Adsorption of methylene blue on sawdust-derived biochar and its adsorption isotherms

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ABSTRACT

The adsorption of methylene blue (MB) onto sawdust biochar and biochar was formed by pyrolyzing of sawdust of the rubber wood (Heveabrasilensis). The experimental equilibrium data were analyzed using the isotherms of Langmuir, Freundlich, Tempkin. The Langmuir isotherm shows the maximum value of adsorption capacity was 333.33 mg/g and the correlation coefficient ($R^2$) was 0.999. Sawdust biochar is a fast and effective adsorbent for removing MB from aqueous solutions.

Keywords: Adsorption isotherms, Sawdust biochar, Methylene blue

1. Introduction

Azo dyes are important colorants having extensive application in the leather, textile, paper mill, additive, foodstuff, and cosmetic industries. However, approximately (10 to 15) % of the overall production of azo dyes is released into the environment, which is very dangerous because some of the azo dyes and their degradation products have a toxic, carcinogenic, or mutagenic influence on living organisms (Chen et al., 2010).
Dyes are colour organic compounds which can colorize other substances. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies (Crini, 2006).

Dyes are widely used in industries such as the textile, paper, pulp mill, leather, dye synthesis, printing, food, and plastics industries. Since many of the organic dyestuffs are harmful to human beings and toxic to microorganisms, removal of dyestuffs from wastewater has received considerable attention over the past decades (Weng and Pan, 2007; Bhattacharyya and Sharma, 2005). Most of these dyes pose acute problems for the ecological system, as they are toxic and have carcinogenic properties, which make the water contaminated with dyes inhibitory to aquatic life. Textile industries produce significant amounts of wastewater containing dyes. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the fabric dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity (El-Qada et al., 2006).

Many types of dyes, such as direct, reactive, acid, and basic dyes, are used in the textile industry (El-Qada et al., 2006). With industrialization, the discharge of industrial wastewater has increased. At the same time, there are environmental concerns, and there is the need to find cheap and efficient methods for the treatment of industrial wastewater prior to disposal into natural waters (Gurses et al., 2006; Wang et al., 2005). The most efficient method for the removal of dyes from aqueous effluents is the adsorption process [8]. Various adsorbents, such as activated bituminous coal (El-Qada et al., 2006), clay (Gurses et al., 2006), neem (Azadirachta indica) leaf powder (Bhattacharyya and Sharma, 2005), jute fiber carbon (Senthilkumar et al., 2005), Abu-Tartour phosphate rock (Malash and El-Khaiary, 2010), black stone cherries (Arana and Mazzoco, 2010), Jordanian diatomite (Al-Ghouti et al., 2009), hazelnut shell (Dogan et al., 2009), spent activated clay (Crini, 2006), bamboo activated carbon (Hameed et al., 2007), coir pith carbon (Kaavitha and Namasiyayam, 2007), Egyptian rice hull (El-Halwany, 2010), vetiver root activated carbon (Altenor et al., 2009), rattan sawdust (Hameed et al., 2007), activated carbon from oil palm wood (Ahmad et al., 2007), garlic peel (Hameed et al., 2009), and montmorillonite clay (Almeida et al., 2009) have been studied for adsorption of methylene blue from aqueous solutions. Among the adsorbents mentioned, the activated carbons (ACs) have the highest dye removal efficiency due to their large surface area and the functional groups on their surface that facilitate interactions with various dyes. Methylene blue (MB) is the cationic dye that is most commonly used for coloring. It is generally used for dyeing cotton, wool, and silk. MB can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea (Senthilkumaran et al., 2005). This dye has been studied because of its known strong adsorption onto solids, and it often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions (Hameed et al., 2007). Previous studies described the preparation, characterization, and optimization based on response surface methodology (Vargas et al., 2011; Vargas et al., 2010), of microporous activated carbon produced from flamboyant pods (Delonix regia). The objective of this work was to study the removal of MB from aqueous solutions using this sawdust-derived biochar under optimized conditions. In
order to establish the removal capacity of this adsorbent, different models of isotherms were fitted to the experimental data. Finally, some possible mechanisms of adsorption are discussed.

2. Materials and methods

2.1 Adsorbent

The biochar sample (SDB) used in this study was obtained by pyrolyzing sawdust of the rubber wood (Heveabrasilensis). It was obtained from a local furniture manufacture (Selangor, Malaysia).

2.2 Adsorbate

The cationic dye, methylene blue (MB) (B. Herzog, Germany), was used as an adsorbate in this work. It has the molecular formula $C_{16}H_{18}N_{3}SCl$ and the molecular weight of 319.85 g mol$^{-1}$. The chemical structure of MB is shown in Fig. 1.

