Activated Carbon Tailored Surfaces for Pharmaceutical Pollution Control

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World waterday 22 March 2017
Hospitals, Clinics & Pharmaceutical Companies

- Medical waste received attention as it is biohazardous
Hospital wastewater (HWW)

- Little attention is paid to Hospital wastewater
- Hospitals generate ~ 400-1200 L /bed/day
- (SQUH 960 L/day)
- Effluents are loaded with

Pharmaceuticals & metabolites
Heavy metals
Radioactive elements
Dyes and pigments
Pathogens
Disinfectants
Chloro-organics
Endocrine chemicals
Pharmaceuticals in Aquatic Environment

Sources:

point source

- Hospitals
- Medical and health care facilities
- Medical institutions
- Pharmaceutical Companies
- Pharmacies
- Animal farms

Diffuse source: Flushing unused or expired drugs down the sink or toilets

Pharmaceuticals detected in Aquatic Environment

- Antibiotics
- Pain killers
- Hormones
- Anti-cancer drugs
- Lipid regulators
- Anti-epiliptics
- Cytotoxic compounds
- Endocrine chemicals

U.S. EPA has detected 400 toxic and hazardous pollutants in hospital wastewater.

Impact of Hospital Waste Water

• Directly affects human health: as many compounds are *Genotoxic*
  Suspected of **increased cancer** worldwide
• Antibiotic-resisting bacteria
• Biological imbalance
• Very **dangerous** to the **biodiversity** in the aquatic environment as they can **contaminate the food chain**.
In the last 40 years in Sultanate of Oman

1970  12  Hospital beds (2 hospitals)
1972  526  Hospital beds
1986  3348 Hospital beds
2013  4821 Hospital beds (49 hospitals)

Population increase

1970: 774,000
2015: 3,219,775

The Royal Hospital Muscat
The Challenge

- Many pharmaceuticals, radioactive elements, chloro-organics **survive** the conventional wastewater treatment (biological treatment).
- Many drugs are **persistent**
- High levels were **detected in effluents** from WWTP
- Levels **detected in surface water, ground water, soil**
- Accumulation in **vegetables and crops**

Date palm leaflets

~180,000 tons of palm leaflets are produced annually with no use

Limitation of Activated Carbons

- Non selective for organics
- Depends on the surface area
- Slow adsorption
- Limited capacity
Chemical classification of pharmaceuticals

• Acidic: like Ibuprofen

• Basic Chloropheniramine

• Zwittter-ion: Levofloxacin
Objectives

- To provide tailored carbon surfaces for pharmaceutical control
- Acidic carbons for basic drugs and amphoteric
- Basic carbons for acidic drugs and amphoteric
- Hydrophobic carbon for less ionized

- Carbon characterization
- Test for drug removal
- Assemble a filter for pharmaceuticals
AC functionalization

\[ \text{AC} \xrightarrow{\text{HNO}_3, 80 \degree C} \text{OAC} \xrightarrow{\text{SOCl}_2, 70 \degree C} \]

- Ethylene diamine, 90 \degree C
  - BAC-EDA
  - BAC-PDA

- Propylene diamine, 90 \degree C
  - BAC-PDA

- Ethylamine, 90 \degree C
  - HAC-EA

- Aniline, 90 \degree C
  - HAC-AN
SEM

(AC)

(OAC)

(BAC-EDA)

(BAC-PSA)

(HAC-FA)

(HAC-AH)
TGA- ACs

The graph shows the weight percentage of various ACs as a function of temperature. The curves represent different ACs, each identified by a specific color:
- AC
- OAC
- BAC-EDA
- BAC-PDA
- HAC-EA
- HAC-AN

The x-axis represents temperature in degrees Celsius (°C), ranging from 0 to 900. The y-axis represents weight percentage, ranging from 110 to 40.
DTA- ACs

The graph shows the DSC (mV/mg) response against temperature (°C) for various ACs. The DTA graphs for different ACs are represented by different line colors, indicating distinct thermal behavior and transitions. The graph highlights the comparison of AC, OAC, BAC-EDA, BAC-PDA, HAC-EA, and HAC-AN across the temperature range from 0 to 900 °C.
### Surface chemistry ACs

