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# **Hysteretic Desorption of Perfluorooctane Sulphonates within Sediment Components under Aerobic and Anoxic Conditions**

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*Author's contribution*

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# **ABSTRACT**

The fate of organic contaminants in sediment can be better accurately predicted through knowledge of desorption. Complex formation between perflurooctane sulphonates (PFOS) and active sites on sediment components, especially, the level of organic matter plays significant role in desorption process. Assessment of successive desorption steps shows that the percent of expected desorption at constant distribution coefficient is better described by ideal and linear model. Desorption of PFOS from the various component at varied organic carbon contents was observed to follow a linear isotherm. Significant negative correlation ( $R^2$ =0.934) was observed between fractional desorption of PFOS and percent organic carbon content of each sediment component. The study observed that significant percentage of initially desorbed PFOS is readily available to partition into the porewater as freely dissolved PFOS. Our findings suggest the stimulation of iron (III) reduction for the bioremediation of subsurface environments contaminated with redox active contaminants such as PFOS.

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## **1. INTRODUCTION**

Reviews of many reports indicate that sediments are major targets of contaminants and consequently pose a potential risk to the environment and in particular, human health. To accurately predict the availability, mobility, fate and toxic potency of any contaminant from sediment, knowledge of desorption of such contaminant is required. While most studies in environmental chemistry have focused on sorption processes, researchers often neglect desorption reactions, assuming that sorption and desorption rates are the same [1]. Desorption involves remobilization of sorbed species. Perflurooctane sulphonates (PFOS) is an emerging pollutant that is unique unlike most organic contaminants because of its hydrophilic and hydrophobic nature. Thus, unlike many other organic pollutants, its desorption from sediment may follow unusual trend.

Diffusion of molecules with sediment organic matter (SOM) matrices and micro-and mesopores connecting the external solution phase and SOM has been identified as limiting factors that can affect the rate of sorption and subsequent desorption of molecules within solid matrices [2-3]. Several studies had shown that desorption from kerogen containing shale is much slower than humic acid dominating peak samples, which was attributed largely to retarded sorbate diffusion within SOM matrices and microporous inorganic matrices [3-5]. Several processes are capable of remobilizing sorbed organic contaminants such as PFOS back into solution. Consequently, simple partitioning model has remained conceptually inconsistent with a wide range of reported sorption phenomena including non-linearity of isotherm, sorption-desorption hysteresis, organic carbon normalized capacities e.t.c [6-7]. These processes are often observed to significantly impact the fate and transport of organic contaminant through soils/sediment to ground-water and surface-water systems. In spite of several studies, information on desorption patterns of PFOS, particularly, under anaerobic conditions are rarely available.

The purpose of the present study was to better understand how metal oxides, particularly of Fe and Mn along with sediment organic matter influences the rate of desorption under aerobic and more importantly, anaerobic environmental conditions. In this study, sediments were treated with different reagents to isolate specific components which are later characterized. This study reports for the first time the trend in desorption of PFOS under anaerobic and attempts in addition to providing description pattern of PFOS with different sediment components. This approach provided multiple points of comparison in the study of PFOS and serves as basis for further studies.

## **2. MATERIALS AND METHODS**

## **2.1 Standards and Reagents**

The potassium salt of perfluorooctane sulfonate (PFOS,≈ 98%) and ammonium acetate (≈ 99.0%) were purchased from Fluka (Milwaukee, WI, USA). Sodium perfluoro-[1,2,3,4]-<br><sup>13</sup>C<sub>4</sub>-octanesulfonate (MPFOS, 99%, 50µg/mL solution in methanol) was obtained from Wellington Laboratories (Canada). HPLC-grade methanol was supplied by Fisher Scientific (USA). Milli-Q water prepared by Millipore (Boston, USA) was used throughout the experiment. All the other reagents used in the experiment were of analytical grade.

# **2.2 Sediment and Water Sampling**

The procedure has been reported for the sorption study (paper under review). Briefly, surface sediment (top 1-5cm) was collected from Taihu Lake, China with a clean methanol rinsed stainless steel trowel. Water sample was also collected on the same spot of sediment collection. All the samples were kept in polypropylene (PP) bags at 4±2ºC for analysis. The sediments were air-dried, passed through a 0.2mm sieve, and stored in closed containers at room temperature prior to use. The sediment samples were characterized following the conventional methods [8]. Selected sediment characteristics including pH, organic carbon, cation exchange capacity (CEC) and particle size are summarized in Table 1.

