



Effect of temperature on the sorption and desorption of perfluorooctane sulfonate on humic acid

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Abstract

Sorption and desorption of perfluorooctane sulfonate (PFOS) on humic acid at different temperatures were studied. It was found that the sorption process could be modeled with power kinetic equation very well, suggesting that diffusion predominated the sorption of PFOS on the humic acid. The sorption capacity was doubled when the temperature increased from 5 to 35°C, and thermodynamics parameters ΔG^0 was calculated to be -7.11 to -5.04 kJ/mol, ΔH^0 was 14.2 kJ/mol, and ΔS^0 was 69.5 J/(mol·K), indicating that the sorption was a spontaneous, endothermic, and entropy driven process. Desorption hysteresis occurred at all studied temperatures which suggested that humic acid may be an important sink of PFOS in the environment.

Key words: perfluorooctane sulfonate; sorption; desorption; temperature; humic acid

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Introduction

Perfluorooctane sulfonate (PFOS) is both an intentionally produced substance and an un-intentional degradation product of sulfonyl-based fluorochemicals. PFOS and its precursors are widely used as surface-active agents in different applications including fire fighting foams, textiles, paper and packaging, coatings, cleaning products, pesticides, photographic industry, semiconductor, hydraulic fluids, and metal plating (UNEP, 2007). PFOS is ubiquitous in environmental phases, including atmospheric particulate, water, sediment, and biotic sample (OECD, 2002; UK Environment Agency, 2004; Higgins et al., 2005; Nakata et al., 2006; Jahnke et al., 2007; Beckera et al., 2008). In the third meeting of the Persistent Organic Pollutants Review Committee of the Stockholm Convention on Persistent Organic Pollutants, PFOS, as well as its salts and perfluorooctane sulfonyl fluoride, have been listed among the Annex A or B of the Convention (UNEP, 2007). This would lead to elimination (Annex A) or severe restriction (Annex B) of the production, use, export and import of these chemicals.

After the global limitation being taken, the PFOS environmental fate has become one of the most important issues due to that this chemical is extremely persistent and difficult to be degraded in natural environment (UK Environment Agency, 2004). Beckera et al. (2008) considered that river sediments constituted a sink of PFOS released from the wastewater treatment plant, while other studies

reported that water or biota was the sink of PFOS rather than the sediment or soil (Sanderson et al., 2002; Nakata et al., 2006). Knowledge of sorption and desorption behaviors would be helpful to better understand this puzzle. Using laboratory batch sorption experiments, Higgins and Luthy (2006) reported the sorption of PFOS increased with increasing total organic carbon (TOC) in sediments. And other studies also demonstrated the significant sorption of PFOS to sediments from field data (Higgins et al., 2005). However, to date, desorption behavior of PFOS has been seldom studied although it is very important to clarify the reversibility of the sorbed chemical on sediment.

Sorption and desorption of organic contaminants in sediment are affected by multiple factors, including the physical properties of water phase (such as, cosolvent, pH) and sediment phase (such as, TOC, iron oxide content), and temperature (ten Hulscher and Cornelissen, 1996). PFOS ($\text{C}_8\text{F}_{17}\text{SO}_3^-$) is an anionic organic compound comprised with a fully fluorinated carbon chain length of C8 and a sulfonyl group, which is expected to behave differently from traditional hydrophobic contaminants since it has both hydrophobic and hydrophilic functionalities (UK Environment Agency, 2004). In previous studies, much attention had been paid to the effects of sediment composition and cosolvent on the sorption of PFOS (Higgins and Luthy, 2006; Johnson et al., 2007; Pan and You, 2010; You et al., 2010). Little knowledge is available about the effect of temperature on the sorption and desorption behaviors of PFOS, although temperature is an important parameter influencing the equilibrium and rate of sorption

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and desorption (ten Hulscher and Cornelissen, 1996).

