Coadsorption of copper and perfluorooctane sulfonate onto multi-walled carbon nanotubes

Yanping Zhou^a, Bei Wen^{a,*}, Zhiguo Pei^a, Guangcai Chen^b, Jitao Lv^a, Jing Fang^c, Xiaoquan Shan^a, Shuzhen Zhang^a

^a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

^b Research Institute of Subtropical Forestry, Chinese Academy of Forestry, Fuyang, Zhejiang 311400, China

^c School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310012, China

H I G H L I G H T S

- ▶ Sorption and desorption of PFOS and Cu(II) on MWCNTs in single- and bi-solute systems were studied.
- ▶ Sorption capacities of PFOS and Cu(II) in bi-solute system were higher than those in single-solute system.
- ▶ Desorption behaviors of PFOS and Cu(II) in bi-solute system were different from those in single-solute system.
- ▶ Cu formed inner-sphere complexes without PFOS, while out-sphere complexes with PFOS.

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Multi-walled carbon nanotubes (MWCNTs) are superadsorbents for perfluorooctane sulfonate (PFOS) and heavy metals, which coexist in wastewater. The interaction between PFOS and Cu(II) with regard to their adsorption and desorption on MWCNTs was evaluated in this study. The adsorption of PFOS on MWCNTs enhanced with an increase of Cu(II). Desorption of PFOS showed no hysteresis without Cu(II), while pronounced hysteresis with Cu(II). Increases of the adsorption and the occurrence of desorption hysteresis of PFOS in the presence of Cu(II) may due to the PFOS adsorption via a Cu(II) bridge. The adsorption of Cu(II) increased with an increase of PFOS. The desorption hysteresis factors in the presence of PFOS were lower than those in the absence of PFOS. Increases of the adsorption and decreases of desorption hysteresis factors may be attributed to the Cu(II) adsorption via a PFOS bridge. Results obtained by X-ray absorption spectroscopy verified the formation of inner-sphere complexes between Cu(II) and functional groups of MWCNTs without PFOS, while out-sphere complexes with large amount of PFOS. The effect of Cu(II) and PFOS adsorption on the zeta potential of MWCNTs was also studied. The results showed that the coexistence of Cu(II) and PFOS greatly affects their sorption and desorption behaviors on MWCNTs thereby their fate and transport in wastewater.

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1. Introduction

Perfluorooctane sulfonate (PFOS) is an anthropogenic organic chemical, which has been employed in industrial and commercial applications for over 40 years. It is the stable end product of the degradation of most perfluorooctanesulfonyl fluoride (POSF)-based perfluorochemicals, and resistant to hydrolysis, photolysis, biodegradation and metabolism, thus persistent in the environment [1]. PFOS has been found in various environmental and biological

matrices [2], and is recognized as an emerging persistent organic pollutant.

Much attention has been paid on the source and exposure pathways of PFOS in the environment. Industrial and municipal wastewater has recently been identified as a significant source [3]. A few studies reported the occurrence of PFOS in the wastewater [3–6]. It was found that the concentration of PFOS in the wastewater treatment plant (WWTP) effluent was higher than that in the influent [3,6]. One of the reasons was the limitation of conventional biological treatments in removing PFOS from aqueous streams because of its biodegradation-resistant nature. It has been demonstrated in many cases that, adsorption is an economical method to remove pollutants from wastewater. The adsorption of PFOS onto non

* Corresponding author. Tel.: +86 10 62923560; fax: +86 10 62923563.

E-mail address: bwen@cees.ac.cn (B. Wen).

ion-exchange polymers [7], activated carbon [7,8], chitosan-based molecularly imprinted polymer adsorbents [9] and resins [8] were reported. Ion exchange, electrostatic and hydrophobic interactions were suggested to be involved in the sorption.

In addition to PFOS, high concentrations of heavy metal cations, such as Cu(II), Zn(II), Co(II), Cd(II) and Pb(II) are typically found in industrial and municipal sewage influents and effluents [10,11]. Heavy metal cations are reported to affect the sorption of ionizable organic contaminants [12]. However, little information is available about the impact of heavy metals on the adsorption of PFOS so far. Effect of alkaline-earth metal ions, such as Ca(II) on the adsorption of PFOS has been reported. Higgins and Luthy found that in the presence of Ca(II), the sorption of anionic PFOS on sediments increased significantly [13]. Similar observation of sorption capacity increases as a result of Ca(II) addition was reported for PFOS sorption on oil-derived black carbon [14] and minerals [15]. However, results obtained by Wang and Shih showed that the adsorption of PFOS on alumina decreased with an increase in Ca(II), due to the compression of the electrical double layers and formation of bridges between calcium ions and PFOS anions in solution [16].

