Sorption of Perfluorooctanoic Acid, Perfluorooctane Sulfonate and

Perfluoroheptanoic Acid on Granular Activated Carbon

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Abstract

The sorption of perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluoroheptanoic acid (PFHpA) on granular activated carbon (GAC) was characterized and compared to explore the underlying mechanisms. Sorption of the three perfluoroalkyl acids (PFAAs) on GAC appeared to be a rapid intra-particle diffusion process, which were well represented by the pseudo-second-order rate model with the sorption rate following the order PFOS > PFOA > PFHpA. Sorption isotherm data were well fitted by the Freundlich model with the sorption capacity (K_f) of PFOS, PFOA and PFHpA being 4.45, 2.42 and 1.66 respectively. This suggests that the hydrophilic head group on PFAAs, i.e. sulfonate vs carboxylic, has a strong influence on their sorption. Comparison between PFOA and PFHpA revealed that hydrophobicity could also play a role in the sorption of PFAAs on GAC when the fluorocarbon chain length is different. Analyses using Attenuated Total Reflection (ATR)-Fourier Transform Infrared (FTIR) spectroscopy suggested possible formation of a negative charge-assisted H-bond between PFAAs and the functionalities on GAC surfaces, including non-aromatic ketones, sulfides, and halogenated hydrocarbons.

Keywords: Perfluorinated alkyl substances (PFAAs); Granular activated carbon (GAC); Attenuated Total Reflection -Fourier Transform Infrared (ATR-FTIR); Sorption isotherm; Sorption kinetics

1. Introduction

Perfluoroalkyl acids (PFAAs), such as perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluoroheptanoic acid (PFHpA), have been widely used in industrial and consumer products over the past 50 years. The chemical structure of each PFAA includes a hydrophobic alkyl tail in which all hydrogens are replaced by fluorine and a hydrophilic acid head group. They are thus relatively soluble in water, and, because the carbon-fluorine bond is the strongest covalent bond, they are extremely stable. These stable chemical characteristics enable a wide range of applications, such as carpet and fabric surface protection, and fire-fighting agents (Moody and Field, 2000; Houtz and Sedlak, 2012). PFAAs have been detected all over the world in various environmental matrices, including soils (Sun et al., 2011; Zareitalabad et al., 2013), sediments (Ferrey et al., 2012), surface water (Cheng et al., 2008; Brede et al., 2010; Hu et al., 2011), and groundwater aquifers (Kunacheva et al., 2012; Post et al., 2012b). PFOA, PFOS and PFHpA are among the most commonly detected PFAAs in the water environment (Clarke et al., 2010; Lu et al., 2011; Cai et al., 2012a; Cai et al., 2012b).

PFAAs have been found to be bio-accumulative and toxic (Pistocchi and Loos, 2009; Houtz et al., 2013). This, in combination with their environmental persistence, causes potential hazardous effects on ecological receptors and human health (Hart et al., 2008; Bao et al., 2011; Liu et al., 2011). PFOS has been included in the Stockholm treaty on persistent organic pollutants (POPs) due to its persistence, bioaccumulation potential and toxicity (Kwok et al., 2010; Beskoski et al., 2013). The U.S. Environmental Protection Agency (USEPA) has placed PFOS and PFOA on the Contaminant Candidate List 3 (CCL 3) and on the Unregulated Contaminant Monitoring Rule 3 (UCMR 3) List (Post et al., 2012a). The USEPA Office of Water has also established Provisional Health Advisories for PFOS (0.2 µg/L) and PFOA (0.4

µg/L) based on a risk assessment performed by the European Food Safety Authority (Clarke et al., 2010; Kwok et al., 2010; Zhang et al., 2011; Shaw et al., 2013).