In the present study, the effects of temperature on the sorption and desorption behaviors of PFOS were investigated using humic acid, one of the main components of the organic matter in sediment, as sorbent (Stevenson, 1994). The objective of this study is to illustrate the sorption kinetics and thermodynamic characteristics of PFOS to the humic acid at different temperatures, and to elucidate the underlying sorption/desorption mechanism related to the transport and fate of PFOS in environment.

1 Materials and methods

1.1 Chemicals and materials

Heptadecafluorooctanesulfonic acid potassium salt (PFOSK) (purity $\geq 98\%$) and ammonium acetate (for mass spectroscopy, purity $\geq 99\%$) were purchased from Fluka (Milwaukee, USA). High performance liquid chromatograph (HPLC)-grade methanol and acetonitrile was purchased from Fisher Scientific (Leicestershire, UK). Humic acid was purchased from Tianjin Chemical Reagent Co., Ltd. (Tianjin, China).

1.2 Sorption kinetics experiments

To determine the sorption equilibrium time at different temperatures, batch sorption kinetic experiments were carried out at 5, 25, and 35°C. All of the sorption/desorption experiments were conducted in 50 mL polypropylene bottles. Teflon-lined caps were avoided. Sorption kinetics experiments of PFOS to the humic acid carried out at an initial PFOS concentration of 2.0 mg/L (solution volume: 45 mL) at 5, 25, and 35°C. A high concentration of PFOS was used in the experiment to reduce the detection error. Duplicate sets of tubes contained 3.0 g humic acid and a background solution containing 0.005 mol/L CaCl_2 . The suspensions were shaken (250 r/min) on 2D-shaker in the dark at needed temperature. After distinct time intervals, the tubes were centrifuged at 9000 $\times g$ for 30 min, and 1 mL of the supernatant liquid was transferred to an autosample vial for high performance liquid chromatography mass spectrometry (HPLC/MS) (Alliance 2695/Micromass ZQ 4000, Waters, USA) analysis.

1.3 Sorption and desorption experiments

Sorption/desorption experiments were conducted at 5, 25, and 35°C. Preliminary sorption experiments were carried out to determine appropriate sorbent to solution ratio to achieve 30%–70% reduction in initial aqueous-phase solute concentration (Chen et al., 2007). Duplicate sets of polypropylene tubes were filled with 3.0 g of the humic acid and 45 mL of a solution containing 0.005 mol/L CaCl_2 solutions. The initial PFOS concentration ranged between 0.5 and 10 mg/L. The suspensions were shaken (250 r/min) on a 2D-shaker in the dark at needed temperature. Parallel control tests in the absence of humic acid showed that the total PFOS loss (e.g., sorption on the tube wall, bio- and/or photo-degradation) was less than 5%, which was neglected in the experiments. After 24 hr sorption equilibration,

determined in the kinetics experiments, the suspension was centrifuged at 9000 $\times g$ for 30 min, and 1 mL of the supernatant liquid was transferred to an autosample vial for HPLC/MS analysis. The sorbed amounts were computed from the difference of the initial and final solute concentrations.

Following the sorption equilibrium, select samples were subjected to further desorption isotherm experiments following the successive dilution method (Pan et al., 2009). First of all, 40 mL of the centrifuged supernatant was removed by pipette, and replaced with the same volume of a solution that contains the same background compositions but free of PFOS. The mixtures were then shaken under the identical conditions used for the sorption experiments. Upon equilibrium, the distribution of PFOS between the humic acid and solution was analyzed following the same procedures as that for the sorption experiment. The dilution and re-equilibration procedures were repeated successively to yield the desorption isotherms.

1.4 Analysis

The concentration of PFOS in water phase was measured using a HPLC (Alliance 2695, Waters, USA) interfaced with an electrospray mass spectrometer (Waters ZQ4000, Waters, USA) as described in our previous study (Pan et al., 2009). The mass spectrometer parameters were optimized to transmit the $[\text{M}-\text{K}]^-$ ion for PFOS using atmospheric pressure ionization, operated in the electrospray negative ion mode. PFOS ion was monitored using selected reaction monitoring for ion 499 for quantitative determination of PFOS. The limit of detection for PFOS was 1.5 $\mu\text{g/L}$, and the relative standard deviation was less than 4.8%.

