



# Electrochemically enhanced removal of perfluorinated compounds (PFCs) from aqueous solution by CNTs-graphene composite electrode

Zhijuan Niu<sup>a</sup>, Yujuan Wang<sup>a</sup>, Hui Lin<sup>a</sup>, Fangyuan Jin<sup>a</sup>, Yang Li<sup>a</sup>, Junfeng Niu<sup>a,b,\*</sup>

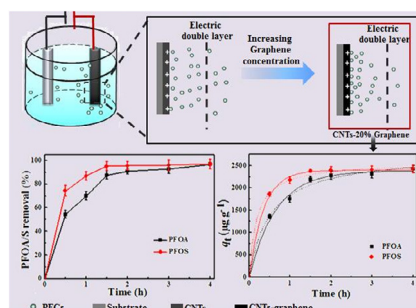
<sup>a</sup>State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing 100875, PR China

<sup>b</sup>School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan, Guangdong 523808, PR China

## HIGHLIGHTS

- Electro sorption removal of PFCs from aqueous solution is investigated.
- Ti/Ebonex/CNTs electrode is more stable than Ti/CNTs electrode to remove PFCs.
- CNTs-20% graphene electrode exhibits maximal sorption capacities.
- The incorporation of graphene into CNTs enhances the removal rate of PFCs.
- The removal ratios of PFOA decrease with the increasing plate distance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electrochemical removal of environmentally persistent perfluorinated compounds (PFCs) from aqueous solution by Ti/activated carbon fiber (ACF), Ti/Ebonex/carbon nanotubes (CNTs), and CNTs-graphene composite electrode was investigated. The results indicated that the CNTs with 20 wt% graphene (CNTs-20% graphene composite electrode) exhibited the optimal capacitive behavior and electrochemical property for the removal of perfluorooctanoate (PFOA) from aqueous solution. The removal ratio and sorption capacity of PFOA on CNTs-20% graphene electrode were 96.9% and  $2421.7 \mu\text{g g}^{-1}$  after 4 h of electro sorption, respectively. The sorption equilibriums of PFOA and perfluorooctane sulfonate (PFOS) by CNTs-20% graphene electrode were approximately 4.0 h and 2.0 h, respectively. The electro sorption rates were 9.7 times (PFOA) and 12.7 times (PFOS) higher than those by powder CNTs-20% graphene composite material, respectively. The maximal sorption capacities of PFOA and PFOS on CNTs-20% graphene electrode were  $491.9 \text{ mg g}^{-1}$  and  $555.8 \text{ mg g}^{-1}$ , respectively. The results indicated that the incorporation of graphene into CNTs could effectively enhance the electrochemical removal of PFCs from aqueous solution. These results provide an effective and alternative method to remove PFCs from wastewater with low energy consumption and mild experimental conditions.

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\* Corresponding author at: School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan, Guangdong 523808, PR China.

E-mail addresses: [niuzj88@sohu.com](mailto:niuzj88@sohu.com) (Z. Niu), [wangyu198732@gmail.com](mailto:wangyu198732@gmail.com) (Y. Wang), [linhui@bnu.edu.cn](mailto:linhui@bnu.edu.cn) (H. Lin), [jinfangyuan@mail.bnu.edu.cn](mailto:jinfangyuan@mail.bnu.edu.cn) (F. Jin), [liyang\\_bnu@bnu.edu.cn](mailto:liyang_bnu@bnu.edu.cn) (Y. Li), [junfengn@bnu.edu.cn](mailto:junfengn@bnu.edu.cn) (J. Niu).

## 1. Introduction

Perfluorooctanoate ( $\text{C}_7\text{F}_{15}\text{COOH}$ , PFOA) and perfluorooctanesulfonate ( $\text{C}_8\text{F}_{17}\text{SO}_3\text{H}$ , PFOS) have been extensively used for decades in different products such as fire-fighting foams, surface treatment agents, polymer additives and surfactants due to its unique properties of chemical stability and high surface activity [1–3]. The wide-

spread distribution of PFOA and PFOS has been frequently detected in various environmental and biological matrices, including water, sediment, air, wildlife, and human blood serum [4–7]. Recent studies indicated that PFOA and PFOS can accumulate in organisms and human being, and it might pose a risk to human health [8–10]. Therefore, it is urgent and of great significance to develop reliable and effective technologies to remove PFOA and PFOS from water.

Some technologies including photochemical oxidation, ultraviolet irradiation, electrochemical oxidation, ultrasonic irradiation, sorption, coagulation, zerovalent iron reduction have been developed to remove PFOA and PFOS from aqueous solution [11–13]. However, these methods are not sufficiently effective and economical for the removal of PFOA and PFOS at low concentration level. It is still imperative to develop an effective technology to remove PFOA and PFOS with low energy consumption and under mild experimental condition.

Sorption method has been widely applied in the elimination of various contaminants from aqueous solution. Previous researches found that many adsorbents could effectively remove perfluorinated compounds (PFCs) from aqueous solution [14,15]. The sorption of PFCs on granular active carbon indicated that the removal ratio of PFCs was more than 99% [16]. In turn, the low sorption rate and sorption capacity restricted the application in the practical treatment of PFCs in water. In addition, some adsorbents always need constant regeneration. Because the hydraulic retention time in the practical treatment process is limited, it is easy for the adsorbed layer to be penetrated due to a low sorption rate before reaching the saturated sorption capacity. For example, the sorption of PFCs on activated carbon filters was fast penetrated in the surface and drinking water samples [17]. Anion-exchange resin exhibits higher adsorption capacity for PFCs, but its sorption rate is quite low [18]. Lampert et al. [18] investigated the sorption of PFCs on ion-exchange resin, and the results found that the ion-exchange resin column was penetrated at merely 45 times column volume, which was far less than its sorption capacity of PFCs. Therefore, it is necessary to develop new adsorbents or sorption technologies with high sorption capacity and sorption rate.

