Mechanistic study of PFOS adsorption on kaolinite and montmorillonite

Ruiming Zhang, Wei Yan, Chuanyong Jing*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

HIGHLIGHTS

- The mechanisms of PFOS adsorption on clay minerals are examined at molecular level.
- XANES analysis provides direct evidence for chemical adsorption.
- FTIR spectra in situ monitors the interaction process of PFOS with clay minerals.
- PFOS could insert into the interlayers of montmorillonite.
- The HA coating decreased PFOS adsorption on kaolinite and montmorillonite.

GRAPHICAL ABSTRACT

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ABSTRACT

Adsorption of perfluorooctane sulfonate (PFOS) on clay minerals is pivotal in the fate and transport of PFOS in the environment. Understanding the PFOS adsorption mechanisms, however, presents challenges, especially in the presence of natural organic substances. In this study, the adsorption mechanism of PFOS on kaolinite and montmorillonite, with and without humic acids (HA), were investigated using batch experiments, ATR-FTIR spectroscopy, zeta potential, NEXAFS, and XRD. The results showed that PFOS had a higher adsorption capacity on kaolinite than on montmorillonite, both with a rapid formation of an outer-sphere complex followed by a slow ligand exchange reaction with the elimination of adsorbed H_2O molecules. In addition to nonspecific hydrophobic and electrostatic interactions, specific chemisorption also exists between sulfonate group of PFOS and hydroxyl group on surfaces of clay minerals. The HA coating on clay materials inhibited PFOS adsorption due to its occupation of adsorption sites and increased electrostatic repulsion. The insights gained from this study improve our understanding on the mechanism of multilateral forces on PFOS adsorption at the molecular level.

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1. Introduction

Perfluorooctane sulfonate (PFOS), widely used as surfactant, fire retardant, and paint [1,2], has been categorized as a persistence organic pollutant since 2009 Stockholm convention [3]. PFOS is

detected in air, water, sediment, soil, human blood, and wildlife tissues around the world [4–6]. The ubiquitous occurrence of PFOS has motivated extensive studies on its mineral–water interfacial behavior [4–6], which is crucial in the fate and transport of PFOS in the environment [7].

Clay minerals participate in many important environmental processes [8,9]. Kaolinite and montmorillonite are widely used model clay minerals in mechanistic adsorption studies [10,11]. The two clay minerals have similar components but with stark

* Corresponding author. Tel.: +86 10 6284 9523; fax: +86 10 6284 9523.
E-mail address: cjying@rcees.ac.cn (C. Jing).

structural difference. Specifically, kaolinite consists of one tetrahedral silica sheet fused to one octahedral alumina sheet, whereas montmorillonite contains one octahedral and two tetrahedral layers [12,13]. We speculate that the structural difference of kaolinite and montmorillonite may result in the different PFOS adsorption behaviors and mechanisms.

PFOS adsorption on clay minerals is mainly ascribed to electrostatic interactions and hydrophobic effect [9,14–16]. For example, electrostatic interactions as well as hydrophobic effect contribute PFOS adsorption on Ottawa sand, iron-coated sand, kaolinite, and goethite [14]. As a further evidence of electrostatic interactions, the increase in pH which consequently enhanced the electrostatic repulsion, decreased the PFOS adsorption on silica [15] and kaolinite [9]. In addition, PFOS adsorption would rise as the enhancement of the hydrophobic interaction by increasing the organic carbon content of adsorbents and perfluorocarbon chains [16]. Previous studies, however, intensively rely on macroscopic experimental results such as kinetics, isotherms, and pH adsorption envelopes to propose adsorption mechanisms. The motivation of our study is, therefore, to investigate the mechanisms of PFOS adsorption on clay minerals at the molecular level to understand its fate and transport in the environment.

Humic acid (HA) is a major component of organic matter and plays a predominant role in many physical, chemical and geochemical processes in the environment [17,18]. HA is generally attached with clay minerals, and thus significantly affects their surface electrostatic properties. HA can also compete with pollutant molecules for available surface adsorption sites and subsequently impact the pollutant's interaction with clay minerals [19,20]. Thus, in this study, HA was coated on clay minerals to simulate the real environment in exploring the HA effect on PFOS adsorption.

The objective of this work was to explore the adsorption mechanism of PFOS on kaolinite and montmorillonite at the molecular level. Multiple complementary techniques were used including adsorption experiments, zeta potential, in situ attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray diffraction (XRD), and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The insights gained from this study would improve our understanding of the fate and transport of PFOS in the environment.

