Adsorption of Phenol from Refinery Wastewater Using Rice Husk Activated Carbon


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Abstract: Industries such as petroleum refineries continuously generate large volumes of wastewater that contain high concentrations of phenol; therefore wastewater treatment as an integral part of their activities is required. The main objective of this paper is to demonstrate the applicability of rice husk activated carbon in an adsorption column for the treatment of phenolic refinery wastewater. Effects of bed depth (of the obtained rice husk activated carbon) and flow rate (of the waste water) on the sorption of phenol from the waste water were investigated. Column models such as Bed Depth Service Time, Thomas and Yoon Nelson models were employed to analyze the experimental data. The column adsorption experiment attained adsorption capacity of 28mg/g at breakthrough point of 0.5, flow rate of 4.5ml/min and bed depth of 7.5cm. The performance of the column adsorption was affected by bed depth and flow rate and models such as Thomas and Yoon Nelson could be employed in estimation of design parameters and scale-up operations during pilot or full scale application.

Key words: Rice husk • Adsorption model • Adsorption column • Refinery wastewater

INTRODUCTION

Adsorption is a process which involves a solid phase (sorbent material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solutions. The degree of sorbent affinity for the sorbate determines its distribution between the solid and the liquid phases [1].

The discharge of industrial wastewaters with high concentrations of chemical contaminants results in chemical hazards on the receiving environmental component [2]. These hazards include injury and damage to environmental resources among which are aesthetic nuisance, health disorder, damage to aquatic life and degradation of environmental resources [3-5]. Phenols are among the most common water pollutants that can cause hazards including health hazards which mostly results in death of living organisms including man. Processing industries such as petroleum refineries continuously generate large volumes of wastewaters that contain high concentration of phenols and other hydrocarbons. These phenolic compounds are among the main dominant group of compounds in refinery waste waters and this group has also been reported to be one of the difficult hydrocarbons to degrade biologically [6, 7]. The enhancement of the environmental friendliness and sustainability of the processing industries entails wastewater treatment to remove these phenolic compounds as an integral part of these processing activities of these plants. This will minimize the environmental damage from the discharge of the resulting wastewaters from the processing industries including the petroleum refineries. Ultimately, the cost of such treatment adds to the overall cost of production. From economic and environmental considerations, this necessitates the continuous search for simple, cleaner and cost-effective treatment option.
Most of the treatment methods for wastewaters are not without their drawbacks such as high capital and operational cost, regeneration cost and residue disposal [8-10]. Consequently, biosorption has been identified as one of the most efficient technique for the removal of wastewater contaminants because of the potential for low-cost adsorbent especially activated carbon from agricultural wastes [11-15]. Hence there is increased attention on utilization of agricultural wastes in adsorption processes [37]. More increasing demands for food production will lead to additional generation of agricultural wastes such as rice husk which increase additional challenge in solid waste disposal. For example, in an attempt to become self-sufficient in rice production, Nigeria has been on the path of boosting its rice production which will invariably lead to increased generation of rice husk (as solid waste) in the environment [16]. Undoubtedly, the fulfilment of increased rice production will generate additional environmental challenge in sustainable solid waste management of the resulting rice husk. There is little or no information on the application of rice husk derived activated carbon in the biosorption of phenolic components using column adsorption from refinery wastewaters. Therefore, the objective of this paper is to highlight the applicability of rice husk activated carbon in the biosorption of phenolic components from refinery wastewaters using a column adsorption arrangement.

**MATERIALS AND METHOD**

**Laboratory Materials/Reagents:** Furnace, ceramic flat surface, oven drier, de-ionized water, measuring cylinder, digital weighing balance, standard flask, conical flask, retort stand and clamp, micro filter, syringe, centrifuge, UV spectrophotometer, quartz cuvettes, glass column, glass wool, connecting pipe and valve, H₃PO₄, and phenol.

**Production of Activated Carbon:** The natural precursor used in the preparation of adsorbent is rice husk which was collected from National Cereal Research Institute, Badeggi. When collected from NCRI Rice Mill, rice husk was washed with distilled water to remove dirt and surface impurity, then oven-dried at 100°C for 24h [17]. In the thermal pretreatment, rice husk was placed on a ceramic flat surface, charged into a furnace and heated to a temperature of 441.46°C (optimum condition developed in preliminary studies) at a heating rate of 20-25°C/min and residence time of 1h. The charred residue was collected and cooled at room temperature. In the chemical pretreatment, the carbonized rice husk (charred residue) was activated with 1M H₃PO₄ for 3h at impregnation ratio of 2:1 (volume ml of acid/mass g of rice husk) and later oven-dried overnight at 200°C to ensure proper drying [18, 19]. The material was then removed from the oven, cooled for 2h and then washed with distilled water to bring the pH to 7.0 and again oven-dried overnight at 100°C [19].

