



## Intercalation of rigid molecules between carbon nanotubes for adsorption enhancement of typical pharmaceuticals

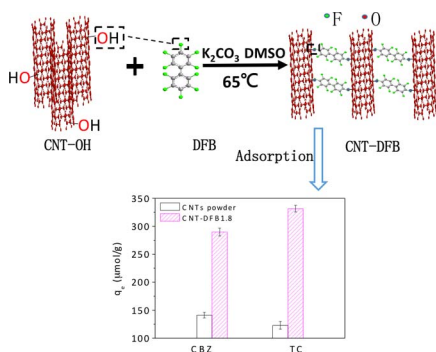


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### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Porous carbon nanotubes  
Adsorption kinetics  
Adsorption capacity  
Pharmaceuticals  
Thermal regeneration

### ABSTRACT

A nucleophilic aromatic substitution reaction was proposed to synthesize porous carbon nanotubes (CNTs) to avoid their aggregation in solution. Hydroxylated carbon nanotubes (CNTs-OH) were reacted with different concentrations of rigid decafluorobiphenyl (DFB) to form the different CNTs-based adsorbents (CNT-DFB0.9, CNT-DFB1.8, CNT-DFB2.7 and CNT-DFB3.6). Among them, CNT-DFB1.8 exhibited the highest adsorption capacity for carbamazepine (CBZ) and tetracycline (TC) due to its higher specific surface area and pore volume than powdered CNTs. The proposed reaction was verified and the textural properties of the CNT-DFB adsorbent were characterized. The CNT-DFB1.8 adsorbent exhibited faster adsorption for CBZ than TC, and the maximum adsorption capacities for CBZ and TC were 403.0 and 456.5 μmol/g respectively, according to the Langmuir fitting. With the increase of solution pH, TC adsorption on CNT-DFB1.8 decreased while CBZ adsorption increased. In addition, a simple thermal method was applied to regenerate the spent CNT-DFB1.8 by heating in air at 400 °C, and the adsorption capacity changed little in the five adsorption cycles. This study provided a novel method to increase the dispersion of CNTs in the prepared adsorbent, showing the potential application for the removal of pharmaceuticals in water or wastewater treatment.

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<http://dx.doi.org/10.1016/j.cej.2017.09.054>

Received 15 July 2017; Received in revised form 6 September 2017; Accepted 8 September 2017

Available online 09 September 2017

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## 1. Introduction

Numerous pharmaceuticals have been discovered in various surface and ground waters, and wastewaters globally, some of which have been linked to ecological impacts, even at trace concentrations [1–3]. Reports on pharmaceuticals for environmental risk and public health assessments have raised substantial concerns between both the public and regulatory agencies [4,5]. Various conventional and advanced water and wastewater treatment processes have been investigated in terms of pharmaceutical removal from aqueous phase [6,7]. It is worth mentioning that nanotechnology enabled remediation applications have captured enormous attention during the past years and gradually become the focus of research.

CNTs have been proven to possess the versatility in different areas such as electrochemical devices, biosensors and environmental remediations [8,9]. Besides high surface area, the superior thermal and chemical stability, mechanical properties [10], fantastic conductivities and extended  $\pi$ -electron structure unique network of  $sp^2$  carbon atoms make CNTs stand out in solving water shortage and water pollution problems in many fields especially in adsorption [11]. However, one of the restrictive factors in CNT adsorbents large-scale use is the tendency to hold strongly together as bundles or aggregations because of the strong van der Waals forces [12]. For this consideration, the modification of pristine CNTs prior to use is an inevitable step in adsorption to remove pollutants. On one hand, chemical functionalization in deed provides a valid approach to make CNT-based adsorption method play a winning game compared with others. Heating oxidation and acid treatment have been proved to be effective in enhancing the dispersion of CNTs in water [13,14]. However, there are still some disadvantages existing in normal methods mentioned above. One is the difficulty in controlling the modification process and insufficient oxidation degree of CNTs owing to its chemical stability. Another major concern is the rising separation challenge since oxygen-containing functional groups on CNTs surface lead to a better dispersion. On the other hand, several studies have focused on conquering separation issue. For example, the regenerable and easy-separation granular CNTs cake adsorbent was prepared by a simple heating-filtration method [15]. The adsorption capacity of oxidized CNTs towards three pharmaceuticals increased approximately 40%, which was not high enough considering its large surface area. Besides, heating temperature at 450 °C was energy-intensive [15]. The granular CNTs/ $Al_2O_3$  hybrid adsorbent can be prepared by a sol-gel method, but it is suitable for the removal of some pharmaceuticals with small molecular size [16]. None of these materials performed well enough with respect to the adsorption capacity and separation ability.

