Adsorption of Methylene Blue by Agricultural Solid Waste of Pyrolyzed EFB biochar

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ABSTRACT

The adsorption equilibrium and kinetics of methylene blue (MB) dye on Empty Fruit Bunch (EFB) char were evaluated. The equilibrium adsorption data were compared using Langmuir and Freundlich isotherm models. The equilibrium adsorption followed a Langmuir isotherm which indicates that the char adsorption is homogeneous and monolayer. The Langmuir adsorption capacity ($Q_0$) was recorded to be 55.25 mg/g at temperature of 30°C. The kinetic studies were performed by using pseudo-first-order and pseudo-second-order kinetic modeling. The adsorption of methylene blue dye was found to be best fitted by the pseudo-second-order model. The adsorption capacity of EFB char in this study illustrates that it has the potential to remove dyes in the waste water industry.

Keywords: Biochar; methylene blue (MB); Langmuir isotherm; Freundlich isotherm.
1. Introduction

Malaysia has abundant oil palm biomass residues increasing yearly. This can be proven where there was around 15.8 million tons of Empty Fruit Bunch (EFB) produced in 2006 (Sumathi et al., 2008). Therefore it is important to utilize the wastes to good use rather than dumping them in the landfill. The EFB has the potential to be processed into biochar to reduce the volume of waste and at the same time produce bio fuel to generate energy. Biochar is a carbon rich product that remains when biomasses such as palm kernel, bagasse, rice husk and EFB are pyrolyzed in a closed container. It can be produced by several thermal treatments such as pyrolysis, gasification and combustion of biomass resources (Gary, 1943). However pyrolysis is proven to be the best method to produce biochar. Pyrolysis of biomass generates biochar together with bio oil and syngas that are useful to generate energy and produce transportation fuel. The biochar production depends on the pyrolysis temperature where biochar are produced more at temperature between 400°C to 500°C. As the pyrolysis temperature increases, the surface area and the pH of the char increases. Large surface area and high cation exchange capacity increases the effectiveness of the char to adsorb phosphates and therefore improving the soil fertility (Lehmann, 2007). Biochar are also processed in order to reduce the volume and sizes of agriculture and industry wastes (Lehmann and Joseph, 2009). Pyrolysis can reduce the weight of waste to 75% to 98%. Therefore it is beneficial to make good use of biochar as an added value studies to be applied in the industry as the agro-resource is inexpensive and renewable.

The wastewater industry, especially dye removal plant facilities in the factories can benefit from the usage of biochar to remove pollutants. Methylene blue dye is frequently used in the fabrics industry to dye cottons, silks and sheets. The substance is hazardous as it can cause eye burns and short period of breathing difficulty if inhaled continuously (Ghosh et al, 2002). There are many treatments methods to remove contaminants from the water system that has been studied such as anaerobic biological method (Turgay et al, 2011), usage of alkaline and acidic media (El-Rahim et al, 2009), nanomembrane filtration (Amini et al, 2011) and adsorption by using activated carbon (Mahmoodi et al, 2011). Since synthetic dyes in wastewater could not be removed by traditional methods, adsorption on solid supports such as activated carbon is considered simple and efficient (Forgacs et al, 2004). Biochar may be beneficial to replace activated carbon in order to reduce cost of operation. Given that Malaysia has abundant amount of agricultural waste produced yearly, there are many adsorption test performed to utilize and evaluate the ability of biomasses such as papaya seeds (Hameed, 2009), rattan sawdust (Hameed et al, 2007), oil palm empty fruit bunch (Zahangir et al, 2007) and bamboo (Ahmad et al, 2009) to adsorb dyes or hazardous compounds in the wastewater. Furthermore, several studies have been made to evaluate the adsorption capacity of fly ashes generated from coal firing power station which indicates that biochar has the potential to remove dyes (Wang et al, 2008; Janoset et al, 2003; Vasanth et al., 2005; Woolar et al., 2002).
In this paper, EFB char was utilized as adsorbent to remove methylene blue dye. Adsorption capacity of the EFB biochar has been evaluated and verified with their adsorption kinetic analyses using Langmuir and Freundlich isotherm models. In the study, the char was used as received to make the most of the waste at its utmost capacity without further treatment.