Multi-walled carbon nanotubes (MWCNTs) have aroused widespread attention as a new type of adsorbents due to their outstanding ability for the removal of various organic and inorganic pollutants from large volumes of wastewater [17–21]. Adsorption and desorption of pollutants onto and from MWCNTs in aqueous phases is a critical process for environmental application of MWCNTs in water treatment [22–24]. This process is also important for determining the environmental and health impacts of both MWCNTs and pollutants [17,25–27]. In our previous work, Cu(II) were found to diminish the sorption of atrazine [28] and trichlorophenol [29] on MWCNTs, whereas atrazine or trichlorophenol had no influence on Cu(II) sorption. The mechanisms ascribed were the formation of surface or inner-sphere complexes of Cu(II) through carboxylic groups and hydration, which may occupy part of the surface of MWCNTs. Moreover, the large hydration shell of metal cations may intrude or shield the hydrophobic and hydrophilic sites and indirectly compete with atrazine or 2,4,6-trichlorophenol for surface sites, leading to the inhibition of their adsorption around the metal-complexed moieties.

Previous works have reported the sorption of heavy metal ions and PFOS on MWCNTs separately [30,31]. However, there are currently few studies on the dual effects of metals on the sorption of PFOS and conversely of PFOS on metal adsorption on MWCNTs. In this manuscript we focus on the dual effect between PFOS and Cu(II) on their sorption onto and desorption from MWCNTs. The interaction between PFOS and Cu(II) in solution was also discussed.

2. Materials and methods

2.1. Chemicals

Perfluorooctane-sulfonic potassium (PFOS, >98%) was purchased from Sigma-Aldrich Chemical Co. and was used as-received. It has a water solubility of 570 mg/L [31] and density of 1.95 g/cm³ (taken from the website by SPARC: <http://ibmcl2.chem.uga.edu/sparc>). Stock solution of Cu(II) was prepared from copper nitrate. All chemicals are of analytical reagent grade or better.

2.2. Adsorbents

Pristine and oxidative multi-walled carbon nanotubes (referred as Pri-MWCNTs and O-MWCNTs) were purchased from Chengdu Organic Chemistry Co. Ltd., Chinese Academy of Sciences. According to the manufacturer, the MWCNTs were synthesized by CVD method and have a purity of +95%, length of 10–30 µm, outer

diameter of 10–20 nm, and inner diameter of 5–10 nm. The TEM images of Pri-MWCNTs and O-MWCNTs are shown in Fig. 1. Detail information about the surface oxygen-containing groups was reported in our previous work [28,29]. Nitrogen adsorption/desorption isotherms at 77 K and carbon-dioxide adsorption isotherms at 273 K of MWCNTs were obtained by using a Nova 4200e surface area and pore size analyzer (Quantachrome Instruments, USA). Specific surface areas (SSA) and mesopore volume (V_{mes}) of MWCNTs were calculated from the isotherms using Brunauer-Emmett-Teller (BET), micropore volume (V_{mic}) using DFT method. The oxygen content and surface functional groups on MWCNTs were determined by X-ray photoelectron spectroscopy (ESCALab220i-XL electron spectrometer from VG Scientific, USA) using 300 W Al K α radiation under the base pressure about 3×10^{-9} mbar and Boehm titration. Zero points of charge (ZPC) of MWCNTs were obtained by plotting zeta potentials, which were measured in triplicate with Malvern ZetaSizer Nano S90 (Malvern Instrument Ltd., UK), versus pH.

2.3. Sorption and desorption experiment

A batch technique was utilized for the sorption of PFOS, or Cu(II), or cosorption of PFOS and Cu (II). 15 mg of MWCNTs were combined with the test 25 mL of electrolyte solution (0.01 M NaNO₃ and 0.1 g/L NaN₃, pH 5.5) containing different concentrations of PFOS (0.02–0.45 mmol/L), or Cu (II) (0.05–0.5 mmol/L), or the mixture of PFOS and Cu(II) in 50-mL polypropylene tubes. Reactors were mixed completely by shaking at 100 rpm at 20 ± 0.5 °C for 2 day. The pH value of the background solution was monitored three times during the sorption processes at every 12 h intervals and adjusted to 5.5 for all isotherms by dropwise addition of 0.1 mol/L HNO₃ or 0.1 mol/L NaOH if necessary. The preliminary experimental results showed that the pH value of the equilibration suspensions remained unchanged during the adsorption process, and apparent equilibration was reached in 1 and 2 d for Cu(II) and PFOS respectively. After centrifugation at 5000g for 20 min, supernatants were withdrawn and final PFOS and Cu concentrations were determined.

PFOS desorption experiments were conducted using a sequential decant-refill technique immediately following the completion of sorption experiments. A portion of the supernatant (10 mL) was withdrawn using a pipet and immediately replaced by the same volume of fresh desorption solution (0.01 mol/L NaNO₃ + 0.1 g/L NaN₃, pH 5.5). As for the sorption experiments at the end of each desorption cycle (2 d), the supernatant was sampled and determined. Desorption process was repeated for three complete cycles and as was done in the sorption experiments the solution pH during desorption processes was readjusted to 5.5 ± 0.1 three times at 12 h intervals.

Single point sorption experiments were performed at an initial concentration of 0.26 mmol/L PFOS, or 0.26 mmol/L Cu(II) as nitrate. Single point sorption experiments were performed to test the effects of Cu(II) concentrations on the sorption of PFOS and conversely of PFOS concentrations on metal adsorption on MWCNTs.

