Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Carter, Kimberly E. and Farrell, James(2010) 'Removal of Perfluorooctane and Perfluorobutane Sulfonate from Water via Carbon Adsorption and Ion Exchange', Separation Science and Technology, 45: 6, 762 — 767
To link to this Article: DOI: 10.1080/01496391003608421
URL: http://dx.doi.org/10.1080/01496391003608421

Separation Science and Technology, 45: 762–767, 2010
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496391003608421

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Removal of Perfluorooctane and Perfluorobutane Sulfonate from Water via Carbon Adsorption and Ion Exchange

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This research investigated the removal of perfluorooctane sulfonate (PFOS) and perfluorobutane sulfonate (PFBS) from water by Filtrasorb®400 granular activated carbon (GAC) and Amberlite®IRA-458 ion exchange resin. Kinetic experiments showed that the time required for the uptake equilibrium was ~50 hours for the GAC and ~10 hours for the resin. Sorption isotherms showed that PFOS and PFBS uptake was endothermic and was promoted by hydrophobic effects on the GAC, and by a combination of hydrophobic adsorption and ion exchange on the resin. The aqueous solubility of PFOS was highly dependent on the ionic composition of the solution. PFOS and PFBS uptake by the resin was hysteretic and nearly irreversible using conventional regeneration methods.

Keywords adsorbents; granular activated carbon; perfluorobutane sulfonate; perfluorooctane sulfonate; PFAS; PFBS; PFOS; surfactants

INTRODUCTION

Perfluoroalkyl sulfonates are widely used in a variety of industries and are also contained in consumer products. The semiconductor industry uses these compounds in electroplating, electronic etching baths, as a photographic emulsifier, and as a photoacid generator (1). Industrial and consumer products containing perfluoroalkyl sulfonates include: paper protectors, refrigerants, pharmaceuticals, lubricants, adhesives, cosmetics, Teflon® coatings, firefighting foams, and insecticides (2). The widespread use of these compounds has resulted in their accumulation in the environment. For example, perfluorooctane sulfonate (PFOS) has been reported in water, biota samples, human blood and liver samples, and wildlife worldwide (3–6).

Due to their ubiquitous occurrence in the environment and the unknown health effects that PFOS and other perfluorinated compounds may cause, the U.S. Environmental Protection Agency (EPA) banned PFOS from the U.S. market in 2000 (7). However, in 2002 the U.S. EPA proposed a significant new use rule (SNUR) for PFOS and its salts that gave the semiconductor industry a waiver allowing their continued use. This waiver came with a stipulation that the semiconductor industry find alternatives to PFOS with lower potentials for bioaccumulation, such as perfluorobutane sulfonate (PFBS), or a practical a way of disposing of or destroying these compounds.

Recent studies have shown that PFOS, and one of its proposed replacements in the semiconductor industry, PFBS, can be rapidly removed from water via electrochemical oxidation (8,9). This process could be used by the semiconductor industry to remove PFOS and PFBS from dilute rinse waters that are normally discharged into sanitary sewer systems (7). However, to make the process cost effective, it is necessary to concentrate the compounds from low ionic strength aqueous solutions with concentrations ranging from saturation down to non-detectable levels.

The goal of this research was to determine the feasibility of using adsorption or ion exchange to concentrate PFOS and PFBS from solutions with compositions similar to those generated during semiconductor manufacturing. The aim was to identify an adsorbent that could be thermally regenerated on site or an ion exchange resin that could be regenerated using NaOH or NaCl solutions. Towards this end, adsorption kinetics and equilibrium isotherms were measured for PFOS and PFBS uptake by GAC and a strong-base ion exchange resin from ultrapure water and dilute electrolyte solutions.

MATERIALS AND METHODS

The Filtrasorb®400 GAC was obtained from Calgon Corporation (Pittsburgh, PA) and was used as received. Amberlite®IRA-458 strong base anion exchange resin was obtained in the chloride form from Rohm and Haas (Philadelphia, PA) and was used as received. The resin is a cross-linked acrylic gel with quaternary ammonium ion functional groups. These two commercially available media were selected for study because previous investigations have shown that they were capable of removing PFOS from dilute aqueous solutions (7,10).

