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Regeneration of PFOS loaded activated carbon by hot water and subsequent aeration enrichment of PFOS from eluent

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ABSTRACT

Regeneration and reuse of spent activated carbon (AC) as well as recovery of the desorbed pollutants are challenging in the application of adsorption technology. In this study, the regeneration of perfluorooctanesulfonate (PFOS)-saturated coal-based granular AC by hot water and subsequent aeration method to enrich PFOS from eluent were investigated. The regeneration time, water temperature and solid-liquid ratio affected the regeneration efficiency of PFOS treated AC. PFOS was desorbed quickly from the AC within 30 min by hot water. High water temperature (92 °C) and low solid-liquid ratio (0.5) led to the highest desorption of 36.7% in one cycle (6 h). Over 90% PFOS on the spent AC was desorbed by 92 °C hot water with the solid-liquid ratio of 0.5 after six cycles. Subsequent experiments were conducted to enrich PFOS, and aeration of the regeneration eluent achieved the enrichment factors of 50.6–62.0 for PFOS at initial PFOS concentrations of 10–100 μg/L. The concentration of PFOS in the concentrated solution was 2.2 g/L following sequential sorption, regeneration and aeration treatments when the influent PFOS concentration was 2.7 μg/L.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) have attracted considerable attention recently because of widespread use in various commercial and industrial applications for the past sixty years as water and oil repellents, fire retardants, and chromium fog inhibitor [1–3]. Perfluorooctanesulfonate (PFOS) is one of the typical PFASs, and is considered to be a threat to environments because of its strong stability under most environmental conditions [4]. PFOS has been detected in wastewater, oceans, surface water, groundwater and tap water in the world [1,5–7], with concentrations of up to 5.7 μg/L reported in surface water near industrial zone [8]. Recently, the United States Environmental Protection Agency has established the health advisory level for PFOS and perfluorooctanoate (PFOA) at 70 ng/L.

To remove PFOS from water, different treatment methods such as adsorption, sonochemical degradation and advanced oxidation processes have been reported [3,9]. Due to the high chemical stability, PFOS resists conventional oxidation processes [9]. In contrast, adsorption has been reported as an effective method for PFOS removal from aqueous solutions [10], and many adsorbents exhibit good adsorption ability for PFOS [11]. Activated carbon (AC) is suitable for PFOS removal due to its low-cost and relatively high adsorption capacity [10,12]. Although coexisting compounds affected the adsorption of PFOS on AC, PFOS was still completely removed from chrome plating wastewater and the AFFF-impacted groundwater by AC at doses of 200 mg/L and at 100 mg/L, respectively [13,14]. Compared with the coexisting PFASs, AC showed the highest removal efficiency for PFOS [14].

Normally, AC after PFOS adsorption is treated as hazardous waste [15], and thus it is attractive to regenerate the spent AC and reuse the adsorbent. In the regeneration process, we hope to desorb PFOS from the spent AC as much as possible (over 90% desorption), and thus the regenerated AC may maintain high adsorption capacity for PFOS in the next adsorption cycle. The regeneration of spent AC has been widely studied using different methods such as thermal, chemical, electrochemical, biological, irradiation, ultrasound, microwave and photochemical treatments [13,15]. Solvent

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and oxidation methods can effectively regenerate the PFOS-saturated AC (less than 10% PFOS left on the adsorbent) according to our previous study [16]. However, these methods suffer from some drawbacks such as using chemicals and large loss (5–20% for the thermal regeneration) of the adsorbent during regeneration process and producing byproducts [17,18]. More importantly, these regeneration methods cannot recover PFOS from water and PFOS was still in the regeneration solution or became byproducts. From the environmental point of view, it is meaningful to find a new treatment method for the regeneration of activated carbon and reuse of PFOS.

According to our previous study [3], PFOS adsorption on AC might be related to the interaction between the hydrophobic and oleophobic C–F chain of PFOS and the hydrophobic parts of AC, and air bubbles on adsorbent surfaces play an important role. There are many air nanobubbles adsorbed on the hydrophobic adsorbent surfaces [3,19], and PFOS molecules may accumulate on the gas-liquid interfaces of air bubbles, resulting in the high adsorption of PFOS. Hence, removing the air bubbles from the surfaces of hydrophobic materials by increasing temperature might lead to the desorption of the adsorbed PFOS molecules and regenerate the spent adsorbents. Additionally, Ebersbach et al. [20] found that fluorosurfactants in solution could be effectively collected through aerosol-mediated separation and the enrichment multiple was up to 1309 at the initial concentration of 6.12 mg/L. The removal of PFOS from water is based on high concentrations of fluorosurfactant at the gas-liquid interfaces. When air bubbles are generated in solution, fluorosurfactants can be separated from solution due to their accumulation on air bubbles [21,22]. Therefore, it may be possible to regenerate PFOS-saturated AC using hot water treatment and subsequently enrich PFOS from the regenerating solution.

