Adsorption of ofloxacin on carbon nanotubes: Solubility, pH and cosolvent effects

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A B S T R A C T

The adsorption of ofloxacin (OFL) on carbon nanotubes (CNTs) has been investigated using the solubility, pH and cocolvent effects. In this work, solubilities of OFL and sorption of OFL on three multi-walled CNTs at different pHs and different methanol volume fractions (f_c) of methanol/water mixture solutions were systematically measured. The solubilities of different OFL species were obtained based on the analysis of pH-dependent solubility. Cationic and anionic OFL showed much higher solubilities than zwitterionic OFL. The highest sorption was not observed at the pH with lowest OFL solubility, indicating hydrophobic interaction was not the dominant sorption mechanism. The sorption decreasing in pH range of 5–8 was consistent with cationic OFL species distribution, suggesting cation exchange may play an important role. With the increased methanol fraction, both OFL solubility and sorption decreased, which was different from hydrophobic organic contaminants (HOCs). Analysis of methanol-fraction-dependent OFL sorption suggested that cosolvent–sorbent (methanol–CNTs) interactions were much stronger than solute–cosolvent (OFL–methanol) interactions. This statement was also confirmed in sorption isotherm study as evidenced by decreased sorption and increased linearity of the isotherms in methanol than those in water.

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1. Introduction

To evaluate the environmental risks of an organic contaminant, it is fundamental to understand its environmental fate. Thus, the relationship between the environmental behavior and physico-chemical properties of organic chemicals is of a major research interest. Sorption is an important process affecting environmental behavior of organic chemicals. For hydrophobic organic contaminants (HOCs), it has been widely reported that the sorption was controlled by hydrophobicity. Thus, the sorption behavior of HOCs is often estimated using the relationship between K_{OC} (organic carbon normalized sorption coefficient) and C_s (the solubility of the chemical in aqueous phase) [1] or between K_{ow} (octanol–water partition coefficient) and C_s [2].

However, for ionizable organic contaminants, the sorption may not be controlled by hydrophobic interaction alone. Generally, several mechanisms (such as H-bond, cation exchange, ligand exchange, electrostatic interaction, and electron-donor–acceptor interaction) function simultaneously [3]. A systematic investigation between the solubility and sorption of ionizable organic contaminants may provide evidence for a better insight into sorption mechanisms of this type of chemicals.

The potential risks of a class of ionizable organic contaminants, antibiotics, to human and the environment are of a major concern to the public as well as to scientific community. Quinolone antibiotics are widely used to prevent and treat a large variety of infectious disease in human and veterinary medication activities [4]. For example, ofloxacin (OFL) is a quinolone antibiotic which is effective against most Gram-negative and Gram-positive aerobic bacteria [5,6]. This type of chemicals could not be removed completely using current water treatment technologies [7], and thus can enter the environment through different pathways. A wide range of antibiotics have been identified in the environment [6].

Therefore, understanding the environmental fate of antibiotics is essential in assessing human- and ecology-health risks of this class of contaminants. However, their environmental behavior is not clear yet, mostly because of the complicated interaction mechanisms of antibiotics with environmental matrix, such as soils and sediments.

We proposed in our previous study that carbon nanotubes (CNTs) could be used as very good model adsorbents, because of their unique and well-defined structures. In addition, CNTs may enter the environment during their wide application [8,9]. CNTs are also regarded as an emerging contaminant because of their significant toxic effects. Numerous studies also reported strong interactions between CNTs and heavy metal ions or organic compounds because of CNT surface functional groups and hydrophobic surfaces [10]. Therefore, CNTs are considered to be an effective

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adsorbent to control the environmental behavior of various contaminants. The understanding of antibiotic–CNT interaction mechanisms are expected to offer important information on assessing risks and potential applications of both CNTs and antibiotics. Therefore, CNTs are used in this study as model adsorbents.

The primary goal of this study was to investigate the relationship between antibiotic (OFL) solubility and its sorption with CNTs at different pH and solvents of various methanol fractions. The aqueous phase condition was varied by its pH values (OFL species change) and methanol fraction (cosolvent effect). OFL solubility and sorption were studied in these conditions simultaneously. The relationship between solubility and sorption is analyzed analogous to HOCs. The possible mechanisms of OFL sorption on CNTs will be discussed based on the above-mentioned analysis.

2. Experimental

2.1. Materials

Adsorbents used in the study were three multi-walled CNTs (purity > 95%) which were graphitized (MG), carboxylized (MC) and hydroxylized (MH). They were purchased from Chengdu Organic Chemistry Co., Chinese Academy of Sciences. All the CNTs were characterized for their zeta potential (Zetasizer, Malvern Instruments), surface area (Autosorb-1C, Quantachrome), elemental composition (MicroCube, Elementar, Germany), and surface functional groups (X-ray photoelectron spectroscopy). Adsorbate used in the study was ofloxacin which was obtained from Bio Basic Inc. All the other chemicals were higher than analytical grade (purity > 99.5%).