The application of electrosorption techniques in water treatment has drawn considerable attention in recent years [19,20]. This technology was found to be able to enhance the sorption capacity and sorption rate by applied electric field, and could operate at room temperature conditions without adding extra reagents, which is a novel water purification technology with less energy consumption and cost-effective. Electrosorption has been successfully applied in the elimination of inorganic salt and heavy metal ions from water [21–23]. At present, the electrosorption technology has been successfully adopted in industrial and municipal wastewater desalination and achieved the engineering and large-scale application. More than thirty companies have used this technology for desalination, and the results showed that it run well with a stable effluent [24]. However, only a limited number of researches reported the application of this technology for the removal of organic pollutants. Li et al. [25] fabricated the CNTs electrode by electrophoretic deposition (EPD) method, and further investigated the adsorption ability of PFCs on CNTs electrode. The results indicated that the sorption capacity and sorption rate of PFCs increased under the electrochemical assistance, suggesting that the electrosorption technology may have a great potential for the elimination of PFCs from aqueous solution.

The performance of the electrode depends mainly on the physical properties and structure of the electrode materials including specific surface area, pore size distribution and electrical conductivity and so on [26,27]. The high specific surface area and high conductivity are the important advantages of carbon materials [28]. It was reported that carbon aerogels, activated carbon fiber (ACF), CNTs, nanofibers, graphene, and mixtures of these materials

were used as the electrosorption electrodes in the removal of recalcitrant organic pollutants from aqueous solution [29–32]. In this work, the feasibility of removing PFCs from aqueous solution using ACF, CNTs and CNTs-graphene composite electrodes were investigated. Batch experiments were conducted to evaluate the sorption kinetics and isotherms of PFCs on the composite electrode. The influence factors including initial solution pH, bias potentials and plate distance were evaluated for the removal of PFOA from aqueous solution.

## 2. Materials and methods

### 2.1. Materials

PFOA (98.0%), PFOS (98.0%), methanol (99.9%) and acetonitrile (99.9%) were purchased from Sigma-Aldrich Chemical Co., Ltd. (St. Louis, MO). Magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), isopropanol, graphene, and carbon nanotubes (CNTs) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). ACF was supplied by Shanghai Union Soldiers Environmental Protection Technology Co., Ltd. (Shanghai, China). All chemicals and reagents used in the experiments were of analytical grade or higher. Deionized water with the conductance of  $18.2 \text{ M}\Omega \text{ cm}$  at  $25 \pm 1 \text{ }^\circ\text{C}$  was prepared by Millipore water system. Prior to the preparation of the electrodes, ACF, graphene and CNTs materials were first washed repeatedly with the deionized water to remove impurities and then washed in  $80 \text{ }^\circ\text{C}$  deionized water for 2 h. Finally, ACF, graphene and CNTs materials were dried for 48 h at  $105 \text{ }^\circ\text{C}$ . The oxygen-containing functional groups on CNTs by acid treatment were prepared to obtain a stable colloidal solution [33]. The acid treatment of CNTs was described in detail by Wepasnick et al. [34].

### 2.2. Fabrication of electrodes

The CNTs suspensions were prepared as follows: CNTs (25 mg) were first added into 100 mL anhydrous isopropanol followed by 60 min sonication at room temperature. A small amount ( $65 \mu\text{mol L}^{-1}$ ) of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was added into the CNTs suspension and continue sonicating for another 15 min to obtain  $\text{Mg}^{2+}$ -adsorbed CNTs suspension. Previous study showed that the presence of  $\text{Mg}^{2+}$  plays an important role in increasing the adhesion of CNTs to the electrodes [35].  $\text{Mg}^{2+}$  was then added in order to charge the CNTs positively [35]. The addition of  $\text{Mg}^{2+}$  could facilitate the movement of negative charged PFOA to the electrode surface and consequently enhanced the electrosorption rate eventually.

An EPD method was utilized for the preparation of Ti/CNTs, Ti/Ebonex/CNTs, and CNTs-graphene composite electrodes. Firstly, Ti and Ti/Ebonex electrodes were sonicated for 10 min to remove impurities. After sonication, Ti and Ti/Ebonex electrodes ( $50 \text{ mm} \times 50 \text{ mm}$ ) were used as cathode, and Ti electrode ( $50 \text{ mm} \times 50 \text{ mm}$ ) was used as anode.  $\text{Mg}^{2+}$ -adsorbed CNTs suspension was loaded in a polymethylmethacrylate vessel, the distance between the two electrodes was kept at a constant gap distance of 10 mm and the applied voltage was 160 V. The weight ratio of CNTs to graphene varied as 100%:0%, 95%:5%, 90%:10%, 80%:20% and 60%:40%, and the resulting composites were named as CNTs-0% graphene, CNTs-5% graphene, CNTs-10% graphene, CNTs-20% graphene and CNTs-40% graphene, respectively.

### 2.3. Characterization of electrodes

The specific surface area and pore size distributions of ACF, CNTs and graphene were measured with a surface area analyzer (Quadrasorb SI, Quantachrome, USA). The Brunauer-Emmett-

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