Adsorption behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) on boehmite

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HIGHLIGHTS

- The influence of surface properties of boehmite and γ-alumina on PFCs adsorption.
- The electrostatic interactions and ligand exchange between PFCs and boehmite.
- The influences of pH and salt concentrations on the PFCs adsorption on boehmite.

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ABSTRACT

Understanding the interaction of perfluorochemicals, persistent pollutants with known human health effects, with mineral compounds in surface water and groundwater environments is essential to determining their fate and transport. Kinetic experiments showed that adsorption equilibrium can be achieved within 48 h and the boehmite (AlOOH) surface is receptive to perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) adsorption. The adsorption isotherms estimated the maximum adsorption capacities of PFOS and PFOA on boehmite as 0.877 l/gm2 and 0.633 l/gm2, respectively. Compared to the adsorption capacity on γ-alumina, the abundant hydroxyl groups on boehmite surfaces resulted in the 2–3 times higher adsorption of PFOS and PFOA. Increasing solution pH led to a moderate decrease in PFOS and PFOA adsorption, owing to an increase in ligand exchange reactions and the decrease of electrostatic interactions. The presence of NaCl and CaCl2 in solution demonstrated negative effects for PFOS and PFOA adsorption on boehmite surfaces, with potential mechanisms being electrical double layer compression, competitive adsorption of chloride, and the Ca2+ bridging effect between perfluorochemicals.

1. Introduction

Perfluorochemicals (PFCs) are a type of anionic surfactant exhibiting environmental persistence. Within the PFC group, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the most commonly used and found compounds in the natural environment, being either directly released into wastewater or surface water through losses from consumer products or generated by the microbial degradation of other perfluorinated compounds (Paul et al., 2009; Yu et al., 2009; Müller et al., 2011). In 2009, PFOS was listed as a persistent organic pollutant in Annex B of the Stockholm Convention (Wang et al., 2009). In addition, PFOS and PFOA have been found in the blood of virtually all Americans tested during the last decade (Calafat et al., 2007). Steenland et al. (2010) reported that the higher serum levels of PFOS and PFOA were associated with a higher prevalence of hyperuricemia, an abnormally high blood uric acid level. The results of Melzer et al. (2010) indicated that higher serum PFOS and PFOA concentrations were related to current thyroid disease in the U.S. general adult population.

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 (Higgins and Luthy, 2006; Johnson et al., 2007; Tang et al., 2010; Wang and Shih, 2011). Higgins and Luthy (2006) reported that both organic matter and minerals played important roles in the PFC sorption process. 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. Previous studies have reported the adsorption behavior of PFOS on five mineral-based materials (goethite, kaolinite, Ottawa sand, iron oxide-coated sands, and sediment from Lake Michigan). The results indicate that the uptake of these compounds declined with an increase in pH and suggest the important role of electrostatic interaction in PFOS adsorption on minerals (Johnson
et al., 2007). To better understand the effect of solution chemistry on electrostatic interaction, Tang et al. (2010) varied pH, ionic strength, and Ca$^{2+}$ concentration in order to investigate the adsorption of PFOS onto goethite and silica. The results demonstrate that different types of minerals have different adsorption mechanisms toward PFOS. The results of our previous study indicate that the sorption of PFOS and PFOA on -alumina was similar to that on goethite and in both cases predominated by electrostatic interaction (Wang and Shih, 2011). However, the adsorbed concentration of PFOS on -alumina was 10 times lower than that on goethite. Besides the intrinsic difference between iron oxide and aluminum oxide, the difference between the surface hydration properties of the minerals has also been reported to be crucial to the sorption behavior of the adsorbate (Morterra and Magnacca, 1996; Yoon et al., 2004; Yang et al., 2007).

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 (Navrotsky, 2001). Boehmite is also an important industrial mineral used as a catalyst or adsorbent because of its ability to retain high surface area (Navrotsky, 2001; Yoon et al., 2004). As the point of zero charge (PZC) of boehmite has been determined to be between 7.7 and 9.4 (Kasprzyk-Hordern, 2004), 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 Ca$^{2+}$ concentrations were then performed to observe their effect on the adsorption process.

