Perfluorooctane sulfonate adsorption on powder activated carbon: Effect of phosphate (P) competition, pH, and temperature

Jin Qian [a, b, *], Mengmeng Shen [a, b], Peifang Wang [a, b, **], Chao Wang [a, b], Kun Li [a, b], Jingjing Liu [a, b], Bianhe Lu [a, b], Xin Tian [a, b]

[a] Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, Hohai University, Nanjing, 210098, PR China
[b] College of Environment, Hohai University, Nanjing, 210098, PR China

HIGHLIGHTS

- Effect of P competition, pH and temperature on PFOS adsorption on PAC was investigated.
- PFOS adsorption with or without P competition followed pseudo-second-order model.
- Adsorption in the binary system was limited by P competing for adsorption sites.
- PFOS adsorption in single/binary systems increased with temperature.
- PFOS adsorption in binary system decreased more sharply with pH increasing.

ARTICLE INFO

ABSTRACT

Powdered activated carbon (PAC), as an adsorbent, was applied to remove perfluorooctane sulfonate (PFOS) from aqueous solution. Laboratory batch experiments were performed to investigate the influences of phosphate (P) competition, temperature, and pH for PFOS adsorption onto PAC. The results showed that higher temperature favored PFOS adsorption in single and binary systems. The kinetic data fitted very well to the pseudo second-order kinetic model. Thermodynamically, the endothermic enthalpy of the PFOS adsorption in single and binary systems were 125.07 and 21.25 kJ mol^{-1}, respectively. The entropy of the PFOS adsorption in single and binary systems were 0.479 and 0.092 kJ mol^{-1} K^{-1}, respectively. And the Gibbs constants were negative. These results indicated that the adsorption processes were spontaneous. The adsorption isotherms of PFOS agreed well with the Langmuir model. In the single system, PFOS adsorption decreased with increased pH value. The difference in the amount of PFOS adsorption between the single and binary systems increased at higher pH. Frustrated total internal reflection (FTIR) demonstrated that P competition increased the hydrophilicity of the PAC and the electrostatic repulsion between PFOS and PAC, then the PFOS adsorption amount decreased. It also demonstrated that, at higher temperature, increased PFOS adsorption was mainly due to the higher diffusion rate of PFOS molecules and greater number of active sites opened on the PAC surface.

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1. Introduction

Perfluorooctane sulfonate (PFOS) is a persistent organic pollutant (POP) (Giesy and Kannan, 2002; Loos et al., 2008), and has attracted considerable scientific and public attention due to its environmental persistence, bioaccumulation, potential toxicity, and widespread distribution in aquatic environments (Giesy and Kannan, 2001; Powley et al., 2008; White et al., 2015). PFOS contamination of ground and surface waters may come from industries that use PFOS-containing compounds as raw materials, e.g., the manufacture of paper, textiles, and leather, as well as in semi-conductors and fire-fighting foam (Tsai et al., 2002; Zareitalabad et al., 2013). Its stable characteristics mean that PFOS is difficult to eliminate using conventional techniques such as

biological degradation, oxidation, and reduction (Vecitis et al., 2009; Yu et al., 2009). Sorption has been demonstrated as an effective and economical method for removing PFOS from wastewater (Yu et al., 2009; Li et al., 2011; Jeon et al., 2011; Deng et al., 2012; Zhou et al., 2012). As one of the most effective adsorbents (Baccar et al., 2009), activated carbon (AC) has been widely used to remove organic and inorganic contaminants from drinking water and wastewater (Luo and Guo, 2001), because of its large surface area, porous structure, and diverse surface chemistry (Zhang et al., 2016). Several studies have investigated the adsorption of PFOS onto AC (Yu et al., 2009; Zhang et al., 2016; Schaefer, 2006).

The effect of phosphate (P) on PFOS adsorption, however, remains unclear, and is therefore of interest for further investigation. Phosphorus, as an additional nutrient, is very important for the growth of photosynthetic macro- and microorganisms in aquatic bodies (Cai et al., 2012; Liu et al., 2002). However, excess discharge of P into water bodies may present serious threat to freshwater ecosystems and human health (Yan et al., 2010). P can convey negative charges to the adsorbent surface, thereby changing the adsorption capacity of another pollutant (Wang et al., 2013; Gimsing and Borggaard, 2007). Wang and Xing (2002) reported that the adsorption of P onto iron oxides may enhance cation adsorption. They found that the adsorption of Cd onto goethite apparently increased following the addition of P, which was attributed to increasing surface negative charges of goethite and decreasing electrostatic potential near the solid surface. Previous studies reported that PFOS and P are likely present in wastewater simultaneously (Qian et al., 2017a,b; Battistoni et al., 2006; Park et al., 2008; Grzmil and Wronkowski, 2006), and the sorption behavior of PFOS onto AC may be strongly modified by P.

