REMOVAL OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION BY ADSORPTION USING LOW COST ADSORBENT OBTAINED FROM centella asiatica LEAVES

S.NIRMALA*, A.PASUPATHY**, M.RAJA***

Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu

Abstract—This work deals with the study of the removal of methylene blue dye from aqueous solution using low cost adsorbent obtained from the leaves of centella asiatica. Batch adsorption studies were carried out by observing the effects of various experimental parameters, such as effect of pH, adsorbent dose, dye concentration, contact time and temperature. The data were fitted into the Langmuir and Freundlich adsorption isotherm equations. Thermodynamic parameters like change in free energy, enthalpy and entropy were calculated. Results indicate that centella asiatica is a promising adsorbent for the removal of methylene blue from aqueous solution.

Index terms— Methylene blue, Isotherm models, Adsorbent, Thermodynamic Parameters.

I. INTRODUCTION

Industries such as leather, paper, plastics, textiles and rubber use lot of synthetic dyes in order to colour their products. As a result, the effluents discharged from these industries contain these dyes. Over 10^5 commercial available dyes exist and more than 7x10^5 tonnes are produced every year. As a result approximately 7x10^5 tonnes of dyes are released into the water bodies every year. The pollution caused by the discharge of untreated effluents from these industries is a major concern. The presence of colour in water is highly visible and undesirable as it reduces sunlight penetration into the water, thus affecting aquatic plants leading to a disturbance of the ecosystem. Once the dyes enter the water it is no longer good and sometimes difficult to treat as the dyes have a synthetic origin and a complex molecular structure, which makes them more stable and difficult to be biodegraded.

Generally biological aerobic wastewater systems are not successful for decolourization of majority of dyes. Therefore colour removal was extensively studied with various methods such as adsorption, coagulation, ultrafiltration, electro-chemical adsorption and photo oxidation. Among these adsorption is one of the effective methods for removing dyes from waste water. Granulated activated carbon (GAC) is commonly used for dye removal, but its high cost limits its use. Recently, numerous approaches have been made for the development of cheaper and effective adsorbents. Many low-cost adsorbents including natural and waste materials from industry and agriculture, have been employed by several workers. Some of these include Bagasse pith, Maize cob, Coconut shell, Chitosan, Peat, Biomass, Orange peel, Papaya seed, Tamarind fruit shell, Pumpkin seed hull. In the present study we utilized the adsorbent obtained from the leaves of centella asiatica for the removal of Methylene blue dye from the aqueous solution.

II. EXPERIMENTAL

Preparation of the adsorbate

Methylene blue dye (chemical formula C_{16}H_{18}ClN_{3}S, Molecular weight-373.91 and λ_{max} 664nm) was obtained from Merck, India. 1000 mg of Methylene blue was dissolved in one litre of double distilled water to get the stock solution. Desired concentration of the dye solution was obtained from the stock solution by dilution.

Preparation of adsorbent

Centella asiatica leaves was collected locally and washed with tap water several times to remove soil dust and finally washed with DD water. It was then dried in sun shade. The dried leaves were powdered and soaked in con.H_{2}SO_{4} (1:1, w/w), for a day, then filtered and dried. The charred mass was kept in a muffle furnace at 400°C for 1 hour, it was taken...
out, ground well to fine powder and stored in vacuum desiccators. The characteristics of the adsorbent is presented in the table-1

<table>
<thead>
<tr>
<th>Characteristics of the adsorbent</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.5</td>
</tr>
<tr>
<td>Moisture Content, %</td>
<td>13.5</td>
</tr>
<tr>
<td>Ash Content, %</td>
<td>10.2</td>
</tr>
<tr>
<td>Volatile Matter, %</td>
<td>21.3</td>
</tr>
<tr>
<td>Water Soluble matter, %</td>
<td>0.45</td>
</tr>
<tr>
<td>Acid Soluble Matter, %</td>
<td>0.89</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>48.1</td>
</tr>
<tr>
<td>Micropore volume cm$^3$/g</td>
<td>0.194194</td>
</tr>
<tr>
<td>Average pore width $\AA$</td>
<td>28.2065</td>
</tr>
<tr>
<td>BET Surface Area, m$^2$/g</td>
<td>604.27</td>
</tr>
</tbody>
</table>

Adsorption studies

Adsorption experiments were carried out in 250ml Erlenmeyer flasks. A known weight of *centella asiatica* adsorbent was added to 50ml of the dye solutions with an initial concentration of 10mg/l to 50mg/l. Flasks were shaken in an orbital shaker with a speed of 120 rpm at room temperature for 90min. The solution was then filtered at preset time intervals and the residual dye concentration was measured spectrophotometrically. The percentage of MB dye removal was calculated by using the following equation.

$$\% \text{ Dye Removal} = \frac{(C_0 - C_e)}{C_0} \times 100$$

Where $C_i = \text{initial concentration}(\text{mg/l})$, $C_e = \text{equilibrium concentration}(\text{mg/l})$.