# **2.3 Selective Extraction of Fe Oxides, Mn Oxides and Organic Materials**

Sediments samples were prepared with four different reagents to extract target components. 0.1 mol/L NH<sub>2</sub>OH·HCl and 0.01 mol/L HNO<sub>3</sub> for 30 min was used to remove manganese oxides [9]. Both NaOCl and  $H_2O_2$  were employed to remove organic matters (OMs) based on previous reports [10]. Extraction with 3.0mL  $H_2O_2$  (30%) involves heating at 40°C while treatment with 1 M NaOCl adjusted to pH 8.0 was shaken over 6 h. 0.2mol/L (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> buffered at pH 3.0 with  $H_2C_2O_4$  and shaken in the dark for 4 h was employed to extract both Fe and Mn hydrous oxides [11]. All the samples were centrifuged at 3800rpm for 30min, and supernatant filtered (0.45 *µ*m) into 50mL PP tube for the determination of Fe and Mn. The extracts were washed 3-4 times with filtered lake water (FLW) and air-dried.

## **2.4 Samples Characterization**

The total extractable amounts of Fe and Mn were determined using the modified sequential extraction procedure (MSEP) [12-13]. Organic matter was quantified by measuring the total organic carbon (TOC) using a TOC-VCPH instrument (Shimadzu, Japan). Pseudo-total amounts of Fe and Mn were obtained by a flame atomic absorption spectrometer (FAAS) (AA6300, Shimadzu, Japan) after digestion with HNO3/HClO4. Specific surface area (BET) of the sample was determined on a surface area and pore size analyzer (ASAP 2000, Micromeritics, USA).

## **2.5 Sorption Experiments**

## **2.5.1 Aerobic and anaerobic sorption**

In this study, aerobic condition was achieved only by the spontaneous oxygen exchange between the overlaying water and the atmosphere at room temperature while anaerobic box was used for the anoxic experiment. The procedure has been submitted (paper under review). Briefly, 0.5g of air-dried samples was added into each 50mL PP tube and mixed with 20mL of 0.5mM NaCl solution prepared with FLW. The initial concentrations of PFOS ranged from 400–1500ng/L, which was of the environmental level. 2mL of water containing 200mg/L NaN<sub>3</sub> was added to each tube to inhibit any microbial activity. Preliminary sorption kinetic showed that the sorption equilibrium was reached at 24h. All tubes were shaken for 24 h at 25±0.1ºC in a 2D-shaker at 250rpm at pH = 7±0.1M solution each of HCl and NaOH were used for pH adjustment. The tubes were centrifuged at 9000rpm for 30min. 2mL of supernatant were taken out, filtered through 0.22um PP membrane filter and analyzed by UPLC-MS/MS. All the experiments, included controls and blanks, were carried out in duplicate. The amount of PFOS adsorbed by unit mass of sediment (*C*s, ng/g) was

calculated from the difference between initial aqueous phase concentration (C<sub>0</sub>, ng/L) and the PFOS equilibrium concentration after adsorption (*C*e, ng/L) (equation 1);

$$
Cs = \frac{(C_0 - C_e)V_0}{S_m}
$$
\n(1)

where  $V_0$  is the initial volume of the aqueous phase in contact with sediment during the adsorption experiments and  $S_m$  is the mass (g) of sediment used in each assay. Same procedure was followed for the anaerobic experiment except that the tubes were purged continuously with high-purity  $N_2$  gas at 20 kPa for about 2 min inside the anaerobic box, capped and allowed to stand in darkness for several days. At different day's interval during incubation, two anaerobic surrogate tubes were opened inside the  $N<sub>2</sub>$  atmosphere glove box to determine their pH, redox potential (ORP). When the ORP in the surrogate tubes was negative in all the samples, the other experimental tubes were then injected with a volume of aqueous PFOS solution to obtain different initial concentrations (400-1500ng/L).