2. Materials and methods

2.1. Materials

Perfluorooctane sulfonate (PFOS, potassium salt; purity $\geq 98\%$) was obtained from AccuStandard, Inc. (New Haven, CT, USA). Humic acid (HA) was purchased from Fluka (Chemie AG, Chemika/Biochemika, Buchs, Switzerland). Ammonium acetate, sodium hydroxide, and sodium chloride in analytical reagent grade were obtained from Sinopharm chemical reagent Co., Ltd. (Shanghai, China). Acetonitrile (HPLC grade) was from Fisher Scientific (Fair lawn, NJ, USA). The reagents were used without further purification. Milli-Q water ($18.2\text{ M}\Omega$, Millipore, USA) was used in all experiments.

Kaolinite (KGa-1b) and montmorillonite (STx-1b) were from the Clay Minerals Society (The Source Clays Repository, Purdue University, USA). The particle size of montmorillonite and kaolinite are $842.9 \pm 125.9\text{ nm}$ for KGa-1b, and $1187.0 \pm 380.8\text{ nm}$ for STx-1b [21]. The BET surface areas of kaolinite and montmorillonite are $11.9\text{ m}^2\text{ g}^{-1}$ and $82.9\text{ m}^2\text{ g}^{-1}$, respectively. Kaolinite and montmorillonite were purified with NaCl solution according to our previous report [22]. Briefly, Na-clays were prepared by adding 10 g clay minerals in 200 mL 0.1 M NaCl solution, then the samples were stirred for 8 h and washed till chloride free. The extractions of

minerals at a solid/water ratio of 1:10 showed no existence of PFOS in KGa-1b and STx-1b.

2.2. Preparation of HA coated clay minerals

The coating of HA on clay minerals was modified from a previous report [19]. Briefly, the HA solution was prepared by dissolving 100 mg HA in 1.0 L water, and the pH was adjusted to 10.0 with NaOH. The solution was sonicated for 10 min before passing through a $0.45\text{-}\mu\text{m}$ filter. After filtration, the solution pH was adjusted to 7.0. Then, 100 mL above HA solution was mixed with 10 g minerals for two weeks at room temperature ($22 \pm 1^\circ\text{C}$). The suspension was centrifuged at 8000 rpm for 30 min and the solid was dried at 60°C . The TOC contents before and after the HA coating process were determined using a Phoenix 8000 Total Organic Carbon (TOC) Analyzer (Tekmar-Dohrmann, USA).

2.3. Batch adsorption experiments

Adsorption experiments were performed in the 50 mL polypropylene centrifuge tubes containing 40 mL of $1.9\text{ }\mu\text{mol L}^{-1}$ PFOS and 0.2 g (5.0 g L^{-1}) clay minerals in 10 mM NaCl solution at $\text{pH } 7.0 \pm 0.1$. Triplicate suspension samples were mixed on a rotator at 40 rpm for 48 h before centrifugation at 8000 rpm for 30 min. The dissolved PFOS concentration was then analyzed using a high performance liquid chromatography-mass spectrometer (HPLC-MS, Waters ZQ4000, Waters, USA) with a detection limit of $1.5\text{ }\mu\text{g L}^{-1}$ according to a previous report [23]. Triplicate control tests in the absence of clay minerals verified that the loss of PFOS is negligible. The solid samples for the following NEXAFS and XRD analysis were prepared in the same way with an initial PFOS concentration of $370\text{ }\mu\text{mol L}^{-1}$, which is lower than the reported Critical Micelle Concentration (CMC) of PFOS in water (1 mmol L^{-1} [24]).

2.4. Zeta (ζ) potential measurements

Zeta (ζ) potential measurements were carried out on a Malvern Zetasizer Nano ZS (Malvern Instruments, U.K.). The pH of the suspensions containing 0.2 g L^{-1} clay minerals and $18.5\text{ }\mu\text{mol L}^{-1}$ PFOS in 10 mM NaCl solution was adjusted in a range of 3.0–11.0 using NaOH and HCl. Suspension samples were placed on a rotator at 40 rpm for 48 h and the final pH was measured. The reported ζ potential value was the average of three measurements.

