

Batch and Column Adsorption of Perfluorooctane Sulfonate on Anion Exchange Resins and Granular Activated Carbon

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ABSTRACT: Perfluorooctane sulfonate (PFOS) has been detected widely in the natural water matrix and is persistent, bioaccumulative, and toxic. To prevent the adverse effects of PFOS contamination on human health and the environment, effective removal techniques are needed. Adsorption is considered an effective technique for PFOS removal. In this study, five anion exchange resins and granular activated carbon (GAC) were examined to evaluate their performance for the removal of PFOS in both batch and column experiments. Experimental adsorption data for all of the adsorbents exhibited a high correlation with the Freundlich isotherm ($R^2 = 0.95 - 0.98$). Most of the anion exchange resins demonstrated a higher adsorption capacity than the GAC. PFA300 had the highest adsorption capacity (455 mg/g). Continuous adsorption of PFOS was performed in column experiments using the same adsorbents that had been used in the batch experiments. The experimental breakthrough curves were set at $C/C_0 = 0.1$. PFA300 showed the longest operation time before reaching the breakthrough point. The Yoon and Nelson model was used to predict the half-saturation time of the anion exchange resins. Moreover, the anion exchange resins exhibited high recovery of PFOS by an organic solvent. Continuous PFOS adsorption on a column can be achieved using anion exchange resins for water/wastewater treatment. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39782.

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INTRODUCTION

Perfluorinated compounds (PFCs) have increasingly received attention as trace micropollutants. PFCs are anionic surfactant compounds that are fully fluorinated carbon chains with different functional head groups. Among the PFCs, perfluorooctane sulfonate (PFOS) is the most commonly used, and it is present in natural water. PFOS is used in many applications, such as the coatings for carpets, textiles, leather, paper, cardboard, food packing, electronic, photographic, and fire-fighting foams.¹ PFOS has been detected in a variety of water bodies, including wastewater, surface water, groundwater, and even tap water throughout the world.² High concentrations of PFOS have often been detected in industrial wastewater. Wastewater discharged from a semiconductor plant in Taiwan was found to contain 12.6 mg/L PFOS,³ and a PFOS concentration of 552.8 ng/L was reported for the central industrial wastewater treatment plant in Thailand.⁴ PFOS is persistent, bioaccumulative, and toxic. In 2009, PFOS was listed as a persistent organic pollutant in Annex B of the Stockholm Convention.⁵ PFOS can bioaccumulate through the food chain. It has been detected in a variety of fish species, and the PFOS concentrations in fish were 8850-fold greater than in the surface water.⁶ PFOS represents the predom-

inant compound detected in the serum, tissues, and milk of both the occupationally exposed and general human populations. Apelberg et al.⁷ found that the PFOS concentration in cord serum affected the birth weight and size of newborns.

To minimize PFOS contamination in the aquatic environment, effective removal techniques are needed. There are several available methods, such as photolysis and photocatalysis,⁸ advanced oxidation,⁹ thermal degradation,¹⁰ sonochemical degradation,¹¹ and membrane filtration.¹² Adsorption has been widely used for the treatment of industrial wastewater and this technique is effective as well as economical for the treatment of large amounts of wastewater. Granular activated carbon (GAC) is the conventional material used in wastewater treatment. However, it was reported that GAC became saturated at a fast rate. Senevirathna et al.¹³ found that GAC had faster breakthrough than non-ion exchange resins (Dow V493, Dow L493, and Amb XAD4). In addition, a water treatment plant in Germany reported poor performance of GAC for the elimination of PFCs.¹⁴

Alternative adsorbents have also been studied, particularly polymeric resins for the removal of PFOS. Resins have a favorable physicochemical stability, a large sorption capacity, good selectivity,

Table I. Physicochemical Properties of PFBS and PFOS Used in This Study

PFCs	Abbreviation	Chemical formula	Molecular weight	Solubility (g/L) ^a	pK _a
Perfluorobutane sulfonated	PFBS	CF ₃ (CF ₂) ₃ SO ₃ K	338	46.2	0.14 ^b
Perfluorooctane sulfonated	PFOS	CF ₃ (CF ₂) ₇ SO ₃ K	538	0.57	-3.27 ^c

