Adsorption of perfluorooctane sulfonate on carbon nanotubes: influence of pH and competitive ions

Yue Bei, Shubo Deng, Ziwen Du, Bin Wang, Jun Huang and Gang Yu

ABSTRACT

Perfluorooctane sulfonate (PFOS) is one of the persistent organic pollutants that has aroused global concern. Carbon nanotubes (CNTs) have drawn much research attention due to their unique properties. This study was aimed to investigate the adsorption behaviour of PFOS with relation to CNTs and clarify their interactions. Electrostatic repulsion suppressed the sorption of PFOS to multi-walled carbon nanotubes (MWCNTs), resulting in low sorption at high pH. With the increase of anion concentration, the removal of PFOS decreased by 20 to 30% because ionic strength changed the aggregation of the MWCNTs. Unlike inorganic anions, cationic metals including Cu(II) and Pb(II) had a significant impact on the sorption of PFOS onto the MWCNTs. At low concentrations of Cu(II) and Pb(II), PFOS removal decreased due to the suppressive effect of ionic strength, while the removal of PFOS increased rapidly with increasing metal concentrations, especially for functionalized MWCNTs. The enhanced adsorption of PFOS at high Cu(II) and Pb(II) concentrations was attributed to the adsorbed cationic metals which might further adsorb PFOS.

Key words | carbon nanotubes, competitive adsorption, perfluorooctane sulfonate, sorption mechanism

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INTRODUCTION

Perfluorooctane sulfonate (PFOS) is one of the typical perfluorinated compounds (PFCs) widely distributed in the aquatic environment; it is very persistent and has a water solubility up to 570 mg/L (Nakata et al. 2006; Yu et al. 2009). Hence, PFOS can exist and be transported in water for a long time, and has become a global concern in aquatic environments (Giesy & Kannan 2002; Wang et al. 2009). Although PFOS was listed as one of the new persistent organic pollutants in 2009, it is still being produced and used in some special industries in developing countries (Wu 2008). PFOS has been detected in wastewater, surface water, groundwater and even tap water throughout the world (Ju et al. 2008; Takagi et al. 2011). For example, the average concentration of PFOS found in the Yangtze River was 5.4 ng/L; tap water in Guangzhou and Shenzhen contained more than 10 ng/L of PFOS (Jin et al. 2009). In addition, it has been reported that PFOS can cause weight loss, alveolar wall thickening, mitochondrial damage, gene induction, larval mortality increase as well as deadly diseases and other adverse biological effects when a certain dose of PFOS is ingested (Schroder & Meesters 2005; Loos

et al. 2008). Therefore, it is important to investigate the adsorption of PFOS on solid-liquid interfaces in the aquatic environment.

Carbon nanotubes (CNTs) have been widely used in many areas (Zhang et al. 2009), and they continually enter the aquatic environment with increasing production and application. Many researchers have reported the sorption of traditional hydrocarbon pollutants on CNTs (Wang et al. 2010; Yu et al. 2012) but there is little research about the adsorption of PFOS on CNTs. It is necessary to understand their interactions in an aquatic environment, providing theoretical support for their transport and fate in the environment (Colvin 2003; Wiesner et al. 2006).

To date, few papers have reported the adsorption of PFOS on CNTs. Li et al. (2011a, b) found that the adsorption of PFOS on CNTs was enhanced by electrochemical assistance and influenced by the oxygen content of CNTs. Zhou et al. (2012) studied the adsorption of PFOS at high concentrations onto CNTs in the presence of copper in wastewater. Our previous study also investigated the adsorption of six PFCs on CNTs, and the adsorption mechanism was

discussed (Deng *et al.* 2012). However, the competitive adsorption of PFOS with inorganic anions and cations on CNTs has not been fully studied, especially at low PFOS concentrations in surface water. In this study, the sorption of PFOS at low concentrations on CNTs was investigated, and experiments to show the effects of some coexisting ions (sulphate, chloride, chromate, copper and lead) and solution pH on the adsorption of PFOS were performed to explore the adsorption mechanism between PFOS and CNTs.

