Metal nanoparticles by doping carbon nanotubes improved the sorption of perfluorooctanoic acid

Longfei Liu[a], Deyun Li[a], Chengliang Li[a,*], Rong Ji[b,*], Xiaofei Tian[a]

[a] National Engineering Laboratory for Efficient Utilization of Soil and Fertilizer Resources, College of Resources and Environment, Shandong Agricultural University, Tai'An, 271018, China
[b] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, 210046, China

GRAPHICAL ABSTRACT
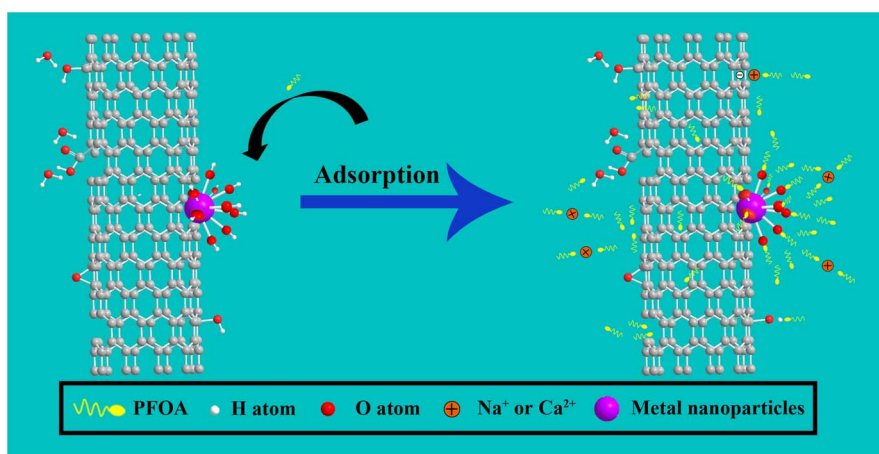
ABSTRACT

Due to considerable application of perfluorooctanoic acid (PFOA) and its refractory degradation, the widespread distribution of PFOA has already resulted in its' risks to environment and organisms. However, the intrinsic characteristic of pristine multi-walled carbon nanotubes (MWCNTs) limited their application for removing PFOA from aqueous medium. Therefore, three nano-metals (nano-crystalline iron, copper and zinc) grafted MWCNTs were synthesized and characterized by BET-N_2, TEM, FTIR, XPS and XRD as well as MWCNTs (as the control treatment) in this study. The results showed that nano metals were well grafted on the surface of MWCNTs. Adsorption were investigated by using radioactive labeled PFOA (^{14}C-PFOA) to quantify the trace PFOA. Adsorption kinetics showed the adsorption of PFOA on the metal doped MWCNTs (MDCNTs) was controlled by intra-particle diffusion. Adsorption isotherms showed the sorption amounts on the MDCNTs were higher than the control. This attributed much to the hydrophobic interaction, electrostatic interaction and the formation of the inner sphere complexes. Ionic strength (0-100 mM) and ionic species (Ca^{2+}) had little effects on the sorption of MDCNTs. PFOA adsorption on MDCNTs strongly depended on pH value in the medium. These results provide an innovative approach for removing trace PFOA from liquid medium.

* Corresponding authors.
E-mail addresses: chengliang_li11@163.com (C. Li), ji@nju.edu.cn (R. Ji).

1. Introduction

Perfluorooctanoic acid (PFOA) is widely used in many products in the past more than half a century because of its high surface activity, resistance to acid and alkali and unique thermal stability [1–4]. Due to the large-scale application of PFOA and its precursors, considerable PFOA was released to the environment [5–7]. The high stability of PFOA is mainly due to the huge energy of C−F covalent bond (531.5 kJ mol^{-1}) [8]. Therefore, considerable PFOA existed in the surface water, soil, atmosphere, sediment and biota for a long time, and PFOA significantly possessed biological accumulation and amplificative characteristics [1,2,9–12]. Some researchers concluded that water was one of the most important backgrounds for PFOA entering human body [13], and PFOA showed a series of toxic effects [14,15]. PFOA had a half-life of about 3.8 years in the human body [16], and the detriment to human is persistent, so it is urgent to remove PFOA from water, especially in drinking water.

Nevertheless, because of the chemically inert and high thermal stability, PFOA molecules are difficult degraded by natural processes [17,18]. As reported, there are several common methods for PFOA degradation [19–21]. However, some of these methods are very expensive or require vast amounts of energy in the degradation processes. In addition, some of these methods use hydroxyl radicals to scavenge PFOA, which was reported that the removal efficiency was not good [22].

Adsorption method for removing perfluorinated compounds is comprehensively accepted as an effective, low energy consumption and environment friendly method [23,24]. Some common adsorbents, such as activated carbon, had been used to adsorb perfluorochemicals in aqueous solution [25–30]. But the adsorption capacities were not optimistic. Some studies found that biological activated carbon was not effective enough for removing trace PFOA in drinking water [31]. In addition, there was an experiment to prove that after using one kind of conventional coagulants (FeCl$_3$·6H$_2$O) for adsorbing PFOA, the removal ratio of PFOA was only about 12% [32]. Hence, new adsorbents with high adsorption capacity, good recyclability, and low cost are urgently needed to be invented or ameliorated.

