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Regeneration and Reusability of Anion Exchange Resin Used in Perfluorooctane Sulfonate Removal by Batch Experiments

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ABSTRACT: Perfluorooctane sulfonate (PFOS) has been increasingly considered an environmental micropollutant in recent years. The adsorption of PFOS by anion exchange resins and granular activated carbon was studied in this work. Additionally, the regeneration and reusability of the selected resin were further studied. The equilibrium adsorption data were fitted well by the Freundlich isotherm for all adsorbents. PFA300 had the highest adsorption capacity (455 mg/g) and the fastest adsorption rate. Regeneration studies of PFA300 were conducted using different types of regeneration solutions. The regeneration efficiency of PFA300 exceeded 99%. Regenerated PFA300 was reused as an adsorbent and showed high PFOS removal efficiency for six cycles. In this study, PFA300 had the highest adsorption capacity as well as good regeneration and reusability. Therefore, PFA300 is a promising adsorbent that can be used to remove PFOS in aqueous solution. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 884–890, 2013

KEYWORDS: adsorption; polystyrene; recycling; resins; surfactants

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INTRODUCTION

Perfluorinated compounds (PFCs) are microorganofluorine compounds in which all the C—H bonds are replaced by C—F bonds. PFCs contain a hydrophobic fluorinated carbon chain with a polar, hydrophilic head attached to one end.[1] PFCs include perfluorooctane sulfonate (PFOS), which is often found in natural water and wastewater.[2] PFOS has received a great deal of attention in recent years due to its endocrine disrupting effect and multiple toxicities, such as hepatotoxicity and immune toxicity, as well as its effects on reproduction and development.[3,4] PFOS and its derivatives have been widely used as a coating material on paper, packaging, and textile products as they repel both water and oil.[1] Because they are stable even at high temperature, they have been used as foams for combating hydrocarbon fuel fires, especially fires associated with fuel spills.[5,6] High concentrations of PFOS are most common in industrial effluent wastewater, which has been identified as a major source of PFOS.[7,8] Recent studies have reported the potential risk of PFOS to living things. Due to its persistence, bioaccumulative nature, and toxic effects, PFOS was recognized as a persistent organic pollutant by the Stockholm Convention in May 2009.[9]

A number of techniques are available for degrading or removing PFOS from aqueous environments, including advanced oxidation processes, photocatalysis, adsorption, and reverse osmosis membrane filtration.[10] However, these techniques have some drawbacks and limitations, such as requiring high-energy and/or extreme reaction conditions. Adsorption is a versatile, practical removal technique that is widely used for wastewater treatment. Activated carbon has been used to remove a variety of toxic organic pollutants, including PFOS.[11–13] Recently, some researchers have reported the effectiveness of anion exchange resins for PFOS adsorption.[14,15] Because the resins can be regenerated, resin-based water treatment is economical. Generally, anion exchange resins are regenerated by high concentrations of NaCl and NaOH. However, Deng et al.[15] reported that high concentrations of NaCl and NaOH could not desorb PFOS adsorbed on resin. Therefore, a suitable regeneration solution for PFOS adsorbed on resin must be identified. Moreover, there is no information about the reusability of regenerated resin used for PFOS removal. Therefore, the results reported here are critical for contributing new information to this research topic.

In this study, five anion exchange resins and granular activated carbon (GAC) were studied in batch experiments to determine the PFOS adsorption capacity and adsorption rate. The selected resin was studied with the suitable regeneration solutions. Next, the identified solutions were used to investigate the regeneration rate. Finally, the reusability of the regenerated resin after six cycles of PFOS removal was evaluated.

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MATERIALS AND METHOD

Chemicals and Adsorbents

PFOS (98%), methanol (LC/MS grade), and acetonitrile (LC/MS grade) were purchased from Wako Chemicals (Japan). Five types of anion exchange resin were used in this study: three anion exchange resins were obtained from Purolite Company (Japan), coded as PFA300, PFA400, and PFA444, and the remaining two were Dow Marathon A (Dow Chemical, Japan) and Amb IRA400 (Sigma Aldrich, Japan). The properties of all anion exchange resins are shown in Table I. The resins were washed with deionized water followed by methanol to remove dirt and PFCs. Next, all resins were washed again by deionized water to remove the remaining methanol and dried at 50°C until reaching constant weight. The five anion exchange resins in this study were classified as Types I or II based on their functional groups: those resins containing strongly basic trimethylbenzylammonium groups were classified as Type I and those containing dimethylethanolamino groups as Type II. Filtrasorb 400 (GAC) was purchased from Dow Chemical (Japan). The GAC was washed with room-temperature deionized water several times and were then washed with 80°C deionized water for 2 h to remove impurities. After drying at 105°C for 48 h, the GAC was crushed and sieved through 1.0–1.4 mm mesh. The surface area of the GAC was 900–1100 m^2/g and its diameter was 0.25–0.50 mm. The total pore volume was 0.61 cm^3/g and the pore size distribution of macropores, mesopores, and micropores were 0.04, 0.09, and 0.48 cm^3/g, respectively.