2. Materials and methods

2.1. Materials

Boehmite was purchased from Sasol Ltd. (Hamburg, Germany). PFOS (potassium salt) and PFOA were purchased from Sigma–Aldrich Co. (St. Louis, MO). Sodium chloride and calcium chloride were purchased from BDH Ltd. (Poole, Dorset, UK). Optim 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. Characterization of boehmite

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$^{-1}$. The boehmite's PZC (pHpzc) 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).

2.3. Sorption experiments

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 kinetic sorption experiments used an initial PFOS or PFOA concentration of 200 μg L$^{-1}$. The sorption isotherm experiments were carried out with PFOS or PFOA concentrations ranging from 50 μg L$^{-1}$ to 1000 μg L$^{-1}$. In preliminary tests, the standard deviations of quality control experiments were lower than 8%, which indicated the reproducibility of the experiment in current study.

2.4. PFOS and PFOA determination

After the adsorption experiments, 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). Further details of the quantification procedure utilized in this study can be found in Ma and Shih (2010).

3. Results and discussion

3.1. Sorption kinetics

Fig. 1 shows the adsorption kinetics of PFOS and PFOA on boehmite, which indicates that approximately 48 h of agitation were required to reach equilibrium for both PFOS and PFOA adsorption, similar to the ranges reported in studies of PFOS adsorption on a variety of minerals (Johnson et al., 2007; Zhou et al., 2010). This result shows that the mineral–water interfaces are accessible for PFOS and PFOA molecules, and thus equilibrium was rapidly reached. However, to ensure that equilibrium was achieved, an agitation time of 72 h was chosen for the subsequent sorption experiments. Overall, the kinetic behavior of PFOS or
PFOA on boehmite consists of a fast adsorption followed by a slow adsorption, which is consistent with the two-step model for surfactant adsorption on solid surfaces (Tabor et al., 2010). According to this model, the slow adsorption process observed in this study may be attributed to the slow transport of PFOS or PFOA to the boehmite surface when the concentration of PFOS or PFOA in the aquatic phase dramatically decreases (around 70–80%) after a rapid adsorption within the initial 3 h.

As shown in Fig. 1, the adsorption capacity \( (q_e = 0.105 \ \mu g \ m^{-2}) \) of PFOS was found to be slightly larger than that of PFOA \( (q_e = 0.09 \ \mu g \ m^{-2}) \), suggesting the sorption of PFOS on boehmite is more favorable than for PFOA. Given the similar ranges of -CF₂-chain length, the distinctly different degrees of adsorption capacity are presumably due to the different functional groups of PFOS and PFOA, which were further investigated and are described in the subsequent sections.

### 3.2. Sorption isotherms

The adsorption isotherms of PFOS and PFOA on boehmite at pH 7 are shown in Fig. 2. The Langmuir and Freundlich equations (Langmuir, 1918; Freundlich, 1922) were applied to model the experimental data, and the derived constants are provided in Table 1. The model equations can be expressed as follows: Langmuir model:

\[
q_e = \frac{K_q q_m C_e}{1 + K_q C_e}
\]  

(1)

Freundlich model:

\[
q_e = K_F C_e^n
\]  

(2)

where \( q_e \) is the adsorbate amount on the surface of the adsorbent at equilibrium \( (\mu g \ m^{-2}) \), \( C_e \) is the equilibrium concentration of adsorbate in solution \( (\mu g \ L^{-1}) \), \( q_m \) is the maximum sorption capacity \( (\mu g \ m^{-2}) \), and \( K_q \) is the Langmuir adsorption constant \( (L \ \mu g^{-1}) \). \( K_F \) is the Freundlich adsorption constant \( (\mu g \ m^{-2}(\mu g \ L^{-1})^{-n}) \), which suggests the adsorption capacity, and \( n \) represents the measure of the nonlinearity involved.

The adsorption isotherms for PFOS and PFOA were found to fit well with both the Langmuir and Freundlich equations, judging from the correlation coefficients \( (R^2) \) in Table 1. The goodness-of-fit to the Langmuir equation indicates that the adsorption of PFOS and PFOA might occur on the boehmite surface with monolayer coverage (Ünlü and Ersoz, 2006). The goodness-of-fit to the Freundlich equation as well as the Langmuir equation reveals the importance of PFOS and PFOA concentrations in the adsorption process.