MATERIALS AND METHODS

Materials

Three multi-walled carbon nanotubes (MWCNTs) with outer diameters of 10–20 nm were selected as adsorbents in this study. The pristine MWCNTs (MWCNTs-Pri), COOH-functionalized MWCNTs (MWCNTs-COOH) and OH-functionalized MWCNTs (MWCNTs-OH) were purchased from Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences, and used as received. Some parameters of these MWCNTs are presented in Table 1. PFOS was purchased from Sigma-Aldrich Company (USA). Other reagents were all of analysis grade.

Sorption experiments

In all batch experiments, 5 mg of adsorbent were placed in 100 mL of PFOS solution in 250 mL polypropylene bottles with lined screw caps. All adsorption experiments were carried out in an orbital shaker at 180 rpm for 48 h (the preliminary experiment indicated that sorption equilibrium was reached), and the temperature was controlled at $25 \pm 1\,°C$. 0.1 M NaOH and HCl were used to adjust pH, and the pH values were controlled at 7 ± 0.1 (except in the metal competitive

experiment) by adjusting every 12 h. All experiments were run in duplicate. For the sorption isotherm experiments, the MWCNTs-Pri, MWCNTs-COOH and MWCNTs-OH were added to a 100 mL solution with PFOS concentrations ranging from 0.0001 to 0.5 mmol/L. The effect of solution pH on sorption of PFOS on the MWCNTs-Pri, MWCNTs-COOH and MWCNTs-OH was examined in 100 mL of 0.5 μmol/L PFOS solution at pH from 3 to 10. In the anion competitive sorption experiments, 100 mL of 0.5 μmol/L PFOS solution and 100 mL of SO_4^{2-} (10–500 μmol/L), Cl^- (10–500 μmol/L), or $Cr_2O_7^{2-}$ (2.5–100 μmol/L) were mixed. In the cationic metal competitive sorption experiments, 100 mL of 0.5 μmol/L PFOS solution and 100 mL of Cu(II) or Pb(II) (2.5–100 μmol/L) were mixed, followed by adjusting pH to 5. In the control experiments, 5 mg of MWCNTs-Pri and MWCNTs-OH were also used to adsorb Cu(II) at the same concentrations in the absence of PFOS.

The removal percentage (R, %) and adsorbed amount (q_e, mmol/g) of PFOS on the MWCNTs were calculated as follows:

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of PFOS in solution (mmol/L), m is the MWCNTs mass (g), and V is the solution volume (L).

Measurement of zeta potentials of MWCNTs

The zeta potentials of MWCNTs were analyzed with a Delsa Nano C zeta potential instrument (Beckham Coulter, USA). An amount of 0.01 g MWCNTs was placed into each conical flask, and the solution pH was adjusted in the range of 3–10

Table 1 | Physical and chemical parameters of CNTs used in this study

MWCNTs	Elemental content (%)[a]			Purity[b] (%)	SA[c] (m²/g)	COOH[d] (%)	OH[d] (Ω)
	C	H	O				
MWCNTs-Pri	98.07	0.12	0.66	98.98	122.03	/	/
MWCNTs-COOH	87.88	0.35	8.54	96.72	127.95	1.00	/
MWCNTs-OH	85.23	0.41	10.90	95.17	139.09	/	1.53

[a]Dry-weight-based elemental content of the CNTs was determined by a Vario ELII elemental analyzer.
[b]Measured by thermo gravimetric analysis.
[c]Surface area was calculated from the adsorption-desorption isotherm of N_2 at 77K using the multipoint BET (Brunauer–Emmett–Teller) method.
[d]Characterized by Boehm's titration.

using 0.01 M HCl or NaOH solution. All data were determined three times and the average value was adopted.