#### **2.5.2 Desorption experiment**

The fraction of PFOS that is resistant to desorption were measured using multiple cycles of decant-refill approach. The percent organic carbon in residues remaining in each component after adsorption experiment was determined. Desorption experiment was performed on sediment residues immediately after adsorption experiments. All of the supernatant solution was removed and replaced with 20ml fresh 0.5M NaCl prepared with Milli-Q water. (N.B: All Milli-Q water used during desorption in anaerobic experiments only was flushed with nitrogen gas for 24 h and stored inside the anaerobic box for at least 2days before use). Sediment residues were equilibrated using an end-over-end mechanical shaker for 24h at  $25±1°C$  at pH = 7. Thereafter, desorbed PFOS was measured in filtrates as described in adsorption experiments after centrifuging the sample at 9000 × *g* for 30min and filtering through a 0.22μm nylon syringe filters. A similar desorption experiment was also performed on the sediment residues obtained from anaerobic PFOS adsorption experiments by maintaining anaerobic conditions throughout the procedure using  $N<sub>2</sub>$  gas, as described previously.

## **3. RESULTS AND DISCUSSION**

## **3.1 Sorption and Desorption Isotherms**

Fig. 1 presents the sorption and desorption isotherms of PFOS measured for all the sediment components. A detail report on sorption has been reported (paper under review). Very briefly, the results show that anaerobic isotherms are more non-linear in all cases than the aerobic isotherms. The isotherms indicate that all exhibit sorption-desorption hysteresis. The data in Tables 1 and 2 were the  $K_d$ 's computed at constant Ce condition (highest concentration in each case). The log  $K_d$  ranged from 1.75-1.50L/g and 1.60-1.28L/g under aerobic and anaerobic experimental conditions respectively. The K<sub>oc</sub> under aerobic were equally higher than those of anaerobic experiment across all components. This may be attributed to the solubilization of organic matter during anaerobic experiment caused by the reduction process. Also, the desorption  $K_d$  is highest in STHP and STSH and least in UNTD. In practical terms, the increased desorption  $K_d$ 's implies reduced chemical activity of sorbed PFOS at constant *C*e, suggesting a reduced biological reactivity and decreased toxicity of PFOS. Similar trend had been reported for some chemicals [14]. In general, desorption process seems to be better enhanced under aerobic condition based on the standard free energy, ∆*G* 0 (KJ/mol) reported in the study.



**Fig. 1. Sorption and desorption isotherms of PFOS on treated and untreated sediments under aerobic and anaerobic conditions at pH 7.0±0.2 at 250C. Background electrolyte: 0.5 mM NaCl. Solid symbols: sorption experimental data; hollow symbols: desorption experimental data; solid lines: modeled sorption isotherms; dashed lines: modeled desorption isotherms. Data given as the mean of duplicates**



#### **Table 1. Characterization and contents of metal oxides in the sediment particles pretreated by different procedures including sequential and selective extractions**

*Abbre: abbreviation; SA: Surface Area; TEM: Total extractable metals from sequential extraction. Average (n = 2) ± standard deviation. UNTD: Untreated (original) soil sample; STAOx: soil treated with ammonium oxalate; STHA: soil treated with hydroxyl amine hydrochloride; STHP: soil treated with hydrogen peroxide*

## Table 2. PFOS desorption parameters to contents of distribution coefficients,  $K_{d}$ , organic carbon normalized distribution **coefficient,** *K***oc and standard free energy, ∆Gº under aerobic and anaerobic conditions**



*N as defined earlier is 14 and 4 for sorption and desorption respectively*

#### **3.2 Desorption Hysteresis**

Sorption alone is of little environmental significance compared to desorption. The sorption reversibility is of crucial importance for the prediction of PFOS migration in the aquatic environment and as a guide towards remediation approach. Desorption isotherms of the various components are carried out at the highest initial equilibrium concentration (Fig. 1). Desorption experiments of initially high PFOS concentration showed higher desorption releases in all the components. The extent, to which the PFOS adsorbed could be desorbed by water, reflects the strength of the bonds with each component. However, these enhanced desorption release (70 to 79% across all components) at the highest (i.e. first) initial PFOS concentration (1500ng/L) was considered to result from enhanced PFOS competition for sorption sites. Because of the competition at higher initial concentration, some PFOS possibly would not bind tightly to the sorption sites, and would be released more easily when 0.5mmolL<sup>-1</sup> NaCl solution containing the same background compositions but free of PFOS was added to the sample. This desorbed component is of great environmental significance as it constitutes bioavailable fraction of PFOS in the porewater phase within the sediment as freely dissolved components. In addition, the undesorbed portion of the PFOS in the component could be ascribed to the complex formation between the PFOS and the active sites on each component, and hence the inability of the desorbing water to completely desorb the PFOS. No significant differences in desorption release between UNTD and STAOx were found in the study (Fig. 2). However, the variation in desorption rate between the mineral phases (STSH and STHP) explains why experimental data can only be compared based on treatment procedures. each component, and he<br>
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**Fig. 2. Variation in amount of total PFOS desorbed under aerobic and anaerobic experimental conditions. Successive desorption experiments were diluted with solutions containing 0.5mM NaCl at a pH of 7.0 and at 25ºC**