The purpose of this study was to investigate the performances of regenerating PFOS-saturated AC using hot water and subsequent recovery of PFOS from the regenerating solution using air bubbling method. Firstly, the effects of regeneration time, water temperature and solid-liquid ratio on the regeneration efficiency of PFOS treated AC were investigated. Secondly, the recovering of PFOS from the regenerating solution with different initial concentrations was studied. Finally, the reusability of AC for PFOS adsorption in successive adsorption-desorption cycles was evaluated.

2. Materials and methods

2.1. Chemicals and materials

Perfluorooctane sulfonate (PFOS, potassium salt, purity ≥ 98%) was purchased from Tokyo Kasei Kogyo Co. (Japan). Commercial coal-based activated carbon (AC) was obtained from Guangfu Technology Development Co. (Tianjin, China). The ultrapure water used in the experiments was produced by a Milli-Q integral water purification system (Millipore, USA). All chemicals used are analytical reagent grade or better.

2.2. Preparation and characterization of activated carbon

Before adsorption experiments, AC was rinsed with ultrapure water and dried at 105 °C for 12 h. The dried AC was crushed and sieved in the size range of 0.42–0.71 mm. The elemental compositions were obtained by an elemental analyzer (EA3000, Italy) shown in Table S1. The carbon element content was measured to be 81%, indicating a relatively pure carbon in the sample. The content of surface oxygen functional groups (carboxylic, lactonic, phenolic and carbonyl) was 0.985 mmoL/g. The specific surface area of AC was determined by nitrogen adsorption at 77 K using a gas adsorption instrument (Autosorb iQ, Quantachrome Corp., US). The BET surface area was measured to be 323 m^2/g (242 m^2/g for micropore, and 81 m^2/g for mesopore and macropore), and all pore volume was 0.32 cm^3/g.

2.3. Adsorption experiments

Sorption isotherm experiments were conducted to evaluate the adsorption capacity. An amount of 10 mg AC was added into 250 mL polypropylene flasks containing 100 mL of PFOS solution at the concentrations from 20 μg/L to 200 mg/L, and the flasks were then shaken in an orbital shaker at 170 rpm and 25 °C for 48 h. In the preliminary adsorption kinetic experiment, the equilibration time of PFOS was less than 48 h (Fig. S1). Due to little change of pH values (<± 0.2) after adsorption experiments, no pH adjustment was made during the sorption process. The equilibrium adsorption capacity was calculated as follows.

$$q_e = \frac{(C_i - C_e) \times V}{m_{AC}} \tag{1}$$

Where q_e is the adsorbed amount of PFOS on the AC (μg or mg PFOS/g AC), C_i and C_e are the initial and equilibrium concentrations of PFOS in solution, respectively (μg/L or mg/L), V is the volume of PFOS solution (L), and m_{AC} is the mass of AC (g).

2.4. Regeneration experiments

An amount of 10 mg AC was added into 2 L polypropylene flasks containing 1.5 L of 5.7 μg/L PFOS solutions for 48 h adsorption at 170 rpm and 25 °C. To compare with the high equilibrium concentrations and clarify the desorption mechanism, 10 mg of AC was added into 0.25 L of 20 mg/L PFOS solutions for 48 h adsorption. The AC saturated with PFOS in the adsorption experiment was filtered with 0.45 μm polyether sulphone (PES) and then used for regeneration experiment. The adsorption equilibrium concentrations of PFOS after adsorption were mainly less than 5 μg/L, consistent with the concentrations of PFOS in actual water and wastewater. Regeneration experiments were conducted in a constant temperature water bath shaker at 150 rpm for 6 h (0–360 min for the desorption kinetics of PFOS from the AC). In the investigation of regeneration temperature effect, 10 mg of PFOS-adsorbed AC was added into 25 mL flasks containing 10 mL hot water at the temperatures from 50 °C to 92 °C. To investigate the influence of solid-liquid ratios, 10 mg of PFOS-adsorbed AC was added into different volume of hot water varying from 5 mL to 20 mL at the temperature of 92 °C. After the sorption of 0.25 L of 20 mg/L PFOS solution on 10 mg AC for 48 h, the spent AC was separated and regenerated using hot water for 6 cycles, followed by drying at 85 °C for 12 h and using in the next adsorption cycle. To investigate the regeneration of other PFASs load AC by hot water, 10 mg AC was added into 0.25 L of 20 mg/L PFASs solutions for 48 h adsorption, and then the spent AC was regenerated at solid-liquid ratio of 0.5 and hot water temperature of 92 °C.

2.5. Aeration and enrichment experiments

Two cylindrical plexiglass devices were prepared for the aeration experiments with different PFOS concentrations (Fig. 1). Before aeration treatment, the PFOS concentration in solution (C_0) was measured. Apparatus II (Fig. 1b) (internal diameter of 4.4 cm, the total volume of 456 mL) was used for the enrichment of PFOS at high concentrations above 10 mg/L since the stable foams can be formed. When PFOS concentrations were less than 10 mg/L, stable foams were difficult to form and cannot steadily rise along the