



# Adsorption mechanism of different organic chemicals on fluorinated carbon nanotubes



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## HIGHLIGHTS

- Carbon nanotubes were fluorinated using PTFE as a fluorine source.
- Organic contaminant adsorption on CNTs was enhanced after fluorination.
- BPA butterfly structure resulted in its strong sorption and desorption hysteresis.
- OFL exothermic sorption resulted in its strong desorption hysteresis.

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## ABSTRACT

Multi-walled carbon nanotubes (MC) were fluorinated by a solid-phase reaction method using polytetrafluoroethylene (PTFE). The surface alteration of carbon nanotubes after fluorination (MC-F) was confirmed based on surface elemental analysis, TEM and SEM. The incorporation of F on MC surface was discussed as F incorporation on carbon defects, replacement of carboxyl groups, as well as surface coating of PTFE. The adsorption performance and mechanisms of MC-F for five kinds of representative organic compounds: sulfamethoxazole (SMX), ofloxacin (OFL), norfloxacin (NOR), bisphenol a (BPA) and phenanthrene (PHE) were investigated. Although BET-N<sub>2</sub> surface area of the investigated CNTs decreased after fluorination, the adsorption of all five chemicals increased. Because of the glassification of MC-F surface coating during BET-N<sub>2</sub> surface area measurement, the accessible surface area of MC-F was underestimated. Desorption hysteresis was generally observed in all the sorption systems in this study, and the desorption hysteresis of MC-F were stronger than the pristine CNTs. The enhanced adsorption of MC-F may be attributed to the pores generated on the coated PTFE and the dispersed CNT aggregates due to the increased electrostatic repulsion after fluorination. The rearrangement of the bundles or diffusion of the adsorbates in MC-F inner pores were the likely reason for the strong desorption hysteresis of MC-F. The butterfly structure of BPA resulted in its high sorption and strong desorption hysteresis. The exothermic sorption character of OFL on CNTs resulted in its strong desorption hysteresis.

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## 1. Introduction

Since carbon nanotubes (CNTs) was discovered by Iijima in 1991 (Iijima, 1991), which has aroused extensive attentions due to their unique and superior physicochemical properties. CNTs have potential applications in many areas including manufacturing, electronics, construction, and medicine (Eatemadi et al., 2014). CNTs exhibited a very strong affinity for organic contaminants and heavy metal ions, thus it is proposed as a superior and promising sorbent applied in wastewater treatment (Ren et al., 2011; Yu et al., 2014).

In order to maximize the selectivity of adsorption and to improve the adsorption performance of CNTs, surface modification of CNTs has drawn a widely attention (Lu et al., 2008; Ghobadi et al., 2014). In most cases, acidic or oxidizing reagents were applied to treat CNTs, and thus oxygen containing functional groups (such as hydroxyl and carboxyl groups) were incorporated on the surface of CNTs (Liao et al., 2008; Chand et al., 2009). The oxygen-containing functional groups will facilitate the wettability properties of the surface, and then enhance the adsorption for polar compounds (Patino et al., 2015). And also, the oxygen-containing functional groups will make the CNTs more negatively charged in neutral condition, which could enhance the dispersion of CNTs in solutions due to the electrostatic repulsion, leading to a higher adsorption than pristine

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CNTs. However, the interactions between oxide-carbon nanotubes and hydrophobic compounds will dramatic decrease in adsorption as the increasing extent of CNTs oxidation (Zhang et al., 2009). Li et al. reported that PHE exhibited a much lower adsorption capacity on oxidized CNTs than on pristine CNTs (Li et al., 2013). The oxygen-containing groups on surface of CNTs can form strong hydrogen bond with water molecules, resulting in decreasing adsorption of organic compounds, especially hydrophobic organic compounds (Wu et al., 2012). Therefore, CNT surface modification may result in the increased sorption of certain chemicals, but will also decrease its sorption with other chemicals. In most of the circumstances, various organic contaminants with different properties simultaneously present in wastewater or the environment. Effective removal of organic contaminants with a wide range of chemical physical properties is a major challenge for researchers.

Fluorination is one of the most effective routes to modify and control physico-chemical properties of carbon materials (Lee, 2007; Lu et al., 2016). Fluorinated CNTs was reported to enhance surface polarity, electroconductivity and capacitive character, and is widely used in lithium batteries, solid lubricants and nano-composites (Zhang et al., 2010; Maiti et al., 2012). Recent study has reported that fluorinated CNTs exhibited great performance in removing chromium ions (Osikoya et al., 2014). However, the study using fluorinated CNTs as adsorbent to retain organic compounds from aqueous is relatively rare. Due to the utmost electronegativity of F, the C–F bond on fluorinated CNTs enables CNTs to act as a strong  $\pi$ -acceptor, which could enhance the adsorption controlled by  $\pi$ -acceptor and  $\pi$ -donor interaction. The strong electronegativity of F will also make the CNTs strongly negatively charged, and thus facilitate the dispersion of CNTs. In addition, different from oxygen containing groups, the C–F bond can hardly form hydrogen bond with water molecules (Dunitz and Taylor, 1997). Therefore, incorporating F into CNTs will not suppress the adsorption of hydrophobic compounds. We thus hypothesized that fluorination will enhance the adsorption of organic compounds on CNTs.

