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Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge

Valeria Ochoa-Herrera, Reyes Sierra-Alvarez *

Department of Chemical and Environmental Engineering, University of Arizona, Tucson, AZ 85721-0011, USA

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ABSTRACT

Perfluorinated surfactants are emerging pollutants of increasing public health and environmental concern due to recent reports of their world-wide distribution, environmental persistence and bioaccumulation potential. Treatment methods for the removal of anionic perfluorochemical (PFC) surfactants from industrial effluents are needed to minimize the environmental release of these pollutants. Removal of PFC surfactants from aqueous solutions by sorption onto various types of granular activated carbon was investigated. Three anionic PFC surfactants, i.e., perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonate (PFBS), were evaluated for the ability to adsorb onto activated carbon. Additionally, the sorptive capacity of zeolites and sludge for PFOS was compared to that of granular activated carbon. Adsorption isotherms were determined at constant ionic strength in a pH 7.2 phosphate buffer at 30 °C. Sorption of PFOS onto activated carbon was stronger than PFOA and PFBS, suggesting that the length of the fluorocarbon chain and the nature of the functional group influenced sorption of the anionic surfactants. Among all adsorbents evaluated in this study, activated carbon (Freundlich K_F values = 36.7–60.9) showed the highest affinity for PFOS at low aqueous equilibrium concentrations, followed by the hydrophobic, high-silica zeolite NaY (Si/Al 80, K_F = 31.8), and anaerobic sludge (K_F = 0.95–1.85). Activated carbon also displayed a superior sorptive capacity at high soluble concentrations of the surfactant (up to 80 mg l⁻¹). These findings indicate that activated carbon adsorption is a promising treatment technique for the removal of PFOS from dilute aqueous streams.

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1. Introduction

Perfluorinated (PFC) surfactants are emerging pollutants that have been used for the last 50 years in a wide variety of industrial processes and consumer-based products, including polymer additives, lubricants, fire retardants and suppressants, pesticides, and surfactants (Kissa, 2001). Quantitatively, perfluorooctane sulfonate (PFOS, C₈F₁₇SO₃H) and perfluorooctanoic acid (PFOA, C₇F₁₅COOH) are the most important anionic PFC surfactants detected in the environment. Large quantities of PFOS (e.g., 3500 metric tons in 2000) and PFOA (1200 metric tons in 2004) have been produced and utilized world-wide during the last decades (Lau et al., 2007). In addition, these two chemicals are the final degradation products of a variety of precursor perfluorinated chemicals including fluorotelomer alcohols and fluorinated polymers (Ellis et al., 2001, 2004; Dinglasan et al., 2004; Dimitrov et al., 2004; Wang et al., 2005).

Long chain PFC surfactants including PFOS and PFOA are under increased scrutiny as global environmental pollutants due to recent reports of their global distribution, persistence, toxicity and

bioaccumulation potential (Houde et al., 2006; Lau et al., 2007). In response to these concerns, regulatory agencies in numerous industrialized countries have initiated studies to quantify the use of perfluorinated chemicals, assess their potential risks, and consider regulations restricting or banning their use. More environmentally sound chemicals are also being developed to replace long chain PFC surfactants. Perfluorobutane sulfonate (PFBS, C₄F₉SO₃⁻) has been commercialized recently as an alternative to PFOS in a variety of applications (3M, 2002). PFBS is a homologous compound of PFOS that has a four-carbon backbone. The shorter carbon chain makes PFBS less bioaccumulative compared to PFOS (Martin et al., 2003).

Ionic PFCs have been detected in municipal effluents, surface and ground water in various countries at concentrations ranging from below detection level to the ng l⁻¹ range (Alzaga and Bayone, 2004; Higgins et al., 2005; Sinclair and Kannan, 2006; Skutlarek et al., 2006; Loganathan et al., 2007). Elevated concentrations of PFCs have been detected near sites impacted by manufacturing plants or accidental emissions of PFCs (Moody et al., 2003; Anonymous, 2004). As an example, sum concentrations of PFCs as high as 43 348 ng l⁻¹ have been detected in a river of a highly industrialized area in Germany, with the major components being PFOA (33 900 ng l⁻¹) and PFOS (3160 ng l⁻¹) (Skutlarek et al., 2006).

