Two-Stage Batch Adsorber Optimisation for Malachite Green Removal Using Activated Waste Biomass

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Outline

• Introduction and Objectives
• Experimental Systems
• Modeling Theory and Models
• Results
• Conclusion
INTRODUCTION
Waste Biomass

**Sources:**
- Straws (wheat, rice husk...)
- Shells (coconut, pistachio, palm kernel, walnut...)
- Fruit stones (olive, dates, peaches, mango...)
- Pine, wood, bamboo, lignin....

Source: filtrasystems
Activated Carbons

- **Activation**: controlled oxidation of carbon atoms in the raw material – expanding the internal surface area
- **Physical and chemical activation**
- **Strong physical adsorption and chemical reactions**
- **Low density**
- **High porosity**: pore volume (0.2 to 0.6 cm³/g)
- **Brunauer-Emmett-Teller (BET)**: surface area (500 to 1500 m²/g)

Source: yet2.com marketplace
Dyes (Malachite Green)

- Dyes are applied to textiles, paper, leather, food, drugs, cosmetics and other products.
- More than 2000 dyes are currently used (reactive orange, congo red, malachite green).
- Major environmental problems (increase in COD, decrease in DO, toxic, carcinogenic, mutagenic, prevent light penetration into water).

Source: Alibaba.com
Adsorption

Factors affecting adsorption:

- pH and Temperature
- Time
- Initial concentration
- Porosity (pore size, volume, and distribution)

Low cost
Low energy
Eco-friendly
Sustainable
Objectives

- Characterize date stones
- Develop suitable activation methods
- Test and compare the performance of the activated date pits adsorbents on the target pollutant of Malachite Green
- Understand the adsorption mechanisms
- Design a two stage adsorption system

The waste product of the seedless date products industry is the date “pit” or date “stone” which is a sustainable and economical resource that can be used to enhance the treatment of water.
EXPERIMENTAL SYSTEMS
Experimental Systems
Properties of the date stones

<table>
<thead>
<tr>
<th>Date stone</th>
<th>Total volume of pore (cm³/g)</th>
<th>Mean pore diameter (nm)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDS</td>
<td>0.21</td>
<td>2.31</td>
<td>85.74</td>
</tr>
<tr>
<td>PADS</td>
<td>0.55</td>
<td>2.48</td>
<td>908.6</td>
</tr>
</tbody>
</table>

Adsorption Tests
- Carried out at 20°C
- 3g of adsorbent with MG
- Shaking at 250 rpm
- Measuring initial and final concentrations
- Mass balance
(amount of dye adsorbed = amount of dye removed)
Two-Stage Batch Adsorber Optimisation

Stage 1
- $S_{s1}$ g-Adsorbent $q_o$, mg/g
- $L_s$, dm$^3$
  Solution $C_1$, mg/L

Stage 2
- $S_{s2}$ g-Adsorbent $q_o$, mg/g
- $L_s$, dm$^3$
  Solution $C_2$, mg/L

$L_s$, dm$^3$
Solution $C_0$, mg/L
MODELING THEORY AND MODELS
Isotherms

- qe: amount of contaminant adsorbed
- Ce: equilibrium concentration of the contaminant

**Models:**
- Langmuir
- Freundlich
- SIPS

**Model information:**
- Prediction
- Type of adsorption
- Molecular interaction

**Errors:**
SSE, chi-square statistic, g-square statistic, relative errors, absolute errors, percentage errors, and fractional errors, etc.

Source: researchgate
### Isotherms (Cont.)