In this study, fluorinated CNTs was synthesized by the solid-phase reaction method. Five representative organic contaminants including sulfamethoxazole (SMX), ofloxacin (OFL), norfloxacin (NOR), bisphenol A (BPA) and phenanthrene (PHE) were selected as adsorbates. Batch adsorption, desorption and thermodynamics experiments were conducted to evaluate the adsorption characteristics and to investigate the adsorption mechanisms of MC-F. In addition, with the wide applications of fluorinated CNTs, it will be inevitably released into the aqueous environment. Therefore, investigating the interactions between fluorinated CNTs and organic contaminants is of great environmental significance. The aim of this work is to illustrate the sorption mechanisms of organic contaminants on fluorinated CNTs, which will be an important input for CNT applications in wastewater treatment.

## 2. Materials and methods

### 2.1. Materials

Carboxylized multiwall carbon nanotubes (MC, purity > 95%, diameter: 8–15 nm) were purchased from Chengdu Organic

Chemistry Co., Chinese Academy of Sciences. It was synthesized in the CH<sub>4</sub>/H<sub>2</sub> mixture at 700 °C by the chemical vapor deposition method and was purified by mixed HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> solutions to reduce the contents of metal catalyst and amorphous carbon. Fluorinated multiwall carbon nanotubes were synthesized by the solid-phase reaction method. Briefly, the MC and PTFE (5  $\mu$ m, Aladdin-reagent Co. Ltd., China) fine particles were mixed in an enclosed vessel according weight ratio: 1:2 (MC:PTFE), then the mixture was put in a temperature-controlled furnace which was purged continuously with N<sub>2</sub>. The temperature was controlled at 460–500 °C for 4–6 h to generate the source of fluorine for fluorination. The resulted particles were chilled and grinded. This particle is noted as MC-F. SMX (AR, 99.0%), OFL (AR, 99.0%) and NOR (AR, 99.0%) were obtained from Bio Basic Inc. PHE (AR, 97%) was obtained from Acros Co., Belgium. BPA (AR, 99.0%) was obtained from Sinopharm Chemical Reagent Co., Ltd, China. Both MC and MC-F were characterized for their surface area (Autosorb-1C, Quantachrome, US), elemental composition (MicroCube, Elementar, Germany), surface elemental composition (X-ray photoelectron spectroscopy, PHI5000 VersaProbe II, ULVACPHI, INC.) scanning electron microscopy (SEM, Tescan, VEGA3 SBH) equipped with energy-dispersive X-ray spectrometer (EDAX, Thermo Fisher Scientific, NORAN System 7), transmission electron microscopy (TEM, JEM 2100) and zero point of charge (pH<sub>ZPC</sub>, ZetaPlus, Brookhaven, US). For SEM-EDAX tests, MC or MC-F particles were mounted on aluminum stubs, and then gold-coated using a sputter coater. The accelerating voltage was set at 20 kV. For TEM tests, the MC and MC-F solutions were ultra-sonicated for 5 min, and then a drop of solution containing MC or MC-F was put onto a copper TEM grid. After air-dried, the measurements were operated with the accelerating voltage of 200 kV. The properties of compounds studied are listed in Table 1.

### 2.2. Batch adsorption experiments

Batch adsorption experiments were separately conducted for SMX, BPA, OFL, NOR and PHE in 4 mL (for MC) and 15 mL (for MC-F) amber glass vials with Teflon-lined screw caps. According to our preliminary work, the aqueous:solid ratios were 2000:1 and 15000:1 (w/w) for MC and MC-F sorption experiments, respectively. The different aqueous:solid ratios were to ensure comparable equilibrated aqueous phase concentrations in two sorption systems. The initial concentration ranges were 0.2–1.24 mg L<sup>-1</sup> for PHE and 1–50 mg L<sup>-1</sup> for the other four chemicals, and all the adsorbates were dissolved in background solution containing 0.02 M NaCl and 200 mg L<sup>-1</sup> NaN<sub>3</sub>. We did not use CaCl<sub>2</sub> in the background solution to avoid possible impact of Ca<sup>2+</sup> on SMX sorption. The adsorbate solutions without adsorbents were referred to as the initial concentration references. All vials were kept in the dark and were continuously shaken in an air-bath shaker (80 rpm) at 25 °C or in a refrigerator at 4 °C for 7 d. According to our preliminary study, 7 d was enough to reach apparent sorption equilibrium. All vials were then centrifuged at 1000 g for 10 min, and the supernatants were sampled for adsorbates quantification.

For desorption experiment, the equilibrium supernatant was removed from the vials and then re-filled with the same volume of

**Table 1**  
Property comparison of MC and MC-F.

CNTs	SSA (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cc g <sup>-1</sup> )	Pore radius (Å)	XPS			Elemental analysis			pH <sub>ZPC</sub>
				C	O	F	C	O	H	
MC	118.8	0.454	9.6	95.8	4.2	0	97	0.5	2.7	4.0
MC-F	17.5	0.083	12.2	57.5	3.3	39.3	56.7	0.2	2.1	2.1

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