2.5. In situ ATR-FTIR spectroscopy

The in situ FTIR experiments were carried out on a Nicolet 6700 Fourier transform infrared spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. A multibounce ZnSe ATR crystal with 45° beveled faces (infrared angle of incidence, θ) was used and the infrared spectra were collected using 256 scans per spectrum at a resolution of 4 cm^{-1} . A 10 mM NaCl solution at pH 5.0 was used for electrolyte solution and PFOS solution. The FTIR measurements were described in our previous publication [25]. Briefly, each 0.5 mL of 1.0 g L^{-1} clay materials suspension was added to ZnSe crystal, and evaporated the water at 60°C to form a thin film. The flow cell with the coated film was washed with 10 mM NaCl solution using a LC pump (LC 10A, Shimadzu Corp.) at a flow rate of 0.3 mL min^{-1} to flush out the uncoated particles and to reach equilibrium at the experimental pH values. The background IR spectrum was collected and saved. The electrolyte solution was then changed to 0.7 mmol L^{-1} PFOS at the same pH value as that of electrolyte solution. When PFOS adsorption reached equilibrium, the

solution was then changed back to the electrolyte for the desorption cycle. All of the samples were purged with N_2 in dark during the spectra collection. All data collection and spectral calculations were performed using OMNIC software (version 8.0, Nicolet Instrument Corp.).

2.6. NEXAFS study

The solid residues were freeze-dried, finely grounded, and dusted on a sulfur-free Mylar tape. The sulfur K-edge NEXAFS spectra were collected on the beamline 4B7A at Beijing Synchrotron Radiation Facility (BSRF), China. The spectra for adsorption samples were collected in fluorescence mode using a silicon drift detector positioned 45° to the incident beam. The total electron yield mode was used to collect spectra for the standards including PFOS, SOS, SDS, Na_2S , KSCN, H_2HCSNH_2 , $NaHSO_3$, Na_2SO_3 , $FeSO_4$, and K_2SO_4 . The spectra were energy calibrated by setting the K-edge of K_2SO_4 to 2482.6 eV [26], and background corrected, and normalized using Athena [27].

2.7. XRD analysis

The basal spacing of kaolinite and montmorillonite with adsorbed PFOS were investigated using XRD analysis. The wet solid residues from the batch adsorption experiments were evenly coated on the platinum platform to obtain thin clay films. The XRD patterns were recorded from 4° to 25° using an X'Pert PRO instrument (PANalytical, The Netherlands) with Cu $K\alpha$ radiation ($n = 1.5418 \text{ \AA}$) at $25^\circ C$.

3. Results and discussion

3.1. Batch adsorption experiment

The PFOS adsorption on kaolinite and montmorillonite at pH 7.0 reached 77.6 ± 3.3 and $54.5 \pm 7.2 \mu g g^{-1}$, respectively, with an initial concentration of $1.9 \mu mol L^{-1}$ PFOS and $5.0 g L^{-1}$ clay minerals (Fig. 1). The surface area normalized adsorption were 7.4×10^{-3} molecules per nm^2 for kaolinite and 0.7×10^{-3} molecules per nm^2 for montmorillonite (Table S1). The results show that more than 10

Fig. 1. Adsorption capability of 1.0 mg L^{-1} PFOS on 5.0 g L^{-1} adsorbents at pH 7.0 in 10 mM NaCl solution.

times of PFOS molecules were adsorbed on kaolinite rather than on montmorillonite, suggesting kaolinite could provide more active sites for PFOS adsorption than montmorillonite.

Fig. 2 shows the zeta potentials of kaolinite and montmorillonite in the presence and absence of PFOS. The point of zero charge (PZC) of kaolinite was 3.2, whereas that of montmorillonite was less than 2.0. The results indicate that in the pH range 5.0–7.0, the clay minerals were negatively charged and kaolinite resulted in an even less negative charge than montmorillonite at the same pH values. Because PFOS was negatively charged in a wide pH range ($pK_a = -3.27$ [3]), the electrostatic repulsion between PFOS and clay minerals should inhibit the uptake of PFOS (Fig. 2), and such repulsion is greater on montmorillonite than on kaolinite. If only electrostatic interactions presented between PFOS and clay minerals, no PFOS adsorption would occur. Conversely, the PFOS adsorption on these two clay minerals was observed in our experiments, suggesting that adsorption mechanisms other than electrostatic interactions should exist.

Fig. 2. Zeta potentials of 0.2 g L^{-1} kaolinite (A) and montmorillonite (B) with/without HA coating in the presence (closed symbols) and absence (open symbols) of 10 mg L^{-1} PFOS as a function of pH in 10 mM NaCl solution. Symbols for kaolinite (squares); HA-kaolinite (triangles); montmorillonite (circles); HA-montmorillonite (oblique squares).

Fig. 3. ATR-FTIR spectra of PFOS adsorption and desorption onto kaolinite and HA-kaolinite at pH 5.0 in 10 mM NaCl as a function of time with a rate of 0.3 mL min^{-1} .

