Removal of Perfluoroalkyl Substances (PFAS) from Water Using Tailored and Highly Porous Organosilica Adsorbents

Paul L. Edmiston
The College of Wooster

University of Illinois
Illinois Sustainable Technology Center
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The College of Wooster (Ohio)
Perfluoroalkyl Substances (PFAS)

Recently, it was discovered that drinking water for more than 600 million Americans was contaminated with PFASs, exceeding the Environmental Protection Agency’s (EPA) 2016 lifetime exposure limit of 70 ppt (Hu et al., 2016).
PFAS Adsorbents: Challenges

Fluoroalkyl groups have limited intermolecular interactions.

Need to adsorb all types:
  Chain length varies
  Polar group varies

Reversible adsorption preferred.

Selectivity is preferred.
Sol-Gel Derived Mesoporous Silicas

**Sol-Gel Process**

1. Alkoxy silane + Hydrolysis
   - Neuterification
   - Hydrolysis
   - Condensation
   - Alcohol

2a. Silanol + Silanol + Silanol + Water
   - Siloxane + Alcohol

2b. Silanol + Alkoxy silane + Alcohol
   - Siloxane + Alcohol

**Ordered Templated Materials**

- Polysilsesquioxanes

**Aerogels**

- Sol
- Gel
- Aerogel

**Sol-Gel Technologies and Their Products**

- Ceramic fibers
π-stacking interactions of aryl groups lead to rapid formation of organosilica nanoparticles which then arrange by covalent bonding into a strong but flexible network.

1,4-bis(trimethoxysilylethyl)benzene (BTEB)
Osorb®-Swellable Organically Modified Silica (SOMS)

Osorb media is a macroporous organosilica that possesses a flexible and hydrophobic pore structure. The pores have affinity for organics leading to swelling when exposed to organic solvents.

Swelling is due to nanomechanical expansion of a mesoporous silica matrix. Osorb does not absorb water. Osorb is chemically inert and hydrophobic.
Swelling Mechanism

Surface area: 550 m$^2$/g
Dry state pore volume: 0.71 mL/g
Swelling Mechanism

Volume change: 2-3 x (>35 x has been observed)
Volume absorbed: 5 mL /g
Mechanism

Pore structure of the swollen state is generally unknown.
Swelling Mechanism

Dry

Swollen

No solvent

Surface area: 400-600 m²/g
Pore volume: 0.6-1.5 mL/g

+Solvent

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Mechanical Force Generation Upon Swelling

**Organic liquids**

- Max force: 600 N/g (61,000 w/w)
- Work: $0.8 \pm 0.1$ J/g
- $\Delta H_{\text{swell}}$: $5.2 \pm 1.2$ J/g

Entropically driven process
- 300% $\Delta V$, 650% $\Delta \text{mass}$

**Hydrocarbon vapors**

- Max 1x w/w change for condensable vapors when $p=p_0$ 13% volume,
Absorption Characteristics Vapor

Molecules absorbed:
  All organics, condensable better
  Not water

Capacity:
  Max 110% swell at $p=p_0$
  Non-specific

Rate:
  Varies depending on boiling point

Force:
  Relative to partial pressure
Vapor Absorption

Acetone Vapor Ab/Adsorption

Osorb pre-saturated with phenol

Regular clean Osorb

400% total mass gain
4.8mL/g Osorb added

$\frac{w}{w_i}$ vs. Time (min)
Permeability to Organics vs. Water Vapor

**Diagram Description:**

- **Gas cell (100 mL):**
  - **Propane + H₂O(g) sat** input
  - **N₂, 1 mL/min** output

- **IR spectrometer**
- **Osorb disk**
- **Diffusion cell – Osorb separated flow cells**

**Graph:**

- **Infrared Absorbance in Collection Chamber**
  - **Time (min):** 0 to 60
  - **Propane**
  - **H₂O**

**Notes:**

- **Vent**
- **8 mm**
- **1 mm**
Entrapment Inside Pores

Evaporation
## Composite Adsorbents

- **Cu(II)-Osorb**

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Bulk Density (g/mL)</th>
<th>Ammonia Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Osorb</td>
<td>0.83</td>
<td>135</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>0.45</td>
<td>6</td>
</tr>
<tr>
<td>Activated carbon - chloride§</td>
<td>0.63</td>
<td>15</td>
</tr>
<tr>
<td>Activated carbon – acid treated*</td>
<td>0.72</td>
<td>27-45</td>
</tr>
<tr>
<td>3M 6004 Ammonia Cartridge</td>
<td>0.7</td>
<td>37</td>
</tr>
<tr>
<td>St. Cloud Zeolite**</td>
<td>0.9</td>
<td>24</td>
</tr>
</tbody>
</table>
Composition of Adsorbents for PFAS

Osorb

F-Osorb

QA-Osorb

poly-QA-Osorb
Adsorption Kinetics: PFOA

The graph shows the adsorption kinetics of PFOA over time for different materials:
- GAC
- Osorb
- F-Osorb
- QA-Osorb
- poly-QA-Osorb

The y-axis represents the concentration ratio $C/C_0$ and the x-axis represents time in hours (hr). The data points indicate a decreasing concentration over time, with different materials showing varying rates of adsorption.
## Percent Removal