PFOS was obtained as heptadecafluorooctane sulfonic acid (Aldrich) and its potassium salt (Fluka). PFBS was obtained as nonafluorobutane-1-sulfonic acid and its

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Received 17 July 2009; accepted 4 January 2010.

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potassium salt from Aldrich. PFOS and PFBS solutions were prepared in 6-liter glass flasks using either ultrapure water (18 MΩ cm) alone or ultrapure water with a 10 mM $NaClO_4$ background electrolyte solution. All solutions were stirred for at least 12 hours before use. Initial solution pH values ranged from 4.4 ± 0.1 to 5.8 ± 0.1, depending on the amount of PFOS or PFBS added to the solution. Given that the pKa of PFOS is −3.2711, PFOS should be fully ionized under these experimental conditions. Although no data is available on the pKa of PFBS, its similar structure to PFOS suggests that will also be fully ionized under these experimental conditions.

Rates of PFOS and PFBS uptake by GAC and the resin were measured in 6-liter flasks with initial PFOS and PFBS concentrations of 0.35 mM and 0.55 mM, respectively. The experiments commenced by adding 10 grams of one of the media to a flask containing either PFOS or PFBS. The flasks were stirred continuously at 200 rpm and sampled over time to determine solution phase concentrations of PFOS or PFBS.

Adsorption isotherms for uptake of PFOS and PFBS from ultrapure water were measured by adding 100 mL of solution with concentrations of 25 or 250 mg/L to 250 mL amber glass vials containing 0.15 to 1.5 grams of one of the media. The jars were periodically shaken and allowed to equilibrate at temperatures of 22, 38, 48, and 58°C for 48 hours. After 48 hours 25 mL samples were taken and tested for PFOS or PFBS concentrations.

Because ionic strength differences between different vials may have impacted PFOS and PFBS uptake by the resin, adsorption isotherms were also measured for this media in 10 mM $NaClO_4$ solutions. In these experiments, 10 g of the resin were added to 6 liters of solution. The solutions were continuously stirred at 200 rpm at constant temperatures of 3, 22, and 35°C. The solutions were then spiked with 200 mg of either PFOS or PFBS. Aqueous samples were taken after 48 hours and the solutions were then spiked again with another 200 mg of either PFOS or PFBS. The sampling and spiking procedure was repeated up to 10 times in order to generate the isotherms. This procedure resulted in monotonically increasing ionic strength with increasing PFOS or PFBS concentrations.

Regeneration experiments for the resin were performed using different concentrations of NaCl or NaOH solutions at temperatures of 7, 22, or 50°C. Resin loaded with PFOS or PFBS was packed in 1 cm-diameter by 10 cm-long glass columns (VWR, West Chester, PA). One liter of regenerant solution was then circulated for 12 hours at 20 mL/min through each column using a peristaltic pump. Solutions were then sampled for PFOS or PFBS concentrations.

Two methods were used to determine aqueous phase concentrations of PFOS and PFBS. Concentrations greater than 1 mg/L were determined using a Dionex (Sunnyvale, CA) ICS-3000 ion chromatograph (IC) equipped with a conductivity detector. Mixtures of 20 mM boric acid and 95% acetonitrile in water were used as the mobile phase. Concentrations below 1 mg/L were determined using a Shimadzu model VSH TOC analyzer (Columbia, MD), which had a detection limit of 1 μg/L, as carbon. The TOC method was verified by comparing it to the IC method for concentrations above 1 mg/L.

RESULTS AND DISCUSSION

Figure 1 shows the concentrations of PFOS and PFBS as a function of time in continuously stirred 6-liter flasks. Assuming the uptake at 48 hours elapsed represents the equilibrium uptake, both PFOS and PFBS reach >95% of their equilibrium uptake by the resin after 4 hours elapsed. For uptake by the GAC ~15 hours were required to reach >95% of the equilibrium uptake. The faster uptake kinetics by the resin suggests that it may take less time to regenerate than the GAC.

