Polymeric Resins
for VOC Removal
from Aqueous Systems

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Polymeric Resins for VOC Removal:

Outline

• Motivation
• Attributes of polymeric resins
• Adsorption capacities
• Performance in dynamic column adsorption processes
• Regeneration
• Summary
Separation Processes to the Rescue!

Clean Air

Impurity

Raw Material → Separation → Process → Separation

Effluent Water → Recycle

By Products

Clean Water

Products

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Some Application Areas

- Chemical Analysis
- Ion-exchange resins
- Non-adsorbing aqueous size exclusion chromatography (SEC) resins
- Affinity resins for Liquid chromatography
- Adsorption of organics from aqueous systems
- Organic liquid-liquid separations

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Adsorption of a Mixture of Chlorinated Pesticides in a Packed-Bed

## Polymer Resins and Activated Carbon

<table>
<thead>
<tr>
<th>Polymeric Resins</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>?</td>
<td></td>
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</tbody>
</table>

- **Activated Carbon**
  - High surface area ( > 1000 m²/g)
  - High heat of adsorption ( >10 kcal/mol)
  - Thermal regeneration (e.g., steam regeneration).
  - 5%-10% degradation per cycle
  - Readily available, low cost ( ~ $2/kg), general adsorbent material
  - Spent carbon may have to be treated as hazardous waste
Polymeric Resins: Major Performance Issues

- Are the surface area and pore size distribution suitable for sorption of VOCs?
- Can solute-polymer affinity be controlled?
- Can polymeric resins be easily regenerated?
- Are polymeric resins stable for cyclic operation?
- Are there severe mass transfer limitations?
Area, Volume and Wettability

- Pore size/volume distribution
- Surface area
- Inaccessible pore volume and wettability
Surface Area Improvements
<table>
<thead>
<tr>
<th>RESIN</th>
<th>SURFACE AREA (M²/G)</th>
<th>PORE VOLUME (CM³/G)</th>
<th>PORE RADIUS (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-400 (Activated Carbon)</td>
<td>1078</td>
<td>0.652</td>
<td>14.7</td>
</tr>
<tr>
<td>XAD-2 (SDVB)</td>
<td>353</td>
<td>0.78</td>
<td>48.3</td>
</tr>
<tr>
<td>XAD-4 (SDVB)</td>
<td>870</td>
<td>1.18</td>
<td>24.5</td>
</tr>
<tr>
<td>XAD-16 (SDVB)</td>
<td>889</td>
<td>1.75</td>
<td>39</td>
</tr>
<tr>
<td>XAD-8 (Poly(methylacrylate)\textsuperscript{a})</td>
<td>126</td>
<td>0.63</td>
<td>98</td>
</tr>
<tr>
<td>Reillex-425 Polyvinylpyridine-divinylbenzene</td>
<td>110</td>
<td>0.63</td>
<td>156</td>
</tr>
<tr>
<td>Polyclar-AT Polyvinylpyrrolidone, crosslinked\textsuperscript{b}</td>
<td>1.2</td>
<td>&lt;0.004</td>
<td>&lt;10</td>
</tr>
<tr>
<td>XUS (43493.01)</td>
<td>1100</td>
<td>1.3</td>
<td>23.5</td>
</tr>
<tr>
<td>MN-150</td>
<td>821</td>
<td>1.01</td>
<td>39.9</td>
</tr>
<tr>
<td>MN-170</td>
<td>1066</td>
<td>1.4</td>
<td>26</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Poly(methylacrylate)

\textsuperscript{b} Polyvinylpyrrolidone, crosslinked
### Macropores, Micropores and Inaccessible Pore Volume

<table>
<thead>
<tr>
<th>Resin</th>
<th>$A_{\text{total}}$ (cm$^2$/g)</th>
<th>$A_{\text{micro}}$ (cm$^2$/g)</th>
<th>$V_{\text{total}}$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>$V_{\text{ina}}/V_{\text{total}}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XUS</td>
<td>1100</td>
<td>772</td>
<td>1.30</td>
<td>0.39</td>
<td>0.11</td>
</tr>
<tr>
<td>Mn150</td>
<td>698</td>
<td>554</td>
<td>1.01</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>Mn170$^{(a)}$</td>
<td>1066</td>
<td>836</td>
<td>1.40</td>
<td>0.43</td>
<td>0.31</td>
</tr>
<tr>
<td>XAD-4</td>
<td>845</td>
<td>114</td>
<td>1.10</td>
<td>0.05</td>
<td>0.43</td>
</tr>
<tr>
<td>XAD-16</td>
<td>889</td>
<td>71</td>
<td>1.75</td>
<td>0.02</td>
<td>0.46</td>
</tr>
</tbody>
</table>

$^{(a)}$ Laboratory grade
Prewetting of Hydrophobic Resins

Bulk Fluid

Pore Fluid

a Cluster of Hydrophobic Micro-spheres

Water

Methanol

Air or Vapor
Solute-Polymer Affinity

- Hanson solubility parameter approach
- Adsorption and swelling (absorption)
- Unexpected multi-solute behavior

