



Superhigh adsorption of perfluorooctane sulfonate on aminated polyacrylonitrile fibers with the assistance of air bubbles

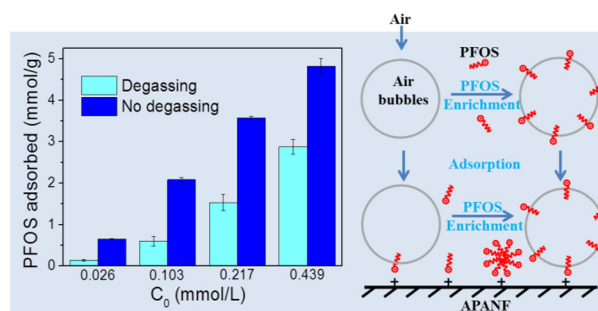
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HIGHLIGHTS

- APANFs possess a superhigh adsorption capacity for PFOS up to 15 mmol/g.
- Air bubbles are involved in the adsorption of PFOS on APANFs.
- Contribution of air bubbles increases with the decrease of PFOS concentrations.
- New sorption mechanism of PFOS on APANFs based on air bubbles is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The role of air bubbles in the adsorption of perfluorooctane sulfonate (PFOS) is normally overlooked, and particularly the influence of air bubbles on PFOS adsorption onto hydrophilic adsorbents remains unclear. In this study, for the first time we propose that air bubbles originally existing in solution or being formed during shaking play an important role in the adsorption of PFOS on the aminated polyacrylonitrile fibers (APANFs). The APANFs possess a superhigh adsorption capacity of 15.0 mmol/g for PFOS at pH 3 with the assistance of air bubbles. The contribution of air bubbles to PFOS adsorption increases with the decrease of initial PFOS concentrations and the increase of solution pH. The adsorbed amount of PFOS on the APANFs decreases by 79% when 0.026 mmol/L PFOS solution at pH 6 is degassed at 0.01 atm for 24 h. By contrast, degassing the APANFs shows no influence on PFOS adsorption, suggesting the dominant contribution of air bubbles in solution rather than on the APANFs. PFOS is adsorbed on the APANFs via not only the electrostatic attraction and micelles, but also the adsorbed air bubbles with accumulated PFOS at gas-liquid interfaces. A new schematic sorption model of PFOS on the APANFs with the assistance of air bubbles is proposed, and this finding is helpful for developing PFOS removal strategy and understanding PFOS transport and fate in aquatic environments.

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1. Introduction

Perfluorinated compounds (PFCs) are a class of persistent organic pollutants with all the hydrogen atoms replaced by fluorine atoms [1–3]. Among all the PFCs, perfluorooctane sulfonate

(PFOS) has drawn great attention for its widely production and consumption in the past decades [4–8]. Although it has been nearly fifteen years since its largest producer, 3M company, phased out the production of PFOS, PFOS is still produced and used in some developing countries [9–14]. Due to the tremendous and worldwide discharge of PFOS in history, it has been detected in the drinking water in many areas around the world [15–21]. Recently, the United States Environmental Protection Agency has established

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the health advisory level for PFOS and perfluorooctanoate (PFOA) at 70 ng/L [22]. The contamination of PFOS in aquatic environments is a long-term issue.

Because of the high energy of carbon-fluorine bonds in the fluorocarbon chain of PFOS, some conventional techniques including biological degradation, oxidation and reduction are difficult to degrade PFOS in ambient environments, [23–25], while the degradation of PFOS under severe conditions is normally an energy-intensive process [3,23]. By comparison, adsorption is considered as an efficient and cost-effective method to remove PFOS from water or wastewater [26–28], and many efficient adsorbents such as activated carbon, resin and modified clays have been reported [8,29–31]. However, most adsorbents exhibit low adsorption capacity for PFOS, and the adsorption rate in the porous adsorbents is normally very slow [1]. Hydrophobic and electrostatic interactions are reported to be mainly involved in the adsorption of PFOS [30–33]. Besides, we have found that the accumulation of PFOS at the interface of air bubbles on some hydrophobic carbonaceous adsorbents also plays an important role in the adsorption process [34], since PFOS is not only hydrophobic, but also oleophobic, preferring to staying at the water-air interfaces [4,35–37]. However, the role of air bubbles in the adsorption of PFOS on hydrophilic adsorbents remains unclear.

Unlike on the hydrophobic adsorbents, air bubbles hardly exist on the hydrophilic adsorbent surfaces [38,39]. However, in consideration of the preferable PFOS accumulation at the air-water interfaces [35,36], air bubbles may first accumulate PFOS, and then be adsorbed on the hydrophilic adsorbents via electrostatic interaction between the anionic PFOS and positive sites on the adsorbents. Due to the high accumulation of PFOS on the surface of air bubbles, the adsorption of an air bubble might result in the adsorption of many PFOS molecules at one adsorption site. Therefore, air bubbles are also possibly involved in the adsorption of PFOS on hydrophilic adsorbents. Besides some effective hydrophilic adsorbents, lots of hydrophilic particles are also widely present in the natural aquatic system [40–43], and thus it is very important to clarify the role of air bubbles in the adsorption of PFOS on the hydrophilic surfaces, which is helpful for understanding the adsorptive removal mechanism of PFOS and its fate in aquatic environments.