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>SIPS isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_e = \frac{q_m b C_e}{1 + b C_e} )</td>
<td>( q_e = k_F C_e^{\frac{1}{n}} )</td>
<td>( q_e = \frac{q_m K_{LF} C_e^{1/n_{LF}}}{1 + K_{LF} C_e^{1/n_{LF}}} )</td>
</tr>
<tr>
<td>- (mg/g) adsorption capacity constant</td>
<td>- adsorption capacity constant</td>
<td>- ( k_{LF} ) constant</td>
</tr>
<tr>
<td>- ( b ) (L/mg) energy constant</td>
<td>- ( n ) constant (surface heterogeneity)</td>
<td>- ( n_{LF} ) isotherm exponent</td>
</tr>
</tbody>
</table>

**Assumptions:**
- Ideal gas behavior of adsorbate
- Molecules do not interact among each other
- Uniform monolayer adsorption

**Freundlich isotherm**
- Empirical equation
- Multilayer adsorption
- Heterogeneous system

**SIPS isotherm**
- Combination of Langmuir and Freundlich
- High concentrations ~ Langmuir
RESULTS
## Isotherm Study Parameters

<table>
<thead>
<tr>
<th>Isotherms</th>
<th></th>
<th>PADS</th>
<th>RDS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir Model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>0.174</td>
<td>0.00583</td>
<td></td>
</tr>
<tr>
<td>q&lt;sub&gt;m&lt;/sub&gt;</td>
<td>64.7</td>
<td>29.5</td>
<td></td>
</tr>
<tr>
<td>SSE</td>
<td>52.4</td>
<td>3.53</td>
<td></td>
</tr>
<tr>
<td><strong>Freundlich Model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;F&lt;/sub&gt;</td>
<td>26.7</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>1/n</td>
<td>0.165</td>
<td>0.476</td>
<td></td>
</tr>
<tr>
<td>SSE</td>
<td>404</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td><strong>SIPS Model</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K&lt;sub&gt;LF&lt;/sub&gt;</td>
<td>14.8</td>
<td>0.203</td>
<td></td>
</tr>
<tr>
<td>a&lt;sub&gt;LF&lt;/sub&gt;</td>
<td>0.221</td>
<td>0.0016</td>
<td></td>
</tr>
<tr>
<td>b&lt;sub&gt;LF&lt;/sub&gt;</td>
<td>0.840</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>SSE</td>
<td>36.2</td>
<td>1.30</td>
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</tr>
</tbody>
</table>
Isotherm Study
Results (Cont.)

SIPS Isotherm

- Experimental- PAADS
- PAADS- SIPS
- Experimental- NDS
- NDS- SIPS

Ce, mg/L vs. qe, mg/g
# Single Stage vs Two Stage Adsorption

## Amount of PADS adsorbent required

<table>
<thead>
<tr>
<th>Removal %</th>
<th>99.50%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$ (mg/L)</td>
<td>$S$ (g)</td>
<td>$S1+S2$ (g)</td>
</tr>
<tr>
<td>50</td>
<td>11.5</td>
<td>2.5</td>
</tr>
<tr>
<td>100</td>
<td>13.5</td>
<td>3.5</td>
</tr>
<tr>
<td>150</td>
<td>15.1</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>16.4</td>
<td>5.0</td>
</tr>
<tr>
<td>250</td>
<td>17.7</td>
<td>5.9</td>
</tr>
<tr>
<td>300</td>
<td>18.8</td>
<td>6.4</td>
</tr>
<tr>
<td>350</td>
<td>19.9</td>
<td>7.5</td>
</tr>
<tr>
<td>400</td>
<td>21.0</td>
<td>8.3</td>
</tr>
<tr>
<td>450</td>
<td>22.0</td>
<td>9.2</td>
</tr>
<tr>
<td>500</td>
<td>23.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>
CONCLUSION
Conclusion

• Date pits are hard lignocellulosic materials with high carbon content and low impurities, and are excellent precursors for the production of activated carbons
• Langmuir-Freundlich (SIPS) isotherm is the best fit among the studied isotherms for both adsorbents and should be used for design purposes
• The total amount of adsorbent increases with increasing initial concentration of malachite green dye, higher removal rate, and with an increase in the dye solution volume
• The two-stage system resulted in a decrease of around 33% of the total adsorbent requirement compared to the one-stage system to remove the same amount of MG
• For a commercial treatment process, the economic comparison between the adsorbent saving versus the increased cost of the two-stage adsorber over the single-stage adsorber needs to be investigated
Thank You
Any Questions?