^aFujii et al.²^bSteinle-Darling and Reinhard.¹⁵^cBrooke et al.¹⁶

structural diversity, and benefit of generation. One of the major advantages of these resins over GAC is their onsite regenerability. The ability to regenerate resins onsite potentially offers economic advantages over GAC, which typically requires offsite high-temperature incineration for regeneration. In addition, regeneration of the resin can be accomplished by simple techniques, such as solvent washing, thereby providing the potential for solute recovery. Because PFOS is present as an anion in aqueous solution, anion exchange may be an effective removal technique. However, studies investigating the practical removal of PFOS are lacking. Although resins are used in column mode in general practice, most studies focus only on the batch adsorption mode; therefore, the results of this study are important for implementing PFOS removal in a practical setting. Moreover, the column study was conducted at a low PFOS concentration, which is close to the actual level detected in wastewater. The objectives were to (i) perform batch studies to examine PFOS adsorption using five anion exchange resins and GAC, (ii) perform column studies to investigate the possibility of continuous removal of PFOS, and (iii) examine the PFOS recovery from the resins used.

MATERIALS AND METHODS

Chemicals and Adsorbents

PFOS and PFBS (perfluorobutane sulfonate) were purchased from Wako Chemicals (Japan). The physicochemical properties of PFOS and PFBS are shown in Table I. Five types of anion exchange resins and GAC were used in this study. Three anion exchange resins were from Purolite (Japan) coded as PFA300, PFA400, and PFA444, and the other two resins were from Dow Marathon A (Dow chemical, Japan) and Amb IRA400 (Sigma Aldrich, Japan). The anion exchange resins were washed with methanol and Milli-Q water and then dried at 50°C until reaching a constant weight. The characteristics of the anion exchange resins are shown in Table II. Filtrasorb 400 (GAC) was purchased from Dow Chemicals (Japan). The GAC was washed several times in Milli-Q water and then in Milli-Q water at 80°C for 2 h. Next,

the GAC was crushed into 1–1.4-mm particles after drying at 105°C for 48 h. The surface area of GAC was 900–1100 m²/g, and the diameter was 0.25–0.50 mm. The total pore volume was 0.61 cm³/g, and the pore sizes of the macropores, mesopores, and micropores were 0.04, 0.09, and 0.48 cm³/g, respectively.

Batch Adsorption Experiments

Adsorption isotherms were conducted to examine the adsorption capacity of each adsorbent by using a bottle-point technique. A mass of 1 mg of each adsorbent was added to 125 mL polypropylene (PP) bottles containing 100 mL of PFOS of varying concentrations (0.01, 0.05, 0.10, 0.50, and 1.00 mg/L). The bottles were placed in a thermostatic shaker (EYELA-NTS4000), which was set at 120 rpm at 25°C and shaken for 96 h. After shaking, the sample solutions were immediately separated by filtration and diluted into 40% acetonitrile. PFA400 and PFA444 were also examined for their adsorption of PFBS under similar experimental conditions as those used for PFOS. Equilibrium concentrations of PFBS and PFOS were determined by Agilent 1200SL high-performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS) Agilent, Japan.

Fixed-Bed Column Adsorption Experiment

Continuous removal of the PFOS system was performed by a fixed-bed column and was carried out using a PP column. The inner diameter of the column was 2 cm, and the length was 30 cm. The column, PP tube, mesh, tank and all equipment were rinsed with methanol and Milli-Q water before starting the experiment. The mesh was placed at the top and bottom of the column to prevent resin loss. The amount of adsorbent placed into each column was 20 cm³. One column was run without adding the adsorbent as a control unit. The column experimental set up is shown in Figure 1. Before starting the experiment, methanol was fed into the column to remove the PFCs and followed by Milli-Q water to remove dirt and the remaining methanol. Each column was filled with Milli-Q water for 24 h to ensure that all entrapped air bubbles in the adsorbents were

Table II. Characteristics of the Anion Exchange Resins Used in This Study

Adsorbent	Matrix	Functional group	Diameter (mm)	Ion exchange capacity (eq/L)
PFA300	Polystyrene cross-linked DVB	R-(CH ₃) ₂ (C ₂ H ₄ OH)N ⁺ (Type II)	0.56	1.4
PFA400	Polystyrene cross-linked DVB	R-(CH ₃) ₃ N ⁺ (Type I)	0.57	1.3
PFA444	Polystyrene cross-linked DVB	R-(CH ₃) ₃ N ⁺ (Type I)	0.57	1.1
Dow Marathon A	Styrene-DVB	R-(CH ₃) ₃ N ⁺ (Type I)	0.58	1.3
IRA400	Styrene-DVB	R-(CH ₃) ₃ N ⁺ (Type I)	0.60–0.75	1.4