**Column Experiment:** The optimum operating condition developed in our previous study was applied in the column experiment. That is rice husk activated carbon was produced at optimum temperature of 441.46°C and the optimum dosage of 4g was the basis for the establishment of the bed height/depth of 6cm. The column experiment was conducted using a glass column of 12cm length, 2cm internal diameter, 3.142cm² surface area and 37.7cm³ empty bed volume. The column was packed with a known quantity of rice husk activated carbon to yield the desired bed depth/height. Glass wool was placed at the bottom as a support and also at the top to prevent flotation of rice husk activated carbon in excess wastewater [20]. Process wastewater, which is the wastewater generated from various unit processes/operations, was collected from Kaduna Refinery and Petrochemical Company before treatment. Phenol composition of the process wastewater was analyzed and found to be 51.32mg/l. This initial concentration was used throughout the experiment. The wastewater was fed to the column in a downward flow mode through a pipe having a valve as the flow regulator. The effluent wastewater was collected from the column outlet at predetermined time interval for analysis of unadsorbed phenol concentration.

The effect of the following variables on the column performance was investigated:

- Bed depth: 7.5cm (5g), 6cm (4g), 4.5cm (3g); keeping the flow rate constant at 3ml/min
- Flow rate: 3ml/min, 4.5ml/min; keeping the bed depth constant at 6cm (4g).

**Breakthrough Curve:** The breakthrough curves for different bed depths and flow rates were generated by plotting \( \frac{C_t}{C_0} \) against \( t \). The breakthrough characteristics for each point were thereafter obtained from the curves.

**Breakthrough Capacity:** \( q_B \) Breakthrough capacity was determined using the equation [21]:

\[
q_B = \frac{t_B f C}{m}
\]
Volume of Effluent Treated $V_{eff}$: Volume of effluent treated was determined using the equation [22]:

$$V_{eff} = t_q f$$  \hspace{1cm} (2)

**Removal Efficiency:** Removal efficiency was determined using the equation [23-25]:

$$RE = \left(\frac{C_r - C_{eq}}{C_r}\right) \times 100$$ \hspace{1cm} (3)

where: $q_b =$ breakthrough adsorption capacity (mg/g), $V_{eff} =$ volume of effluent (L), $C_r$, $C_i =$ influent concentration of solute at breakthrough or time $t$ (mg/l), $t_q$, or $t =$ breakthrough time or time (min), $C_e =$ equilibrium concentration of solute (mg/l), $m =$ mass of activated carbon used (g), $RE =$ removal efficiency (%).

**Column Adsorption Models:** For the column adsorption study, the column models below were used to analyze the experimental data.

**Bed Depth Service Time (Adam Bohart) Model:** The Bed Depth Service Time (BDST) model equation given below was used by plotting service time $t$ against bed depth $z$. Model parameters were obtained from the slope and intercept of the plot [26, 27]:

$$t = aZ - b$$ \hspace{1cm} (4)

The equation above can be written as [26, 28]:

$$t = aZ - b$$ \hspace{1cm} (5)

where:

$$a = \text{slope} = \frac{N}{C_f C_e}, b = \text{intercept} = \frac{1}{C_f K_a} \ln \left(\frac{C_r}{C_{eq}} - 1\right)$$

**Thomas Model:** The Thomas model equation given below was used to analyze the column experimental data by plotting $\ln \left(\frac{C_i}{C_r} - 1\right)$ against $t$. Model parameters were obtained from the slope and intercept of the plot [29]:

$$\ln \left(\frac{C_i}{C_r} - 1\right) = \frac{K_{Th} q m}{f} - k_{Th} C_i t$$ \hspace{1cm} (6)