* Corresponding author. Tel.: +1 520 626 2896; fax: +1 520 621 6048.

E-mail address: rsierra@email.arizona.edu (R. Sierra-Alvarez).

Considerably higher concentrations of PFCs can be found in effluents from chemical plants manufacturing fluorochemicals and from other industrial activities that utilize ionic PFCs. As an example, PFOS concentrations of 1650 mg l^{-1} have been reported in effluents generated from semiconductor manufacturing (Tang et al., 2006). The semiconductor manufacturing industry has secured a temporary exemption to utilize PFOS in wafer photolithography (Anonymous, 2002).

The application of conventional treatments for removing anionic PFC surfactants from aqueous streams containing elevated concentrations of these contaminants is restricted by technical and/or economical constraints. PFOS and PFOA are not amenable to biological treatment due to their outstanding stability against microbial attack. Similarly to its longer chain homologues, PFBS appears to be highly persistent in the environment (NICNAS, 2005). Literature data on the removal of PFOS and related compounds by physico-chemical treatment methods are limited. The strategies investigated include membrane processes (Tang et al., 2006), and decomposition by chemical approaches involving high-temperature conditions such as sonochemical treatment (Moriwaki et al., 2005) and reduction with zero-valent iron in subcritical water (Hori et al., 2006). These treatment technologies present some drawbacks and limitations, mainly due to their high energy demand and/or interference by other compounds present in the wastewater.

Adsorption of anionic PFC surfactants onto granular activated carbon (GAC) could offer a viable alternative for the removal from aqueous streams. Activated carbon adsorption is widely applied in the removal of organic contaminants in wastewaters due to the effectiveness, versatility, and relatively low-cost of this approach. Although published data on the removal of PFC surfactants are lacking, there is some evidence that non-fluorinated alkyl sulfonated compounds can be adsorbed onto activated carbon (Ihara, 1992; Zor, 2004).

The objective of this study is to evaluate the adsorption of PFOS from aqueous solutions onto various commercial grades of granular activated carbon. The adsorption of two related PFC surfactants, PFOA and PFBS, was also evaluated on the best performing activated carbon. The capacity of GAC to adsorb PFOS was compared to that of alternative sorbents, including several types of zeolites and wastewater treatment sludges. Adsorption isotherms were determined at constant ionic strength in a pH 7.2 phosphate buffer at 30 °C.

2. Materials and methods

2.1. Chemicals

Perfluorooctane sulfonic acid potassium salt, PFOS (98%), was purchased from SynQuest Laboratories (Alachua, FL). Perfluorobutane sulfonic acid potassium salt, PFBS (98.2%), was kindly provided by the 3M Company (St. Paul, MN). Perfluorooctanoic acid, PFOA (96%), and sodium fluoride (99%) were obtained from Sigma-Aldrich (St. Louis, MO). HPLC chemicals, sulfuric acid (95–98% ACS grade) was purchased from Sigma-Aldrich (St. Louis, MO), acetonitrile (99.8% HPLC grade) and boric acid (99.5% ACS grade) were obtained from Mallinckrodt Chemicals (Phillipsburg, NJ). All chemicals were used as received.

2.2. Sorbents

The sorbents evaluated included different grades of granular activated carbon (GAC), i.e., Filtrasorb 300, Filtrasorb 400, abbreviated as F300 and F400, respectively, and URV-MOD 1 (Calgon Carbon Corp., Pittsburg, PA), as well as several zeolites (microporous crystalline hydrated aluminosilicates) differing in their molar Si/Al ratio, i.e., zeolite 13X (Si/Al 2.8, Fluka product 96096, Sigma-

Aldrich, St. Louis, MO), zeolite NaY (Si/Al 5.5, product HS-320 from Wako Chemicals, Richmond, VA), and zeolite NaY80 (Si/Al 80, product CBV 780 from Zeolyst Int., Valley Forge, PA). The activated carbon utilized in the experiments was washed thoroughly with deionized water and dried at 70 °C to minimize interferences by soluble organic residues in the material.

