IMPROVING THE ADSORPTIVE PROPERTIES OF BIOMATERIALS FOR THE REMOVAL OF HEAVY METALS

Dr. Abel E. Navarro
Science Department, Borough of Manhattan Community College, CUNY
Heavy Metals

- Present in human activities, from food to mechanic and paints.
- Are not biodegradable
- Can be bioaccumulated and transferred to humans through the food chain.
Use of biological techniques to remove pollutants from air, soil and water.

- Bioaccumulation: Living organism
- Biosorption: Dead biomass
Use of non-living biomasses to passively remove pollutants
- Driven by physico-chemical processes
- Algae, crustacean shells, eggshell, nutshell, fruit peels, fruit seeds, TEALEAVES.
- Fast kinetics (saturation time).
- Potential recyclability of waste
ADVANTAGES

- Competitive performance.
  - Pollutant selectivity.
  - Cost effectiveness.
  - Pollutant recovery.
- No sludge generation.
Our Adsorbents

- Domestic waste found in the kitchen:
  - Why? High content of functional organic groups such as alcohol (fiber and carbohydrates), carboxylic acids and amines (structural polysaccharides).
  - Widespread use of green tea as a hot/cold drink. Massive collection from green tea industries (i.e. Arizona and other bottled tea-based drinks).
ALGINATE BEADS

- Alginate and other polymers gelify in contact with divalent cations (Calcium ions).
- High porosity and stability.
- Encapsulating matrix
Teabags were boiled, dried, stored and used in adsorption experiments.

Solutions of pollutants were prepared and taken to proper pH, mass of adsorbent, dye concentrations, salinity, and crowding.
METHODOLOGY

- Duplicate experiments were carried out at room temperature and shaken during 24h.

- Metal concentrations were measure by the color of the complex with Zincon.

- Adsorbents were characterized using Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Infrared Spectroscopy (FTIR), X-ray Energy Dispersion Spectroscopy (EDS). Surface and porosity were determined by colorimetric and redox experiments.
METHODOLOGY
Characterization of the Adsorbents

TGA: Temperature resistance and presence of volatile compounds

Surface Area and Porosity: Compared to Activated carbon (SA+ 1000 – 2500 cm²/g)

### Results

<table>
<thead>
<tr>
<th>ADSORBENT</th>
<th>Surface Area (m²/g)</th>
<th>Micropore Volume (cm³/g)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>228</td>
<td>0.056</td>
<td>0.137</td>
</tr>
<tr>
<td>CM</td>
<td>1063</td>
<td>0.397</td>
<td>0.578</td>
</tr>
<tr>
<td>CT</td>
<td>231</td>
<td>0.149</td>
<td>0.529</td>
</tr>
<tr>
<td>DGT</td>
<td>274</td>
<td>0.219</td>
<td>0.592</td>
</tr>
<tr>
<td>GT</td>
<td>2736</td>
<td>0.692</td>
<td>1.106</td>
</tr>
<tr>
<td>PGT</td>
<td>221</td>
<td>0.058</td>
<td>0.411</td>
</tr>
<tr>
<td>PM</td>
<td>946</td>
<td>0.892</td>
<td>0.961</td>
</tr>
</tbody>
</table>
RESULTS
RESULTS

GT

DGT
RESULTS
X-RAY EDS – ADSORPTION

PM
PM + Co
PM + Cu
RESULTS

pH Effect
- Ionization of adsorbent’s surface and metals (aquo- and hydroxo-complexes.
- Higher pH promotes higher adsorption.
RESULTS

Mass Effect
- Minimize amount of adsorbent.
- Higher adsorption promotes formation of aggregates.
Isotherms were modeled by Langmuir, Freundlich, Dubinin-Radushkevich and Temkin theories.
### RESULTS