**Yoon Nelson Model:** The Yoon Nelson model equation given below was also used to analyze the column experimental data by plotting $\ln \left(\frac{C_i}{C_r} - 1\right)$ against $t$. Model parameters were obtained from the slope and intercept of the plot [9]:

$$\ln \left(\frac{C_i}{C_r} - 1\right) = k_{YN} t - k_{YN} \tau$$ \hspace{1cm} (7)

where: $K_r =$ adsorption rate constant (l/mg. min), $f =$ linear flow velocity to bed (m/min), $C_r =$ effluent concentration of solute at breakthrough (mg/l), $C_o =$ influent concentration of solute (mg/l), $N_r =$ adsorption capacity (mg/l), $Z =$ bed depth (m), $t =$ time (min), $K_{Th} =$ Thomas rate constant (l/(min mg)), $F =$ volumetric flow rate (l/min), $q_b =$ adsorption capacity (mg/g), $m =$ mass of the adsorbent (g), $K_{YN} =$ Yoon Nelson rate constant, $\tau =$ breakthrough time at 50% (min)

**RESULTS AND DISCUSSION**

**Column Adsorption Capacity and Removal Efficiency:** It was observed that as the column adsorption proceeds with time, the adsorption capacity increases while the removal efficiency decreases. This is because as the influent stream pass through the bed, more solute molecule are captured and retained by the activated carbon and this continuously increases the adsorption capacity until the bed becomes saturated. But as this continues with time, the amount of solute captured from the stream and retained by the activated carbon decreases and this result in an increase in the amount of solute concentration in the effluent stream, hence removal efficiency will be observed to be decreasing. It was deduced from Fig. 1 that at breakthrough point of 0.5, the bed attained adsorption capacity of 28mg/g.
Table 1: Break-through Characteristics

<table>
<thead>
<tr>
<th>Breakthrough points (b.p)</th>
<th>0.1</th>
<th></th>
<th>0.2</th>
<th></th>
<th>0.4</th>
<th></th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z (cm)</td>
<td>f (ml/min)</td>
<td>t_b (min)</td>
<td>V_w (ml)</td>
<td>q_e (mg/g)</td>
<td>t_b (min)</td>
<td>V_w (ml)</td>
<td>q_e (mg/g)</td>
</tr>
<tr>
<td>4.5</td>
<td>3</td>
<td>23</td>
<td>69</td>
<td>1.180</td>
<td>54</td>
<td>162</td>
<td>2.771</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>44</td>
<td>132</td>
<td>1.694</td>
<td>77</td>
<td>231</td>
<td>2.974</td>
</tr>
<tr>
<td>7.5</td>
<td>3</td>
<td>69</td>
<td>207</td>
<td>2.125</td>
<td>103</td>
<td>309</td>
<td>3.172</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>21</td>
<td>94.5</td>
<td>1.212</td>
<td>42</td>
<td>189</td>
<td>2.425</td>
</tr>
</tbody>
</table>

**Effect of Process Variables**

**Effect of Bed Depth:** From Fig. 2 it could be observed that the breakthrough time increases with increase in bed depth. This observation is similar to that of Zhang et al., [30]; Ji et al., [31] and it is probably due to increased surface area and availability of more binding sites for sorption as the bed depth increases [32]; thereby resulting in a broadened mass transfer zone. This means that as the bed depth is increased the length of the bed which the wastewater passes through also increases. Table 1 shows the breakthrough characteristics with respect to increase in bed depth. From the table also, at any breakthrough point, the corresponding breakthrough time, capacity and volume of wastewater treated increases with increase in bed depth. It can also be observed from the table that the larger the breakthrough time, the higher the breakthrough capacity of the column. This could be as a result of the fact that increase in bed depth provides the solute (phenol) molecule with more time to get adsorbed into the broadened mass transfer zone and this also result in treating more volume of effluent [22, 27]. Therefore, a decrease in the phenol composition of the effluent can be achieved in a column design approach by increasing the bed depth at the same time [27, 33]. Hence, higher bed depth favours better column performance.

**Effect of Flow Rate:** Fig. 3 shows that the breakthrough time decreases with increase in flow rate. This observation is in agreement with the trend reported by Zhang et al., [30] and Kundu et al., [34]. Table 1 also shows the breakthrough characteristics with respect to increase in flow rate. The table also shows that relative breakthrough time, capacity and volume of waste water at any breakthrough point decreases as the flow rate increases. This is because as the flow rate is increased, more volume of the wastewater is made to pass through the adsorption zone thereby providing insufficient residence time for the solute molecule to adequately transverse to the functional group–containing pores [22]. This leads to the exit of solute in the wastewater from the column before the establishment of equilibrium [35] and usually results in shorter breakthrough time and capacity. Hence, lower flow rate favours better column performance.
Table 2: Bed Depth Service Time (BDST) model parameters

