



## Adsorption of ionizable organic contaminants on multi-walled carbon nanotubes with different oxygen contents

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### ABSTRACT

Multi-walled carbon nanotubes (MWNTs), which are considered to be promising candidates for the adsorption of toxic organics, are released into aqueous environment with their increasing production and application. In this study, the adsorption behaviors of five structurally related ionizable organic contaminants namely perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-n-nonylphenol (4-NP) onto MWNTs with different oxygen contents (3.84–22.85%) were investigated. The adsorption kinetics was investigated and simulated with pseudo-second-order model. The adsorption isotherms were found to be fitted with Freundlich model and influenced by both the properties of organic chemicals and the oxygen contents of MWNTs. As adsorption capacity decreases dramatically with the increasing of oxygen contents, the MWNTs with the lowest oxygen contents possess the highest adsorption capacity among four MWNTs. For the MWNTs with the oxygen contents of 3.84%, the adsorption affinity related with hydrophobic interaction and  $\pi$ -electron polarizability decreased in the order of 4-NP > PFOSA > PFOS > 2,4-D > PFOA. Furthermore, the adsorption characters of five contaminants were affected by solution pH and solute  $pK_a$  considering electrostatic repulse force and hydrogen bonding, which showed the adsorption of MWNTs with lower oxygen content is much sensitive to solution chemistry.

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### 1. Introduction

Multi-walled carbon nanotubes (MWNTs) possess splendid potential applications in energy storage [1], environmental remediation [2] and medical delivery [3] due to their unusual one-dimensional hollow nanostructures and unique chemical and physical characteristics. The rapid growth in commercial application of MWNTs leads to their increasing production rates. So far, except for preparation in laboratory, MWNTs have also been found from common fuel-gas-air combustion, propane-air kitchen stove top burners as well as methane-air-flame exhausts [4]. Therefore, MWNTs are ubiquitous in natural environment, and their impacts on human health and environmental risk have received more and more attention.

The strong adsorption affinity of carbon nanotubes (CNTs) towards organic contaminants [5], such as dioxin [6], trihalomethanes [7], aromatic organic chemicals [8,9], antibiotics [10] and organic pesticides [11] was approved. Also, the influence of different purification and oxidation methods of CNTs with  $HNO_3$ ,  $HNO_3/H_2SO_4$ ,  $H_2O_2$  or  $KMnO_4$  etc. was explored since these treat-

ments could prepare stable dispersed mixtures, which are needed in many fields including medicine delivery agents or polymer composites [3,12]. The influence of MWNT surface oxidation on the adsorption of several typical hydrophobic organic chemicals (HOCs) and radioactive metals has been reported [13–16]. Ionizable organic contaminants with higher water solubility disperse widely in aqueous solution, and are likely to transfer in natural environment, but few studies have discussed the adsorption characters of ionizable organic chemicals on different oxidized MWNTs, especially those of aliphatic compounds bearing sulfonic, carboxyl or sulfonamide functional groups [9,17].

In this work, the adsorption of five ionizable contaminants including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorooctanesulfonamide (PFOSA), 2,4-dichlorophenoxyacetic acid (2,4-D) and 4-n-nonylphenol (4-NP) onto MWNTs with different oxygen contents was studied. PFOS and PFOA were widely used in many fields such as surfactants, lubricants, pesticides, firefighting foams, food packaging and other consumer products due to its unique characters of chemical stability, high surface activity, thermal resistance, hydrophobicity and olephobicity, and PFOS has been listed as one of the prominent persistent organic pollutants (POPs). In recent years, reports on the environmental persistence and potential bioaccumulation of perfluorochemicals (PFCs), and the global distribution of these

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compounds in biota [18,19] and humans [20] have drawn considerable attention. The adsorption of PFCs on sediments [21], zeolite and sludge [22], activated carbon [23,24], resin [24] has been studied, but still no report about the adsorption of PFCs on CNTs. PFOSA, a precursor of PFOS, was selected as comparison to explore the effect of oxidation of MWNTs and aqueous solution environment towards adsorption. 2,4-D was an anionic ionizable herbicides which was widely used on crops to control broad-leaf weeds. Despite its relatively short half life in soils [25], it is frequently detected in waters and posed a threat on surface and ground water contamination in the region of intensive agriculture due to its weak adsorption by soils [26]. 4-NP as an intermediate in anaerobic degradation of nonylphenol ethoxylates, occurs widespread in the environment, and is recognized as an environmental endocrine disrupting chemical [27]. The solubility and partition behavior of 4-NP could be affected by different media since it behaves as a weak acid and may be ionizable under neutral to alkaline conditions.

The target of this study is to examine the adsorption properties of ionizable organic chemicals on MWNTs, investigate the influence of MWNT surface oxidation and structure characters of contaminants (aromatic compounds, aliphatic compounds, hydrophobicity and polarity, etc.) towards the adsorption, discuss the possible interaction mechanisms controlling adsorption, and understand the environmental fate and health risk of MWNTs and ionizable organic chemicals in natural environment.

## 2. Materials and methods

### 2.1. Materials

The pristine multi-walled carbon nanotubes (MWNTs) produced by a chemical vapor deposition method using nickel or cobalt as catalysts were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences (out diameters <8 nm, inner diameters <5 nm, length 10–30  $\mu\text{m}$ ). Before adsorption experiment, the MWNTs were heated at 350 °C for 30 min to remove amorphous carbon, and purified with hydrochloride acid (HCl) according to Datsyuk's method [28]. Approximately 0.5 g of MWNTs were transferred into 200 mL 36.5% HCl and refluxed for 24 h at room temperature. The oxidation of MWNTs was performed by three different methods: (a) 0.5 g of MWNTs were added into 200 mL concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  (1:3) and refluxed for 24 h at room temperature [29]. (b) 0.5 g of MWNTs were added into 100 mL aqueous solution with 70% sodium hypochlorite solution, which was heated to 85 °C and kept for 3 h [30]. (c) 2 g pristine MWNTs were put into 500 mL of  $\text{HNO}_3$ – $\text{H}_2\text{SO}_4$  (1:3), and sonicated for 16 h at room temperature to obtain the stable suspension. The MWNTs were collected by filtration from above reaction solution, then washed with Milli Q water and filtered through 0.22  $\mu\text{m}$  fiber filter for several times until pH of the filtrate was nearly neutral. The resulted MWNTs were dried at 105 °C for 24 h and stored in desiccator. Above purified and oxidized MWNTs were labeled as M–O (3.84%), M–O (10.08%), M–O (18.01%) and M–O (22.85%) according to their oxygen contents, respectively. The physicochemical characters of these MWNTs are listed in Table 1. The specific surface area ( $S_{\text{BET}}$ ) and total pore volume ( $V_{\text{total}}$ ) of MWNTs were calculated from the adsorption–desorption isotherms of  $\text{N}_2$  at 77 K by multi-point BET and BJH methods, respectively. The length of MWNTs was measured with transmission electron microscope (TEM). Elemental compositions were obtained from an elemental vario EL III analytensysteme.

