Removal of PFAS Precursor Compounds Using GAC

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RESEARCH GOALS

DEVELOP DATA SET FOR PFAS PRECURSOR REMOVAL
• RSSCTs – well-established method, relatively quick to run
• Target compounds: 4 fluorotelomers & 1 sulfonamide
• Compare multiple carbon types (5)
• PFOA & PFOS included in “background”

BETTER UNDERSTAND ROLE OF CARBON PROPERTIES
• Can pore volume distribution explain results?
• Can more “simple” test methods correlate to results?
PREVIEW – RESULTS - 1

Effluent Concentration (ng/L) vs. Bed Volumes (10 min EBCT)

- Reagg Bit - Virgin
- Reagg Bit - React
- Lignite
- Sub-bituminous
- Enh. Coconut

4:2 Fluorotelomer Sulfonic Acid
**PFAS OVERVIEW**

**WHAT ARE PFAS?**
- Poly- and perfluoroalkyl substances
- Class of man-made fluorinated compounds

**Health Advisory:**
- 70 ppt
- Combined PFOA / PFOS

**WHY ARE THEY A PROBLEM?**
- Contaminates drinking water and food
- Highly persistent / resistant to degradation
- Accumulate in the body

**WHERE DO THEY COME FROM?**
PFAS are used in a variety of products as a surface-active agent
PFAS Molecular Characteristics

- **CHEMICALLY STABLE**
  - Carbon Chain backbone
  - C-F Bond
- **RELATIVELY HIGH MOLECULAR WEIGHT**
- **LOW VAPOR PRESSURE**
- **EASILY INFILTRATES INTO GROUNDWATER & SOIL**
- **BIOACCUMULATES IN ORGANISMS**

**PFOS MOLECULE**
- Carboxylic Acid Head Group
- Sulfonic Acid Head Group

**PFOA MOLECULE**
- C-F Bond
- C-C Bond
- Carboxylic Acid Head Group
PFAS PRECURSORS

4:2 Fluorotelomer Sulfonic Acid (4:2 FTS)

6:2 Fluorotelomer Sulfonic Acid (6:2 FTS)

8:2 Fluorotelomer Sulfonic Acid (8:2 FTS)

Perfluorooctane Sulfonamide
# PFAS Treatment Technology

<table>
<thead>
<tr>
<th>Treatment Option</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
</table>
|                  | • Significantly lower capital costs  
• Significantly lower O&M costs  
• Reactivation saves cost, destroys PFASs, & removes liability  
• Established BAT for a long list of organic contaminants | • High Natural Organic Matter (NOM) can increase use rates  
• Removal efficacy varies by size/weight/solubility of contaminant |
|                  | • Removes salts / inorganics that GAC cannot | • Concentrated waste water disposal liabilities & costs  
• More energy / CO₂ intensive  
• High maintenance cleaning and replacement of fouled membranes  
• Removes healthy minerals |
|                  | • Resin can be regenerated  
• May be more economical at high concentrations of PFAS (generally much higher than drinking water applications – primarily remediation applications only) | • High cost of media  
• Regeneration produces disposal liabilities & costs  
• Regeneration requires both brine and a solvent (e.g. methanol) |
STRUCTURE OF ACTIVATED CARBON

**Adsorption Pores**
- Finest pores in structure
- Termed “micropores”
- <20 Å diameter

**Transport Pores**
- Diffusion pathways to transport adsorbates
- Termed “mesopores”
- 20 Å - 500 Å diameter
CALGON CARBON
PFAS TREATMENT LOCATIONS

40+ INSTALLATIONS ACROSS THE US
TREATMENT METHODOLOGY

DUAL VESSEL TREATMENT
- Maximize carbon loading
- Simplify carbon exchange logistics
- Redundancy

SUFFICIENT CONTACT TIME IS CRITICAL FOR EFFECTIVE REMOVAL
- Kinetics and Thermodynamics of adsorption must be considered
- 10 minutes EBCT per vessel minimum
### Five GAC products evaluated under identical equivalent full-scale operating conditions and influent water quality

<table>
<thead>
<tr>
<th>GAC Source Material</th>
<th>Full-Scale Mesh Size</th>
<th>Apparent Density</th>
<th>Iodine Number (mg/g)</th>
<th>Xylenol Orange Dye Number (mg/g/hr)</th>
<th>Molasses Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagglomerated Bituminous Coal - Virgin</td>
<td>12 × 40</td>
<td>0.543</td>
<td>1030</td>
<td>13.5</td>
<td>189</td>
</tr>
<tr>
<td>Reagglomerated Bituminous Coal – React.</td>
<td>12 × 40</td>
<td>0.546</td>
<td>905</td>
<td>13.4</td>
<td>236</td>
</tr>
<tr>
<td>Lignite Coal</td>
<td>12 × 40</td>
<td>0.377</td>
<td>605</td>
<td>17.4</td>
<td>416</td>
</tr>
<tr>
<td>Sub-Bituminous Coal</td>
<td>12 × 40</td>
<td>0.350</td>
<td>1015</td>
<td>21.7</td>
<td>154</td>
</tr>
<tr>
<td>Coconut Shell</td>
<td>12 × 30</td>
<td>0.414</td>
<td>1290</td>
<td>13.5</td>
<td>288</td>
</tr>
</tbody>
</table>
GAC COMPARISON
TEST CONDITIONS - 1