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Adsorption of VOCs onto Polymeric Resins - A Simple Correlation
PCE Adsorption Isotherms
ADSORPTION onto POLYSTYRENE XAD-4

FUGACITY INTERPRETATION

SURFACE CONCENTRATION (mmole/m²)

○ Phenol
△ TCE
▼ CHCl₃
□ PCE
◇ CH₂Cl₂

FUGACITY (atm)

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Adsorption/Regeneration System

1 a-f Solvent Reservoirs
2 Solvent Select Valve
3 a,b Piston Pumps
4 a,b High Pressure Mixer

5 Adsorber column
6 UV Detector
7 SIM Box
8 386sx Computer

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Cyclic Adsorption/Regeneration Process

- In Water
- In Methanol

Diagram showing the process with stages labeled a to e, and time axis indicating progression through the stages.
Column Regeneration

- In-situ solvent regeneration of resin with aliphatic alcohols
- Cyclic Adsorption/regeneration process
Breakthrough Curve for Chlorobenzene in XUS Column

\[ Q = 20 \text{ ml/min} \]
\[ C_0 = 250 \text{ mg/l} \]
Regeneration Curve for Fixed-Bed XUS Column Saturated with Chlorobenzene.
Recovery of Chlorobenzene from XUS Resin
Adsorption of Benzoic Acid onto MN-170
Flow rate = 2 ml/ min
Bed volume 3.53 cm³
C₀ = 400 mg/l
Regeneration of MN-170 Column Saturated with Benzoic Acid
1 - 400 mg/l
2 - 300 mg/l
3 - 200 mg/l
4 - 100 mg/l
Isotherms: Benzoic Acid Adsorption onto MN-170
Multiple Regenerant Passes

Benzoic Acid Recovery from MN-170 column using a recycled Methanol Stream

Concentration of Benzoic Acid in methanol (g/l)
Multiple Regenerant Passes

Benzoic Acid Recovery from MN-170 column using a recycled Methanol Stream
Solute Recovery and Solvent Regeneration

- Solute is concentrated in the regenerating stream
- Concentration factor: 10-100
- Solvent can be recycled up to 3-4 cycles
- Regenerate solvent using appropriate separation method
Chlorobenzene adsorption on MN-150 in a column relative to the initial equilibrium adsorption capacity. Every other cycle is plotted for clarity.
Column Adsorption Regeneration Cycles

Relative mass of chlorobenzene adsorbed onto XUS resin for repeated adsorption/regeneration cycles

Resin Stability
Resin Stability

Resin’s Performance for Repeated Adsorption/Regeneration Cycles

Relative mass of benzoic acid adsorbed onto XUS resin over repeated process cycles
Resin Stability

- Adsorption capacity is retained over many adsorption/regeneration cycles
# Mass Transfer Limitations

<table>
<thead>
<tr>
<th>Source</th>
<th>Adsorbent</th>
<th>Temperature (K)</th>
<th>Intraparticle Diffusivity $x10^{11}$ $[m^2/s]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Macronet</td>
<td>293</td>
<td>1.05</td>
</tr>
<tr>
<td>Huang et al. (1994)</td>
<td>Macoreetricular</td>
<td>300</td>
<td>2.71</td>
</tr>
<tr>
<td>Takeuchi and Suzuki (1984)</td>
<td>Activated Carbon</td>
<td>298</td>
<td>0.41</td>
</tr>
</tbody>
</table>
## Polymeric Resins and Activated Carbon

### Polymeric Resins
- High surface area (>1000 m²/g)
- Low heat of adsorption (<4 kcal/mol)
- Solvent regeneration (e.g., using aliphatic alcohols)
- No loss in performance over many cycles
- Limited choice and high cost (~ $20/kg)
- Chemical selectivity is feasible

### Activated Carbon
- High surface area ( > 1000 m²/g)
- High heat of adsorption ( >10 kcal/mol)
- Thermal regeneration (e.g., steam regeneration).
- 5%-10% degradation per cycle
- Readily available, low cost (~ $2/kg), *general adsorbent* material
- Spent carbon may have to be treated as hazardous waste
SUMMARY

• Polymeric sorption resins can be regenerated in-situ by solvent regeneration or thermal recovery.
• Cyclic adsorption/regeneration process is feasible.
• Solvent regeneration and solute recovery from the solvent may be the costly part of the process.
• The dominance of low cost activated carbon is an important reason for the small market share of polymeric resins and thus their high cost.
SUMMARY (Cont’d)

- Capital cost for polymeric resin packed-beds should is expected to be at the same level as for granular activated carbon adsorption.
  - Virtually no attrition of resin
  - Resin stability is maintained over many cycles
  - Regeneration can be done in-site under mild conditions
- Pilot-scale demonstration is the next step
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Pertinent Publications:


