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Adsorption of perfluorooctanoic acid (PFOA) onto anion exchange resin, non-ion exchange resin, and granular-activated carbon by batch and column

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ABSTRACT

Perfluorooctanoic acid (PFOA) has become a global concern due to its toxicity and persistent nature. It has been detected in water environments in recent years. Therefore, removal techniques are essential for minimizing human health risks and environmental impacts. The main objective of this study is to investigate the efficiency of adsorbents in the removal of batch and column PFOA. Batch adsorption experiments were conducted to study four adsorbents (PFA300, Dow Marathon A, XAD4, and GAC). The equilibrium adsorption data fitted well to the *Freundlich* isotherm for all adsorbents. PFA300 exhibited the maximum adsorption capacity (*Freundlich* K_f value = 117). The continued removal of PFOA was conducted by column. PFA300 exhibited the best performance over the longest duration of operation. The Yoon–Nelson model was employed to predict the half-saturation times of all adsorbents. The adsorbents were tested for regeneration. PFA300 and XAD4 yielded high regeneration percentages. Based on the results, PFA300 was the most effective material for removing PFOA in water and wastewater because it exhibited the highest adsorption capacity, the longest duration of operation, and the highest PFOA recovery percentage.

Keywords: Adsorption; Anion exchange resin; GAC; PFOA and regeneration

1. Introduction

Perfluorooctanoic acid (PFOA) has been widely used as a surfactant in industry, especially in the fields of polymer synthesis, photolithography, and the fabrication of fire retardants, carpet cleaners and paper coatings [1–3]. PFOA is a bio-accumulative and persistent organic pollutant that poses potential harm to humans [4]. PFOA has been detected in wastewater, surface water, groundwater, and tap water throughout the world [5–8]. High concentrations of PFOA compounds are frequently detected in the effluents of industrial wastewater treatment plants [9–10].

Conventional treatment techniques are ineffective for treating PFOA. Thus, alternative treatment methods for the removal of PFOA are required to minimize their adverse effects on human health and the environment. Existing research has focused on decomposition by chemical approaches that involve strict temperature or pressure conditions, such as sonochemical degradations [11], reduction with

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zero-valent iron in subcritical water [12], and photo catalysis using various catalysts [13]. However, these techniques have certain limitations because they require high energy and/or are interfered by other compounds in wastewater [14]. The adsorption process is an economical and effective technique for removing pollutants from water and wastewater [15]. Conventional adsorbents, such as activated carbons, are utilized by some PFOA manufacturers to remove PFOA from wastewater. Because the adsorption capacities of activated carbon are minimal [14,15], PFOA has been discharged from treatment systems to water environments. Therefore, further examination of highly effective materials for the adsorption of PFOA is required. The amount of published data on the continued removal of PFOA using anion exchange resin, non-ion exchange resin, and granular activated carbon (GAC) in column mode remains negligible. Therefore, the results of this study are critical to the implementation of practical PFOA removal.

The main objective of this study was to identify the effectiveness of two anion exchange resins, one non-ion exchange resin, and GAC for the removal of PFOA by batch and column experiments. The regeneration of adsorbents was conducted after all adsorbents reached a breakthrough point.

2. Material and methods

2.1. Chemicals and adsorbents

PFOA (95%) and other chemicals, such as methanol (LC/MS grade) and acetonitrile (LC/MS grade), were purchased from Wako Chemicals (Japan). Two types of anion exchange resins were employed in this study. Resins coded as PFA300 and Dow Marathon A were obtained from the Purolite Company (Japan) and Dow Chemical (Japan), respectively. The non-ion exchange resin was XAD4 (Sigma-Aldrich, Japan). Filtrasorb 400 (GAC), which was purchased from Dow Chemicals (Japan), was also used in this study. The resins were washed with ultrapure water and methanol to remove dirt and PFOA. They were washed with ultrapure water second time to remove any remaining methanol and were subsequently dried at 50°C to obtain a constant weight. The GAC was washed several times with room-temperature ultrapure water and subsequently washed with ultrapure water at a temperature of 80°C for 2 h to remove impurities. After drying at 105°C for 48 h, the GAC was crushed and sieved through mesh sizes ranging from 1.0 to 1.4 mm. The surface areas of the GAC ranged from 900 to 1,100 m^2/g and the diameters ranged from 0.25 to 0.50 mm. The total pore volume was 0.61 cm^3/g and the pore-size distributions of the macropores, mesopores, and micropores were 0.04, 0.09, and 0.48 cm^3/g, respectively. The properties of each resin are shown in Table 1.

