



Enhanced adsorption of perfluorooctane sulfonate and perfluorooctanoate by bamboo-derived granular activated carbon

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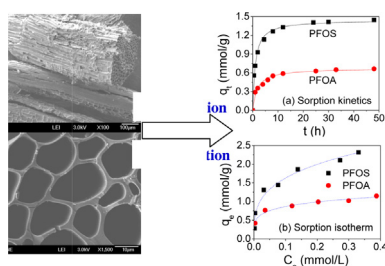
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HIGHLIGHTS

- Granular bamboo-derived activated carbon is successfully prepared by KOH activation.
- The micron and nano-sized pores are suitable for PFOS/PFOA diffusion and sorption.
- The activated carbon has fast and high PFOS/PFOA adsorption.
- Spent activated carbon can be regenerated in 50% methanol solution.

GRAPHICAL ABSTRACT



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ABSTRACT

A bamboo-derived granular activated carbon with large pores was successfully prepared by KOH activation, and used to remove perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from aqueous solution. The granular activated carbon prepared at the KOH/C mass ratio of 4 and activation temperature of 900 °C had fast and high adsorption for PFOS and PFOA. Their adsorption equilibrium was achieved within 24 h, which was attributed to their fast diffusion in the micron-sized pores of activated carbon. This granular activated carbon exhibited the maximum adsorbed amount of 2.32 mmol/g for PFOS and 1.15 mmol/g for PFOA at pH 5.0, much higher than other granular and powdered activated carbons reported. The activated carbon prepared under the severe activation condition contained many enlarged pores, favorable for the adsorption of PFOS and PFOA. In addition, the spent activated carbon was hardly regenerated in NaOH/NaCl solution, while the regeneration efficiency was significantly enhanced in hot water and methanol/ethanol solution, indicating that hydrophobic interaction was mainly responsible for the adsorption. The regeneration percent was up to 98% using 50% ethanol solution at 45 °C.

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1. Introduction

PFOS and PFOA are the typical perfluorinated compounds (PFCs), and they have been produced and used in many industries. Although PFOS was listed as one of the persistent organic pollutants in 2009 [1], it is still allowed to be used in some special industries such as chrome plating in China. PFOA is often used as an emulsifier in the production of fluoropolymers [2,3], and it is also used in semiconductor industry. The wastewater from the

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photolitho process was estimated to have 1000 mg/L of PFOA [4]. It has been reported that the concentrations of PFOS and PFOA in surface water near industrial zone were up to 5.7 $\mu\text{g/L}$ and 19.2 $\mu\text{g/L}$, respectively [5]. Therefore, it's very important to find some effective techniques to remove PFOS and PFOA from industrial wastewater and contaminated surface water.

Adsorption is an effective method to remove PFOS and PFOA from wastewater [6–8], and some efficient adsorbents such as activated carbon, resin [7,9], chitosan [10,11], hydrotalcite [5], alumina [12], and organo-montmorillonite [13] have been reported. Among these adsorbents, the anion-exchange resins and crosslinked chitosan have the highest sorption capacity for PFOS and PFOA, but the sorption velocity is not satisfactory due to the slow intraparticle diffusion in the porous materials [7,9], and especially the two adsorbents are expensive. In consideration of actual application, the cheap activated carbon is preferred. The granular activated carbons (GAC) have the sorption capacity of 160–229 mg/g for PFOS and 112–161 mg/g for PFOA [6,7,14]. The powdered activated carbons (PAC) have the sorption capacity of 374–550 mg/g for PFOS and 175–524 mg/g for PFOA [5,7,15,16]. It is obvious that the PAC has higher adsorption capacity for PFOS and PFOA than the GAC. Similarly, the PAC has faster adsorption velocity than the GAC. The reason is that these commercially available activated carbons mainly contain micropores, unfavorable for PFOS/PFOA diffusion and adsorption in the inner pores of the GAC [7]. The formed micelles or hemi-micelles of PFOS and PFOA may block the micropores of activated carbon, making some inner surfaces unavailable for adsorption [7]. Although the PAC has the relatively fast and high adsorption of PFOS and PFOA, it cannot be reused due to the difficult separation of powder. Therefore, it is a challenge to prepare GAC with fast and high adsorption of PFOS and PFOA. If the prepared GAC has bigger pores than the commercially available GAC, the adsorption of PFOS and PFOA may be enhanced.