2.2. Batch adsorption experiments

Two types of batch adsorption experiments were conducted. (a) Adsorption study of OFL on CNTs at different pHs (pH 2.0–12.0). OFL (10 mg/L) was dissolved in background solution containing 0.02 M NaCl (background electrolyte) and 200 mg/L NaN$_3$ (bio-inhibitor) as a stock solution. Adsorption experiments were conducted in 4 mL glass vials with teflon-lined screw caps. According to preliminary studies, the liquid:solid ratio was 4000:1 for OFL, in order to ensure 20–80% adsorption. The pH of suspension was adjusted using HCl or NaOH and sequentially distributed in the range of pH 2.0–12.0. All the vials were placed in dark and shaken in an airbath shaker (150 rpm) at 25 °C for 7 d which were sufficient to reach apparent equilibrium. After equilibrated for 7 d, all the vials were centrifuged at 1000 × g for 10 min and the supernatants were subjected to solute quantification. Solution pH at equilibrium was measured by a pH electrode (Leici Instruments, Shanghai, China).

(b) Adsorption of OFL on CNTs at different volume fractions of methanol. The initial concentration of OFL was fixed at 10 mg/L in this experiment. The volume ratio of methanol of the solutions were distributed in the range of water:methanol (v:v) = 0.0–1.0. The other experimental procedure was the same as experiment (a). The sorption isotherms of OFL on CNTs from water and methanol were also obtained using batch sorption experiment.

2.3. Measurement of OFL solubilities

OFL C_s values were measured in two series. (a) OFL C_s at different pHs (pH 2.0–12.0) in water. Aliquots of 3 mg OFL were weight and separately put into 1.5 mL glass vials with teflon-lined screw caps. The pH of background solution (0.02 M NaCl and 200 mg/L NaN$_3$) was adjusted using HCl or NaOH and sequentially distributed in the range of pH 2.0–12.0. One mL of the pH-adjusted background solution was injected in each vial. All the vials were kept in dark and shaken in an air-bath shaker at 25 °C for 2 d. Subsequent 3 mg

OFL were added in the vials until solid residuals were observed. Then, these vials were shaken for another 5 d. All the vials were centrifuged at 1000 × g for 10 min and the supernatants were subjected to quantification of solute. Solution pH at equilibrium was measured using a pH electrode (Orion 91-25/26).

(b) OFL C_s at different volume fractions of methanol (water:methanol (v:v) = 0.0–1.0). The conducted procedure was same as in section (a).

2.4. Detection of OFL

OFL was quantified by an HPLC (Agilent Technologies 1200) equipped with a reversed-phase C8 column (5 μm, 4.6 mm × 150 mm). The mobile phase was 10:90 (v:v) of acetonitrile and deionized water with 0.8% acetic acid. The flow rate was 1 mL/min. The retention time for OFL is 4.6–5.0 min. OFL concentration was quantified using a UV detector at 286 nm.

2.5. Data analysis

The relationship between equilibrium sorption coefficients in aqueous system (K_d) and in mixed solvent system (K_m) was described by the following model [11]:

$$\log K_m = \log K_d - \alpha \sigma f_c \tag{1}$$

where α is an empirical constant hypothesized to reflect cosolvent–sorbent interactions, the parameter σ is an index of the solubilizing power of the cosolvent, which describes solute–cosolvent interactions. f_c is the volume fraction of cosolvent. For a given solute, σ values may be approximated from the slope of the solute solubility profile (log C_s vs f_c).

The apparent solubility could be viewed as the sum of different species. Thus, the following equation was applied for this calculation:

$$C_s = C_s^+ \delta^+ + C_s^0 \delta^0 + C_s^- \delta^- \tag{2}$$

where C_s (mg/kg) is the apparent solubility. C_s^+, C_s^0, and C_s^- are solubilities for cationic, neutral, and anionic species, respectively. δ^+, δ^0, and δ^- are the percentages of cationic, neutral, and anionic species at a certain pH, respectively.

The sorption isotherms were fitted using Freundlich equation:

$$\log S_e = \log K_F + n \log C_e \tag{3}$$

where S_e (mg/kg) and C_e (mg/L) are the equilibrium solid phase and aqueous phase concentrations. K_F [(mg/kg)/(mg/L)^n] is the Freundlich affinity coefficient and n is the Freundlich nonlinearity factor. The above model regression was performed using SigmaPlot 10.0 and statistical analysis was conducted with the aid of SPSS 17.0.