2.2. Adsorption isotherms

Adsorption isotherm experiments were performed with four adsorbents using a bottle-point technique. Adsorbent (1 mg) was placed in 125 mL polypropylene (PP) bottles that contained 100 mL of PFOA in initial concentrations ranging from 0.01 to 1.00 mg/L. Three samples with a replication ($n = 3$) were prepared for each concentration. The thermo shaker (EYELA-NTS4000) was set at 120 rpm and 25°C and shaken for 96 h. To establish a control, each concentration of PFOA was added to PP bottles without adsorbents. After shaking, the adsorbent was immediately separated from the sample and the sample was diluted in 40% acetonitrile. The samples were analyzed by high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS).

2.3. Column experiment

The continued removal of PFOA was performed using a fixed-bed column. The diameter of the column was 2 cm and the length of the column was 30 cm. All of the equipment, including the column, PP tube, mesh, and tank, were rinsed with methanol and

Table 1
Physical properties of anion exchange resins and non-ion exchange resin

Type	Adsorbent	Matrix	Functional group	Diameter (mm)
Anion exchange resin	PFA300	Polystyrene crosslinked DVB	$R–(CH_3)_2(C_2H_4OH)N^+$	0.56
	Dow Marathon A	Styrene-DVB	$R–(CH_3)_3N^+$	0.58
Non-ion exchange resin	XAD4	Macroreticular crosslinked aromatic polymer	–	0.35–1.18

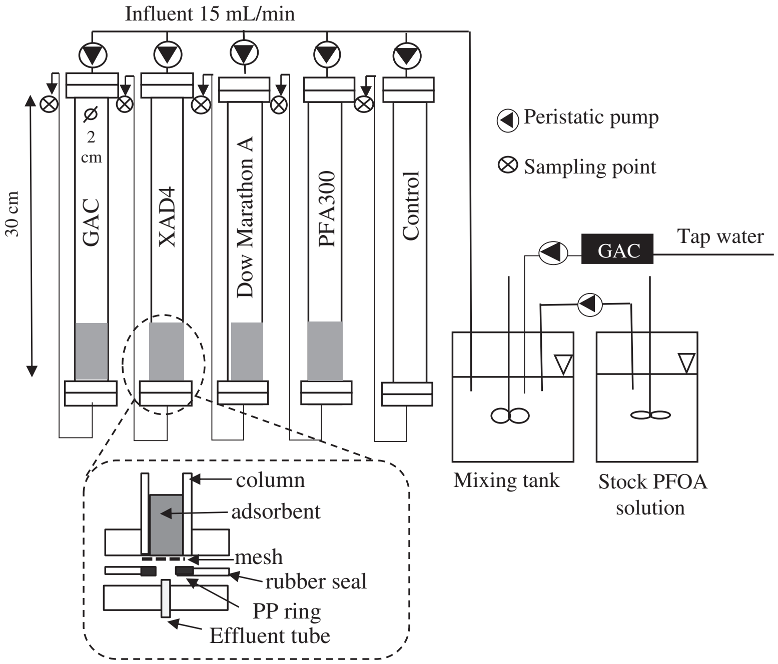

Fig. 1. Schematic of the experimental arrangement for PFOA removal in the column experiments.