Three types of wastewater treatment sludge were also evaluated for their effectiveness for PFOS biosorption. The sludges were obtained from different wastewater treatment plants and they included anaerobic granular sludge, return aerobic activated sludge (RAS) and anaerobically digested sewage sludge (ADS). The anaerobic granular sludge was obtained from an industrial anaerobic reactor treating wastewater from alcohol distillery wastewater (Nedalco, The Netherlands). The samples of RAS and ADS were obtained from the Ina Road municipal wastewater treatment plant in Tucson, AZ. The content of total suspended solids (TSS) in the granular anaerobic sludge, RAS and ADS was 7.45, 1.64 and 17.20%, respectively. The organic matter content of the sludges was estimated by determination of their content in volatile suspended solid (VSS). The VSS content in the anaerobic granular sludge, RAS and ADS was 6.98, 1.04 and 11.76%.

2.3. Adsorption of perfluorinated surfactants

Sorption isotherm experiments with activated carbon and zeolites were conducted in duplicate using Nalgene flasks (200–500 ml) supplemented with the sorbent (0.1 g) and a known volume of 3 mM phosphate buffer (pH 7.2) spiked with the target perfluoroalkyl compound. The solution volume was 100 ml and the final PFC concentrations were 15, 25, 50, 75, 100, 125 and 150 mg l^{-1} . Samples of activated carbon were also contacted with 200, 300 and 400 ml of 3 mM phosphate buffer spiked with $150 \text{ mg PFC l}^{-1}$ in order to test the feasibility of obtaining increasing loadings of PFC on the sorbent. Additional sorption experiments were conducted to evaluate the partitioning of PFOS in more diluted solutions onto activated carbon. In the latter experiments, the initial adsorbate concentrations were 0.05, 0.125, 0.25, 0.35 and 0.5 mg l^{-1} , and the solution volume was 130 ml.

Sorption isotherm experiments with wastewater treatment sludges ($0.12\text{--}1.76 \text{ g VSS l}^{-1}$) were performed in duplicate using Nalgene flasks (200 ml) supplied with 100 ml of a 3 mM phosphate buffer (pH 7.2) spiked with known concentrations of PFOS (e.g. 15, 25, 50, 75, 100 and 150 mg l^{-1}). Sludges were also contacted with 150 ml of an aqueous solution spiked with $150 \text{ mg PFOS l}^{-1}$ to obtain increasing loadings of the adsorbate on the sorbent.

Control flasks lacking sorbent were run in parallel to correct for possible removal of PFCs by other mechanisms than adsorption. Flasks were shaken in an orbital shaker (Innova 4300, New Brunswick Scientific, Edison, NJ) at 150 rpm for 2 d at 30 °C. Removal of PFCs from solution was determined using a total organic carbon (TOC) analyzer and/or HPLC with suppressed conductivity detection following centrifugation and filtration ($0.45 \mu\text{m}$) of the samples to remove insoluble matter. All liquid samples were analyzed by HPLC with the exception of samples from adsorption experiments with the activated carbons Filtrasorb 300 and URV-MOD 1 which were analyzed using the TOC analyzer. Liquid samples containing less than $0.5 \text{ mg PFOS l}^{-1}$ were concentrated by solid phase separation prior to analysis.

2.4. Solid phase extraction

Solid phase extraction (SPE) was conducted to concentrate liquid samples containing less than $0.5 \text{ mg PFOS l}^{-1}$. Solid phase extraction (SPE) cartridges (3 ml, 500 mg ODS-C18, Agilent Technologies, New Castle, DE) were mounted in a vacuum manifold and conditioned with methanol (6 ml) and then deionized water

(6 ml). Subsequently, the sample (125 ml) was loaded at a rate of 1–2 ml min⁻¹. SPE cartridges were rinsed with deionized water (6 ml) and then centrifuged at 4000 rpm for 25 min. Analytes were eluted with methanol (4 ml) and collected in Nalgene flasks. Phosphate buffer blanks spiked with known PFOS concentrations were extracted in parallel to determine recovery efficiencies (106 ± 18% for triplicate samples).

