Efficient Sorptive Removal of PFOS by Layered Double Hydroxides: Behavior and Mechanisms

Zhihao Hu and Xin Song*
Institute of Soil Science, Chinese Academy of Sciences, Nanjing, China

Adelaide, 2019
**Chemical Introduction**

- Industrial use and consumer goods: leather, surfactant, fire foam, hard chromium plating, cosmetics, etc.
- Easy to transport in surface water and groundwater
- Strong bioaccumulation and potential health risk
- USEPA set up advisory health value of PFOS and PFOA: 70 ng/L, 2016

---

**PFOS**

**Name**

Perfluorooctane Sulfonate (PFOS)

**Abbreviation**

PFOS

**Formula**

C₈F₁₇O₃SK

**Molecular weight**

538

**Solubility (25°C)**

680 mg/L

**pKa**

-3.3

**Half-life period**

> 41 年

---

**C-F bond**

**Sulfonate group**

**Chemical Structure**

---

**Industrial use and consumer goods:** leather, surfactant, fire foam, hard chromium plating, cosmetics, etc.

**Easy to transport in surface water and groundwater**

**Strong bioaccumulation and potential health risk**

**USEPA set up advisory health value of PFOS and PFOA: 70 ng/L, 2016**
# PFOS Occurrence

<table>
<thead>
<tr>
<th>Samples</th>
<th>concentration</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>0.05 ~ 2.41 ng/g</td>
<td>Hu et al., 2013</td>
</tr>
<tr>
<td>Sediments</td>
<td>1.17 ~ 15.12 ng/g</td>
<td>Cristian et al., 2011; Lutz et al., 2010; Yang et al., 2011; Zhang et al., 2012</td>
</tr>
<tr>
<td>Surface water</td>
<td>1.1 ~ 10,980 ng/L</td>
<td>Yang et al., 2011; Wang et al., 2012; Flores et al., 2013; Panlilio er al., 2014</td>
</tr>
<tr>
<td>Groundwater</td>
<td>182 ~ 14,600 ng/L</td>
<td>Melissa et al., 2004; Paustenbach et al., 2007; Hoffman et al., 2011</td>
</tr>
<tr>
<td>Tap water</td>
<td>0.16 ~ 22 ng/L</td>
<td>Takagi et al., 2008; Mak et al., 2009</td>
</tr>
<tr>
<td>Serum</td>
<td>20 ~ 30 µg/L</td>
<td>Geary et al., 2006; Kyunghee et al., 2012; Beesoon et al., 2012</td>
</tr>
</tbody>
</table>
**Treatment technologies**

- **UV photolysis**
- **Ultrasonic degradation**
- **Oxidation and reduction**
- **Electrochemical degradation**
- **Coagulation**
- **Membrane**
- **Sorbents**

**Chemical degradation**

- UV photolysis
- Ozonation

**Physical separation**

- Coagulation
- Membrane
- Sorbents

- Reverse osmosis membrane
- Ion exchange resin
Layered Double Hydroxides: LDHs

Interlayer waters and anions

Host layers

Formula: \([M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O\)
Hypothesis: Sorptive Removal of PFOS by LDHs

- Strong anion exchange ability
- Able to remove inorganic anions
Methodology

Synthesis and characterization (Prior to sorption)
- Coprecipitation
- X-ray diffraction (XRD)
- Fourier transform infrared spectra (FTIR)

Sorption performance
- Sorption kinetics
- Sorption isotherms
- Effect of solution chemistry

Sorption mechanisms (Post-sorption)
- Effect of solution chemistry
- XRD
- FTIR
The sharp basal reflections at lower 2θ values correspond to the successive orders of the basal spacing.

$d_{003}$ is the total thickness of the LDH sheet and the interlayer region. For the nitrate, carbonate and chloride LDHs, the $d_{003}$ is 8.11, 7.80 and 7.76 Å.

The order of anion exchangeability: $\text{Mg}_3\text{Al-NO}_3 > \text{Mg}_3\text{Al-Cl} > \text{Mg}_3\text{Al-CO}_3$
Sorption removal efficiency

With the initial concentration of 1 mg/L, the removal efficiencies of PFOS by nitrate, carbonate and chloride LDHs are 95.5%, 50.3% and 90.6%.

The removal efficiency of PFOS by nitrate LDHs reached 99.7% even at elevated concentrations.
Pseudo-second order model

\[ \frac{dq_t}{dt} = k_2(q_e - qt)^2 \]

\[ t = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e \times v_0} + \frac{t}{q_e} \]

$q_e$: amount of solute sorbed at equilibrium
$q_t$: amount of solute sorbed at $t$
$k_2$: rate constant
$v_0$: initial sorption rate

Table – Constants of pseudo-second-order model for various initial concentrations

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$q_{e, exp}$ (mg/g)</th>
<th>$q_{e, cal}$ (mg/g)</th>
<th>$k_2$</th>
<th>$v_0$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>99.25</td>
<td>105.49</td>
<td>0.0063</td>
<td>70.11</td>
<td>0.998</td>
</tr>
<tr>
<td>50</td>
<td>199.45</td>
<td>202.43</td>
<td>0.0038</td>
<td>155.72</td>
<td>0.998</td>
</tr>
<tr>
<td>75</td>
<td>298.82</td>
<td>307.69</td>
<td>0.0021</td>
<td>198.81</td>
<td>0.998</td>
</tr>
<tr>
<td>100</td>
<td>398.75</td>
<td>408.16</td>
<td>0.0009</td>
<td>149.94</td>
<td>0.998</td>
</tr>
</tbody>
</table>
Intraparticle diffusion model

\[ q_t = k_i \times t^{0.5} + C_i \]