ultrapure water prior to beginning the experiment. Mesh was placed at the top and bottom of the column to prevent adsorbent loss. Twenty cm^3 of adsorbent was placed in each column. As a control unit, one column was run without adsorbent added. The experimental arrangement of the column is shown in Fig. 1. Prior to beginning the experiment, methanol was fed into the column to remove the PFOA; ultrapure water was subsequently fed into the column to remove dirt and the remaining methanol. Each column was filled with ultrapure water for 24 h to ensure that all of the entrapped air bubbles in the adsorbents were released. Tap water, which was passed through the GAC to remove chlorine residue, was pumped to the mixing tank. In the mixing tank, a PFOA concentration of 5 μg/L was fed into each column at 15 mL/min. The total operation was completed in 117 days. Column studies were terminated when the PFOA removal efficiency of all of the columns reduced to 90%. To measure the PFOA removal, effluent samples (50 mL) were collected every three days from each column in the PP tube. A PresepC-Agri (C_{18}) cartridge (Wako, Japan) was used to concentrate the PFOA in the samples. The cartridges were conditioned by 10 mL of methanol and 2 × 10 mL of ultrapure water prior to loading the samples into the cartridges. They were dried for 1.5 h by manifold vacuum. The samples in the dried cartridges were eluted with 2 × 2 mL methanol and 2 mL acetonitrile into a PP tube. The eluted samples were dried by N_2 gas prior to reconstitution with 1 mL of 40% acetonitrile in ultrapure water. The PFOA concentration was analyzed by HPLC/MS/MS. Effluent concentrations were periodically measured by HPLC/MS/MS and breakthrough curves were predicted by the Yoon–Nelson model.

2.4. Regeneration of adsorbents

The continued removal of PFOA by column was stopped when all of the adsorbents reached a breakthrough point (90%). Prior to beginning the regeneration, each column was washed with ultrapure water at 15 mL/min for 2 h. Generally, anion exchange resins are regenerated by high concentrations of NaCl and NaOH. However, because PFOA exhibits hydrophobic properties, it is soluble in organic solvents. Deng et al. [16] discovered that perfluorooctane sulfonate (PFOS)-adsorbed anion exchange resin was successfully regenerated by a mixture of 1% NaCl and 70% methanol. Because PFOA exhibits properties similar to PFOS, a similar regeneration solution was applied in this study. Thus, the ratio of methanol/ultrapure water (7:3) was employed in this study. The amount of NaCl was increased to 5% for faster regeneration. Anion exchange resins (PFA300 and Dow Marathon A) were generated with 5% NaCl in methanol/ultrapure water (7:3). Using 100% methanol, XAD4 exhibited a high PFOS recovery percentage [17]. In other studies, organic solvent was also successful for GAC regeneration [18,19]. Therefore,

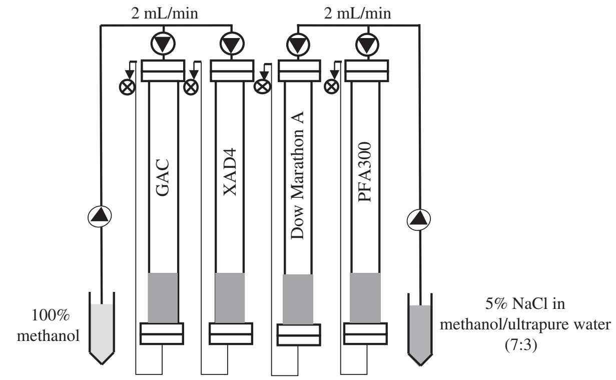

Fig. 2. Experimental setup for regeneration of adsorbents.

non-ion exchange resin (XAD4) and GAC were generated with 100% methanol. The flow rate of the regenerant was 2 mL/min. Regenerated samples were collected and diluted in 40% acetonitrile and analyzed by HPLC/MS/MS. The experimental arrangement is illustrated in Fig. 2.

2.5. HPLC-electrospray tandem mass spectrometry

Ten µL of extract was injected into a 2.1 × 100 mm (5 µm) Agilent Eclipse XDB-C18 column. The mobile phase consisted of (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 of the mobile phase (B) began at 30% and subsequently increased to 45% after 1 min and to 60% after 8 min. The percentage increased to 90% after 8.5 min and was maintained at this concentration for 6.5 min; it subsequently decreased 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 an electrospray ionization negative mode. The analyte ion was monitored using a multiple-reaction monitoring mode with a retention time of 3.4 min. The calibration curves for quantification consisted of seven points ranging from 0.01 to 10 µg/L. The determination coefficient (R^2) for the linear calibration curve exceeded 0.99. The instrumental detection limit and instrumental quantification limit were 0.01 and 0.02 µg/L, respectively. The recovery percentages were calculated by spiking the normal PFOA and surrogate standard ($^{13}C_4$-PFOA) in the duplicated samples. The recovery percentages of normal PFOA and $^{13}C_4$-PFOA exceeded 98%.