<table>
<thead>
<tr>
<th>PFAS Solute</th>
<th>Percent Removal (%)</th>
<th>50 mM NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DI Water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Osorb</td>
<td>F-Osorb</td>
</tr>
<tr>
<td>PFDA</td>
<td>50</td>
<td>57</td>
</tr>
<tr>
<td>PFNA</td>
<td>94</td>
<td>88</td>
</tr>
<tr>
<td>PFOA</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>PFHpA</td>
<td>79</td>
<td>75</td>
</tr>
<tr>
<td>PFHxA</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>PFPeA</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>PFBA</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PFOS</td>
<td>50</td>
<td>89</td>
</tr>
<tr>
<td>PFHxS</td>
<td>11</td>
<td>27</td>
</tr>
<tr>
<td>PFBs</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>PFOSaAm</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>PFOSA</td>
<td>94</td>
<td>89</td>
</tr>
</tbody>
</table>

2,000 ppb initial concentration, 200 mg/L dosage, 18 hr contact time
Adsorption Capacity ($C_e = 200$ ppb)
Adsorption Capacity

PFAS in 50 mM NaCl

- Osorb
- F-Osorb
- poly-QA-Osorb
- GAC

Adsorption Capacity (mg/g)
Adsorption Capacity

![Graph showing adsorption capacity of different PFAS in 50 mM NaCl solution.](image)

- **Osorb**: Blue bars
- **F-Osorb**: Orange bars
- **poly-QA-Osorb**: Grey bars
- **GAC**: Black bars

**PFAS in 50 mM NaCl**

- PFDA
- PFNA
- PFOA
- PFHpA
- PFHxA
- PFPeA
- PFBA
- PFOS
- PFHXS
- PFBS
Effect of Ionic Strength

Adsorption isotherm measured in DI Water

Adsorption isotherm measured in 50 mM NaCl
Adsorption of PFAS Mixtures (DI water)

Poly-QA-Osorb (200 ppb each PFAS) accumulated PFAS: 81 mg/g
## Treatment of Groundwater

<table>
<thead>
<tr>
<th>Compound</th>
<th>Site Water (Influent)</th>
<th>Concentration (µg/L)</th>
<th>Effluent – Composite 0-1800 applied bed volumes (Percent Reduction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>F-Osorb (2 bed vol /min)</td>
<td>Poly-QA-Osorb (2 bed vol/min)</td>
</tr>
<tr>
<td>Perfluorobutanesulfonic acid (PFBS)</td>
<td>0.96± 0.07</td>
<td>0.369 (61.7)</td>
<td>0.015 (98.4)</td>
</tr>
<tr>
<td>Perfluorohexanesulfonic acid (PFHxS)</td>
<td>7.6± 0.3</td>
<td>0.280 (59.4)</td>
<td>0.140 (98.1)</td>
</tr>
<tr>
<td>Perfluorooctanesulfonic acid (PFOS)</td>
<td>40.7± 0.3</td>
<td>0.537 (98.7)</td>
<td>0.279 (99.3)</td>
</tr>
<tr>
<td>Perfluorooctanoic acid (PFHβA)</td>
<td>0.30 ± 0.01</td>
<td>0.040 (86.7)</td>
<td>0.020 (93.5)</td>
</tr>
<tr>
<td>Perfluorooctanoic acid (PFOA)</td>
<td>0.84± 0.5</td>
<td>0.050 (94.0)</td>
<td>0.053 (93.7)</td>
</tr>
<tr>
<td>Total PFOS + PFOA</td>
<td>42</td>
<td>0.588</td>
<td>0.332</td>
</tr>
</tbody>
</table>
Treatment of Groundwater: Breakthrough

- Bump
- Out

Bioswale
Conclusions and Future Work

Current organosilica based adsorbents have 3-5 times more capacity than GAC. Equivalent or 2 times better than ion exchange.

PFAS can be recovered with a methanol rise.
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PFAS can be recovered with a methanol rise.

How is PFAS adsorption in the presence of other solutes? Ex: landfill leachate

What are the total economics of PFAS treatment?

Is there a role for high technology in water treatment?
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Other Specialty Applications

Passive Samplers
- Passive sampling of volatile and semi-volatile analytes for GC/MS and LC/MS analysis.
- Designed for long-term placement in surface water or wastewater to capture: (1) volatile organics, (2) EPA 525 compounds, (3) EPA Suite of 16 compounds.

Drinking Water
- Osorb Coated Sand for addition to municipal sand filters for removal of trace (ppb level) chemical contaminants.

Metals Binding
- Osorb materials specifically designed to capture Zn(II), Cu(II), Cu(I), Pb(II), Hg(II), and other transition metals.

Catalytic Materials
- Osorb embedded with catalytic nanoparticles for accelerated rates of reaction.

Specialty Materials
- Extraction and recovery of valuable species
- Extraction of high value essential oils
- Personal Care Osorb for dry shampoos, controlled fragrance release, cosmetics, etc.
Drinking Water: Osorb Treatment Concept

Contaminated water

Flow

Biology impacted by toxic chemical

Indicates biomass heath

Little removal of contaminants

Sorbent-coated sand

Flow

Biological health preserved

Zero valent iron

ZVI breaks down contaminants in sorbent layer, desorb to microorganisms

Removal of contaminants