Removal of Methylene Blue Dye from Aqueous Solutions by Using Treated Animal Bone As A Cheap Natural Adsorbent

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Abstract - The adsorption behaviors of treated animal bone (TAB) with methylene blue dye (MBD) were studied. The aim of this study is to remove MBD from wastewater. A synthetic solution of 25 mg/L of the dye was used. The adsorption process was affected by contact time, doses of adsorbent, concentration of dye and temperature. It was carried out at constant pH (7.1). The optimum contact time was 90 min and 0.15 g was a suitable dose of adsorbent. Different concentrations of MBD ranging from 25 to 70 mg/L were used in the batch process. The uptake percentage, distribution coefficient (Kd), dimensionless separation factor (Rf) and maximum adsorption capacity (Qm) were calculated. 80% of MBD was removed by TAB at 25°C, reaching 90% at 55°C. The isothermal adsorption curves of MBD onto TAB indicate that the ratio matches Freundlich equation. The obtained results show that TAB is a suitable cheap adsorbent for the elimination of methylene blue dye from wastewater.

Keywords - Isothermal models, removal, methylene blue, treated animal bone.

I. INTRODUCTION

Many dyes are widely used in different industries, such as textile, paper, rubber, plastics, leather, food and pharmaceutical [1,2]. These industries release colored wastewater which may present an ecotoxic hazard and introduce the potential danger of bioaccumulation, which affect the human food chain. Wastewater containing small amounts of dyes can affect the aquatic life because of its toxicity and resistance to breakdown with time [3,4]. Most of the dyes are toxic and carcinogenic, causing allergy, skin irritation [5]. Chemical, physical and biological methods were used for removing dyes from wastewater. Adsorption is an effective and low-cost physical and chemical method for removing dyes from wastewater [6]. Natural adsorbents play an important role in removing dyes from wastewater, such adsorbents include, activated corn husk Carbon [7], Jute fiber [8], wheat shells [9], rice husk [10], bamboo dust [11], sugarcane [12], Zeolites [13-16], activated carbon from bituminous coal [17], pillared clays [18] and pine tree [19-20].

Animal bone plays an important role on the adsorption of dyes and heavy metals from wastewater. Basic dye rhodamine B was removed from aqueous solution by using animal bone meal [21]. Pb, Cd and Zn were removed from industrial wastewater by adsorption onto animal bone [22-24]. In this study, treated animal bone was used as a natural absorbent for methylene blue dye (MBD) from wastewater.

The effects of contact time, adsorbent doses, dye concentration and temperature were studied. Langmuir and Freundlich isotherms were used for analyzing the adsorption process.

II. EXPERIMENTAL

A. Materials and adsorption study :

The residual animal bone was collected from the butcher's. It was prepared by washed with tap water, and then burnt at 600°C, ground and then washed over night with distilled water. Finally, it was dried at 100°C and mechanically sieved to give suitable grain size used in the adsorption process (0.2 mm). The physical characteristics of (TAB) are surface area 907.7 m²/g, total pore volume 0.357 ml/g and average pore radius 7.86Å. Bone is mainly composed of tricalcium phosphate Ca₃(PO₄)₂. The chemical analysis of the bone refers to presence of (49.50%) Ca, (42.21%) P, (1.29%) Mg, (0.31%) Al, (0.69%) Na, (0.21%) Fe, (3.70%) Si, (0.05%) K, (0.02) Cu, (0.02) Sr and (0.22%) Cl. The infrared absorption spectra of (TAB) are given in figure (1). The plots in figure 1 show, an absorption peak at 3574 cm⁻¹ which is characteristics to intermolecular alcohol, an absorption peak at 2016cm⁻¹ which is characteristics to keterimines (X = Y = Z) and an absorption peak at 1460 cm⁻¹ which is characteristics to stretching carboxylate group (-CO₂⁻). It also show an absorption peaks at 1414 cm⁻¹,1051 cm⁻¹ and 963 cm⁻¹ which are characteristics to stretching carboxylate group (-C=O-O), primary oxygen single bond (-C-O-H) and trans-disubstituted vinyl group (C=C-H).
Figure 1: IR. Spectra Of Animal Bone Powder

Methylene blue dye (C.I. 52015) was supplied from Fluka and was used without purification. It is a cationic dye having the molecular formula C_{16}H_{18}N_{3}SCl, its chemical structure is shown in figure 2.

Figure 2: Structural Formula Of Methylene Blue Dye.