- \( q_t \): amount of solute sorbed at time \( t \)
- \( k_i \): intraparticle diffusion rate constant at time \( t \)
- \( C_i \): intercept

**Stage 1: Diffusion**

**Stage 2: Chemical reaction**

- \( t=0-8 \) min, diffusion of PFOS into LDHs interlayer region
- \( t=8-30 \) min, the reaction between PFOS and LDHs takes place
Sorption isotherm

Fitting models: Langmuir and Freundlich

Table – Constants of Langmuir and Freundlich fittings for three types of LDHs

<table>
<thead>
<tr>
<th>LDHs type</th>
<th>q_m (mg g⁻¹)</th>
<th>b (L mg⁻¹)</th>
<th>R²</th>
<th>K_F (mg¹⁻¹/n L⁻¹/n g⁻¹)</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₃Al-NO₃</td>
<td>821.08</td>
<td>2.38</td>
<td>0.98</td>
<td>468.56</td>
<td>5.79</td>
<td>0.85</td>
</tr>
<tr>
<td>Mg₃Al-CO₃</td>
<td>329.11</td>
<td>0.018</td>
<td>0.99</td>
<td>18.28</td>
<td>1.94</td>
<td>0.96</td>
</tr>
<tr>
<td>Mg₃Al-Cl</td>
<td>210.51</td>
<td>0.15</td>
<td>0.99</td>
<td>47.39</td>
<td>3.33</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Effect of solution chemistry: initial pH

Mechanisms of LDHs removal of anionic surfactants include:

1. Surface sorption via electrostatic interactions including hydrogen bond
2. Intercalation via anion exchange

\[ \text{Mg}_3\text{Al} - \text{OH} + H^+ \rightarrow \text{Mg}_3\text{Al} - \text{OH}_2^+ \]

\[ \text{Mg}_3\text{Al} - X + \text{C}_8\text{F}_{17}\text{SO}_3^- \rightarrow \text{Mg}_3\text{Al} - \text{SO}_3\text{C}_8\text{F}_{17} + X^- \]

- The sorption of PFOS by the nitrate LDHs was slightly affected by the initial pH, indicating anion exchange is the main mechanism in the sorption removal of PFOS.
Effect of solution chemistry: initial pH

With the increase of pH, the sorption of PFOS by the carbonate and chloride LDHs decreased due to the reduced electrostatic attraction.
With the increase of ionic strength, the sorption of PFOS by the nitrate and chloride LDHs decreased due to the suppressed anion exchange process.

Different trend of sorption was observed under acidic and alkaline conditions for carbonate LDHs.
With the increase of coexisting ions, the sorption of PFOS by the nitrate and chloride LDHs decreased due to the suppressed anion exchange process.

For carbonate LDHs, Mg$^{2+}$ and Ca$^{2+}$ increased the sorption of PFOS through bridging effect.
The sorption process was significantly suppressed by the coexisting sulfate and carbonate anions.

- The results showed the role that anion exchange played in the sorption of PFOS by different LDHs.
Characterizations of LDHs

- For nitrate and chloride LDHs, the basal spacing decreased to 0.77 nm after PFOS sorption while the basal spacing remained unchanged for carbonate LDHs.

- For nitrate LDHs, the absorption of the band that correspond to the intercalated nitrate ion significantly decreased after PFOS sorption and the newly appeared peaks are related with the groups of intercalated PFOS anion.
Sorption mechanisms

Chloride-LDHs
Medium anion exchangeability
Surface adsorption and anion exchange

Nitrate-LDHs
Highest anion exchangeability
Anion exchange

Carbonate-LDHs
Lowest anion exchangeability
Surface adsorption
## Summary for PFOS sorbents

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Equilibrium time (h)</th>
<th>Sorption capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granular activated carbons</td>
<td>48-168</td>
<td>160-229</td>
</tr>
<tr>
<td>Anion–exchange resins</td>
<td>48-168</td>
<td>2960</td>
</tr>
<tr>
<td>Crosslinked chitosan bead</td>
<td>100</td>
<td>2745</td>
</tr>
<tr>
<td>Non-ion resins</td>
<td>10-90</td>
<td>37-41</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>24</td>
<td>83-99</td>
</tr>
<tr>
<td>Quaternized cotton</td>
<td>12</td>
<td>1647</td>
</tr>
<tr>
<td>Powdered activated carbons</td>
<td>3-5</td>
<td>374-550</td>
</tr>
<tr>
<td>Zeolites</td>
<td>3-5</td>
<td>8-126</td>
</tr>
<tr>
<td>Metal organic framework</td>
<td>0.17</td>
<td>45</td>
</tr>
<tr>
<td><strong>Layered double hydroxides (LDHs)</strong></td>
<td><strong>0.17</strong></td>
<td><strong>865-998</strong></td>
</tr>
</tbody>
</table>

(Du et al., 2014; Li et al., 2017)
Conclusions

- The synthesized LDHs are able to remove PFOS from water with high capacities, especially nitrate-LDHs.
- LDHs sorption performance can be affected by the coexisting anions.
- The sorption mechanisms include surface adsorption and interlayer anion exchange.
Thank you!
xsong@issas.ac.cn