OPERATING PARAMETERS

- 10 minutes empty-bed contact time (EBCT).
- Pennsylvania groundwater spike with PFAS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Avg. Influent Concentration (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:2 Fluorotelomer Sulfonic Acid</td>
<td>4:2 FTS</td>
<td>130</td>
</tr>
<tr>
<td>6:2 Fluorotelomer Sulfonic Acid</td>
<td>6:2 FTS</td>
<td>43</td>
</tr>
<tr>
<td>8:2 Fluorotelomer Sulfonic Acid</td>
<td>8:2 FTS</td>
<td>56</td>
</tr>
<tr>
<td>Perflurooctanesulfonic Acid</td>
<td>PFOS</td>
<td>153</td>
</tr>
<tr>
<td>Perfluoroctanoic Acid</td>
<td>PFOA</td>
<td>177</td>
</tr>
<tr>
<td>Perfluoroctane Sulfonamide</td>
<td>PFOSA</td>
<td>39</td>
</tr>
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</table>
## WATER QUALITY

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.1</td>
<td>-</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>670</td>
<td>mg/L</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>105</td>
<td>mg/L as CaCO3</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>0.3</td>
<td>mg/L</td>
</tr>
</tbody>
</table>
REFRESHER: READING BREAKTHROUGH CURVES

REMEmBER
- Usually shown as normalized values.
- C/Co - What is influent concentration?
- “Bed Volumes” does not equal actual run time.
PFAS BREAKTHROUGH CURVES
REAGGLOMERATED BITUMINOUS GAC (VIRGIN)

Effluent Concentration (ng/L)

Bed Volumes (10 min EBCT)

1 Year of Service
PFAS BREAKTHROUGH CURVES
6:2 FTS

Short-term spike in feed concentrations
PFAS BREAKTHROUGH CURVES
8:2 FTS

Short-term spike in feed concentrations
PFAS BREAKTHROUGH CURVES
PFOS

Effluent Concentration (ng/L) vs. Bed Volumes (10 min EBCT)
Influent
PFAS BREAKTHROUGH CURVES

PFOA
PFAS BREAKTHROUGH CURVES
PFOSA

Short-term spike
In feed concentrations
INITIAL CONCLUSIONS

ALL 4 PRECURSORS REMOVABLE WITH GAC

- 4:2 FTS most difficult
  - Lower molecular weight (shorter chain).
  - Large variation in removal.
  - Most-favorable performance with reaggl. bituminous GACs.

SENSITIVITY TO VARYING INFLUENT CONCENTRATIONS

- Reaggl. bituminous GAC minimally affected.
- Sub-bituminous & enhanced coconut showed rapid increase in breakthrough during spike.
- Some sensitivity evident in lignite breakthrough curve.
PROPERTIES vs. PERFORMANCE

In addition to surrogate adsorbate tests, porosity of test GACs was evaluated using nitrogen adsorption isotherms and compared to performance.

<table>
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<th>GAC Source Material</th>
<th>BV to 50% Breakthrough</th>
<th>Apparent Density</th>
<th>Iodine Number (mg/g)</th>
<th>Xylenol Orange Dye Number (mg/g/hr)</th>
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GAC POROSITY: ~5 - 500 Å

**Parking Lots**

**Highways**

Discrete Pore Volume (cc/g)

Pore Width (Å)

- Reagg. Bit. - Virgin
- Reagg. Bit. - React.
- Lignite
- Sub-Bituminous
- Enh. Coconut
GAC POROSITY: ~5 - 100 Å

- Parking Lots
- Highways

Discrete Pore Volume (cc/g)

Pore Width (Å)
GAC POROSITY: NORMALIZED TO VOLUME IN BED

Dramatic shifts in relative amounts of porosity.
GAC POROSITY: RELATED TO PERFORMANCE?

Key is porosity per volume, not per weight!
IODINE NUMBER: RELATED TO PERFORMANCE?

Does not account for variation in density of GACs.

Bed Volume to 50% Breakthrough - 4:2 FTS

Iodine Number (mg Iodine / g GAC)

$R^2 = 0.002$
NORMALIZED IODINE NUMBER: RELATED TO PERFORMANCE?

Bed Volume to 50% Breakthrough - 4:2 FTS

Normalized Iodine Number (mg Iodine / RSSCT bed)

$R^2 = 0.81$

Normalized to actual volume of carbon in bed.
**IODINE & DYE NUMBER COMBINED: RELATED TO PERFORMANCE?**

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**AD x (0.1 x Iodine + 3.2 x Dye Number)**

![Graph showing relationship between weighted sum of iodine and dye number and bed volumes to 50% breakthrough.](image-url)
CONCLUSIONS

PRECURSORS ARE REMOVABLE ALONG WITH PFOA & PFOS
- Compound structure impacts removal as expected
- GAC performance varies widely among source materials
- Reactivated GAC can offer performance on-par, or nearly on-par, with its virgin counterpart, depending on the target contaminant

GAC SELECTION MUST CONSIDER INTERPLAY BETWEEN PROPERTIES
- No single specification can adequately guide carbon selection
- Porosity is key, but only when considered alongside bed density
- “Old” methods such as Iodine Number are still valuable, especially when combined with some measure of adsorption rate, such as Dye Number
Thank you for your time.
Questions?

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