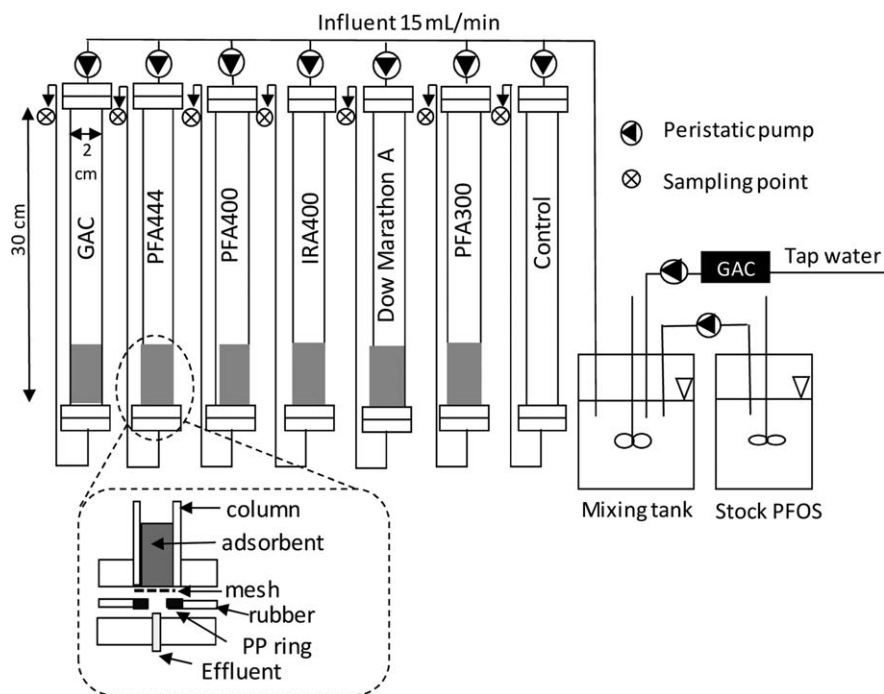


Figure 1. Column adsorption experiment of PFOS with different adsorbents.

released. Tap water was passed through the GAC to remove the chlorine residue, and it was pumped into a mixing tank. The PFOS concentration in the mixing tank was $5 \mu\text{g/L}$, and it was fed to each column at 15 mL/min . The total operation time was 122 days. Column studies were terminated when the PFOS removal efficiency of all columns dropped to 90%. The effluent from each column was collected (50 mL) every 3 days to measure the PFOS removal. A PresepC-Agri (C_{18}) cartridge (Wako, Japan) was used to concentrate the PFOS in the samples. The cartridges were conditioned by 10 mL of methanol and $2 \times 10 \text{ mL}$ of Milli-Q water before loading the sample into the cartridges. The cartridges were dried by a manifold vacuum for 1.5 h. The samples in the dried cartridges were eluted into a PP tube by $2 \times 2 \text{ mL}$ methanol and 2 mL acetonitrile. The eluted samples were dried under N_2 gas before reconstitution with 1 mL of 40% acetonitrile in ultrapure water. The PFOS concentration was analyzed by HPLC-MS/MS. The effluent concentrations were periodically measured by HPLC-MS/MS, and the breakthrough curves were predicted by Yoon and Nalson model.

PFOS Recovery

All of the adsorbents were removed from the column and washed with Milli-Q water. They were homogenized by mechanical shaking. The ratio of methanol/deionized water (7 : 3) was used in this experiment because it was effective for resin regeneration.¹⁷ Each adsorbent (1 mg) was placed into a 125-mL PP bottle filled with 50 mL of solution (5% NaCl in methanol/deionized water (7 : 3) or 100% methanol). PFOS was eluted from the used resins with 5% NaCl in methanol/deionized water (7 : 3), while GAC was eluted with 100% methanol. The PP bottles were shaken at 120 rpm and 25°C . The samples were collected at varying time intervals (1, 2, 4, 8 and 12 h) and analyzed by HPLC-MS/MS.

