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# Three-dimensional α-$Fe_2O_3$/amino-functionalization carbon nanotube sponge for adsorption and oxidative removal of tetrabromobisphenol A

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ABSTRACT

Tetrabromobisphenol A (TBBPA) is one most widely used brominated flame retardant worldwide. In this study, a three-dimensional α-$Fe_2O_3$/amino-functionalization carbon nanotube (α-$Fe_2O_3$/CNT-N) sponge was synthesized and applied for adsorption removal of TBBPA from aqueous solution. The maximum adsorption capacity of TBBPA on the α-$Fe_2O_3$/CNT-N sponge was 41.35 ± 6.09 $mg{\cdot}g^{-1}$ at 303 K and pH 7.0 ± 0.1 and the adsorption capacity was maintained in the pH range of 3–7. The adsorbed TPPBA on the α-$Fe_2O_3$/CNT-N sponge can be easily degraded after adding peroxymonosulfate (PMS) to generate hydroxyl and sulfate radicals. The functional groups such as $-CONH_2$, $-C{=}O$ and $\pi$–$\pi^*$ bonds played an important role in the activation of PMS. The α-$Fe_2O_3$/CNT-N sponge may be considered to use for water treatment due to its good adsorption capacity, easy separation from water and simple regeneration procedures.

## 1. Introduction

Tetrabromobisphenol A (TBBPA) is the most widely used brominated flame retardants (BFR) around the world, accounting for around 60% of the total brominated flame retardant products in market, which has been recognized as an emerging contaminant and a potentially toxic endocrine-disruptor [1]. TBBPA has been widely detected in different environment matrices, including soil, water, sediments, dust and organisms [2]. Even though TBBPA is currently unregulated worldwide, there is an urgent need to remove it from the aquatic environment due to its extensive usage, persistence and toxicity aforementioned [3]. Thus, it is necessary to develop effective techniques for removal of TBBPA from contaminated environment.

There are different methods to remove TBBPA from water such as photocatalytic degradation [4], adsorption [5], microbial degradation [6,7]. Among these methods, the adsorption process is attractive due to its simple operation and possible regeneration for multiple uses [8]. Various adsorbents such as activated carbon, clay minerals, metal oxides, natural and synthetic materials have been generated for removing TBBPA from the contaminated environment [9–11]. In recent years, carbon nanotube (CNT) has received great attention for the potential applications in environmental remediation due to its large specific surface area and adsorption capacity. It has been reported that CNT could be used as a promising adsorbent for the removal of gas, dyes, heavy metal ions and organic compounds [12–15]. To improve the adsorption capacity for target pollutants, modification methods, such as oxidation, ammonification and doped nanoparticles were generally applied [16]. Modified CNTs showed good adsorption removal efficiency of TBBPA in comparison to pristine CNT. Ji et al. [17] used a one-step thermal decomposition method to prepare monodispersed magnetite nanoparticles on multi-walled carbon nanotubes (MWCNTs/$Fe_3O_4$), which were further modified with amino groups (MWCNTs/$Fe_3O_4$-$NH_2$). The maximum adsorption capacity for TBBPA on MWCNTs/$Fe_3O_4$ and MWCNTs/$Fe_3O_4$-$NH_2$ was 22.04 and 33.72 $mg{\cdot}g^{-1}$ at 303 K at pH 7, respectively. Zhou et al. [18] studied the TBBPA adsorption performance of the MWCNTs/$CoFe_2O_4$-$NH_2$ and chitosan modified MWCNTs/$CoFe_2O_4$-$NH_2$ hybrid materials, which showed the maximum adsorption capacity of 30.65 and 42.68 $mg{\cdot}g^{-1}$ for TBBPA at 303 K at pH 6.3, respectively. One major concern of using CNT is the difficulty to separate from water after adsorption. Recently, we have developed porous sponge-like materials consisting of three-dimensional (3D) interconnected CNT networks with high structural

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flexibility and robustness [19,20]. It showed effective adsorption removal of nanoparticles, dye molecules and oil from water [21,22]. The 3D structure of the CNT sponge makes its separation from water easily and has the potential use in water treatment for pollutant removal [20].