The model compounds included perfluorooctane sulfonate (PFOS, 98%, Sigma–Aldrich, Matrix Scientific, Columbia), perfluorooctanoic acid (PFOA, 96%, Acros Organic, New Jersey, USA), perfluorooctanesulfonamide (PFOSA, 98%, J&K Chemical. Ltd.), 2,4-

dichlorophenoxyacetic acid (2,4-D, 95%, TCI, Tokyo, Japan) and 4-n-nonylphenol (4-NP, 98%, Alfa Aesar). Their typical physico-chemical properties are listed in Table 2. Acetonitrile (99.8% HPLC grade) was obtained from Fisher Scientific (USA). Milli Q water was used for HPLC–MS analysis, standard stock solution with different concentrations were prepared by dissolving solid standards in methanol, and stored in 4 °C.

### 2.2. Adsorption experiments

Adsorption experiments of 2,4-D and 4-NP were conducted in 50 mL quartz vessels with 30 mL adsorption solution. As for PFOS, PFOA and PFOSA, the recovery of controls from polystyrene (PS) tubes was reported to be higher than glass vials and polypropylene (PP) tubes [21], accordingly, all adsorption experiments of PFOS, PFOA and PFOSA were conducted in 15 mL PS centrifuge tubes containing 12 mL solution, and the vessels avoid touching with the materials of polytetrafluoroethylene. Background solution containing 0.5 mM  $\text{CaCl}_2$  and 200 mg/L  $\text{NaN}_3$  was mixed with about 1 mg MWNTs. The batch adsorption experiments were conducted at 200 rpm on an orbital shaker at fixed temperature of  $20 \pm 1$  °C. The concentration of solution was in the range of 50  $\mu\text{g/L}$  to 50 mg/L expect for 4-NP (10  $\mu\text{g/L}$  to 5 mg/L), since the water solubility of 4-NP is lower than 10 mg/L. The volume ratio of methanol in solution of each vial was controlled to be less than 0.1% to minimize cosolvent effect. The vials were sealed and placed in the shaker for 7 days (kinetics experiments indicated that apparent equilibrium was reached before 7 days). After adsorption equilibrium, the solid and aqueous phases were separated by centrifugation (1500 rpm for quartz tubes, and 3500 rpm for PS tubes). Then, 0.2 mL supernatant was added to 0.2 mL methanol for quantitative analysis.

The pH was adjusted with HCl or NaOH. The final pH of the solution after adsorption equilibrium was nearly the same as before. Experimental uncertainty was conducted in the vials without MWNTs. The results showed that the total uncertainty of glass tubes and PS tubes was in the range of  $98.9 \pm 8.4\%$  and  $104.0 \pm 7.2\%$ , respectively. So it is feasible to calculate the adsorbed contaminants directly by mass loss.

### 2.3. Chemical analysis

The concentrations of PFOS, PFOA, PFOSA and 2,4-D were determined by LC–MS (LC–MS 2010A, Shimadzu Co., Japan). The part of LC was consisted of a SIL-10ADvp automatic injector (sample injector volume 2  $\mu\text{L}$ ), a DGU-12AM degasser, two LC-10ADvp pumps, a CTO-10Avp column oven (40 °C), a protecting column (Shimpack GVP-ODS Guard Column 5 mm  $\times$  2.0 mm) and an Agilent column (Zorbax eclipse plus  $\text{C}_{18}$  2.1 mm  $\times$  150 mm, 5  $\mu\text{m}$ ). The flow rate was controlled at 0.2 mL/min with a mobile phase of 10 mM ammonium acetate in water (A) and acetonitrile (B). The gradient program was conducted to elute the components of the samples. Negative electrospray ionization (ESI) model was employed to obtain the mass spectra information. The selected ion monitoring (SIM) model was employed to quantify the analytes ( $m/z = 499.05$  for PFOS,  $m/z = 413.05$  for PFOA,  $m/z = 497.90$  for PFOSA and  $m/z = 219.80$  for 2,4-D). The instrumental parameters were set at the following levels: the rate of nebulize gas (nitrogen) 1.5 L/min, the rate of drying gas (nitrogen) 5 L/min, probe bias  $-3.5$  kV, CDL voltage 35 V, CDL temperature 250 °C, the block temperature 200 °C, and the detector voltage  $-1.6$  kV.

Waters 2695 high-performance liquid chromatography (HPLC) with waters 2475 fluorescence detector (Waters company, USA) was utilized to determine the concentration of 4-NP equipped with a SunFire ODS reverse-phase column (150 mm  $\times$  4.6 mm, 5.0  $\mu\text{m}$ ). The mobile phase was acetonitrile/water (80:20, v/v) with the flow

**Table 1**  
Selected physical and chemical parameters of MWNTs.

Adsorbent	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	Length ( $\mu\text{m}$ )	N (%)	C (%)	H (%)	O (%)
M-O (3.84%)	562.5	0.780	10–30	0.24	95.76	0.15	3.84
M-O (10.08%)	519.7	0.568	<3.0	0.16	89.40	0.35	10.07
M-O (18.01%)	383.9	0.333	<0.5	0.03	81.24	0.72	18.00
M-O (22.85%)	142.5	0.131	<0.3	0.19	76.13	0.82	22.85

rate of 1.0 mL/min, and the Ex/Em wavelength was 228 nm and 305 nm, respectively.

#### 2.4. Zeta potential

The zeta potential ( $\zeta$ ) of MWNTs at different pH was measured with zetasizer nano ZS equipment (Malvern instrument company, USA). MWNTs treated with different methods were dispersed in 2.5 mM  $\text{CaCl}_2$  solution for 24 h and the pH of suspension was adjusted by HCl (0.5 M and 6 M) and NaOH (0.05 M and 0.5 M). The zeta potentials were measured according to the method reported by Chen et al. [37]. In aqueous media, zeta potential was affected by many factors, such as pH, conductivity of solution, concentration of sample and other additive ingredients. The pH is one of the most important factors affecting the zeta potential, and the point where the zeta potential equal to zero, is called the isoelectric point ( $\text{pH}_{\text{iep}}$ ).