Blank experiments indicated that MWCNTs contained no detectable levels of PFOS or Cu(II), and the losses caused by degradation, adsorption onto polypropylene tubes, removal and replacement operation were less than 3%. Therefore, the amount of PFOS, Cu(II) adsorbed was directly calculated by mass differences between the initial and final concentrations.

2.4. Analysis

An ultra performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was used to determine the concentrations of PFOS, with an UPLC system (ACQUITY, Waters Corp., USA) equipped with a C18 column (2.1 × 150 mm, 5 µm, Waters Corp.,

Fig. 1. TEM images of MWCNTs: (a and b) Pri-MWCNTs; (c and d) O-MWCNTs.

USA) and MS system Quattro Premier XE tandem quadrupole mass spectrometer (Waters Corp., USA) equipped with an electrospray ionization source. The mixture of acetonitrile/10 mM ammonium acetate (v/v, 45/55) was used as the mobile phase at a flow rate of 0.2 mL/min. Cu(II) concentrations in the equilibrium solutions were determined by ICP-AES at 224.7 nm (Optima DV2000, Perkin-Elmer, USA).

2.5. Determination of free copper ion (Cu^{2+}) concentrations in the presence of PFOS

Copper ion selective electrodes (Cu-ISE) in combination with a voltmeter of 0.1 mV resolution (model 9629, Orion Research, Cambridge, MA) were used to measure Cu^{2+} concentrations in solutions containing 50 $\mu\text{mol/L}$ Cu(II) and different concentrations of PFOS. Solution containing 50 $\mu\text{mol/L}$ Cu(II) but no PFOS was used as control. The Cu-ISE was activated in 0.5 mol/L $\text{Cu}(\text{NO}_3)_2$ for 2 h and rinsed with Milli-Q water before use. The limit of detection was 0.7 $\mu\text{mol/L}$ Cu^{2+} . The activity of Cu^{2+} at each calibration point was calculated using the speciation program ChemEQL based on the total Cu concentration together with other parameters including pH, alkalinity, and major ion concentrations constituting inputs to the model.

2.6. Zeta potential (ξ -potential) measurement

The suspension for ξ -potential measurements was prepared by mixing MWCNTs (15 mg) with 0.01 M NaNO_3 solution (25 mL) containing 0.3 mmol/L Cu(II), or 0.3 mmol/L PFOS. The solution pH was adjusted to 3–6 using 0.1 M HNO_3 or NaOH. The suspensions were

rotated continuously for 24 h at room temperature ($20 \pm 1^\circ\text{C}$). The ξ -potentials were determined following the method described by Pei et al. [32].

2.7. X-ray absorption measurements and data analyses

The adsorbed samples were prepared according to the above sorption procedures, where the initial concentration of Cu(II) is 0.1 mmol/L, and the PFOS to Cu(II) ratios are 0, 1 and 5, respectively. After the adsorption reached equilibrium, samples were centrifuged to replace the supernatant with fresh adsorbate solution of initial composition. This procedure was repeated three times. The X-ray Absorption Near-Edge Structure (XANES) spectra of Cu were collected at Beijing Synchrotron Radiation Facility on 4W1B beamline. The conditions of X-ray absorption spectroscopic measurements were described previously [32]. The X-ray absorption spectra at Cu K-edges were recorded at a wiggler beamline and EXAFS end station of the Beijing Synchrotron Radiation Facility (China) using a homemade Si(111) double-crystal monochromator. During the experiment, the storage ring was operated at 2.2 GeV, with a beam current of approximately 80 mA. To suppress the unwanted high-order harmonics, the parallelism of the two crystals in the monochromator was adjusted to mistune the incident beam by 30%. The incident beam intensities were monitored and recorded using a nitrogen gas-flow ionization chamber. The fluorescence signals were measured using a Lytle-type fluorescence detector (EXAFS Company, Pioche, NV, USA) with filter (EXAFS Materials, Danville, CA, USA). Absorption data were collected in an energy range from 8920 to 9080 eV, covering the K-edge absorption of Cu atoms. Three scans were made and averaged for

both the adsorbed soil samples and the chemical standards. Processing of XANES data and least-square linear combination fitting (LCF) analyses were carried out using WinXAS program (version 3.1). LCF analyses of the Cu K-edge XANES spectra was performed in the region between 8960 and 9020 eV.

2.8. Adsorption data fitting

Adsorption isotherms were fitted using the Dubinin-Ashtakhov [33] and Freundlich models.

Dubinin – Ashtakhov model (DA) : $\log q_e = \log Q_m + (\epsilon/E)^b$ (1)

Freundlich model (FM) : $q_e = K_F C_e^N$ (2)

The concentration-dependent solid-water distribution ratio, K_d (L/kg), indicating adsorption affinity, was calculated based on the following equation:

$K_d = q_e/C_e = K_F C_e^{N-1}$ (3)

where C_e and q_e (mmol/kg) are the equilibrium adsorbate concentrations in the aqueous and solid phases; Q_m (mmol/kg) is the maximum loading capacity; ϵ (kJ/mol), $\epsilon = -RT \ln(C_e/C_s)$, is the effective adsorption potential; C_s (mmol/L) is the water solubility of solute; R (8.314×10^{-3} kJ/mol/K) is the universal gas constant; and T (K) is the absolute temperature; E (kJ/mol) is the correlating divisor; b is a fitting parameter. The K_F [(mmol/kg)/(mmol/L)^N] is the Freundlich adsorption coefficient and N (dimensionless) is the isotherm nonlinearity factor.