Determination of PFOS and metal concentrations

After sorption experiments, the supernatant was filtered with a 0.45 μm polyether sulphone membrane (PFOS adsorbed on the membrane was negligible). A high pressure liquid chromatography-tandem mass spectrometer (HPLC-MS/MS) was used to determine the concentrations of PFOS with an HPLC system (API 3200, Applied Biosystems Inc., USA) equipped with an Agilent C18 column (2.1 mm × 100 mm i.d., particle size 3.5 μm) and a Quattro Premier XE tandem quadrupole mass spectrometer with an electrospray ionization source. The mobile phase consisted of a binary mixture of 2 mmol/L ammonium acetate (solvent A) and 0.3 mL/min methanol (solvent B). The gradient started with 85% A and 15% B, and was linearly ramped to 0% A and 100% B from 1 to 20 min, and ramped to 85% A and 15% B from 30 to 30.1 min and kept constant until 40 min. The injection volume was 10 μL. The PFOS concentrations above 2 μmol/L were determined using an LC-10ADvp HPLC with a CDD-6A conductivity detector (Shimadzu, Japan). The detailed method was reported in our previous paper (Deng *et al.* 2010). Metal ions such as

Cr(VI), Cu(II), and Pb(II) were all detected by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Sorption isotherm

Figure 1 illustrates the sorption isotherm of PFOS on MWCNTs-Pri, MWCNTs-COOH and MWCNTs-OH, and it can be seen that the sorption amount of PFOS decreased in the order of MWCNTs-OH > MWCNTs-COOH > MWCNTs-Pri. Langmuir and Freundlich (Li *et al.* 2005) equations were used to describe the sorption data. The Langmuir equation can be expressed as $q_e = kC_e q_m/(1 + kC_e)$, where q_e and C_e are the equilibrium PFOS concentration on the adsorbent and in aqueous solution, respectively; q_m is the maximum adsorption capacity; k is the Langmuir constant. The Freundlich equation can be expressed as $q_e = K_F C_e^n$, where K_F is the Freundlich affinity coefficient; and n is the Freundlich linearity index. As is shown in Table 2 and Figure 1, the Langmuir model described the data better in the whole range than the Freundlich equation, indicating the possible monolayer adsorption of PFOS on the MWCNTs. Because the MWCNTs used in this study had a similar length and external diameter, different surface areas might play an important role in the sorption. The sorption amount increased with increasing surface areas (MWCNTs-OH > MWCNTs-COOH > MWCNTs-Pri). Since the functionalized groups of MWCNTs are hydrophilic, they can be dispersed well in water, making more surface available for PFOS adsorption. In contrast, MWCNTs-Pri are prone to aggregation in water due to the hydrophobic surface.
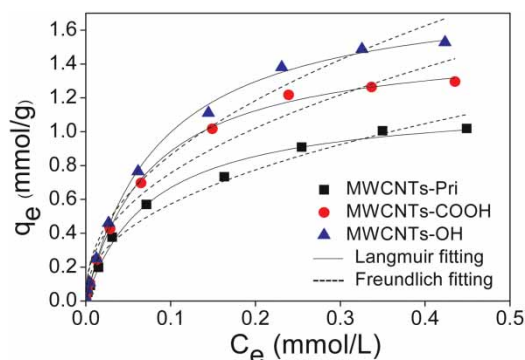
Effect of solution pH

Figure 2(a) shows the effect of solution pH on the adsorption of PFOS on the different MWCNTs. With increasing pH, the removal of PFOS by the MWCNTs decreased significantly.

Figure 1 | Adsorption isotherms of PFOS on different MWCNTs and modeling with the Langmuir and Freundlich equations.