3. Results and discussion

3.1. Adsorption isotherms

The adsorbents selected in this study are generally employed for water and wastewater treatment. The shaking duration of the isotherm experiment is 96 h to ensure that all adsorbents attain their equilibrium concentrations. The adsorption capacity of the anion exchange resins with different concentrations (in the range of 0.01–1.00 mg/L) of PFOA was determined by fitting the resulting values to the *Freundlich* model. The *Freundlich* isotherm is utilized to describe the adsorption solutes from a liquid-to-solid surface. It is also widely used to describe the adsorption processes of heterogeneous surfaces of many compounds [20], which is defined by following equation:

$$q_e = K_f C_e^{1/n} \tag{1}$$

where K_f (mg/g)/(mg/L)$^{1/n}$ is the *Freundlich* adsorption constant or capacity factor and n is the *Freundlich* exponent that provides a measure of adsorption intensity. If $n = 1$, the partition between the two phases is independent of concentration and the isotherm becomes linear. q_e (mg/g) is a concentration of the adsorbate on the adsorbent, whereas C_e (mg/L) is an equilibrium concentration of the adsorbate.

All adsorbents fitted well to the *Freundlich* isotherm ($R^2 = 0.97$–0.98). The established *Freundlich* constants are listed in Table 2.

K_f is the *Freundlich* constant in relation to the adsorption capacity. Among the four adsorbents used in this study, PFA300 exhibited the highest adsorption capacity followed by Dow Marathon, GAC, and XAD4. Anion exchange resins (PFA300 and Dow Marathon A) exhibited better performance for the adsorption of PFOA than the non-ion exchange resin and GAC. Because PFOA is present as an anion in aqueous solution, the effective adsorbent method is anion exchange. PFA300 contains an ethanol group (–C_2H_4OH) in a functional group, causing PFA300 to become more hydrophilic and possess a more open structure [16] than Dow Marathon A; this results in a

Table 2
Freundlich isotherm constants for the adsorption of PFOA onto adsorbents

Adsorbent	K_f	n	R^2
PFA300	117	1.04	0.98
Dow Marathon A	93	1.13	0.97
XAD4	18	1.37	0.98
GAC	40	1.37	0.97

Note: K_f (mg/g)/(mg/L)$^{1/n}$.

higher diffusion of PFOA molecule into the anion exchange sites. In this study, XAD4 and GAC yield comparatively higher *Freundlich* exponents (*n*) than anion exchange resins; *n* is an indicator of non-linearity of the *Freundlich* curve. Non-linearity can occur for many reasons, including the heterogeneity of the adsorption site and the sorbate–sorbate interactions. The reason for higher *n* for XAD4 and GAC may be the heterogeneity of the adsorption site, which is higher than the heterogeneity of the anion exchange resins.

3.2. Column experiment

Fig. 3 displays the removal efficiency of PFOA against operation time. Different types of adsorbents, anion exchange resins, non-ion exchange resins, and GAC were tested in this study. The breakthrough point was set at 10% of the influent concentration (C_0), which was 0.5 μg/L. The flows through columns were continued until the PFOA concentration of all detected column effluents exceeded 0.5 μg/L. The removal efficiency of PFOA decreased in the following order: PFA300 > XAD4 > GAC > Dow Marathon A. At 90% removal, PFA300 exhibited the best performance over 111 operation days, whereas XAD4, GAC, and Dow Marathon A performed for 60, 51, and 30 operation days, respectively. At 99% removal efficiency, PFA300 exhibited the highest performance for 68,040 bed volumes or 1,361 L. At a 90% breakthrough point, PFA300 demonstrated the largest amount of treated water (119,880 bed volumes or 2,398 L), whereas XAD4 (68,040 bed volumes or 1,361 L), GAC (55,080 bed volumes or 1,102 L), and Dow Marathon A (32,400 bed volumes or 648 L) demonstrated the second, third, and fourth highest amounts of treated water, respectively.

