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# **Sorption Kinetics, Isotherm and Mechanisms of PFOS on Soils with Different Physicochemical Properties**

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## Abstract

Perfluorooctane sulfonate (PFOS) is environmentally persistent, bioaccumulative and toxic to human health and ecosystems. It has been widely detected in groundwater, surface water, soil and sediment. So far, very few research has reported on the PFOS sorption behaviors onto soils, one of the primary processes that influence its fate and transport in the subsurface. In this study, the sorption of PFOS onto six soils with different physicochemical properties were investigated. Kinetic and equilibrium studies of PFOS sorption onto six soils were carried out in batch experiment. The well-fitted pseudo-second-order kinetic model to experimental data suggested that chemisorption was involved in PFOS sorption on soils. The intraparticle diffusion model results indicated that both film diffusion and intraparticle diffusion were the rate-limiting steps for five of the six soil samples, while the intraparticle diffusion was the only limiting step in the PFOS sorption on the sixth soil. PFOS sorption isotherms can be described by the Freundlich model well for all soils ( $R^2=0.979-0.999$ ). The correlation analysis between  $K_{\rm F}$  of PFOS and the physicochemical properties of the soils showed that a positive correlation between  $K_{\rm F}$  and  $Al_2O_3$ , SOC and  $Fe_2O_3$ . The FTIR data demonstrated hydrophobic interaction, ion exchange, surface complexing and hydrogen bonding might all play a role in the PFOS sorption onto soil samples. PFOS sorption onto soil minerals, especially iron oxide minerals, needs to be further explored in future.



## **Materials and Methods**



different provinces in China.



Soil samples were collected from agricultural land (0-20 cm) from different provinces, namely Heilongjiang (HLJ, Isohumosols), Jiangsu (JS, Cambosols), Jiangxi (JX, Ferrosols), Chongqing (CQ, Cambosols), Guangdong (GD, Ferrosols) and Guangxi (GX, Ferrosols) (Fig. 1).

The concentrations of PFOS were determined using an HPLC-MS/MS system (API 3200, AB-Sciex, USA). The mobile phase is a mixture of 10 mmol/L of ammonium acetate in double DI water (phase A) and methanol (phase B) at a volume ratio of 15/85. The flow rate of the mobile phase was 0.8 mL/min and the injection volume was 10  $\mu$ L. The specific surface areas (SSA) measurement was conducted with a BEL SORP-MAX analyzer (MicrotracBEL, Japan). The FTIR spectra were obtained from samples mixed with KBr using the Nicolet iS 10 FTIR spectrometer (Thermo, USA).

Soil		JX	HLJ	JS	CQ	GD	GX
Properties		Ferrosols	Isohumosols	Cambosols	Cambosols	Ferrosols	Ferrosols
pН		5.46	7.90	7.90	4.99	4.31	4.81
SOC (%)		1.27	2.25	0.87	0.99	2.71	1.46
$Fe_2O_3$ (g/kg)		49.58	8.44	9.57	18.35	80.66	62.60
$Al_2O_3$ (g/kg)		6.26	2.19	0.75	0.69	17.75	3.78
CEC (cmol /kg)		8.00	33.30	5.58	16.90	10.70	7.63
	Sand (%)	14	16	46	51	36	47
son texture	<b>Silt (%)</b>	76	50	48	29	33	16
	<b>Clay (%)</b>	10	34	6	20	31	37
$SSA_{BET} (m^2/g)$		76.09	122.32	6.25	15.08	47.09	25.93
Average pore diameter/nm		14.86	4.79	10.07	9.29	10.37	12.72
Total pore volume/(cm <sup>3</sup> /g)		0.283	0.146	0.016	0.035	0.122	0.082

### Results





#### Fig. 2. Sorption kinetics of PFOS to six soils. (a) Pseudo-first-order kinetic model (b) Pseudo-second-order model (c) Elovich model (d) Power function model.

