCNTs.

3.3 Adsorption in the presence of Cu(II) and Ni(II)

In Fig. 3, the adsorption isotherms of tetracycline to the four MWCNTs in the absence and presence of Cu(II) or Ni(II) (initially at 0.1 mmol/L) are compared to understand the effects of metal ions on tetracycline adsorption. Interestingly, different influence trends were observed. As shown in Fig. 3, Cu(II) and Ni(II) had a negligible effect on the adsorption of tetracycline by G-MWCNTs. For OH-MWCNTs, the adsorption affinity of tetracycline was increased in the presence of Cu(II), but was slightly decreased in the presence of Ni(II). For COOH-MWCNTs, the adsorption of tetracycline was slightly increased in the presence of Cu(II) or Ni(II), and the enhancement effect was stronger for Cu(II) than that for Ni(II). For NH_2-MWCNTs, significant adsorption enhancement was observed for both Cu(II) and Ni(II), especially at low concentrations of the metal ion.

It is well recognized that the presence of O-/N-functionalities on the surface of MWCNTs could undergo polar interactions (Sun *et al.*, 2002; Tasis *et al.*, 2006; Karousis and Tagmatarchis, 2010). For example, it has been reported that Cu(II) and Ni(II) can easily adsorb to MWCNTs through the mechanisms of cation exchange, cation bridging, and surface complexation between the charged/polar sites (e.g., surface O- and N-functionalities) of MWCNTs and the metal ions (Lu and Liu, 2006; Chen J.Y., *et al.*, 2007; Kandah and Meunier, 2007; Rao *et al.*, 2007). These attached Cu(II) and Ni(II) ions on the MWCNTs surface are also considered as favorable sites for surface reactions with tetracycline (Wang *et al.*, 2008). At the tested pH range (4.1–6.0), tetracycline is predominated by the zwitterions (TCH_2^0), and the deprotonated C1–C3 tricarbonyl methane moiety of tetracycline is capable of forming water-soluble complexes with Cu(II) and Ni(II) (Albert and Rees, 1956; Doluisio and Martin, 1963; Baker and Brown, 1966; Lambs and Berthon, 1988; Jezowska-Bojczuk *et al.*, 1993; Wang *et al.*, 2008). Accordingly, Cu(II) and Ni(II) could serve as the bridging agent between tetracycline and O-/N-functionalities of MWCNTs, and the formation of ternary surface complexes (MWCNTs-Cu(II)/Ni(II)-tetracycline) are expected to significantly enhance tetracycline adsorption (Ji *et al.*, 2010b). Note that the stability constant of Cu-tetracycline complexes is 63 times larger than that of Ni-tetracycline complexes (Albert and Rees, 1956), thus, tetracycline could react with Cu(II) in aqueous solution much more strongly than with Ni(II), which is consistent with the much stronger adsorption enhancement for Cu(II).

To better understand the surface complexation mechanism, the UV spectrums of tetracycline with Cu(II) and Ni(II) in the absence and presence of NH_2-MWCNTs were measured (Fig. 4). As shown in Fig. 4, the characteristic sorption peak of tetracycline alone was at a wavelength of 360 nm, whereas the peak was significantly shifted to a higher wavelength in the presence of Cu(II) or Ni(II), indicating the formation of complexes in aqueous solution (Gu and Karthikeyan, 2005), and similar peak shift phenomena were observed in solution in the presence of NH_2-MWCNTs.