3. Results and discussion

3.1. OFL solubilities as affected by pH

The solubilities of organic chemicals were generally detected as the total dissolved concentrations. However, for chemicals with different species, the total dissolved concentrations provide limit information to understand the properties of the chemicals. It is well documented that OFL exists as different species with the change of pH because of its pK_as. Therefore, OFL solubilities were measured at different pHs to study the solubility variation with species.

At 6 < pH < 8, OFL is zwitterionic. As shown in Fig. 1, the solubilities for OFL were the lowest at this pH range. This result could be easily understood from the hydrophobicity of different chemical species. At higher or lower pHs, OFL molecules were negatively or positively charged, respectively. The electrostatic repulsion
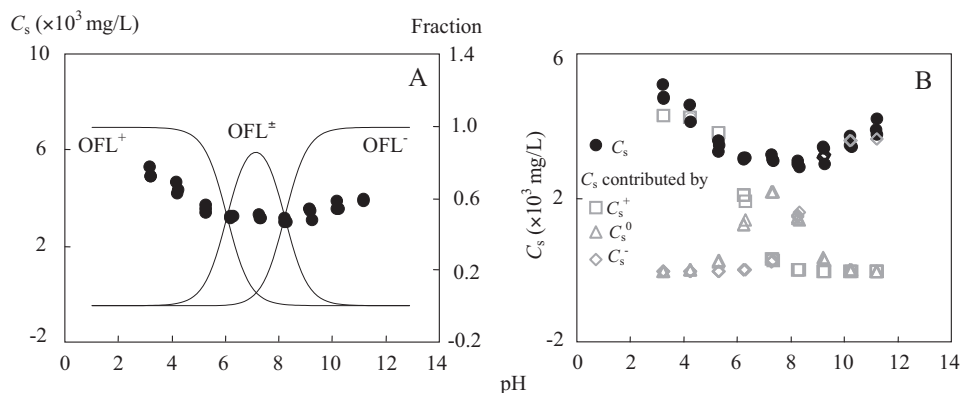
Fig. 1. Solubility (C_s) in relation with pHs (black solid circles). The distribution of cationic (OFL$^+$), zwitterionic (OFL$^\pm$), and anionic (OFL$^-$) OFL in aqueous solution as a function of pH (Panel A) was calculated based on OFL pK_a values (pK_{a1} = 6.1, pK_{a2} = 8.28). Panel B presents OFL solubilities as contributed by cationic (C_s^+), zwitterionic (C_s^0), and anionic (C_s^-) molecules in aqueous solution as a function of pH.

between the charged molecules could enhance their stabilities in aqueous phase and thus OFL solubility was increased either at pH higher than 9, or at pH lower than 6. The systematically measured solubilities at different pHs enabled the calculation of OFL solubilities of different species. Eq. (2) was applied for this calculation and the regression results were listed in Table 1. The zwitterionic OFL has a solubility of $(2.55 \pm 0.22) \times 10^3$ mg/L, significantly lower ($P < 0.01$) than that of cationic OFL ($C_s^+{}_{OFL}$, $(4.31 \pm 0.14) \times 10^3$ mg/L) and anionic OFL ($C_s^-{}_{OFL}$, $(3.67 \pm 0.15) \times 10^3$ mg/L). The higher solubility of cationic OFL in comparison to that of anionic OFL is probably related with their different charged functional groups, which deserves further study.

3.2. OFL adsorption on carbon nanotubes at different pHs

The adsorption edge study was conducted for OFL on three types of CNTs and the K_ds varied with pH are depicted in Fig. 2. The maximum K_ds were observed at pH 5 for all CNTs. It is important to notice that the highest adsorption was not observed at the lowest solubility, which indicated that hydrophobic interaction may not be a controlling mechanism. This statement could be further discussed by comparing the following two results.

3.2.1. Solubility normalized K_ds vs pH

Normalization of the sorption coefficient by solubility could exclude the effect of hydrophobicity [15]. No K_d ($K_d = \log (S_e/C_e)$) variation will be expected if hydrophobic effect is the only interaction mechanism. However, the solubility normalized K_ds ($K_d' = \log(S_e/(C_e/C_s))$) varied by one order of magnitude for a given type of CNTs as presented in Fig. 3A. The K_d' increased when pH values increased from 2 to 5, and decreased as pH increased from 5 to 9.

As pH values further increased, K_d' hardly changed. The K_d' decrease in pH range of 5–9 was consistent with the contribution change of OFL$^+$ in OFL speciation distribution (Fig. 1). This result suggested that cationic OFL contribute greatly to the overall OFL sorption at pHs lower than 9, probably through electrostatic attraction and cation exchange. The lower K_d' as pH decreased below 5 may be explained by the electrostatic repulsion between OFL$^+$ and the positively charged CNTs. When OFL and the functional groups in CNTs were completely dissociated at pHs higher than 10, further increase of solution pH did not result in any obvious sorption change. Still, very high sorption (with $\log K_d$ in the range of 4–5, Fig. 2B) was observed at this pH range, probably because of hydrophobic interaction.

