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Adsorption behavior of perfluorochemicals (PFCs) on boehmite: influence of solution chemistry

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Abstract

With global distribution, persistence nature, and strong bioaccumulation, the fate and transport of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) in natural environment have recently attracted strong attentions. As boehmite is a common form of hydrated aluminum oxide existing in soils and sediments, this study successfully revealed the adsorption behavior of PFOS and PFOA on boehmite and the influence from solution chemistry. The results of kinetic experiments show that the adsorption equilibrium can be achieved within 48 hours and the boehmite surface is generally receptive to PFOS and PFOA adsorption. The adsorption isotherms estimated the maximum adsorption capacities of PFOS and PFOA on boehmite to be 0.877 $\mu g/m^2$ and 0.633 $\mu g/m^2$, respectively. The increase of pH can lead to a moderate decrease of PFOS and PFOA adsorption, owing to the increase of ligand exchange reaction and the decrease of electrostatic interaction. With the compression of electrical double layers, the competitive adsorption from the other ions and the Ca^{2+} bridging effect between perfluorochemicals have demonstrated their negative influence for PFOS and PFOA adsorption on boehmite surface. Finally, humic acid (HA) also showed significant retardant effects on the sorption of perfluorooctanesulfonate (PFOS) and perfluorobutanesulfonate (PFBuS) on boehmite.

Keywords: PFOS; PFOA; isotherm; pH; ionic strength; humic acid

1. Introduction

Perfluorochemicals (PFCs) are a type of anionic surfactant with high-energy carbon-fluorine (C-F) bonds that render them persistent in the environment [1]. Within the PFC group, the compounds perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) have been widely found in sediment, sludge, municipal wastewater, coastal water, and even tap water [2-5]. Due to the wide distribution and

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bioaccumulation of PFOS and PFOA in the environment, they have been proposed as persistent organic pollutants (POPs) [6]. Different from other POPs, however, PFOS and PFOA are highly water-soluble; thus, they are easy to transport in an aquatic environment. At the same time, the hydrophobic chain and hydrophilic functional groups may provide opportunities for PFOS and PFOA to adsorb onto the surfaces of a variety of environmental solid matrices.

Because of the persistent nature of PFOS and PFOA in the environment and these compounds' harmful effects on human beings, studies to understand their fate and transport in aquatic environments is important [3, 7-9]. It was reported that both organic matter and minerals played important roles in the PFC sorption process [3]. In groundwater systems, the fate and transport of PFCs presumably has a strong dependence on interactions with surrounding mineral surfaces, however, the interactions between PFCs and minerals are not well characterized. Boehmite (AlOOH) is a common form of hydrated aluminum oxide that usually exists as fine-grained constituents in soils and sediments due to its thermodynamic stability under hydrous conditions [10]. Boehmite is also an important industrial mineral used as a catalyst or adsorbent because of its ability to retain high surface area [10-11]. As the point of zero charge (PZC) of boehmite has been determined to be between 7.7 and 9.4 [12], it is likely to exist with positive charges on its surface in nature. Boehmite's protonated surface renders it easy for compounds with negative charges to be attached by electrostatic attraction and thus PFOS and PFOA, which are anionic, are likely to be adsorbed on the surface of boehmite and this mechanism may play an important role in the fate and transport of these compounds in the environment.

The adsorption behavior of PFOS and PFOA on boehmite has not yet been systematically investigated; therefore the first goal of this study was to quantify the adsorption capacities of PFOS and PFOA on boehmite through sorption kinetics and isotherm experiments. Experiments observing the adsorption behavior of PFOS and PFOA on boehmite under different solution pH, ionic strengths, and humic acid (HA) concentrations were then performed to observe their effect on the adsorption process.