3.2. FTIR analysis

To monitor the real-time interactions between PFOS and clay minerals, in situ ATR-FTIR spectroscopy was employed. The dissolved PFOS was used as a reference, and its spectrum and peak assignments are shown in Fig. S1 and Table S2, respectively. The characteristic peaks of PFOS were resolved at 1244 and 1152 cm^{-1} , corresponding to asymmetric and symmetric stretching bands of CF_2 [28], respectively.

The spectra of adsorbed PFOS on the two clay minerals were similar to that of the aqueous PFOS (Figs. 3 and 4 and Fig. S2). This high similarity in FTIR spectra suggested that the adsorption of PFOS as an outer-sphere complex should play a dominant role, in line with a previous report [28]. Here, the driving force for the outer-sphere adsorption of PFOS might be hydrophobic interaction [9,13,15].

Notably, the negative peaks in the range $800\text{--}1200 \text{ cm}^{-1}$ were resolved which were ascribed to the dissolution of silicic group (e.g. 1006 , 1031 , 1090 , 1114 cm^{-1} for Si–O stretching vibration) and aluminous group (e.g. 912 cm^{-1} for Al–OH deformation) on the clay minerals (Figs. 3 and 4, Table S3). Before FTIR signals were collected, the clay minerals films had been equilibrated with the electrolyte solution, and therefore, the dissolution should be facilitated by the surface reactions between PFOS and clay minerals. These interactions may be ligand exchange [29], and acid–base reaction [21,30]. Because the sulfonate group is a hard base and clay minerals are hard acids [9,21], the hard base is readily adsorbed on clay surfaces based on the hard-soft-acid-base (HSAB) reaction theory. The results indicate that both the hydrophobic C–F chain and the functional sulfonate group could affect PFOS adsorption on clay minerals. This conclusion was further justified by the following kinetic study using the parabolic diffusion model.

3.3. Adsorption–desorption kinetics of PFOS

To understand the adsorption dynamics, the kinetics of adsorption and desorption were characterized by the change in FTIR

peak intensity of $\nu_{\text{as}}(\text{CF}_2)$ band centered at 1244 cm^{-1} (Fig. 5). The kinetics of PFOS adsorption and desorption followed the parabolic diffusion model well ($R^2 > 0.842$, Fig. 5, Table S4). Generally, the parabolic diffusion indicates that the diffusion-controlled phenomena are rate-limiting. In our study, PFOS adsorption process was similar to those of anionic surfactants and can be divided into two processes including a rapid formation of an outer-sphere complex followed by a slow ligand exchange reaction with the elimination of adsorbed H_2O molecules [31,32]. The second slow process lasted about 80 min which was the rate controlling step in PFOS adsorption. In addition, the PFOS desorption process also showed a two-step process (Fig. 5). The initial rapid decrease was mainly due to the removal of weakly adsorbed PFOS [33]. Our FTIR kinetics results indicated that physical and chemical interactions occurred for PFOS adsorption on clay minerals. To testify the chemical nature in PFOS adsorption, we employed the following NEXAFS study.

3.4. NEXAFS analysis

NEXAFS is sensitive to the structure change near the target atom, and is used as a probe for the chemical state of sulfur in minerals and chemical compounds [34]. Because sulfonate group serves as the functional and active moiety in PFOS molecules, S K-edge NEXAFS can be applied to the structural analysis for PFOS surface complex. The PFOS spectrum exhibited a strong white line peak at 2481.2 eV (Fig. 6), which originates from the excitation of S $1s$ core electrons into unoccupied S $3p$ orbitals [35]. The broad peak in the range $2479.0\text{--}2484.0 \text{ eV}$ was primarily attributed to the number and nature of first coordination shell around the scattering S atom (S–O, S=O, S–C), and also to the next nearest-neighbor atoms including K, C, and F, as well as metal atoms on surfaces [26].

Upon PFOS adsorption, three pre-edge peaks were observed at 2467.8 , 2473.8 , and 2476.4 eV for kaolinite, and 2473.8 , 2476.4 and 2478.4 eV for montmorillonite (Fig. 6B). The pre-edge peaks are usually ascribed to the presence of low oxidation state of S

Fig. 4. ATR-FTIR spectra of PFOS adsorption and desorption onto montmorillonite and HA-montmorillonite at pH 5.0 in 10 mM NaCl as a function of time with a rate 0.3 mL min^{-1} .