Freundlich equation-derived thermodynamic irreversible index (TII) was calculated to quantify the degree of desorption irreversibility [34]:

$TII = 1 - N_d/N_a$ (4)

where N_a and N_d are nonlinear factors for sorption and desorption isotherms, respectively. The TII values lies between 0 and 1, with 0 indicating a completely reversible system and 1 complete irreversibility.

2.9. Data analysis

All statistical analyses were conducted with the software Origin version 7.5. One-way ANOVA was used to assess the significance of the difference between groups, and nonlinear regression analyses were conducted by the least-squares method. Statements of significant differences are based on $P < 0.05$.

3. Results

3.1. Characterization of MWCNTs

Selected structural properties of MWCNTs are listed in Table 1. O-MWCNTs have a larger surface area and pore volumes than Pri-MWCNTs due to the removal of amorphous carbon and hemispherical caps on the nanotubes. Both Pri-MWCNTs and O-MWCNTs

Table 2

Determination of Cu²⁺ concentrations in solutions measured by Cu-ISE in the absence and presence of PFOS.

PFOS to Cu(II) ratios	Percentage of Cu ²⁺ to total Cu(II) (%) ^a			
	pH 3	pH 4	pH 5.5	pH 6
Control	98.6 (1.7) ^a	96.9 (1.3) ^a	96.9 (1.0) ^a	97.7 (1.0) ^a
0.5:1	98.2 (1.1) ^a	97.1 (1.7) ^a	96.5 (1.7) ^b	96.2 (1.1) ^a
1:1	98.2 (1.3) ^a	96.9 (1.5) ^a	96.6 (1.2) ^a	97.0 (1.9) ^a
5:1	97.6 (1.4) ^a	94.8 (1.3) ^a	95.5 (0.7) ^a	95.9 (0.8) ^a
10:1	92.9 (1.4) ^b	91.9 (0.6) ^b	90.5 (0.7) ^b	90.5 (0.7) ^b

^a Means within each column with the same letter are not significantly different at the 5% level.

have oxygen-containing functional groups. Oxidation introduced more oxygen-containing groups on the outermost surface and defect sites, resulting in the decrease of the point of zero charge (PZC) (Table 1).

3.2. Effect of PFOS on free copper ion (Cu²⁺) concentration in solution

Effect of PFOS on Cu²⁺ concentrations that measured by Cu-ISE are shown in Table 2. More than 95% of total Cu in control solution is Cu²⁺. The presence of PFOS affected Cu²⁺ concentration slightly. When the ratios of PFOS to Cu(II) increased from 0.5 to 5, the percentages of Cu²⁺ were equivalent to that of the control. When the ratio of PFOS to Cu(II) was 10, Cu²⁺ concentrations were 90.5–92.9% of the total Cu(II) concentrations in solution.

3.3. Sorption and desorption of PFOS onto and from MWCNTs as affected by Cu(II)

Adsorption isotherms of PFOS at pH 5.5 on MWCNTs with or without Cu(II) are shown in Fig. 2. All the isotherms fitted by both DA and FM well, with the R^2 values higher than 0.981 and 0.988 for DA and FM respectively (Fig. 2, Table 3). The FM parameters suggested that the PFOS sorption isotherms on MWCNTs were all practically nonlinear, with N values ranging from 0.319 to 0.569. A precise comparison cannot be made according to the K_F values because of their different units as a result of nonlinearity. Therefore, the concentration-dependent sorption coefficient K_d at two selected equilibrium concentrations (C_e) (0.05 and 0.3 mmol/L), and the maximum loading capacity (Q_m) derived from DA model were employed to compare the sorption capacity. The K_d and Q_m values of Pri-MWCNTs were higher than those of O-MWCNTs. The maximum surface coverage of PFOS was calculated by dividing Q_m by the calculated monolayer adsorption capacity (Q_m/Q_{cal} , Table 3). In the absence of Cu(II), the Q_m/Q_{cal} values of PFOS for Pri-MWCNTs and O-MWCNTs were 0.643 and 0.348, respectively.

In the presence of Cu(II), PFOS adsorption on both Pri-MWCNTs and O-MWCNTs was significantly higher than those in the absence of Cu(II) (Fig. 2). The larger the Cu(II) concentrations, the greater the quantity of PFOS adsorbed (Fig. 3). The enhanced factors of O-MWCNTs were larger than that of Pri-MWCNTs. The Q_m values

Table 1

Selected structural properties of the MWCNTs.