1.5 Characterization of humic acid

CPMAS ^{13}C NMR spectrum of humic acid was acquired on a Bruker Avance 300 MHz NMR spectrometer (Bruker Analytic GmbH, Germany). The spectrum was divided into the six major regions: alkyl (0–40 ppm), O-alkyl (40–100 ppm), aromatic (100–140 ppm), phenolic (140–165 ppm), carboxyl and amide (165–185 ppm), and aldehyde and ketone (185–220 ppm). The Fourier transform infrared (FT-IR) spectrum of the humic acid was obtained on KBr disk (contained 1 mg of the sample and 200 mg of dried KBr) in the 500–4000 cm^{-1} range on a FT-IR spectrophotometer (NEXUS 670, Nicolet, USA). The resolution of FT-IR spectroscopy was 2.0 cm^{-1} . The average particle size of the humic acid was 34 μm determined by Mastersizer 2000 laser particle size analyzer (Malvern Instruments Ltd., UK). Content of total organic carbon was 55.5% determined by elemental analyzer (Elementar Analysen Systeme GmbH, Germany).

2 Results and discussion

2.1 Characterization of humic acid

The humic acid contained a large percentage of aromatic compounds (63.9%), and had a high hydrophobic index

(Table 1). The ^{13}C NMR and FT-IR spectra in Fig. 1 were interpreted according to Wen et al. (2007) and Swift (1996). It was found that the humic acid spectrum contained an intense signal from C-substituted aromatic carbon at 124 ppm, which was corroborated by its high IR absorbance at 1620 cm^{-1} (stretching of $\text{C}=\text{C}$ —aromatic). The high resonance at 207 ppm might be attributable to the C of the carboxyl group, which corroborated by its high IR absorbance at 1280 cm^{-1} (deformation of the O—H of COOH) and 1720 cm^{-1} (stretching of the $\text{C}=\text{O}$ of COOH). The aliphatic region (0–50 ppm) of the NMR spectrum reflected a high presence of nonsubstituted saturated aliphatic carbon. The resonance at 165 ppm reflected phenolates, which were corroborated by the IR absorbance at 1270 cm^{-1} (stretching and deformation of the phenolic O—H). The broad band observed at 3420 cm^{-1} was assigned to the stretching vibration of hydroxyl groups. The $1420\text{--}1450\text{ cm}^{-1}$ in the lipid fraction was the deformation of aliphatic C—H. The absorbance at 1130 cm^{-1} was C—OH stretching of aliphatic O—H. The peak that appeared at 1040 cm^{-1} represented C—O stretching of polysaccharides or polysaccharide-like substances.

2.2 Sorption kinetics of PFOS to humic acid at different temperatures

As shown in Fig. 2, sorption of PFOS to the humic acid took about 1440 min to reach the steady state at

Table 1 Distribution of carbon intensity in different regions of CPMAS ^{13}C NMR spectrum of the humic acid presented by carbon content

Function group	Chemical shift (ppm)	Content (%)
Alkyl	0–40	12.8
Alkyl-O	40–100	8.3
Aromatic	100–140	52.0
Phenolic	140–165	11.9
Carboxyl	165–185	4.5
Carbonyl	185–220	10.3
Aromaticity ^a		63.9
Aliphaticity ^b		21.1
Hydrophobic index ^c		2.6

^a $(100\text{--}165\text{ ppm})/(0\text{--}240\text{ ppm})$; ^b $(0\text{--}100\text{ ppm})/(0\text{--}240\text{ ppm})$; ^c $((0\text{--}40\text{ ppm}) + (100\text{--}140\text{ ppm})) / ((40\text{--}100\text{ ppm}) + (140\text{--}185\text{ ppm}))$.

