Effect of salinity and sediment characteristics on the sorption and desorption of perfluorooctane sulfonate at sediment-water interface

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Salinity is an important environmental parameter affecting the transport and fate of PFOS in aquatic environment.

Article info
Article history:
Received 27 September 2009
Received in revised form
21 December 2009
Accepted 11 January 2010

Keywords:
Perfluorooctane sulfonate
Sorption
Desorption hysteresis
Salinity
Salting-out effect
Ca-bridging effect

Abstract
This study investigated the influence of solution salinity, pH and the sediment characteristics on the sorption and desorption of perfluorooctane sulfonate (PFOS). The results showed that the sorption of PFOS onto sediment increased by a factor of 3 as the CaCl₂ concentration increased from 0.005 to 0.5 mol L⁻¹ at pH 7.0, and nearly 6 at pH 8.0. Desorption hysteresis occurred over all salinity. The thermodynamic index of irreversibility (TII) values increased with increasing concentration of CaCl₂. Maximum irreversibility was found in the sorption systems with CaCl₂ in the concentration of 0.5 mol L⁻¹. The results suggested that PFOS can be largely removed from the water with increasing salinity, and get trapped onto sediments irreversibly. These phenomena could be explained by salting-out effect and Ca-bridging effect. Studies also suggested that the content of total organic carbon is the dominant psychochemical properties of sediment controlling the sorption of PFOS.

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1. Introduction

Recently, the environmental fate of PFOS has raised public and scientific concerns for its high bioaccumulation, extreme persistence, and toxic properties, such as endocrine-disrupting activity and carcinogenesis (Beach et al., 2006). Many studies have shown that PFOS is ubiquitously detected in the environment, even in remote arctic areas (Giesy and Kannan, 2001; Report RIKZ/2002.043, 2002). Because of the low volatility and high solubility of PFOS, the transport of PFOS in the aquatic environment is considered an important process in controlling its distribution and fate.

Sorption and desorption behaviors are important processes that control the distribution, transport and fate of chemicals in aquatic environment. Since PFOS contains both hydrophobic and hydrophilic functionalities, it is expected to behave differently from traditional hydrophobic pollutants (Villagrasa et al., 2006). Significant sorption of PFOS onto sediment has been reported from laboratory and field data (Higgins and Luthy, 2006; Nakata et al., 2006), and sediment has been confirmed as one of the final sinks of perfluorocarboxylates (Prevendouros et al., 2006). Higgins and Luthy (2006) have reported that the total organic carbon (TOC) of sediment is the dominant parameter affecting the sorption, and that hydrophobic interaction is the underlying sorption mechanism. When organic carbon is not presented, such as sorption on sand, clay, and iron oxide, surface electrostatic interaction is considered as the main sorption mechanism for PFOS (Johnson et al., 2007).

On the other hand, field data from Rivers in America and Japan show that the concentrations of PFOS in water are detectable, while the concentrations in sediment are below the quantification limit, which suggest that the distribution of PFOS into sediment due to sorption is negligible (Hansen et al., 2002; Senthilkumar et al., 2007). These results suggest that the sorption behavior of PFOS may vary greatly under different sorption conditions, which mean that besides the physiochemical characteristics of the sorbent, environmental parameters of aquatic system, such as salinity and pH, also affect the sorption of PFOS. For the ionic organic chemicals, such as PFOS, salinity and the solution pH not only influence the speciation of sorbate in solution, but also influence the properties of sorbent, such as surface charge and structure of sediment organic matter (SOM), which consequently affect the extent of sorption of hydrophilic organic pollutants (Liu et al., 2001).

Martin et al. (2004) suggest that sediments are the major sources of perfluoroalkyl introduction into the food web in Lake Ontario. Consequently, this puts forward an important issue on the bioavailability of sediment-bound PFOS, whether sediments serve as long-term sources of PFOS to the biosphere. Understanding the
sorption and desorption mechanisms of PFOS onto sediment in different aquatic environment is very important to speculate the bioavailability of sediment-bound PFOS in aquatic environment. Unfortunately, no scientific report has been presented to answer this salient question up to date. Therefore, systematic studies on the sorption and desorption behavior of PFOS is pertinent to understand the fate and distribution of PFOS in water–sediment system, as well as the bioavailability and potential risk to ecosystem.