In this study, α-$Fe_2O_3$ doped on amino-functionalization carbon nanotube (α-$Fe_2O_3$/CNT-N) sponge was synthesized and used for remediation of TBBPA-contaminated water. The aims of this study are (i) to investigate the adsorption properties of TBBPA from aqueous solutions, (ii) to investigate the activity and stability of α-$Fe_2O_3$/CNT-N for TBBPA degradation in the catalytic peroxymonosulfate (PMS) oxidation solution, (iii) to illustrate the mechanism of TBBPA degradation.

## 2. Materials and methods

### 2.1. Chemicals

TBBPA and 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo [4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU) were purchased from Aladdin Industrial Corporation (China). Peroxymonosulfate (PMS) was purchased from Industrial Corporation (China). $FeCl_3 \cdot 6H_2O$, ferrocene, dichlorobenzene, sodium hydroxide and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (China). Ethylenediamine was purchased from Tianjin Damao Industrial Corporation (China). All experimental solutions were prepared with ultrapure water.

### 2.2. Synthesis and characterization of α-$Fe_2O_3$/CNT-N sponge

CNT sponge was synthesized by a chemical vapor deposition (CVD) method in a horizontal tubular furnace (860 °C for 1 h) using ferrocene and dichlorobenzene as the catalyst precursor and carbon source, respectively, as reported in our early work [19]. To fabricate the α-$Fe_2O_3$/CNTs-N sponge composite, the as grown CNTs sponges were cut into rectangular block ($12 \times 12 \times 1\ mm^3$) and exposed to UV (254 nm) for 1 hand immersed in 2 M NaOH for 2 h and then treated with $HNO_3$ for 2 h at 120 °C. CNT sponge dispersed in ethylenediamine (200 mL) with HATU (30 mg) and sonicated for 4 h at 40 °C. The obtained sponge blocks (CNT-N sponge) were immersed into 30 mL $FeCl_3$ ethanol/aqueous (50:50, v/v) precursor solution with a concentration in the range of 0.1, 0.3, 0.5 M. The mixture was sealed in a 50 mL Telfon-lined autoclave and hydrothermally treated at 120 °C for 2 h. Then, the sponges were taken out, washed repeatedly with deionized water, and freeze-dried. Finally, the composite was annealed in air using an atmospheric pressure tubular furnace to obtain α-$Fe_2O_3$/CNT-N sponge. The annealing temperature and time were 300 °C and 3 h. The heating rate was set as $10\ °C \cdot min^{-1}$.

The morphology of the α-$Fe_2O_3$/CNT-N sponge was observed using a scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, JEM-2100F, Japan). The Raman spectrum was collected using a LabRAM-HR Confocal Raman Microprobe (Jobin Yvon Instruments, France) equipped with a 514.5 nm argon ion laser. Fourier Transform Infrared (FTIR) Spectroscopy (Thermo iS50, USA) was used to determine the surface functional groups in the sponge in the wavenumber range from 400 to $4000\ cm^{-1}$. Magnetization measurements were carried out at room temperature using a vibrating sample magnetometer (LakeShore VSM-7307). The static contact angles (CA) were measured on a Kruss DSA100 contact angle testing system at room temperature. Thermogravimetric analysis (TGA) was conducted on a simultaneous thermal analyzer coupled with a Fourier transform infrared spectrometer (STA449F3) from 20 to 800 °C in air atmosphere at a heating rate of $20\ °C\ min^{-1}$. The powder X-ray diffraction (XRD) pattern was recorded on a Philips X'Pert Pro Super X-ray diffractometer equipped with monochromatized Cu Ka radiation. X-ray photoelectron spectroscopy (XPS) was conducted on a thermoelectron instrument (Thermo Scientific ESCALAB 250, USA) with Al Ka radiation as the excitation source (1486.8 eV, 500 mm).