MWCNTs	Out diameter ^a (nm)	Inner diameter ^a (nm)	Length (μm)	Oxygen ^b content (%)	A_{surf} ^c (m ² /g)	V_{meso} ^c (cm ³ /g)	V_{micro} ^c (cm ³ /g)	PZC
Pri-MWCNTs	10–20	5–10	10–30	1.52	149.3	0.305	0.016	4.0
O-MWCNTs	10–20	5–10	10–30	7.07	185.2	0.756	0.024	1.4

^a Determined by high-resolution transmission electron microscopy (TEM).

^b Oxygen content was analyzed by energy-dispersive X-ray spectroscopy.

^c Surface area (A_{surf}), and mesopore pore volume (V_{meso}) were calculated from the adsorption–desorption isotherm of N₂ at 77 K by multi-point BET, BJH methods, respectively. The micropore volume (V_{micro}) was measured by carbon dioxide sorption with Quantachrome instruments v2.2 and calculated with DFT method.

Fig. 2. Effect of Cu(II) on the sorption and desorption of PFOS from MWCNTs at pH 5.5. (a) Adsorption and desorption isotherms of PFOS on Pri-MWCNTs as affected by 0.26 mmol/L Cu(II); (b) Adsorption and desorption isotherms of PFOS on O-MWCNTs as affected by 0.26 mmol/L Cu(II); Lines: fitting to Freundlich model.

for Pri-MWCNTs and O-MWCNTs in the presence of Cu(II) were about 5.5 and 6.0 times, respectively, those in the absence of Cu(II). In the presence of Cu(II) the Q_m/Q_{cal} values of PFOS for both Pri-MWCNTs and O-MWCNTs were higher than 1.

Desorption of PFOS from Pri-MWCNTs and O-MWCNTs showed no desorption hysteresis in the absence of Cu(II), whereas a pronounced hysteresis was observed in the presence of Cu(II) (Fig. 2). The TII was used to quantify the hysteresis. The TII values

for PFOS desorption were -0.14 to 0.11 and 0.58 – 0.78 for MWCNTs in the absence and presence of Cu(II), respectively.

3.4. Sorption and desorption of Cu(II) onto and from MWCNTs as affected by PFOS

Adsorption isotherms of Cu(II) at pH 5.5 on MWCNTs with or without PFOS are shown in Fig. 4. All the isotherms fitted FM well (Fig. 4, Table 4). The parameters derived suggested that the Cu(II) adsorption on O-MWCNTs was higher than that adsorption on Pri-MWCNTs. In the presence of PFOS, Cu(II) adsorption increased significantly. For instance, the K_d value for O-MWCNTs at low C_e (0.05 mmol/L) in the presence of PFOS was 1.72 times higher than that in the absence of PFOS. The larger the PFOS concentrations, the greater the quantity of Cu(II) adsorbed (Fig. 5).

Desorption of Cu(II) from Pri-MWCNTs and O-MWCNTs showed significant desorption hysteresis with and without PFOS (Fig. 4). The TII values in the presence of PFOS were in the range of 0.07–0.43, which was smaller than those in the absence of PFOS (0.38–0.80).

3.5. Effect of Cu(II) and PFOS sorption on zeta potential of MWCNTs

Zeta potentials of Pri-MWCNTs and O-MWCNTs were measured before and after adsorption of 0.3 mmol/L Cu(II) or 0.3 mmol/L PFOS as a function of pH (Fig. 6). Zeta potentials of Pri-MWCNTs and O-MWCNTs were more negatively charged with increasing solution pH. The sorption of Cu(II) made the zeta-potentials of MWCNTs surface less negative charged, while the sorption of PFOS made the zeta-potential of Pri-MWCNTs and O-MWCNTs more negative charged.

3.6. X-ray absorption spectroscopic investigation of coordination environment of Cu

Cu K-edge X-ray absorption near edge structure (XANES) spectral features are very sensitive to molecular coordination. Thus, interpretation of the XANES spectra can be used to determine molecular structure of Cu(II) adsorbed on MWCNTs.

Fig. 7 shows Cu K-edge spectra (a) and their first derivatives (b) for Cu(II) adsorbed on O-MWCNTs, along with two standard compounds $\text{Cu}(\text{OH})_2$ precipitation, and $\text{Cu}(\text{NO}_3)_2$ in aqueous solutions. The normalized K-edge XANES spectra are very similar. The pre-edge peak in the first derivative spectra is due to the 1s to 3d electron transition, and is invariant in the Cu(II) XANES spectra in this study. The obvious two peaks (α and β peaks) in Fig. 7b were qualitatively related to the difference between the equatorial and axial Cu–O distances in the CuO_6 octahedron [35]. The energy separation and intensity of the α and β peaks is dependent on molecular

Table 3
Freundlich and Dubinin–Ashtakhov (DA) model isotherm parameters for PFOS with and without Cu(II).