3.2.2. The relationship between K_ds and C_ss for different species

Analyzing the relationship between solubilities and sorption coefficients of various HOCs (several to hundreds of different chemicals) is a useful method to discuss HOC sorption mechanisms [16]. This method could be applied in the current study. Different OFL species may be regarded as different chemicals because of their different properties. Thus, the solubilities and sorption coefficients of different OFL species were plotted in Fig. 3B. No trend of negative relationship (as expected for HOCs) was observed in this figure. For example, the positively charged molecules have very high solubilities, and at the same time showed very high sorption. This much higher-than-expected sorption of cationic OFL again suggested that cation exchange may be an important mechanism for OFL sorption on CNTs. The site for cation exchange may be the oxygen-containing functional groups (such as carboxyl groups) on CNTs (Table 2). Cation exchange has been considered to be an important mechanism in the sorption of quinolone antibiotics to

Table 1
Selected physicochemical properties of ofloxacin.

Name	C_s^{+a} ($\times 10^3$ mg/L)	C_s^{0a} ($\times 10^3$ mg/L)	C_s^{-a} ($\times 10^3$ mg/L)	C_s (water, pH 7)	C_s (methanol)	K_{ow}	pK_a^f	Structure
Ofloxacin	4.31 ± 0.14^b	2.55 ± 0.22^b	3.67 ± 0.15^b	3400[c] 3230[d]	1210[c]	0.446[c] 0.407[e]	6.10/8.28	

[a] Calculated based on Fig. 1.
[b] Standard deviation.
[c] Measured at 25 °C.
[d] From [12].
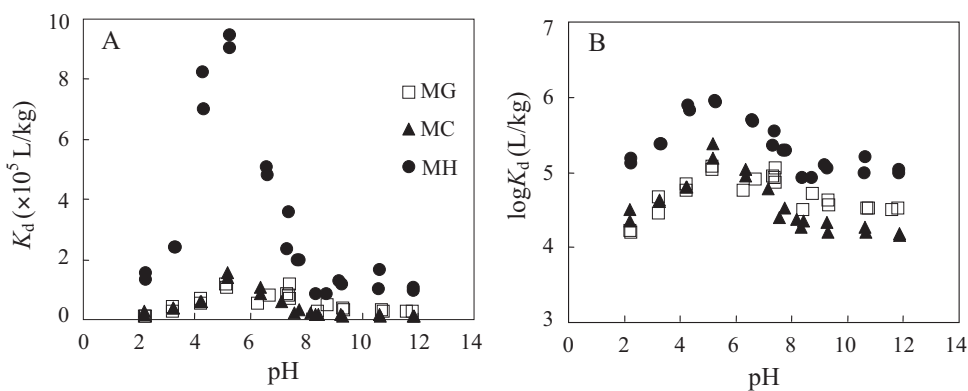[e] From [13].
[f] Obtained from [14].

Fig. 2. Adsorption coefficient of OFL on CNTs at different pHs. Panel A is K_d vs pH, while panel B presents $\log K_d$ vs pH.

inorganic mineral [17] and soils [18,19]. As shown in Fig. 2, at pH 5.0 where the OFL sorption reached maximum; the cationic OFL form account for about 80% of all the species (Fig. 1). Accordingly, cation exchange participated in the adsorption process because the positively charged piperazinyl group of OFL exchanged the H$^+$ on the CNT surface. This mechanism can be confirmed by the solution pH decrease after OFL sorption at pH 5.0–9.0 (data not shown).

CNTs with different functional groups showed very different sorption properties with OFL. As could be observed in Figs. 2 and 3, MH always showed the highest sorption in comparison to other two types of CNTs. OFL could act as π-acceptors because the fluorine group has a strong electron-withdrawing ability. Carboxyl functional groups on benzene rings make MC π-acceptor [20], while hydroxyl groups on benzene rings make MH π-donor [21]. Thus, high sorption of MH with OFL is expected because the interactions between a π-donor compound and a π-acceptor compound are much stronger than donor–donor or acceptor–acceptor pairs [22].

3.3. OFL solubilities as affected by methanol fraction

Methanol is a widely used organic solvent in both academic research and engineering application. The solubility of a certain organic chemical in methanol is determined by its physicochemical properties and determines its application strategy. Therefore, the solubilities of OFL in methanol were determined in methanol as well as in methanol/water mixtures. The obtained solubilities depending on methanol fractions were presented in Fig. 4.