HPLC-Electrospray Tandem Mass Spectrometry

Ten microliters of each sample was injected onto a $2.1 \times 100 \text{ mm}$ ($5 \mu\text{m}$) Agilent Eclipse XDB-C18 column. The mobile phase was (a) 5 mM ammonium acetate in ultrapure water (LC/MS grade) and (b) 100% acetonitrile (LC/MS grade). The flow rate was set at 0.25 mL/min . The separation process was started with mobile phase (B) at 30%, which increased to 45% at 1 min and then increased to 60% at 8 min. Then, the percentage of (B) was increased to 90% at 8.5 min and was maintained for 6.5 min before ramping down to 30%. The total running time for each sample was 21 min. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). The mass spectrometer was operated with the electrospray ionization negative mode. The analyte ions were monitored using the multiple reactions monitoring mode.

RESULTS AND DISCUSSION

Adsorption Isotherms

Five commercial anion exchange resins were selected in this study, and these were generally used for water and wastewater treatment. The shaking duration of the isotherm experiment was 96 h to ensure that all adsorbents reached their equilibrium concentrations. The adsorption isotherms of five anion exchange resins and GAC determined their adsorptive capacities. The Freundlich isotherm is an empirical relationship describing the adsorption of solute on a solid phase and a liquid phase. The Freundlich isotherm is defined by the followed equation:

$$q_e = K_f C_e^{1/n} \quad (1)$$

where q_e is the adsorbate amount on the surface of the adsorbent at equilibrium (mg/g), C_e is the equilibrium

Table III. Freundlich Isotherm Constants for the Adsorption of PFOS and PFBS onto Different Adsorbents

Adsorbent	PFCs	K_f (mg/g)/(mg/L) ^{1/n}	n	R^2
PFA300	PFOS	455	1.18	0.97
Dow Marathon A	PFOS	432	1.10	0.98
IRA400	PFOS	426	1.00	0.95
PFA400	PFOS	159	1.02	0.97
	PFBS	256	1.09	1.00
PFA444	PFOS	97	1.16	0.97
	PFBS	113	1.02	0.99
GAC	PFOS	163	1.22	0.98

concentration of the adsorbate in solution (mg/L). K_f is the Freundlich constant (mg/g)/(mg/L)^{1/n}, which indicates the adsorption capacity. n represents the measure of the nonlinearity involved.

The experimental data for all of the adsorbents in this study were fitted by the Freundlich isotherm, and their coefficients of determination ranged from 0.95 to 0.98 (Table III). Most of the anion exchange resins had a higher capacity to adsorb PFOS compared with GAC. PFA300 had the highest adsorption capacity followed by Dow Marathon A, IRA400, GAC, PFA400, and PFA444, respectively. Among the five anion exchange resins, PFA300 has a dimethylethanolamine functional group (Type II resin). Type II resins have a quaternary ammonium functional group, and one of the methyl groups ($-\text{CH}_3$) in the Type I resins is replaced with an ethanol group ($-\text{C}_2\text{H}_4\text{OH}$). It has been observed that Type II resins have a slightly greater capacity than Type I.¹⁸ The presence of one $-\text{OH}$ group close to the quaternary nitrogen can make PFA300 more hydrophilic and provide a more open structure

Table IV. Parameters of Yoon-Nelson Model for PFOS Column Adsorption

Adsorbent	k_{YN} (1/day)	τ (day) ($C_i/C_0 = 0.5$)	R^2
PFA300	0.043	172.4	0.84
Dow Marathon A	0.039	167.5	0.95
IRA400	0.036	161.2	0.88
PFA400	0.033	157.7	0.92
PFA444	0.033	142.6	0.87

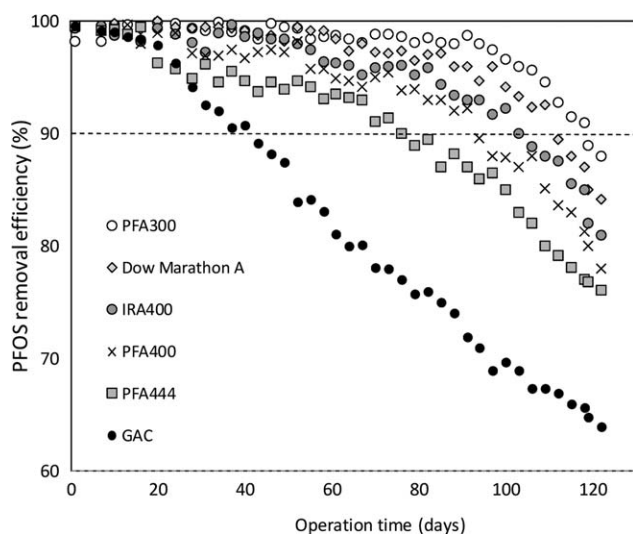
than the other resins in this study, causing the PFOS molecules to diffuse into the anion exchange sites.