2.5. Analytical methods

HPLC analysis of PFCs in aqueous samples was conducted using a chromatographic system fitted with a suppressed conductivity detector (Dionex ICS-3000, Sunnyvale, CA, USA). An Acclaim Polar Advantage II C18-guard column (4.3 mm i.d., 1 cm length) and an Acclaim Polar Advantage II C18-column (4.6 mm i.d., 25 cm length), both from Dionex, were used for chromatographic separation and they were maintained at 35 °C in a thermostated column compartment. A mixture of 20 mM boric acid (pH 8.0) and 95% acetonitrile was used as the mobile phase at a flow rate of 1 ml min⁻¹. The ratio of boric acid to acetonitrile varied with linear gradient program was 0 min from 75:15 (v/v) to 45:55 (v/v) at 13.2 min. The volume of sample injected on the column was 100 µl. Blanks were continuously run to assure that the column was clean and traces of the analyte were not carried over between samples. The total concentration of PFCs in liquid samples was obtained by linear calibration curves ($r^2 > 0.99$) using known concentrations of the respective compounds in methanol or 3 mM phosphate buffer (pH 7.2), depending on the experiment, ranging from 0.5 to 25 mg l⁻¹. The detection limit of PFOS, PFBS and PFOA was 0.5 mg l⁻¹.

Dissolved organic carbon analyses were performed using a total organic carbon analyzer (Shimadzu TOC-V CSH/CSN system, Columbia, MD). All liquid samples, including blanks and standards, were acidified with HCl to pH 2.20–2.50 prior to analysis. Instrument calibration was performed using potassium hydrogen phthalate standards ranging from 0.40 to 25 mg TOC l⁻¹. The coefficient of determination (r^2) for each calibration was >0.99. Calibration lines obtained using potassium hydrogen phthalate and PFCs standards were nearly identical confirming the suitability of TOC measurements for PFC quantification.

3. Results and discussion

3.1. PFOS adsorption onto activated carbon

The adsorption of PFOS from aqueous solutions onto three different types of granular activated carbon, Calgon F300, Calgon F400 and Calgon URV-MOD 1, was evaluated. These activated carbons are widely used for the treatment of surface and ground water sources for the production of drinking water. The physical properties of the various GAC tested are described in Table 1. The adsorption isotherms obtained for the removal of PFOS by the three GAC types are depicted in Fig. 1A.

Table 1
Physical properties of GAC Calgon F300, Calgon F400 and Calgon URV-MOD 1

Property	F300	F400	URV-MOD 1
Total pore volume, ml/g	0.709*	0.767*	0.643
Micropore, ml/g	0.378–0.408*	0.312–0.391*	0.386
Mesopore, ml/g	0.063–0.378*	0.071–0.172*	n/a
Micropore average diameter, nm	0.841*	0.817*	n/a
Porosity	0.608*	0.627*	0.592
Particle diameter, mm	0.85–1.70	0.85–1.70	n/a
Iodine number, mg/g (min)	900	1000	1250
Effective size, mm	0.8–1.0	0.55–0.75	1.0–1.18

Sources: Calgon F300 and F400 (Calgon Carbon Corporation and * Gauden et al. (2006); Calgon URV-MOD 1 (Huling et al., 2005).

The adsorptive capacity of the various activated carbons over a range of different concentrations was determined by fitting the experimental data to Langmuir and Freundlich models. The Langmuir isotherm is defined by

$$C_s = \frac{a \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (1)$$

where C_s is the concentration of the solute in the solid phase (mg PFC g⁻¹ sorbent), C_e is the equilibrium concentration of the solute in solution (mg PFC l⁻¹), a and b are Langmuir adsorption constants; a represents the maximum achievable surface concentration of the solute, and b is the equilibrium constant for the sorption reaction. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It also assumes that once a sorbate molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption occurs.

The Freundlich equation is an empirical relationship describing the sorption of solutes from a liquid to a solid surface. The equation is widely used and has been found to describe adequately the adsorption process for many compounds in dilute solution. The Freundlich equation is defined by

$$C_s = K_F \cdot C_e^n \quad (2)$$

where K_F [(mg PFC g⁻¹ sorbent)(mg PFC l⁻¹)⁻ⁿ] is the Freundlich adsorption constant or capacity factor and n is the Freundlich exponent which provides a measure for the sorption intensity. For $n = 1$ the partition between the two phases is independent of the concentration and the isotherm becomes linear. The K_F value represents the carbon loading in mg compound per gram of carbon at an aqueous equilibrium concentration of 1.0 mg l⁻¹ of the compound.