2. Materials and Methods

2.1. Materials and Characterization

Boehmite was purchased from Sasol Ltd. (Hamburg, Germany). PFOS (potassium salt) and PFOA were purchased from Sigma-Aldrich Co. (St. Louis, MO). Humic acid was obtained from Fluka Co. (Buchs, Switerland) and the carbon content was determined to be around 32% by Total Organic Carbon (TOC) Analyzer (Shimadzu, Japan) Sodium chloride and calcium chloride were purchased from BDH Ltd. (Poole, Dorset, UK). Optima grade methanol was purchased from Fisher Scientific (Pittsburgh, PA), and the ammonium acetate used to prepare the mobile phase in LC/MS/MS analysis was obtained from VWR International Ltd. (Poole, Dorset, UK). Using an X-ray powder diffractometer (D8 Advance, Bruker, Germany), the as-received boehmite was found to be dominated by a nanocrystalline AlOOH. The surface area of the boehmite was measured with a surface area analyzer (Coulter SA 3100, Beckman, Fullerton, CA) as 299.2 ± 1.8 m^2/g. The boehmite's PZC (pH$_{pzc}$) was determined to be pH 8.4 by a zeta-potential analyzer (Coulter Delsa 440SX, Beckman, Fullerton, CA). The average particle size (d$_{50}$) of as-received boehmite was approximately 37.02 μm, as measured by a particle counter (Coulter Multisizer II, Beckman, Fullerton, CA). Boehmite was purchased from Sasol Ltd. (Hamburg, Germany). PFOS (potassium salt) and PFOA were purchased from Sigma-Aldrich Co. (St. Louis, MO). Humic acid was obtained from Fluka Co. (Buchs, Switerland) and the carbon content was determined to be around 32% by total organic carbon (TOC) analyzer (Shimadzu, Japan). Sodium chloride and calcium chloride were purchased from BDH Ltd. (Poole, Dorset, UK). Optima grade methanol was purchased from Fisher

Scientific (Pittsburgh, PA), and the ammonium acetate used to prepare the mobile phase in LC/MS/MS analysis was obtained from VWR International Ltd. (Poole, Dorset, UK).

2.2. Sorption Experiments and PFC Determination

All sorption experiments were conducted in 50 ml polypropylene copolymer (PPCO) Nalgene centrifuge tubes (Rochester, NY) containing 0.1 g of boehmite and 20 ml of solution with varying PFOS or PFOA concentrations. The tubes were shaken at 150 rpm and kept at 25 °C for 72 h. The pH was adjusted by 0.1 M HCl and 0.1 M NaOH solutions, and the ionic strengths were controlled by adding 1 M stock solutions of $NaCl_{(aq)}$ and $CaCl_{2(aq)}$. The HA concentrations in the working solutions were adjusted within the range of 2 mg/L to 50 mg/L. The kinetic sorption experiments used an initial PFOS or PFOA concentration of 200 µg/L. The sorption isotherm experiments were carried out with PFOS or PFOA concentrations ranging from 50 µg/L to 1000 µg/L. After the sorption experiments, the working solutions were centrifuged at 4000 rpm for 10 min, and then 10 ml supernatant solution was transferred to the glass bottle for TOC analysis.1.5 ml of sample solution was diluted with 3.5 ml methanol (v/v = 3/7). The mixture was then filtered with a 0.2 µm Whatman inorganic membrane filter (Maidstone, UK), and the initial 3 ml of the mixture was discarded to reduce the potential effect of membrane adsorption. The concentrations of PFOS (or PFOA) were determined using a Waters Acquity ultra-performance LC/MS/MS system (UPLC/MS/MS) equipped with a 50 × 2.1-mm Waters BEH C18 column (1.7-µm particle size) and tandem quadrupole mass spectrometers (Milford, MA).

3. Results and Discussion

3.1. Sorption Kinetics and Isotherm Study

Fig. 1(a) shows the adsorption kinetics of PFOS and PFOA on boehmite, which indicates that approximately 48 h of agitation were required to reach the equilibrium for both PFOS and PFOA adsorption, similar to the ranges reported in studies of PFOS adsorption on a variety of minerals [7,13]. This result shows that the mineral-water interfaces are accessible for PFOS and PFOA molecules, and thus equilibrium was rapidly reached.
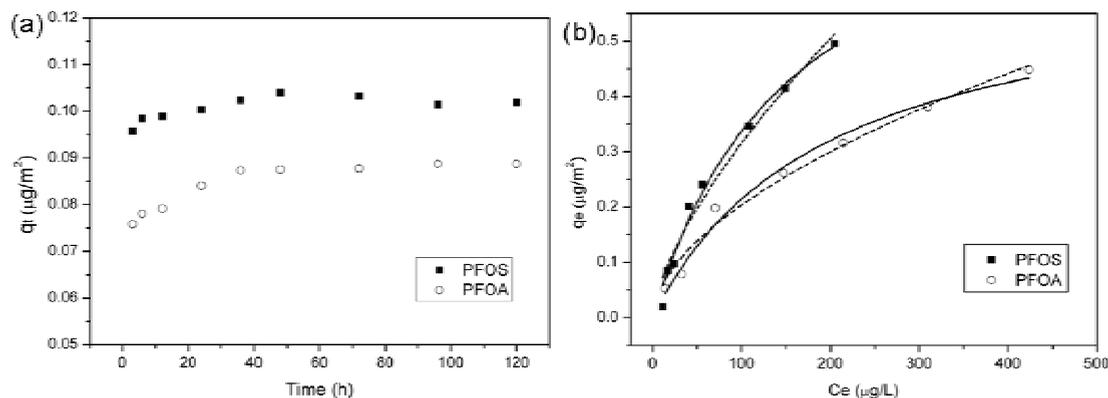