This study aimed at investigating sorption and desorption behavior of PFOS under varying environmental variables. In addition, we can elucidate the underlying sorption mechanisms related to the transport and fate of PFOS in the aquatic environment.

2. Materials and methods

2.1. Chemicals and materials

Heptadecafluorooctanoic acid potassium (PFOS) (technical grade, purity ≥ 98%) and ammonium acetate (for mass spectroscopy, ≥99.0%) were purchased from Fluka (Milwaukee, WI, USA). Natural sediment samples TH1–TH10 were taken from the Taihu Lake, Jiangsu Province, China. Natural sediment samples MY1–MY5 were taken from the Miyun reservoir, Beijing, China. Sediment samples were air-dried and sieved through 0.18 mm mesh. Salient physicochemical characteristics of sediments were determined according to the methods described by Tao et al. (2006)

2.2. Batch sorption and desorption experiments

All the sorption and desorption experiments were conducted in 50 mL polypropylene (PP) centrifuge tubes. Teflon caps or vessels were avoided throughout the experiment as interferences may be introduced to the samples (Hansen et al., 2002). Duplicate sets of PP tubes were filled with 3.0 g sediment and 45 mL solutions containing 0.005, 0.05, and 0.5 mol L⁻¹ CaCl₂. The initial PFOS concentration ranged from 0.5 to 10 mg L⁻¹. The mixture was equilibrated in a 2D-shaker at 250 rpm at 25 ± 1 °C. During the experiment, the solution pH was kept at the required values (pH = 7.0 or 8.0) by intermittent adjustment with HCl or NaOH. Parallel control tests in the absence of sediment showed that the total PFOS loss (e.g., sorption on the tube wall, bio- and/or photo-degradation) was less than 5%, which was neglected in the experiment. Sorption equilibrium time was 24 h as reported in our previous study (Pan et al., 2009). After equilibration, the mixture was centrifuged at 9000 rpm for 30 min. Then 1 mL of each supernatant was transferred to 2 mL GC autosampler vial for analysis.

At the attainment of the sorption equilibrium, selected samples were subjected to the desorption experiments using the successive dilution method (Zhao et al., 2002). Briefly: 40 mL of the centrifuged supernatant was removed, and replaced with the same volume of a solution that contained the same background solution but free of PFOS. The mixtures were then re-equilibrated for 24 h under similar experimental conditions (pH, temperature, and rotating velocity) as for the sorption experiments. After equilibrium, the distribution of PFOS between the sediment and solution was analyzed following the same procedure used for the sorption experiment. The dilution and re-equilibration procedures were repeated successively to yield the desorption isotherms.

2.3. Chemical analyses

The concentration of PFOS in the sample was measured using a high performance liquid chromatograph (HPLC) (Waters, Alliance 2695) (Boston, USA) interfaced with an electrospray mass spectrometer (Waters, ZQ4000) (Manchester, UK) as described in our previous study (Pan et al., 2009). The mass spectrometer parameters were optimized to transmit the [M – K]⁻ ion for PFOS using atmospheric pressure ionization, operated in the electrospray negative ion mode. PFOS was monitored using selected reaction monitoring for ion 499 for quantitative determination. The limit of detection (LOD) for PFOS was 1.5 μg L⁻¹, and the relative standard deviation (RSD) was less than 8.28%.

2.4. Data analysis

The data obtained from the sorption and desorption experiments were fitted using the Freundlich isotherm equation, presented below:

\[ \log C_e = n \log C_s + \log K_f \]  

where \( C_s \) and \( C_e \) were the concentrations of PFOS on the sediment and in the solution, respectively. \( K_f \) was the Freundlich capacity coefficient, and \( n \) indicated the nonlinearity of the sorption isotherm. Comparison of results using \( K_f \) values extrapolated from nonlinear isotherms under different solution conditions could lead to biased results. Thus, concentration-specific distribution coefficients \( (K_{d}) \) were interpolated at equilibrium concentrations of 1 mg L⁻¹ (Higgins and Luthy, 2006):

\[ K_d = K_f C^{-1} \]  

Over the low concentration range of the sorbate in solution, most isotherms were linear. Thus, sorption experiments were conducted with initial PFOS concentrations that ranged between 0.5 mg L⁻¹ and 2.5 mg L⁻¹ to achieve linear sorption isotherm. Linear sorption model was used to interpret equilibrium data on different sediments using the formula:

\[ C_e = K_d C_s \]  

The sediment organic carbon-normalized distribution coefficient \( (K_{oc})\) was obtained from the formula:

\[ K_{oc} = \frac{K_d}{f_{oc}} \]  

\( f_{oc} \) was fraction of organic carbon in sediments.