Because of their high chemical stability, PFAAs have not been shown to be effectively degraded using biological or chemical treatment technologies, and thus physical sorption is the primary option currently available for their removal from water. Activated carbon (AC) has a long history in environmental applications as a sorbent for purifying drinking water and wastewater (Karanfil and Kilduff, 2000; Li et al., 2002), including for PFAAs removal (Yu et al., 2009; Li et al., 2012). AC exhibits superior adsorptive capacity for organic pollutants in aqueous solution because of its porous structure, large surface area and diverse surface chemistry (Rozwadowski et al., 1979; Qu et al., 2009). It has been demonstrated in numerous cases that AC adsorption is an effective and economical method to remove polar organic pollutants from water (Tzabar and Grossman, 2012; Qin et al., 2014).

Sorption of PFOS and PFOA on AC by long-term batch experiments have shown high sorption capacities ranging from 60 to 200 mg of PFAA per gram of AC (Yu et al., 2009; Senevirathna et al., 2010b). While it is believed that sorption capacity is mainly controlled by the sorbent properties, sorption kinetics is influenced by the properties of both the sorbents and the sorbates (Ahrens et al., 2011; Bao et al., 2014). It has been shown that the kinetics of PFAA sorption onto porous sorbents was closely related to the particle diameter and pore size of sorbents (Dubinin, 1983; Senevirathna et al., 2010b). It has also been shown that the hydrophobic interactions between the porous sorbents and PFOS are much stronger than the electrostatic repulsion that governs the sorption of PFOS (Senevirathna et al., 2010a).

Sorption of PFAAs was also influenced by solution chemistry and other factors in addition to the properties of the sorbent and sorbates. The sorption efficiencies of PFOS on black

carbon decreased with increasing solution pH and $[Ca^{2+}]$ (Wang and Shih, 2011). Co-existing natural organic matter greatly reduces the sorption capacity of PFOS on powdered activated carbon (Zhou et al., 2010b; Zareitalabad et al., 2013). It was also found that the organic carbon content rather than mineral content dominates the sorption of PFAAs in sediment (Ahrens et al., 2011).

In this study, we investigated the sorption of PFOS, PFHpA, and PFOA on granular activated carbon (GAC) with both sorption isotherm and kinetics examined. Conducting both isotherm and kinetic experiments for three model PFAAs that are closely related in molecular structures in one study under consistent conditions enabled systematic comparisons to probe the mechanisms of PFAA sorption on GAC.

2 Materials and Methods

2.1 Materials

PFOS ($\geq 98\%$ purity), PFOA ($\geq 96\%$ purity), PFHpA (99% purity) and GAC were purchased from Sigma-Aldrich (St. Louis, MO, USA). Calcium chloride, sodium hydroxide, hydrochloric acid, and ammonium acetate of analytical grade, and methanol and acetonitrile of HPLC grade were purchased from Fisher Scientific (New Jersey, USA).

2.2 Characterization of GAC

The property of the GAC used in this study, including the surface area, pore volume, and pore size distribution, was characterized using N_2 sorption isotherm (Autosorb-IQ3, Quantachrome Corp., Boynton, FL). The surface area of the GAC is $534.44 \pm 1.5 \text{ m}^2/\text{g}$ and the

other properties are summarized in Table 1. Gas adsorption was used to measure the pore size distribution of GAC particles.

2.3 Sorption rates

Prior to the sorption experiments, the GAC was soaked in Milli-Q water for 24 h, dried in an oven at 103°C for 48 h, and then stored in a desiccator until use. All sorption experiments were conducted in 50 mL polypropylene conical tubes (FALCON, Japan) containing 10.0 mg of GAC and 50 mL of a solution containing PFOS, PFOA, or PFHpA with each at an initial concentration of 10 mg/L. Control samples without GAC added were also prepared with the same PFAA solutions. The solutions were prepared by diluting 500 mg/L stock solutions in methanol with Milli-Q water, and the methanol volume fraction in each solution was maintained at less than 0.02 to avoid possible co-solvent effects. The pH of the solution was adjusted to 5.0 by adding 0.01M HCl or 0.01M NaOH solution. Batch experiments were conducted at 25 ± 1 °C in an incubator shaker. Triplicate tubes were sampled at predetermined time intervals, and the solution was centrifuged at 8000 g for 10 minutes. A 1-mL aliquot of the supernatant was mixed with 2 mL Milli-Q water, and then filtered through a GF/B glass membrane (0.45 µm; Whatman, Inc., United States). The initial 1.5 ml of the filtrate was discarded to reduce the potential effect of membrane adsorption, and then 0.5 ml of the filtrate was collected and diluted with methanol to 1 ml for subsequent analysis of PFAA concentration. The pH values of the reaction solutions during the sorption process were monitored, and have shown essentially no change.