Solutions of (MBD) were prepared by dissolving the required quantity in distilled water. The volume prepared was 1L. The adsorption process of methylene blue by treated animal bone was carried out by using a batch contact adsorption method. The equilibrium was established at 90 min. A 0.15 g of adsorbent was mixed with 100 ml dye solution of appropriate concentration in 250 ml Erlenmeyer flasks. The flasks were then shaken at 150 rpm at a pre-settled temperature for 12 h in a shaker. Samples were filtered and the concentrations of MBD at equilibrium (C_e) were determined. The effect of contact time, adsorbent dose, concentration of dye and temperature were studied. The amount of MBD adsorbed per unit mass of adsorbent at equilibrium (uptake %) was calculated from equation (1): Uptake % = \left[ C_o - C_e \right] / C_o \times 100 \text{ } (1)

Where C_o and C_e are the initial and equilibrium concentrations of MBD in solution. The amount of equilibrium adsorption Q_e (mg/g) was calculated from equation (2):

\[ Q_e = \frac{C_o - C_e}{m} \times v \text{ } (2) \]

Where C_o and C_e are the initial and equilibrium concentrations of MBD in solution, V is the volume of the solution (ml) and m is the mass of the adsorbent (TAB). The distribution coefficient K_d was calculated from equation (3):

\[ K_d = \frac{\text{amount of dye in adsorbent} \times V}{\text{amount of dye in solution} \times m} \text{ } (3) \]

Where V is the volume of the solution (ml) and m is the weight of the adsorbent (g).

B. Analysis:

The concentration of MBD was analyzed by UV/vis. Spectrophotometer. A standard MBD solution was taken and the absorbance was determined at different wavelengths to obtain a plot representing the absorbance versus wave length. The wave length corresponding to maximum absorbance as obtained from this plot was 664 nm. Linear calibration curve between absorbance and concentration was obtained with MBD concentration in the range 10-70 mg/L (R^2 = 0.9917).

C. Instruments and apparatus:

UV/vis. spectrophotometer Unicam (Philips) PU 8670 was used for spectrophotometric measurements. The IR spectrometric measurements were applied by FTIR spectrophotometer Mattson, m 100 series Unicam, pH meter, Schottgreate, GmbH, D 6238, Hofheim, Germany was used and flask shaker, Gallen Kamp with timer, Cat. No. SGL 700-010V was used for samples shaking. The specific surface area of (TAB) was measured with a Micromeritics (ASAP- 2020 instrument, (Norcros, USA).

III. RESULTS AND DISCUSSION

A. Effect of adsorbent dose:

Doses of animal bone from 0.05 g to 0.30 g were used in studying this effect. 100 ml of 25 mg/L of dyes solution were used. The results in figure 3 show that, the uptake percentage of MBD increased with the increase of TAB dose up to 0.15 g. This was attributed to the increase the surface area of adsorbent from 0.05 g to 0.15 g, and availability of more adsorption sites. Therefore, 0.15 g of adsorbent and 100 ml dye solution were selected in these experiments.
B. Effect of contact time:

This factor plays an important role in the adsorption process. This experiment was carried out at variation of time of contact (0-150 minutes). Generally, high adsorption was obtained at the first hour and low adsorption was obtained later. Figure 4 shows the adsorption of MBD reaching the equilibrium in 90 minutes. The mechanism of adsorption process takes place in three steps, firstly, the molecules of dyes reach the boundary layer, then they diffuse to the surface of adsorbent and finally they diffuse to the porous structure of adsorbent. Therefore the adsorption process may be take a relatively long contact time [8].

C. Effect of MBD concentration on adsorption:

The adsorption of MBD onto TAB was affected by the dye concentration. Figure 5 shows that the uptake percentage of the dye decreased with the increase of dye concentration. That is because, at lower concentration, the ratio of the initial number of MBD molecules to the available surface area is low and the available sites are high. But at high concentrations of dye, the available sites are fewer [7]. Table I gives the equilibrium parameters of the adsorption process.

D. Effect of MBD concentration on distribution ratio (Kd):

Figure 6 shows that the distribution ratio (Kd) as a function of concentrations. The Kd values decrease with the increase in dye concentration.

E. Effect of temperature on dye adsorption:

The effect of temperature on the uptake % of MBD by using TAB was studied at (25-55°C) as shown in figure 7. This figure shows that the removal % of dye increases with the increase of temperature, where the maximum adsorption (90%) is achieved at 55°C. Increasing the temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer. It also increases the internal pores of the adsorbent particle [25].
TABLE I
Equilibrium Parameters Of The Adsorption Of MBD On Tab.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C_(e)/(Q_(m))</th>
<th>pH</th>
<th>55</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.04</td>
<td>73.9</td>
<td>66</td>
<td>60</td>
</tr>
<tr>
<td>35</td>
<td>0.13</td>
<td>72.6</td>
<td>58</td>
<td>51</td>
</tr>
<tr>
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<td>0.29</td>
<td>72.2</td>
<td>52</td>
<td>50</td>
</tr>
<tr>
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<td>0.45</td>
<td>71.4</td>
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<td>45</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Q_(max) (mg/g)</th>
<th>pH</th>
<th>55</th>
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</thead>
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<tr>
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<td>0.04</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C_(e) (mg/L)</th>
<th>pH</th>
<th>55</th>
<th>70</th>
</tr>
</thead>
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<tr>
<td>25</td>
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<td>73.9</td>
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<td>55</td>
<td>0.45</td>
<td>71.4</td>
<td>46</td>
<td>45</td>
</tr>
</tbody>
</table>

F. Adsorption isotherm:

The adsorption isotherm describes the mechanism of the adsorption process between the adsorbate molecules and the adsorbent. There are many isotherm equations. For this study, Langmuir and Freundlich isotherms were selected. The Langmuir isotherm assumes that the adsorption process is the formation of a homogenous monolayer of adsorbate on the outer surface of the adsorbent, and after that, no further adsorption takes place. The Langmuir linear equation [26] is expressed as equation (4).