In all the components, the desorption isotherm is located above sorption isotherm. This is indicative of hysteretic sorption of PFOS. The Hysteresis suggests that sorption of PFOS on treated and untreated sediment samples are not completely reversible. To characterize sorption Hysteresis quantitatively, sorption and desorption isotherms were fitted to the

Freundlich equation (Table 3). Hysteresis was quantified using the thermodynamic index of irreversibility (*TII*) (equation 2)

International Research Journal of Pure & Applied Chemistry, 4(6): 773-784, 2014  
ion (Table 3). Hysteresis was quantified using the thermodynamic index of  
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$$
T II = \frac{In C^y - In C^p}{In C^s - In C^p}
$$
(2)  

$$
T^D = \frac{In C^y - In C^p}{In C^s - In C^p}
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(2)

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3). Hysteresis was quantified using the thermodynamic index of<br>
2)<br>  $\frac{I n C^y - I n C^b}{I n C^s - I n C^b}$  (2)<br>
observed solute concentrations at the where  $C^{S}$  and  $C^{D}$  are the observed solute concentrations at the sorption and desorption points and C<sup>y</sup> is the solute concentration of the hypothetical reversible desorption state on the sorption branch at the same sorbed concentration as the observed desorption point [15].

The *TII* recorded in the study (Table 2) lies within those reported in previous studies [16-17]. The order of increasing *TII* from 0.37 (STHP) to 0.64 (STAOx) is indicative of the relative pattern in which PFOS is being increasingly desorbed from the components. The results of *TII* are in good agreement with previous desorption experimental results reported in Table 3. International Research Journal of Pure & Applied Chemistry, 4(6): 773-784, 2014<br>
ion (Table 3). Hysteresis was quantified using the thermodynamic index of<br>
(equation 2)<br>  $T \cdot I = \frac{I_n C^{-\gamma} - I_n C^{-\delta}}{I_n C^{-\delta}}$  (2)<br>
<sup>D</sup> are the

#### **3.3 Desorption Steps**

Three successive desorption steps were undertaken for each of the components after the 24h adsorption period. The stepwise desorption from the solid phase of each component was evaluated using the following equation (*3*):

$$
\Delta Cs_{i,desorbed} = [C_{e,i} - C_{e,i-1}(1-r)]\frac{V}{W}
$$
\n(3)

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Table 3). Hysteresis was quantified using the thermodynamic index of<br>  $= \frac{f_n C^* - Ir C^P}{\pi C^* - Ir C^P}$  (2)<br>  $\pm \frac{f_n C^* - Ir C^P}{\pi C^* - Ir C^P}$  (2)<br>
( *International Research Journal of Pure & Applied Chemistry, 4(6): 773-784, 2014*<br> *V* **Crigidion 2**) Hysteresis was quantified using the thermodynamic index of<br>
equation 2)<br>  $II = \frac{I \pi}{I \pi} \frac{C}{C} \frac{v}{s} - I \pi \frac{C}{C} \frac{v}{c}$ where ∆Cs*i*,desorbed is the change in solid phase PFOS concentration (ng/g) during the *i*th desorption step, *C*e*<sup>i</sup>* and *C*e,*i-1* are the solution phase PFOS concentrations (µg/L) between successive steps, and *r* is the fraction of supernatant that may not be removed prior to desorption and consequently determined gravimetrically. The cumulative fraction of PFOS desorbed in the experiment (*CFD*<sub>experimental</sub>) after *n* desorption steps was calculated according to equation 4: *i* and phase of each component<br> *i* (3)<br>
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as calculated according<br>  $\frac{i, desorbed}{t}$  (4)<br>  $\frac{1}{rbed}$ <br>
and linear model, two *i*  $\frac{1}{\sqrt{N}}$  (3)<br>
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results reported in Table 3.<br>
of the components after the<br>
phase of each component<br>
component ation<br>