To show the effect of size exclusion, PFA400 and PFA444 were selected in this experiment because they had lower K_f values for adsorption of PFOS than other resins. Adsorption of PFBS (C4) onto PFA400 and PFA444 were conducted under the same experimental conditions as PFOS (C8) adsorption. Both resins showed higher K_f values for PFBS than PFOS (Table III). PFBS has a shorter carbon chain, which was more hydrophilic than PFOS. Thus, PFBS easily entered the small pores and adsorbed onto the resins. This result confirms that the poor adsorption of PFOS onto PFA400 and PFA444 occurred due to the effect of size exclusion.

Furthermore, GAC has a higher K_f value for PFOS than PFA400 and PFA444. GAC has a smaller diameter than PFA400 and PFA444, increasing its surface area. Additionally, GAC has heterogeneous adsorption sites, including micropores, mesopores, and macropores. Therefore, PFOS has a higher probability of entering the larger pores and adsorbing onto GAC. In comparison to the K_f value from the Freundlich equation with the other adsorbents, PFA300 had a higher K_f than GAC (Table III), Zeolite (0.7 mg/g),¹⁹ and ash (26.8 mg/g).²⁰ This indicates that the PFA300 is highly effective for PFOS removal from water/wastewater.

Column Experiment

An experiment to observe the continuous removal of PFOS by the five resins and GAC was conducted over 122 operational days. A PFOS solution (5 $\mu\text{g/L}$) was fed into the column at a flow rate of 15 mL/min with 0.75 bed volume/min. The retention time was 1.3 min. Figure 2 shows the removal efficiencies of PFOS in each column compared with operation time. The breakthrough point was set at 90% ($C/C_0 = 0.1$) removal efficiency. The flows through columns were continued until the PFOS concentration of all the detected column effluents exceeded 0.5 $\mu\text{g/L}$. The removal efficiencies of all adsorbents were greater than 99% for 14 operation days ($\sim 15,000$ bed volumes). PFA300 showed the best operation performance by removing more than 99% of PFOS for the first 52 operation days (56,000 bed volumes). Longer operation days indicate that a large volume of water can be treated. At the breakthrough point ($C/C_0 = 0.1$), the number of operation days decreased in the order of PFA300 > Dow Marathon A > IRA400 > PFA400 > PFA444 and GAC. GAC showed the fastest breakthrough at 40 days. It was reported that GAC was not effective for PFOS removal because it had a low

**Figure 2.** Removal efficiency of PFOS with an operation time (122 days) for different adsorbents in the column experiment.