Isotherms for PFOS and PFBS on the GAC in ultrapure water are shown in Figs. 2a and b. The final solution pH values were within ±0.1 pH units of the initial values. All the isotherms are highly non-linear and do not readily conform to standard isotherm models (12). The isotherms in Fig. 2 for both compounds are very steep at low concentrations, indicating that there are a limited number of adsorption sites with very favorable adsorption energies. For PFOS uptake, the isotherms show a decrease in slope at adsorbed phase concentrations of ~65 mg/g. This suggests that there may be two types of PFOS adsorption sites. Based on the molecular structure and the van der Waals diameters of the atoms (13,14), the PFOS molecule is approximately 1.4 nm long by 0.4 nm wide, and therefore should require $0.56\,nm^2$ of surface area per PFOS

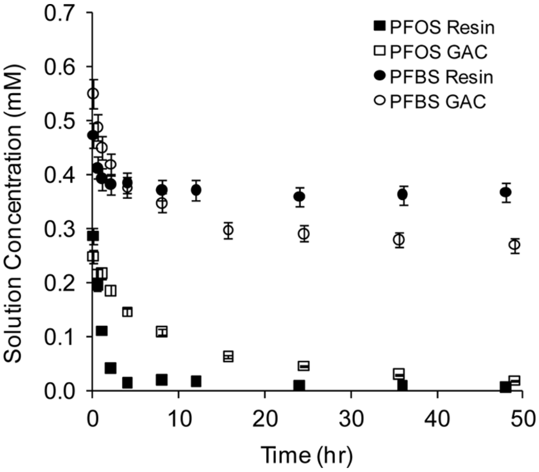
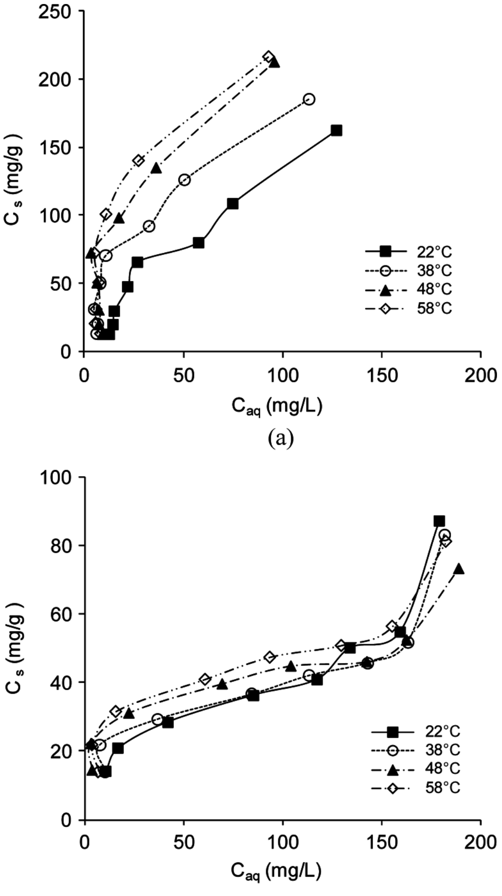


FIG. 1. PFOS and PFBS concentrations versus elapsed time after addition of 10 grams of GAC or resin to well-stirred 6 liter flasks at 22°C. Error bars represent the 95% confidence intervals of concentration measurements.



(a)

(b)

FIG. 2. Adsorbed concentration (C_s) versus aqueous concentration (C_{aq}) for: (a) PFOS and (b) PFBS on GAC from ultrapure water.

adsorbed. Based on this surface area per molecule, a loading of 65 mg-PFOS per gram of adsorbent requires only 0.44 m^2. This is less than three orders of magnitude smaller than the surface area of the carbon (15). Therefore, only a small fraction of the GAC surface area is associated with this highly favorable adsorption. Alternatively, the highly favorable adsorption could be associated with the small anion exchange capacity of the carbon.