Adsorption Experiments

Adsorption isotherm experiments were carried out with five types of anion exchange resins using a bottle-point technique. The adsorbent (1 mg) was placed into 125 mL polypropylene (PP) bottles containing 100 mL of 0.01, 0.05, 0.10, 0.50, and 1.00 mg/L PFOS solutions (initial concentrations) in deionized water. Five samples were prepared for each concentration ($n = 5$). The samples were shaken at 120 rpm and 25°C for 96 h using a thermo shaker (EYELA-NTS4000). As controls, PFOS solutions were also added to PP bottles without any adsorbents. After shaking, the adsorbent was immediately separated from the sample by filtration, and filtrate sample was diluted with 40% acetonitrile in deionized water. The samples were analyzed by Agilent 1200SL high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS; Agilent, Japan).

A kinetic study was also conducted on an initial concentration of 0.50 mg/L (PFOS) with the shaking conditions described above and 10 mg of adsorbent. Samples were collected at 1, 3, 6, 12, 24, 48, and 72 h of contact ($n = 5$) and analyzed by HPLC-MS/MS.

Regeneration Experiments

Sample Preparation: PFOS Adsorption. PFA300 was selected for the regeneration and reusability study due to its PFOS adsorption performance being the best of the five resins. The adsorbent was prepared for the regeneration study by placing 2 mg of adsorbent into a 15 mL PP tube with 10 mL of PFOS solution (10 mg/L). The mixture was shaken for 48 h at 120 rpm and 25°C using a thermo shaker. After shaking, the PFOS concentrations in the liquid samples were below the instrumental quantification limit (IQL) when analyzed by HPLC-MS/MS. The adsorbents were then washed by deionized water to remove the PFOS remaining in the PP tubes.

Regeneration Solutions of Selected Resin. Various types of solutions were used for the regeneration of PFA300, as shown in Table II. PFA300, prepared in Section "Sample preparation: PFOS adsorption," was regenerated by adding 10 mL of each regeneration solution and shaking in a thermo shaker at 120 rpm and 25°C for 48 h. Next, the PFOS concentration in the aqueous solution was analyzed by HPLC-MS/MS. High-concentration NaCl and NaOH solutions are commonly used to regenerate spent anion exchange resin. PFOS has hydrophobic properties, so it is soluble in organic solvents, such as methanol, ethanol, hexane, acetone, and dimethyl sulfoxide (DMSO).[16] Thus, NaCl, NaOH, and methanol were used as regeneration solutions for PFA300. A previous study indicated that 1% NaCl and 1% NaOH in 70% methanol were effective for regenerating IRA67 resin after PFOS adsorption.[15] Therefore, a 7 : 3 ratio of MeOH/deionized water was used in this study with different concentrations of NaCl and NaOH. Regeneration efficiency was calculated by eq. (1).

$$\frac{E_i}{E_0} \times 100 = \text{regeneration efficiency} \quad (1)$$

E_i = PFOS concentration (mg/L) in the liquid phase at different intervals.

E_0 = Initial PFOS concentration (mg/L) used in the adsorption experiment.

Table I. Properties of Anion Exchange Resins in This Study

Adsorbent	Matrix	Functional group[a]	Diameter (mm)	Ion exchange capacity (eq/L)
PFA300[b]	Polystyrene cross-linked DVB	R-$(CH_3)_2(C_2H_4OH)N^+$ (Type II)	0.56	1.4
PFA400[b]	Polystyrene cross-linked DVB	R-$(CH_3)_3N^+$ (Type I)	0.57	1.3
PFA444[b]	Polystyrene cross-linked DVB	R-$(CH_3)_3N^+$ (Type I)	0.57	1.1
Dow Marathon A[c]	Styrene-DVB	R-$(CH_3)_3N^+$ (Type I)	0.58	1.3
IRA400[d]	Styrene-DVB	R-$(CH_3)_3N^+$ (Type I)	0.60–0.75	1.4

Note: All resins are gel type. DVB is divinylbenzene.
[a]The functional groups are trimethylbenzylammonium for Type I resin and dimethylethanolaminium for Type II.
[b]Purolite (www.purolite.com).
[c]Dow Chemical (www.dowex.com).
[d]Sigma-Aldrich (www.sigmmaldrich.com).