### 2.3. Adsorption experiments

Batch adsorption experiments were carried out in 100 mL Erlenmeyer flasks containing 50 mL $2\ mg \cdot L^{-1}$ of TBBPA water/methanol solution (98:2, v/v) at pH 7.0 ± 0.1 in a temperature controlled shaker at 120 rpm in dark at 303 K. 0.02 ± 0.005g of as-grow CNT sponge, 25%, 35%, 56% α-$Fe_2O_3$ deposed CNT-N sponge was added into a series of Erlenmeyer flasks. Samples were collected at different time intervals. pH varying from 10.0 to 3.0 were also used with 0.02 ± 0.005g of 56% (wt.) α-$Fe_2O_3$/CNT-N sponge. To obtain the adsorption isotherms, the adsorption experiments were carried out in 100 mL Erlenmeyer flasks containing 50 mL of TBBPA water/methanol solution (90:10, v/v) at pH 7.0 ± 0.1 on a temperature-controlled shaker at 120 rpm in dark at 303 K for 2 h with 0.02 ± 0.005g of 56% (wt.) α-$Fe_2O_3$/CNT-N sponge. The initial concentrations of TBBPA were 1.0, 2.0, 3.0, 5.0, 10, 15 and $20\ mg \cdot L^{-1}$.

Adsorption capacity $Q_e$ ($mg \cdot g^{-1}$) and removal efficiency (%) were calculated using the following equations:

$$Q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

$$Removal\,(\%) = \frac{C_i - C_e}{C_i} \times 100\% \tag{2}$$

where $Q_e$ ($mg \cdot g^{-1}$) is the amounts of TBBPA adsorbed per unit mass of the α-$Fe_2O_3$/CNT-N sponge, $C_i$ and $C_e$ (mg/L) are the initial and final concentrations of TBBPA in solution.

### 2.4. Catalytic experiments

Time dependent catalytic degradation of TBBPA was investigated by using 56% (wt.) α-$Fe_2O_3$/CNT-N sponges as catalysts for PMS activation. The stock suspension of α-$Fe_2O_3$/CNT-N sponge (50 ± 0.1 mL, $0.4\ g \cdot L^{-1}$), stock solution of TBBPA (50 mL, $2\ mg \cdot L^{-1}$) that was adjust pH 7.0 ± 0.1 without methanol for 30 min. The initial concentration of PMS was 5 mM. In recyclability experiment, the adsorption process is same as batch adsorption experiments, and the clean PMS solution for degradation process was 50 mL of 5 mM PMS.

### 2.5. Analytical methods

The concentrations of TBBPA were analyzed on a HPLC system (Accucore C18 250 mm × 4.6 mm × 5 μm, Thermo Fisher Scientific) and a DAD detector at 230 nm [23]. The mobile phase used for the HPLC experiments was a mixture of HPLC-grade methanol and water (85:15, v:v) [23]. The electron paramagnetic resonance (EPR) were obtained at room temperature on a Bruker A300 spectrometer (Germany) to detect free radicals during the PMS activation using 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 98%, Adams Reagent Co., Ltd.) as the spin-trapping agent [24]. The determination of PMS concentration in reaction solution was conducted based on a modified 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) method [25].

## 3. Results and discussion

### 3.1. Characterization of α-$Fe_2O_3$/CNT-N sponge

The facile preparation process of α-$Fe_2O_3$/CNT-N sponge is showed in Fig. 1(a), which includes surface amination and $Fe_2O_3$ deposition. The inset of Fig. 1(b) clearly showed the sponges maintained block structure even after functionalization and $Fe_2O_3$ nanoparticles deposition. The SEM image (Fig. 1(b)) showed the α-$Fe_2O_3$ nanoparticles aggregated with irregular shape and deposited on the CNT-N sponges,