The constants determined for the different Freundlich and Langmuir isotherms are listed in Table 2. The experimental data obtained at intermediate to high equilibrium concentrations of PFOS ($C_e > 0.5$ mg l⁻¹) fitted well to both isotherm models and showed a tendency to attain a maximum adsorption capacity (plateau) as the concentration of PFOS in solution increased. In contrast, adsorption data determined with F400 at low equilibrium concentrations of PFOS (12.4–290.0 µg l⁻¹) fitted best to a linear Freundlich model ($n \approx 1$). Linear isotherms are often determined for dissolved species in dilute solutions that are present at concentrations significantly lower than their aqueous solubility.

The isotherms obtained show a strong adsorption of PFOS at low aqueous equilibrium concentrations (<2 mg l⁻¹) followed by a low to moderate adsorption at higher PFOS concentrations, and they indicate that the affinity of GAC for PFOS is moderate when compared to chemical compounds traditionally considered as suitable for activated carbon treatment. For instance, the K_F determined for the adsorption of PFOS by F300 was 38.5, which is in the same order of magnitude as the Freundlich distribution coefficients reported with the same activated carbon for phenol (21 mg g⁻¹), trichloroethylene (28 mg g⁻¹) and 2-chlorophenol (51 mg g⁻¹) (Dobbs and Cohen, 1980). These K_F values are one-order magnitude lower compared to those determined for highly hydrophobic compounds known to have a high affinity for GAC such as lindane (256 mg g⁻¹) or hexachlorobenzene (450 mg g⁻¹) (Dobbs and Cohen, 1980).

F400 was the most effective activated carbon as evidenced by the stronger adsorption of PFOS observed at all the concentrations tested (Fig. 1A). Nonetheless, at high aqueous concentrations the adsorption capacity of the three sorbents was relatively close. The superior performance of F400 at low equilibrium concentrations cannot be attributed to the variation in specific surface areas or pore size of the materials, since all three GAC have similar characteristics (Table 1). The stronger adsorption of PFOS might be