Table II. Summary of Experimental Conditions in This Study

Experiment	Adsorbent	Concentration of PFOS (mg/L)	Sample volume (mL)	Shaking condition	Type of regeneration solution
Adsorption isotherm ($n = 5$)	PFA300 PFA400 PFA444 Dow Marathon A IRA400 GAC	0.01, 0.05, 0.10, 0.50, and 1.00	100	120 rpm, 25°C at 96 h	-
Kinetics ($n = 5$)	PFA300 PFA400 PFA444 Dow Marathon A IRA400 GAC	0.50	100	120 rpm, 25°C at 1, 3, 6, 12, 24, 48, and 72 h	-
Regeneration solution ($n = 5$)	PFA300	10	10	120 rpm, 25°C at 48 h	100% Methanol, 1% NaOH, 5% NaOH, 1% NaCl, 5% NaCl, 1% NaOH in MeOH/deionized water (7 : 3), 5% NaOH in MeOH/deionized water (7 : 3), 1% NaCl in MeOH/deionized water (7 : 3), and 5% NaCl in MeOH/deionized water (7 : 3)
Regeneration rate ($n = 5$)	PFA300	10	10	120 rpm, 25°C at 1, 2, 4, 8, and 12 h	1% NaOH in MeOH/deionized water (7 : 3), 3% NaOH in MeOH/deionized water (7 : 3), 5% NaOH in MeOH/deionized water (7 : 3), 1% NaCl in MeOH/deionized water (7 : 3), 3% NaCl in MeOH/deionized water (7 : 3), and 5% NaCl in MeOH/deionized water (7 : 3)
Reusability ($n = 5$)	PFA300	10	10	120 rpm, 25°C at 48 h	5% NaCl in MeOH/deionized water (7 : 3)

Regeneration Rate of Selected Resin. The mixture of NaCl and NaOH in MeOH/deionized water (7 : 3) solution was used to study the regeneration of PFA300 with different contact times. The regeneration solutions (10 mL) were shaken together with the PFA300 prepared in Section "Sample preparation: PFOS adsorption". Samples were collected at different intervals (0, 1, 2, 4, 8, and 12 h), as shown in Table II. All samples were diluted into 40% acetonitrile in deionized water and analyzed by HPLC-MS/MS. Finally, the regeneration percentages were calculated ($n = 5$).

Reusability of Selected Resin. To test the reusability of the selected resin, the regenerated PFA300 was washed with deionized water. It was then reused as the adsorbent for a 10 mL solution of PFOS at a concentration of 10 mg/L (Table II). The regeneration and reuse cycles were repeated for up to six cycles ($n = 5$).

HPLC-Electrospray Tandem Mass Spectrometry

A sample (10 μL) was injected into a 2.1 × 100 mm (5 μm) Agilent Eclipse XDB-C18 column. The mobile phase was (A)

5 m*M* 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 started with mobile phase (B) at 30%, which then increased to 45% at 1 min, 60% at 8 min, and 90% at 8.5 min, where it remained 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 mass spectrometer (MS/MS, Agilent, Japan). The mass spectrometer was operated in the electrospray ionization negative mode. Analyte ions were monitored using multiple reaction monitoring mode. The retention time was 4.6 min. The instrumental detection limit and IQL were 0.02 and 0.08 μg/L, respectively.

RESULTS AND DISCUSSION

Adsorption Isotherms

The adsorptive capacities of five anion exchange resins and GAC were examined by fitting the experimental data to the Freundlich equation and determining the Freundlich constant. The Freundlich isotherm provides an empirical relationship describing the adsorption of the solute onto solid and liquid phases. It is defined by

$$q_e = K_f C_e \quad (2)$$

where q_e is the equilibrium adsorption uptake of PFOS in mg/g and C_e is the equilibrium concentration of PFOS in mg/L. K_f (mg/g)/(mg/L)$^{1/n}$ is the Freundlich constant related to adsorption capacity. n is *Freundlich* exponent; values of $n > 1$ represent favorable adsorption. This model is widely used to describe the adsorption capacity of many compounds onto heterogeneous materials, including activated carbon, resins, zeolite, and chitosan.[12,17] The Freundlich isotherm constants of PFOS adsorbed onto anion exchange resins and GAC are shown in Table III.