all studied temperatures. We then tested several kinetic models including pseudo first-order, pseudo second-order, Elovich, power, and parabolic diffusion kinetics equations to analyze the data of kinetics experiment. The coefficients of determination (r^2) and the standard error of estimate (SEE) were used to describe the fitness of the kinetics models as described by Shirvani et al. (2007). SEE provides a measure of agreement between the calculated and observed values and is defined as Eq. (1).

$$\text{SEE} = \left(\frac{\sum (q_m - q_c)^2}{n - 2} \right)^{\frac{1}{2}} \quad (1)$$

where, q_m and q_c are the measured and calculated PFOS sorption amount, respectively, and n is the number of measurements. The r^2 and SEE values for PFOS sorption to the humic acid of the kinetic models are summarized in Table 2. In view of r^2 , models of power, Elovich, and pseudo second-order kinetics equations all well fitted to the experimental data ($r^2 > 0.96$). While in view of the SEE value, the SEE value of power kinetics equation was much lower than those of other equations. This suggested that the power kinetics equation was the most suitable model in describing PFOS sorption onto the humic acid at 5, 25, and 35°C . Since the power kinetics equation derived directly from the transient equation for Fickian diffusion (Wells et al., 2004), and could mathematically reflect a process of diffusion (Aharoni et al., 1991), the good fitness of power kinetics equation indicated that diffusion should be an important process in controlling kinetics of PFOS sorption to the humic acid.

2.3 Sorption and desorption of PFOS to humic acid at different temperatures

Sorption and desorption tests of PFOS to the humic acid at 5, 25, and 35°C were conducted with electrolyte $0.005\text{ mol/L CaCl}_2$. The initial concentration of PFOS ranged from 0.5 to 10.0 mg/L . As determined in sorption kinetics, sorption equilibrium time was 24 hr for all studied temperatures. Sorption of the PFOS to the humic acid increased with the increase of temperature and the sorption capacity doubled when temperature increased from 5 to 35°C . The sorption data were fitted using the linear sorption model

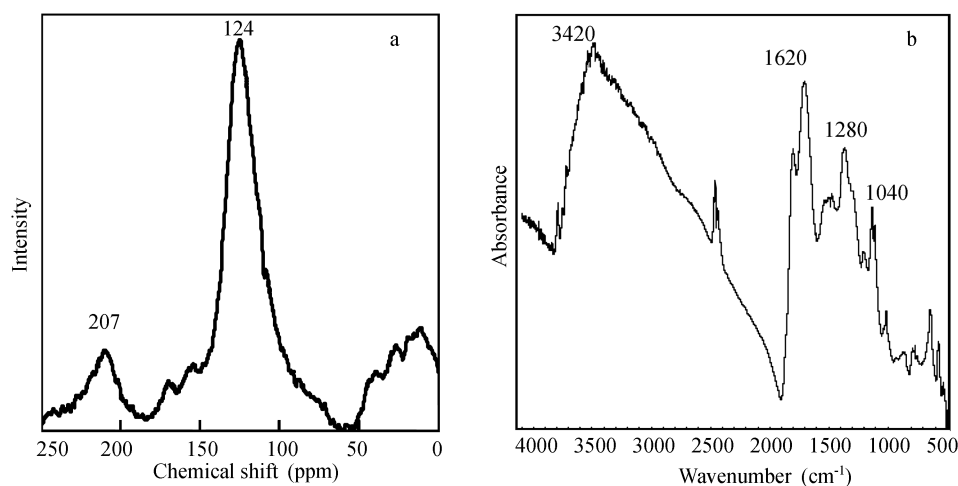
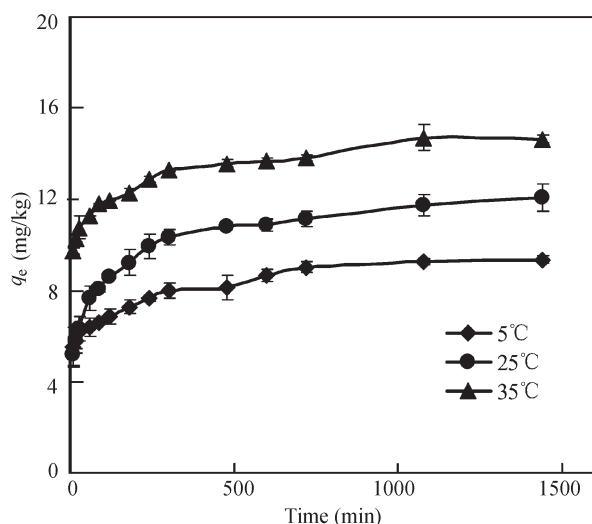
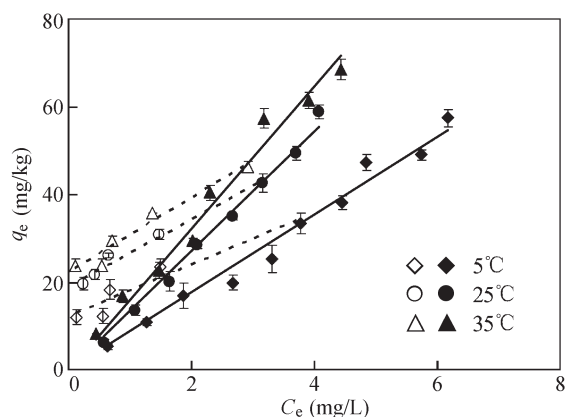