Table 2 | Calculated constants of Langmuir and Freundlich models for the adsorption of PFOS on three MWCNTs

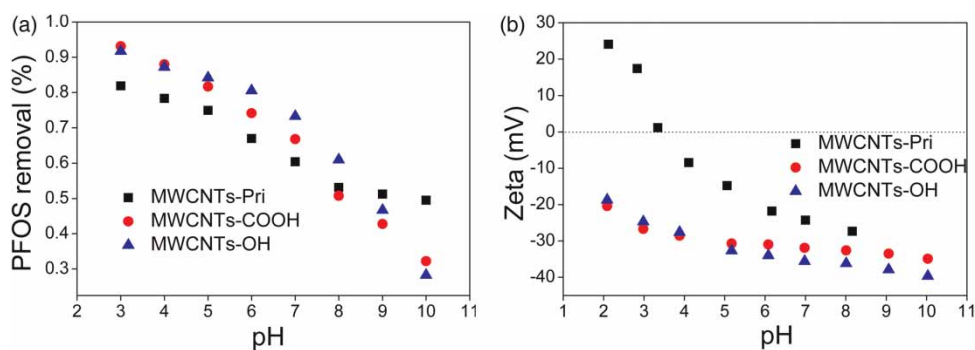| Adsorbents	Langmuir constants			Freundlich constants		
	q_m	k	R^2	K_F	n	R^2
MWCNTs-Pri	1.18 ± 0.03	12.98 ± 1.43	0.993	1.56 ± 0.09	2.29 ± 0.19	0.977
MWCNTs-COOH	1.54 ± 0.02	13.39 ± 0.72	0.998	2.05 ± 0.15	2.30 ± 0.23	0.966
MWCNTs-OH	1.85 ± 0.03	11.58 ± 0.73	0.998	2.47 ± 0.16	2.19 ± 0.19	0.976

Figure 2 | Effect of pH on PFOS adsorption on the different MWCNTs (a) and zeta potential of three MWCNTs (b).

The functionalized MWCNTs had higher PFOS removal than the MWCNTs-Pri at pH less than 8, but the removal was lower at pH above 8. The decreased removal of PFOS with increasing solution pH indicated that electrostatic interaction was involved in the adsorption of PFOS on the MWCNTs. The MWCNTs-Pri had a zero point of zeta potential at pH 3.3 (Figure 2(b)), and thus the surface of the MWCNTs-Pri was negative at pH above 3.3, while the functionalized MWCNTs were all negatively charged in the pH range studied. Since PFOS exists as anions in solution due to the low pK_a (-3.27) (Campbell *et al.* 2009), electrostatic repulsion should occur to prevent the adsorption of PFOS to the three MWCNTs. It has been reported that electrostatic interaction is involved in the adsorption of PFOS on alumina (Wang & Shih 2011), goethite (Tang *et al.* 2010), activated carbon (Yu *et al.* 2009), chitosan (Zhang *et al.* 2011) and montmorillonite (Jeon *et al.* 2011). The high adsorption of PFOS at low pH was due to the enhanced electrostatic attraction between the negatively charged PFOS molecules and positively charged adsorbent surface (Tang *et al.* 2010). The higher PFOS adsorption on the functionalized MWCNTs compared to the MWCNTs-Pri at pH below 8 may be related to their high surface areas, and hydrophobic interaction might dominate the adsorption of PFOS on the three MWCNTs. As OH$^-$ ions became dominant in solution at pH >8, electrostatic repulsion prevented the PFOS from approaching the surface of MWCNTs. For the functionalized MWCNTs, the hydrophilic surface groups would lead to the formation of water clusters (Pan & Xing 2008; Zhang *et al.* 2010), and then it would be more difficult for PFOS to approach the surface of the MWCNTs, resulting in the significant decrease of PFOS removal.

Effect of anions

Chloride and sulphate are the most common anions in water, and chromate widely exists in electroplating

wastewater which also contains PFOS. Figure 3 presents the effects of three anions on the adsorption of PFOS on the three MWCNTs. It can be seen that the percentage removal of PFOS on the three adsorbents decreased with increasing anion concentrations, and the removal decreased by about 15–30% at high concentrations of anions. The influence of chloride on the adsorption of PFOS was relatively lower than sulphate and chromate. As the initial concentrations of NaCl, Na$_2$SO$_4$ and K$_2$Cr$_2$O$_7$ increased, ionic strength was enhanced. Lower removal at high anion concentrations may be related to the influence of solution ionic strength (Campinas & Rosa 2006). The increase of ionic strength might compress the electric double layers of MWCNTs and caused particles to aggregate, which would reduce the effective adsorption sites and result in lower removal of PFOS.