### 3. Results and discussion

#### 3.1. Characterization of MWNTs

The element analysis showed that the components of carbon decrease along with the increasing of hydrogen and oxygen components in different MWNTs prepared by four treatment methods. The FTIR spectra (Fig. 1) confirmed the existence of the carboxyl ( $1700$  and  $1580 \text{ cm}^{-1}$ ), lactonic ( $1210$  and  $1700 \text{ cm}^{-1}$ ) and phenolic groups ( $3430 \text{ cm}^{-1}$ ) after oxidation, and there is no obvious difference of the FTIR spectra between M-O (3.84%) and pristine

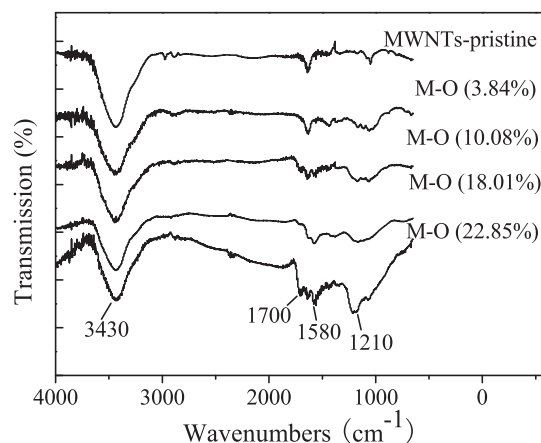


Fig. 1. Infrared spectra of pristine, purified and oxidized MWNTs.

MWNTs, which indicated purification with HCl only remove amorphous carbon and metal catalyst without the oxidation of MWNTs [28]. TEM analysis (Fig. 2) displayed that the length of MWNTs is shorten along with the amounts of oxygen increased, which is consistent with Cho et al.'s report [13]. Raman spectroscopy (Fig. 3) of MWNTs was also conducted. A strong peak at  $\sim 1584 \text{ cm}^{-1}$  (G band) stands for the formation of graphitized structure, and the peak at  $\sim 1330 \text{ cm}^{-1}$  is the D band relative to the C–C stretching vibrations. As shown in Table 3, the intensity ratios of D band and G band ( $I_{\text{D}}/I_{\text{G}}$ ) of MWNTs with different oxygen contents exhibit no distinct dif-

**Table 2**  
Selected physicochemical properties of model chemicals.

Chemicals	Mol. formula	Structure	MW (g/mol)	$\text{pK}_a$	Solubility (mg/L)
PFOS	$\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$		538.15	-3.27 [31]	570 [31]
PFOA	$\text{C}_7\text{F}_{15}\text{COOH}$		414.20	-0.5 [32]	3400 [33]
PFOSA	$\text{C}_8\text{F}_{17}\text{SO}_2\text{NH}_2$		499.14	6.52 [34]	-
2,4-D	$\text{C}_8\text{H}_6\text{Cl}_2\text{O}_3$		221.04	2.87 [35]	618.9 [36]
4-NP	$\text{C}_{15}\text{H}_{24}\text{O}$		220.35	10.7 [27]	5.4–8.0 [27]



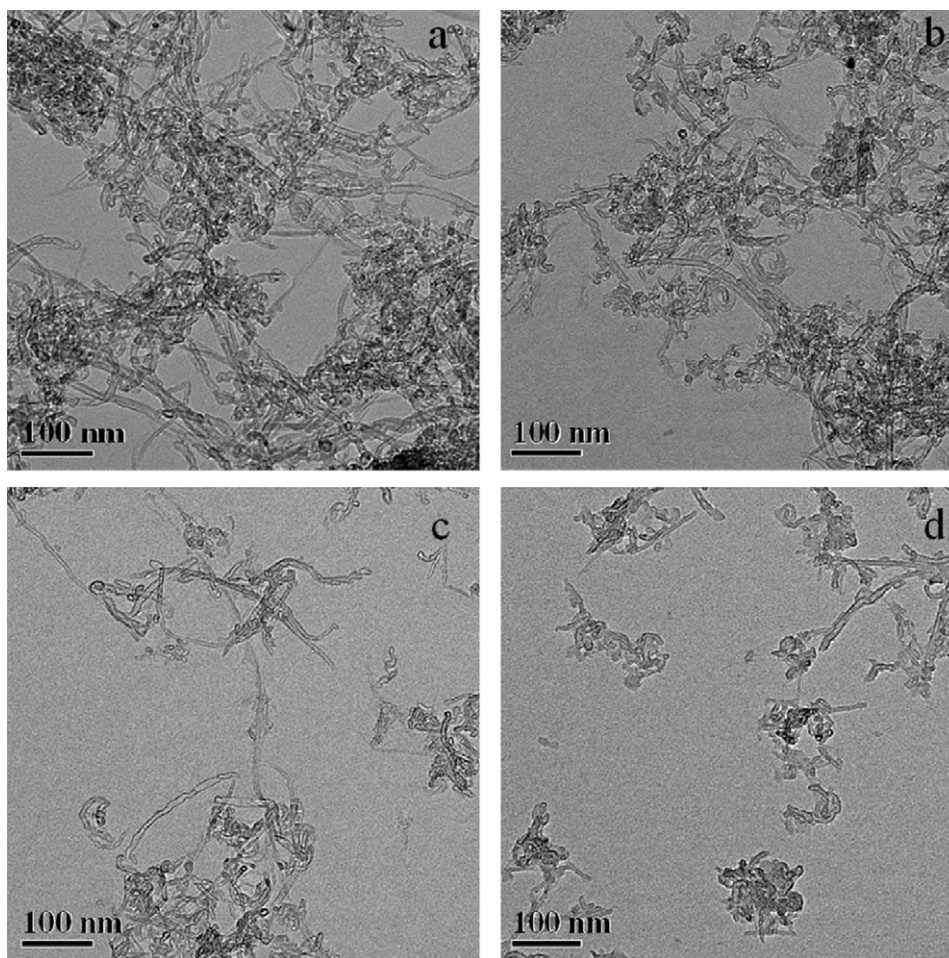


Fig. 2. TEM images of M-O (3.84%) (a), M-O (10.08%) (b), M-O (18.01%) (c) and M-O (22.85%) (d).

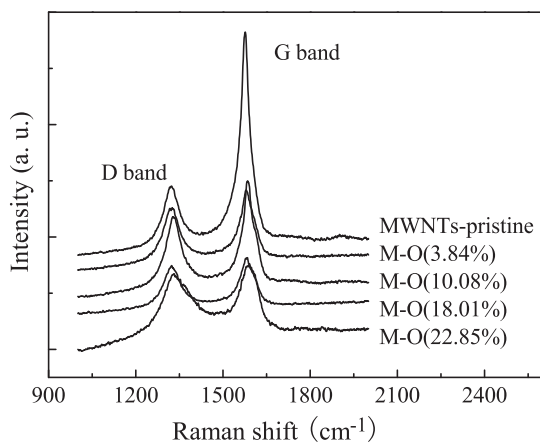


Fig. 3. Raman spectra of pristine, purified and oxidized MWNTs.

ference but higher than pristine MWNTs. Therefore the adsorption equilibrium was expected to be mainly affected by surface areas and functional groups of MWNTs, which was also approved by the adsorption of naphthalene and other synthetic organic toxics on carbon nanotubes [9,13,14].

