



# Electro-oxidation of perfluorooctanoic acid by carbon nanotube sponge anode and the mechanism



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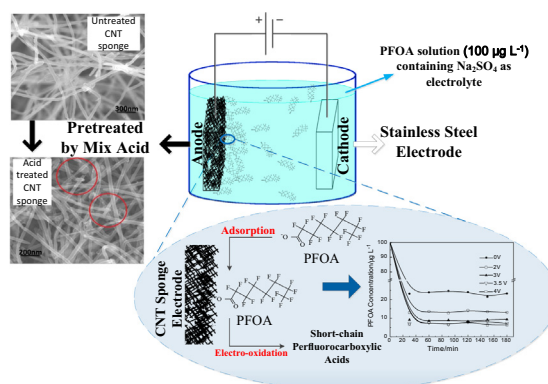
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## HIGHLIGHTS

- Carbon nanotube sponge was used as electrode to enhance PFOA electro-oxidation.
- More than 90% PFOA was decontaminated from low-concentration ( $100 \mu\text{g L}^{-1}$ ) solutions.
- PFOA was concentrated and adsorbed on CNT sponge and then electro-oxidized.

## GRAPHICAL ABSTRACT



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## ABSTRACT

As an emerging persistent organic pollutant (POPs), perfluorooctanoic acid (PFOA) exists widely in natural environment. It is of particular significance to develop efficient techniques to remove low-concentration PFOA from the contaminated waters. In this work, we adopted a new material, carbon nanotube (CNT) sponge, as electrode to enhance electro-oxidation and achieve high removal efficiency of low-concentration ( $100 \mu\text{g L}^{-1}$ ) PFOA from water. CNT sponge was pretreated by mixed acids to improve the surface morphology, hydrophilicity and the content of carbonyl groups on the surface. The highest removal efficiencies for low-concentration PFOA electrolyzed by acid-treated CNT sponge anode proved higher than 90%. The electro-oxidation mechanism of PFOA on CNT sponge anode was also discussed. PFOA is adsorbed on the CNT sponge rapidly increasing the concentration of PFOA on anode surface. When the potential on the anode is adjusted to more than 3.5 V, the adsorbed PFOA undergoes electrochemically oxidation and hydrolysis to produce shorter-chain perfluorocarboxylic acids with less  $\text{CF}_2$  unit. The efficient electro-oxidation of PFOA by CNT sponge anode is due to the combined effect of adsorption and electrochemical oxidation. These findings provide an efficient method to remove actual concentration PFOA from water.

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## 1. Introduction

Perfluorooctanoic acid (PFOA) has been produced and used worldwide for many decades (Post et al., 2012). It is both

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chemically and biologically stable and highly resistant to heat (Fujii et al., 2007; Singh et al., 2012), and therefore persists in natural environment as an anthropogenic contaminant. One serious problem that PFOA causes is the water pollution (Emmett et al., 2006; Weiss et al., 2012). Various technologies have been developed to degrade PFOA in water to harmless species, including photocatalytic degradation (Estrellan et al., 2010), chemical oxidation (Lee et al., 2010; Liu et al., 2012), electrochemical oxidation (Ochiai et al., 2011a) and sonochemical decomposition (Moriwaki et al., 2005). Among them, electrochemical oxidation is the favored approach because of its strong oxidation performance, mild treatment conditions and environmental compatibility without secondary pollutants (Lin et al., 2012).

As electrode is the key component of the electrochemistry reactor, the utility of high efficiency PFOA-degradation electrode has been a subject of considerable interest. Due to the high bonding energy (approximately  $110 \text{ kcal mol}^{-1}$ ) of C–F in fluorocarbon, perfluorinated compounds (PFCs) have high chemical stability (Du et al., 2014). Electrode materials, such as Pb, platinum, Ti/IrO<sub>2</sub>, Ti/RuO<sub>2</sub>, and Ti/IrO–RuO<sub>2</sub>, could not effectively remove PFOA from aqueous solutions. Recently, there are some studies that explored boron-doped diamond (BDD) and Ti/SnO<sub>2</sub>–Sb/PbO<sub>2</sub> as electrodes (Zhuo et al., 2011, 2012; Lin et al., 2012). Hydrothermal method (Xiao et al., 2011) and photocatalysts (Ochiai et al., 2011b) were used to enhance electrochemical oxidation of PFOA. The pathway of PFOA electro-oxidation was also discussed in previous studies, which revealed that the degradation of PFOA followed a stepwise CF<sub>2</sub> flake-off manner. PFOA was gradually oxidized to shorter-chain perfluorocarboxylic acids and finally mineralized to CO<sub>2</sub> and F<sup>−</sup> completely (Ochiai et al., 2011a; Zhuo et al., 2011).