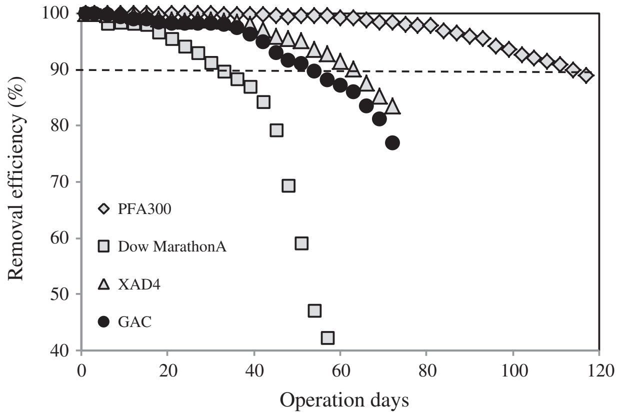

Fig. 3. Removal efficiencies of PFOA with operation time (117 days).

The column adsorption process requires a prediction of the breakthrough curve for the effluent [21]. Yoon and Nelson developed a relatively simple model. The model is based on the assumption that the rate of decrease for the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [22–24]. The half-saturations of five anion exchange resins were predicted by the Yoon–Nelson model. The Yoon–Nelson equation for a single component system is expressed as follows [25]:

$$\frac{c_t}{c_0 - c_t} = \exp\,(k_{YN}t - \tau k_{YN}) \tag{2}$$

The linearized version of the Yoon–Nelson model can be expressed as:

$$\ln\left(\frac{c_t}{c_0 - c_t}\right) = k_{YN}t - \tau k_{YN} \tag{3}$$

where k_{YN} is the rate constant (1/day), τ is the time required for a 50% adsorbate breakthrough (day), and C_t and C_0 are the effluent and influent concentrations (μg/L), respectively. t is the breakthrough (sampling) time (day). The values of the correlation coefficients (R^2), k_{YN}, and τ are displayed in Table 3. The constant k_{YN} decreased with a decrease in the 50% breakthrough time. The performance of each column can be described by the Yoon–Nelson model, which is based on correlation coefficients ranging from 0.94 to 0.98. The theoretical prediction of the breakthrough curves for all of the adsorbents used in this study was demonstrated by the calculation of k_{YN} and τ, as depicted in Fig. 4. The longest half-saturation time can be expected from PFA300, which exhibited the highest τ value, followed by XAD4, GAC, and Dow Marathon A.

3.3. Regeneration of adsorbents

Generally, adsorbent is regenerated onsite. Anion exchange resins (PFA300 and Dow Marathon A) were regenerated by 5% NaCl in methanol/ultrapure water

Table 3
Parameters of Yoon–Nelson model for PFOA column adsorption

Adsorbent	τ (days)	k_{NY} (1/days)	R^2
PFA300	142.9	0.06	0.98
Dow Marathon A	57.5	0.09	0.94
XAD4	94.3	0.07	0.98
GAC	87.7	0.07	0.97

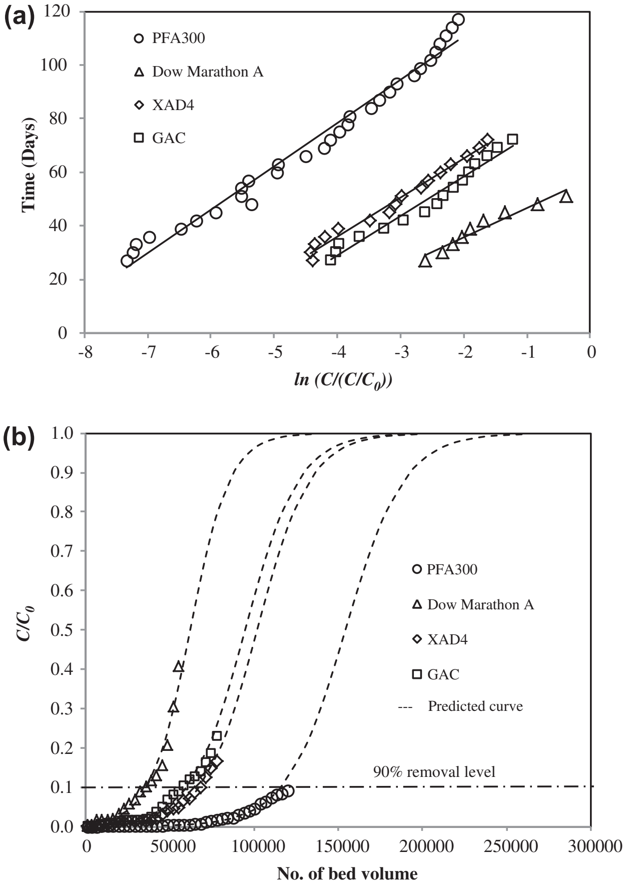

Fig. 4. (a) Linear plot of time vs. ln $(C/(C/C_0)$ and (b) comparison of the observed and predicted (dotted line) breakthrough curves of PFOA adsorption in columns with different adsorbents.