The degree of sorption hysteresis was quantified using the thermodynamic index of irreversibility (TII) proposed by Sander et al. (2005), the calculated TII values usually lied in the range of 0–1, with 1 indicating the maximum irreversibility.

3. Results and discussion

3.1. Sorption of PFOS at different salinity and pH

Sample MY3 was used as a model sorbent to study the effects of salinity and pH on the uptake of PFOS. The sorption experiments were carried out in 0.005, 0.05 and 0.5 mol L⁻¹ of CaCl₂ at two pH values (7.0 and 8.0) with an initial PFOS concentration ranged between 0.5 mg L⁻¹ and 10 mg L⁻¹. As shown in Fig. 1 and Table 1, sorption of PFOS increased by a factor of 3 as the CaCl₂ concentration increased from 0.005 mol L⁻¹ to 0.5 mol L⁻¹ at pH 7.0, and
PFOS was 307 mg L⁻¹ in pure water. The calculated values of log \( K_d \) also increased by a factor of 6 at pH 8.0. The calculated values of log \( K_d \) also increased from 1.75 to 2.97 at pH 7.0 as the CaCl₂ concentration increased from 0.005 mol L⁻¹ to 0.5 mol L⁻¹, while it increased from 2.03 to 3.41 at pH 8.0. The authors also found that the solubility of seawater (OECD, 2002). The authors also found that the solubility of seawater increased from 0.005 mol L⁻¹ to 0.5 mol L⁻¹ as the CaCl₂ concentration increased. Electrolyte CaCl₂, in the concentration of 0.005 mol L⁻¹ was often used as mineral background to simulate freshwater (Higgins and Luthy, 2006; Zhou et al., 2004). In order to evaluate the effect of salinity on the sorption and desorption, 0.05 and 0.5 mol L⁻¹ CaCl₂ were used as the background electrolyte for this study. The results suggested that PFOS tended to exist as dissolved species in low salinity water, such as freshwater, but sorbed to sediment in high salinity water, such as seawater.

Turner and Rawling (2001) showed that the sorption of organic chemicals generally increased with increasing salinity via a mechanism of salting-out effect. Salting-out effect referred to the reduction solubility of neutral solute in aqueous in the presence of dissolved ions. This was because water molecule became more ordered and compressible in the presence of dissolved ions, and the cavity volume available to accommodate neutral solute reduced (Turner and Rawling, 2001), which meant the aqueous solubility of organic chemicals was inversely related to the content of dissolved ions. It had been reported that the solubility of PFOS potassium salt in pure water was 680 mg L⁻¹ at 24–25 °C (Brooke et al., 2004), and was 370 mg L⁻¹ in freshwater and reduced to 25 mg L⁻¹ in filtered seawater (OECD, 2002). The authors also found that the solubility of PFOS was 307 mg L⁻¹ in 0.005 mol L⁻¹ CaCl₂ (Pan et al., 2009).

Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>CEC (cmol kg⁻¹)</th>
<th>f_soc (%)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Granulometry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;2 µm</td>
</tr>
<tr>
<td>MY1</td>
<td>7.55</td>
<td>1.49</td>
<td>15.2</td>
<td>2.95</td>
</tr>
<tr>
<td>MY2</td>
<td>5.12</td>
<td>0.67</td>
<td>15.2</td>
<td>0.94</td>
</tr>
<tr>
<td>MY3</td>
<td>6.87</td>
<td>0.75</td>
<td>21.3</td>
<td>2.61</td>
</tr>
<tr>
<td>MY4</td>
<td>6.35</td>
<td>0.85</td>
<td>11.4</td>
<td>2.15</td>
</tr>
<tr>
<td>MY5</td>
<td>6.96</td>
<td>0.63</td>
<td>19.5</td>
<td>2.00</td>
</tr>
<tr>
<td>TH1</td>
<td>9.52</td>
<td>1.27</td>
<td>27.5</td>
<td>4.37</td>
</tr>
<tr>
<td>TH2</td>
<td>9.82</td>
<td>1.31</td>
<td>24.1</td>
<td>4.82</td>
</tr>
<tr>
<td>TH3</td>
<td>9.69</td>
<td>1.25</td>
<td>22.5</td>
<td>4.99</td>
</tr>
<tr>
<td>TH4</td>
<td>9.00</td>
<td>1.21</td>
<td>26.4</td>
<td>2.38</td>
</tr>
<tr>
<td>TH5</td>
<td>8.90</td>
<td>1.14</td>
<td>26.9</td>
<td>4.91</td>
</tr>
<tr>
<td>TH6</td>
<td>7.72</td>
<td>0.93</td>
<td>29.6</td>
<td>7.38</td>
</tr>
<tr>
<td>TH7</td>
<td>9.33</td>
<td>0.55</td>
<td>35.2</td>
<td>6.23</td>
</tr>
<tr>
<td>TH8</td>
<td>9.66</td>
<td>0.18</td>
<td>40.9</td>
<td>5.59</td>
</tr>
<tr>
<td>TH9</td>
<td>10.1</td>
<td>0.16</td>
<td>63.3</td>
<td>7.16</td>
</tr>
<tr>
<td>TH10</td>
<td>10.3</td>
<td>0.16</td>
<td>74.9</td>
<td>6.61</td>
</tr>
</tbody>
</table>

Table 1

Freundlich model-fitted sorption and desorption parameters and thermodynamic index of irreversibility (TII) for PFOS.

<table>
<thead>
<tr>
<th>pH</th>
<th>CaCl₂ (mol L⁻¹)</th>
<th>Sorption</th>
<th>Desorption</th>
<th>TII</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>log ( K_d )</td>
<td>( C_d = 1000 ) (µg L⁻¹)</td>
<td>n ± SD</td>
</tr>
<tr>
<td>7.0</td>
<td>0.005</td>
<td>1.75 ± 0.33</td>
<td>0.82</td>
<td>2.94</td>
</tr>
<tr>
<td>7.0</td>
<td>0.05</td>
<td>2.56 ± 0.09</td>
<td>1.36</td>
<td>3.48</td>
</tr>
<tr>
<td>8.0</td>
<td>0.005</td>
<td>2.03 ± 0.17</td>
<td>0.92</td>
<td>3.04</td>
</tr>
<tr>
<td>8.0</td>
<td>0.05</td>
<td>2.86 ± 0.16</td>
<td>1.48</td>
<td>3.60</td>
</tr>
</tbody>
</table>

Notes:
- \( K_d \) (µg L⁻¹ n L kg⁻¹) is sample numbers.
- SD is standard deviation.
- \( K_d \) is concentration-specific distribution coefficients (L kg⁻¹).
- \( K_m \) is sample numbers.
- \( K_m \) is sample numbers.
- \( S.D. \) is concentration-specific distribution coefficients (L kg⁻¹) calculated from formula (2).
- \( S.D. \) is concentration-specific distribution coefficients (L kg⁻¹) calculated from formula (2).
- \( N \) is sample numbers.
2003), and increased the sorption of calcium (II) ion onto the sediment surface, which enhanced the sorption of PFOS through electrostatic effect and Ca-bridging mechanism.

3.2. Desorption of PFOS

Desorption hysteresis occurred over all the salinity conditions we studied, with the two pH values. As shown in Table 1, the $TII$ values increased with increasing concentration of CaCl$_2$, and approached nearly 1 in the three-sorption systems, with electrolyte background of 0.5 mol L$^{-1}$ CaCl$_2$ at pH 7.0, 0.05 and 0.5 mol L$^{-1}$ CaCl$_2$ at pH 8.0 respectively. Under the same salinity condition, the desorption hysteresis at pH 8.0 was higher than that in pH 7.0. The results suggested that PFOS possibly existed as dissolved species in low salinity water, but sorbed to sediment in high salinity water.