The applicability of these four kinetic models (Fig. 2) was further validated by the normalized standard deviation ( $\Delta Q_{a}$ ), and the pseudo-second-order model (Fig. 2b) was considered the most suitable equation to describe the sorption kinetics of



Fig. 3 (a)Intraparticle diffusion model for PFOS sorption kinetics, (b) pore size distribution and (c) nitrogen adsorptiondesorption isotherm of six soils.

The intraparticle diffusion model suggests that PFOS sorption onto JS Cambosols is mainly controlled by the intraparticle diffusion only, whereas both film diffusion and intraparticle diffusion play a role in PFOS sorption on all other five soils. However, in the case of HLJ Isohumosols, the external film diffusion is more limiting than the intraparticle diffusion in the PFOS sorption process (Fig. 3a). To further verify the theory of intraparticle diffusion model, the pore size distribution and nitrogen adsorption–desorption isothermal measurements were carried out (Fig. 3b and 3c). It was proposed that film diffusion mainly occurs in macropore transport and intraparticle diffusion mainly occurs in micropore/mesopore transport. The pore size distribution data support the conclusions drawn from the intraparticle diffusion model analysis.

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Call		Freundlich	Linear		
5011	n	$K_F(\text{mg/kg}) (L/\mu g)^{1/n}$	<b>R</b> <sup>2</sup>	<i>K</i> <sub>d</sub> (L/g)	$r^2$
JX	0.57	4.34×10 <sup>-4</sup>	0.985	<b>48</b>	0.900
HLJ	0.67	3.15×10 <sup>-3</sup>	0.996	66	0.951
JS	0.59	<b>1.99×10<sup>-4</sup></b>	0.999	18	0.925
CQ	0.45	1.28×10 <sup>-5</sup>	0.979	29	0.861
GD	1.43	0.40	0.988	63	0.930
GX	1.19	3.91×10 <sup>-2</sup>	0.992	14	0.995

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Table 2 Freundlich	isotherm model	parameters and	l linear model f	or sorption (	of PFOS on soils.
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#### Table 3 Correlation coefficients and p values of the $K_{\rm p}$ related to physicochemical properties of soils.

Soil properties	<b>Correlation coefficient</b>	р
pН	-0.523	0.145
SOC	0.756	0.042
Fe <sub>2</sub> O <sub>3</sub>	0.735	0.049
$Al_2O_3$	0.950	0.003
CEC	-0.165	0.379
Sand	0.065	0.452
Silt	-0.275	0.300
Clay	0.364	0.240
<b>SSA</b> BET	-0.038	0.472
Average pore diameter	0.031	0.478
Total pore volume	0.027	0.480

In order to identify the factors influencing PFOS sorption on soils, coefficient correlations as well as p values were calculated to explain the relationship between  $K_{\rm F}$  and soil properties. The results showed a positive correlation between  $K_{\rm F}$  and Al<sub>2</sub>O<sub>3</sub>, SOC and  $Fe_{2}O_{3}$ , i.e., the higher the contents of  $Al_{2}O_{3}$ , SOC and  $Fe_2O_3$ , the higher  $K_F$ , hence the stronger sorption tendency of PFOS towards soils (Table 3).





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The bands at WNs around 912 cm<sup>-1</sup>, 1027 cm<sup>-1</sup>, 3447 cm<sup>-1</sup> and 3630 cm<sup>-1</sup> were an Al-OH bending vibration. The band at 795 cm<sup>-1</sup> was Fe-OH bending vibration. The absorbance intensity for the Fe-O bands at 535 cm<sup>-1</sup> and 473 cm<sup>-1</sup> changed, with the exception of JS Cambosols (Fig. 6). The FTIR data showed that SOC, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> influenced the PFOS sorption by electrostatic interaction, hydrophobic interaction, ligand and ion exchange, and hydrogen bonding.

## Conclusion



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