Figure 2b shows that there are two changes in slope for the PFBS isotherms. The decrease in slope at an adsorbed phase concentration of 20 mg/g is similar to that observed for PFOS at a concentration of 65 mg/g. The increase in slope at an adsorbed phase concentration of ~50 mg/g is suggestive of multilayer adsorption or a pore condensation phenomenon (12). For all aqueous concentrations, there was greater uptake of PFOS as compared to PFBS, both on a molar and weight basis. This is consistent with previous studies showing that surfactants with longer alkyl chain lengths adsorb to GAC at higher loadings than their shorter counterparts (16).

Isosteric heats of adsorption (Q_{iso}) were calculated from the data in Figs. 2a and b using:

$$Q_{iso} = R\left[\frac{d(\ln C_{aq})}{d\left(\frac{1}{T}\right)}\right]_{loading} \tag{1}$$

where C_{aq} is the aqueous concentration for fixed adsorbed phase loading, R is the universal gas constant, and T is the temperature (K). For PFOS, Q_{iso} values ranged from 25 to 32 kJ/mol for adsorbed phase loadings between 25 and 150 mg/g. The endothermic heat of adsorption can likely be attributed to the increase in enthalpy associated with taking a charged species and its ion pair from water and placing it in the hydrophobic environment of the carbon micropore. For PFBS, the Q_{iso} decreased monotonically from 41 to 5 kJ/mol for adsorbed phase loadings ranging from 20 to 50 mg/g. The mechanism responsible for this trend is unknown. For adsorbed phase concentrations above 50 mg/g, there was no apparent trend in the effect of temperature on adsorption. This observation also supports that there was a different adsorption mechanism for PFBS loadings greater than 50 mg/g.

The positive Q_{iso} values indicate that PFOS and PFBS adsorption by the carbon was promoted by entropic effects. At constant temperature and pressure, the Gibbs energy of the system will be a minimum at equilibrium. Thus, for adsorption to proceed, the Gibbs energy change for the adsorption process must be negative. Given that $\Delta G = \Delta H - T\Delta S$, the positive enthalpies of adsorption (ΔH) must therefore be accompanied by increases in entropy (ΔS). This increase in entropy can be attributed to removing the hydrophobic portions of PFOS and PFBS from the solution (17). When solvated, the hydrophobic portions of surfactants require the solvating water molecules to lose rotational degrees of freedom in order to both maintain their hydrogen bonding with other water molecules and form a solvation cavity around the solute (18). Therefore, solvation of hydrophobic moieties decreases the rotational entropy of the solvating water molecules.

Isotherms for PFOS and PFBS on the resin in ultrapure water are shown in Figs. 4a and b. The final solution pH values were within ±0.1 pH units of the initial values. The unusual shape of these isotherms can be attributed to hysteresis effects resulting from the combination of irreversible adsorption (vide infra) and exposing the resin to different initial adsorbate concentrations. Differences in ionic strength associated with initial adsorbate concentrations of 25 and 250 mg/L may have also impacted the isotherm shape, since the solubility of PFOS and PFBS are highly dependent on the solution ionic strength (vide infra). The effect of possible micelle formation in some of the solutions was investigated using a fluorescence method (19). However, the presence of micelles was not observed

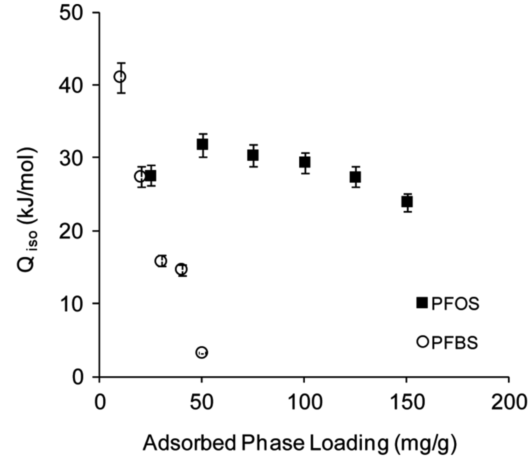


FIG. 3. Isosteric heats of adsorption (Q_{iso}) on GAC from ultrapure water as a function of the adsorbed phase loading based on the data in Fig. 2. Error bars represent 95% confidence intervals for the regression slopes based on Eq. 1.