Fig. 1 Solid state CPMAS ^{13}C NMR (a) and FT-IR (b) spectra of humic acid.

Table 2 Coefficient of determination (r^2) and standard error of estimate (SEE) for sorption of PFOS to the humic acid according to different kinetic models

Temperature (°C)	Pseudo first-order		Pseudo second-order		Elovich		Power		Parabolic diffusion	
	$q_t = q_e(1 - e^{-k_1 t})$		$q_t = \frac{q_e k_2 t}{1 + k_2 q_e t}$		$q_t = A + B \ln t$		$q_t = at^b$		$q_t = kt^{\frac{1}{2}} + \beta$	
	r^2	SEE	r^2	SEE	r^2	SEE	r^2	SEE	r^2	SEE
5	0.81	0.029	0.99	2.31	0.96	0.26	0.98	0.026	0.95	0.31
25	0.73	0.058	0.99	1.85	0.99	0.20	0.98	0.040	0.88	0.82
35	0.77	0.046	0.99	1.12	0.99	0.17	0.99	0.011	0.91	0.48

**Fig. 2** Sorption kinetics of PFOS to the humic acid at 5, 25, and 35°C. Data were given as the mean of duplicates \pm standard deviation.**Fig. 3** Sorption isotherms of PFOS to the humic acid at 5, 25, and 35°C. Data were given as the mean of duplicates \pm standard deviation.

presented as Eq. (2):

$$q_e = K_d \times C_e \quad (2)$$

where, q_e and C_e are the concentrations of PFOS on the humic acid and in the solution, respectively. K_d is the distribution coefficient.

It was obvious that linear sorption model fitted well the sorption data at 5, 25, and 35°C ($r^2 > 0.98$). The linear model is generally used to describe partitioning sorption process. The good fitness of linear sorption model demonstrated that the partitioning was the main sorption mechanism in the PFOS sorption as suggested by Higgins and Luthy (2006). The calculated K_d values were 8.86, 13.6, and 16.1 L/kg at 5, 25, and 35°C, respectively, which were much lower than those of weakly polar and non-polar

