



Effect of effluent organic matter on the adsorption of perfluorinated compounds onto activated carbon

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HIGHLIGHTS

- The presence of EfOM significantly reduced the adsorption capacities and rates of PFCs.
- Low-molecular-weight EfOM compounds (<1 kDa) compete for adsorption sites of PFCs directly.
- Large-molecular-weight EfOM compounds (>30 kDa) affect the adsorption through pore blockage or restriction effect.
- Changes in surface properties of PAC caused by preloaded EfOM could affect PFCs adsorption.

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ABSTRACT

Effect of effluent organic matter (EfOM) on the adsorption of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) onto powdered activated carbon (PAC) was quantitatively investigated at environmentally relevant concentration levels. The adsorption of both perfluorinated compounds (PFCs) onto PAC followed pseudo-second order kinetics and fitted the Freundlich model well under the given conditions. Intraparticle diffusion was found to be the rate-controlling step in the PFC adsorption process onto PAC in the absence and presence of EfOM. The presence of EfOM, either in PFC–EfOM simultaneous adsorption onto fresh PAC or in PFC adsorption onto EfOM-preloaded PAC, significantly reduced the adsorption capacities and sorption rates of PFCs. The pH of zero point of charge was found to be 7.5 for fresh PAC and 4.2 for EfOM-preloaded PAC, suggesting that the adsorbed EfOM imparted a negative charge on PAC surface. The effect of molecular weight distribution of EfOM on the adsorption of PFCs was investigated with two EfOM fractions obtained by ultrafiltration. The low-molecular-weight compounds (<1 kDa) were found to be the major contributors to the significant reduction in PFC adsorption capacity, while large-molecular-weight compounds (>30 kDa) had much less effect on PFC adsorption capacity.

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1. Introduction

Perfluorinated compounds (PFCs) have emerged as a new class of environmentally persistent pollutants, which have been widely used in different applications, such as surfactants and surface protectors in carpets, leather, paper, food containers, fabric, and upholstery as well as fire-fighting foams, floor polishes, and shampoos [1]. Perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) have been detected in a wide array of environmental matrices including biota, water, sediment and sludge. In wastewater, it was observed that PFOS and PFOA were ubiquitous in effluents of waste water treatment plants (WWTPs). Schultz et al. [2] reported that PFOS and PFOA occurred

in the influent and effluent of 10 WWTPs in USA. For example, in the effluents of those 10 WWTPs, the concentration of PFOS was in the range of 1.1–130 ng/L, while that of PFOA varied from 2.5 to 97 ng/L. However, higher concentrations of PFOS (48–4980 ng/L) and PFOA (42–2280 ng/L) were found in effluents of publicly owned treatment works [3]. The discharge of municipal and industrial wastewater is one of the major routes for introducing PFOS and PFOA into aquatic environment. In rivers near the PFCs-related factories, high PFOS and PFOA concentrations were reported. In drinking water, U.S. Environmental Protection Agency (USEPA) set a “provisional health advisory” of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS as safe level [4]. Therefore, it is urgent to develop effective technologies to remove PFCs from wastewater.

PFOS and PFOA are considered stable and persist in environment without natural degradation. Studies on fate and behavior of these pollutants in WWTPs implied that they could not be effectively removed by biological treatment process [5]. Various physical-chemical treatment processes, including adsorption

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[6–8], sonochemical treatment [9], reduction with zero-valent iron in subcritical water [10], and membrane filtration [11], have been employed to remove these compounds. Activated carbon adsorption is one of the most promising methods to remove PFCs in aqueous stream due to the effectiveness and low cost. Ochoa-Herrera et al. [5] reported that PFOS could be effectively removed by granular activated carbon (GAC). Senevirathna et al. [12] compared a few adsorbents and found that GAC could effectively remove PFOS even at low concentrations (at ng/L equilibrium concentration). Yu et al. [13] found that PAC possessed significantly higher adsorption rate and capacity for both PFOS and PFOA in comparison with GAC, which indicates that PAC could be a promising adsorbent for PFCs removal. However, the above studies were conducted in pure water. Further information on PFC adsorption kinetics and isotherms in field water is necessary for its application.

Effluent organic matter (EfOM) is highly heterogeneous, containing molecules of various molecular weights ranging from simple compounds such as acetic acid to complex polymers. The composition of EfOM is a combination of natural organic matter (NOM), soluble microbial products (SMPs), and trace harmful chemicals [14,15]. It is known that NOM adversely affected the adsorption of trace organic compounds, such as pesticides, onto activated carbons [16,17] through two major competitive mechanisms: direct site competition and pore constriction/blockage [18,19]. When background NOM was present during activated carbon treatment of water containing trace organic compounds, NOM would compete for adsorption sites with the target compounds. As a consequence, the adsorption of trace organic compounds would usually be reduced [16,17]. In addition, preloaded NOM was found to reduce adsorption capacity primarily through direct site competition and decrease adsorption kinetics primarily by pore blockage [19,20]. In continuous flow adsorption systems, pore blockage effect caused by NOM is the 'preloading' phenomena commonly found in fixed bed GAC columns. In fact, all adsorption systems in which activated carbon is held in the system while water continuously flows through, such as GAC column, floc blanket reactors with PAC addition, and PAC/membrane systems, are vulnerable to pore blockage effect. In these systems, activated carbon is partially loaded with NOM before trace organic compounds enter the system, resulting in pore blockage when the surface concentration of NOM gets high enough. However, few data is available about the effect of EfOM on adsorption kinetics and isotherm of PFCs onto PACs, which is needed for the application of PAC to remove PFCs in wastewater treatment.