2.4 Sorption isotherm

All sorption isotherm experiments were conducted in 50 mL polypropylene conical tubes

(FALCON, Japan), each containing 10.0 mg GAC and 50 mL of a solution of PFOS, PFOA, or PFHpA at a concentration ranging from 0.5 mg/L to 10 mg/L (pH = 5.0, adjusted by 0.01 M HCl and NaOH solutions without a pH buffer). Control samples without GAC added were also prepared with the same PFAA solutions. All tubes were incubated in a shaker incubator at 25 °C and 150 rpm for 144 h to reach sorption equilibrium. After incubation, the solution was centrifuged at 8000 g for 10 minutes, and 1 mL of the supernatant was sampled and mixed with 2 mL Milli-Q water, and then passed through a GF/B glass membrane (0.45 µm, Whatman, Inc., United States). The initial 1.5 ml of the filtrate was discarded to reduce the potential effect of membrane adsorption, and then 0.5 ml of the filtrate was collected and diluted with methanol to 1 ml for subsequent analysis of PFAA concentration.

2.5 Analytical method

The concentrations of PFAAs were determined using an HPLC-MS/MS system comprising a Waters 2690 HPLC coupled to a Waters Micromass Quattro tandem mass spectrometer (Waters, Milford, MA). The separation was performed on an Ascentic C18 reversed phase column (25 × 4 mm, 5 µm, Supelco, St. Louis, MO). The mobile phase consisted of 2 mM ammonium acetate water solution (A) and methanol (B) at a flow rate of 0.4 mL/min. The gradient program lasted 17 min and programmed as follows: 50% B was increased linearly to 90% in 3 min, and hold 90% till 14 min, and then reduced to 50% at 14.1 min, and held for additional 3 min. The electrospray ionization in a negative mode was used with the following parameters: capillary voltage 20 V, cone voltage 11 V. Desolvation temperatures was at 300 °C, and the source block at 100 °C. Nitrogen (Airgas, > 99.999% purity) was used as the nebulizer and drying gas at the flow rates of 34, and 198 L/hour, respectively. Quantitative analysis was

performed using selected reaction ion monitoring for PFAAs: transition $m/z = 413 > 369$ for PFOA, $m/z = 499 > 80$ for PFOS, $m/z = 363 > 319$ for PFHpA. Five point calibration curves were generated using standard PFAA concentrations ranging from 0.01 mg/L to 10 mg/L.

2.6 FTIR spectroscopy and functional group analysis

ATR-FTIR spectra were collected on selected GAC samples with or without sorption of a PFAA to probe the interactions between PFAAs and GAC. The wet samples were dried in a fume hood at 25 °C until constant weight, grinded, and then passed through a 1-mm sieve. The infrared spectra were measured at room temperature using a 330 Thermo Nicolet FTIR spectrometer equipped with a diamond horizontal attenuated reflectance resonance device (ATR-FTIR), for scanning between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} against an air background. The instrument was purged with nitrogen gas to water vapor and CO_2 .

2.7 Modeling

The sorption amount of PFAA on GAC was calculated using the following equation: $q_t = (C_c - C_t) \times V \times M / m$, where q_t is the sorption amount of PFAAs at time t ($\mu\text{g/g}$), C_t is the PFAA concentration in liquid phase at time t ($\mu\text{mol/L}$), C_c is the PFAA concentration ($\mu\text{mol/L}$) in the corresponding control sample (without GAC added) at time t , V is the volume of the reaction solution (L), M is the molar mass (g/mole) and m is the mass of sorbent (g).