![Chemical Structure of Methylene Blue.](image)

2.3 Batch adsorption study

A stock solution of 1.0 g L$^{-1}$ was prepared by dissolving the appropriate amount of MB in 100 mL and completing to 1000 mL with distilled water. Batch adsorption was performed in a set of 50 mL plastic flasks containing 25 mL of MB solutions with various initial concentrations (100–1000 mg L$^{-1}$). The amount of 0.2019 g of SDB was added to each flask and kept at 30°C on a shaker. For equilibrium studies, the experiment was carried out for 2.4 h to ensure equilibrium was reached. All samples were filtered prior to analysis (using 0.45 µm membrane filters) in order to minimize interference of small particles of the activated carbon.

The MB concentration was determined by comparing absorbance to a calibration curve previously obtained. All experiments were duplicated and only the mean values were reported.

The amount of MB adsorbed onto SDB, $q_e$ (mg/g) was calculated by Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{M}$$
Where $C_o$ and $C_e$ (mg/L) are the initial and equilibrium liquid phase concentrations of MB, respectively, $V$ (L) is the volume of the solution, and $W$ (g) is the mass of dry adsorbent used. For batch kinetic studies, the same procedure was followed, but the aqueous samples were taken at preset time intervals. The concentrations of MB were similarly measured. The amount of MB adsorbed at anytime, $q_t$ (mg/g), was calculated by Eq. (2):

$$q_t = \frac{(C_o - C_t)V}{M}$$

Where $C_t$ (mg/L) is the liquid-phase concentration of MB at any time. Initial concentrations of 120, 300 and 430 mg/L of the dye for different time intervals (10, 20, 40, 80, 160, 220 and 1440 min) at 30 °C studied. The dye removal percentage can be calculated by Eq. (3)

$$\%C = \frac{(C_o - C_e)}{C_o} \times 100$$

Where $C_o$ and $C_e$ (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

3. Adsorption isotherm

The application of adsorption isotherms is very useful to describe the interaction between the adsorbate and the adsorbent of any system. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the adsorbent. There are several equations for analyzing experimental adsorption equilibrium data, being that the most accepted surface adsorption models for single solute systems are the Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906) and Temkin (Temkin and Pyzhev, 1940) models. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters (Hamdaoui, 2006; Kannan and Sundaram, 2001; Basar, 2006; Senthilkumaar et al., 2005; Royer et al., 2009).

The adsorption isotherm is representing the relationship between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of adsorbate (Lata et al., 2007), where the values of isotherm yields constants can express the properties of the surface and affinity of the sorbent (Ofomaja and Ho, 2007). The isotherm results were analyzed using three forms of Langmuir, Freundlich and Temkin isotherm.
3.1 Langmuir isotherm

The Langmuir isotherm model (Langmuir, 1918) assumes that the adsorption occur at homogeneous sites at adsorbent surface, and saturation happen when the dye molecule fill the site where no more adsorption can occur at that site. Langmuir isotherm can represent by the following equation:

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

(4)

Where, \(q_e\) is the Amount of adsorbate adsorbed at equilibrium (mg/g), \(q_{\text{max}}\) is the Maximum monolayer adsorption capacity of the adsorbent (mg/g), \(C_e\) is the Equilibrium concentration of adsorbate (mg/L) and \(K_L\) is the Langmuir adsorption constant related to the free energy adsorption (L/mg).

Since the estimation of the adsorption isotherms parameters interference by the method of linearization (Hamdaoui, 2006), therefore three forms of Langmuir isotherm equations used to determine the constants \(K_L\) and \(q_{\text{max}}\). Equation 4 can be linearized in to these three forms of Langmuir isotherm equations (Hamdaoui and Naffrechoux, 2007):

Form (1)

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

(5)

Form (2)

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

(6)

Form (3)

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

(7)

The constants values can be evaluated from the intercept and the slop of the linear plot of experimental data of \((C_e/q_e)\) versus \(C_e\) or \((1/q_e)\) versus \((1/ C_e)\) or \(q_e\) versus \((q_e / C_e)\). The essential feature of the Langmuir isotherm can be expressed by the separation factor \(R_L\), and can be calculated using the following equation:

\[
R_L = \frac{1}{1 + K_L C_o}
\]  

(8)
where, $K_L$ = Langmuir adsorption constant related to the free energy adsorption (L/mg), $C_o$ is the highest initial adsorbate concentration (mg/L). The value of separation factor $R_L$ indicates the adsorption process as given: Unfavorable ($R_L>1$), Linear ($R_L =1$), Favourable ($0< R_L<1$), Irreversible ($R_L = 0$)

### 3.2 Freundlich isotherm

The Freundlich isotherm can be used for adsorption that involves heterogeneous surface energy systems (Al-Ghouti et al., 2009), where the adsorption not involved homogeneous site energies and there are no limited levels of sorption (Aksu, 2005). The Freundlich model (Freundlich, 1906) equation is expressed as:

$$q_e = K_F C_e^{1/n}$$ (9)

Where $K_F$ and $n$ are Freundlich constants. $K_F$ (mg/g (L/mg)^{1/n}) is the adsorption capacity of the sorbent and $n$ giving an indication of how favourable the adsorption process. If the value of exponent $n$ was greater than 1 ($n>1$) then the adsorption represent favourable adsorption condition (Namasivayam et al., 1994).