Sorbents	Cu contents (mmol/L)	Freundlich					Dubinin-Ashtakhov					
		^a K _F	<i>N</i>	<i>R</i> ²	<i>K</i> _d (L/kg)		<i>Q</i> _m (mmol/kg)	<i>E</i> (kJ/mol)	<i>b</i> (mmol/kg)	<i>R</i> ² (mmol/kg)	^c <i>Q</i> _{cal.} (mmol/kg)	<i>Q</i> _m / <i>Q</i> _{cal} (mmol/kg)
						^b <i>C</i> _e = 0.05 mmol/L	^b <i>C</i> _e = 0.30 mmol/L					
Pri-MWCNTs	0	319 (7) ^d	0.319 (0.010)	0.992	2454	724	232 (15)	16.2 (0.3)	2.1 (0.2)	0.981	361	0.643
	0.26	1206 (50)	0.560 (0.018)	0.995	4507	2048	1266 (159)	9.8 (0.9)	0.9 (0.1)	0.997		3.78
O-MWCNTs	0	169 (5)	0.462 (0.017)	0.988	847	323	156 (22)	12.6 (0.6)	1.1 (0.1)	0.990	448	0.348
	0.26	1129 (30)	0.569 (0.012)	0.998	4107	1897	932 (85)	10.9 (0.6)	1.2 (0.1)	0.997		2.08

^a The unit of K_F is (mmol/kg)/(mmol/L)^N; $K_d = K_F C_e^{N-1}$.

^b $C_e = 0.05$ mmol/L and $C_e = 0.3$ mmol/L are the liquid-phase equilibrium concentrations at 0.05 and 0.3 mmol/L, respectively.

^c Q_{cal} is the monolayer adsorption capacity (mmol/kg) calculated by $A_{surf}/(A_m \times N) \times 10^{10}$, where A_{surf} is the CNT surface area (m²/kg), A_m is the projecting area of PFOS (cm²) estimated by $\pi \times (3/[(4\pi \times D \times N)]/2/3$, where N is the Avogadro constant, D is the density of PFOS, 1.84 g/cm³.

^d Standard deviation (σ).

Fig. 3. K_d of PFOS (0.26 mmol/L) as a function of initial Cu (II) concentrations.

composition and coordination, and can be used to qualitatively assess Cu speciation on MWCNTs. The first derivatives for Cu(II) adsorbed on O-MWCNTs were quite different from that of $\text{Cu}(\text{OH})_2$, indicating that the formation of $\text{Cu}(\text{OH})_2$ did not account for the

adsorption of Cu(II) on MWCNTs. Compared to that of aqueous $\text{Cu}(\text{NO}_3)_2$, the α peak intensity of Cu adsorbed in the absence of PFOS (Cu-MWCNTs) decreased significantly (Fig. 7b), suggesting that the stronger field water molecules in the tetragonal plane had exchanged with different field organic moieties such as carboxylic and hydroxylic groups. The decreased α peak intensity in Cu adsorbed on MWCNTs also suggested that O-MWCNTs were sterically hindered due to their three-dimensional structure and that when Cu approached the surface, Cu could not be bound in the equatorial plane with the same degree of angular overlap as that of water. These indicated that the adsorbed Cu was present in a disordered geometry of an inner-sphere complex. When the PFOS to Cu(II) ratio is 1, the first derivative spectrum is similar to that in the absence of PFOS. Fitting the first derivative spectrum of Cu(II) adsorbed on O-MWCNTs (PFOS/Cu = 1) using both the aqueous $\text{Cu}(\text{NO}_3)_2$ and Cu-MWCNTs spectra resulted in 3.6% $\text{Cu}(\text{NO}_3)_2$ and 96.4% Cu-MWCNTs, with a residual of 5.5% (Fig. 8a), which indicated that Cu(II) adsorbed mainly as an inner-sphere complex when PFOS to Cu ratio is 1. When the PFOS to Cu ratio increased from 1 to 5, the position of the α and β peaks for the XANES spectrum match well with the hydrated Cu(II). Using aqueous Cu(II) XANES spectrum as a standard to fit that of Cu(II) adsorbed on MWCNTs (PFOS/Cu = 5), the fit residual was 13.4%. Using both the aqueous $\text{Cu}(\text{NO}_3)_2$ and Cu-MWCNTs spectra resulted in 80.9% $\text{Cu}(\text{NO}_3)_2$ and 29.1% Cu-MWCNTs, with an improvement in fit residual of 5.8% (Fig. 8b), indicating that when

Fig. 4. Effect of PFOS on the sorption and desorption of Cu(II) from MWCNTs at pH 5.5. (a) Adsorption and desorption isotherms of Cu(II) on Pri-MWCNTs as effect by 0.26 mmol/L PFOS; (b) Adsorption and desorption isotherms of Cu(II) on O-MWCNTs as effect by 0.26 mmol/L PFOS. Lines: fitting to Freundlich model.

Table 4

Freundlich model isotherm parameters for Cu(II) with and without PFOS.

Sorbent	PFOS mmol/L	K_f (mmol ^{1-N} L ^N kg ⁻¹)	N	R^2	^a K_d (L/kg)	
					^b $C_e = 0.05$ mmol/L	$C_e = 0.5$ mmol/L
Pri-MWCNT	0	112.7 ± 5.2 ^c	0.262 ± 0.018	0.987	1028	188
Pri-MWCNT	0.26	231.5 ± 12.0	0.403 ± 0.035	0.986	1384	350
O-MWCNT	0	173.3 ± 4.4	0.315 ± 0.016	0.982	1348	279
O-MWCNT	0.26	1768.8 ± 120.0	0.929 ± 0.043	0.994	2188	1858

^a $K_d = K_f C_e^{N-1}$.^b $C_e = 0.05$ mmol/L and $C_e = 0.5$ mmol/L are the liquid-phase equilibrium concentration at 0.05 and 0.5 mmol/L, respectively.^c Standard deviation (σ). **Fig. 5.** K_d of Cu (II) (0.26 mmol/L) as a function of initial PFOS concentrations.