Two adsorption isotherm models, i.e. Langmuir and Freundlich, in their linear forms were employed to model sorption equilibriums. The pseudo-first order and pseudo-second order models and the Weber and Morris intra-particle diffusion (IPD) model were used to describe the adsorption rates. The details of these models are provided in Supporting Information.

3 Results and Discussion

3.1 Sorption rate

The sorption data shown in Figure 1 indicates a similar sorption trend among the three PFAAs, but their kinetic profiles were quite different. The sorption rate of PFOS was the highest, with the sorbed amount reaching 15.8 mg/g at 24 h, while that of PFOA and PFHpA was respectively 10.3 mg/g and 7.5 mg/g at 24 h. The sorption equilibrium of PFOS was reached after 24 h, while that for PFOA and PFHpA was about 120 h. These were different from an earlier report about PFOS sorption on GAC (Senevirathna et al., 2010b), in which the sorption equilibrium reached within a very short time (< 4 h) on F400 GAC. The different kinetics may arise from the different characteristics of the granular activated carbons. F400 GAC used as the sorbent in the earlier study has a surface area of $900\text{--}1100\text{ m}^2\text{ g}^{-1}$, while as shown in Table 1 the GAC used in this study has a surface area of $534\text{ m}^2\text{ g}^{-1}$. It has been shown that the particle surface area strongly influences the sorption rate of PFAAs onto porous sorbents (Appleman et al., 2013). In addition, the pore volumes and surface chemistry would also strongly influence sorption behaviors of different GAC materials.

Despite the same carbon chain length of PFOA and PFOS, the sorption of PFOS is apparently greater in both rate and amount. This suggests that the hydrophilic head group on PFAAs has a strong influence on their sorption. The sorption of PFOA is somewhat greater than PFHpA while both reached equilibrium within the same timeframe. The difference in the sorption of PFOA and PFHpA was probably attributed to their difference in hydrophobicity. While earlier studies involving PFOA and PFOS have indicated the importance of electrostatic interactions in their sorption to GAC (Deng et al.; Ochoa-Herrera and Sierra-Alvarez, 2008; Yu et al., 2009; Deng et al., 2012), the study here comparing PFOA and PFHpA suggests that

hydrophobic effect could also play a role when the fluorocarbon chain length differs.

In an attempt to further understand the factors controlling sorption rates, the kinetic data shown in Figure 2 was fitted with different rate models, including the pseudo first-order model, the pseudo second-order model (Ho and McKay, 1998), and the intra-particle diffusion model (Kannan and Sundaram, 2001) with details provided in Supporting Information. The parameters obtained through model fitting are shown in Table 2. According to the estimated correlation coefficient (R^2), the pseudo second-order rate model provided the best fit for the sorption rate data over the entire period of experiment ($R^2 = 0.99$), and the model fit was illustrated in Figure S2. The adsorbed amount at equilibrium, q_e , obtained through data fitting were 12.6 mg/g for PFOA, 15.3 mg/g for PFOS, and 9.9 mg/g for PFHpA, which are close to the experimental data (12.8mg/g for PFOA, 15.8 mg/g for PFOS, 10.5 mg/g for PFHpA, Figure 1).

According to the pseudo-second order rate equation (Eq 2 in Supporting Information), the rate constant k_2 is inversely related to the sorption rate, and it is theoretically determined solely by the property of the sorbate for a given sorbent. As seen from the fitted k_2 values in Table 2, the sorption rate on GAC follows the order PFOS > PFOA > PFHpA. The pseudo-second order rate model was based on an assumption that the rate-limiting step is chemisorption involving sharing or exchange of electrons between sorbent and sorbate (Sharma and Forster, 1996). As such, the better fit of the pseudo-second order rate model found in this study may suggest the occurrence of electronic interactions between PFAAs and GAC. Such interactions can be justified by invoking a theory recently proposed by Xing and coworkers (Li et al., 2013), negative charge-assisted H-bond, (-)CAHB, as discussed later. The fit of the data to the pseudo-first order rate model was not as good as the pseudo-second order rate model (Table 2). A close examination revealed that the pseudo-first order rate model captured the initial sorption period (<

12 h) better than the latter period (Figure S1). This may imply that the electronic interaction between PFAAs and GAC may take effect after the initial sorption period when the sorption sites were occupied to certain extent (Zhu et al., 2015).