OFL solubility decreased gradually with the increased methanol fraction. This phenomenon is very different from the solubility change of HOCs in methanol/water mixture. For example,

according to the calculation using SPARC online calculator (http://ibmlc2.chem.uga.edu/sparc/), the solubility of phenanthrene (1.21 mg/L) increased 600 times when the solvent was changed from water to methanol (7080 mg/L) [23]. The lab-measured results showed even higher extend of phenanthrene solublility increase (more than 4 orders of magnitude) with the increased methanol content [23]. The increased solubility of HOCs in methanol could be understood from the increased solvent hydrophobicity with increased methanol content. However, the opposite solubility change with the addition of methanol was observed for OFL. As presented in Fig. 4A, OFL solubility decreased 3 times as methanol fraction increased from 0 to 1.0. As Park et al. [24] has stated previously, H$_2$O and the polar groups of OFL have stronger intermolecular interactions (such as hydrogen bond) than methanol–OFL interactions. The decreased solvent–solute interaction would decrease solute solubility.

Another possible explanation of the decreased OFL solubility with increased f_c could be viewed through dielectric constant (ε). The ε value describes the ratio of the electrical capacity of a capacitor filled with the solvent to the electrical capacity of the evacuated capacitor. In another word, ε defines the ability of a solvent to "screen off" the electrostatic interactions between solute molecules. At pH around 7, OFL zwitterionic molecules may interact with each other through their opposite charges. Water has a ε value of 78.54, which is much bigger than that of methanol (32.63) [25]. The addition of methanol could decrease solution ε [26]. Thus, water molecules could block the attractions between OFL molecules and thus facilitates OFL dissolution. With the addition of methanol, OFL molecular interactions may be increased because of the decreased ε, which consequently resulted in decreased OFL solubility.
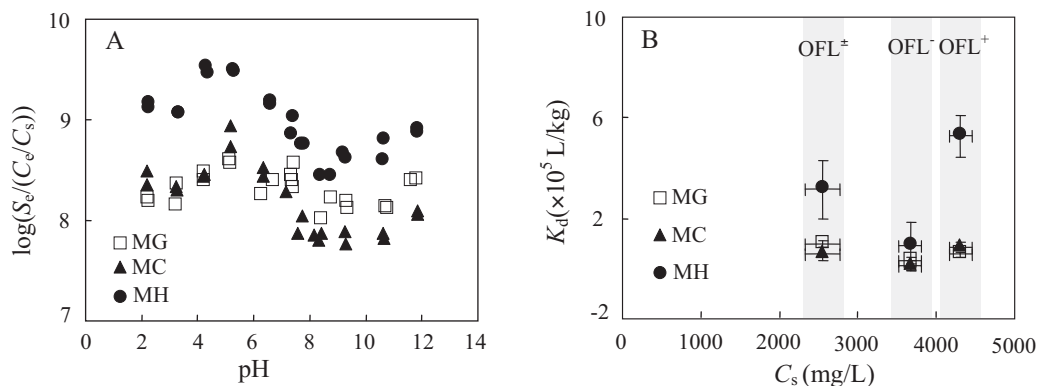

Fig. 3. OFL solubilities and sorption coefficients on CNTs. The solubility-normalized adsorption coefficients were plotted against pH (Panel A). The K_ds and C_ss for different OFL species were presented in panel B.
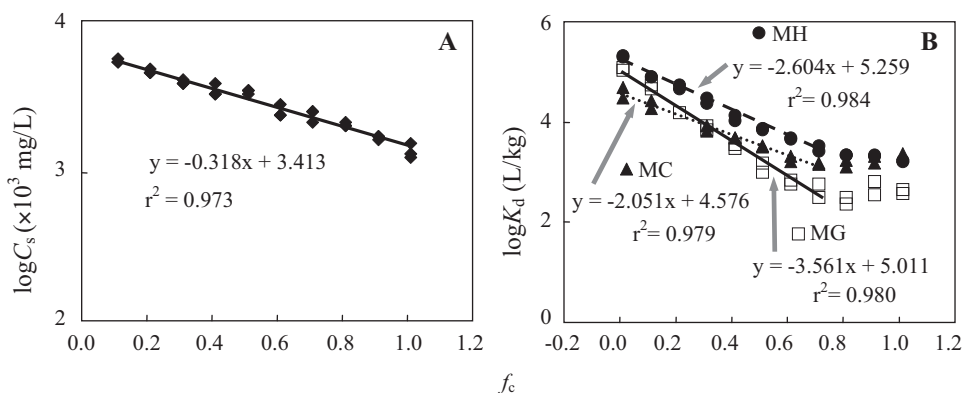
Fig. 4. OFL solubility and sorption as affected by methanol addition in aqueous phase. The solubilities variation with methanol volume fractions (f_c) are presented in panel A, while adsorption coefficients varied f_c are illustrated in panel B.