Fraction-solute-desorbed (experimental) = 
$$
\frac{\sum_{i=1}^{i=n} \Delta C s_{i,desorbed}}{q_{adsorbed}}
$$
 (4)

Considering the fits of the experimental data to both Freundlich and linear model, two assumptions can be made at this point with respect to the desorption pattern and PFOS distribution coefficients,  $K_d$ : desorption can be assumed ideal and linear and that  $K_d$  remains constant or non-ideal and non-linear with desorption specific K<sub>d</sub>. In either case, the fraction of PFOS desorbed (*CFD*,<sub>predicted</sub>) after *n* desorption steps can be calculated with the following equation (*5*): r)  $\frac{1}{W}$  (3)<br>
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Fraction-solute-desorbed (predicted) =

(CFD<sub>predicted</sub>)

\n
$$
\frac{r}{K_d \frac{M_{s}}{V_w} + (1 - r)} \sum_{i=1}^{i=n} \left( \frac{K_d \frac{M_{s}}{V_w} + (1 - r)}{K_d \frac{M_{s}}{V_w} + 1} \right)_i
$$
\n(5)

*i*

Table 3 summarizes the results of three successive desorption steps obtained in the study. The table equally displays the values of *CFD*<sub>experimental</sub> and *CFD*<sub>predicted</sub> calculated from equation 4 and 5 respectively. Across all components, the predicted fractions of PFOS desorbed at constant  $K_d$  are less (0.751 – 1.448) but not significantly different from those predicted with desorption-specific  $K_d$  (0.901 – 1.902). The data reflects the extent to which PFOS desorption process in each component can best be described or correlated with their respective adsorption processes. The percent of expected desorption is expected to be 100% for a perfect description. However, with the limited data obtained in the present study as indicated in Table 3, the percent of expected desorption varies from 34% to 58% and 31% to 52% at constant and desorption-specific  $K_d$  respectively. These indicate that none of the components including the untreated sample were able to desorb the expected predicted values from adsorption isotherm. It is however noteworthy the higher values of the percent of expected desorption at constant  $K_d$  which shows that the desorption process is better described by ideal and linear model. A critical assessment of Tables 1 and 3 indicates that SOM plays vital role in desorption. Thus, the fractional desorption of PFOS was found to be significantly negatively correlated ( $R^2$  = 0.934) with the percent organic carbon content of each components (Figs. 3a and 3b) as well with least desorption from organic-matter-rich UNTD and STAOx samples. It could therefore be suggested that desorption resistant (irreversible) component is related to the extent of mechanical entrapment of the sorbed PFOS within the SOM matrices. Especially for sediment with very low total organic carbon (TOC) as the case in the present study, such entrapment into the meso- and microporous structures within the sediment aggregates is possible [18]. The data equally suggests that reduction in OC% due to various treatments enhances the remobilization of PFOS into the aqueous phase, though, at different rates. The trend corroborates the inverse relationship between organic matter and desorption of lindane in anaerobic soils as well with least desorption from organic-matter-rich sample earlier reported [19].



Fig. 3. Correlation analysis of desorption  $K_d$  and percent organic carbon of sediment **components under (a) aerobic and (b) anaerobic experimental conditions**



## **Table 3. Summary of PFOS desorption from treated and untreated sediment components of Taihu Lake under anaerobic condition**

*ARB: Aerobic; ANRB: Anaerobic; const and d-sp: constant and desorption specific distribution coefficient (Kd's) respectively. K<sup>d</sup> (const): constant Kd; <sup>K</sup><sup>d</sup> (des-spec): desorption specific <sup>K</sup>d.\*Mean value*

## **4. CONCLUSIONS**

This study has found that sediment physical and chemical properties affects desorption of PFOS from lake sediments. The study equally reveals that a significant percentage of the initially desorbed PFOS may find their ways into the porewater or be readily available to partition into the porewater as freely dissolved PFOS. This trend may be related to the less hydrophobic fraction of PFOS. With the limited data obtained in the study, organic matter seems to play negative role in desorption of PFOS. However, more information may be necessary on the properties of the organic matter. The study suggests that porewater in lake sediments enriched with organic matter are less prone to PFOS contamination. This may also imply a complex formation between PFOS and soluble organic matter in the sub surface environment based on the anaerobic environment. Therefore, we suggest, based on reduced desorption under anaerobic experiment, the stimulation of iron (III) reduction for the bioremediation of subsurface environments contaminated with redox active contaminants such as PFOS. The chemically induced reductive dissolution of iron (III) oxides is thought to play a key role in PFOS sorption and subsequent desorption. This is of great significance in the management of ground water.