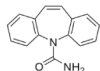
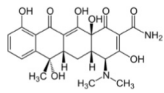
The objective of this study is to prepare the CNTs-based novel adsorbent with the advantages of high adsorption capacity towards different pharmaceuticals, easy-separation in water and efficient regeneration. A nucleophilic aromatic substitution reaction is proposed to introduce a rigid molecule among CNTs for inhibiting the aggregation thus creating the porous CNTs with high specific surface area and pore volume. Two frequently detected pharmaceuticals including CBZ and TC in water and wastewater were selected as adsorbates [1,17]. Batch adsorption and column adsorption experiments were conducted to investigate the adsorption behavior of CBZ and TC on the prepared CNTs. The regeneration and reusability of the spent adsorbent were also carried out.

## 2. Materials and methods

### 2.1. Materials

Multiwalled carbon nanotubes (CNTs, outer diameter: 10–20 nm, Length: 10–20  $\mu$ m) were purchased from Chengdu Organic Chemicals Co. Ltd. DFB,  $K_2CO_3$  and ferrous sulphate-7 hydrate were purchased from Aladdin Reagent. Two pharmaceuticals including carbamazepine

**Table 1**  
Physicochemical properties of selected pharmaceuticals.

Adsorbates	Molecular formula	Structure	MW	$\log K_{ow}$	$pK_a$
Carbamazepine (CBZ)	$C_{15}H_{12}N_2O$		236	2.47	2.313.9 3.3 7.7
Tetracycline (TC)	$C_{22}H_{24}N_2O_8$		444	-1.37	9.7 12.0

(CBZ, purity > 97%) and tetracycline (TC, purity > 98%) were purchased from J & K Scientific Co. (Beijing, China). All solvents including dimethyl sulfoxide (DMSO), methanol and dichloromethane ( $CH_2Cl_2$ ), toluene, pentane, ethanol and hydrogen peroxide ( $H_2O_2$ ) were obtained from Beijing chemical Works, and their physicochemical properties are listed in Table 1. All chemical solutions were prepared in ultrapure water produced by a Milli-Q system (Millipore, USA).

### 2.2. Preparation of porous CNT-based adsorbents

CNTs-OH was synthesized in our lab according to the reported method [18]. The specific procedures were as follows, 5 g of multi-walled-CNTs and 576 mL toluene were mixed and sonicated for 45 min. The resulting mixture was filtered and washed first with toluene and then pentane, followed by drying under vacuum at 80 °C. Thereafter, 750 mL  $H_2O$  and 2.5 g of the above product were mixed together and sonicated for 30 min. After the addition of 1.25 g ferrous sulphate-7 hydrate and 250 mL of 30%  $H_2O_2$ , the mixture was stirred for 24 h. Before being dried under vacuum at 80 °C, the mixture was washed with first  $H_2O$  and then ethanol. The preparation of porous CNTs was divided into four stages. Firstly, 0.1 g of CNTs-OH and 50 mL of DMSO were added in 100 mL glass vials, and the mixture was sonicated for 15 min, followed by adding the DFB (0.9, 1.8, 2.7 and 3.6 mmol/L) and  $K_2CO_3$  (0.60 g) and sonicating for 10 min in an ice bath. Secondly, the mixture was bubbled with  $N_2$  gas for 10 min, and the mixture was placed on a hot stirring plate (65 °C) and stirred at 500 rpm for 2 days. Thirdly, the final suspension was cooled and then filtered, and the residual  $K_2CO_3$  was removed by washing the solid on the filter paper with 1 mol/L HCl until  $CO_2$  evolution stopped. The recovered solid was isolated and activated by soaking for 15 min in  $H_2O$  (200 mL), methanol (100 mL), and  $CH_2Cl_2$  (50 mL), respectively. Finally, the solid was dried under high vacuum at 77 K in a liquid nitrogen bath for 10 min, and then dried at room temperature for 3 days. The obtained materials were denoted as CNT-DFB0.9, CNT-DFB1.8, CNT-DFB2.7 and CNT-DFB3.6 based on different intercalating molecules and their concentrations.

### 2.3. Characterization

The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured by an automated gas sorption analyzer (Quantachrome, autosorb-iQ, USA). Adsorbent size was measured by a laser particle analyzer (Mastersizer 2000, UK). The surface morphology was observed by a scanning electron microscope (SEM, Merlin Compact, Japan) and a high-resolution transmission electron microscopy (TEM, JEM-2100F, Japan). Raman spectra were obtained with an excitation line at 532 nm from an Ar laser (Renishaw inVia Manual, UK). XRD patterns were recorded on an X-ray diffractometer (Rigaku S2, Japan). Elemental and functional group analysis was carried out using a X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, USA). The thermal properties of CNTs, CNTs-DFB1.8 and DFB were investigated by a thermo-gravimetric analyzer (Mettler Toledo, TGA/DSC 1 Stare, Switzerland) in an oxidative (air) atmosphere (30 mL/min) at a

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