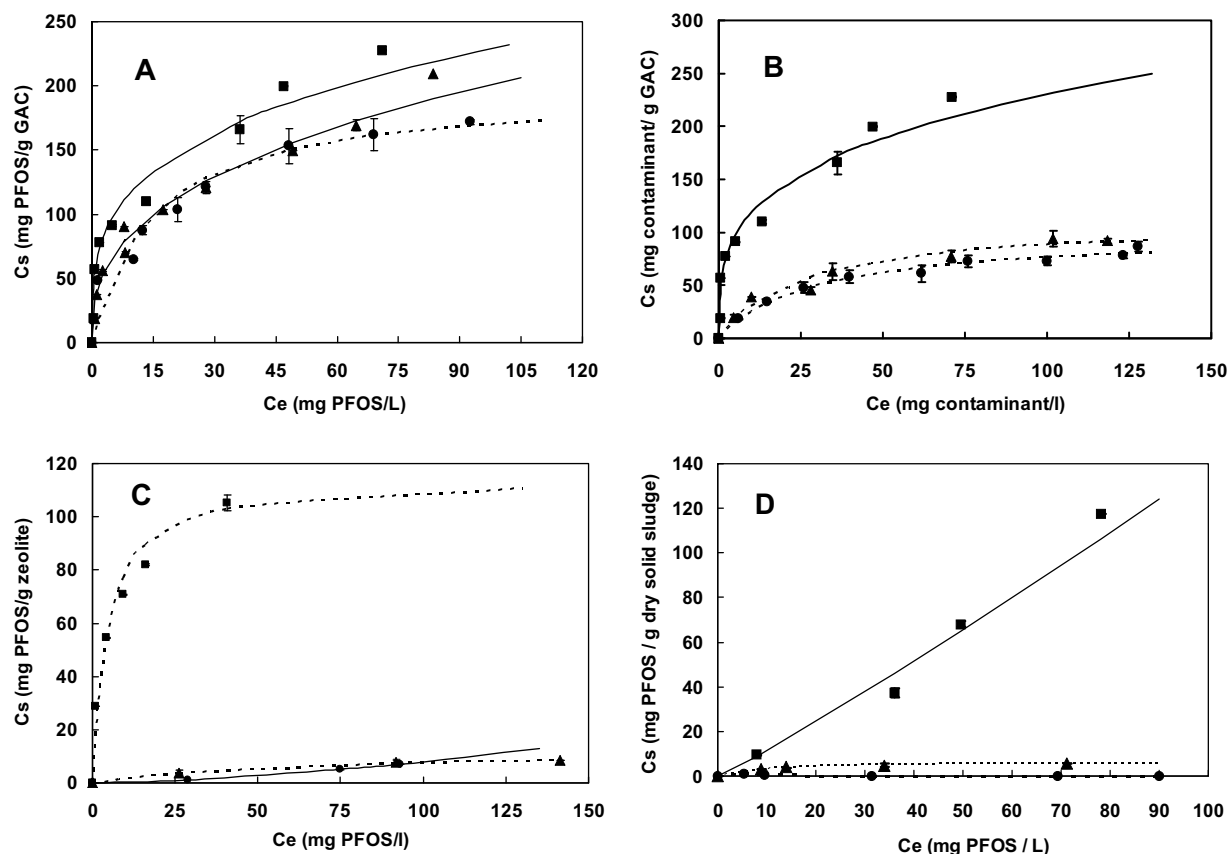


Fig. 1. (A) Adsorption isotherms of PFOS onto granular activated carbon at intermediate-high equilibrium concentrations. Legend: Calgon F400 (■), Calgon F300 (●), and Calgon URV-MOD 1 (▲). (B) Adsorption isotherms of PFOS (■), PFOA (▲), and PFBS (●) onto activated carbon Calgon F400. (C) Adsorption isotherms of PFOS onto various zeolite types: NaY80 (Si/Al 80) (■), NaY (Si/Al 5.5) (●), and 13X (Si/Al 2.8). (D) Adsorption isotherms of PFOS onto different wastewater treatment sludges: anaerobic granular sludge (■), anaerobic digested sludge or ADS (▲), aerobic activated sludge or RAS (●). Experimental data fit to Langmuir model (dashed line); experimental data fit to Freundlich model (solid line). Error bars (shown if larger than the symbols) represent standard deviations of duplicate assays.

Table 2

Langmuir isotherm constants a (mg PFAS/g sorbent) and b (l/mg PFAS) and Freundlich isotherm constants K_F [(mg PFOS/g sorbent)(mg PFAS/l) $^{-n}$] and n for the adsorption of PFAS onto various sorbent materials at 30 °C and solution pH 7.2

Contaminant	Sorbent	Langmuir isotherm			Freundlich isotherm		
		a	b	r^2	K_F	n	r^2
PFOS	GAC Calgon F300	196.2	0.068	0.977	38.5	0.332	0.939
PFOS	GAC Calgon URV-MOD1	211.6	0.080	0.947	36.7	0.371	0.979
PFOS	GAC Calgon F400	236.4	0.124	0.959	60.9	0.289	0.969
PFOS	GAC Calgon F400-low range	−0.245	−29.71	0.854	25.9	1.123	0.979
PFOA	GAC Calgon F400	112.1	0.038	0.968	11.8	0.443	0.955
PFBS	GAC Calgon F400	98.70	0.034	0.985	9.3	0.463	0.959
PFOS	NaY zeolite	–	–	–	0.01	1.577	1.000
PFOS	13X zeolite	12.0	0.018	0.993	0.73	0.507	0.976
PFOS	NaY80 zeolite	114.7	0.218	0.991	31.8	0.339	0.988
PFOS	Anaerobic granular sludge*	–	–	–	0.95	1.083	0.983
PFOS	ADS	6.137	0.115	1.000	1.85	0.262	0.957

* The sludge concentrations were expressed as gram dry solids (total suspended solids, TSS).

accounted for by differences in the chemical composition of the surface layer of F400. Surface chemistry is known to have a great impact on the sorption behavior of activated carbon (Haghsereht et al., 2002; Dąbrowski et al., 2005).

3.2. PFOA and PFBS adsorption onto activated carbon

Sorption of PFOS by activated carbon F400 was compared to PFOA and PFBS, which are two other perfluoroalkyl surfactants of environmental concern. For the three surfactants, adsorption

tended to reach a plateau as their aqueous equilibrium concentration exceeded about 40–50 mg l $^{-1}$, suggesting saturation of the available adsorption sites (Fig. 1B). Both Langmuir and Freundlich isotherms provide a good fit for the sorption of PFOA and PFBS onto F400 (Table 2).

