Application of Sewage Sludge Derived Hydrochar as an Adsorbent for Removal of Methylene Blue

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It is estimated that India would produce ~3955 thousand metric tonnes dry sewage sludge, annually (Singh et al., 2020).

SS generated during wastewater treatment is a huge management problem and responsible for 60% of the total wastewater treatment plant (WWTP) operational cost (Pilli et al., 2015).

Common sludge disposal techniques in India are landfiling of centrifuged SS and anaerobic digestion (AD).

Microbiological degradation of sludge to CH₄ and CO₂ by AD is a slow process and requires high retention time and larger digester volume (García-Cascallana et al., 2021).

Hydrothermal pretreatment (HPT) is an emerging process due to its potential for enhancing resources recovery options from the SS (Barber, 2016; Malhotra and Garg, 2019).

The hydrochar (HC), a hydrothermally carbonized product, has attracted significant attention in recent years due to its potential applications in various fields including agriculture, energy, and environmental remediation.

One of the simplest ways for HC recycling is in the form of adsorbent within the same or other WWTP.

In the present study, the HC samples recovered after HPTs (thermal hydrolysis and hydrothermal carbonization) of SS and centrifuged sewage sludge (CSS) were tested as an adsorbent.
Solids fraction of SS after thermal hydrolysis at 160°C for 0.5 h (HC_160_0.5) and 160°C for 1 h (HC_160_1). Solid fraction of CSS after HTC at 200°C for 3 h (HC_200_3) and modified HC_200_3 by 2M KOH (HC_200_3_KOH).
Methodology (2/2)

Detailed characterization of hydrochars

Methylene blue removal (Dose = 1 g/L, time = 24 h, pH = 3.24-7, Concentration = 50-500 mg/L, temp = 30°C, Shaker speed = 100 rpm)

Kinetic and thermodynamic studies

Hydrochar (a) HC_160_0.5, (b) HC_160_1, (c) HC_200_3, (d) HC_200_3_KOH
### Results and Discussion: Characterisations (1/6)

**Proximate and ultimate analysis of SS, CSS and HC samples**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>SS</th>
<th>CSS</th>
<th>HC_160_0.5</th>
<th>HC_160_1</th>
<th>HC_200_3</th>
<th>HC_200_3_KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (w/w)</td>
<td>2.1±0.01</td>
<td>10.5±1.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Volatile solids (w/w)</td>
<td>57.3±0.03</td>
<td>61±0.19</td>
<td>51.2±0.28</td>
<td>52.5±0.2</td>
<td>47.7±0.78</td>
<td>-</td>
</tr>
<tr>
<td>Fixed carbon (w/w)</td>
<td>3±0.3</td>
<td>4±0.8</td>
<td>5.2±0.09</td>
<td>5.4±0.13</td>
<td>5.2±0.15</td>
<td>-</td>
</tr>
<tr>
<td>Ultimate analysis on dry basis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (%)</td>
<td>26.7</td>
<td>32.1</td>
<td>26.2</td>
<td>28.1</td>
<td>28.6</td>
<td>24.5</td>
</tr>
<tr>
<td>H (%)</td>
<td>4.75</td>
<td>3.4</td>
<td>3.5</td>
<td>3.8</td>
<td>3.2</td>
<td>3.1</td>
</tr>
<tr>
<td>N (%)</td>
<td>1.95</td>
<td>5.6</td>
<td>2.57</td>
<td>2.99</td>
<td>1.86</td>
<td>1.68</td>
</tr>
<tr>
<td>O (%)</td>
<td>26.6</td>
<td>22.9</td>
<td>18.46</td>
<td>17.48</td>
<td>13.81</td>
<td>23.16</td>
</tr>
<tr>
<td>*Ash (w/w)</td>
<td>39.6</td>
<td>35.3±0.2</td>
<td>43.6±0.71</td>
<td>42±0.58</td>
<td>47±0.4</td>
<td>48±0.6</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>13.6</td>
<td>13.3</td>
<td></td>
<td>13.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Ash = 100 – (C+H+N+S+O)
Results and Discussion: Characterisations (2/6)