When bamboo was used as the precursor to prepare the GAC, many micron-sized pores were formed in the adsorbent prepared by KOH activation [17], which should be favorable for PFOS and PFOA diffusion in the activated carbon. If the micropores in the bamboo-derived activated carbon are enlarged, they should facilitate the adsorption of PFOS and PFOA, resulting in the high adsorption. In this study, the bamboo-derived GAC was optimized to have high sorption capacity for PFOS and PFOA, and then the batch adsorption experiments including adsorption kinetics, isotherms and effect of solution pH were conducted to investigate their adsorption behavior on the optimum activated carbon. Finally, the regeneration of the spent activated carbon was also evaluated using different regeneration agents. The novelty of this study is to prepare the bamboo-derived activated carbon through KOH activation to achieve the fast and high adsorption of PFOS and PFOA, and the suitable regeneration agents were also found to successfully regenerate the spent activated carbon. Although the bamboo-derived activated carbons prepared by different activation methods have been studied before [17,18], this activated carbon prepared via KOH activation for PFOS/PFOA adsorption was not reported.

2. Materials and methods

2.1. Chemicals and materials

The bamboo was obtained from a local market in Beijing, and crushed and sieved into the particle size in the range of 20–30 mesh (0.85–0.60 mm). Perfluorooctane sulfonate (PFOS, potassium salt) and perfluorooctanoate (PFOA, sodium salt) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Japan), and their properties are listed in Table 1. Other chemicals including KOH, HCl, NaCl, methanol and

ethanol were purchased from Beijing Modern Eastern Fine Chemical Co., Ltd., and they were reagent grade.

2.2. Preparation of bamboo-derived GAC

In the carbonization process, the bamboo particles were heated to 500 °C in a tubular furnace and maintained at this temperature for 1.5 h under N_2 flow protection. In the activation process, the carbonized particles were impregnated by KOH solution at the KOH/C mass ratios of 1–6, and the mixture was dried at 105 °C for 12 h. The obtained material was placed in a tubular furnace, followed by heating to the activation temperature (700, 800 and 900 °C) at an increasing rate of 10 K/min, and maintaining at the temperature for 1.5 h under N_2 flow protection. Thereafter, the obtained GAC was washed by 1 M HCl solution, followed by washing with deionized water until the pH of the wash water was neutral. Finally, the bamboo-derived GAC was dried in an oven at 105 °C for 12 h.

2.3. Characterization of activated carbon

The surface morphologies of the carbonized bamboo and bamboo-derived activated carbon were observed by a scanning electron microscopy (SEM, JSM-6460LV, JEOL, Japan). The specific surface area (SSA) and pore size distribution of the activated carbons were characterized by N_2 adsorption at 77 K in a gas adsorption instrument (Autosorb iQ, Quantachrome Corp., US). Before each measurement, the sample was outgassed at 300 °C for 6 h in vacuum to clean its surface. SSAs were calculated with the Brunauer–Emmett–Teller (BET) equation from N_2 adsorption data in the relative pressure (P/P_0) range of 0.01–0.25. The pore-size distribution was obtained according to the nonlocal density functional theory [19]. The zeta potentials of bamboo-derived activated carbon were measured with a zeta potential instrument (Delsa Nano C, Beckman Coulter, USA). The granular sample was crushed into powders below 200 mesh and suspended in ultrapure water at the dose of 0.05 g/L, following by adjusting solution pH with NaOH or HCl solution in the range of 2.0–10.0 before the zeta potential measurement at 25 °C. The elemental composition of bamboo-derived GAC prepared at the KOH/C ratio of 4 and 900 °C was measured by an elemental analyzer (EA3000, Italy). The surface oxygen-containing functional groups were obtained by Boehm titration.

2.4. Adsorption experiments

In all batch adsorption experiments, 10 mg of activated carbon was added into 250-mL flasks containing 100 mL of PFOS/PFOA solution. All the adsorption experiments were carried out at 175 rpm in an orbital shaker for 48 h, and the temperature was controlled at 25 °C. Since solution pH changed little ($<\pm 0.2$) after the sorption experiments, no pH adjustment was conducted in the adsorption process. In the investigation of the sorption kinetics, the initial solution pH was 5.0, and the initial concentrations of PFOS and PFOA were 100 and 81 mg/L, respectively. The experiments of sorption isotherms were conducted in solution at pH 5.0 with initial PFOS/PFOA concentrations ranging from 20 to 250 mg/L. In the investigation of pH effect, the initial concentrations of PFOS and PFOA were 100 and 81 mg/L, respectively, and solution pH varied in the range of 3.0–10.0. The concentrations of PFOS and PFOA used in this study were comparable with those in some actual wastewaters [4,20].

2.5. Regeneration and reuse experiments

After the adsorption experiment was conducted with 10 mg of activated carbon in 100 mL of 100 mg/L PFOS solution at pH 5.0