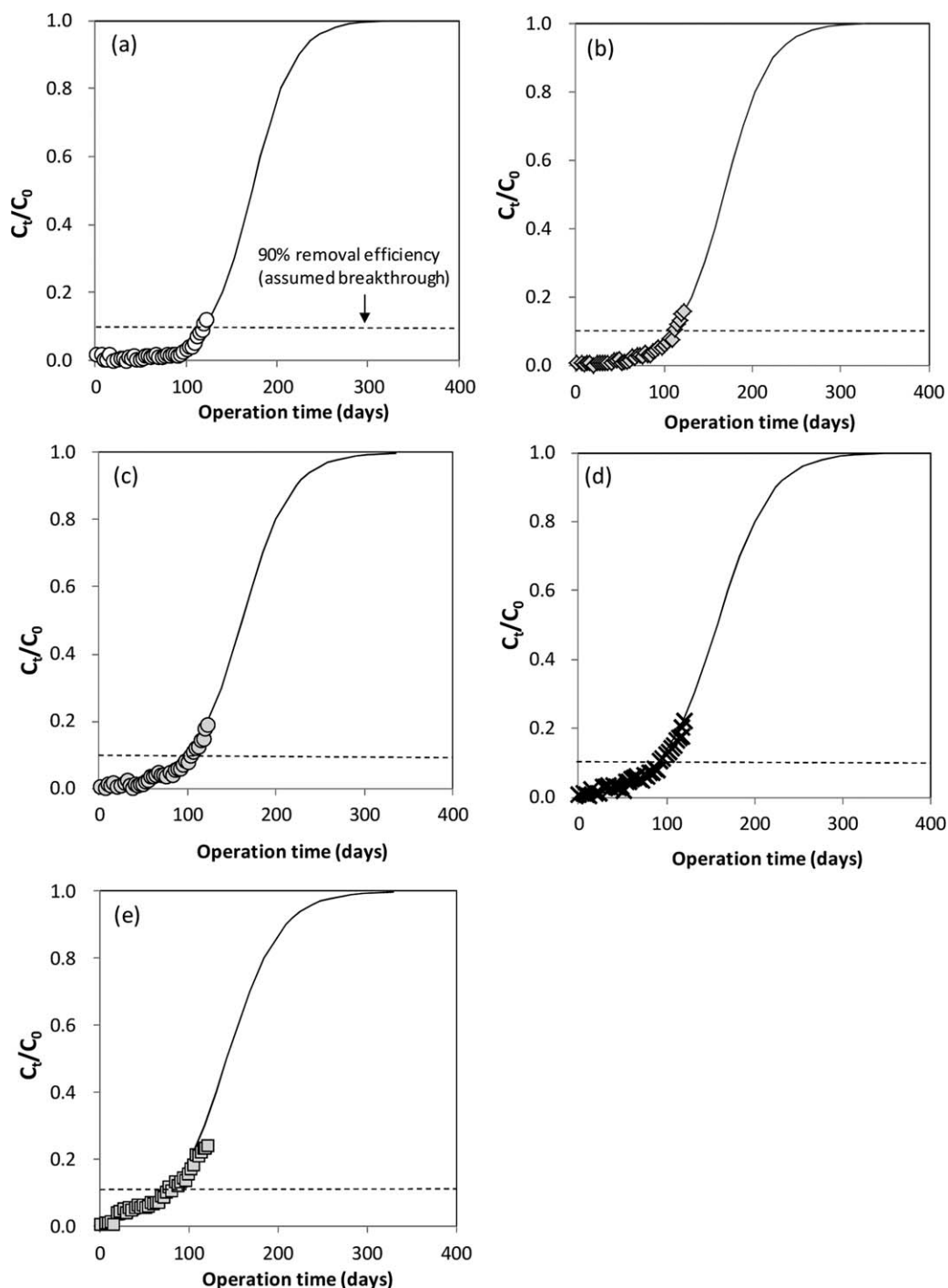


Figure 3. Predicted curves of PFOS adsorbed onto the anion exchange resins vs. operation time according to the Yoon and Nelson model (a) PFA300, (b) Dow Marathon A, (c) IRA400, (d) PFA400, and (e) PFA444.

adsorption capacity and it was easy to reach super saturation. This result could be the reason for the fast breakthrough of perfluorinated surfactants when the activated carbon filter was applied in a German water works.¹⁴ Of the six adsorbents, PFA300 has the highest adsorption capacity of PFOS (455 mg/g), and it also showed the best performance for the removal efficiency of PFOS in a column experiment compared with the other resins in this study.

Prediction of the Breakthrough Curve

The column adsorption process requires the prediction of the breakthrough curve for the effluent.²¹ Yoon and Nelson have developed a relatively simple model for a single component system. This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on

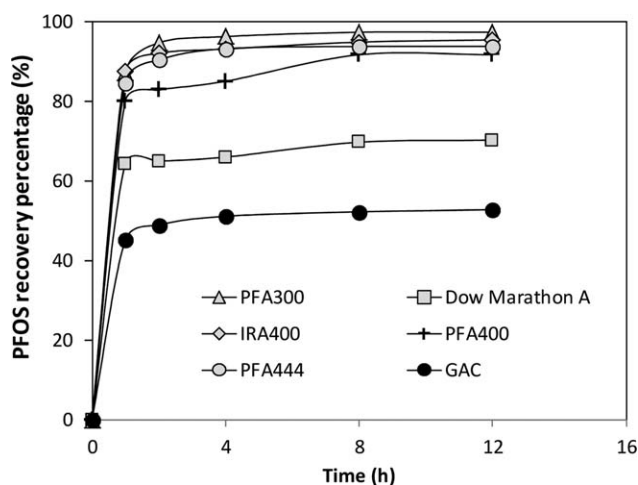


Figure 4. Percentage of PFOS recovery from the used resins after the column experiment.

