Thermodynamic and Kinetic Analysis on the Removal of METHYLENEBLUE Dye Using Senna Alata Bark

M. Chidambaran and S. Arivoli

Abstract – The feasibility of using Senna alata bark for the cationic dye (Methylene Blue) adsorption has been investigated. Batch adsorption studies were conducted to study the effects of contact time, initial concentration, pH and adsorbent dose on the removal of methylene blue (MB) at temperature of 30°C. The equilibrium data were analyzed by the Langmuir, the Freundlich. The data fitted well with the Langmuir model with a maximum adsorption. The pseudo-second-order kinetics was the best for the adsorption of MB by SAC with good correlation. The results demonstrated that the SAC is very effective to remove methylene blue from aqueous solutions.

Keywords – MB-Methylene Blue, SAC-Senna Alata Bark Carbon.

I. INTRODUCTION

The presence of dyes into streams and rivers constitutes a category of pollutants that cannot be neglected. For industrial liquid effluents, color is the first indication of water pollution. In the dyeing industry, ennobler discharge in the environment large volume of strongly colored effluents that are heavily loaded with pollutants and highly concentrated in salts. After reviewing the characteristics of these effluents, Hessel et al. [1] compare the current legislation on the dyeing industry emission. They examine more closely the discharge legislation, first in France and then in other countries around the world. Considering six of the most representative parameters (color, BOD5, COD, suspended solids, salinity, detergents and oil and grease) it was shown how different the applied constraints are in different countries. The industrial dumping of effluents containing dyes not only marks the natural aspect of the rivers but also perturbs the aquatic life interfering in the transmission of sunlight and thus reducing the action of photosynthesis because some azo dyes and their degradation products are highly toxic and even carcinogenic [2].

A convenient alternative for the classical treatment for the discoloration of wastewaters from the textile industry is the usage of some non-conventional adsorbents (natural materials, biosorbents and waste materials from industry and agriculture) with lower cost and high efficiency [3-6].

There exists an extensive research work in this field, systematized by Crini [3]. The review represents a critical analyses of these adsorbents with characteristics, advantages, limits and tendencies in their use, as well the possible mechanisms of sorption.

Our attention was focused on the Senna alata plant stem. This adsorbent obtained from the SA plants in and around Thiruvarur District, Tamilnadu, India.

II. EXPERIMENTAL METHOD

A. Preparation of Biosorbents:

Senna Alata used in this study was collected from the local Agriculture land of Thiruvarur, Tamilnadu, India. The raw biosorbent was cut into small sizes and then washed thoroughly with hot-distilled water followed by double-distilled water to remove any unwanted particles. It was then dried at 333 K in oven drier. The dried material was sieved to get uniform size particles <177µm (80mesh). The same SAC was used throughout the experiment.

B. Properties of Biosorbents:

Particle size analysis of the SA was carried out as per IS 2720 standard using standard sieves of different sizes. Scanning electron micrographs were obtained on a scanning electron microscope (Model Hitachi S-3000N) to understand the morphology of the original SAC. The particles were coated with gold using a sputter coater and the SEM images were then taken.

C. Preparation of Methylene Blue Solutions

Methylene blue used in this study was of commercial purity (C.I 52015; FW, 319.86; MF, C16H18N3SCl) and was used without further purification. Stock solution of methylene blue (500 mg L⁻¹) was prepared by dissolving the required quantity of the dye in double-distilled water.
Experimental dye solution was prepared by diluting the stock solution with suitable volume of double-distilled water to the desired concentration.

**D. Determination of Methylene Blue Contents in the Solutions**

The free dye content of the solution in the effluent before and after treatment was determined colorimetrically using UV-Vis spectrophotometer (Model Hitachi 2800). Standard calibration curve was prepared by recording the absorbance values of various concentrations of methylene blue dye at maximum absorbance of wavelength (663).

**E. Influence of Agitation Speed**

The biosorption capacity was determined at different agitator speeds ranging from 120 to 400 rpm using a fixed amount of SAC and methylene blue solution (20 mg L⁻¹) at 313 K in the incubator shaker, (Model Innova 42, New Brunswick Scientific, Canada). The initial and final concentrations of the solution were determined using UV-Vis spectrophotometer. Subsequently, adsorption capacities of the adsorbents were calculated based on the initial and final concentrations.

**F. Influence of pH**

Adsorption of dye on SAC was carried out through batch method. After loading the biosorbent, Acetic acid and sodium bicarbonate were added to adjust the initial pH of solution. The pH of the resulting mixture was determined by pH meter (model, EUTECH make digital microprocessor) for all the experiments. The pH meter was calibrated using different buffer solution (pH 4, 7, and 10 buffer tablets). 25 mg of SAC was added to 100 mL of 50 mg L⁻¹ concentrated dye solution in each of the 250mL Erlenmeyer flasks, and pH was maintained using acetic acid and sodium bicarbonate. The pH of the resulting solution was measured for all the experiments at the before and after adsorption experiments. pH of the solution were varied from pH 3 to 10. These 250-ML flasks were stirred in a digital incubator shaker at 120 rpm at a constant temperature (313 K), and samples were collected from the flasks at particular time interval. The collected samples solution was analyzed using UV-Vis spectrophotometer to determine the dye concentration.