Park et al. [24] also observed that the fluorescence emission spectrum of OFL in aqueous solution was stronger than that in methanol solution. In addition, a red shift of main emission band was observed in methanol in comparison to that in aqueous solution. Combining the evidence from experiments and theoretical calculations, the authors suggested that OFL exists as neutral zwitterionic form in water, but as molecular form in methanol. Both zwitterionic and molecular OFL may be adsorbed on CNTs through hydrophobic interaction, hydrogen bond, and EDA mechanisms. Additionally, the zwitterionic molecules have positively charged sites and thus may be adsorbed on the negatively charged CNTs at pH 7 through electrostatic attraction. This electrostatic interaction is not expected for molecular OFL and thus the OFL sorption was higher in water (zwitterionic OFL) than in methanol (molecular OFL).

3.4. OFL adsorption on carbon nanotubes from water/methanol mixed solvent

OFL sorption decreased greatly with the addition of methanol. Two orders of magnitude K_d-decrease could be observed in Fig. 4B. The sorption isotherms of OFL on CNTs from water and methanol are also presented in Fig. 5. Thus, the decreased OFL sorption in methanol in comparison to that in water was demonstrated in both sorption isotherm study (Fig. 5) and sorption variation with methanol fractions (Fig. 4B). The decreased sorption of HOCs with the addition of methanol in aqueous phase was generally reported. However, the same methanol-fraction-depended sorption for OFL and HOCs should be discussed differently. For HOCs, the decreased sorption with increased methanol content was explained by the increased solubility [23]. But this is not the case for OFL. A positive relationship between K_d and C_s could be observed in Fig. 4

(by comparing panels A and B). Thus the solubility-normalized OFL sorption isotherms actually enlarged the difference between the sorption from water and methanol (Fig. 6). The analysis of sorption coefficients in mixed solvent system was enabled by Eq. (1) and thus this equation was applied in our study.

The solubility-f_c relationship profile of OFL was plotted in Fig. 4A. Regressing of $\log C_s$ vs f_c yield coefficient of determination (r^2) of 0.973, and the resulted slope ($\sigma = -0.318$) was the solubilizing power of methanol for OFL. In the plot of $\log K_d$ vs f_c, $\log K_d$ decreased linearly with f_c increased up to 0.7. As f_c further increased, $\log K_d$ did not show obvious change. Clearly, it is not proper to include the points of $f_c > 0.7$ in the linear regression of $\log K_m$ vs f_c (Eq. (1)). Therefore, the data analysis using Eq. (1) was based on the data points at $f_c \leq 0.7$ as in literature [26,27]. The regression results were also listed in Fig. 4B, and the r^2 values were about 0.98. From Eq. (1), the obtained slope of $\log K_m$ vs f_c was the product of α and σ. The α values could be calculated to 11.2, 6.4, and 8.2 for MG, MC, and MH, respectively. These very high α values in comparison to σ values indicated that cosolvent–sorbent (methanol–CNTs) interactions were much stronger than solute–cosolvent (OFL–methanol) interactions. The strong methanol–CNT interactions may also be understood from the analysis of OFL sorption isotherms in water and methanol.

OFL sorption isotherms in Fig. 5 were also fitted using Freundlich equation. Very strong nonlinear sorption was observed for sorption in water as noted by the n values in the range of 0.14–0.18. These low n values indicating a highly heterogeneous site energy distribution for OFL sorption on all three CNTs. But in methanol, the sorption decreased with significant increase of n values (0.67–1.09). This phenomenon is well consistent with competitive sorption [28]. In another word, methanol may interact with CNTs and occupy sorption site with high energy which consequently resulted in more
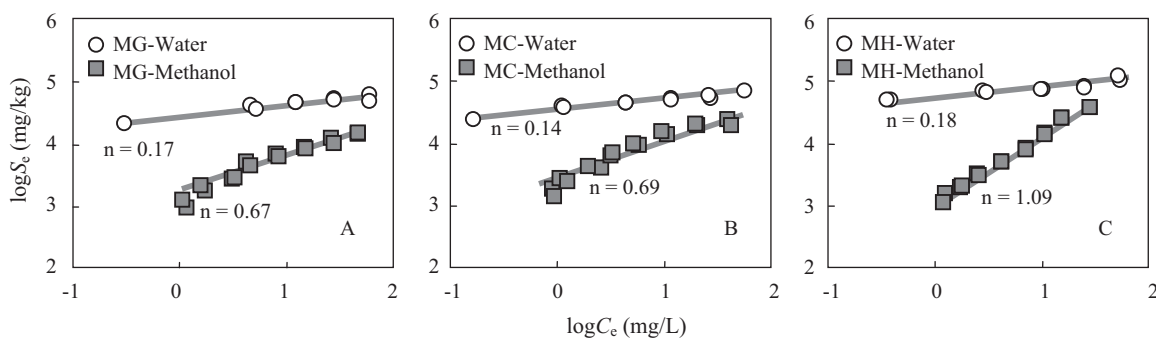