SEM images of sludge and HC samples: (a) SS, (b) HC_160_0.5, (c) HC_160_1, (d) CSS, (e) HC_200_3, and (f) HC_200_3_KOH

FTIR spectra of HC and chemically modified HC samples
Results and Discussion: Adsorption Studies (3/6)

**Effect of Contact Time**

(a. Adsorbent = HC_160_1, C₀ = 200 mg/L, adsorbent dose = 1 g/L, unadjusted pH = 3.24, shaker speed = 100 rpm and temperature = 30°C)

(b. C₀ = 200 mg/L, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

(c. pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

**Effect of Initial pH and MB concentration**

(b. Adsorbent = HC_160_0.5, HC_160_1, HC_200_3, HC_2003_KOH, Initial pH = 7, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

(c. pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)
### Results and Discussion: Adsorption Kinetics Studies (4/6)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>(q_{e, \text{ex}}) (mg/g)</th>
<th>(q_e) (mg/g)</th>
<th>(k_1) (h(^{-1}))</th>
<th>(R^2)</th>
<th>(q_e) (mg/g)</th>
<th>(k_2) (g*m(^{-1})*mg(^{-1})*h(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC_160_1</td>
<td>192.36</td>
<td>133.8</td>
<td>0.103</td>
<td>0.91</td>
<td>200</td>
<td>0.44</td>
<td>0.98</td>
</tr>
<tr>
<td>HC_160_0.5</td>
<td>190</td>
<td>134.3</td>
<td>0.122</td>
<td>0.94</td>
<td>200</td>
<td>0.47</td>
<td>0.99</td>
</tr>
<tr>
<td>HC_200_3</td>
<td>178</td>
<td>24.5</td>
<td>0.267</td>
<td>0.65</td>
<td>178.6</td>
<td>11.2</td>
<td>1</td>
</tr>
<tr>
<td>HC_200_3_KOH</td>
<td>194</td>
<td>22.2</td>
<td>0.193</td>
<td>0.46</td>
<td>192.3</td>
<td>13</td>
<td>1</td>
</tr>
</tbody>
</table>

(initial MB concentration = 200 mg/L, pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

- **Lagergern’s pseudo-first order model**
  \[ \log(q_e - q_t) = \log(q_e) - k_1 t \]

- **Lagergern’s pseudo-second order models**
  \[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} (t) \]

- \(q_{e, \text{ex}}\) = Experimental adsorption capacity (mg/g)
- \(q_e\) = Calculated adsorption capacity (mg/g)
- \(q_t\) = Amount of adsorbent adsorbed at time \(t\)
- \(k_1\) and \(k_2\) are pseudo first order and second order model rate constant
<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( q_{\text{max}} ) (mg/g)</th>
<th>( K_L ) (L/mg)</th>
<th>( R^2 )</th>
<th>( K_f )</th>
<th>n</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC_160_0.5</td>
<td>370</td>
<td>82</td>
<td>0.996</td>
<td>54</td>
<td>2.53</td>
<td>0.88</td>
</tr>
<tr>
<td>HC_160_1</td>
<td>370</td>
<td>84</td>
<td>0.998</td>
<td>53.9</td>
<td>2.5</td>
<td>0.83</td>
</tr>
<tr>
<td>HC_200_3</td>
<td>322</td>
<td>40</td>
<td>0.992</td>
<td>65.5</td>
<td>3.4</td>
<td>0.79</td>
</tr>
<tr>
<td>HC_200_3_KOH</td>
<td>454</td>
<td>95</td>
<td>0.981</td>
<td>66.2</td>
<td>2.3</td>
<td>0.75</td>
</tr>
</tbody>
</table>

(initial MB concentration = 200 mg/L, pH = 7, adsorbent dose = 1 g/L, reaction time = 24 h, shaker speed = 100 rpm and temperature = 30°C)

- **Langmuir isotherm**
  \[
  q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
  \]
- **Freundlich isotherm**
  \[
  q_e = k_f C_e^{1/n}
  \]