chemicals, such as dichlorobenzene, trichlorobenzene, and phenanthrene (Zhou et al., 2004; Lu and Pignatello, 2004; Pignatello et al., 2006). Solubility is usually considered as an important factor affecting the distribution coefficient of organic contaminants (Nakata et al., 2006). The solubility of the potassium salt of PFOS reaches 550 mg/L in pure water and 307 mg/L in 0.005 mol/L CaCl_2 solution at 25°C which are much higher than those of hydrophobic contaminants (approximately 10^{-2} – 10^{-4} mg/L) (OECD, 2002; Pan et al., 2009; Nakata et al., 2006). The low K_d values observed in this study may be due to the relatively higher water solubility and its consequent partitioning of PFOS to water phase. Similar phenomenon was observed in the sorption of imidacloprid to soil humic acid, which has a K_d value of 5 L/kg and a solubility of 510 mg/L at 20°C (Filipe et al., 2009). Usually, the solubility of the humic acid may increase with the rise of temperature, which would enhance the interaction between dissolved humic acid and PFOS. Considering the humic acid and PFOS are both negative charged in water (Kretzschmar et al., 1997), the interaction between the dissolved humic acid and anionic PFOS molecule would be difficult due to electrostatic repulsion. Tremblay et al. (2005) had demonstrated that dissolved humic acid has a weak ability to compete with sediment in the sorption process of fluoranthene, and deemed that the effect of dissolved humic substances on the sorption was negligible or minor. Therefore, the impacts of the increased humic acid on sorption of PFOS were neglected in this study, and due to the high concentration of humic acid (3 g/45 mL), the loss of humic acid in the sorbent due to dissolving was neglected.

Desorption hysteresis occurred at all studied temperatures as presented in Table 3. The degree of desorption hysteresis was quantified using the thermodynamic index of irreversibility (TII) proposed by Sander et al. (2005). Usually, the calculated TII values lies in the range of 0 to 1, where the value 1 indicating the maximum irreversibility. Previous study has demonstrated that desorption hysteresis correlated well with rigidity and aromaticity of the organic matter (Yang et al., 2004). The high TII values in this study may be due to the high content of aromatic compounds in humic acid. For nonionic organic chemicals, desorption hysteresis is proportion to rigidity and aromaticity of the organic matter (Pignatello et al., 2006), while for ionic organic chemicals, the electrostatic interactions between the ions in solution with the sorbate and sorbent would significantly affect the extent of desorption hysteresis. Our previous study found that desorption hysteresis of PFOS to natural sediment increased remarkably in the presence of cationic surfactant cetyltrimethylammonium bromide

Table 3 Linear sorption model fitted sorption and desorption parameters, thermodynamic index of irreversibility (TII), and sorption thermodynamic parameters for PFOS to humic acid

Temperature (°C)	Sorption isotherm	r^2	n	Desorption isotherm	r^2	n	TII	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))
5	$q_e = 8.86C_e$	0.98	10	$q_e = 5.93C_e + 12.1$	0.93	5	0.48	-5.04	14.2	69.5
25	$q_e = 13.6C_e$	0.99	8	$q_e = 7.50C_e + 19.3$	0.98	5	0.51	-6.46		
35	$q_e = 16.1C_e$	0.98	9	$q_e = 8.48C_e + 21.9$	0.96	5	0.51	-7.11		

n : sample numbers.

(Pan et al., 2009). The TII values of PFOS to the humic acid have no significant difference at 5, 25, and 35°C. Sorption models in previous studies suggested that glassy domains (rigid) and rubbery domains (flexible) were coexistent in the sediment organic matter (Xing and Pignatello, 1997). Glassy domains are related to desorption hysteresis, whereas rubbery domains are proposed to account for reversible sorption. Humic acid was the mixture of macromolecules, and exhibit certain bulk physicochemical properties similar to those of organic polymeric materials (Huang et al., 2003). The rigidity of a macromolecular structure was reflected by the glass transition temperature T_g , which has been discovered for humic acids with differential scanning calorimetry analysis and ranged between 43 and 72°C (Schaumann and Antelmann, 2000; Katherine et al., 2000; LeBoef and Weber, 2000; Young and LeBoeuf, 2000). According to the temperature isotherms below the T_g of humic acid in this study, the structure and properties of the humic acid should be unchanged (Gunasekara, 2003). It may be the reason for the similarity of TII values observed at 5, 25, and 35°C.