As shown in Table III, all adsorbents were well fitted by the Freundlich model, with good correlation coefficients (R^2 in the range of 0.95–0.98). The Freundlich model is based on multilayer adsorption. Because of the hydrophobicity of the C—F chains in PFOS, multilayer adsorption occurs at higher equilibrium concentrations. The five resins were different in terms of functional groups, ion exchange capacity, and size, which influence the PFOS adsorption capacity. PFA300 had the highest adsorption capacity (455 mg/g), followed by Dow Marathon A (432 mg/g), IRA400 (426 mg/g), PFA400 (159 mg/g), and PFA444 (97 mg/g). The resins had higher adsorption capacities than GAC (163 mg/g), except for PFA400 and PFA444. Among the five resins used in this study, PFA300 had the highest ion exchange capacity (1.4 eq/L) and was categorized as Type II (Table I). Both Types I and II have a quaternary ammonium functional group; however, a methyl group (—CH_3) in Type I is replaced by an ethanol group (—C_2H_4OH) in Type II resins. Because Type II is more hydrophilic than Type I, PFOS can more easily adsorb onto the Type II resins. Type II resin has been noted to have a slightly greater capacity than Type I.[18] Therefore, the resin functional groups influenced the adsorption of PFOS. However, PFOS adsorption on other four resins in this study can be explained by their ion exchange capacity. The ion exchange capacity of Dow Marathon A, IRA400, and PFA400 were similar (1.3–1.4 eq/L) whereas PFA444 had the lowest ion exchange capacity (1.1 eq/L), meaning that the latter can adsorb less PFOS than the other resins.

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

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

All resins in this study have a similar gel-type structure with very small pores (few Å). The hydrophilic properties of the gel phase enhance the transportation of PFOS into the resins. Additionally, the resin matrix influences the adsorption capacity of the resin. The five resins used in this study are polystyrene-divinylbenzene resins, which are more hydrophobic than polyacrylic resins. The hydrophobicity of resin leads to an increase in the hydrophobic interactions between resins and PFOS. Therefore, the gel type and polystyrene-divinylbenzene composition may affect PFOS adsorption.

The Freundlich exponent (n), an indicator of nonlinearity, was higher for GAC than for anion exchange resins due to adsorption site heterogeneity and adsorbate-adsorbent interactions.[19] GAC is likely comprised of heterogeneous adsorption sites, based on its different pore sizes (micropores, mesopores, and macropores). However, GAC had a higher adsorption capacity than PFA400 and PFA444. Two possible explanations for this finding are that GAC has a smaller diameter than PFA400 and PFA444, increasing its surface area, and that PFA400 and PFA444 may contain a high percentage of divinylbenzene, leading to the size exclusion of PFOS.

Adsorption Kinetics

The adsorption kinetics in Figure 1 show that the equilibrium state was established more rapidly in PFA300 than in Dow Marathon A, PFA400, PFA44, IRA400, and GAC due to the presence of an ethanol group in PFA300 (Type II), leading to increased hydrophilicity. The diffusion of PFOS into PFA300 was higher than into the other adsorbents in this study. PFA300 was also the smallest resin and reached the equilibrium state most quickly. Smaller particles lead to a higher surface area for film diffusion and require less time for equilibration. The structure of gel-type resin also affects PFOS adsorption by the diffusion of the gel phase in aqueous solution; thus, all five resins reached the equilibrium state more quickly than did GAC. Moreover, GAC had a high proportion of micropores, slowing the entry of PFOS; hence, it took the longest time to reach the equilibrium state.

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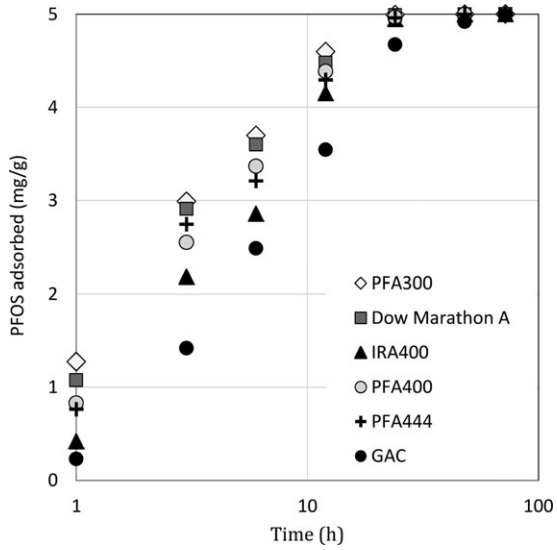


Figure 1. Adsorption kinetics of PFOS on five anion exchange resins and GAC.

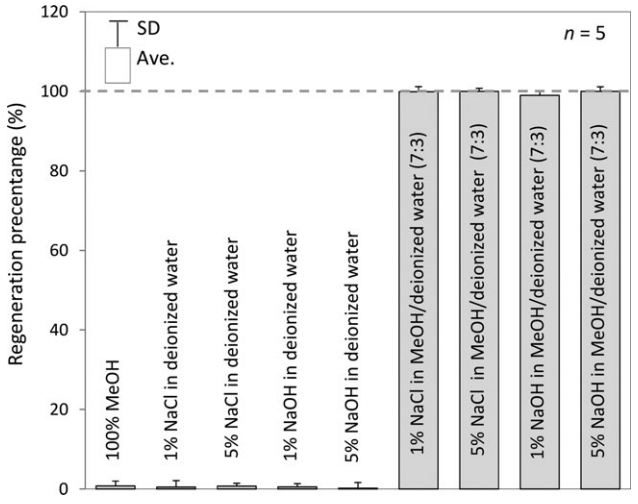


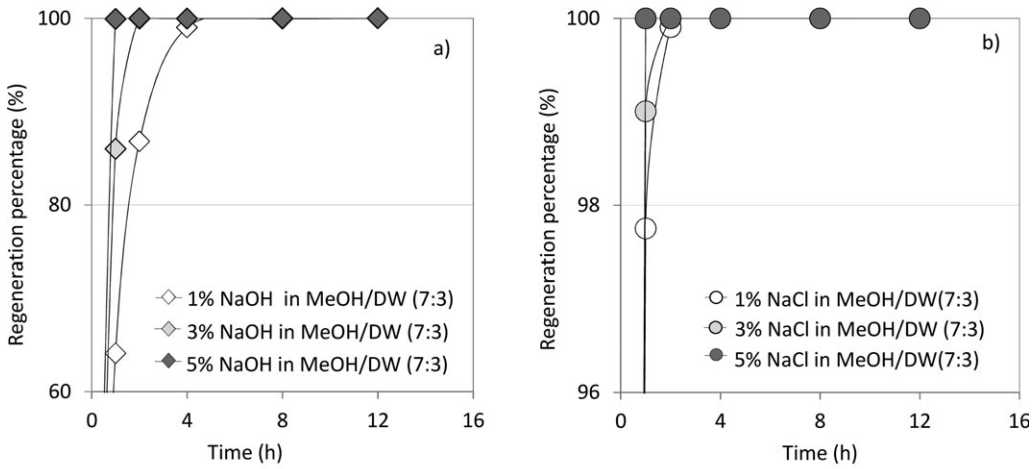
Figure 2. Regeneration percentage of PFA300 by different regeneration solutions after 48 h.

Regeneration Solutions of Selected Resin

The benefit of using adsorbent is its ability to be regenerated after reaching its capacity. For this purpose, the regeneration of the selected resin was studied using the solvent regeneration technique. This technique is convenient and can be performed onsite. Among the five resins in this study, PFA300 was selected in this experiment because it showed the highest PFOS adsorption performance. The regeneration of anion exchange resins occurred by ion exchange processes. The adsorbed PFOS on the resins was replaced by anions from the regeneration solutions to reactivate the resin. Figure 2 shows the different types of regeneration solutions used for PFA300. The results showed that solutions of pure methanol and of NaCl and NaOH in deionized water were unable to regenerate PFA300. When the concentrations of NaCl and NaOH (in 100% deionized water) were increased from 1 to 5%, they were still ineffective for desorbing PFOS from PFA300 because PFOS has low water solubility at high salt concentrations and ionic strengths.[6] In the case of methanol, PFOS was unable to directly desorb into methanol. Thus, mixed solutions of NaOH or NaCl in MeOH/deionized water (7 : 3) were applied in this study. Each concentration (1% NaCl, 5% NaCl, 1% NaOH, and 5% NaOH) was mixed in MeOH/deionized water (7 : 3) and used for resin regeneration. The adsorbed PFOS was first desorbed from the binding sites on the resin surface and then dissolved in methanol. After shaking for 48 h, the regeneration efficiency was over 99% for all solutions. Mixing with methanol enhances the solubility of PFOS. Therefore, the solutions of NaCl and NaOH in MeOH/deionized water (7 : 3) were suitable for PFA300 regeneration.

Regeneration Rate of Selected Resin

The regeneration rate of PFA300 was investigated. Figure 3 shows the regeneration rate of PFA300 for different



Note: DW is deionized water.

Figure 3. Regeneration rate of the spent PFA300 after PFOS adsorption: (a) using NaOH in MeOH/DW (7 : 3) and (b) using NaCl in MeOH/DW (7 : 3).

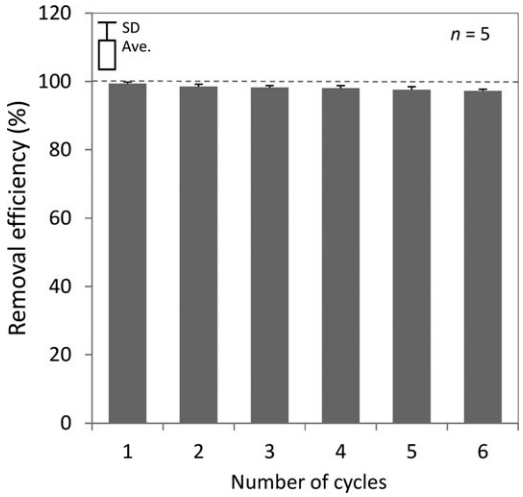


Figure 4. Reusability efficiency of PFA300 using 5% NaCl in MeOH/deionized water (7 : 3) for regeneration.

regeneration solutions at different time intervals. The solutions of NaOH and NaCl in MeOH/deionized water (7 : 3) were highly effective for the regeneration of PFA300 in this study. The regeneration rate increased with increasing concentrations of NaOH and NaCl. After 1 h of shaking, 1% NaCl in MeOH/deionized water (7 : 3) yielded a regeneration efficiency of >97%, whereas 1% NaOH in MeOH/deionized water (7 : 3) yielded a regeneration efficiency of 64%. Because chloride has higher ion selectivity than hydroxide ($Cl^- > OH^-$), the NaCl solution desorbed PFOS more quickly than the NaOH solution did. When the NaOH concentration was increased from 1 to 3%, the regeneration efficiency increased from 64 to 86%. Finally, when the NaOH concentration was increased to 5%, the regeneration efficiency was over 99% after 1 h of shaking. After 4 h, all of the regeneration solutions had completely desorbed PFOS. Deng et al.[15] reported a similar result for IRA67 resin using 1% NaCl and 1% NaOH solutions mixed with 70% methanol. PFOS adsorption on resin occurred by ion exchange and adsorption at the outer surface of the resin, which may be explain the fast regeneration of resin. As shown by the results reported herein, PFA300 is easily regenerated, and *in situ* regeneration is feasible.

Reusability of Selected Resin

For this experiment, 5% NaCl in MeOH/deionized water (7 : 3) was selected because it regenerated PFA300 at the fastest rate. The performance of the regenerated PFA300 was investigated over six cycles. Figure 4 shows the reusability efficiency of PFA300 for PFOS adsorption. The first cycle obtained the highest removal efficiency (over 99%) because the adsorbent was fresh. The removal efficiency dropped slightly from 99 to 97% in subsequent cycles. As the removal efficiency was still high after six cycles, PFA300 has high reusability.

CONCLUSIONS

The adsorption of PFOS on anion exchange resins by PFA300, Dow Marathon A, IRA400, PFA400, PFA444, and GAC were investigated. All adsorbents were well fitted by the Freundlich model, with high correlation coefficients (R^2). Among the adsorbents, PFA300 had the highest PFOS adsorption capacity and fastest adsorption rate. The resin functional groups affected PFOS adsorption. Moreover, PFA300 was also successfully regenerated by NaOH and NaCl in MeOH/deionized water (7 : 3). The solution of 5% NaCl in MeOH/deionized water (7 : 3) showed the fastest regeneration rate. The reusability of regenerated PFA300 was high for PFOS removal for up to six cycles. Based on these results, PFA300 has the highest adsorption capacity, a high regeneration efficiency, and high reusability. Therefore, PFA300 is an effective material for removing PFOS in aqueous solution.

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