The intra-particle diffusion rate model also provided a good fit of the data, although not as good as the pseudo-second order rate model (Table 2). Based on the intra-particle diffusion rate model (Eq. 3 in Supporting Information), if q_t and $t^{0.5}$ is linearly correlated and the correlation curve passes through the origin point, it indicates that the intra-particle diffusion of the sorbate is the only process controlling the sorption rate (Viegas et al., 2014). As seen in Figure S3 (Supporting Information), the correlations between q_t and $t^{0.5}$ was highly linear for all PFAAs, but they do not pass the origin point. This suggests that the sorption process was controlled by both surface and pore diffusion with surface diffusion controlling at the earlier stage followed by pore diffusion. The greater slope of the curve for PFOS in Figure S3 reflected its stronger pore diffusion, while the comparison between that of the PFOA and PFHpA suggested that the one-carbon longer fluorocarbon chain also slightly enhanced the pore diffusion of PFOA from the water phase into the solid phase. The lengths of PFOA and PFOS, and PFHpA were calculated to be in the range of approximately 7–10 Å (Table S1), and the average pore diameter of activated carbons is approximately 25 Å (Table 1). Therefore with regard to their sizes, it is possible for PFAAs to diffuse into GAC's inner pores and become sorbed therein.

3.2 Sorption isotherms

The sorption isotherms of PFAAs onto GAC are displayed in Figure 2, and data fitting with the Freundlich and Langmuir models is described in Supporting Information III and the

parameters obtained are summarized in Table 3.

As seen in Table 3, the sorption isotherms were fitted well by both the Freundlich and Langmuir models. For Freundlich model, a higher K value represents a larger sorption capacity while a higher $1/n$ value represents a more homogeneous distribution of the sorption site energy on the sorbent, and as $1/n$ approaches 1 the sorption becomes concentration-independent and the isotherm is linear. The results from Freundlich model fitting indicate that PFOS has a greater sorption capacity, while the sorption site energies are quite homogenous for all three PFAAs with $1/n$ ranging from 0.91 to 0.94. Note that the concentration range (0.5-10 mg/L) is relatively narrow in this study. This concentration range is much higher than those typically found in natural waters (ng - $\mu\text{g/L}$), but may be seen in contaminated areas. In an earlier study, the sorption capacity of activated carbon exhibited great differences between a high concentration range (15–150 mg/L) and a low concentration range (50–400 $\mu\text{g/L}$) (Yu and Hu, 2011).

Unlike the Freundlich model, Langmuir model can illustrate the maximum sorption. The results of Langmuir model fitting indicate that the sorption capacity of PFOS (72.2 ± 19.0 mg/g) was higher than that of PFOA (52.8 ± 17.1 mg/g) and PFHpA (41.3 ± 9.2 mg/g). Although the initial concentrations were close among three PFAAs, the equilibrium concentrations of PFOS were much lower than those of PFOA and PFHpA, implying the greater affinity of PFOS to GAC. A similar trend was observed in earlier studies about the sorption of PFAAs on sediment, activated sludge and organo-montmorillonites (Zhou et al., 2010a; Zhou et al., 2010b).

It is evident in Figure 2 that the sorption isotherm data were nonlinear; suggesting that more than one process affected the sorption and multilayer sorption of PFAAs on GAC is plausible. This is supported by the higher R^2 values of the fits by Freundlich model for the isotherm data and the intra-particle diffusion model for the rate data. Because of the highly

hydrophobic perfluorinated chain of PFAAs, multilayer sorption is considered favorable at higher equilibrium concentrations (Chen et al., 2009; Chen et al., 2011).