The adsorption capacity $Q_e$ (mg/g), is obtained from the following equation.

$$q_e = (C_0 - C_e) \frac{V}{M}$$

Where, $Q_e = \text{adsorbent capacity}(\text{mg/g})$, $C_i = \text{initial MB concentration (mg/l)}$, $V = \text{volume of the solution(l)}$, $M = \text{mass of the adsorbent (g)}$.

III. RESULTS AND DISCUSSION

Effect of pH

The pH is an important controlling parameter in the adsorption process. The interaction between dye molecule and adsorbent is basically a combined result of the charges on dye molecules and the surface of the adsorbent$^{20}$. The influence of pH of the solution on the removal of the dye was studied with an initial dye concentration of 10mg/l, adsorbent dosage of 100mg, contact time 90min, temperature 303K and 120 rpm and varying the pH of the solution from 2 to 10. The pH of the working solution was controlled by adding 1NHCl or 1NNaOH solution. The results are presented in the fig-1. As the pH of the solution increased the percentage of the adsorption also increased and reaches the maximum at pH-6 and thereafter no appreciable change was observed. At low pH the dye is protonated and the surface of the adsorbent is positively charged which reduces the adsorption of the cationic form of the dye. In addition to that, the H$^+$ ions also compete with the dye for the available vacant sites of the adsorbent. With increase in the pH of the medium the positive charge on the adsorbent surface decreases which facilitates the adsorption of the dye molecules. Maximum adsorption was observed at pH -6. Hence the pH of the medium was maintained at 6 for further studies.

![Fig:1 Effect of pH on the adsorption of MB on to the adsorbent](image)

Effect of adsorbent dose

Effect of adsorbent dose on the removal of Methylene blue dye from aqueous solution was investigated by varying adsorbent dose from 25mg to 150mg for 10mg/l of dye concentration, keeping the other parameters constant, and the results are presented in the fig-2. As the adsorbent dose increases, the MB dye removal also increases and reaches the maximum at 100mg of adsorbent dosage thereafter there was no appreciable increase in the percentage of dye removal. Therefore the adsorbent dosage was maintained at 100mg for further studies. The increase in the dye removal with an increase in the adsorbent dosage can be attributed to increased carbon surface area and the availability of more adsorption sites. This is an agreement with already reported$^{21}$.

![Fig:2 Effect of adsorbent dose on the adsorption of MB on to the adsorbent](image)

Effect of dye concentration
The effect of initial dye concentration on the removal of MB dye is illustrated in fig-3. When the initial MB dye concentration increased from 10mg/l to 50mg/l, keeping the other parameters constant, the percentage removal of MB dye decreased from 83% to 46%. As the initial concentration is increased the ratio of the number of vacant sites on the adsorbent to the dye molecules decreases. This leads to a decrease in the percentage of adsorption of the dye.

**Effect of contact time**

The effect of contact time on the removal of the dye is shown in fig-4. It is observed that initially the percentage removal of dye increases rapidly and later increases in a slow and gradual manner till it reaches the equilibrium state. Maximum adsorption was found to be at 90min. This is because the initial stage is film diffusion which is very rapid followed by pore diffusion which is a slow process. Therefore, 90min shaking time was found to be appropriate for the maximum adsorption and was maintained in all subsequent experiments.

**IV. ADSORPTION ISOTHERMS**

**Langmuir Adsorption Isotherm**

In our study Langmuir and Freundlich isotherms were utilized to describe the adsorption of methylene blue on to the adsorbent. The Langmuir model assumes monolayer surface coverage, equal availability of adsorption sites and no interaction among the adsorbed dye molecules. The linear form of Langmuir equation is expressed as follows

\[
\frac{C_e}{Q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_0b}
\]

The values of \( Q_0 \) and \( b \) were calculated from the slope and intercept of the linear plots of \( C_e/Q_e \) verses \( C_e \). Langmuir adsorption isotherm is presented in fig-5. Higher value of correlation co-efficient (\( R^2=0.999 \)) indicates that the experimental data fits well with the Langmuir equation. The values of \( Q_0 \) and \( b \) are given in Table-2.