The constants $K_F$ and $n$, can be determined from the linear form of Freundlich isotherm equation from the graph of ln$q_e$ against ln$C_e$ as expressed from the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$ (10)

In general, as the $K_F$ value increases the adsorption capacity of adsorbent will also increase (Al-Ghouti et al., 2009).

### 3.3 Temkin isotherm

Temkin and Pyzhev (1940) studied the heat of adsorption and the adsorbate-adsorbent interaction on adsorption isotherms, where they assumed that because of the adsorbate-adsorbent interactions, the energy of the molecules adsorption will decrease linearly with coverage (Sekar et al., 2004).

The Temkin isotherm (Temkin and Pyzher, 1940) has been generally applied in the following form:

$$q_e = \left(\frac{RT}{b_t}\right) \ln(A_t C_e)$$ (11)

The linear form is shown as:

$$q_e = B \ln A_t + B\ln C_e$$ (12)
Where $B = RT/b_t$. $B$ is the Temkin constant related to heat of sorption (J/mol); $A_t$ is the Temkin isotherm constant (L/g), $R$ the gas constant (8.314 J/mol K) and $T$ the absolute temperature (K). Therefore, by plotting $q_e$ versus $\ln C_e$ enables one to determine the constants $A_t$ and $B$.

4. Results and discussion

4.1 Effect of initial concentration of dye

To study the effect of the initial concentration of MB on the rate of dye adsorption onto sawdust biochar, the experiments were carried out at a fixed adsorbent dose (0.2019 g) and at different initial dye concentrations of methylene blue (120, 300 and 430 mg/L) for different time intervals (10, 20, 40, 80, 160, 220 and 1440 min) at 30 °C as shown in Fig. 2. The amount of MB adsorbed increase with the increase in the initial MB concentration. For MB dye adsorption onto SDB at 30°C it was observed that the amount of MB adsorbed increased from 106.423 mg/g to 283.447 mg/g with increasing dye concentration from 120 to 430 mg/L. The initial MB concentration provides an important driving force to overcome all mass transfer resistance. Hence a higher initial concentration of dye will enhance the adsorption process. Fig. 3 shows that the percentage removal of MB adsorbed decreased from 99.308 to 74.696 % as the initial concentration was increased from 120 to 430 mg/L. This may be due to the saturation of the adsorption sites at higher MB concentrations (Ozer et al., 2007).

Fig. 2 Effect of initial dye concentration and contact time on MB uptake at 30 °C
4.2 Isotherm data analysis

Equilibrium isotherm for the sorption of methylene blue dye is shown in Fig. 4-6. The values of the maximum adsorption amount ($Q_o$), correlation coefficient ($R^2$), and the other parameters for all the isotherms are shown in Table 1. The Langmuir isotherm assumes that adsorption occurs on a homogeneous surface containing sites with equal energy and that are equally available for adsorption. This is valid for the complete monolayer of adsorption, on which there is no transmigration of adsorbate on the surface plane. The $Q_o$ value of 333.33 mg/g obtained for this isotherm and the value of $R^2$ of 0.999 shows good fitting of this isotherm to the experimental data (Fig. 4a).

The Freundlich isotherm is an empirical equation that can be used for heterogeneous systems with interaction between the molecules adsorbed. The $n$ parameter, known as the heterogeneity factor, can be used to indicate whether the adsorption is linear ($n = 1$), whether it is a chemical process ($n < 1$), or whether a physical process is favourable ($n > 1$). On the other hand, the values of $1/n < 1$ and $1/n > 1$ indicate a normal Langmuir isotherm and cooperative adsorption, respectively. The values of $n = 4.807$ and $1/n = 0.208$ indicate that the physical process and the normal Langmuir isotherm are favourable. The fitting of the Freundlich isotherm to the experimental data ($R^2 = 0.950$) is shown in Fig. 5. Like the Freundlich isotherm, the Tempkin isotherm considers the interactions between adsorbates assuming that the adsorption heat of all molecules decreases linearly when the layer is covered and that the adsorption has a maximum energy distribution of uniform bond. The constant $A_T$ is related to the heat of adsorption, and the positive value found ($A_T = 37.250$) indicates an exothermic process. The fit to experimental data ($R^2 = 0.978$) in Fig. 6 shows that the Tempkin isotherm is less adequate to explain the adsorption of MB onto SDB, as compared to the Langmuir and Freundlich isotherms. Based on Table 2, it could be seen that the adsorption capacity obtained
for the adsorption of MB onto sawdust biochar is good compared with other reported values. The absorption capacity of saw dust biochar is very high which indicate that it is a good adsorbent for removal of MB from the solution.