<table>
<thead>
<tr>
<th>Adsorption Isotherm</th>
<th>Parameters</th>
<th>AB</th>
<th>CT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td>( q_{\text{max}} ) (mg/g)</td>
<td>79.87</td>
<td>16.28</td>
</tr>
<tr>
<td></td>
<td>( b ) (L/mg)</td>
<td>0.0162</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>( p)-value</td>
<td>&lt; 0.0001</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.984</td>
<td>0.930</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>( k_F ) (L/g)</td>
<td>2.045</td>
<td>3.142</td>
</tr>
<tr>
<td></td>
<td>( n )</td>
<td>1.349</td>
<td>3.199</td>
</tr>
<tr>
<td></td>
<td>( p)-value</td>
<td>0.00062</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.959</td>
<td>0.982</td>
</tr>
<tr>
<td><strong>Dubinin-Radushkevich</strong></td>
<td>( q_{\text{DR}} ) (mg/g)</td>
<td>46.84</td>
<td>14.59</td>
</tr>
<tr>
<td></td>
<td>( B \times 10^4 ) (mol^2.J^2)</td>
<td>0.235</td>
<td>0.892</td>
</tr>
<tr>
<td></td>
<td>( E ) (J/mol)</td>
<td>146</td>
<td>75</td>
</tr>
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<td>( p)-value</td>
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<tr>
<td></td>
<td>( R^2 )</td>
<td>0.969</td>
<td>0.823</td>
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<tr>
<td><strong>Temkin</strong></td>
<td>( a_t )</td>
<td>0.291</td>
<td>0.406</td>
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<tr>
<td></td>
<td>( b_t \times 10^4 ) (J/mol)</td>
<td>0.312</td>
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<tr>
<td></td>
<td>( p)-value</td>
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<td>&lt; 0.0001</td>
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<tr>
<td></td>
<td>( R^2 )</td>
<td>0.924</td>
<td>0.987</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Isotherm Theory</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q = \frac{q_{\text{max}} \times b \times C_{eq}}{1 + b \times C_{eq}} )</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( q = k_F \times C_{eq}^{1/n} )</td>
</tr>
<tr>
<td>Dubinin-Radushkevich</td>
<td>( q_e = q_{\text{DR}} \times \exp \left(-K_{DR} \times \varepsilon^2\right) )</td>
</tr>
<tr>
<td>Temkin</td>
<td>( q_e = \frac{RT}{b_t} \ln \left(a_t \times C_{eq}\right) )</td>
</tr>
</tbody>
</table>
Salinity Effect:

- Decreases adsorption due to competition for the adsorption sites.
- Higher the charge, the stronger the effect.
- Mild acidic conditions were enough to desorb both dyes.
- Competition of hydronium for active sites.
- Water has weak desorbing properties.
X-RAY EDS – DESORPTION
(HCl treatment)
RESULTS

- Challenge in Remediation: Real Conditions.
- Crowding Agent: Ficoll, Polyethylene glycol.
- Steric Hindrance, access to active sites
FUTURE WORK

- Mixtures of metals: Cu + Zn
- Explore other more toxic metals, proteins, PAHs, emerging pollutants.
- Column studies
- Chemical modification of adsorbents
- Characterization: Elemental Analysis, Potentiometric Titration, BET, AFM.
NEW DIRECTIONS

Emerging Pollutants – Antibiotic Enrofloxacin
pH effect and kinetics

Continuous-flow experiment: Chamomile as an adsorbent of Cu(II) ions. Conditions: 1.8g of CM, flow 7mL/min, pH 6, 100ppm Cu(II).
NEW DIRECTIONS
NEW DIRECTIONS

Enhance adsorption affinity by the incorporation of more reactive functional groups: Carboxyl, thiol, sulfonic

Table: Acidic Group content (mmol/g) of all the adsorbents
Adsorption of heavy metals onto raw and modified adsorbents: Copper (red), Zinc (blue), and Cobalt (green) at pH 6, using 50mg of adsorbent in a 100 ppm metal solution.
Tealeaves have proven to be promising adsorbents for model metals and other pollutants. They also serve as scaffold for chemical modifications.

Characterization studies report advantages of tealeaves and alginate beads as an alternative adsorbent.

pH has a strong effect on the adsorption. Likewise, salinity and crowding effects have a negative impact.

Carboxylation and sulfonation improve the adsorption of metals.
REFERENCES


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