For the MWCNTs-Pri, the three anions did not differ much in terms of their effects on the sorption of PFOS, but for functionalized MWCNTs, the three anions had obvious effects. The ionic strength of chromate and sulfate were greater than chloride at the same initial concentrations, which may lead to a greater impact on PFOS removal. In the control experiment, the adsorption of chromate on the three MWCNTs was negligible, and thus the decrease of PFOS adsorption in the presence of chromate was not caused by the competitive adsorption of chromate.

Effect of Cu(II) and Pb(II)

Figure 4 presents the adsorption of PFOS on three MWCNTs in the presence of Cu(II) or Pb(II). It is interesting that removal of PFOS on the three MWCNTs all first decreased and then increased with increasing Cu(II) or Pb(II) concentrations. The possible reason for the enhanced adsorption of PFOS in the presence of Cu(II) or Pb(II) is that Cu(II) or Pb(II) serve as a bridging agent between
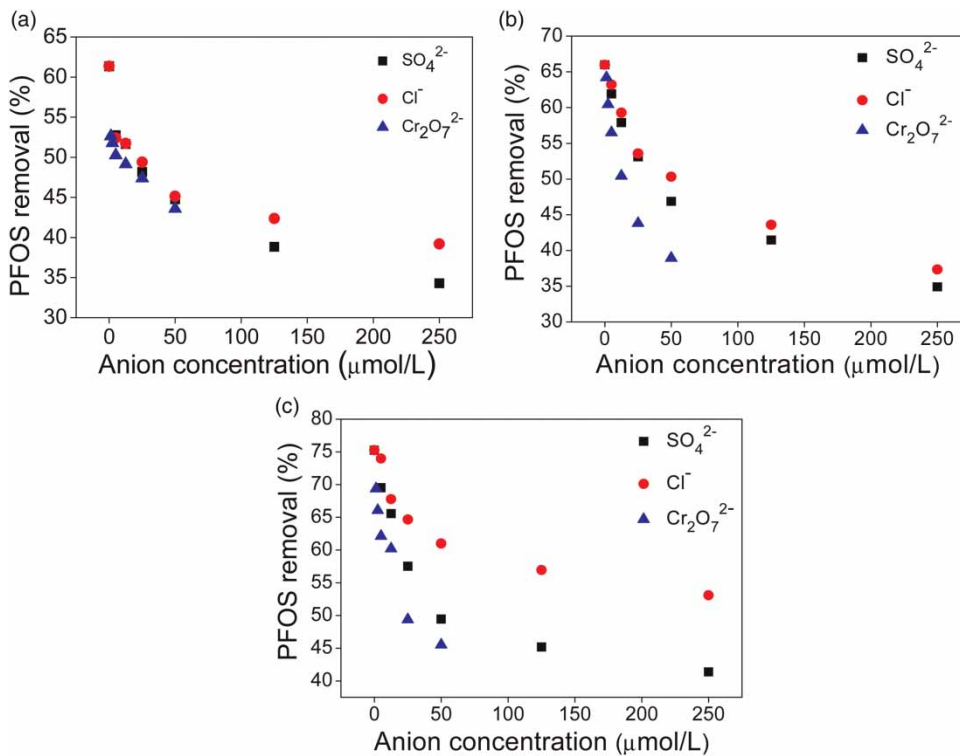
Figure 3 │ Influence of different anions on MWCNTs-Pri (a), MWCNTs-COOH (b) and MWCNTs-OH (c).
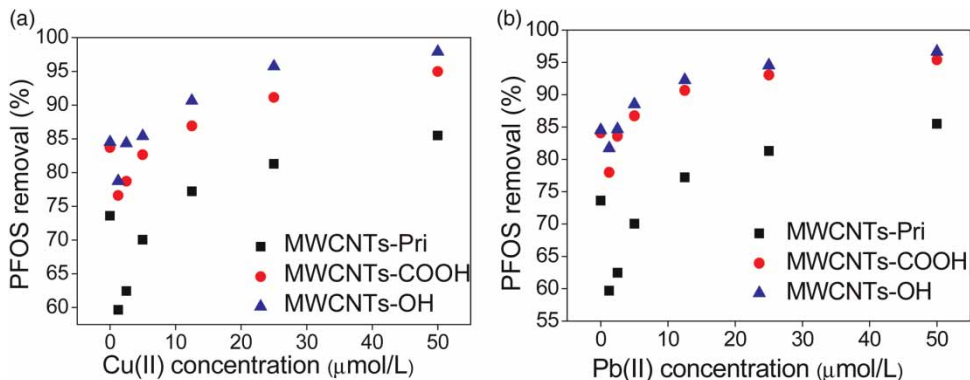