The nitrogen adsorption and desorption isotherms and the pore volume data (Table 1) revealed the surface areas and total pore volume decrease as the amounts of oxygen increase, which suggests the oxygen-containing functional groups occupy part of adsorption sites [38]. The same trend was also observed by Cho et al. [39] and Salam and Burk [40]. The results in Fig. 4 show zeta potential decreases with the amounts of oxygen increasing. The  $\text{pH}_{\text{iep}}$  of M-O (3.84%) and M-O (10.08%) was measured to be 3.76 and 2.13, respectively. For M-O (18.01%) and M-O (22.8%),  $\zeta < 0$  was found in the range of pH 1.8–11.0, which means oxygen-containing groups change the charge characters of MWNT surfaces.

### 3.2. Adsorption kinetics

According to the batch experiment condition, the adsorption kinetics experiments of PFOA, 2,4-D, PFOS, PFOSA (50 mg/L) and 4-

**Table 3**  
Intensity ratio of D band and G band ( $I_D/I_G$ ) of MWNTs with different oxygen contents.

	Adsorbent				
	MWNTs-pristine	M-O (3.84%)	M-O (10.08%)	M-O (18.01%)	M-O (22.85%)
$I_D/I_G$	0.34	0.80	0.87	0.72	0.88

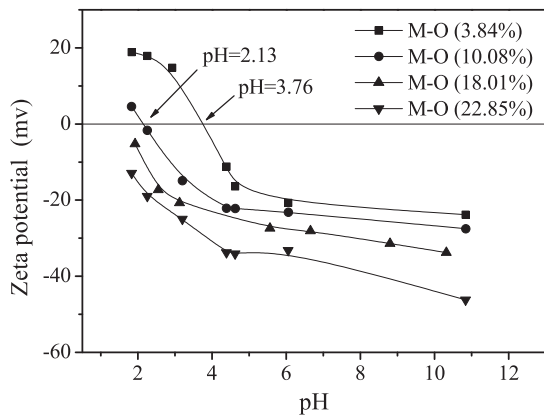


Fig. 4. Zeta potential of MWNTs as a function of solution pH.

NP (5 mg/L) on M-O (3.84%) were conducted at pH 5.0 ± 0.3. Change of the adsorbed contaminants amounts with the contact time is given in Fig. 5. As shown in Fig. 5, fast initial adsorption from liquid to the MWNTs was observed within the first 1.5 h for the five compounds, which suggests a rapid initial transfer of toxics into the near surface boundary layers of MWNTs. This process is followed by a slow diffusion from external sites to internal sites of MWNTs. Finally, the adsorption equilibrium was reached in 3 h (for PFOSA, 4-NP), 10 h (for PFOA, PFOS) and 50 h (for 2,4-D).

The pseudo-second-order model was used to simulate the experimental data. This model is depicted by Eq. (1) [24]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t = \frac{1}{\nu_0} + \frac{1}{q_e} t \quad (1)$$

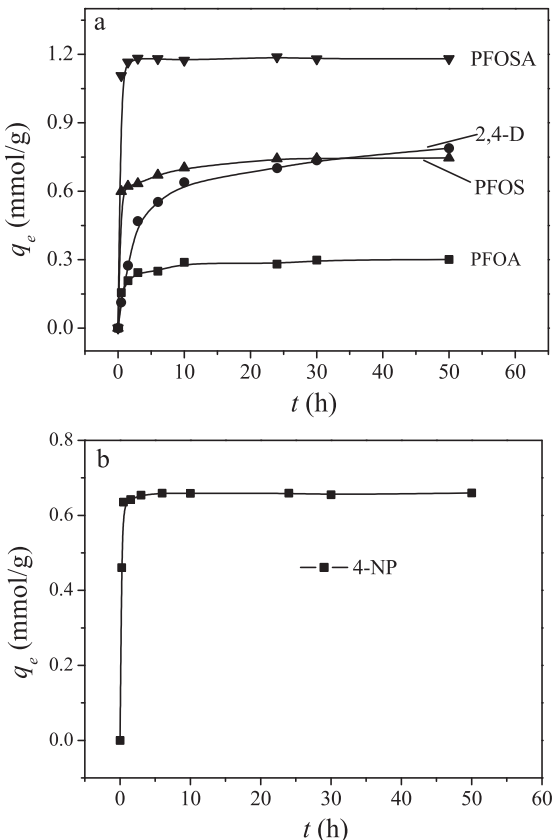


Fig. 5. Adsorption kinetics of five compounds on M-O (3.84%).

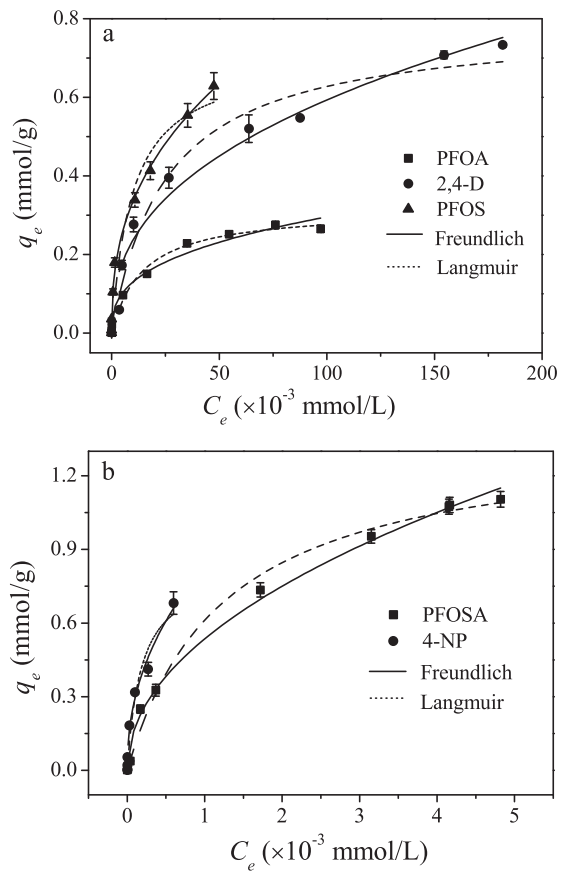


Fig. 6. Adsorption isotherms of five compounds on M-O (3.84%) modeling with Freundlich equation and Langmuir equation.

where  $q_e$  and  $q_t$  (mmol/g) are the amount of contaminants adsorbed on the adsorbents at equilibrium and time  $t$  (h), respectively.  $k_2$  is the adsorption rate constant (g/mmol/h).  $\nu_0$  is the initial adsorption rate (mmol/h/g). The related model parameters are listed in Table 4. It was found that the pseudo-second-order model fits well with correlation coefficient ( $R^2$ ) up to 0.997–0.999 for the five contaminants, indicating the chemical adsorption is involved and adsorption capacity is proportional to the number of active sites of MWNTs [24]. Compared with granular activated carbon (GAC) and resin, the initial adsorption rates for PFOA and PFOS are higher and the corresponding adsorption equilibrium is also more rapid on MWNTs [24]. As for 2,4-D, the equilibrium time on MWNTs is similar to that on GAC and the  $q_e$  on MWNTs is 2.2 times of that on GAC [41].