For most neutral hydrophobic chemicals, each sediment-contaminant combination exhibits a fixed maximum irreversible adsorption (Kan et al., 1997), which is proportional to the sediment organic carbon content (Chen et al., 2000). As described in distributed reactivity model, sorption in glassy organic matter was typically nonlinear and irreversible (Weber et al., 1998). The presence of calcium (II) ion in solution could function as cross-linking agents, and increased the glassy character of organic matter of sediment, and therefore enhanced the irreversibility and nonlinearity (Lu and Pignatello, 2004). The Freundlich exponent ($n$) which denoted the degree of deviation from isotherm linearity also decreased with the increase of CaCl$_2$ concentration at pH 7.0 and 8.0, which corroborated the influence of Calcium (II) on the sorption for PFOS.

3.3. Effect of sediments properties

In order to understand the effects of sediment properties on the sorption of PFOS onto the sediment, sorption experiments were conducted at pH 7.0 in 0.005 mol L$^{-1}$ CaCl$_2$, using fifteen different types of sediments with varying properties. The physiochemical characteristics of the sediments were presented in Table 2. The initial PFOS concentration ranged between 0.5 mg L$^{-1}$ and 2.5 mg L$^{-1}$. In all the sorption systems studied, PFOS showed apparent affinity to the sediment. Linear sorption model was used to analyze the sorption data ($R^2 > 0.91$) and the results were presented in Table 3. The calculated log $K_{oc}$ values ranged between 2.97 L kg$^{-1}$ and 3.20 L kg$^{-1}$, with an average of 3.10 L kg$^{-1}$. These values were comparable with the results reported by other workers (2.57–3.1 L kg$^{-1}$) (Higgins and Luthy, 2006).

Correction analysis between $K_d$ and sediment physicochemical parameters were conducted, only the content of organic carbon ($f_{oc}$) was correlated with $K_d$. The result in Fig. 2 showed that the correlations of $f_{oc}$ with $K_d$ was high ($r = 0.96$, $n = 15$, $p < 0.01$), which suggested $f_{oc}$ was the dominant factor controlling the sorption of PFOS. There was no significant correlation between $K_d$ and cation exchange capacity (CEC), specific surface area, and granularity of the sediments. The result was consistent with the report of Higgins and Luthy (2006), and indicated that partitioning interactions between sediment–water interfaces was the main sorption mechanism for PFOS.

3.4. Implication on the environmental fate of PFOS

The discharge of municipal wastewater has been considered as a major source of PFOS in the aquatic environment (Becker et al., 2008). Due to significant bioaccumulations and the persistence of PFOS, possible transfer from water to the sediment, and ultimately to higher trophic level animals is an issue that must not be neglected. From a critical analysis of the sorption and desorption results in this study, it could be inferred that PFOS would be largely removed from the water column with increase in salinity and pH, and get trapped in the sediments with little bioavailability. Estuary was an important area in the transport of PFOS to open ocean, where had frequent changing of environment conditions, such as pH and salinity. Our results would be helpful to understand the transport and fate of PFOS in this area.

4. Conclusions

Sorption and desorption of PFOS on sediment were affected, significantly, by salinity and pH. Sorption of PFOS increased by a factor of 3 as the CaCl$_2$ concentration increased from 0.005 to 0.5 mol L$^{-1}$ at pH 7.0, and nearly 6 times at pH 8.0. The thermodynamic index of irreversibility ($TII$) values increased with increasing CaCl$_2$ concentration, and approached 1 in the three sorption systems (0.5 mol L$^{-1}$ CaCl$_2$ at pH 7.0; 0.05 and 0.5 mol L$^{-1}$ CaCl$_2$ at pH 8.0). These phenomena could be explained by salting-out effect and Ca-bridging sorption mechanism. The correlations between the calculated $K_d$ values and the fraction of organic carbon was significant ($r = 0.96$, $n = 15$, $p < 0.01$), suggesting hydrophobic partitioning was important to the sorption of PFOS on sediments.
Acknowledgements

The study is supported by a CAS project [KJCX2.YW.H04] and the National Natural Science Foundation of China [20621703].

The authors wish to thank Nurudeen A. Oladoja for his valuable comment.

References