Carbon nanotubes have attracted more and more attention due to their unique one-dimensional hollow tubular structure, large specific surface area, and strong adsorption capacity [33]. The adsorption of multi-walled carbon nanotubes (MWCNTs) on some pollutants showed excellent results than traditional adsorbents [34]. However, after being treated by strong acid to remove the independent amorphous carbons and residual catalysts, the surface of MWCNTs were loaded by hydrophilic functional groups (e.g. hydroxyl and/or carboxyl). This would encourage MWCNTs to combine with water molecules or to weaken the hydrophobic interaction, and consequently inhibit the adsorption amount of PFOA [35].

In the last several years, most researches of nano-complexes focused on the fields such as catalyst, super capacitor and super battery [36–38]. Some researchers reported that the residual of metal catalyst particles remaining on MWCNTs can promote the adsorption of PFOA on MWCNTs [24]. Nowadays, there is no literature on the adsorption of PFOA in aqueous solution by metal doped MWCNTs. Therefore, a conjecture was proposed that compared with the MWCNTs and commonly used treatment (strong acid or strong oxidant treatment) of MWCNTs, metal doped MWCNTs may improve the adsorption capacity of PFOA.

In this study, different metal nanoparticles were grafted on the surface of MWCNTs by various approaches, and the metal doped MWCNTs were characterized. The adsorption mechanism(s) of PFOA on them was determined by batch technique. Simultaneously, the effects of ionic strengths, ionic species, and electrolyte pH values on the adsorption of PFOA were also investigated. It is hoped that the data and results of this study are helpful for understanding the adsorption behavior of PFOA on metal doped MWCNTs in water environment.

2. Materials and methods

2.1. Chemicals

Non-labeled PFOA (96% purity) and ^{14}C-labeled PFOA (99% radiochemical purity and 55 mCi mmol^{-1} specific activity) were purchased from KMF Laborchemie Handels GmbH (Germany) and American Rediolabeled Chemicals. Inc. (USA), respectively. The selected physical-chemical properties of PFOA are listed in Table S1. Stock solutions were prepared by mixing non-labeled and ^{14}C-labeled PFOA in Milli-Q water and stored at 4 °C. MWCNTs were purchased from Shenzhen Nanotech Port Co., China. Other chemical reagents for grafting metal nanoparticles (MNPs) are analytical reagent levels.

The grafted MWCNTs were synthesized according to available literatures [39,40]. Nano zinc loading method was referenced to loaded nano iron, and then marked as Fe/Fe$_2$O$_3$-CNTs, Cu/CuO-CNTs and Zn/ZnO-CNTs (X/XO$_y$-CNTs, X = Fe, Cu, Zn and y = 1 or 3/2), respectively.

In order to avoid the adsorption of PFOA by the independent MNPs, all of the complexes were washed repeatedly with ultrasonic treated 95% ethanol by suction filtration (0.45 μm filter membrane), to remove the MNPs that did not firmly load on the surface of the MWCNT.

2.2. Characterization of X/XO$_y$-CNTs and MWCNTs

The zeta potentials of X/XO$_y$-CNTs and MWCNTs were probed by the zeta potentials-pH curves using a laser particle size analyzer (Zetasizer Nano S, UK). The specific surface area (SSA) of adsorbents were determined by nitrogen adsorption-desorption isotherms at 77 K that were measured using NOVA 4000e (Quantachrome, USA) through multipoint Brunauer-Emmett-Teller (BET) method. Microscopy images were observed by field emission transmission electron microscopy (FETEM, Tecnai G2 F20, USA) and the crystalline interplanar spacing were demarcated and measured by Gatan DigitalMicrograph 3.9. Powder X-ray diffraction (XRD, Bruker D8 Venture, Germany) with Cu Kα radiation was used to identify the phase composition and crystal lattice parameters of texted samples and the patterns were analyzed by MDI Jade 5.0 software. The diffraction patterns were collected at room temperature by step scanning in the range of 15°–85° at a scanning rate of 12° min^{-1}. The surface functional groups were observed by X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, USA) and Fourier transform infrared spectroscopy (FTIR, Thermo Fisher, USA). The XPS data were collected with an energy step size of 1.00 eV and the spectra were analyzed by Thermo Avantage software. The FTIR spectras were recorded on the spectrum in the 4000–400 cm^{-1} region with a resolution of 2 cm^{-1} in transmission mode.

2.3. Adsorption and desorption experiments

Adsorption kinetics and isotherms were investigated by using batch equilibration technique and all the experiments were performed in three replications. Some studies found that equilibration time had no effect on initial environmental factors [41]. Therefore 500 μg L^{-1} of PFOA as the initial concentration was to determine adsorption kinetics. The adsorbents (1.2 mg) were weighted into polypropylene tubes, and pre-wetted with 10 mmol L^{-1} NaCl and 200 mg L^{-1} NaN$_3$ (to prevent biodegradation) electrolyte solution (12 mL) for 24 h. The electrolyte solution had been adjusted to pH 6.50 ± 0.10 using 0.1 mol L^{-1} HCl or NaOH. Then aliquot of ^{14}C- and non-labeled PFOA stock solution (20 μL) was added into tubes. All tubes were mixed at 150 rpm on a horizontal shaker at 25 ± 1 °C and the whole process was carried out under shading conditions. The solid and liquid phases were separated by centrifugation for 20 min at 10,000g [24]. The radioactivity in the supernatant was detected using liquid scintillation counter.

For adsorption isotherms, adsorbents were weighted into polypropylene tubes respectively and pre-wetted with electrolyte solution as