PFOA and PFBS were effectively sorbed by GAC, although to a lower extent than PFOS. For instance, for an equilibrium concentration of the surfactant in the aqueous phase of 27 mg l $^{-1}$, the estimated concentrations of PFOA and PFBS sorbed onto activated carbon are 57 mg g $^{-1}$ GAC and 48 mg g $^{-1}$ GAC, respectively,

compared to 182 mg PFOS g⁻¹ GAC. These results are in agreement with a recent study reporting stronger sorption onto sediments for sulfonates as compared to carboxylates of equal perfluorocarbon chain length (Higgins and Luthy, 2006), observation which was attributed to the larger size of the sulfonate substituent (Higgins and Luthy, 2007). Adsorption of perfluoroalkyl sulfonates onto sediments has also been reported to increase with increasing chain length, with distribution coefficient (K_d) values increasing in a regular fashion for each additional CF₂ moiety (Higgins and Luthy, 2006).

3.3. Adsorption of PFOS onto faujasite zeolites

Zeolites are an important class of aluminosilicates widely used in catalysis as well as in the separation and purification fields due to their uniform, small pore size, high internal surface area and controlled chemistry (Bailey et al., 1999; Tao et al., 2006). Three faujasite zeolites with different Si/Al ratios, zeolite 13X (Si/Al = 2.8), NaY (Si/Al = 5.5) and NaY80 (Si/Al = 80), were evaluated for their ability to adsorb PFOS. The physical properties of the zeolites are summarized in Table 3. PFOS was found to adsorb strongly to the NaY80 (Si/Al 80) zeolite, but poorly to the 13X (Si/Al 2.8) and NaY (Si/Al 5.5) zeolites (Fig. 1C). As an example, the K_F value determined for NaY80 was 31.8, compared to only 0.73 and 0.01 for 13X and NaY, respectively (Table 2). It is interesting to note that the capacity of zeolite NaY80 to adsorb PFOS from aqueous solutions was of the same order of magnitude as that of the GACs evaluated in this study which had K_F values ranging from 36.7 to 60.9.

The aluminum content of the zeolites evaluated seems to control the adsorption process, as evidenced by the increase in adsorption capacity with increasing molar Si/Al ratio. Similar trends were observed in sorption studies of sodium dodecylbenzene sulfonate with zeolites of varying Si contents (Kawai and Tsutsumi, 1995). No adsorption of the alkylbenzene sulfonate surfactant occurred on low siliceous NaY zeolites, while sorption was enhanced on the high siliceous NaY zeolites. Hydrophobic interactions appear to play an important role on the adsorption of PFOS since the most hydrophobic zeolite, NaY80, showed the highest adsorption capacity. It is well established that the silica content is the main parameter determining the hydrophobic properties of zeolites. High-silica zeolites such as NaY80 have hydrophobic surface properties, while low-silica zeolites such as NaY and 13X preferentially adsorb polar molecules. Although PFOS is a strong acid (estimated pK_a -3.27) (Brooke et al., 2004) which is completely dissociated under environmental conditions, the compound has a dual hydrophobic-hydrophilic nature.

The entrance to the micropores of the zeolites 13X and NaY is 1.0 and 0.8 nm in diameter, respectively, while the zeolite NaY80 is 0.6 nm in diameter. The smaller pore aperture of the zeolite showing the best sorptive capacity, NaY80, suggests that the poor sorptive capacity of the two other zeolites was not due to molecular exclusion.

3.4. Adsorption of PFOS onto wastewater treatment sludge

Biosorption has been proposed as an alternative to replace current removal processes of hazardous contaminants from wastewater.

Table 3
Physical properties of the faujasite zeolites evaluated in this study

Zeolite	Pore apertures (nm)	SiO ₂ /Al ₂ O ₃ (mol ratio)	Unit cell (Å)	Surface area (m ² /g)
13X	1.0	2.8	4.0	n/a
NaY	0.8	5.5	24.6	700
NaY80	0.6	80	24.2	780

Sources: Zeolite 13X (Sigma-Aldrich), NaY (Wako Chemicals) and NaY80 (Zeolyst International).

ters (Aksu, 2005). The potential of wastewater treatment sludge as an adsorbent has received attention due to its ability to adsorb hydrophobic organic compounds and low-cost as compared to conventional adsorbents. PFOS and related perfluoroalkyl surfactants have been detected in sewage sludge from several wastewater treatment plants at ng g⁻¹ concentrations, suggesting partitioning of these compounds from the aqueous phase to the biosolids during the treatment process (Boulanger et al., 2005; Higgins et al., 2005; Nakata et al., 2006; Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007).