**G. Batch Adsorption Experiment**

Table1. Equilibrium parameter for adsorption of METHYLENE BLUE on SAC

<table>
<thead>
<tr>
<th>M₀ (mg/L)</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>Qₑ(mg/g)</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
<th>Removed(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.419</td>
<td>1.73</td>
<td>1.14</td>
<td>0.78</td>
<td>95.1</td>
<td>96.5</td>
<td>97.7</td>
<td>98.4</td>
<td>95.1</td>
<td>96.5</td>
</tr>
<tr>
<td>100</td>
<td>17.75</td>
<td>14.8</td>
<td>10.92</td>
<td>8.11</td>
<td>164.4</td>
<td>170.7</td>
<td>178.1</td>
<td>183.7</td>
<td>82.2</td>
<td>85.1</td>
</tr>
<tr>
<td>150</td>
<td>40.69</td>
<td>34.2</td>
<td>27.98</td>
<td>22.49</td>
<td>218.6</td>
<td>231.5</td>
<td>244.0</td>
<td>255.0</td>
<td>72.8</td>
<td>77.1</td>
</tr>
<tr>
<td>200</td>
<td>78.35</td>
<td>70.1</td>
<td>61.50</td>
<td>52.93</td>
<td>243.2</td>
<td>259.7</td>
<td>276.9</td>
<td>294.1</td>
<td>60.8</td>
<td>64.9</td>
</tr>
<tr>
<td>250</td>
<td>109.9</td>
<td>99.5</td>
<td>89.09</td>
<td>79.61</td>
<td>280.0</td>
<td>300.8</td>
<td>321.8</td>
<td>340.7</td>
<td>56.0</td>
<td>60.1</td>
</tr>
</tbody>
</table>

C. Effect of solution pH on dye adsorption

The effect of solution pH on the equilibrium up-take capacity of SAC was studied at 50 mg/L initial dye concentration and temperature 30°C between pH value of 2 and 10. As shown in Fig. , the dye up-take was found to increase with an increase in pH. It increased from 15.5 to 98.4 mg/g for an increase in pH from 2 to 10. A consistent increase in adsorption capacity of the SAC was noticed as
the pH increased from 2 to 4, but further increase in pH from 4 to 9 seemed not affect the sorption in any wise. A similar trend was reported for the adsorption of MB onto wheat shells [29].

At lower pH as 2, the surface charge may be positively charged, thus making (H\(^+\)) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher pH the surface of SAC, may be negatively charged which enhance the positively charged dye cations through electrostatic force at attraction [30].

### D. Adsorption isotherms

In order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system, two common isotherm models were tested: the Langmuir and Freundlich models. The applicability of the isotherm equations was compared by judging the correlation coefficients, \( R^2 \).

The Langmuir adsorption [32] model is based on the assumption that maximum adsorption corresponds to saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can describe by:

\[
Ce = \left(\frac{1}{Q_b}b\right) + \left(\frac{1}{Q_b}\right)\frac{C_e}{C_e} ------- (1)
\]

Where \( Ce (\text{mg/L}) \) is the equilibrium concentration of the adsorbate, \( q_e (\text{mg/g}) \) is the amount of adsorbate per unit mass of adsorbent; \( Q_b \) and \( b \) is Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The linear plot of specific adsorption (\( C_e/q_e \)) against the equilibrium concentration (\( C_e \)) (Fig.9) shows that the adsorption obeys the Langmuir model.

The Langmuir constants \( Q_b \) and \( b \) were determined from the slope and intercept of the plot and are presented in Table 2. The \( R^2 \) values (0.998) suggest that the Langmuir isotherm provides a good fit to the isotherm data. A similar observation was reported for adsorption of MB on fly ash [33], pomelo (citrus grandis) [26], silk worm [34], cedar sawdust and crushed brick [35].

The Freundlich isotherm [23] is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy system and is expressed by the following equation:

\[
q_e = K_f C_e^{1/n} ------- (2)
\]

Where \( K_f (\text{mg/g(L/mg)}^{1/n}) \) is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. In general, as the \( K_f \) value increases the adsorption capacity of adsorbent for a given adsorbate increases. The magnitude of the exponent, 1/n gives an indication of the favorability of adsorption. Value n>1 represents favorable adsorption condition [24–27]. The linear form or Eq.(3) is:

\[
\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \------ (3)
\]

Values of \( K_f \) and n are calculated from the intercept and slope of the plot (Fig.) and are listed in Table 2. The value of Freundlich exponent n (2.97) is the range of n>1. indicating a favorable adsorption [28, 29, 30, 31].