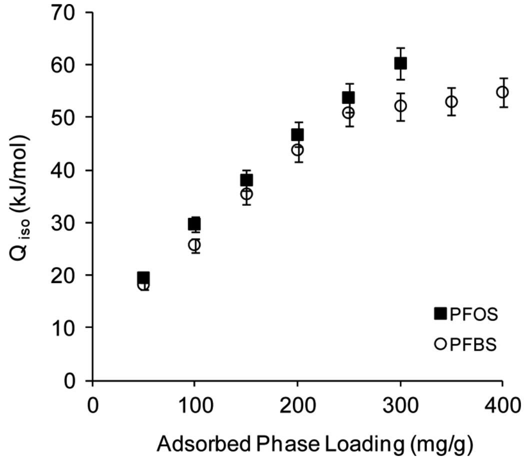
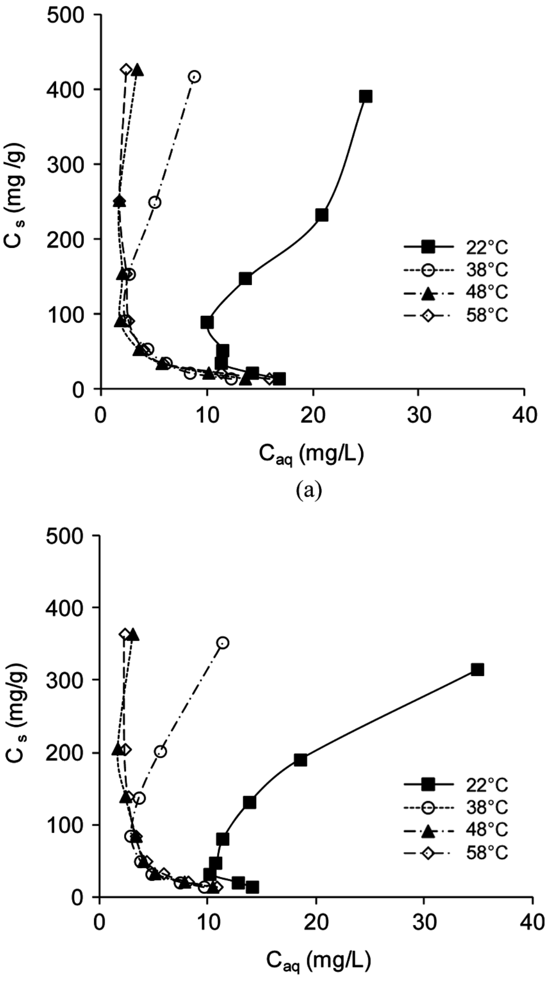


FIG. 5. Isosteric heats of adsorption (Q_{iso}) on the resin from ultrapure pure water as a function of the adsorbed phase loading based on the data in Fig. 4. Error bars represent 95% confidence intervals for the regression slopes based on Eq. 1.

for PFOS concentrations as high as 1.8 g/L or for PFBS concentrations as high as 2.5 g/L.

The isosteric heats of adsorption for the isotherms in Fig. 4 are shown in Fig. 5. The increasing Q_{iso} values with increasing loading may be impacted by the increasing ionic strength of the solutions with increasing initial concentration. However, similar to the heats of adsorption for the activated carbon, the heats of adsorption for both PFOS and PFBS were endothermic. This indicates that hydrophobic adsorption in addition to ion exchange may also be promoting uptake by the resin, since hydrophobic effects increase with increasing ionic strength due to the salting out effect (18).



