Adsorption of perfluorooctanoic acid (PFOA) using graphene-based materials

Supriya Lath
(PhD Student, The University of Adelaide)

Prof. Mike McLaughlin (UofA, School of Agriculture Food & Wine)
Dr. Divina Navarro (UofA, School of Agriculture Food & Wine; CSIRO Land & Water)
Prof. Dusan Losic (UofA, School of Chemical Engineering)
Dr. Anu Kumar (CSIRO Land & Water)
PFOA (Perfluorooctanoic acid)

- hydrophobic fluorinated tail
- anionic polar head

Applications

University of Adelaide
Concerns and Challenges

• Bioaccumulation; long-range transport
• Exposure through soil, water, dust
• Linked with human and animal health
• Phased out, but ubiquitous
• Resistant to degradation; stable
Remediation Strategies for PFOA & PFASs

- Photocatalysis
- Sonochemical degradation
- Advanced oxidation

**Physical & Chemical**
(scope for *in situ* and *ex situ*)

- Adsorptive immobilisation (*in situ*)
e.g. activated carbon

- Thermal
  (energy intensive; *ex situ* only)

- Biological
  (PFOA resistant to degradation)
Graphene Materials

- Single layer of graphite
- 2-D carbon sheet
- High surface area
- Versatile surface chemistry
Project Aims

• Develop graphene-based materials with capabilities for immobilisation of PFOA.

• Evaluate efficiency of prepared materials for PFOA-sorption, and compare with a commercial remediation agent.

  • effect of pH
  • effect of ionic strength
  • effect of PFOA concentration
Materials Used

*Commercial adsorbent:*

- RemBind™ RemB
  (mixture of activated C, gibbsite and kaolinite)

*Prepared graphene adsorbents:*

- Graphene oxide GO
- Iron-modified graphene FeG
Synthesis of GO & FeG

Graphite + KMnO₄ + conc. H₂SO₄ : H₃PO₄ (9:1)

Δ 50°C, 15 hrs
Ice + 30% H₂O₂

Multiple wash cycles with HCl, water & ethanol
(centrifuge, decant)

FeG hydrogel

FeG aerogel
Freeze-dry

Hydrothermal reduction
Self-assembly

FeSO₄·7H₂O
Δ 90°C
8 hrs

Well-exfoliated
GO suspension (2 mg/mL)

GO, oven dry at 30°C

Structural Characterisation

**GO:** SEM and TEM images

**FeG:** SEM and TEM images

Additional characterisation:
- XRD spectra
- FTIR spectra

Idealised Structure of Graphene Oxide

iron oxide particles (goethite mineral)
Surface Characterisation

Specific surface area (25 °C)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Specific surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>434.6 m²/g</td>
</tr>
<tr>
<td>FeG</td>
<td>242.4 m²/g</td>
</tr>
<tr>
<td>RemB</td>
<td>123.4 m²/g</td>
</tr>
<tr>
<td>Kaolinite¹</td>
<td>~ 25 m²/g</td>
</tr>
</tbody>
</table>

Surface zeta potential (25 °C)

Experimental methods & PFOA analysis

Radiochemical Analysis:

Isotopically labelled \(^{(14C)}\) PFOA, (ARC Inc., USA)

Liquid scintillation β-counting measures \(^{14}\)C activity.

Specific activity = 2035 MBq/mmol

Note: PFOA concentration calculations were corrected for any sorption that occurred on the reaction vessels during batch sorption.
PFOA sorption: equilibrium time

- Time: 0 – 96 hrs
- Initial [PFOA] ~ 30 ng/mL
- pH 5.5
- 10 mM CaCl₂ background
- 25 °C
PFOA sorption: effect of pH

- pH: 3 – 9
- Initial [PFOA] 100 ng/mL
- 10 mM CaCl₂ background
- 48hrs
- 25 °C
PFOA sorption: effect of ionic strength

- 0 – 100 mM CaCl₂ background
- Initial [PFOA] 20 ng/mL
- pH 5.5
- 48hrs
- 25 °C

<table>
<thead>
<tr>
<th>Background electrolyte</th>
<th>Elec. conductivity mS/cm = dS/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM CaCl₂</td>
<td>2.11 (non-saline soil)</td>
</tr>
<tr>
<td>25 mM CaCl₂</td>
<td>4.93 (saline soil)</td>
</tr>
<tr>
<td>50 mM CaCl₂</td>
<td>9.24 (landfill leachate)</td>
</tr>
</tbody>
</table>
PFOA sorption: effect of concentration (isotherm)

- Initial [PFOA] 0 – 650 ng/mL
- 10 mM CaCl₂ background
- pH 5.5
- 48hrs
- 25 °C
Summary

✓ GO & FeG successfully adsorbed PFOA

✗ Surface area did not correlate with sorption performance

✓ Effect of pH and ionic strength
  • Efficiency of GO ↓ with ↑ in pH
  • FeG & RemB resistant to changes

✓ No saturation of binding sites to concentrations up to 650 μg/L PFOA

✓ Binding related to non-ionic interactions with surfaces
  • Hydrophobic interactions
  • Possible role of Important role of minerals Fe, Al, Si
Acknowledgements

Prof. Mike McLaughlin (UofA, School of Agriculture Food & Wine)
Prof. Dusan Losic (UofA, School of Chemical Engineering)
Dr. Divina Navarro (UofA, School of Agriculture Food & Wine)
Dr. Anu Kumar (CSIRO Land & Water)

Dr. Richard Stewart (Ziltek Pty. Ltd.)

Funding: Australian Postgraduate Award and Ziltek Soil Science Scholarship (Ziltek Pty. Ltd.)