Fig. 1. PFOS and PFOA adsorption kinetics (a) and adsorption isotherms (b) on boehmite. The solid lines are the fitted Langmuir isotherms, and the dashed lines are the fitted Freundlich isotherms.

The adsorption isotherms of PFOS and PFOA on boehmite at pH 7 are shown in Fig. 1(b). The Langmuir and Freundlich equations were applied to model the experimental data, and the derived constants are provided in Table 1. The adsorption isotherms of PFOS and PFOA were found to fit well with both the Langmuir and Freundlich equation, judging from the correlation coefficients (R^2) in Table 1. The good fitness of Langmuir equation hints that the adsorption of PFOS and PFOA may occur on the boehmite surface with monolayer coverage. The good fitness of Freundlich equation as well as Langmuir equation indicates the concentration of PFOS and PFOA may also dominate the adsorption process.

Table 1. Constants of Langmuir and Freundlich equations for the adsorption of PFOS and PFOA on boehmite.

Adsorbate	Langmuir constants			Freundlich constants		
	K_L (L/µg)	q_m (µg/m^2)	R^2	K_F[(µg/m^2)(µg/L)$^{-n}$)]	n	R^2
PFOS	0.00622	0.877	0.985	0.0139	0.678	0.969
PFOA	0.00512	0.633	0.984	0.0155	0.559	0.980

NOTE: "R^2" is the correlation coefficient of fitting result.

It has been suggested that amphiphilic compounds may adsorb onto minerals in hemi-micelles when the organic ions are present at 0.001 to 0.01 of the critical micelle concentration [14]. The critical micelle concentration (CMC) of PFOS and PFOA was reported at around 8 mM and 25 mM [15], respectively. In this study, the PFOS and PFOA concentrations were all controlled below 1 ppm (around 0.002 mM) in experiment, and thus the hemi-micelles were unlikely to form during the adsorption processes. This condition also supports the monolayer adsorption behavior described by Langmuir model.

For adsorption on boehmite, the maximum adsorption capacities were estimated to be 0.877 µg/m^2 for PFOS and 0.633 µg/m^2 for PFOA. This result is similar to our previous result that γ-alumina showed a higher affinity toward PFOS than PFOA. Higgins and Luthy [3] attributed the different adsorption levels between perfluorosulfonate and perfluorocarboxylate to the slightly larger size of the sulfonate moiety as compared to the carboxylate moiety. According to Pearson's concept of hard- and soft-acids/bases, the carboxylate group is a soft base while the sulfonate group is a relatively hard one, and a hard base is more readily adsorbed on oxide surfaces which are hard acids [16,17].

3.2. Effects of pH and Ionic Strength

The effects of varying pH on the adsorption of PFOS and PFOA are shown in Fig. 2. Since the pKa values of PFOS and PFOA are lower than 1, PFOS and PFOA mainly existed in anionic forms within the pH range (4.0-7.5) tested in this study. The PZC of the boehmite in this study was measured at around 8.4, and hence the surface of boehmite was positively charged in the tested pH range. The protonation reaction of boehmite and the electrostatic attraction between anionic PFOS or PFOA and protonated boehmite are as follows:

$$\text{Al-OH} + \text{H}^+ \rightarrow \text{Al-OH}_2^+ \tag{1}$$
$$\text{Al-OH}_2^+ + \text{L}^- \rightarrow \text{Al-OH}_2\text{-L} \tag{2}$$

Therefore, the decrease of solution pH can increase the positive sites on the boehmite surface, which may lead to the increase of PFOS and PFOA adsorption we observed. The adsorption behavior within this pH range can be explained by the increase in electrostatic interactions and/or the formation of surface complexes by ligand exchange [18]. In our previous study, the adsorbed concentrations of PFOS or