**Table-2. Langmuir constants**

<table>
<thead>
<tr>
<th>Q0(mg/g)</th>
<th>b</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5135</td>
<td>0.2710</td>
<td>0.999</td>
</tr>
</tbody>
</table>

The essential characteristics of the Langmuir adsorption isotherm is expressed by a dimensionless constant called separation factor. This value indicates whether the adsorption is favorable or not.

\( R_L \) is defined by the following equation

\[
R_L = 1/(1+bc)
\]

Where, \( R_L \) is dimensionless separation factor, \( C_i \) is initial concentration, \( b \) is Langmuir constant (L/mg), The parameter \( R_L \) indicates the type of the isotherm.

<table>
<thead>
<tr>
<th>Values of ( R_L )</th>
<th>Types of isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L &gt;1 )</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>( R_L = 1 )</td>
<td>Linear</td>
</tr>
<tr>
<td>( 0 &lt; R_L &lt; 1 )</td>
<td>Favourable</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

The \( R_L \) value obtained using the above equation for 10mg/l MB concentration is 0.2695. This \( R_L \) value lies between 0 and 1 indicating the favourability of the adsorption.
Freundlich Adsorption Isotherm

The Freundlich isotherm considers multilayer adsorption with interactions among the adsorbed molecules. The linear form of the Freundlich equation is as follows:

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

Where \( Q_e \), amount of dye adsorbed (mg/g), \( K_f \), (adsorption capacity) and \( n \), (adsorption intensity). By plotting \( \log Q_e \) Vs \( \log C_e \), the values of \( n \) and \( K_f \) were calculated from slope and intercept respectively (fig-6). The values of \( K_f \) and \( n \) are given in table-3. The value of linear regression co-efficient (\( R^2 \)) was found to be 0.963. This indicates that the adsorption process follows Langmuir adsorption isotherm more than Freundlich adsorption isotherm.

\[ \Delta G^0 = -RT \ln K_0 \]
\[ \log K_0 = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \]

Where \( C_i \) is the concentration of the dye at equilibrium and \( C_e \) is the amount of dye adsorbed on the adsorbent.

The values of \( \Delta G^0 \) (KJ/mol), \( \Delta H^0 \) (KJ/mol) and \( \Delta S^0 \) (J/K/mol) can be obtained from the slope and intercept of a linear plot of \( \log K_0 \) versus \( 1/T \) and are presented in table-4.

<table>
<thead>
<tr>
<th>Conc.of MG dye (mg/l)</th>
<th>-( \Delta G^0 ) (KJ/mol)</th>
<th>( \Delta H^0 ) (KJ/mol)</th>
<th>( \Delta S^0 ) (J/K/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.993</td>
<td>6.912</td>
<td>35.88</td>
</tr>
<tr>
<td>20</td>
<td>4.315</td>
<td>8.742</td>
<td>38.14</td>
</tr>
<tr>
<td>30</td>
<td>4.614</td>
<td>9.684</td>
<td>37.83</td>
</tr>
<tr>
<td>40</td>
<td>5.107</td>
<td>10.593</td>
<td>38.42</td>
</tr>
<tr>
<td>50</td>
<td>6.912</td>
<td>11.494</td>
<td>35.67</td>
</tr>
</tbody>
</table>

Table-4 Thermodynamic parameters for the adsorption of MB on to the adsorbent.

The negative values of \( \Delta G^0 \) indicates that the adsorption process is spontaneous and highly favorable . The positive values of \( \Delta S^0 \) indicates the increased randomness at the solid solution interface. The positive values of \( \Delta H^0 \) indicates that the adsorption process is endothermic and physical in nature.

VI. CONCLUSION

The adsorption of methylene blue from aqueous solution by the adsorbent obtained from \textit{Centella asiatica} was studied with various parameters like effect of pH, adsorbent dose, dye concentration, contact time and temperature. It was concluded that maximum adsorption of MB from aqueous solutions occurred at pH 6. The experimental data were correlated well by the Langmuir adsorption isotherm. The result of this study indicates that this adsorbent can be successfully utilized for the removal of MB from aqueous solution.

REFERENCES


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AUTHORS

First Author – S. Nirmala, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu.

Second Author – A. Pasupathy, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu

Third Author – M. Raja, Department of Chemistry, Urumu Dhanalakshmi College, Tiruchirappalli, Tamil Nadu