PFOS to Cu(II) ratio is 5, Cu(II) adsorbed mainly as out-sphere complex. Thus, we deduced that with the PFOS to Cu ratio increasing, the portion of Cu(II) adsorbed as an inner-sphere complex decreased, while those adsorbed as an out-sphere complex increased.

4. Discussion

4.1. Possibility of Cu-PFOS complex formation in solution

PFOS is an organic acid with the PK_a of -3.27. Complex formation between divalent cations (Ca^{2+} and Mg^{2+}) and PFOS in solution was proposed [16]. However, no apparent formation constant between PFOS and Cu(II) was found so far, limiting the performance of PFOS and Cu(II) chemical speciation calculation using computer programs. In this study, ISE was used to measure the concentrations of Cu^{2+} in order to explore the possibility of Cu-PFOS complex formation in solution at different pH. The results showed that the concentration of Cu^{2+} only decreased when PFOS to Cu(II) ratio was 10, suggesting that the formation of complexes between PFOS and Cu(II) in solution is very weak.

4.2. Sorption and desorption of PFOS as affected by Cu(II)

It is suggested that hydrophobic and electrostatic interactions were involved in the sorption of PFOS on sediment [13], activated sludge [36], MWCNTs [31] and granular active carbon [8]. In this study, in the absence of Cu(II), the maximum surface coverage of PFOS were 64.3% and 34.8% for Pri-MWCNTs and O-MWCNTs, respectively (Table 3), indicating that a fraction of surface sites of

Fig. 6. Zeta potential as a function of pH for Pri-MWCNTs (a) and O-MWCNTs (b) without Cu or PFOS (■), with 0.3 mmol/L Cu (II) (●), 0.3 mmol/L PFOS (▲).

Pri-MWCNTs and O-MWCNTs cannot be occupied by PFOS, and the accessible surface sites of Pri-MWCNTs was larger than those of O-MWCNTs. Compared with Pri-MWCNTs, the O-MWCNTs are more hydrophilic and less surface area is accessible to PFOS because the water adsorbed on MWCNTs surface (through H bonding of oxygen), which blocks PFOS approach [37]. Moreover, zeta potential analysis showed that the surface charges of O-MWCNTs are more negative than those of Pri-MWCNTs at pH 5.5 (Fig. 6). Thus compared with that of Pri-MWCNTs, much electrostatic repulsion between the anionic PFOS and deprotonated hydroxylic and carboxylic groups of O-MWCNTs is expected to weak the sorption of PFOS. Li et al. also reported that the adsorption of ionizable organic contaminants decreased with oxygen contents of MWCNTs increasing [31].

Fig. 7. Normalized XANES spectra (pre- and near-edge region) of Cu(II)-O-MWCNTs (a), and the corresponding first derivatives (b).

In the presence of Cu(II), adsorption of PFOS on MWCNTs increased obviously, and the maximum surface coverage for Pri-MWCNTs and O-MWCNTs were higher than 1 (Table 3), indicating that the presence of Cu(II) not only enhanced the PFOS accessibility to MWCNTs, but also provided extra sorption sites. Various mechanisms were postulated to be responsible for the increases of anionic chemical sorption in the presence of divalent cation, including salt-out effect, which decreased the solubility of PFOS [38], and the neutralization of the negative charge on the sorbent surface [13], which reduced the electrostatic repulsion between the negative charged sorbent surface and the anionic PFOS. Moreover, Cu(II) can adsorb onto MWCNT surface sites, resulting in positive Cu sites to which negatively charged PFOS will be attached due to electrostatic interactions. Cu(II) could form a bridge between the anionic MWCNTs functional groups (e.g., carboxyl and hydroxyl groups) and the anionic PFOS could adsorb with Cu-bridging sorption mechanism [12]. Results of zeta potential analysis demonstrated the positive surface sites at pH 5.5 in the presence of 0.3 mmol L⁻¹ Cu(II) (Fig. 6). The adsorption above a simply monolayer adsorption may due to that adsorbed molecules are oblique to the surface of MWCNTs with an angle [39]. In this case, the $-\text{SO}_3^-$ group of PFOS could be responsible for this oblique attachment because these groups can be attracted by the positive surface sites.