The best equilibrium model was determined based on the linear square regression correlation coefficient \( R^2 \). From Table 2, it was observed that the equilibrium sorption data were very best represented by the Langmuir isotherm. The best fit isotherm expressions confirm the monolayer coverage process of MB onto SAC. A similar result was reported for adsorption of MB on adsorbents materials produce from sewage sludge [31–34].

### Table 3: Comparison of adsorption capacities of various adsorbents for MB

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( Q_b (\text{mg/g}) )</th>
<th>( T (\textdegree C) )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>352.26</td>
<td>600\degree C</td>
<td>This study</td>
</tr>
<tr>
<td>Orange peel</td>
<td>18.6</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>Rice husk</td>
<td>40.58</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Pineapple stem</td>
<td>119.05</td>
<td>30</td>
<td>00</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>88.29</td>
<td>26±1</td>
<td>29</td>
</tr>
<tr>
<td>treated</td>
<td>20.8</td>
<td>30</td>
<td>29</td>
</tr>
<tr>
<td>Parthenium(SWC)</td>
<td>16.56</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>Pathenium (PWC)</td>
<td>5.56</td>
<td>30</td>
<td>32</td>
</tr>
<tr>
<td>Wheat shells</td>
<td>0.0068</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>Raw Posidonia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oceanica fibres</td>
<td>142.36</td>
<td>20</td>
<td>36</td>
</tr>
<tr>
<td>Yellow passion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fruit peel</td>
<td>96.61</td>
<td>20</td>
<td>36</td>
</tr>
<tr>
<td>Cedar sawdust</td>
<td>102.04</td>
<td>30–50</td>
<td>43</td>
</tr>
<tr>
<td>Crushed brick</td>
<td>136.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste apricot-based</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>activated carbon</td>
<td>143.20</td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>Bamboo dust carbon</td>
<td>123.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dehydrated peanut</td>
<td>0.80</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>hull</td>
<td>0.24</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>Eggshell membrane</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 lists a comparison of maximum monolayer adsorption capacity of MB on various adsorbents. SAC is found to have a relatively large adsorption capacity of 352.26 mg/g and this indicates that it could be considered a promising material for the removal basic dye from aqueous solution, mostly when compared with waste apricot based activated carbon (102.04-136.92 mg/g) [35] and dehydrated peanut hull (123.5 mg/g) [36,37,38].

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor \( R_L \) [36] given by eq.(2)

\[
R_L = \frac{1}{1 + bC_0} \------ (4)
\]

Where \( C_0 (\text{mg/L}) \) is the highest initial concentration of adsorbent, and \( b (\text{L/mg}) \) is Langmuir constant. The
parameter $R_L$ indicates the nature of shape of the isotherm accordingly:

<table>
<thead>
<tr>
<th>$C_i$</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>50</td>
<td>0.1823</td>
</tr>
<tr>
<td>100</td>
<td>0.1003</td>
</tr>
<tr>
<td>150</td>
<td>0.0691</td>
</tr>
<tr>
<td>200</td>
<td>0.0527</td>
</tr>
<tr>
<td>250</td>
<td>0.0426</td>
</tr>
</tbody>
</table>

$R_L > 1$ - Unfavorable adsorption
$0 < R_L < 1$ - Favorable adsorption
$R_L = 1$ - Linear adsorption

The value of $R_L$ in the present investigation has been found to be 0.0426 at 30°C showing that the adsorption on MB on SAC is favorable at the temperature studied.

### E. Thermodynamic Treatment of the Adsorption Process

Thermodynamic parameters associated with the adsorption, via standard free energy change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$), and standard entropy change ($\Delta S^0$) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant $K_0$ is given by the equation:

$$\Delta G^0 = -RT \ln K_0 \quad \quad (5)$$

Where $\Delta G^0$ is the free energy of adsorption (kJ/mol), $T$ is the temperature in Kelvin and $R$ is the Universal gas constant (8.314 J mol$^{-1}$K$^{-1}$). The adsorption distribution coefficient $K_0$ for the sorption reaction was determined from the slope of the plot of ln(qe/Ce) against Ce at different temperatures and extrapolating to zero Ce according to the method suggested by Khan and Singh [16]. The adsorption distribution coefficient may be expressed in terms of enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$) as a function of temperature,

$$\ln K_0 = \left(\frac{\Delta H^0}{RT}\right) + \left(\frac{\Delta S^0}{R}\right) \quad \quad (6)$$

Where $\Delta H^0$ is the standard heat change of sorption (kJ/mol) and $\Delta S^0$ is standard entropy change (kJ/mol), the value of $\Delta H^0$ and $\Delta S^0$ can be obtained from the slope and intercept of plot of ln K$_0$ against 1/T. The values of thermodynamic parameter calculated from equations 5 and 6 are shown in Table. The thermodynamic treatment of the sorption data indicates that $\Delta G^0$ values were negative at all temperatures.