Fig. 5. FTIR peak intensity of PFOS at 1244 cm^{-1} on different adsorbents at pH 5.0 as a function of time. Symbols for kaolinite ($\square$); montmorillonite ($\circ$); HA-kaolinite (Δ); HA-montmorillonite ($\diamond$). Solid line stands for the parabolic diffusion model fitting.

[36–38]. However, the observed pre-edge peaks in this study were not induced by other lower valence S-compounds, as evidenced by the failure in matching their peak positions with reference compounds (Fig. 6A) [37]. Not surprisingly, PFOS would not transform to other S-containing compounds upon adsorption because of its high chemical stability. Thus, such pre-edge peaks indicated that the symmetry or local coordinates of S atom was changed after PFOS adsorption on kaolinite and montmorillonite.

The hybridization between S 3p and unoccupied transition metal *d* orbitals has been reported to induce S pre-edge peaks [39,40]. Interestingly, such hybridization occurred in spite of the presence of oxygen atom that separate sulfur from transition metal ions [41]. In agreement with our observations, the S and P pre-edge peaks were reported in transition-metal sulphate and phosphate

[41,42]. These pre-edge peaks can arise only if transition metal ion is bounded to S via a bridging O [43], corresponding to an inner-sphere complex at the solid/aqueous interface. Our NEXAFS analysis demonstrated the chemisorption nature of PFOS on clay minerals.

3.5. XRD analysis

To test whether the interlayer intercalation could be an important contributor to PFOS adsorption, the XRD patterns for PFOS-free and PFOS-adsorbed clay minerals were investigated. The XRD patterns of kaolinite with and without PFOS adsorption showed no significant change (Fig. 7), which suggested that PFOS molecules can not occupy the interlayers of kaolinite. In contrast, as shown in Fig. 7, a broad peak at a *d*-spacing of 1.19 nm for the wet paste of montmorillonite without PFOS adsorption indicated the existence of interlayer hydration with monolayer of water molecules [44,45]. Upon PFOS adsorption, a slight increase in *d*(001) spacing from 1.19 to 1.24 nm was observed, which is consistent with a previous report on expansion from 1.34 to 1.46 nm [46]. The magnitude of the *d*-spacing increase (0.05 nm) was significant less than the molecular sectional size of PFOS (OD: $\approx 0.40 \text{ nm}$ [9]), which indicated that PFOS may partially insert into interlayers of montmorillonite during the adsorption. In conclusion, our XRD results indicated that interlayer adsorption existed on montmorillonite, whereas no interlayer adsorption occurred on kaolinite.

3.6. Effects of HA coating

To simulate the natural particulate assembly where clay minerals are associated with organic matter, HA was coated on kaolinite and montmorillonite [19] with the concentration of 60 and $32 \mu\text{g-Cg}^{-1}$ (Table S1), respectively. PFOS adsorption experiments were then performed on such HA-kaolinite and HA-montmorillonite to exploit the impact of the coated HA. The results in Fig. 1

Fig. 6. Sulfur K-edge NEXAFS spectra of PFOS and PFOS adsorbed on two clay minerals.

showed that the coated HA decreased PFOS adsorption by 19.8% on kaolinite and by 25.3% on montmorillonite. This adsorption decrease could be attributed to the negatively charged HA, which may inhibit PFOS adsorption due to adsorption site occupancy and electrostatic repulsion. The HA coating may increase the electrostatic repulsion between PFOS and clay minerals because HA coating decreased the zeta potential of the particle (Fig. 2).

Our FTIR analysis also confirmed the adverse effect of HA coating on PFOS adsorption. The FTIR results showed the Si–O vibration at 1006, 1031, 1090 cm^{-1} on kaolinite and 1095 cm^{-1} on montmorillonite disappeared upon HA coating (Figs. 3 and 4) [10,47], suggesting adsorption sites occupation by HA. In addition, the intensity of C–F bond decreased by 4.8% and 68.0% on HA-kaolinite and HA-montmorillonite, respectively (Fig. 5). However, PFOS adsorption kinetics were not changed in the presence and absence of coated HA (Table S4), suggesting the HA coating would not affect the adsorption mechanisms. The significant

discrepancy of PFOS adsorption decrease by HA coating may be caused by the fact that HA occupied most of the available adsorptive sites on montmorillonite but a large amount of sites still remained on kaolinite.

Contrast to our results, previous study reports that sediment organic carbon should be attributable to PFOS uptake due to hydrophobic partitioning, in which the PFOS distribution coefficient was linearly increased with the organic carbon content increasing from 0.6% to 9.7% [16]. The contrast observations may be due to the amount of HA on surfaces. The high content of HA (OC, 0.6–9.7% [16]) in sediment could serve as organic phase to absorb PFOS, whereas minor HA (<0.1%) on surface may compete with PFOS for adsorption. The results highlight the complex impact of HA, the major composition of nature organic carbon, on the fate and transport of PFOS.