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \rightarrow (4)
\]

Where \( C_e \) is the equilibrium concentration of dye in solution (mg/L), \( Q_e \) is the amount of dye adsorbed on the adsorbent at equilibrium (mg/g), \( Q_m \) is the monolayer adsorption capacity (mg/g) and \( b \) is the Langmuir constant (L/mg). \( Q_m \) and \( b \) were calculated from the slope and interception of the straight lines of the plot \( C_e/Q_e \) versus \( C_e \) [27]. Figure 8 shows the linear Langmuir isotherm for the adsorption of MBD on TAB. Table II gives the parameter constants of Langmuir and Freundlich isotherms.

Figure 8: Langmuir Isotherm For The Adsorption Of MBD Onto Tab.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( R^2 )</th>
<th>( Q_m )</th>
<th>b (mg/g)</th>
<th>( R^2 )</th>
<th>( K_L ) (L/mg)</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.9923</td>
<td>56.18</td>
<td>0.098</td>
<td>0.9953</td>
<td>10.13</td>
<td>2.20</td>
</tr>
<tr>
<td>35</td>
<td>0.9840</td>
<td>56.82</td>
<td>0.114</td>
<td>0.9944</td>
<td>11.39</td>
<td>2.38</td>
</tr>
<tr>
<td>45</td>
<td>0.9888</td>
<td>58.48</td>
<td>0.149</td>
<td>0.9817</td>
<td>13.82</td>
<td>2.69</td>
</tr>
<tr>
<td>55</td>
<td>0.9658</td>
<td>58.3</td>
<td>0.185</td>
<td>0.9766</td>
<td>14.99</td>
<td>2.77</td>
</tr>
</tbody>
</table>
From table II, the Langmuir maximum adsorption capacity \( Q_m \) are 56.18, 56.82, 58.48 and 58.82 (mg/g) at 25, 35, 45 and 55°C respectively. The obtained results from Langmuir isotherm indicate the endothermic nature process involved in the system. The essential characteristic based on the further analysis of Langmuir equation, can be expressed in terms of a dimensionless parameter of the equilibrium or adsorption intensity (\( R_L \)) and can be expressed by equation 5 [19].

\[ R_L = \frac{1}{1 + bC_o} \rightarrow (5) \]

Where \( C_o \) is the initial concentration of dye and \( b \) is the Langmuir constant. The value of \( R_L \) indicated the type of Langmuir isotherm, and to be irreversible (\( R_L = 0 \)), favorable (\( 0 < R_L < 1 \)), unfavorable (\( R_L > 1 \)) and linear (\( R_L = 1 \)). Table III shows the values of \( R_L \) at different temperatures. According to these values, the \( R_L \) values are in a range between 0 and 1, which indicates favorable adsorption process.

**TABLE III**

<table>
<thead>
<tr>
<th>MBD concentration (mg/L)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>25</td>
<td>0.20</td>
</tr>
<tr>
<td>40</td>
<td>0.20</td>
</tr>
<tr>
<td>55</td>
<td>0.10</td>
</tr>
<tr>
<td>70</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 9 shows comparison of \( R_L \) values of adsorption of MBD on TAB in four temperatures as shown in the figure, the \( R_L \) values decrease with the increase of temperature.

Freundlich isotherm is an empirical equation to describe heterogenous systems [28]. The linear form of Freundlich equation presented as follows:

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  

A plot of \( \log Q_e \) versus \( \log C_e \) enables to determine the constant \( K_f \) and \( n \). Where \( K_f \) and \( n \) are roughly an indication of the adsorption capacity of adsorbent and the adsorption intensity, respectively, \( n \) values were calculated from the slope of the straight line of Freundlich isotherm, where slope \( =1/n \) and \( K_f \) values were calculated also from the interception of the same straight line, where interception \( = \log K_f \).
IV. CONCLUSION

The present study indicated that:

1. TAB is a cheap effective adsorbent for the removal of MBD from the wastewater.
2. The uptake % of MBD increases with the increase of contact time, adsorbent dose and temperature, but it decreases with the increase of MBD concentration.
3. Adsorption behavior of TAB is described by Freundlich isotherm, and the results indicate multilayer type adsorption process involved in the system.
4. The Langmuir maximum adsorption capacity \( Q_m \) is 56.18, 56.82, 58.48 and 58.82 (mg/g) at 25, 35, 45 and 55°C respectively.
5. The \( R_p \) values indicate favorable adsorption process, therefore, TAB can be used for the removal of dyes from wastewater.
6. The results indicate that \( n > 1 \), therefore the adsorption process is physical.

REFERENCES