To the best of our knowledge, none of the previous studies have investigated the effect of P competition for PFOS adsorption onto powder activated carbon (PAC). To better understand the potential applications of PAC in PFOS removal, this study investigates: (1) the kinetics, thermodynamics, and isotherms of PFOS adsorption on PAC under various conditions; and (2) the effects of temperature, pH, and P competition for PFOS adsorption onto PAC.

2. Materials and methods

2.1. Chemicals and materials

PFOS (>98% purity) and KH_2PO_4 (>98% purity) were purchased from Sigma-Aldrich Co. (St. Louis, MO). PAC, as the adsorbent in this study, was purchased from Sasol Ltd. (Hamburg, Germany). The value of IEP stated on the product label was 5.02. The PAC was passed through a 0.1 mm sieve. Prior to use, the PAC was first rinsed with deionized water to remove impurities, and then dried in an oven at 105 °C for 48 h, after which it was removed from the oven, cooled, and stored in a desiccator.

The characteristics of the PAC are shown in Table 1. PAC surface area was determined by N^2 adsorption isotherms at 77 K using a surface area analyzer (Micromeritics, USA). The point of zero charge (PZC) of PAC was determined by a zeta-potential analyzer (JS94H, China).

Table 1
Characteristics of powdered activated carbon (PAC).

Characteristics	Value
S_{BET}[a] ($m^2 g^{-1}$)	1000
Particle size (mesh)	≥200
Bulk density ($g cm^{-3}$)	0.4
Ash content (%)	4.5—5.0

[a] By the nitrogen adsorption with t method.

2.2. Sorption experiments

Municipal and industrial wastewaters show very different concentrations of PFOS and phosphate (Qian et al., 2017a,b). It was found that a semiconductor industry generated about 200 tons of wastewater containing 12.566 mg L^{-1} PFOS (Lin et al., 2009). Gong et al. (2002) reported P concentrations of 100—1000 mg L^{-1} in phosphorus-containing wastewater. Consequently, the concentrations of PFOS and phosphate in this experiment were set at 10 mg L^{-1} and 100 mg L^{-1}, respectively.

2.2.1. PFOS adsorption experiments in single system

For each test, 100 mL of aqueous solution of PFOS was added to 250 mL polypropylene (PP) Erlenmeyer flasks together with 0.5 g of PAC. The flasks were placed in a thermostatically controlled shaker at 120 rpm for 2.5 h. The kinetic and thermodynamic experiments were conducted at 293, 303, and 313 K respectively, in the single system using PFOS solution concentrations of 10 mg L^{-1}. Samples were collected from the flasks to measure the PFOS concentrations at different time intervals. Adsorption isotherms were obtained from different PFOS concentrations (0.5, 5, 10, 15, 20, and 25 mg L^{-1}). The pH was adjusted (range 3—10) using 0.1 M NaOH or HCl, to investigate the effect of initial solution pH on PFOS adsorption.

2.2.2. PFOS adsorption experiments in binary system

For each co-adsorption test, 100 mL of aqueous solution of a binary mixture of PFOS and KH_2PO_4 was added to 250 mL polypropylene Erlenmeyer flasks together with PAC (5 g L^{-1}). In the binary system, the initial P concentration was maintained at 100 mg L^{-1}. After adding P and PFOS simultaneously to the same PP centrifuge tube, the experiments on kinetics, thermodynamics, and the effects of pH were conducted using the same methods described for the PFOS adsorption experiments without P addition.

2.3. PFOS analyses

The concentration of PFOS was determined using a Waters Acquity ultra-performance liquid chromatography-tandem mass spectrometry system (UPLC-MS/MS) equipped with a 50 × 2.1 mm Waters BEH C18 column (1.7 μm particle size) and tandem quadrupole mass spectrometers (Milford, MA) (Ma and Shih, 2010; Wang et al., 2015).

The amounts of PFOS adsorbed by the PAC were calculated by the following equation:

$$q_e = (C_0 - C_e) V/S \tag{1}$$

Here, q_e is the amount of PFOS adsorbed (μg m^{-2}); C_0 and C_e are the initial and equilibrium concentrations of PFOS concentration (mg L^{-1}), respectively; V is the volume of the solution (L); and S is the surface area of sorbent mass (m^2).

3. Results and discussion

3.1. Effects of temperature on PFOS adsorption in single and binary systems

3.1.1. Adsorption kinetics

Fig. 1a shows the effect of temperature on the kinetics of PFOS adsorption onto PAC. The adsorption amount of PFOS increased from 5.55 to 6.85 μg m^{-2} with temperature increase from 293 to 313 K. This result indicates that temperature has positive influence on PFOS adsorption kinetics and capacities, which may be because the adsorption of PFOS is endothermic (Qu et al., 2009). Similarly, Xu et al. (2015) reported that the amount of PFOS adsorbed onto