According to the above discussion, the hydrophilic adsorbents such as aminated polyacrylonitrile fibers (APANFs) are able to adsorb more PFOS via air bubbles, which could be formed during the shaking process or originally exist in solution. Therefore, we hypothesize that air bubbles are responsible for PFOS adsorption on the hydrophilic APANFs in this study, and the objectives of this study are to: 1) prepare the positively charged APANFs with super-high adsorption capacity for PFOS, and verify the involvement of air bubbles in the adsorption process, 2) analyze the contribution of air bubbles to PFOS adsorption under different conditions, and 3) propose the adsorption mechanism of PFOS on the APANFs in the presence of air bubbles.

2. Materials and methods

2.1. Materials

PFOS, perfluorohexane sulfonate (PFHxS), perfluorobutane sulfonate (PFBS) (all potassium salts, purity > 98%), and diethylenetriamine (purity > 99 %) were purchased from Sigma-Aldrich Co. Polyacrylonitrile fibers (PANFs) were kindly provided by Daqing Polyacrylonitrile Factory, China. The PANFs contain 90% polyacrylonitrile and 10% vinyl acetate, and have an average diameter of about 25 μm and a density of about 1.18 g/cm^3 . Sodium hydroxide and hydrochloric acid (AR grade) were purchased from Beijing

Chemical Works. Methanol (HPLC grade) was purchased from J.T. Baker, NJ. Ultrapure water was used in all the experiments.

2.2. Preparation of APANFs

APANFs were prepared according to our previous method [44]. An amount of 10 g PANFs was added into 300 mL of 75% (v/v) diethylenetriamine solution in a 500 mL reaction vessel with constantly stirring. The reaction was proceeded at 120 °C with heating under reflux for 24 h. After the reaction, the APANFs were rinsed with ultrapure water till neutral. The rinsed APANFs were dried in a vacuum dryer at 60 °C to constant weight and kept in a desiccator.

2.3. Characterization of APANFs

The amino density of the PANFs and APANFs was measured via acid-base titration. The Brunauer-Emmett-Teller (BET) specific surface area of APANFs was determined by nitrogen adsorption using a gas sorption analyzer (Autosorb iQ, Quantachrome Co., USA). The APANFs before and after the sorption of PFOS were characterized using a Fourier transform infrared (FTIR) spectrophotometer (Thermo Nicolet NEXUS 870, U.S.). The surface morphology and elemental analysis of the APANFs before and after sorption were observed using a field emission scanning electron microscopy (SEM, Zeiss Merlin Compact, Germany) with an energy dispersive spectrometer (EDS).

2.4. Vacuum degassing experiments

Ultrapure water was degassed in a vacuum degasser at a degassing pressure of 0.01 atm for 24 h, and the detailed process could be found in our former research [34]. Different amounts of PFOS methanol stock solutions were added into ultrapure water (with or without degassing) to form the degassed or non-degassed PFOS solution with different PFOS concentrations. The volume ratio of methanol in PFOS solution was controlled less than 2%.

2.5. Sorption experiments

Except for special description, the adsorption experiments with and without degassing were conducted in 40 mL (actual volume: 43 mL) and 60 mL (actual volume: 63 mL) glass vessels respectively, in a back-and-forth shaker with a shaking speed of 150 rpm at 28 °C for 24 h. The dosage of APANFs was 40 mg/L. All sorption experiments were carried out at least twice, and the average values were adopted.

In the adsorption dynamic experiments, 50 mL of PFOS solution at pH 6 and the APANFs were added into vessels for adsorption, and the initial concentrations were 0.093, 0.186, 0.374 and 0.743 mmol/L. When the initial PFOS concentration was 0.374 mmol/L, the solution pH was adjusted to 3, 6 or 10 to explore the effect of solution pH on PFOS adsorption kinetics. In the investigation of adsorption isotherms, 50 mL of PFOS solutions with concentrations from 0.02 to 0.743 mmol/L and APANFs were added into vessels, and the initial pH was adjusted to 3, 6 or 10. To investigate the effect of air volume on PFOS adsorption, different volumes (20–63 mL) of 0.374 mmol/L PFOS solutions at pH 6 were added into the vessels. In the investigation of the effect of shaking speed on PFOS adsorption, 50 mL of 0.374 mmol/L PFOS solution at pH 6 was added into 60 mL vessels for the adsorption with the variable shaking speed from 0 to 210 rpm.

The degassing experiments were conducted to remove air bubbles from the APANFs, solution, or both APANFs and solution, and the detailed degassing procedure was described in our former research [34]. In the investigation of air re-contact experiments,

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