2. Experimental Techniques

2.1 Adsorbent Preparation

The EFB biochar pyrolyzed at 400°C was acquired from Nasmech Technologies in Puchong, Selangor. The as-received EFB char was dried in an oven at 100°C for 1 hour to remove any moisture present. No chemical treatments were performed to ensure that the utilization of the char has low preparation cost and inexpensive. A commercial activated carbon was obtained from K.D. Technology Sdn. Bhd. to compare the effectiveness of adsorption at the initial stage.

2.2 Biochar Characterization

The Brunauer-Emmett-Teller (BET) surface area of the EFB char was analyzed using an automatic Quantacome AS1Win™ – Automated Gas Sorption Data Analyzer. The image of the char’s pore sizes were observed using Scanning Electron Microscopy (SEM) HITACHI S 3400N.

2.3 Adsorption Experiment

Methylene blue dye solutions with the amount of 100 mL each were prepared at several concentrations of 50, 100, 200 and 300 mg/L in an Erlenmeyer flask. The adsorption wavelength of the dye was obtained from UV spectroscopy (Spectronic Helios Alpha, Thermo Electron Corporation, UK) at 661 nm.

The adsorption test was conducted by adding 0.2 gram biochar in each of the flasks. The flasks were then inserted in a shaker set at 150 rpm with temperature of 30°C. The initial and the concentration of mixture were analyzed every hour using UV-Vis Spectroscopy. The method used in this experiment is similar to the method applied in previous studies to evaluate the adsorption capacity of different biomasses for dye removal in wastewater (Hameed et al., 2007; Ahmad et al., 2009).

2.4 Equilibrium Studies

The amount of equilibrium adsorption, \( q_e \) (mg/g) was calculated using the following equation:

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]  
(1)
where $C_0$ is the initial dye concentration (mg/L) and $C_e$ is the dye concentration at equilibrium (mg/L). $V$ and $W$ are the volume of the dye solution (L) and weight of char (gram) respectively.

### 2.5 Kinetic Studies

The amount of adsorption at time $t$, $q_t$ (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W}$$  \hspace{1cm} (2)

Where $C_0$ Initial dye concentration (mg/L) and $C_t$ is the dye concentration at time $t$ (mg/L). $V$ and $W$ are the volume of the dye solution (L) and weight of char (gram) respectively.

### 3. Results and discussion

#### 3.1 Physical Properties of EFB char

The BET surface area result shows a reading of 0.1250m$^2$/g. The total pore volume shows a reading of 0.006cm$^3$/g. The values obtained were lower compared to bamboo-based activated carbon from a study by Ahmad and Hameed (2009) where the activated carbon has a BET surface area of 988.23 m$^2$/g and total pore volume of 0.696cm$^3$/g (Ahmad et al., 2009). Although the BET surface area and pore volume shows low values, the effectiveness of the EFB char adsorption may depend on other factors such as the pore structure, functional groups and surface chemistry (Guo et al, 2003). According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified as micropores (<2nm diameter), mesopores (2-50nm diameter) and macropores (>50nm diameter) (IUPAC, 1972). The average pore diameter was found to be 6.5954nm showing that the char was in the mesopores region. Figure 1 indicates the pore structures obtained from the SEM image where large pores of honey comb shaped were found at the surface of the char. This porous structure of the as-received EFB biochar facilitates the effectiveness of the methylene blue adsorption (Ahmad et al., 2009).
3.2 Effects of dye Concentration as time increases

Fig.2 shows the concentration of MB decreases as time increases. The percentage removal of dye are 91%, 90%, 49% and 36% for 50 mg/L, 100 mg/L, 200 mg/L and 300 mg/L respectively. A short comparison study of dye removal for commercial activated carbon shows a percentage of 99.3% dye removal for 50mg/L as compared to EFB char which gives percentage removal of 91%. This shows that the EFB biochar has the potential to be used as adsorbent. Higher percentage of dye removal are achieved at lower concentration as there are less amount of MB to be adsorbed at lower concentration as compared to high concentration. This can be explained by the fact that at lower concentration of MB solution, adsorption occurs mainly on the surface of the adsorbent. At higher concentration solution, more time is needed for adsorption to take place in the pores (intraparticle diffusion) (Banat et al., 2003).
It is observed that the amount of adsorbate adsorbed onto the EFB char in Fig.3 increases as time increases. The solutions were left for 24 hours to allow the adsorption process to achieve equilibrium. The term equilibrium here means that the process has achieved the limited amount of dye able to be adsorbed after 24 hours at 30°C. As the MB solution concentration increases from 50 ppm to 300 ppm, the MB adsorption increases from 23.8 mg/g to 54.4 mg/g respectively. This result is comparable with a study by Vadivelan and Kumar (2005) who reported similar result of 40.58 mg/g adsorption of dye by rice husk (Vadivelan et al., 2005). A comparable result of study by using coconut bunch waste also shows an adsorption capacity of 70.92 mg/g (Hameed et al, 2008). It is demonstrated from the result that the EFB char has the capacity and ability to adsorb MB dye at 30 °C upon reaching equilibrium. The rate of diffusion of the adsorbate in a substance is proportional to the concentration of the solution. Molecules from high concentration region will flow to regions of low concentration. The greater the difference in concentration, the faster is the diffusion. In the experiment, it took almost 24 hours for the adsorption to reach equilibrium whereby the MB molecules were adsorbed into the adsorbent particles at its active sites.