4. Conclusions

The mechanistic understanding of PFOS adsorption on clay minerals in the presence of humic acid is a fundamental basis in evaluating its fate, transport, and toxicity. The hydrophobic and electrostatic interactions play an important role in PFOS adsorption on kaolinite and montmorillonite, and therefore PFOS mainly forms outer-sphere surface complex. In addition to non-specific physical interactions, specific chemisorption also exists between sulfonate group of PFOS and hydroxyl group on surfaces of clay minerals. Interlayer intercalation can influence the PFOS adsorption, depending on the structure of the clay minerals: no interlayer adsorption exists for PFOS on kaolinite, whereas interlayer insertion occurs on montmorillonite. When the surface of minerals is coated with humic acid, the adsorption of PFOS could be inhibited due to the electrostatic repulsion and occupation of adsorption sites. These dissolved humic substances, once adsorbed on minerals under natural conditions, may hinder the adsorption of PFOS onto clay minerals. Our results highlight the importance of clay minerals and humic acid on the adsorption of PFOS and its fate and transport in the environment.

Fig. 7. X-ray diffraction patterns of kaolinite and montmorillonite wet paste adsorbed with and without PFOS at pH 7.0 in 10 mM NaCl.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.09.019>.

References

- [1] L. Zhang, J.G. Liu, J.X. Hu, C. Liu, W.G. Guo, Q. Wang, H. Wang, The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China, *Environ. Pollut.* 165 (2012) 193–198.
- [2] F. Xiao, K.J. Davids, S. Park, M. Nakayama, B.R. Phillips, Batch and column study: sorption of perfluorinated surfactants from water and cosolvent systems by Amberlite XAD resins, *J. Colloid Interface Sci.* 368 (2012) 505–511.
- [3] D. Brooke, A. Footitt, T. Nwaogu, Environmental Risk Evaluation Report: Perfluorooctanesulphonate (PFOS), UK Environment Agency, 2004.
- [4] K.J. Hansen, H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, L.A. Dick, Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River, *Environ. Sci. Technol.* 36 (2002) 1681–1685.
- [5] A. Beyer, D. Mackay, M. Matthies, F. Wania, E. Webster, Assessing long-range transport potential of persistent organic pollutants, *Environ. Sci. Technol.* 34 (2000) 699–703.
- [6] R. Bossi, F.F. Riget, R. Dietz, C. Sonne, P. Fauser, M. Dam, K. Vorkamp, Preliminary screening of perfluorooctane sulfonate (PFOS) and other fluorochlorinated in fish, birds and marine mammals from Greenland and the Faroe Islands, *Environ. Pollut.* 136 (2005) 323–329.
- [7] G. He, G. Pan, M. Zhang, Assembling structures and dynamics properties of perfluorooctane sulfonate (PFOS) at water–titanium oxide interfaces, *J. Colloid Interface Sci.* 405 (2013) 189–194.
- [8] N.R. Hari, G.S. Grest, C.D. Lorenz, Viscosity of nanoconfined water between hydroxyl basal surfaces of kaolinite: classical simulation results, *J. Phys. Chem. C* 117 (2013) 6096–6104.
- [9] F. Xiao, X. Zhang, L. Penn, J.S. Gulliver, M.F. Simcik, Effects of monovalent cations on the competitive adsorption of perfluoroalkyl acids by kaolinite: experimental studies and modeling, *Environ. Sci. Technol.* 45 (2011) 10028–10035.
- [10] K. Wang, B. Xing, Structural and sorption characteristics of adsorbed humic acid on clay minerals, *J. Environ. Qual.* 34 (2005) 342–349.
- [11] Y. Tsujimoto, C. Chassagne, Y. Adachi, Comparison between the electrokinetic properties of kaolinite and montmorillonite suspensions at different volume fractions, *J. Colloid Interface Sci.* 407 (2013) 109–115.