PFOA on γ-alumina (pH_{pzc}= 8.5) increased three to four times when pH decreased from 6.5 to 4.0. However, only a 20%-30% increase of PFOS or PFOA adsorption levels on boehmite was observed when the pH decreased from 7.0 to 4.0. This comparison indicates that the adsorption behavior of PFOS and PFOA on boehmite may not be fully due to the electrostatic interaction mechanism. The increase of H^+ concentration not only increases $Al-OH_2^+$ sites, but also decreases the Al-OH sites on boehmite surfaces (Eq. 1). Therefore, if the pH is decreased, the ligand exchange reaction will be decreased and the electrostatic interaction (Eq. 2) will be increased. The observed moderate increases of PFOS and PFOA adsorption following the decrease of solution pH may be attributed to electrostatic interaction counteracted by the reduced ligand exchange.
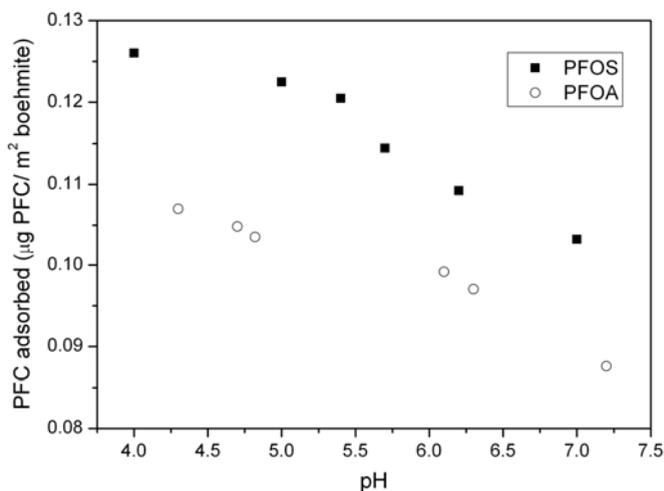

Fig.2. Effect of pH on the adsorption of PFOS and PFOA.

Salts are abundant from natural and anthropogenic sources, and the salinity of surface water and groundwater can vary considerably. For example, NaCl can be used as a road de-icing agent and enters wetlands, lakes and rivers [19]. Thus, the influence of NaCl on PFOS and PFOA adsorption may be important in determining the environmental fates of PFOS and PFOA. Fig. 3(a) shows the influence of different NaCl concentrations on the PFOS and PFOA adsorption on boehmite surfaces, and indicates a decreasing trend of PFOS and PFOA adsorption with the increase of NaCl concentration. A possible explanation of this result is that the higher ionic strength causes a decrease of electrostatic attraction between the positively charged boehmite surface and the negatively charged PFC molecules, due to the compression of the electrical double layer (EDL), and the reduction in ζ-potential [9]. In addition, Regalbuto et al. [20] reported their observation of minor direct uptake of chloride by aluminum oxide. In such a case, the potential hindering effect due to the competitive adsorption of chloride ions on the active adsorption sites may also decrease the adsorption of PFOS and PFOA on the boehmite surface [21]. A study of PFOS adsorption on goethite observed a significant adsorption enhancement with the increase (1 mM to 3 mM) of $CaCl_2$ concentration in the system, and pointed out the increase of surface charge due to the potential binding of calcium ions on the goethite surface [8]. In this study, the influence of $CaCl_2$ concentration on PFOS and PFOA adsorption on boehmite was further tested and the result is illustrated in Fig. 3(b). In contrast to the literature, we found the adsorption of PFOS and PFOA on boehmite to decrease with increasing $CaCl_2$ concentration in the solution. The effect of $CaCl_2$ was similar to the effect of NaCl concentration, both negatively affecting the adsorption of PFOS and PFOA on boehmite,