Fig. 5. OFL sorption on MG (A), MC (B), and MH (C) from water (○) and methanol (■). S_e and C_e are solid-phase and liquid-phase concentrations, respectively. The lines were Freundlich equation ($\log S_e = \log K_F + n \log C_e$) fitting results. The obtained n values were marked for each isotherm.
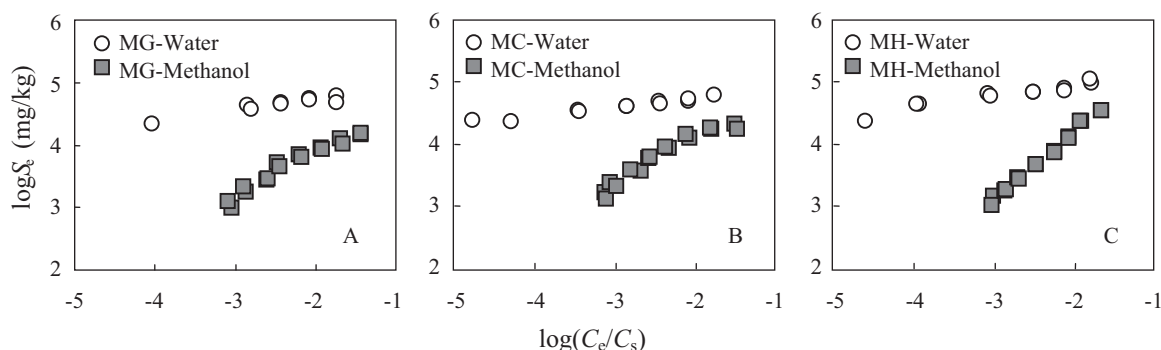
Fig. 6. Solubility-normalized OFL sorption on MG (A), MC (B), and MH (C) from water ($\bigcirc$) and methanol ($\blacksquare$). C_s is OFL solubility in the solvent (water or methanol).

Table 2
Selected CNT properties.

Name	Outer diameter (nm)	Elemental analysis (atom based) (%)				XPS[d] (atom based) (%)		Functionalized surface carbon (%)	SSA[e] (m²/g)
		N	C	H	O	C	O		
MG[a]	8–15	0.19	100	1.49	<0.05	99.3	0.7	<0.70	117
MC[b]	8–15	0.21	96.7	2.65	0.45	95.8	4.2	2.19	164
MH[c]	8–15	0.18	94.2	2.66	2.93	95.9	4.1	4.28	228

[a] Graphitized multi-walled carbon nanotubes.
[b] Carboxylized multi-walled carbon nanotubes.
[c] Hydroxylized multi-walled carbon nanotubes.
[d] X-ray photoelectron spectroscopy.
[e] Specific surface area.

homogeneous site energy distribution for OFL (higher n values). Therefore, the nonlinearity change with the solvent alteration also provided evidence for strong methanol–CNT interaction.

This study conducted experiment with the full range of f_c (Fig. 4B), which is wider than in literature [26,27]. It is interesting to notice that at higher f_c (>0.7), OFL sorption did not change significantly with increased methanol fraction. Current experiment could not provide any explanation for this phenomenon and thus further investigation is needed.

4. Conclusions

Both OFL solubility and sorption on CNTs were monitored at different pHs and methanol fractions. Different OFL species could be viewed as chemicals with different physicochemical properties and their solubilities and sorption coefficients were mathematically calculated based on sorption edge experiment (pH effect). No negative relationship was observed between sorption and solubility for OFL, which was different from HOCs. This result suggested that hydrophobic interaction was not dominant for OFL sorption on CNTs. Other possible mechanisms may include electrostatic interactions, cationic exchange, and hydrogen bond. Both OFL solubility and sorption decreased with the increased methanol fraction. Analysis of methanol-fraction-dependent OFL sorption suggested that cosolvent–sorbent (methanol–CNTs) interactions were much stronger than solute–cosolvent (OFL–methanol) interactions. This result suggested that solute–cosovlent interactions should be incorporated in future studies.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.12.063.