- [12] C.D. Hatch, J.S. Wiese, C.C. Crane, K.J. Harris, H.G. Kloss, J. Baltrusaitis, Water adsorption on clay minerals as a function of relative humidity: application of BET and freundlich adsorption models, *Langmuir* 28 (2012) 1790–1803.
- [13] G. Sposito, N.T. Skipper, R. Sutton, S.-H. Park, A.K. Soper, J.A. Greathouse, Surface geochemistry of the clay minerals, *Proc. Natl. Acad. Sci. U.S.A.* 96 (1999) 3358–3364.
- [14] R.L. Johnson, A.J. Anschutz, J.M. Smolen, M.F. Simcik, R.L. Penn, The adsorption of perfluorooctane sulfonate onto sand, clay, and iron oxide surfaces, *J. Chem. Eng. Data* 52 (2007) 1165–1170.
- [15] C.Y. Tang, Q. Shiang Fu, D. Gao, C.S. Criddle, J.O. Leckie, Effect of solution chemistry on the adsorption of perfluorooctane sulfonate onto mineral surfaces, *Water Res.* 44 (2010) 2654–2662.
- [16] C.P. Higgins, R.G. Luthy, Sorption of perfluorinated surfactants on sediments, *Environ. Sci. Technol.* 40 (2006) 7251–7256.
- [17] B. Gu, J. Schmitt, Z. Chen, L. Liang, J.F. McCarthy, Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models, *Environ. Sci. Technol.* 28 (1994) 38–46.
- [18] X. Wang, X. Shan, L. Luo, S. Zhang, B. Wen, Sorption of 2,4,6-trichlorophenol in model humic acid-clay systems, *J. Agric. Food. Chem.* 53 (2005) 3548–3555.
- [19] K. Yang, B. Xing, Sorption of phenanthrene by humic acid-coated nanosized TiO₂ and ZnO, *Environ. Sci. Technol.* 43 (2009) 1845–1851.
- [20] L. Weng, W.H. Van Riemsdijk, L.K. Koopal, T. Hiemstra, Adsorption of humic substances on goethite: comparison between humic acids and fulvic acids, *Environ. Sci. Technol.* 40 (2006) 7494–7500.
- [21] C.V. Chrysikopoulos, V.I. Syngouna, Attachment of bacteriophages MS2 and (X174 onto kaolinite and montmorillonite: extended-DLVO interactions, *Colloids Surf. B* 92 (2012) 74–83.
- [22] W. Yan, S. Hu, C. Jing, Enrofloxacin sorption on smectite clays: effects of pH, cations, and humic acid, *J. Colloid Interface Sci.* 372 (2012) 141–147.
- [23] G. Pan, C.X. Jia, D.Y. Zhao, C. You, H. Chen, G.B. Jiang, Effect of cationic and anionic surfactants on the sorption and desorption of perfluorooctane sulfonate (PFOS) on natural sediments, *Environ. Pollut.* 157 (2009) 325–330.
- [24] C.Y. Tang, Q.S. Fu, A.P. Robertson, C.S. Criddle, J.O. Leckie, Use of reverse osmosis membranes to remove perfluorooctane sulfonate (PFOS) from semiconductor wastewater, *Environ. Sci. Technol.* 40 (2006) 7343–7349.
- [25] Y. Yang, W. Yan, C. Jing, Dynamic adsorption of catechol at the goethite/aqueous solution interface: a molecular-scale study, *Langmuir* 28 (2012) 14588–14597.
- [26] R. Alonso Mori, E. Paris, G. Giuli, S.G. Eeckhout, M. Kavčič, M. Žitnik, K. Bučar, L.G.M. Pettersson, P. Glatzel, Electronic structure of sulfur studied by X-ray absorption and emission spectroscopy, *Anal. Chem.* 81 (2009) 6516–6525.
- [27] B. Ravel, M. Newville, Athena, artemis, hephaestus data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchrotron Rad.* 12 (2005) 537–541.
- [28] X. Gao, J. Chorover, Adsorption of perfluorooctanoic acid and perfluorooctane sulfonic acid to iron oxide surfaces as studied by flow-through ATR-FTIR spectroscopy, *Environ. Chem.* 9 (2012) 148–157.
- [29] X. Feng, A.J. Simpson, M.J. Simpson, Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces, *Org. Geochem.* 36 (2005) 1553–1566.
- [30] C.L. Lai, J.H. Harwell, E.A. O'Rear, S. Komatsuzaki, J. Arai, T. Nakakawaji, Y. Ito, Adsorption isotherms of perfluorocarbon surfactants from aqueous and non-aqueous solutions and friction measurements of perfluorosurfactant-adsorbed alumina, *Colloids Surf. A: Physicochem. Eng. Asp.* 104 (1995) 231–241.