(a)

(b)

FIG. 4. Adsorbed concentration (C_s) versus aqueous concentration (C_{aq}) for: (a) PFOS and (b) PFBS on the resin from ultrapure water.

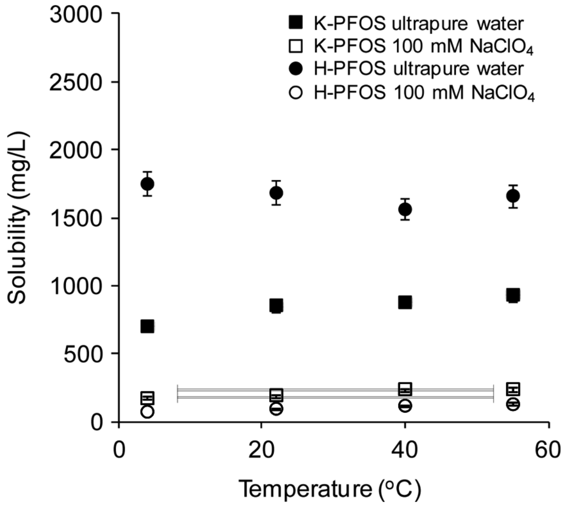
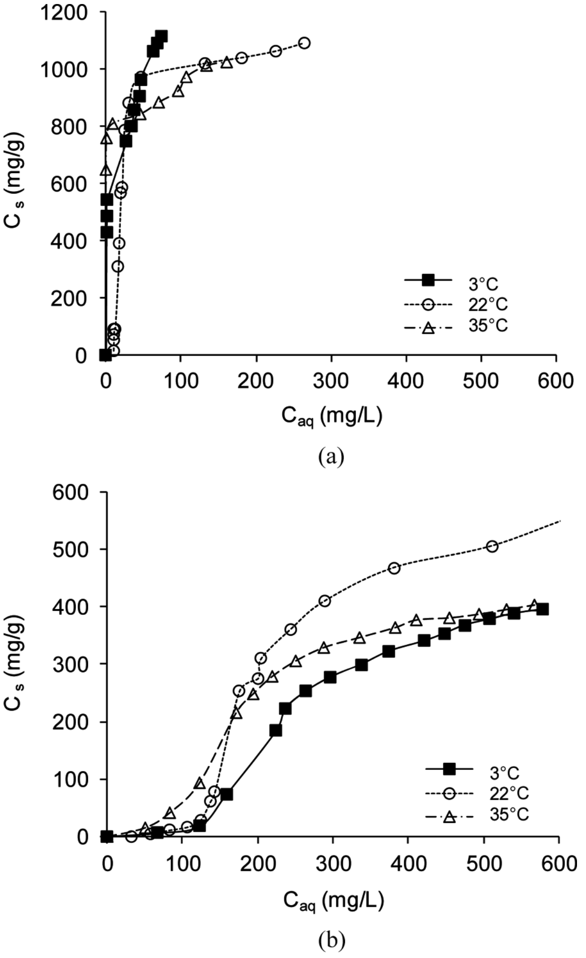


FIG. 6. Aqueous solubility of PFOS in ultrapure water and in 100 mM $NaClO_4$ solutions as a function of temperature. Error bars represent 95% confidence intervals for the analyses.



(a)

(b)

FIG. 7. Adsorbed concentration (C_s) versus aqueous concentration (C_{aq}) for: (a) PFOS and (b) PFBS on the resin from 10 mM $NaClO_4$ solutions.