### 3.3. Adsorption isotherms and comparison of pollutant adsorption characters

Since the surface area is one of the major factors influencing the adsorption capacity, M-O (3.84%) was selected as adsorbent to compare the adsorption characters towards five contaminants. The adsorption batch experiments were conducted at pH of 5.0 ± 0.3. The adsorption isotherms are shown in Fig. 6. All isotherms exhibited non-linear characters and were described with Freundlich model and Langmuir model, which was expressed respectively as:

$$q_e = K_F C_e^n \quad (2)$$

$$q_e = \frac{b q_m C_e}{1 + b C_e} \quad (3)$$

where  $C_e$  and  $q_e$  are the concentration of contaminants in water and adsorbent when the adsorption equilibrium was reached, respec-

**Table 4**  
Kinetics parameters of pseudo-second-order model for five compounds adsorption on M–O (3.84%).

Adsorbate	C (mg/L)	Pseudo-second-order parameter			
		$q_e$ (mmol/g)	$\nu_0$ (mmol/h/g)	$k_2$ (g/mmol/h)	$R^2$
PFOA	50	0.30	0.35	3.94	0.998
2,4-D	50	0.83	0.27	0.39	0.997
PFOS	50	0.75	1.64	2.91	0.998
PFOSA	50	1.18	100	71.8	0.999
4-NP	5	0.66	16.7	38.3	0.999

tively.  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbents. The  $q_m$  is the maximum adsorption capacity, and  $b$  is the adsorption equilibrium constant of Langmuir model. The parameters of two models are listed in Table 5. The correlation coefficient  $R^2$  in Freundlich model is higher than that of Langmuir model of each compound. So, Freundlich model is more suitable to simulate the adsorption isotherms. The  $n$  values varied from 0.36 (PFOS) to 0.49 (PFOSA) as expected for a non-linear fitting. The  $K_F$  value showed that the adsorption capacities of chemicals on the M–O (3.84%) are in accordance with the orders of 4-NP > PFOSA > PFOS > 2,4-D > PFOA. Among the five contaminants, PFOS, PFOA and PFOSA are typical PFCs. As comparison, 4-NP as the structure analog of PFOA by its characteristic long carbon chain and 2,4-D is an aromatic acid versus aliphatic acid of PFOA. It is interesting to compare the adsorption behaviors of these compounds with similar functional groups.

PFOSA, PFOS and PFOA belong to aliphatic hydrocarbons, the long carbon chains are strongly hydrophobic. Therefore, hydrophobic interaction is expected to play important role on the adsorption of these PFCs [24]. Also, according to Vincent and Glenwood's experiments [42], increasing alkyl length improves the hydrophobicity of chemicals. From this point, it is reasonable for the stronger adsorption affinity of PFOS than PFOA on M–O (3.84%). Since 4-NP and 2,4-D are polar aromatics, the  $\pi$  electron polarizability is assumed to make contributions to their adsorption on the MWNTs [8,30]. It is known that MWNTs are more affinitive to the hydrophobic compounds [36]. The octanol–water partition coefficient ( $K_{ow}$ ), as the ratio of a chemical's concentration in octanol phase to its concentration in the aqueous of a two-phase octanol/water system, is an important parameter which is often used to describe the hydrophobicity of contaminants. It was known that  $K_{ow}$  of 4-NP ( $K_{ow} = 4.48$ ) is greater than that of 2,4-D ( $K_{ow} = 2.81$ ) [43], accordingly, 4-NP exhibited superior adsorption capacity than that of 2,4-D. So the hydrophobic mechanism is also assumed to exert important function in the adsorption process of 4-NP except for  $\pi$ -electron polarizability. From another aspect, even lack of the solubility data of PFOSA, the solubility of compounds in Table 2 essentially showed an inverse order with that of adsorption capacities. It was found that 4-NP with the lowest solubility among five contaminants in water exhibits highest adsorption on MWNTs and PFOA with the highest solubility among five contaminants exhibits lowest adsorption on MWNTs. These results also approved that the hydrophobic interaction makes contribution to the adsorption.

**Table 5**  
Adsorption equilibrium constants of Freundlich model and Langmuir model for contaminants adsorption on M–O (3.84%).

Adsorbate	Langmuir constants			Freundlich constants		
	$q_m$ (mmol/g)	$b$ (L/mmol)	$R^2$	$K_F$ (mmol <sup>(1-n)</sup> L <sup>n</sup> /g)	$n$	$R^2$
PFOA	0.32 ± 0.01	69.5 ± 12.6	0.970	0.67 ± 0.08	0.36 ± 0.04	0.982
2,4-D	0.79 ± 0.05	39.6 ± 9.6	0.964	1.48 ± 0.15	0.38 ± 0.02	0.994
PFOS	0.71 ± 0.09	103.1 ± 42.9	0.960	2.07 ± 0.11	0.39 ± 0.01	0.998
PFOSA	1.37 ± 0.07	803.6 ± 135.4	0.994	15.38 ± 2.47	0.49 ± 0.03	0.994
4-NP	0.83 ± 0.13	5481.0 ± 2211.5	0.960	19.37 ± 9.7	0.46 ± 0.08	0.974

### 3.4. Effect of MWNT properties on adsorption

Fig. 7 described the effect of oxygen contents of MWNTs on five chemicals adsorption. The single-concentration point adsorption coefficient ( $K_d$ ), used to describe the relative proportion of the adsorbate distributed to the solid phase and in solution when adsorption balance was reached, was calculated at the concentration of 1 mg/L for 4-NP for its low solubility and 50 mg/L for the other chemicals to compare their adsorption capacities. According to our results,  $K_d$  decreases in the order of M–O (3.84%) > M–O (10.08%) > M–O (18.01%) > M–O (22.85%). The results support the assumption that oxidized MWNTs are more hydrophilic than pristine MWNTs, and less surface area is accessible to contaminants because of the water adsorbed on MWNTs surface (through H bonding of oxygen) which blocks contaminants approach [38]. In fact, naphthalene, phenanthrene, biphenyl and 2-phenylphenol adsorption on CNTs also proved this trend [13,14].