Figure 4 │ Effect of Cu(II) (a) and Pb(II) (b) on the adsorption of PFOS on the three MWCNTs.

PFOS and MWCNTs (Ren *et al.* 2011). In addition, divalent metal ions might complex with negative PFOS directly (Wang & Shih 2011). In the adsorption process, some metal ions approached the surface of the MWCNTs and some reacted with functional groups at the surface of functionalized MWCNTs to form complexes. The positive charged surface would attract negatively charged PFOS, which obviously enhanced the removal of PFOS. To verify the adsorption of Cu(II) on the MWCNTs, the adsorbed

amounts of Cu(II) in the presence/absence of PFOS were measured (Figure 5). It can be seen that both MWCNTs-Pri and MWCNTs-OH can adsorb Cu(II), and that MWCNTs-OH had higher Cu(II) removal than MWCNTs-Pri. In particular, the adsorption of Cu(II) was enhanced in the presence of PFOS, indicating that adsorbed PFOS via hydrophobic interaction on the MWCNT surface can adsorb Cu(II). In addition, at a low concentration of Cu(II) and Pb(II), the inhibition of ionic strength may be
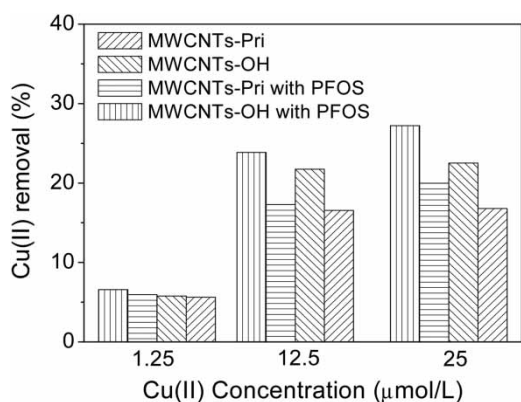
Figure 5 | Adsorption of Cu(II) on MWCNTs-Pri and MWCNTs-OH in the presence/absence of PFOS.

more obvious than the favourable cation-bridging effect of metals, and thus the removal of PFOS decreased.

CONCLUSIONS

The adsorption of PFOS on MWCNTs-Pri, MWCNTs-OH and MWCNTs-COOH was well fitted by the Langmuir equation, and MWCNTs-OH had the highest sorption capacity for PFOS. Hydrophobic interaction was responsible for PFOS adsorption on the MWCNTs, and electrostatic repulsion was unfavourable for PFOS adsorption. In the presence of anions, the removal of PFOS decreased because the enhanced ionic strength increased the aggregation of MWCNTs, making less surface available for PFOS adsorption. In the presence of cationic Cu(II) and Pb(II), the adsorption of PFOS first decreased and then increased with increasing metal concentrations. The enhanced adsorption of PFOS on the MWCNTs at high Cu(II) and Pb(II) concentrations was attributed to the high adsorbed amount of Cu(II)/Pb(II), which might further adsorb PFOS.

ACKNOWLEDGEMENTS

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