The salting out effect for PFOS was confirmed by measuring its aqueous solubility in ultrapure water and in 100 mM $NaClO_4$ electrolyte solutions. Figure 6 shows the PFOS solubility for the acid form (H-PFOS) and the potassium salt (K-PFOS) over a temperature range of 22 to 38°C. H-PFOS is more than 17 times less soluble in the 100 mM perchlorate electrolyte as compared to ultrapure water. This can be attributed to both the salting out effect and to the tendency of PFOS to form ion pairs with cations in solution (20). The effect of ion pair formation can be seen by comparing the solubility of H-PFOS and K-PFOS in ultrapure water. Given that these two solutions have the same ionic strength, the factor of ~2 difference in the solubility of H-PFOS and K-PFOS can be attributed to PFOS ion pair formation with K^+.

To minimize the effect of PFOS or PFBS concentrations on the ionic strength of the solution, uptake isotherms by the resin were measured in 10 mM $NaClO_4$ background electrolyte solutions using the previously described procedure. Figures 7a and b show the isotherms for PFOS and PFBS. In contrast to the behavior shown in Fig. 4, PFOS and PFBS uptake increased with increasing aqueous phase concentration. For PFOS at 22 and 35°C, the isotherms show a change in slope at a loading of ~800 mg/g. This loading corresponds to the ion exchange capacity of the resin, which is 1.8 meq/g. Therefore, resin loadings greater than 800 mg/g are likely the result of hydrophobic adsorption. Measurements of the chloride ions released by the resin support this conclusion. For resin loadings below 800 mg/g, the moles of chloride released by the resin corresponded to the moles of PFOS removed from solution. However, at higher loadings, there was no further release of chloride ions with increasing PFOS uptake.

The PFBS isotherm in Fig. 7b is considerably less steep than that for PFOS, especially at low concentrations. Since both compounds carry the same charge, the large difference in behavior between PFOS and PFBS also indicates that hydrophobic effects play an important role in promoting PFOS uptake at low concentrations.

The endothermic heats of adsorption indicate that the GAC cannot be regenerated on site by mild heating. However, onsite regeneration of the resin may be possible using concentrated NaOH or NaCl solutions. Table 1 shows the percentage of adsorbed PFOS that was recovered from the resin using pH 13 NaOH solutions (320 mM) and 320 mM NaCl solutions at temperatures of

TABLE 1
Regeneration of the resin with 320 mM NaOH or NaCl solutions at 7, 22, and 50°C

Compound	Electrolyte	Initial pH	Final pH	Temperature (°C)	% recovered
PFOS	NaCl	7.5	4.5	7	0.0
PFOS	NaCl	7.5	4.5	22	0.0
PFOS	NaCl	7.5	4.5	50	0.0
PFOS	NaOH	13	13	7	0.0
PFOS	NaOH	13	10	22	0.36
PFOS	NaOH	13	13	50	0.18
PFBS	NaOH	13	10	22	4.0

7, 22, and 50°C. There was no detectable removal of PFOS from the resin by the NaCl solutions at any temperature. The NaOH solutions at 22 and 50°C were able to recover trace amounts of PFOS. Regeneration of PFBS from the resin was also attempted using 320 mM NaOH at 22°C. Although the fractional recovery of PFBS was more than one order of magnitude greater than that for PFOS, only 4% of the PFBS was recovered from the resin.

The low recoveries indicate that PFOS and PFBS uptake by the resin was irreversible using conventional regeneration procedures. This may be attributed to the fact that these two compounds have very low solubilities in the concentrated NaOH and NaCl regenerant solutions. This problem may be overcome by the use of a co-solvent, such as ethanol, in the regenerant solution. However, this would produce an organic waste stream that would be difficult to treat. Therefore, media that combine ion exchange and hydrophobic adsorption, such as Amberlite® IRA-458, do not appear to be a practical method for removing PFOS and PFBS from waste streams produced during semiconductor manufacturing.

ACKNOWLEDGEMENTS

Thanks to the National Science Foundation Chemical and Transport Systems Directorate (CTS-0522790), the Semiconductor Research Corporation/Sematech Engineering Research Center for Environmentally Benign Semiconductor Manufacturing (2001MC425), and the Donors of the American Chemical Society Petroleum Research Fund (PRF 43535-AC5) for support of this work.

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