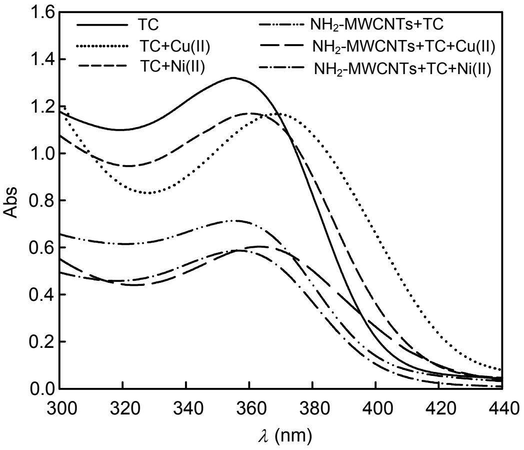

Fig. 4 UV spectra of tetracycline with Cu(II) and Ni(II) in the absence and presence of NH_2-MWCNTs
TC: an aqueous solution of 50 mg/L tetracycline; TC+Cu(II): 50 mg/L tetracycline and 0.1 mmol/L Cu(II); TC+Ni(II): 50 mg/L tetracycline and 0.1 mmol/L Ni(II); NH_2-MWCNTs +TC: 0.25 g/L NH_2-MWCNTs and 50 mg/L tetracycline; NH_2-MWCNTs+TC+Cu(II): 0.25 g/L NH_2-MWCNTs, 50 mg/L tetracycline, and 0.1 mmol/L Cu(II); NH_2-MWCNTs+TC+ Ni(II): 0.25 g/L NH_2-MWCNTs, 50 mg/L tetracycline, and 0.1 mmol/L Ni(II); solutions/suspensions were pre-equilibrated for 72 h before UV measurement

The different adsorption trends observed for the four MWCNTs in the presence of Cu(II) and Ni(II) cannot be explained by surface complexation alone. In fact, the adsorption of tetracycline on OH-MWCNTs was slightly inhibited in the presence of Ni(II), which is probably attributable to the formation of dense hydration shells. As reported in our previous studies (Chen J.Y., *et al.*, 2007; Wang *et al.*, 2012), by strong complexation of metal ions with surface O-functional groups, the formation of hydration shells of water could compete with tetracycline for surface area. Since OH-MWCNTs contained the greatest amount of O-functional groups, the sorption suppression for OH-MWCNTs is relatively profound than that of other MWCNTs in the presence of Ni(II), and thus the slightly suppressed adsorption for Ni(II) on OH-MWCNTs was observed; however, for Cu(II), the suppressive effect of forming hydration shells was not strong enough to prevail over the bridging effects to form ternary surface complexes, and thus Cu(II) can still enhance tetracycline adsorption on OH-MWCNTs.

Besides the mechanisms mentioned above, the cation exchange interaction is still a viable mechanism to account for the overall adsorption within this pH range (Ji *et al.*, 2010b; Sun *et al.*, 2010). As seen from Table 2, in the presence of Cu(II), the solution pH was clearly much lower than that in the presence of Ni(II) for all the MWCNTs, indicating that protons in the surface functional groups of MWCNTs preferred to exchange with Cu(II), and hence the effect of cation exchange interactions can be more stronger for Cu(II) than for Ni(II).

Additionally, electrostatic attractive/repulsive forces between metal ions coordinated to O-/N-functionalities of functionalized MWCNTs and zwitterionic tetracycline molecules are also expected to occur (Ji *et al.*, 2010b; Li *et al.*, 2010; Zhao *et al.*, 2011). Note that when normalizing the adsorption affinities with BET surface area, both in the absence and presence of Cu(II), OH-MWCNTs and COOH-MWCNTs can accumulate more tetracycline than NH_2-MWCNTs (Fig. 5). This may be attributed to the significant amount of negative charge on the two acidic surfaces (as indicated by lower pH_{pzc} values), and the electrostatic attractive forces between the positively charged C4 dimethyl ammonium group of tetracycline and negatively charged surfaces may have an adsorption enhancement effect. Since the surface functionalities of G-MWCNTs were very limited, the mechanisms mentioned above do not obviously affect G-MWCNTs, and thus the presence of Cu(II) and Ni(II) is negligible for the adsorption of tetracycline in this case.