The adsorption was also found to be influenced by pH values of aqueous solution. This effect was showed clearly by adsorption on M–O (3.84%) as shown in Fig. 7, but gradually weakened as the oxygen content increases in MWNTs. As a result, no obvious pH-dependence of  $K_d$  value is observed for adsorption on M–O (18.01%) and M–O (22.8%). Zeta potential analysis (Fig. 4) indicated that the surface charges of M–O (18.01%) and M–O (22.85%) are negative in the range of pH 1.8–11.0. Accordingly, the hydroxy and carboxylic groups of MWNTs are deprotonated, which results in the invariability of adsorption capacities. Similar properties were also observed for bisphenol A adsorption on MWNTs purified by mixed HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [44].

### 3.5. Effect of contaminant solution character on adsorption

The MWNTs with lower surface oxidation contents are more structurally well-defined and chemically homogeneous and sensitive to the environmental conditions [13]. Fig. 7 shows that the structure properties of contaminants were related to the adsorption capacities. The dissociation of organic acid (4-NP, PFOS, 2,4-D and PFOA) and organic bases (PFOSA) mainly depends on the solution pH. As for organic acid, when  $\text{pH} > \text{p}K_a$ , the chemical surface with negative charges is resulted from the acid deprotonation. By contrast, when  $\text{pH} < \text{p}K_a$ , it is surrounded by positive charges and remains as neutral molecules [38]. Yang et al. [9] adopted the Eqs. (4) and (5) to describe the relationships between the fractions of dissociated acid species ( $f_A^1$ ) or basic species ( $f_B^1$ ) and the values of

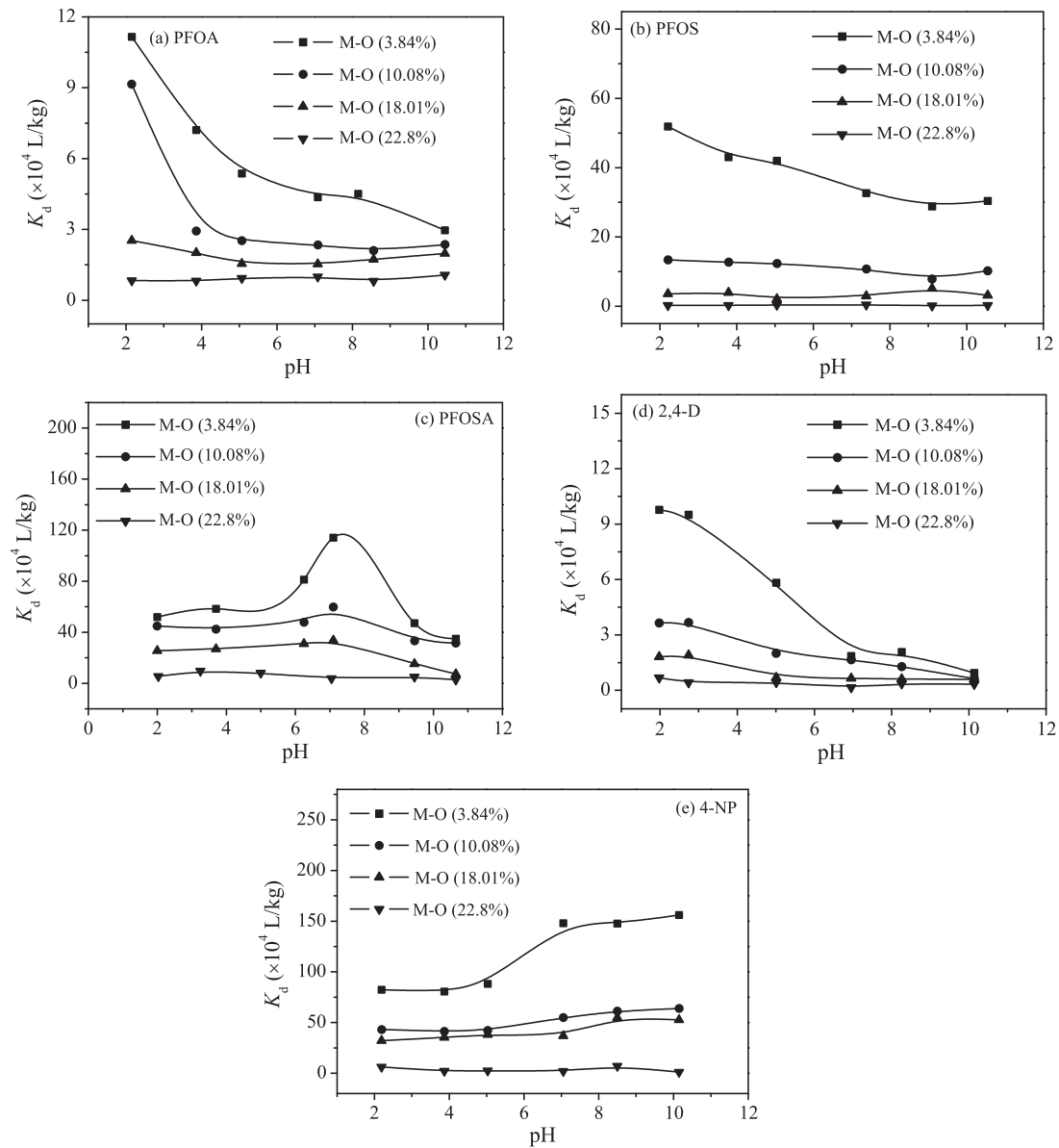


Fig. 7.  $K_d$  as a function of pH for five chemicals adsorption on MWNTs with different oxygen contents.

pH and  $pK_a$ .

$$\text{Acid: } f_A^I = (1 + 10^{pK_a - \text{pH}})^{-1} \quad (4)$$

$$\text{Base: } f_B^I = (1 + 10^{\text{pH} - pK_a})^{-1} \quad (5)$$

The adsorption capacities of PFOA decreased on M–O (3.84%) and M–O (10.08%) with the increasing pH. In the range of pH 1.8–11.0, PFOA ( $pK_a = -0.5$ ) exists as deprotonated form. The electrostatic repulse force becomes stronger with the increasing negative charge of M–O (3.84%) surface, which results in the weak adsorption. PFOS (Fig. 7(b)) displayed the similar trend with PFOA. For PFOSA ( $pK_a = 6.52$ ), when  $\text{pH} < pK_a$ , protonation occurs on the amino group, and the decreased protonation leads to the increased adsorption, but when  $\text{pH} > pK_a$ , PFOSA exists as neutral molecule in water, at the same time negative charges of CNTs increase as well, therefore the electrostatic repulse force between M–O (3.84%) and long carbon chain with fluoride atom increases. This may be the reason for decreased adsorption capacity. The adsorption behavior of 2,4-D ( $pK_a = 2.87$ ) is similar with that of PFOA when  $\text{pH} > pK_a$ , and no obvious change was found when pH is below  $pK_a$  in the range of

our experiments. For 4-NP ( $pK_a = 10.7$ ), no dissociated species exists below pH 10.7 according to Eq. (1), it is possible that the increasing hydrogen bonding interaction between the –OH group of 4-NP and the O-containing groups of MWNTs induce the stronger adsorption.