It has been suggested that amphiphilic compounds may adsorb onto minerals in hemi-micelles when the organic ions are present at 0.001–0.01 of the critical micelle concentration (Schwarzenbach et al., 1993). The critical micelle concentrations (CMC) of PFOS and PFOA have been reported at around 8 mM and 25 mM (Harada et al., 2005), respectively. In this study, the PFOS and PFOA concentrations were all controlled below 1 ppm (around 0.002 mM) in experiments, and thus the hemi-micelles were unlikely to form during the adsorption processes. This condition also supports the monolayer adsorption behavior described by the Langmuir model.

For adsorption on boehmite, the maximum adsorption capacities were estimated to be 0.877 \( \mu g \ m^{-2} \) for PFOS and 0.633 \( \mu g \ m^{-2} \) for PFOA. This result is similar to our previous result that -alumina showed a higher affinity toward PFOA than PFOS. Higgins and Luthy (2006) 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 (Snoeyink and Jenkins, 1980; Walters, 1991).

Our previous study (Wang and Shih, 2011) showed that the maximum adsorption capacities of PFOS and PFOA on -alumina were 0.252 \( \mu g \ m^{-2} \) and 0.157 \( \mu g \ m^{-2} \), which were 2–3 times lower than that on boehmite. Kasprzyk-Hordern (2004) reported that the catalytic or adsorption activity of alumina was mainly dependent on its surface area and surface active sites. In this and our previous study, the results were normalized by the surface areas of boehmite and -alumina, therefore the significantly different adsorption levels of PFOS or PFOA between boehmite and -alumina are attributable to those minerals’ different surface properties. Kummert and Stumm (1980) used a surface coordination model to explain the specific interaction of organic anions with hydrous oxides and indicated that organic anions might replace the surface hydroxyl groups of hydrous oxides by ligand exchange. The ligand exchange reaction can be expressed as follows:

\[
\text{Al}^-\text{OH} + \text{L}^- \rightarrow \text{Al}^-\text{L} + \text{OH}^-
\]  

(3)

Based on this model, the density of hydroxyl groups on the surfaces of different aluminum oxides could strongly affect the adsorption capacity. Therefore, the higher observed adsorbed concentrations of PFOS and PFOA on boehmite may be attributed to the more abundant hydroxyl groups on the surface of boehmite when compared to -alumina.

Tang et al. (2010) and Johnson et al. (2007) reported the maximum adsorption capacities of PFOS on goethite as 2.4 \( \mu g \ m^{-2} \) and 1.2 \( \mu g \ m^{-2} \), respectively, which are one to two times higher than the adsorption capacity of PFOS by boehmite revealed in this study. Such enhanced adsorption on goethite reflects the different surface complexation forms of PFOS on the surfaces of goethite and fig. 2. PFOS and PFOA adsorption isotherms (test condition: 5 g L⁻¹ boehmite, 72 h agitation time, and final pH = 7.0 ± 0.2) on boehmite. The solid lines are the fitted Langmuir isotherms, and the dashed lines are the fitted Freundlich isotherms.

### Table 1

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_L ) (L ( \mu g^{-1} ))</td>
<td>( q_m ) (( \mu g \ m^{-2} ))</td>
</tr>
<tr>
<td>PFOS</td>
<td>0.00622</td>
<td>0.877</td>
</tr>
<tr>
<td>PFOA</td>
<td>0.00512</td>
<td>0.633</td>
</tr>
</tbody>
</table>

Note: \( R^2 \) is the correlation coefficient of fitting result.
boehmite. Infrared spectra studies (Parfitt and Smart, 1977, 1978; Harrison and Berkerheiser, 1982) of sulfate adsorbed on goethite ($\alpha$-FeOOH) and hydrous Fe(OH)$_3$ show the replacement of surface hydroxyl bands and the formation of adsorbed sulfate groups on the surface of iron compounds, and proposed that an inner sphere complex was formed between sulfate and the goethite surface. However, Wu et al. (2002) found that the adsorption of MoO$_4^{2-}$ was not influenced by SO$_4^{2-}$ while the adsorption of SO$_4^{2-}$ was inhibited by MoO$_4^{2-}$, and they attributed such observations to the different complexes formed by MoO$_4^{2-}$ (inner-sphere) and SO$_4^{2-}$ (outer-sphere). Considering the similar sulfur–oxygen bond angles and distances between sulfate and sulfonate (Ruben et al., 1961; Torres et al., 2009), PFOS may similarly form inner sphere bridging with goethite, while forming outer-sphere complexes with aluminas.