potentially due to the EDL compression and the competitive adsorption of chloride ions. Moreover, the bridging effect of Ca^{2+} between PFCs [9] may further lead to a reduction in PFOS and PFOA adsorption on boehmite. Overall, the strong dependence of NaCl and $CaCl_2$ concentrations on PFOS and PFOA adsorption has clearly indicated the importance of electrostatic considerations in predicting the PFC behavior on a hydrated aluminum oxide surface.
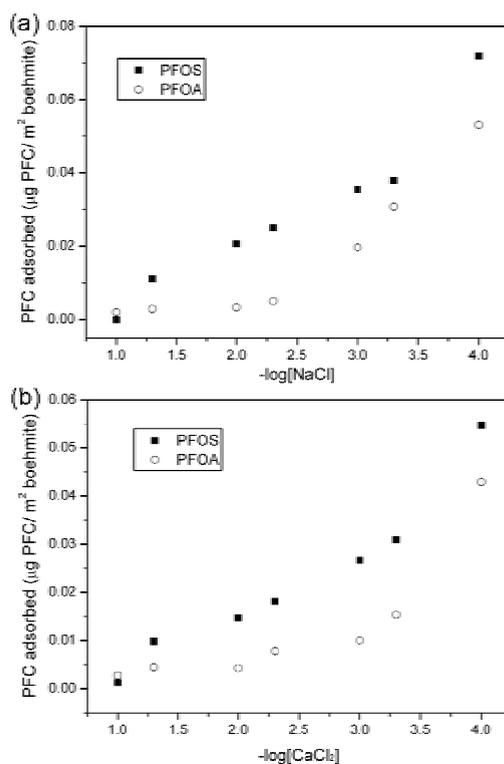

Fig. 3. Effect of NaCl (a) and $CaCl_2$ (b) concentrations on the adsorption of PFOS and PFOA.

3.3. Effects of HA Concentrations

Fig. 4 shows the influences of HA initial concentration on the sorption levels of HA and PFOS on boehmite. It is clear that HA sorption increased while PFOS sorption decreased significantly as HA initial concentration was up to 30 mg/L. It indicated that HA was with a strong competition with PFOS at the surface of boehmite. It has been reported that the sorption mechanisms of HA on minerals mainly included electrostatic interaction, ligand exchange and hydrophobic interaction [22]. Due to the hydrophilicity of boehmite, hydrophobic interaction should not occur between the boehmite surface and HA. The reported interactions between PFC and boehmite include electrostatic interaction and ligand exchange [23]. Thus, a strong competition between HA and PFOS on the positive sites of boehmite surface will occur with a ternary system containing boehmite, HA and PFOS. The sorption sites on boehmite surface were gradually occupied by HA molecules with the increase of HA concentration, which decreases the available sites left for PFOS adsorption. Furthermore, the sorption of HA will initiate the negative charge on the surface of boehmite to repulse the electrostatic sorption of PFOS, since HA

contains numerous carboxylic and phenolic negatively-charged functional groups. As a result, HA shows retardant effect on the sorption of PFOS on boehmite surface, and this finding is different from some previous studies [24-26] for the other type of organic pollutants with their sorption levels enhanced by the competitive sorption of HA.
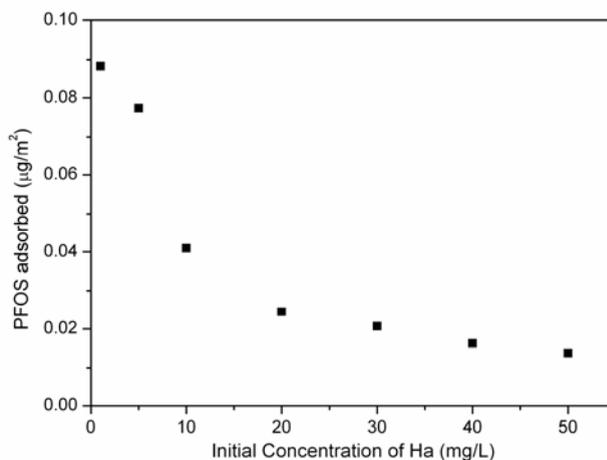

Fig. 4. The influence of HA initial concentration on the levels of PFOS adsorbed on boehmite surface.

4. Conclusion

Kinetic experiments showed that adsorption equilibrium can be achieved within 48 hours and the boehmite (AlOOH) surface is receptive to perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) adsorption. The sulfonate group in PFOS is a relatively harder base than the carboxylate group in PFOA, and a hard base is more readily adsorbed on boehmite surfaces. Therefore, in this study boehmite was observed to exhibit a higher affinity toward PFOS than PFOA. The experimental data suggest a moderate effect of solution pH on PFOS and PFOA adsorption on boehmite, resulting in the increase of electrostatic interaction and the decrease of ligand exchange reaction at lower pH. The NaCl concentrations showed a negative effect for PFOS and PFOA adsorption on boehmite, potentially due to EDL compression and the competitive adsorption of chloride ions. The results of this study indicate that environments of high salt content, such as subsurface pore water, will substantially hinder the adsorption of PFOS and PFOA on boehmite surfaces, and the result of competitive sorption of HA can decrease the sorption of PFOS on boehmite surface.

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