3.3 ATR-FTIR spectroscopy

ATR-FTIR spectroscopy of GAC before and after the sorption of PFOA, PFOS or PFHpA was analyzed to probe possible interactions between PFAAs and the functionalities on GAC's surface. ATR-FTIR spectroscopy is a powerful tool to investigate electronic interactions between functionalities including H-bond (Kimber and Kazarian, 2014). All FTIR spectra are displayed in Figure 3 with detailed peak information. As seen in Figure 3a, GAC without PFAA sorption exhibited several distinct functional groups, including non-aromatic halogenated hydrocarbons (586 cm^{-1}), non-aromatic ethers, acetals and epoxides (1496 cm^{-1}), non-aromatic mercaptans and sulfides (1608 cm^{-1} and 1646 cm^{-1}), non-aromatic ketones (2345 cm^{-1}). This is consistent with the understanding that GACs generally contain surface functional groups like carboxyl, lactones, carbonyl and phenolic hydroxyl, etc (Mehta and Flora, 1997; Chen et al., 2012; Singha et al., 2013).

Some ATR-FTIR responses shifted after sorption, indicating electronic interactions during sorption (see Figure 3-B). After the sorption of PFOA, the peak at the 2345 cm^{-1} attributed to non-aromatic ketones shifted to 2321 cm^{-1} . A similar change was also observed after the sorption of the PFOS and PFHpA on the GAC. This is a strong indication that the sorption of PFAAs on GAC involved the C=O bond. The 24 cm^{-1} downshift of C=O band implied hydrogen bonding between the C=O oxygen and the PFAAs. It is reported that when an H-bond ($\text{X-H}\cdots\text{Y}$) is formed the X-H bond will be weakened with $\gamma_{\text{X-H}}$ stretching vibration shifting to lower wavenumber (Tâme Parreira et al., 2007). Likewise, the $\gamma_{\text{X-H}}$ stretching vibration of non-

aromatic sulfides (1646 cm^{-1}) also shifted downward to 1635 cm^{-1} after the sorption of the PFOS
and PFHpA.

As opposed to the blue shifting of $\gamma_{\text{X-H}}$ stretching vibration, the in-plane bending $\delta_{\text{X-H}}$
vibration will shift to a higher wavenumber when an H-bond ($\text{X-H}\cdots\text{Y}$) is formed (Mangolini et
al., 2011; Li et al., 2013). It was the case with the peak at the 524 cm^{-1} ($\delta_{\text{X-H}}$ vibration, non-
aromatic halogenated hydrocarbons) that shifted to 659 cm^{-1} after the sorption of PFHpA. These
ATR-FTIR results corroborates that (-)CAHB played a significant role in the sorption of PFAAs
with non-aromatic ketones, sulfides and halogenated hydrocarbons likely being involved as
hydrogen bond acceptors. The acid dissociation constant (pK_a) of the three PFAAs are shown in
Table S1, and they would be proton dissociated to carry a negative charge at the experiment
condition ($\text{pH } 4.5 > pK_a$). Therefore, negative charge-assisted H-bonds, (-) CAHB, between the
acid groups of PFAAs and the GAC surface functionalities were likely formed. As suggested by
Xing et al (Ni et al., 2011; Sittijunda et al., 2013) in recent studies that such (-) CAHBs are
exceptionally strong and facilitate the sorption of weak acids.

4. Conclusion

The sorption of PFOA PFOS, and PFHpA on granular activated carbon was characterized
in sorption kinetic and isotherm experiments and the data were fitted to different models and
compared. Sorption of the three PFAAs on GAC appeared to be rapid intra-particle diffusion
processes, which were well represented by the pseudo-second-order rate model with the sorption
rate following the order PFOS > PFOA > PFHpA. Sorption isotherm data were well fitted by the
Freundlich model with the sorption capacity (K_f) of PFOS, PFOA and PFHpA being 4.45, 2.42
and 1.66 respectively. This suggests that the hydrophilic head group on PFAA, i.e. sulfonate vs

carboxylic, has a strong influence on their sorption.

ATR-FTIR analyses indicated the presence of a variety of functional groups on the GAC's surfaces, and that negative charge-assisted H-bonds were formed between the acid groups of PFAAs and certain GAC surface functionalities, like non-aromatic ketones, sulfides and halogenated hydrocarbons, which facilitated the sorption of PFAAs.

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Table 1 The property of the granular activated carbon

Total pore volume	0.375 cm ³ g ⁻¹
Macropores (>500 Å)	11.2%
Mesopores (20–500 Å)	26.93%
Micropores (<20 Å)	57.07%
Average pore Diameter	25 Å
Surface area	534 m ² g ⁻¹
Matrix	Stacked layers of fused hexagonal ring of C atoms
Diameter	20-40 mesh

532 Table 2 Parameters from fitting of the sorption rate data with three different kinetic models

PFAA	The pseudo first-order model			The pseudo second-order model		Intra-particle diffusion model	
	$K_1^a / (\text{min}^{-1})$	$q_e^b (\text{mg/g})$	R^2	$K_2^c / (\text{g mg}^{-1} \text{h}^{-1})$	R^2	$K_{id}^d / (\text{g mg}^{-1} \text{h}^{-0.5})$	R^2
PFOA	0.09 ± 0.01^e	12.6	0.95	4.72	0.99	3.82	0.93
PFOS	0.23 ± 0.04	15.3	0.85	0.35	0.99	5.46	0.26
PFHpA	0.10 ± 0.02	9.9	0.83	5.10	0.99	3.12	0.96

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a k_1 is the rate constant of the pseudo-first order sorption rate model (min^{-1})

536 b q_e is the amount adsorbed at equilibrium (mg g^{-1})

c k_2 is the rate constant of the pseudo-second order sorption rate model ($\text{g mg}^{-1} \text{h}^{-1}$)

538 d k_{id} is the intra-particle diffusion rate constant ($\text{g mg}^{-1} \text{h}^{-0.5}$)

e Mean $\pm$ standard deviation

540 R^2 correlation coefficient

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550 Table 3 Parameters of sorption isotherms for PFAAs on GAC fitted by Freundlich or Langmuir model

Sorbate	Freundlich model parameters			Langmuir model parameters		
	K_f^a	$1/n$	r^2	K_l^b	q_m^c	r^2
	$\mu\text{mol}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$			mg L^{-1}	mg g^{-1}	
PFHpA	1.66 ± 0.13^d	0.89 ± 0.04	0.99	0.04 ± 0.01	41.3 ± 9.2	0.99
PFOS	4.45 ± 0.21	0.89 ± 0.04	0.98	0.07 ± 0.02	72.2 ± 19.0	0.99
PFOA	2.42 ± 0.25	0.89 ± 0.06	0.97	0.05 ± 0.02	52.8 ± 17.1	0.97

552 a K_f is Freundlich capacity coefficient constant ($\mu\text{mol}^{(1-1/n)} \text{L}^{1/n} \text{g}^{-1}$)

b K_l is Langmuir affinity coefficient ($\text{mg} \cdot \text{L}^{-1}$)

554 c q_m is monolayer sorption capacity (mg g^{-1}), calculated by the method described in supporting information
part III

556 d Mean $\pm$ standard deviation

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568 Figure1 PFAAs sorption kinetics. Initial PFAAs concentration 10 mg L^{-1} , GAC dosage 0.2 g L^{-1} , pH 5.0,
 570 room temperature. Values are the means of three replicates and error bars are standard deviations.

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Figure 2. Sorption isotherms of PFAAs (0.5-10 mg L⁻¹) on the GAC at pH 4.3 and 25 ± 1 °C. Curve fitting of sorption isotherms was accomplished by OriginPro 9.0 software. The error bars denote the standard deviation of three replicates.

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Figure3. ATR-FTIR spectrums of GAC with or without sorption of a PFAAs under N_2 atmosphere at room temperature (A) and the difference between them (B). The spectra were collected using 64 scans per spectrum at a resolution of 4 cm^{-1} .