Fig. 1D shows the isotherms for the adsorption of PFOS by two sludge samples obtained from different wastewater treatment plants, i.e., anaerobic granular sludge and anaerobically digested sewage sludge (ADS). The isotherm for return aerobic activated sludge (RAS) is not shown since PFOS adsorption was negligible even at high aqueous equilibrium concentrations (up to 90 mg l⁻¹). The results obtained for ADS show that adsorption appears to reach saturation as the equilibrium concentration of PFOS in solution approaches 14 mg l⁻¹, suggesting monolayer coverage of active sites. In contrast, the anaerobic granular sludge data fit a linear Freundlich isotherm ($n = 1.083$) spanning over the whole range of equilibrium concentrations evaluated (up to 80.9 mg PFOS l⁻¹) (Table 2). Kennedy et al. (1992) studied the sorption of chlorophenols by anaerobic granular sludge and observed linear isotherms for the majority of chlorophenols. This linear adsorption behavior was attributed to the highly porous structure of granular anaerobic sludge which would allow penetration of the adsorbate to sorption sites in the inner surface.

The K_d values determined in this study for ADS ranged from 77 to 277 l kg⁻¹ dry-sludge, and for anaerobic granular sludge from 143 to 209 l kg⁻¹ dry-sludge. A K_d of 120 l kg⁻¹ was previously reported for the adsorption of PFOS onto municipal sewage treatment sludge (Ellefson, 2001). However, the K_d values determined for the adsorption of PFOS onto biosolids are several orders of magnitude lower compared to those of bioaccumulative organic pollutants such as polychlorinated biphenyls and organochlorine pesticides (Katsoyiannis and Samara, 2005), indicating that the perfluoroalkyl surfactant has a lower tendency to partition onto the sludge.

The results obtained clearly demonstrate that the type of the sludge strongly influences the degree of PFOS sorption and suggest that characteristics other than organic matter content must contribute to controlling sorption of PFOS onto wastewater treatment sludge. Indeed, given the dual oleophobic-hydrophobic nature of PFOS, it is unlikely that the adsorption mechanism obeys simple hydrophobic partitioning paradigms. Higgins and coworkers confirmed the importance of hydrophobic interactions on the adsorption of PFOS by sediments, but these authors also demonstrated that electrostatic interactions play a role in the adsorption of anionic PFC surfactants (Higgins and Luthy, 2006, 2007).

4. Conclusions

The adsorption of PFOS, PFOA and PFBS from aqueous solutions onto granular activated carbon was demonstrated in this study. The substitution of the sulfonic group by a carboxylic group as well as a decreasing fluorocarbon chain contributed to a weaker adsorption of the PFCs by activated carbon, as evidenced by the stronger adsorption of PFOS compared to PFOA and PFBS. Activated carbon provided a high adsorptive capacity for PFC surfactants when these compounds were present at low mg l⁻¹ concentrations; however, the adsorptive capacity was only moderate at higher PFC concentrations. Hydrophobic zeolites with a high-silica content (e.g. zeolite NaY80, Si/Al = 80) were also found to adsorb PFOS, while low-silica zeolites (Si/Al < 5.5) showed very poor sorption capacity. Furthermore, biosorption of PFOS by various wastewater treatment

sludges was demonstrated. Comparison of the sorption capacity of GAC with that of various zeolites and wastewater treatment sludges demonstrated that the affinity of the various sorbents for PFOS decreased as follows: GAC > hydrophobic zeolite > anaerobic granular sludge > activated sludge. Taken together these results indicate that GAC sorption is a promising treatment for the removal of anionic perfluoroalkyl surfactants from dilute aqueous streams. These findings also suggest that some removal of PFOS by biosorption should be expected during biological wastewater treatment, and that extent of partitioning will depend on the characteristics of the sludge.

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