<table>
<thead>
<tr>
<th>b.p</th>
<th>C/C₀ -1</th>
<th>ln(C/C₀ -1)</th>
<th>a</th>
<th>b</th>
<th>N₀ (mg/l)</th>
<th>K₀</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>9</td>
<td>2.197</td>
<td>15.333</td>
<td>46.667</td>
<td>751.122</td>
<td>0.000917</td>
<td>0.9975</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
<td>1.609</td>
<td>16.333</td>
<td>20</td>
<td>800.109</td>
<td>0.001568</td>
<td>0.9988</td>
</tr>
<tr>
<td>0.4</td>
<td>2.5</td>
<td>0.916</td>
<td>64.333</td>
<td>202</td>
<td>3151.498</td>
<td>8.84E-05</td>
<td>0.9717</td>
</tr>
</tbody>
</table>

Table 3: Yoon Nelson and Thomas model parameters

<table>
<thead>
<tr>
<th>Z (cm)</th>
<th>f (ml/min)</th>
<th>Kθθ</th>
<th>qₒ (mg/g)</th>
<th>qₒ-max (mg/g)</th>
<th>R²</th>
<th>KYN</th>
<th>τ (min)</th>
<th>tₒ-max (min)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>3</td>
<td>0.00055924</td>
<td>5.468</td>
<td>5.132</td>
<td>0.9916</td>
<td>0.0287</td>
<td>106.554</td>
<td>&gt;97</td>
<td>0.9916</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0.00034295</td>
<td>6.451</td>
<td>6.543</td>
<td>0.9725</td>
<td>0.0176</td>
<td>167.602</td>
<td>&gt;165</td>
<td>0.9725</td>
</tr>
<tr>
<td>7.5</td>
<td>3</td>
<td>0.00017732</td>
<td>9.554</td>
<td>8.930</td>
<td>0.9386</td>
<td>0.0091</td>
<td>310.275</td>
<td>&gt;290</td>
<td>0.9386</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>0.00040725</td>
<td>6.061</td>
<td>6.351</td>
<td>0.8422</td>
<td>0.0209</td>
<td>115.373</td>
<td>&gt;110</td>
<td>0.8422</td>
</tr>
</tbody>
</table>

Column Models: The Bed Depth Service Time (BDST) model parameters were obtained from Fig. 4 and are presented in Table 2. The large value of co-efficient of determination as observed in the table shows that the experimental data fit well in to the model. Therefore, BDST model could be employed in the adsorption of phenol onto rice husk activated carbon for the estimation of column design parameters such as bed depth and breakthrough time.

Thomas model parameters were obtained from the slope and intercept of Fig. 5 and are presented in Table 3. It was observed in the table that the theoretical breakthrough capacity (qₒ) increases as the bed depth increases and decreases as the flow rate increases.

This trend is in agreement with the earlier discussion on the effect of bed depth and flow rate on breakthrough capacity. Similar observation was reported by Han et al., [28]; Noreen et al., [36]. Hence, lower flow rate and higher bed depth favours better column performance. The table also shows that the theoretical breakthrough capacity obtained from Thomas model is close to the experimental breakthrough capacity indicating that Thomas model can be used to describe the column performance on the adsorption of phenol onto rice husk activated carbon.

Yoon Nelson model parameters were obtained from the slope and intercept of the plots in Fig. 6 and are presented in Table 3. The Table shows that the theoretical breakthrough time at 50% (τ) increases with increase in...
bed depth but decreases with increase in flow rate. This observation is in agreement with the earlier report on the effect of bed depth and flow rate on breakthrough time and similar trend was observed by Chowdhury et al., [9]. The 50% theoretical breakthrough time obtained from Yoon Nelson model could be said to be very close to the experimental value as in each case, it was observed to be slightly more than the 40% experimental breakthrough time.

CONCLUSIONS

The column experiment attained adsorption capacity of 28mg/g at breakthrough point of 0.5, flow rate of 4.5ml/min and bed depth of 7.5cm. As the column adsorption proceeds with time, it was observed that the adsorption capacity increases while the removal efficiency decreases. The performance of the column adsorption was significantly affected by bed depth and flow rate, thus improved column performance could be achieved by employing higher bed depth and/or lower flow rate. Analysis of the column experimental data indicates that models such as Thomas and Yoon Nelson can be employed in the estimation of design parameters and scale-up during pilot or full scale operations.

REFERENCES