From the results it can be made out that physisorption is much more favorable for the adsorption of Methylene Blue. The positive values of $\Delta H^0$ show the endothermic nature of adsorption and they governs the possibility of physical adsorption for in the case of physical adsorption, while increasing the temperature of the system, the extent of MB adsorption increases, this rules out the possibility of chemisorptions. The low $\Delta H^0$ value depicts that MB is physisorbed on to the adsorbent SAC [17, 18, 19, 20].

### F. Adsorption Kinetics

Pseudo-first-order and second-order models were applied to test experimental data and thus elucidated the kinetic adsorption process. Lagergren proposed a method for adsorption analysis which is the pseudo-first-order kinetic equation of Lagergren [36] in the form:

$$\log\left(\frac{q_e - q_t}{q_e}\right) = \log q_e - (k_1/2.303) t \quad \quad (7)$$

Where $k_1$ (1/min), is the rate constant, $q_e$ (mg/g) is the amount of solute adsorbed on the surface at equilibrium and $q_t$ (mg/g) is the amount of solute adsorbed at any time. The value of $k_1$ for MB adsorption by SAC was determined from the plot of log(qe-qt) against t. Comparison of the pseudo-first-order adsorption rate constant and calculated and experimental $q_e$ value obtained at different initial MB concentrations.

Although the correlation coefficients ($r^2$) are generally greater than 0.858 for all initial concentrations under the limit of the experimental qe for the pseudo-second-order kinetic model. As such the adsorption of MB on SAC cannot be best described by the pseudo-second-order kinetic. In many cases the second-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [37]. Therefore, the pseudo-second-order kinetic model [38] as shown in eq.(6) was used to study the adsorption kinetic of the present system.

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>$\Delta G$</th>
<th>$\Delta S$</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
<td>50°C</td>
</tr>
<tr>
<td>50</td>
<td>-7504.4</td>
<td>-8658.6</td>
<td>-10078.5</td>
</tr>
<tr>
<td>100</td>
<td>-3861.7</td>
<td>-4545.2</td>
<td>5634.2</td>
</tr>
<tr>
<td>150</td>
<td>-2488.8</td>
<td>-3172.4</td>
<td>-3953.7</td>
</tr>
<tr>
<td>200</td>
<td>-1107.9</td>
<td>-1602.9</td>
<td>-2179.8</td>
</tr>
<tr>
<td>250</td>
<td>-609.4</td>
<td>-1074.5</td>
<td>-1587.3</td>
</tr>
</tbody>
</table>

Table 5: Thermodynamic parameter for the adsorption of METHYLENE BLUE on SAC

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>Pseudo second order</th>
<th>Elovich model</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_e$</td>
<td>$K_2$</td>
<td>$r^2$</td>
</tr>
<tr>
<td>50</td>
<td>95.16</td>
<td>0.044</td>
<td>0.9940</td>
</tr>
<tr>
<td>40</td>
<td>96.54</td>
<td>0.050</td>
<td>0.9953</td>
</tr>
</tbody>
</table>
gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [41]. The plots were not linear over the whole time range, implying that more than one process affected the adsorption.

**IV. CONCLUSION**

The adsorption of MB from aqueous solution using SAC as low-cost adsorbent was investigated under different experimental conditions in batch process. The Langmuir adsorption isotherm was found to have the best fit to the experimental data with maximum adsorption capacity of 352.26 mg/g. The adsorption kinetics can be predicted by pseudo-second-order kinetic. The results of the present investigation indicated that SAC, a low-cost adsorbent could be employed as an alternative to commercial-activated carbon for the removal of MB from aqueous solutions.
Fig. 5a FT-IR spectra for raw Senna Alata Carbon

Fig. 5b FT-IR spectra for the adsorption of Methyleneblue by SAC

Fig. 6. Effect of adsorbent dose on the removal of Methyleneblue 50mg/L: Contact time=60 min; pH=6.5; Temp=30\(^\circ\)C

Fig. 7. Effect of contact time on the removal of Methylene Blue 50 mg/L: adsorbent dose=50mg/50ml; pH=6.5; Temp=30\(^\circ\)C

Fig. 8. Effect initial pH on the removal of Methylene Blue 50 mg/L: Contact time=60 min; Adsorbent dose=50 mg/50 ml

Fig. 9. Linear Langmuir for the adsorption of Methyleneblue
Fig.10. Linear Freundlich isotherm for the adsorption of Methylene Blue by SAC

REFERENCES


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