PFOA concentrations detected in river and the wastewater treatment effluent normally range from ng L<sup>−1</sup> to μg L<sup>−1</sup> levels (Saito et al., 2004; Skutlarek et al., 2006; Sun et al., 2011; Lin et al., 2014). However, most of the previous electrochemical oxidation studies dealt with high PFOA concentrations (5–50 mg L<sup>−1</sup>) but not with low concentration close to actual condition due to the inefficient mass transfer of low-concentration PFOA in solution. The weak adsorption of PFOA on the electrodes in these studies would decrease the rate of mass transfer and diffusion further, and as a result, the contaminant was unable to be degraded on the anode effectively. Therefore, the further exploration should focus on development of electrode materials with high adsorption activity to enhance PFOA decomposition under relatively low concentration close to actual condition.

Carbon nanotube (CNT) sponge is a novel type of macroscopic CNT material. The CNT sponges were synthesized by thermal chemical vapor deposition using ferrocene and 1,2-dichlorobenzene as the catalyst precursor and carbon source (Gui et al., 2010), respectively. Compared with other CNT materials, the CNT sponge show a labyrinth-like pore structure formed by random over-lapping of CNTs, with a porosity of >99%, higher structural flexibility and robustness, and wettability to organics in pristine form (Gui et al., 2010; Li et al., 2010). The average pore size in the CNT sponge is ~80 nm, and the BET surface area was measured to be ~370 m<sup>2</sup> g<sup>−1</sup> (Zhong et al., 2013). Due to these excellent properties, CNT sponge can absorb a wide range of organics and oils with high sorption rates and sorption capacities up to 180 times their own weight, two orders of magnitude higher than activated carbon (Gui et al., 2010; Li et al., 2010; Zhu et al., 2013). Furthermore, CNT sponges have excellent electrical conductivity and electrocatalytic activity. They have shown great promise to be used in fabricating deformable supercapacitor electrodes with stable performance (Li et al., 2013). Therefore, CNT sponges are ideal electrode materials for electro-oxidation theoretically. To our knowledge, there has been no report on CNT sponge electrode for contaminant electro-oxidation.

Herein we report the efficient electro-oxidation of PFOA by using CNT sponge electrode for the first time. Taking graphite electrode as control, we studied the removal efficiency of PFOA in aqueous solution by CNT sponge electrode on different voltages. The feasibility and validity of this method in decontaminating PFOA solution with a concentration close to the real situation were investigated. The mechanism of low-concentration PFOA degradation was discussed by examining the adsorption of PFOA by CNT sponge and the intermediate of PFOA degradation.

## 2. Experimental

### 2.1. Chemicals and materials

CNT sponges were supplied by College of Engineering, Peking University (Gui et al., 2010). A graphite electrode was purchased from Tianjin Aidahengsheng Technology Ltd. (P.R. China). PFOA (C<sub>7</sub>F<sub>15</sub>COOH, chromatographically pure), sodium perchlorate (NaClO<sub>4</sub>·H<sub>2</sub>O) as well as chemicals for chromatographic analysis such as LC grade acetonitrile and ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>) were supplied by J&K Scientific Ltd. All other chemicals used were of analytical grade, and all solutions were prepared with ultra-pure water obtained from a Millipore-MilliQ system with a resistivity of 18 MΩ cm.

### 2.2. Electrode preparation and characterization

The CNT sponges were added into mixed acid (concentrated H<sub>2</sub>SO<sub>4</sub>:concentrated HNO<sub>3</sub> = 3:1) to be refluxed for about 10 min at room temperature, and then washed with ultra-pure water several times until pH of the filtrate was nearly neutral. 0.01 g CNT sponge was wrapped with cotton gauze and equipped with titanium wires to serve as electrode (dimension: 10 mm × 10 mm). Graphite electrode (dimension: 10 mm × 10 mm) was washed with ultra-pure water and dried before use.

Microscopic morphology images of acid treated CNT sponges were taken with a field emission scanning electron microscopy (SEM) (FEI Quanta 200, U.S.). The surface hydrophilicity of the CNT sponge was characterized by measuring the water contact angle with a contact-angle measurement system (Dataphysics OCA20, Germany). X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS Ultra X-ray photoelectron spectrometer (Kratos, U.K.) using a monochromated Al Kα excitation source (1486.7 eV) and its quantitative analysis was performed with CasaXPS software (Version 2.3.12 Dev7).

### 2.3. Electro-oxidation of PFOA

The electrochemical cells were made of glass. The CNT sponge or graphite was used as the anode. In all cases, a stainless steel electrode (dimension: 10 mm × 10 mm) was used as the cathode. The distance between the anode and cathode was 10 mm. A volume of 200 mL PFOA solution containing Na<sub>2</sub>SO<sub>4</sub> as electrolyte (10 mM) was used to conduct the electrochemical experiments with regard to the effects of initial PFOA concentration (10,000 and 100 μg L<sup>−1</sup>) and polarization voltage (0–4 V). All the experiments were operated at 25 ± 1 °C in a batch mode with a magnetic stirrer. 2 mL sample was taken every 30 min and filtered through a 0.22 μm filter before analysis.

To exam the adsorption of PFOA by CNT sponge electrode, adsorption experiments were conducted under the same condition with electrochemical experiments without potential imposed on the electrode. The experiments were operated for 60 min (kinetics experiments which took 120 min indicated that apparent

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