Sannino et al. postulated that there are two types of mechanisms for the adsorption of anionic organic chemicals: a physical and a

chemical adsorption [40]. Physically adsorbed anionic organic chemicals would be easily removed, whereas those via cation-bridge would be more strongly retained, which may be in charge of irreversible desorption. Yang and Xing suggested that the capillary condensation in mesopores or macropores, rearrangement of the bundles or aggregates of MWCNTs, and the formation of covalent bond between oxygen-containing functional groups of MWCNTs and oxygen- or nitrogen-containing functional groups of the organic chemicals are responsible for the desorption hysteresis of organic pollutants from MWCNTs [17]. In this study, no hysteresis was found for PFOS desorption in the absence of Cu(II), indicating that adsorption of PFOS on MWCNTs without Cu(II) are mainly physical adsorption. In the presence of Cu(II), PFOS may adsorb on MWCNTs via Cu-bridge, which would be more strongly retained on the MWCNT surface. Alternatively, rearrangement of the bundles or aggregates of MWCNTs alteration of adsorbent structure or reorganization after Cu(II) adsorption may be another reason to be responsible for the desorption hysteresis in the presence of Cu(II), because Cu(II) could act by cross-linking functional groups on adjacent tubes, creating a more tightly knit bundle [19].

4.3. Sorption and desorption of Cu(II) as affected by PFOS

The mechanisms of heavy metal ion adsorption on MWCNTs include physical adsorption, electrostatic attraction, precipitation and chemical interaction between the heavy metal ions and the surface functional groups of CNTs. Among these, chemical interaction between the heavy metal ions and the surface functional groups of CNTs is the major adsorption mechanism [18]. In this study, the desorption hysteresis of Cu(II) was found for both O-MWCNTs and Pri-MWCNTs, indicating the chemical interaction between Cu(II) and the functional groups on O-MWCNTs and Pri-MWCNTs. The Freundlich parameter K_d values of O-MWCNTs was about 1.5 times that of MWCNTs (Table 4), which was attributed to the higher amount of O contents on O-MWCNTs surface (Table 1). Wu [30] reported that the adsorption of Cu²⁺ on as-produced CNTs and HNO₃-modified CNTs is a chemically specific reaction. The maximum sorption capacity of Cu(II) on HNO₃-modified CNTs was about 1.68 times that of as-produced CNTs. Chen et al. [28] suggested that Cu(II) was adsorbed on MWCNTs through formation of an inner-sphere complex in which the water molecules were partly displaced by the carboxylic and hydroxylic groups of MWCNTs. In this study, the formation of strong inner-sphere complexes between Cu(II) and oxygen containing functional groups of O-MWCNTs in the absence of PFOS was also demonstrated by X-ray absorption spectroscopy (Fig. 7). This inner-sphere complexes were responsible for the desorption hysteresis of Cu(II) from MWCNTs (Fig. 4). In the presence of PFOS, Cu(II) adsorption on MWCNTs significantly increased, and the desorption hysteresis index decreased. The changes of adsorption–desorption behavior of Cu(II) indicated the shift of sorption mechanisms. PFOS mainly adsorbed on the hydrophobic sites of MWCNTs [31], leading to the lower zeta potential of these sites (Fig. 6). The reason for enhanced Cu(II) sorption in the presence of PFOS was possibly due to Cu(II) adsorption not only through the complexation with oxygen containing functional groups of MWCNTs, but also through electrostatic interaction with the adsorbed PFOS, that is, through formation of outer-sphere complex via PFOS bridge. With PFOS concentration increasing, out-sphere complex was the main adsorption mechanism, as verified by X-ray spectroscopy when PFOS to Cu(II) ratio was 5 (Fig. 8).

The results from this study showed that PFOS and Cu(II) exhibited different adsorption and desorption behavior in single- and bi-solute systems, though the formation of complex between PFOS and Cu(II) in solution is very weak. The coexistence of PFOS and Cu(II) could increase their adsorption on MWCNTs significantly,

Fig. 8. Copper K-edge first derivative XANES spectrum of Cu adsorbed on the O-MWCNTs at PFOS to Cu ratios of 1:1 (a) and 5:1 (b) and the LCF results (open circles). The weighted components and corresponding residual are displayed in the figure.

thus enhancing the elimination of PFOS and Cu(II) from wastewater using MWCNTs. In bi-solute system, desorption hysteresis factors of PFOS were larger, while hysteresis factors of Cu(II) were smaller than those in single-solute system. The different sorption and desorption of PFOS and Cu(II) between single- and bi-solute system could be attributed to the Cu(II) adsorption via the PFOS bridge, and the PFOS adsorption via the Cu(II) bridge.

5. Conclusions

In view of the foregoing study, the coexistence of PFOS and Cu(II) enhanced their adsorption onto Pri-MWCNTs and O-MWCNTs, which indicated that the removing efficiency of PFOS and Cu(II) by MWCNTs from wastewater would be enhanced. Desorption of PFOS showed no hysteresis without Cu(II), while pronounced hysteresis with Cu(II). Desorption of Cu(II) without PFOS showed significant desorption hysteresis, while the desorption hysteresis factors decreased with PFOS. The difference of sorption and desorption behavior of PFOS and Cu(II) between those in single-solute and bi-solute systems may be attributed to the sorption of PFOS via a Cu(II) bridge, while the sorption of Cu(II) via a PFOS bridge. Results obtained from X-ray absorption spectroscopy verified the formation of inner-sphere complexes between Cu(II) and functional groups of MWCNTs without PFOS, while out-sphere complexes with large amount of PFOS.

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