The main objective of this study is to investigate the effect of EfOM on the adsorption kinetics and isotherms of PFOS and PFOA onto the PAC at environmentally relevant concentration level. In addition, EfOM was characterized and fractionated to study the effect of molecular weight distribution of EfOM on PFC adsorption. The competitive mechanism caused by EfOM was explored for optimization of system design and operation in order to achieve maximum pollutant removal.

2. Materials and methods

2.1. Chemicals and reagents

Standards of PFOS ($\geq 98\%$), PFOA (96%), methanol (99.8%) and ammonium acetate (97%) were purchased from Sigma–Aldrich (Singapore). Oasis HLB solid phase extraction (SPE) cartridges (500 mg, 6 cm³) were purchased from Waters (Milford, USA). YM series (YM1, YM10, YM30) ultrafiltration (UF) membranes (Millipore, USA) with nominal molecular weight cutoffs of 1, 10, 30 kDa were used in this study. High density polyethylene (HDPE) bottles were used for all adsorption experiments.

Table 1

Characteristics of PAC used in this study.

Primary micropore volume (<8 Å)	0.24 cm ³ /g
Secondary micropore volume (8–20 Å)	0.18 cm ³ /g
Mesopore volume (20–500 Å)	0.07 cm ³ /g
Particle size (nominal)	≤ 40 μ m (75%)
BET surface area	763.8 m ² /g
Mean pore diameter	12.7 Å

2.2. Adsorbent

PAC obtained from [Sigma–Aldrich \(Singapore\)](#) was used as adsorbent in this study and was characterized by nitrogen adsorption at 77 K using a NOVA 3000 surface area analyzer (Quantachrome, USA). The characteristics of the PAC were summarized in [Table 1](#). Prior to adsorption experiments, PAC was soaked in Milli-Q water for 24 h to release potentially adsorbed organics. After dried in an oven at 103 °C for 48 h, the PAC was stored in a desiccator.

2.3. PAC surface titration

The surface charge of PAC was measured by the method described by Newcombe et al. [21]. In brief, 0.5 g PAC was added to 500 mL of 0.01 M NaCl and 0.1 M NaCl solution in a constant temperature titration vessel, respectively. A known amount of NaOH was added to the sample solutions after the titration vessel was stored overnight under protection of nitrogen. After equilibration for 2.5 h, the pH was measured and a small amount of HCl was added with the same equilibration time (2.5 h) between measurements. A blank titration was performed under the same conditions. The relative surface charge was plotted against pH for the two electrolytes concentrations. The pH of point of zero charge (pH_{pzc}) was taken at the point where the two curves crossed.

2.4. Preparation of EfOM solution

EfOM solution was collected from the treated effluent of conventional activated sludge process from a WWTP. Immediately, the treated effluent was filtered by GF/B glass filter (1.0 μ m, Whatman, USA) and stored at 4 °C until use. PFOS and PFOA were detected in treated effluent in the range of 6.3–37.5 ng/L, which was far lower than the adsorption equilibrium concentrations in this study. The fractionation method used in this study was basically based on the procedure developed by Barker et al. [22] with minor modification. The <1 kDa and >30 kDa fractions were obtained and used for adsorption experiments. The fraction of >30 kDa was diluted by synthetic solution with similar ionic strength (0.02 M) to EfOM solution to achieve a same DOC concentration as that of <1 kDa fraction (refer to [supporting document](#) for preparation of synthetic solution).

2.5. Characterization of EfOM solution

The concentration of dissolved organic carbon (DOC) was measured by a 1010 Total Organic Carbon Analyzer (O.I. Analytical, USA). The phenol–sulfuric acid method [23] was used to measure the content of carbohydrate in EfOM solution with glucose as the standard reference, whereas the modified Lowry method [24] was used for protein determination with bovine serum albumin (BSA) as the standard reference. The apparent molecular weight distribution (AMWD) of the EfOM solution was determined using UF membrane in a stirred and pressurized cell (Millipore, USA), operated in a dead end mode. Nitrogen gas regulated at 30 psi was used as a driving force for filtration. Gentle turbulence was created at the membrane surface using a magnetic stirrer to minimize the build-up of a dense macromolecular layer at the membrane