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$\text{pH}_{\text{zpc}}$</th>
<th>CEC (meq/100g)</th>
<th>Surface functionality (meq/g)</th>
<th>Surface basicity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>carboxyl</td>
<td>lactone</td>
</tr>
<tr>
<td>AC</td>
<td>5.0</td>
<td>18.1</td>
<td>0.29</td>
<td>0.47</td>
</tr>
<tr>
<td>OAC</td>
<td>3.2</td>
<td>288.7</td>
<td>2.66</td>
<td>0.88</td>
</tr>
<tr>
<td>BAC-EDA</td>
<td>8.2</td>
<td>22.1</td>
<td>0.21</td>
<td>0.87</td>
</tr>
<tr>
<td>BAC-PDA</td>
<td>8.7</td>
<td>25.7</td>
<td>0.23</td>
<td>0.82</td>
</tr>
<tr>
<td>HAC-EA</td>
<td>7.9</td>
<td>24.2</td>
<td>0.28</td>
<td>0.93</td>
</tr>
<tr>
<td>HAC-AN</td>
<td>7.2</td>
<td>20.4</td>
<td>0.20</td>
<td>0.86</td>
</tr>
</tbody>
</table>
# Surface Area & porosity

<table>
<thead>
<tr>
<th>Carbon</th>
<th>BET Surface area (m²/g)</th>
<th>Vₜ (ml/g)</th>
<th>D (Å)</th>
<th>Mesopore surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>Vₘicro (ml/g)</th>
<th>Vₘeso (ml/g)</th>
<th>Apparent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>823</td>
<td>0.467</td>
<td>22.7</td>
<td>115</td>
<td>708</td>
<td>0.358</td>
<td>0.109</td>
<td>0.167</td>
</tr>
<tr>
<td>OAC</td>
<td>33.8</td>
<td>0.0424</td>
<td>51.4</td>
<td>30.4</td>
<td>3.40</td>
<td>0.0029</td>
<td>0.0405</td>
<td>0.351</td>
</tr>
<tr>
<td>BAC-EDA</td>
<td>4.02</td>
<td>0.0152</td>
<td>152.0</td>
<td>2.75</td>
<td>1.27</td>
<td>0.0006</td>
<td>0.0146</td>
<td>0.350</td>
</tr>
<tr>
<td>BAC-PDA</td>
<td>6.78</td>
<td>0.0316</td>
<td>186.0</td>
<td>4.28</td>
<td>2.50</td>
<td>0.0012</td>
<td>0.0304</td>
<td>0.282</td>
</tr>
<tr>
<td>HAC-EA</td>
<td>9.89</td>
<td>0.0419</td>
<td>168.0</td>
<td>7.76</td>
<td>2.13</td>
<td>0.0010</td>
<td>0.0409</td>
<td>0.326</td>
</tr>
<tr>
<td>HAC-AN</td>
<td>17.7</td>
<td>0.0513</td>
<td>116.0</td>
<td>16.1</td>
<td>1.56</td>
<td>0.0008</td>
<td>0.0505</td>
<td>0.355</td>
</tr>
</tbody>
</table>
Pore size distribution

AC

OAC

Incremental pore volume (cm$^3$/g)

Pore diameter (Å)

Incremental pore volume (cm$^3$/g)

Pore diameter (Å)
Methylene Blue - Equilibrium

![Graph showing the equilibrium of MB sorbed over time for different materials.](image)
## Kinetics constants

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Pseudo second order model</th>
<th></th>
<th>qₑ (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rate const k₂, (g/mg/hr)</td>
<td>Initial adsorption rate, h, (mg/g/hr)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>0.0080</td>
<td>23.3</td>
<td>54.1</td>
<td>0.9971</td>
</tr>
<tr>
<td>OAC</td>
<td>0.0215</td>
<td>69.4</td>
<td>56.8</td>
<td>0.9999</td>
</tr>
<tr>
<td>BAC-EDA</td>
<td>0.0171</td>
<td>38.0</td>
<td>47.2</td>
<td>0.9991</td>
</tr>
<tr>
<td>BAC-PDA</td>
<td>0.0204</td>
<td>34.5</td>
<td>41.2</td>
<td>0.9989</td>
</tr>
<tr>
<td>HAC-EA</td>
<td>0.2110</td>
<td>833</td>
<td>62.9</td>
<td>0.9999</td>
</tr>
<tr>
<td>HAC-AN</td>
<td>0.1020</td>
<td>105</td>
<td>32.2</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

HACs > OAC > AC is rate of reaction
Methylene Blue - Equilibrium

[Graph showing the equilibrium concentration of MB sorbed (mg/g) vs. equilibrium concentration (mg/L) for different materials: AC, OAC, BAC-EDA, BaC-PDA, HAC-EA, HAC-AN.]
## Capacity