### 3.6. Implication

According to our results, the adsorption capacity ( $K_F$ ) of PFOA, PFOS and 2,4-D on purified MWNTs is higher than the adsorption on activated carbons (AC), resin, zeolite and sludge [23,24,41,45]. Rapid adsorption equilibrium of 4-NP on MWNTs than on terrestrial soils was also reported [27]. Although the price of CNTs is higher than AC at present, the regeneration and repeated availability of CNTs could be realized after several recycles of water treatment [46]. Therefore, CNTs would be a potential adsorbent used in water treatment, especially, the price of which will decrease in future with its increasing commercial production [13,47].

On the other hand, the transportation and transformation of toxics as well as the environmental behaviors of CNTs can be affected by the structural characters of compounds, oxygen con-



tents of CNTs and water quality parameters on the basis of high adsorption capacity of contaminants on CNTs. For example, the distribution of contaminants between aqueous solution and solid could be changed once adsorbed by CNTs, and the health risk of CNTs also increases after the adsorption of organic toxics. In summary, it is very valuable to explore the adsorption behaviors of contaminants on CNTs.

#### 4. Conclusions

The adsorption of five ionizable organic contaminants including PFOS, PFOA, PFOSA, 2,4-D and 4-NP onto MWNTs with different oxidation contents was investigated. The pseudo-second-order model well described the adsorption kinetics, and the adsorption isotherms were fitted with Freundlich model for the five contaminants. For the same contaminant, MWNTs with more oxygen contents lead to lower adsorption capacity since less surface areas are accessible to contaminants due to the blockage of absorbed water. The model constant  $K_F$  of contaminants adsorption on M-O (3.84%) listed by an inverse order of the compounds solubility as 4-NP > PFOSA > PFOS > 2,4-D > PFOA, showed that MWNTs are inclined to adsorb hydrophobic organic chemicals. Based on these results, the hydrophobic interactions are assumed to play important role on the adsorption of PFOA, PFOS and PFOSA, while  $\pi$  electron polarizability as well as hydrophobic mechanism dominate the adsorption of 4-NP and 2,4-D. The adsorption is also affected by solution pH and solute  $pK_a$ . This influence is weakened gradually with the increasing oxidation contents of MWNTs, and becomes negligible when oxidation concentrations reached to 18.01%. In summary, our study shows that surface oxidation and solution chemistry have dramatic influence on the adsorption of ionizable pollutants onto MWNTs.