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## **COMPETING INTERESTS**

Author has declared that no competing interests exist.

## **REFERENCES**

- 1. Schultz MF, Benjamin MM, Ferguson JF. Adsorption and desorption of metals on ferrihydride: Reversibility of the reaction and sorption properties of the regenerated solid. Environ. Sci. Technol. 1987;21(9):863–869.
- 2. Johnson M, Keinath T, Weber WJ. A distributed reactivity model from sorption by soils and sediments. XIV. Characterization and modeling of phenanthrene desorption rates. Environ. Sci. Technol. 2001;35:1688–1695.
- 3. Weber Jr WJ, LeBoueuf EJ, Young TM, Huang W. Contaminant interactions with geosorbent organic matter: Insights drawn from polymer sciences Water. Res. 2001;35:853-868.
- 4. Pignatello JJ, Xing B. Mechanisms of slow sorption of organic chemicals to natural particles. Environ Sci. Technol. 1996:30:1–11.
- 5. Werth CJ, Reinhard M. Effects of temperature on trichloroethylene desorption from silica gel and natural sediments. Kinetics. Environ. Sci Technol. 1997;31:697-703.
- 6. Huang W, Weber Jr WJ. A distributed reactivity model for sorption by soils and sediments. 10: Relationships between sorption, hysteresis, and the chemical characteristics of organic domains. Environ. Sci. Technol. 1997;31:2562-2569.
- 7. Xing B, Pignatello JJ. Dual-mode sorption of low- polarity compounds in glassy poly(vinyl chloride) and soil organic matter. Environ. Sci. Technol. 1997;31:792-799.
- 8. Tao QH, Wang DS, Tang HX. Effect of surfactants at low concentrations on the sorption of atrazine by natural sediment. Water Environ. Research. 2006;78(7):653– 660.
- 9. Li FM, Wang XL, Li Y, Guo SH, Zhong AP. Selective extraction and separation of Fe, Mn oxides and organic materials in river surficial sediments. Journal of Environmental Sciences-China. 2006;18(6):1233-1240.
- 10. Mikutta RM, Kleber K, Kaiser K, Jahn R. Review: Organic matter removal from soils using hydrogen peroxide, sodium hypochlorite, and disodium peroxodisulfate. Soil Sci. Soc. Am. J. 2005;69(1):120-135.
- 11. Pei ZG, Shan XQ, Wen B, Zhang SZ, Yan LG, Khan SU. Effect of copper on the adsorption of p-nitrophenol onto soils. Environ. Pollut. 2006;139(3):541-549.
- 12. Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace-metals. Anal. Chem. 1979;51(7):844-851.
- 13. Yu KC, Tsai LJ, Chen SH, Ho ST. Chemical binding of heavy metals in anoxic river sediments. Water Res. 2001;35(17):4086-4094.
- 14. Lucking AD, Huang W, Soderstorm-Schwarz S, Kim M, Weber Jr, WJ. The Chemical structure of soil/sediment organic matter and its role in the sequestration and bioavailability of sorbed organic contaminants. J. Environ. Qual. 200;29:317- 317.
- 15. Pan G, Jia CX, Zhao DY, You C, Chen H, Jiang GB. Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments. Environ. Pollut. 2009;157(1):325-330.
- 16. Sander M, Lu Y, Pignatello JJ. A thermodynamically based method to quantify true sorption hysteresis. J. Environ. Qual. 2005;34:1063–1072.
- 17. Jia C, You C, Pan G. Effect of temperature on the sorption and desorption of perfluorooctane sulfonate on humic acid. J. Environ. Sci. 2010;22(3): 355–361.
- 18. Wahid PA, Sethunathan N. Sorption-desorption of lindane by anaerobic and aerobic soils. J. Agric. Food Chem*.* 1980;28(3):623–635.
- 19. Weber WJ, Huang W, Yu H. Hysteresis in the sorption and desorption of hydrophobic organic contaminants by soils and sediments. II. Effects of soil organic matter heterogeneity. J. Contam. Hydrol. 1998;31:149–165.

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