Removal of Estrone from Water by Adsorption on Zeolites with Regeneration by UV Photolysis

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Introduction
- Endocrine-disrupting compounds (EDCs)
  strong estrogenic effects – estrogens, e.g. estrone (E1)
- Adverse potential effects on the environment
  feminized fish; reproductive abnormalities of fish;
  sharp increase in breast cancer (suspected cause)
- Current wastewater/sewage treatment facilities:
  average removal < 90%
- Recent research on advanced treatment technology
  ozonation; TiO₂/UV; UV; UV/H₂O₂; reverse osmosis;
  nanofiltration; activated carbon

Introduction (Cont.)
- Research interest: removal of estrogens from water
- Hypothesis: hydrophobic zeolites - hydrophobic estrogens
- Target compound: estrone (E1)
- Adsorbents of research:
  dealuminated Y (DAY); silicalite-1;
  Centaur® activated carbon (CAC)
- Challenge: analysis of low E1 concentrations

What does estrone look like?
Analytical Method

Sample preparation

Extraction - SPME fiber

On-fiber derivatization - MSTFA

GC-FID

Quantification approach:
* Internal standard: adjustment for sensitivity of SPME fiber
* Calibration curve: E1 standard conc. vs. Peak area
* Detection limit: 1 µg/l

Experimental Scheme

Screening tests

Adsorbent ability

Adsorption kinetics

Equilibrium time

Adsorption isotherm

Adsorption capacity

UV Photolysis

Possibility of regeneration

Which adsorbents worked effectively?

In screening tests:

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>BET Surface area (m²/g)</th>
<th>SiO₂/Al₂O₃</th>
<th>Framework (number of T atoms/Å)</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAY</td>
<td>692</td>
<td>80</td>
<td>13.3</td>
<td>99.7</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>371</td>
<td>&gt;1000</td>
<td>18.4</td>
<td>38.7</td>
</tr>
<tr>
<td>CAC</td>
<td>NA</td>
<td>/</td>
<td>/</td>
<td>69.3</td>
</tr>
</tbody>
</table>

Zelite Y and Activated Carbon showed promise for estrone removal.


How long to reach equilibrium?

DAY - 4 h vs. CAC - > 8 d
Adsorption isotherm of E1 on DAY at 20°C

Freundlich Equation: $q (\text{mg/g}) = 0.163C_e (\mu\text{g/l})^{1.10}$
$Q_{(\text{max})} = 74$ mg E1/g DAY based on Langmuir equation


Thermal Regeneration at High Temp.

Can UV destroy estrone in aqueous solution?

- Long-wave UV 365 nm (1000µW/cm²) - 10% (6 min - 360 mJ/cm²)
  vs. UV 254 nm (6650 µW/cm²) - 90% (30 sec - 200 mJ/cm²)
- Addition of H₂O₂ no additional degradation.
Can DAY be regenerated by UV?

Can DAY be regenerated by UV?

Cycle – adsorption of E1 on DAY & 254 nm UV radiation for 6 (or 30) minutes (Possible loss of DAY between adjacent cycles)

Conclusions

- A solvent-free analytical method developed
  - SPME followed by on fiber derivatization & GC-FID
- DAY has higher adsorption capacity for estrone than silicalite-1 and Centaur® activated carbon.
- Adsorption of E1 to DAY takes much less time than GAC to reach equilibrium.
- UV 254 nm: readily destroys E1 in aqueous solution.
  No deterioration of adsorption capacity of DAY was observed over nine adsorption-regeneration cycles. H₂O₂ not required.

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