As shown above, sorption of PFOS to humic acid increased with the increase of temperature. Humic acid is the main component of the organic matter in sediment (Stevenson, 1994), and played a major role in the sorption and desorption of organic contaminants in natural aquatic environment. Beckera et al. (2008) reported that river sediments constituted a sink of PFOS released from the wastewater treatment plant, and our result is well supported their conclusion because humic acid is the major component of the sediment organic matter which is proportion to the sorption amount of PFOS to natural sediments (Higgins et al., 2006). The results showed that part of PFOS would be irreversibly bound to the humic acid, and buried in the sedimentation process of sediment. Humic acid in the sediment may be one of PFOS sinks in aquatic environment. The increased sorption with temperature indicated that dissolved PFOS in water would transfer into suspended particles as transporting from warm region to cold region with water body, and more PFOS was irreversible bound to the humic acid.

2.4 Estimation of sorption thermodynamic parameters

The thermodynamic parameters of the sorption including the standard Gibbs free energy (ΔG^0) (kJ/mol), standard enthalpy (ΔH^0) (kJ/mol), and standard entropy (ΔS^0) (J/(mol·K)), were calculated from the Van't Hoff equation:

$$\Delta G^0 = -RT \ln K_d \quad (3)$$

$$\ln K_d = \frac{\Delta H^0}{-RT} + \frac{\Delta S^0}{R} \quad (4)$$

where, the slop and intercept of the plot of $\ln K_d$ versus $1/T$ are used to determine ΔH^0 and ΔS^0 . R is the gas constants and equals 8.314 J/(mol·K), and T (K) is the absolute temperature. The calculated ΔG^0 , ΔH^0 , and ΔS^0 are presented in Table 3.

The standard free energy changes were all negative (-5.04, -6.46, and -7.11 kJ/mol at 5, 25, and 35°C, respectively), suggesting that PFOS sorption to the humic acid is a spontaneous process. The sorption heat of PFOS to the humic acid from water was 14.2 kJ/mol, which indicated that the sorption process is endothermic. For nonionic chemicals sorption to sediment, and the standard enthalpies are usually negative, which means sorption inversely dependent on the temperature, and the enthalpy changes are small (Huang and Weber Jr, 1997). Endothermic processes have been observed for sorption of PFOS to polymer materials, and sorption enthalpies of nonionic chemicals to polymers averaged 3.5 kJ/mol (ten Hulscher and Cornelissen, 1996). The physicochemical properties of humic acid were similar to those of organic polymeric materials (Huang et al., 2003), thus the similar enthalpy change between the sorption to the humic acid and to the polymers is reasonable. For ionic chemicals, the enthalpy-related forces were relatively great due to the additional contribution of electrostatic interactions (Banerjee et al., 2008). The high enthalpy of PFOS suggested that electrostatic interaction was a possible sorption mechanism. This is consistent with the result of Johnson et al. (2007). Sorption of ionic organic contaminant Methylene Blue on pyrolyzed petrified sediment has obtained ΔH^0 values ranged between 14 and 18.5 kJ/mol, and ΔS^0 values ranged between 52.8 and 67 J/(mol·K) (Aroguz et al., 2008), similar to the anionic PFOS sorption to humic acid. The high positive values of standard entropy changes, 69.5 J/(mol·K), was found in this study, suggesting that the sorption was entropy driven process.

3 Conclusions

The power kinetics equation was found to be a suitable model to describe the sorption process at 5, 25, and 35°C, suggesting that diffusion is a rate-controlling process for PFOS sorption to the humic acid. Sorption of PFOS to the humic acid increased with the increase of temperature, and doubled as the temperature increased from 5 to 35°C. Desorption hysteresis occurred at studied temperature, which indicated that the humic acid in sediment may be served as one of PFOS sinks in aquatic environment.

Acknowledgments

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