- [31] T.H. Yoon, S.B. Johnson, C.B. Musgrave, J.G.E. Brown, Adsorption of organic matter at mineral/water interfaces: I. ATR-FTIR spectroscopic and quantum chemical study of oxalate adsorbed at boehmite/water and corundum/water interfaces, *Geochim. Cosmochim. Acta* 68 (2004) 4505–4518.
- [32] R. Xing, S.E. Rankin, Three-stage multilayer formation kinetics during adsorption of an anionic fluorinated surfactant onto germanium. 1. Concentration effect, *J. Phys. Chem. B* 110 (2005) 295–304.
- [33] A.G. Young, A.J. McQuillan, Adsorption/desorption kinetics from ATR-IR spectroscopy. Aqueous oxalic acid on anatase TiO₂, *Langmuir* 25 (2009) 3538–3548.
- [34] S. Asaoka, S. Hayakawa, K. Kim, K. Takeda, M. Katayama, T. Yamamoto, Combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash, *J. Colloid Interface Sci.* 377 (2012) 284–290.
- [35] H. Sekiyama, N. Kosugi, H. Kuroda, T. Ohta, Sulfur K-edge absorption spectra of Na₂SO₄, Na₂SO₃, Na₂S₂O₃, and Na₂S₂O₅ ($x=5-8$), *Bull. Chem. Soc. Jpn.* 59 (1986) 575–579.
- [36] O.A. Baturina, B.D. Gould, A. Korovina, Y. Garsany, R. Stroman, P.A. Northrup, Products of SO₂ adsorption on fuel cell electrocatalysts by combination of sulfur K-edge XANES and electrochemistry, *Langmuir* 27 (2011) 14930–14939.
- [37] G. Sarret, J. Connan, M. Kasrai, G.M. Bancroft, A. Charrière-Duhaut, S. Lemoine, P. Adam, P. Albrecht, L. Eybert-Bérard, Chemical forms of sulfur in geological and archeological asphaltenes from Middle East, France, and Spain determined by sulfur K- and L-edge X-ray absorption near-edge structure spectroscopy, *Geochim. Cosmochim. Acta* 63 (1999) 3767–3779.
- [38] J.R. Prieztel, A. Botzaki, N. Tyufekchieva, M. Brettholle, J.R. Thieme, W. Klysubun, Sulfur speciation in soil by S K-edge XANES spectroscopy: comparison of spectral deconvolution and linear combination fitting, *Environ. Sci. Technol.* 45 (2011) 2878–2886.
- [39] B.O. Leung, F. Jalilehvand, R.K. Szilagy, Electronic structure of transition metal-cysteine complexes from X-ray absorption spectroscopy, *J. Phys. Chem. B* 112 (2008) 4770–4778.
- [40] A. Dey, M. Chow, K. Taniguchi, P. Lugo-Mas, S. Davin, M. Maeda, J.A. Kovacs, M. Odaka, K.O. Hodgson, B. Hedman, E.I. Solomon, Sulfur K-edge XAS and DFT calculations on nitrile hydratase: geometric and electronic structure of the non-heme iron active site, *J. Am. Chem. Soc.* 128 (2005) 533–541.
- [41] N. Okude, M. Nagoshi, H. Noro, Y. Baba, H. Yamamoto, T.A. Sasaki, P and S K-edge XANES of transition-metal phosphates and sulfates, *J. Electron. Spectrosc. Relat. Phenom.* 101–103 (1999) 607–610.
- [42] W. Xiong, J. Peng, Y. Hu, Use of X-ray absorption near edge structure (XANES) to identify physisorption and chemisorption of phosphate onto ferrihydrite-modified diatomite, *J. Colloid Interface Sci.* 368 (2012) 528–532.
- [43] J. Majzlan, S.-C.B. Myneni, Speciation of iron and sulfate in acid waters: aqueous clusters to mineral precipitates, *Environ. Sci. Technol.* 39 (2005) 188–194.
- [44] F.-R.C. Chang, N.T. Skipper, G. Sposito, Computer simulation of interlayer molecular structure in sodium montmorillonite hydrates, *Langmuir* 11 (1995) 2734–2741.
- [45] N. Skipper, G. Sposito, F.-R.C. Chang, Monte Carlo simulation of interlayer molecular structure in swelling clay minerals. 2. Monolayer hydrates, *Clays Clay Miner.* 43 (1995) 294–303.
- [46] Q. Zhou, S. Deng, Q. Yu, Q. Zhang, G. Yu, J. Huang, H. He, Sorption of perfluorooctane sulfonate on organo-montmorillonites, *Chemosphere* 78 (2010) 688–694.
- [47] S. Kang, B. Xing, Phenanthrene sorption to sequentially extracted soil humic acids and humins, *Environ. Sci. Technol.* 39 (2005) 134–140.