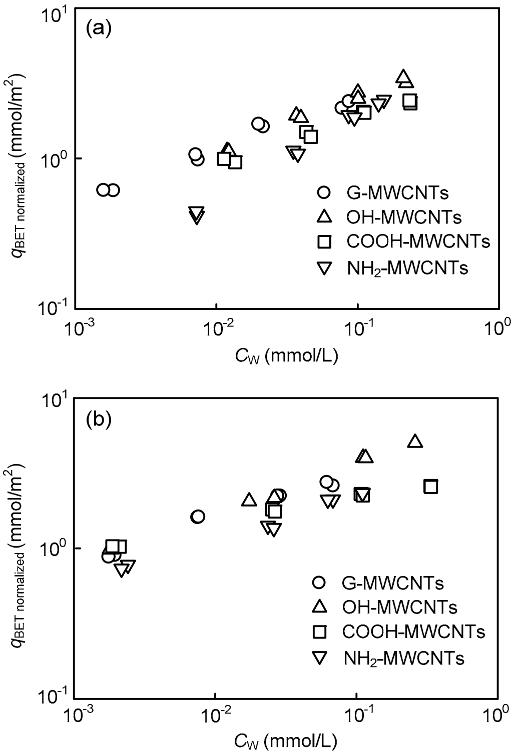

Fig. 5 Effects of Cu(II) on adsorption to different functionalized MWCNTs

(a) Only Na(I); (b) Plus Cu(II)

4 Conclusions

The present study indicates that functionalized MWCNTs may accumulate environmental contaminants in aquatic environments, and the types and abundance of functionalities on the MWCNTs surfaces could play important roles. Moreover, in the presence of complexing agents, such as Cu(II) and Ni(II) ions, the adsorptive interactions between MWCNTs and tetracycline can be further complicated. The strong adsorptive interactions between functionalized MWCNTs and tetracycline observed in the present study can be extrapolated to other polar, ionizable, and organic contaminants. The adsorption enhancement/suppressive effects of Cu(II) and Ni(II) present an important co-contamination scenario where functionalized MWCNTs are being used to accumulate organic contaminants and heavy metals in water and wastewater treatment, but which may result in significant alteration of the adsorption capacities of functionalized MWCNTs, as well as environmental risks from the functionalized MWCNTs and/or the bioavailability of the adsorbed contaminants.

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中文概要：

本文题目： **Cu(II)和 Ni(II)对四环素在官能团化碳纳米管上吸附的影响**

Effects of Cu(II) and Ni(II) ions on adsorption of tetracycline to functionalized carbon nanotubes

研究目的： 探究四环素在不同官能团化碳纳米管上的吸附机制，并揭示 Cu(II)和 Ni(II)对四环素与碳纳米管间作用的影响机制。

创新要点： 1. 碳纳米管对四环素的吸附与其表面官能团种类密切相关；2. 金属离子对碳纳米管吸附四环素的影响能力与金属离子络合性能相关。

研究方法： 采用批量吸附试验和谱学手段表征相结合的研究方法。

重要结论： 四环素在不同官能化碳纳米管上吸附能力的强弱顺序为：石墨化碳纳米管（G-MWCNTs）>羟基化碳纳米管（OH-MWCNTs）>羧基化碳纳米管（COOH-MWCNTs）>氨基化碳纳米管（NH_2-MWCNTs），碳纳米管表面的官能团类型和数量对四环素与碳纳米管间的作用机制有重要影响（表 1 和图 2）。Cu(II)和 Ni(II)对四环素在 G-MWCNTs 上的吸附几乎没有影响，但对在其它三种官能团化的碳纳米管上的吸附表现出不同的影响能力（图 3）。与 Ni(II)相比，Cu(II)与碳纳米管上官能团具有更强的络合能力，因此 Cu(II)对四环素在不同碳纳米管上吸附的影响要比 Ni(II)更显著。

关键词组： 官能团化碳纳米管；四环素；吸附；络合