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir Constants</th>
<th>Freundlich Constants</th>
<th>Correlation Values, ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q ) (mg/g)</td>
<td>( b ) (L/mg)</td>
<td>( 1/n )</td>
</tr>
<tr>
<td>AC</td>
<td>270</td>
<td>0.019</td>
<td>0.9972</td>
</tr>
<tr>
<td>OAC</td>
<td>343</td>
<td>0.16</td>
<td>0.9996</td>
</tr>
<tr>
<td>BAC-EDA</td>
<td>200</td>
<td>0.015</td>
<td>0.9979</td>
</tr>
<tr>
<td>BAC-PDA</td>
<td>182</td>
<td>0.017</td>
<td>0.9961</td>
</tr>
<tr>
<td>HAC-EA</td>
<td>393</td>
<td>0.107</td>
<td>0.9995</td>
</tr>
<tr>
<td>HAC-AN</td>
<td>34.7</td>
<td>0.030</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

HAC-EA > OAC >> AC > BACs

CPM sorption - kinetics
# Kinetics parameters

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Temp.</th>
<th>Pore diffusion constant, $k_d$ (mg/g/ hr$^{0.5}$)</th>
<th>Pseudo second order model</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>6.18</td>
<td>$k_2$ (g/mg/hr)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>AC</td>
<td>35 °C</td>
<td>8.14</td>
<td>0.0476</td>
<td>12.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OAC</td>
<td>25 °C</td>
<td>11.34</td>
<td>0.1216</td>
<td>40.65</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>13.92</td>
<td>0.1692</td>
<td>76.92</td>
</tr>
<tr>
<td>BAC</td>
<td>25 °C</td>
<td>6.21</td>
<td>0.0675</td>
<td>14.27</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>8.50</td>
<td>0.0793</td>
<td>29.67</td>
</tr>
<tr>
<td>HAC</td>
<td>25 °C</td>
<td>10.95</td>
<td>0.2037</td>
<td>86.96</td>
</tr>
<tr>
<td></td>
<td>35 °C</td>
<td>11.51</td>
<td>0.2454</td>
<td>133.3</td>
</tr>
</tbody>
</table>

Faster HAC > OAC > AC > BAC
CPM - equilibrium
Equilibrium Data  

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Temperature</th>
<th>HWW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>AC</td>
<td>100.2</td>
<td>175.49</td>
</tr>
<tr>
<td>OAC</td>
<td>357.1</td>
<td>454.5</td>
</tr>
<tr>
<td>BAC</td>
<td>58.14</td>
<td>95.3</td>
</tr>
<tr>
<td>HAC</td>
<td>454.4</td>
<td>588.2</td>
</tr>
</tbody>
</table>

Faster HAC > OAC > AC > BAC
Hospital wastewater sample collection
Column work
<table>
<thead>
<tr>
<th>Carbon</th>
<th>Temperature</th>
<th>HWW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>AC</td>
<td>45.51</td>
<td>67.98</td>
</tr>
<tr>
<td>OAC</td>
<td>24.38</td>
<td>46.37</td>
</tr>
<tr>
<td>BAC</td>
<td>78.33</td>
<td>88.4</td>
</tr>
<tr>
<td>HAC</td>
<td>84.84</td>
<td>96.5</td>
</tr>
</tbody>
</table>

Equilibrium Data  IBU
**Equilibrium Data**

- **Levofloxacin**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Temperature</th>
<th>HWW</th>
</tr>
</thead>
<tbody>
<tr>
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<td>35</td>
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<tr>
<td>AC</td>
<td>59.92</td>
<td>94.37</td>
</tr>
<tr>
<td>OAC</td>
<td>101.39</td>
<td>184.28</td>
</tr>
<tr>
<td>BAC</td>
<td>46.28</td>
<td>73</td>
</tr>
<tr>
<td>HAC</td>
<td>110.16</td>
<td>182.3</td>
</tr>
</tbody>
</table>
DC functionalization for pharmaceuticals

DC → SOC\(_2\), 70 °C → Ethylene diamine, 90 °C → BDC-EDA

DC → Aniline, 90 °C → Ethylamine, 90 °C → Propylene diamine, 90 °C → BDC-PDA

HDC-AN → HDC-EA
DC functionalization for heavy metals and radionuclides

Conclusions

Modified activated carbons:
Larger Capacity Faster Removal
Faster sorption
Better breakthrough curves
– regardless of the low surface area.
Expected to have a role in the future
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