(7:3), whereas XAD4 and GAC were regenerated by 100% methanol. Fig. 5 shows the PFOA recovery percentages of the adsorbents in the column experiment. For five bed volumes of regeneration solution, XAD4 yielded the largest recovery percentages of PFOA above 90% followed by Dow Marathon A (50%), PFA300 (30%), and GAC (1%). The regeneration solution was fed until constant PFOA recovery was achieved. PFOA was recovered from XAD4 (95%), PFA300 (93%), GAC (67%), and Dow Marathon A (63%), respectively. Non-ion exchange resins and anion exchange resins are manufactured via similar processes. The primary difference between the two resins is that an anion exchange resin contains charged functional groups. PFOA is adsorbed on the outer surface of a non-ion exchange resin. The bonding forces between the adsorbent and the adsorbate are usually weak. Regeneration of the non-ion exchange resin can be accomplished by simple nondestructive means, such as solvent washing, which provides the potential for solute recovery [26,27]. Thus, the fastest desorption of PFOA was demonstrated for XAD4. Senevirathna et al. [17] also discovered high recovery percentages of PFOS from XAD4 using 100% methanol. In this study, 100% methanol was also used to regenerate GAC. The maximum percentage recovery for GAC was 67%. It was difficult to regenerate by organic solvent under normal conditions due to the strong interaction between the PFOA and GAC surfaces. PFOA contained a long chain of C-F, which exhibited hydrophobic properties. Nemethy and Scherage [28] reported that hydrophobic compounds adsorbed more intensely on carbon. Another possible reason for this occurrence is pore diffusion. Because PFOA can diffuse into the deep pores of GAC, the desorption of PFOA into organic solvents is difficult and time-consuming. PFA300 demonstrated the highest performance for the continued removal of PFOA over 117 days and a high PFOA recovery percentage, which was more feasible for onsite regeneration. Thus, PFA300 was a suitable alternative material for PFOA removal in water and wastewater.

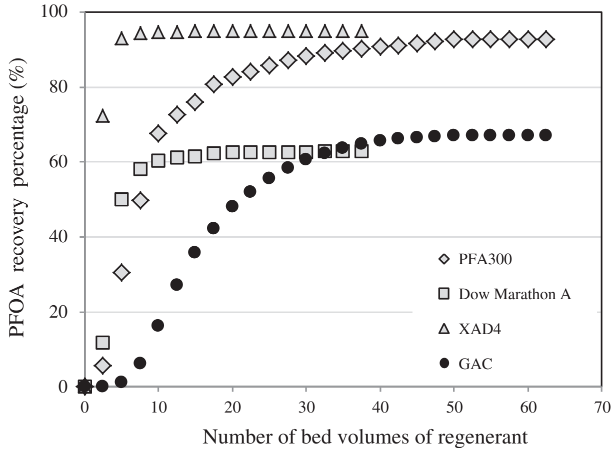

Fig. 5. PFOA recovery percentages of adsorbents in the column experiment.

4. Conclusions

For the adsorption isotherms, all adsorbents fitted well to the *Freundlich* model with high correlation coefficients (R^2). PFA300 exhibited the highest adsorption capacity among all of the adsorbents in this study. The column test demonstrated the best performance of PFA300 for the removal of PFOA with the longest duration of operation. The half-saturations ($C/C_0 = 0.5$) of the columns were predicted using the Yoon–Nelson model. High recovery percentages of PFOA were demonstrated for PFA300 and XAD4. PFA300 exhibited the highest adsorption capacity, the longest duration of operation, and the highest recovery of PFOA, suggesting that PFA300 is a suitable material for PFOA removal in aqueous solutions.

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