3.3. Effects of pH

The effects of varying pH on the adsorption of PFOS and PFOA are shown in Fig. 3. 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 (Brooke et al., 2004; Goss, 2008). The PZC of the boehmite in this study was measured 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:

\[
\text{Al}–\text{OH} + \text{H}^+ \rightarrow \text{Al}–\text{OH}_2^+ 
\]

\[
\text{Al}–\text{OH}_2^+ + \text{L}^- \rightarrow \text{Al}–\text{OH}_2^--\text{L}
\]

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 an increase in electrostatic interactions and/or the formation of surface complexes by ligand exchange (Stumm, 1993). In our previous study, the adsorbed concentrations of PFOS or PFOA on –alumina (pH$_\text{PZC}$ = 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. An increase in H$^+$ concentration in solution not only increases Al–OH$_2^+$ sites, but also decreases the Al–OH sites on boehmite surfaces (Eq. (2)). Therefore, if the pH is decreased, the ligand exchange reaction (Eq. (1)) will be decreased and the electrostatic interaction (Eq. (3)) 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.

3.4. Effect of NaCl and CaCl$_2$

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 (Xiao et al., 2011). Thus, the influence of NaCl on PFOS and PFOA adsorption may be important in determining the environmental fates of PFOS and PFOA. Fig. 4 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 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 $\zeta$-potential (Wang and Shih, 2011). The adsorption of adsorbates (PFOS and PFOA) on adsorbents (boehmite) is usually associated with the free energy between adsorbate and adsorbent, which can be evaluated by the equation as follows:

\[
\Delta G_{\text{total}} = \Delta G_{\text{electrostatic}} + \Delta G_{\text{adsorbate-adsorbent}} = zF\psi_d - F\psi_a = -F\zeta
\]

where $z$ is the charge of PFOS or PFOA ions (−1), $F$ is the Faraday constant (96,485 C mol$^{-1}$), and $\psi_d$ is the diffuse layer potential (V). $\psi_a$ can be approximated by the $\zeta$-potential, as the shear plane is often located close to the inner boundary of the diffuse layer (Kretzschmar et al., 1997; Carnali and Shah, 2008; Xiao et al., 2011). Thus, the reduction of $\zeta$-potential can lead to an increase in free energy, which causes a reduction in PFOS and PFOA adsorption. In addition, Regalbuto et al. (1999) 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 (Hao et al., 2003).

![Fig. 3. Effect of pH on the adsorption of PFOS and PFOA](image)

![Fig. 4. Effect of NaCl concentration on the adsorption behavior of PFOS and PFOA](image)
literature, we found the adsorption of PFOS and PFOA on boehmite a strong dependence of NaCl and CaCl₂ concentrations on PFOS and PFOA. Overall, the increase in PFOS and PFOA adsorption on boehmite with an increase (1–3 mM) of the CaCl₂ concentration in the system, and pointed out the increase of surface charge due to the potential binding of calcium ions on the goethite surface (Tang et al., 2010). In this study, the influence of CaCl₂ concentration on PFOS and PFOA adsorption on boehmite was further tested and the result is illustrated in Fig. 5. In contrast to the literature, we found the adsorption of PFOS and PFOA on boehmite to decrease with increasing CaCl₂ concentration in the solution. The effect of CaCl₂ 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 Ca²⁺ between PFCs (Wang and Shih, 2011) may further lead to a reduction in PFOS and PFOA adsorption on boehmite. Overall, the strong dependence of NaCl and CaCl₂ concentrations on PFOS and PFOA adsorption clearly indicates the importance of electrostatic considerations in predicting the PFC behavior on a hydrated aluminum oxide surface.

4. Conclusion

The kinetic behavior of PFOS or PFOA on boehmite consists of a fast adsorption process followed by a slow adsorption process which may be attributed to the slow transport of PFOS or PFOA into the boehmite pore surface. The sulfonate group in PFOA 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 from the increase of electrostatic interaction and the decrease of ligand exchange reaction at lower pH. Both NaCl and CaCl₂ concentrations showed a negative effect on 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.

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