the adsorbent.^{22,23} The half saturation of five anion exchange resins was predicted using Yoon and Nelson model. The Yoon and Nelson²⁴ equation for a single component system is expressed as:

$$\frac{C_t}{C_0 - C_t} = \exp(k_{YN}t - \tau k_{YN}) \quad (2)$$

where, k_{YN} is the rate constant (1/day), τ is the time required for 50% adsorbate breakthrough (day). t is the breakthrough (sampling) time (day). C_0 and C_t are the influent and effluent concentrations ($\mu\text{g/L}$). According to the Yoon and Nelson model, the rate constant characterizes the shape of the breakthrough curve. A sharp breakthrough curve always has a large rate constant. The linearized form of the Yoon and Nelson model is described below:

$$\ln \frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN} \quad (3)$$

A linear plot of $\ln(C_t/(C_0 - C_t))$ against t determined the values of k_{YN} and τ from the intercept and slope of the plot (not shown by diagram). The values of the correlation coefficients (R^2), k_{YN} and τ are shown in Table IV. The performance of each column can be described by the Yoon and Nelson model based on the correlation coefficients, which range from 0.84 to 0.95. Theoretical predictions of breakthrough curves for all the resins used in this study were demonstrated from the calculation of k_{YN} and τ and presented in Figure 3. The longest half saturation time can be expected from PFA300, which showed the highest of τ value.

PFOS Recovery

The total amount of PFOS adsorbed on the adsorbents was calculated by the integrated area under the curve in Figure 2. PFOS recovery experiments were carried out in batch. The recovery of PFOS by the solvent washing is applicable for onsite regeneration. In this experiment, there were two types of solvent. First, 5% NaCl in methanol/*Milli-Q* water (7 : 3) was used for the anion exchange resins. Because PFOS has hydrophobic properties, methanol was used to increase the solubility of PFOS. Second, 100% methanol was used for GAC. Figure 4

shows the PFOS recovery percentage of each adsorbent. Most of the anion exchange resins showed a recovery percentage of PFOS >93%, except for Dow Marathon A (70%). PFA300 showed the highest percentage of PFOS recovery, followed by IRA400, PFA444, PFA400, Dow Marathon A, and GAC. The faster desorption of PFOS from the anion exchange resin compared with GAC was due to the interaction between the adsorbate and the adsorbent. Adsorption of PFOS on the GAC surface was due to the stronger attraction than that of the resins. Némethy and Scherage²⁵ reported that hydrophobic compounds adsorbed more strongly on carbon. Additionally, PFOS adsorbed in the deep pores of GAC, and it takes time to desorb PFOS into the solvent. Similar results have been reported by Senevirathna et al.,¹³ who showed that the percentage of PFOS recovery by GAC was only 40% after 270 min. In practice, resins are always regenerated using chemicals, while carbon is usually regenerated thermally because the adsorption forces are strong. Therefore, anion exchange resins were suitable adsorbents for PFOS removal in the aqueous phase.

CONCLUSIONS

The treatment performance of five anion exchange resins and GAC were examined for the removal of PFOS by performing both batch and fixed-bed column experiments. The adsorption isotherms were determined to identify the capacity of each adsorbent. The adsorption capacities decreased in order of PFA300, Dow Marathon A, IRA400, GAC, PFA400, and PFA444, respectively. The functional groups of the resins have an influence on the adsorption capacity. The best performance of the column test was given by PFA300. From the experimental data, GAC reached a breakthrough point at a faster rate than the other adsorbents. The Yoon and Nelson model was applied to the data obtained from experimental studies performed on a fixed-bed column to predict the breakthrough curves. PFA300 exhibits the longest operation time to half saturation for PFOS at 172 days. Moreover, the PFOS recovery percentages of all of the anion exchange resins were higher than GAC. The anion exchange resins had high adsorption capacities, long operation days, and high PFOS recovery percentage, suggesting that anion exchange resins are suitable materials for PFOS removal in aqueous solution, particularly PFA300.

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