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#### References

- [1] S.B. Kayiran, F.D. Lamari, D. Levesque, Adsorption properties and structural characterization of activated carbons and nanotubes, *J. Phys. Chem. B* 108 (2004) 15211–15215.
- [2] V.L. Colvin, The potential environmental impact of engineering nanomaterials, *Nat. Biotechnol.* 21 (2003) 1160–1170.
- [3] Z. Liu, M. Winters, M. Holodniy, H.J. Dai, siRNA delivery into human T cells and primary cells with carbon nanotube transporters, *Angew. Chem. Int. Ed.* 46 (2007) 2023–2027.
- [4] L.E. Murr, K.F. Soto, A TEM study of soot, carbon nanotubes, and related fullerene nanopolyhedra in common fuel-gas combustion sources, *Mater. Charact.* 55 (2005) 50–65.
- [5] B. Pan, B.S. Xing, Adsorption mechanism of organic chemicals on carbon nanotubes, *Environ. Sci. Technol.* 42 (2008) 9005–9013.
- [6] R.Q. Long, R.T. Yang, Carbon nanotubes as superior sorbent for dioxins removal, *J. Am. Chem. Soc.* 123 (2001) 2058–2059.
- [7] C.S. Lu, Y.L. Chung, K.F. Chang, Adsorption of trihalomethanes from water with carbon nanotubes, *Water Res.* 39 (2005) 1183–1189.
- [8] K. Yang, L.Z. Zhu, B.S. Xing, Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials, *Environ. Sci. Technol.* 40 (2006) 1855–1861.
- [9] K. Yang, W.H. Wu, Q.F. Jing, L.Z. Zhu, Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes, *Environ. Sci. Technol.* 42 (2008) 7931–7936.
- [10] L.L. Ji, W. Chen, L. Duan, D.Q. Zhu, Mechanisms for strong adsorption of tetracycline to carbon nanotubes: a comparative study using activated carbon and graphite as adsorbents, *Environ. Sci. Technol.* 43 (2009) 2322–2327.
- [11] G.C. Chen, X.Q. Shan, Y.Q. Zhou, X.E. Shen, H.L. Hang, S.U. Khan, Adsorption kinetics, isotherms and thermodynamics of atrazine on surface oxidized multi-walled carbon nanotubes, *J. Hazard. Mater.* 169 (2009) 912–918.
- [12] P. Pieta, G.M. Venukadasula, F.D. Souza, W. Kutner, Preparation and selected properties of an improved composite of the electrochemically deposited single-wall carbon nanotubes, electrochemically coated with a  $C_{60}$ -Pd and polybithiophene mixed polymer film, *J. Phys. Chem. C* 113 (2009) 14046–14058.
- [13] H.H. Cho, B.A. Smith, J.D. Wnuk, D.H. Fairbrother, W.P. Ball, Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes, *Environ. Sci. Technol.* 42 (2008) 2899–2905.
- [14] S.J. Zhang, T. Shao, S.S.K. Bekaroglu, T.J. Karanfil, The impacts of aggregation and surface chemistry of carbon nanotubes on the adsorption of synthetic organic compounds, *Environ. Sci. Technol.* 43 (2009) 5719–5725.
- [15] A. Schierz, H. Zanker, Aqueous suspensions of carbon nanotubes: surface oxidation, colloidal stability and uranium sorption, *Environ. Pollut.* 157 (2009) 1088–1094.
- [16] B. Smith, K.E. Schrote, H.H. Cho, W.P. Ball, D.H. Fairbrother, Influence of surface oxides on the colloidal stability of multi-walled carbon nanotubes: a structure–property relationship, *Langmuir* 25 (2009) 9767–9776.
- [17] G.D. Sheng, D.D. Shao, X.M. Ren, X.Q. Wang, J.X. Li, Y.X. Chen, X.K. Wang, Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes, *J. Hazard. Mater.* 178 (2010) 505–516.
- [18] S. Taniyasu, K. Kannan, Y. Hori, N. Hanari, N. Yamashita, A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan, *Environ. Sci. Technol.* 37 (2003) 2634–2639.
- [19] M.K. So, S. Taniyasu, N. Yamashita, J.P. Giesy, Z. Fang, S.H. Im, P.K.S. Lam, Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea, *Environ. Sci. Technol.* 38 (2004) 4056–4063.
- [20] K. Kannan, S. Corsolini, J. Falandysz, G. Fillmann, S.K. Kumar, B. Loganathan, A.M. Mohd, J. Olivero, V.N. Wouwe, J.H. Yang, K.M. Aldous, Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries, *Environ. Sci. Technol.* 38 (2004) 4489–4495.
- [21] P.H. Christopher, G.L. Richard, Sorption of perfluorinated surfactants on sediments, *Environ. Sci. Technol.* 40 (2006) 7251–7256.
- [22] G. Pan, C.X. Jia, D.Y. Zhao, C. You, H. Chen, G.B. Jiang, Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments, *Environ. Pollut.* 157 (2009) 325–330.
- [23] O.H. Valeria, S.A. Reyes, Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge, *Chemosphere* 72 (2008) 1588–1593.
- [24] Q. Yu, R.Q. Zhang, S.B. Deng, J. Huang, G. Yu, Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: kinetics and isotherms study, *Water Res.* 43 (2009) 1150–1158.
- [25] P. Picton, A. Farenhorst, Factors influencing 2,4-D sorption and mineralization in soil, *J. Environ. Sci. Health B* 39 (2005) 367–379.
- [26] J. Gaultier, A. Farenhorst, J. Cathcart, T. Goddard, Degradation of [carboxyl- $^{14}C$ ] 2,4-D and [ring- $^{14}C$ ] 2,4-D in 114 agricultural soils as affected by soil organic carbon content, *Soil Biol. Biochem.* 40 (2008) 217–227.
- [27] R.A. Doring, S. Krahe, S. Gath, Sorption behavior of nonylphenol in terrestrial soils, *Environ. Sci. Technol.* 36 (2002) 4052–4057.
- [28] V. Datsyuk, M. Kalyua, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, Chemical oxidation of multi-walled carbon nanotubes, *Carbon* 46 (2008) 833–840.
- [29] C.M. Yang, J.S. Park, K.H. An, S.C. Lin, K. Seo, B. Kim, K.A. Park, S. Han, C.Y. Park, Y.H. Lee, Selective removal of metallic single-walled carbon nanotubes with small diameters by using nitric and sulfuric acids, *J. Phys. Chem. B* 109 (2005) 19242–19248.
- [30] W. Chen, L. Duan, D.Q. Zhu, Adsorption of polar and nonpolar organic chemicals to carbon nanotubes, *Environ. Sci. Technol.* 41 (2007) 8295–8300.
- [31] D. Brooke, A. Footitt, T.A. Nwaogu, Environmental Risk Evaluation Report: Perfluorooctane Sulfonate (PFOS), UK Environment Agency, 2004.
- [32] U.G. Kai, The  $pK_a$  value of PFOA and other highly fluorinated carboxylic acids, *Environ. Sci. Technol.* 42 (2008) 456–458.
- [33] Preliminary Risk Assessment of the Developmental Toxicity Associated with Exposure to Perfluorooctanoic Acid and its Salt, U.S. Environmental Protection Agency Office of Pollution Prevention and Toxics Risk Assessment Division, 2003, April 10.
- [34] S.D. Eva, R. Martin, Nanofiltration for trace organic contaminant removal: structure, solution, and membrane fouling effects on the rejection of perfluorochemicals, *Environ. Sci. Technol.* 42 (2008) 5292–5297.
- [35] Y. Qui, X.Y. Xiao, H.Y. Cheng, Z.L. Zhou, G.D. Sheng, Influence of environmental factors on pesticide adsorption by black carbon: pH and model dissolved organic matter, *Environ. Sci. Technol.* 43 (2009) 4973–4978.
- [36] W. Chu, K.H. Chan, The prediction of partitioning coefficients for chemicals causing environmental concern, *Sci. Total Environ.* 248 (2000) 1–10.
- [37] H. Chen, S. Chen, X. Quan, Y.Z. Zhao, H.M. Zhao, Sorption of perfluorooctane sulfonate (PFOS) on oil and oil-derived black carbon: influence of solution pH and  $[Ca^{2+}]$ , *Chemosphere* 77 (2009) 1406–1411.
- [38] Y.N. Yang, Y. Chun, G. Sheng, M. Huang, pH-dependence of pesticide adsorption by wheat-residue-derived black carbon, *Langmuir* 20 (2004) 6736–6741.
- [39] H.H. Cho, K. Wepasnik, B.A. Smith, F.K. Bangash, D.H. Fairbrother, W.P. Ball, Sorption of aqueous Zn (II) and Cd (II) by multiwall carbon nanotubes: the relative roles of oxygen-containing functional groups and graphenic carbon, *Langmuir* 26 (2009) 967–981.
- [40] M.A. Salam, R.C. Burk, Thermodynamics of pentachlorophenol adsorption from aqueous solutions by oxidized multi-walled carbon nanotubes, *Appl. Surf. Sci.* 255 (2008) 1975–1981.
- [41] J.M. Salman, B.H. Hameed, Adsorption of 2,4-dichlorophenoxyacetic acid and carbofuran pesticides onto granular activated carbon, *Desalination* 256 (2010) 129–135.



- [42] C.H. Vincent, K. Glenwood, Structure–activity relationships for sorption of linear alkylbenzenesulfonates, *Environ. Sci. Technol.* 21 (1987) 370–373.
- [43] M. Alel, W. Giger, Partitioning of alkylphenols and alkylphenol polyethoxylates between water and organic solvents, *Chemosphere* 26 (1993) 1471–1478.
- [44] B. Pan, D.H. Lin, H. Mashayekhi, B.S. Xing, Adsorption and hysteresis of bisphenol A and 17 $\alpha$ -ethinyl estradiol on carbon nanomaterials, *Environ. Sci. Technol.* 42 (2008) 5480–5485.
- [45] Y. Qu, C.J. Zhang, F. Li, X.W. Bo, G.F. Liu, Q. Zhou, Equilibrium and kinetics study on the adsorption of perfluorooctanoic acid from aqueous solution onto powdered activated carbon, *J. Hazard. Mater.* 169 (2009) 146–152.
- [46] C.S. Lu, H.T. Chiu, H.L. Bai, Comparisons of adsorbent cost for the removal of zinc (II) from aqueous solution by carbon nanotubes and activated carbon, *J. Nanosci. Nanotechnol.* 7 (2007) 1647–1652.
- [47] R.C. Templeton, P.L. Ferguson, K.M. Washburn, W.A. Scrivens, G.T. Chandler, Life-cycle effects of single-walled carbon nanotubes (SWNTs) on an estuarine meiobenthic copepod, *Environ. Sci. Technol.* 40 (2006) 7387–7393.