References

[1] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, John Wiley & Sons, 2003.
[2] B. Van der Bruggen, L. Braeken, C. Vandecasteele, Flux decline in nanofiltration due to adsorption of organic compounds, Separation and Purification Technology 29 (2002) 23–31.
[3] D. Zhang, B. Pan, H. Zhang, P. Ning, B.S. Xing, Contribution of different sulfamethoxazole species to their overall adsorption on functionalized carbon nanotubes, Environmental Science & Technology 44 (2010) 3806–3811.
[4] Z. Xu, D. Kuang, L. Liu, Q. Deng, Selective adsorption of norfloxacin in aqueous media by an imprinted polymer based on hydrophobic and electrostatic interactions, Journal of Pharmaceutical and Biomedical Analysis 45 (2007) 54–61.
[5] S.P. Velaga, S. Basavoju, D. Boström, Norfloxacin saccharinate-saccharin dihydrate cocrystal - a new pharmaceutical cocrystal with an organic counter ion, Journal of Molecular Structure 889 (2008) 150–153.
[6] S.T. Ulu, Rapid and sensitive spectrofluorimetric determination of enrofloxacin, levofloxacin and ofloxacin with 2,3,5,6-tetrachloro-p-benzoquinone, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 72 (2009) 1038–1042.
[7] S. Zorita, L. Mårtensson, L. Mathiasson, Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden, Science of The Total Environment 407 (2009) 2760–2770.
[8] M.G. Lines, Nanomaterials for practical functional uses, Journal of Alloys and Compounds 449 (2008) 242–245.
[9] A.A. Shvedova, E.R. Kisin, D. Porter, P. Schulte, V.E. Kagan, B. Fadeel, V. Castranova, Mechanisms of pulmonary toxicity and medical applications of carbon nanotubes: two faces of Janus? Pharmacology & Therapeutics 121 (2009) 192–204.
[10] X. Ren, C. Chen, M. Nagatsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management: a review, Chemical Engineering Journal 170 (2011) 395–410.
[11] P.S.C. Rao, A.G. Hornsby, D.P. Kilcrease, P. Nkedi-Kizza, Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: model development and preliminary evaluation, Journal of Environmental Quality 14 (1985) 376–383.

[12] D.L. Ross, C.M. Riley, Aqueous solubilities of variously substituted quinolone antimicrobials, International Journal of Pharmaceutics 63 (1990) 237–250.

[13] S. Zorita, L. Martensson, L. Mathiasson, Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden, Science of the Total Environment 407 (2009) 2760–2770.

[14] H.R. Park, T.H. Kim, K.M. Bark, Physicochemical properties of quinolone antibiotics in various environments, European Journal of Medicinal Chemistry 37 (2002) 443–460.

[15] B. Pan, D.H. Lin, H. Mashayekhi, B.S. Xing, Adsorption and hysteresis of bisphenol A and 17 alpha-ethinyl estradiol on carbon nanomaterials, Environmental Science & Technology 42 (2008) 5480–5485.

[16] F. Wang, J. Yao, K. Sun, B. Xing, Adsorption of dialkyl phthalate esters on carbon nanotubes, Environmental Science & Technology 44 (2010) 6985–6991.

[17] C.-J. Wang, Z. Li, W.-T. Jiang, J.-S. Jean, C.-C. Liu, Cation exchange interaction between antibiotic ciprofloxacin and montmorillonite, Journal of Hazardous Materials 183 (2010) 309–314.

[18] A.A. MacKay, D.E. Seremet, Probe compounds to quantify cation exchange and complexation interactions of ciprofloxacin with soils, Environmental Science & Technology 42 (2008) 8270–8276.

[19] R.A. Figueroa-Diva, D. Vasudevan, A.A. MacKay, Trends in soil sorption coefficients within common antimicrobial families, Chemosphere 79 (2010) 786–793.

[20] M. Keiluweit, M. Kleber, Molecular-level interactions in soils and sediments: the role of aromatic π-systems, Environmental Science & Technology 43 (2009) 3421–3429.

[21] D. Lin, B. Xing, Adsorption of phenolic compounds by carbon nanotubes: role of aromaticity and substitution of hydroxyl groups, Environmental Science & Technology 42 (2008) 7254–7259.

[22] D. Zhu, S. Hyun, J.J. Pignatello, L.S. Lee, Evidence for π-electron donor–acceptor interactions between π-donor aromatic compounds and π-acceptor sites in soil organic matter through pH effects on sorption, Environmental Science & Technology 38 (2004) 4361–4368.

[23] D.C. Bouchard, Cosolvent effects on sorption isotherm linearity, Journal of Contaminant Hydrology 56 (2002) 159–174.

[24] H.-R. Park, T.H. Kim, K.-M. Bark, Physicochemical properties of quinolone antibiotics in various environments, European Journal of Medicinal Chemistry 37 (2002) 443–460.

[25] W. Wang-Fan, E. Küsters, O. Lohse, C.-P. Mak, Y. Wang, Application of centrifugal counter-current chromatography to the separation of macrolide antibiotic analogues. I. Selection of solvent systems based on solubility and partition coefficient investigations, Journal of Chromatography A 864 (1999) 69–76.

[26] S. Hyun, L.S. Lee, Pentachlorophenol sorption by variable-charge soils in methanol–water mixture: pH effect at the low solvent volume fraction, Chemosphere 70 (2008) 503–510.

[27] D.C. Bouchard, Organic cosolvent effects on the sorption and transport of neutral organic chemicals, Chemosphere 36 (1998) 1883–1892.

[28] K. Yang, B.S. Xing, Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application, Chemical Reviews 110 (2010) 5989–6008.