Figure 4 (a)

\[ y = 0.0035x + 0.0084 \]
\[ R^2 = 0.9997 \]

Figure 4 (b)

\[ y = 0.0049x + 0.0037 \]
\[ R^2 = 0.9962 \]
Fig. 4 Langmiur isotherm plots (a): form 1, (b): form 2 and (c): form 3 at 30 °C

Fig. 5 Linearized Freundlich isotherm plot
Fig. 6 Tempkin isotherm plot

\[ y = 37.251x + 117.99 \]
\[ R^2 = 0.9786 \]
Table 1 Three forms of Langmuir, Freundlich and Temkin models constants and correlation coefficients for sorption of MB onto sawdust biochar at 30°C

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir form-1-</td>
<td>$Q_o$ (mg/g)</td>
<td>333.333</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.375</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.006</td>
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<tr>
<td>Langmuir form-2-</td>
<td>$Q_o$ (mg/g)</td>
<td>333.333</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.750</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.003</td>
</tr>
<tr>
<td>Langmuir form-3-</td>
<td>$Q_o$ (mg/g)</td>
<td>273.6</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.737</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.003</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>115.469</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>4.807</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.950</td>
</tr>
<tr>
<td>Temkin</td>
<td>$A_t$ (LJ/g)</td>
<td>37.250</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>23.691</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.978</td>
</tr>
</tbody>
</table>
Table 2 Comparison of the maximum adsorption capacities of various adsorbents for MB dye

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>Temp. °C</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sawdust biochar</td>
<td>MB</td>
<td>30</td>
<td>333.333</td>
<td>This work</td>
</tr>
<tr>
<td>Coconut shell carbon</td>
<td>MB</td>
<td>30</td>
<td>277.900</td>
<td>(Kannan and Sundaram, 2001)</td>
</tr>
<tr>
<td>waste apricot activated carbon</td>
<td>MB</td>
<td>30</td>
<td>102.04</td>
<td>(Basar, 2006)</td>
</tr>
<tr>
<td>jute fiber carbon</td>
<td>MB</td>
<td>28</td>
<td>225.64</td>
<td>(Senthilkumaar et al., 2005)</td>
</tr>
<tr>
<td>oil palm fibre activated carbon</td>
<td>MB</td>
<td>30</td>
<td>277.78</td>
<td>(Tan et al., 2007)</td>
</tr>
<tr>
<td>Sun flower oil cake activated carbons</td>
<td>MB</td>
<td>25</td>
<td>10.21</td>
<td>(Karagoz et al., 2008)</td>
</tr>
<tr>
<td>bamboo-based activated carbon</td>
<td>MB</td>
<td>25</td>
<td>183.3</td>
<td>(Liu et al., 2010)</td>
</tr>
<tr>
<td>oil palm wood activated carbon</td>
<td>MB</td>
<td>30</td>
<td>90.9</td>
<td>(Ahmad et al., 2007)</td>
</tr>
<tr>
<td>walnut shells activated carbons</td>
<td>MB</td>
<td>25</td>
<td>355.5</td>
<td>(Yang and Qiu, 2010)</td>
</tr>
<tr>
<td>coir pith carbon</td>
<td>MB</td>
<td>35</td>
<td>5.87</td>
<td>(Kavitha and Namasivayam, 2007)</td>
</tr>
<tr>
<td>Activated coffee grounds Carbons</td>
<td>MB</td>
<td>25</td>
<td>181.8</td>
<td>(Reffas et al., 2010)</td>
</tr>
<tr>
<td>Carbonized Brazilian pine-fruit shell</td>
<td>MB</td>
<td>25</td>
<td>413</td>
<td>(Royer et al., 2009)</td>
</tr>
<tr>
<td>impregnated Euphorbiari gida activated carbon</td>
<td>MB</td>
<td>20-40</td>
<td>114.45</td>
<td>(Gercel et al., 2007)</td>
</tr>
</tbody>
</table>
5. Conclusion

The results of present investigation show that sawdust has very high adsorption capacity with regard to the removal of methylene blue from its aqueous solution. The experimental equilibrium data obtained were applied to the Langmuir, Freundlich and Temkin isotherm equations to test the fitness of these equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that adsorption of methylene blue obeys Langmuir isotherm, the linearization mode of the Langmuir equation influences the estimation of parameters, the Freundlich model is less suitable than that of Langmuir and the Temkin model shows that the reaction of adsorption is exothermic.

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