- \( q_e \) = equilibrium sorption concentration of solute per gram of adsorbent (mg/g)
- \( C_e \) = equilibrium concentration of solute (mg/L)
- \( q_{\text{max}} \) = maximum adsorption capacity (mg/g)
- \( K_L \) = Langmuir constant (L/mg)
- \( K_F \) and \( n \) = Freundlich constants
Results and Discussion: Adsorption Thermodynamic Studies (6/6)

Thermodynamic parameters for MB adsorption

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$\Delta G^\circ$ (kJ/mol)</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC_160_0.5</td>
<td>-11</td>
<td>7.7</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>-11.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-11.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC_160_1</td>
<td>-11.3</td>
<td>4.7</td>
<td>53.3</td>
</tr>
<tr>
<td></td>
<td>-11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-12.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC_200_3</td>
<td>-10.7</td>
<td>11</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>-11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC_200_3_KOH</td>
<td>-12.1</td>
<td>15.2</td>
<td>90.3</td>
</tr>
<tr>
<td></td>
<td>-13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-13.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Delta G^\circ = -$RT ln K

$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$

$\ln K = (\Delta S^\circ/R) - (\Delta H^\circ/RT)$

$\Delta G^\circ$ = Free energy change; $\Delta H^\circ$ = Heat of adsorption

$\Delta S^\circ$ = Entropy change; R = Universal gas constant (8.314 J/mol.K)

T = Temperature in kelvin; K = Equilibrium constant

Plot between equilibrium constant and temperature for MB on HC samples
Conclusions

- Hydrochar obtained from SS and CSS after HPT have MB removal efficiency of more than 90% and can be used for tertiary treatment of wastewater on the site itself.

- Langmuir isotherm and pseudo-second-order kinetic models provided the best fit with the experimental equilibrium and kinetic data, respectively.

- Thermodynamic analysis confirmed the feasibility of the adsorption process.

- The utilisation of waste derived adsorbent will reduce the requirement of activated carbon from natural sources and lessen environmental impacts.
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Department of Science and Technology (DST), New Delhi, India

ESED, Indian Institute of Technology (IIT) Bombay faculty and staff

SAIF, IIT Bombay

Solid and liquid waste research laboratory group


Thank You
The model is based on adsorption on heterogeneous surface and is a widely used isotherm. The Freundlich isotherm is derived by assuming that the sites on the adsorbent have different affinities for different adsorbates with each site. 

\[ q_e = k_f C_e^{1/n} \]

$q_e$ = equilibrium sorption concentration of solute per gram of adsorbent (mg/g)  
$C_e$ = equilibrium concentration of solute (mg/l)  
$K_F$ and $n$ = Freundlich constants  

$1/n e^{-qk C_e} = q_e$  
$q_e$ = equilibrium sorption concentration of solute per gram of adsorbent (mg/g)  
$C_e$ = equilibrium concentration of solute (mg/l)  
$K_F$ and $n$ = Freundlich constants

The Lagergren’s pseudo-first order model and pseudo-second order models.

\[ \log(q_e - q_t) = \log(q_e) - k_1 t \]

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} \]

$q_e$ and $q_t$ = amount of adsorbent adsorbed at equilibrium and at time $t$ (mg/g)  
$k_1$ and $k_2$ are pseudo first order and second order model rate constant, respectively.

\[ q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \]

Langmuir adsorption is valid for monolayer adsorption. The solid is assumed to have limited capacity ($q_{max}$). All the adsorption sites (i) are assumed to be identical, (ii) each site can retain one molecule of the given compound

$q_{max}$ = maximum adsorption capacity (mg/g)  
$K_L$ = Langmuir constant  
$C_e$ = equilibrium concentration (mg/l)

\[ \Delta G^0 = -RT \ln K \]

Where $R$ is the universal gas constant (8.314 J/(mol.K)), and $T$ is the temperature in Kelvin.  
$\Delta G^0$ is also related to the entropy change ($\Delta S^0$) and the heat of adsorption ($\Delta H^0$) according to the following equation 2.6.  
$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$

$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$