Fig.3 The adsorption capacity of EFB char at different dye concentrations at time (minutes).

3.3 Adsorption Equilibrium Isotherms

The adsorption capacity of biochar to remove dyes is correlated to the measurement of particles dispersion at different phases. The movements of molecules between the liquid phase and solid phase are related to different isotherm studies that can identify whether the distributions processes are homogeneous or heterogeneous. In this study, two different models are used to identify the mechanism of the char adsorption. The first isotherm is the Langmuir isotherm where assumptions on the adsorption mechanism are that the adsorption occurs at
homogeneous surface within the adsorbent and the adsorption at one site does not interfere with the ability of the next side to adsorb dye (Nelson, 2001). The Langmuir isotherm model that has been applied to several adsorption processes is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0} \left( \frac{1}{b} \right) + \frac{1}{Q_0} C_e$$

(3)

where $C_e$ is the methylene blue dye equilibrium concentration (mg/L), $q_e$ is the quantity of methylene blue dye adsorbed per gram char (mg/g), $Q_0$ is the maximum adsorption capacity of the char and $b$ is the adsorption energy. A plot of $C_e/q_e$ versus $C_e$ produces a straight line which indicates homogeneous adsorption distribution of Langmuir isotherm. The values of constant $b$ and $Q_0$ were obtained from the intercept and the slope of the graph as shown in Fig.4.

![Fig.4 Langmuir adsorption model of biochar's methylene blue adsorption at 30°C.](image)

The experimental results fit well into Langmuir isotherm hence attests that each site of the char can accommodate one atom or molecule and signify the homogeneous surface within the EFB char. The Langmuir model also generates a correlation factor, $R^2$ of 0.99 which shows it fits well into the model. It is seen that the EFB char has a maximum sorption of 55.25 mg/g. This value is considered to be comparable with previous studies of fly ash from thermal power plant which has adsorption capacity of 5.574 mg/g (Kumar et al., 2005) and coal fly ash of 12.7 mg/g (Wang et al., 2008).

The Langmuir isotherm can also be articulate as dimensionless constant separation factor $R_L$ (Weber & Chakkravorti., 1974) described as:
\[ R_L = \frac{1}{1 + bC_0} \]  

(4)

Where \( b \) is the Langmuir constant and \( C_0 \) is the highest dye concentration (mg/L). The values of \( R_L \) the types of isotherm whereby when \( R_L > 1 \), the adsorption is unfavorable, linear when \( R_L = 1 \), favorable when \( 0 < R_L < 1 \) or irreversible when \( R_L = 0 \). For this study, the amount of \( R_L \) was calculated to be 0.017. This shows that the adsorption of methylene blue on EFB char is a favorable to adsorption.

The Freundlich isotherm derived from assumptions that the adsorption system includes different types of non uniform surfaces mainly heterogeneous surfaces (Fogler, 2006). The most recognized form of Freundlich model is:

\[
\ln q_e = \ln K_F + \ln C_e \left( \frac{1}{n} \right)
\]

(5)

Where \( q_e \) is the quantity of methylene blue dye adsorbed at equilibrium (mg/g), \( C_e \) is the methylene blue equilibrium concentration (mg/g). The values of \( K_F \) and \( n \) are the constants that can be calculated from the graph’s interception and the slope.

Table 1 Langmuir and Freundlich isotherm constants for Methylene Blue Adsorption Test.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir Isotherm</th>
<th></th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_0 ) (mg/g)</td>
<td>55.25</td>
<td>( K_F ) [(mg/g (L.mg)^b)]</td>
<td>114806.1</td>
</tr>
<tr>
<td>( b ) (mg^{-1})</td>
<td>0.19</td>
<td>( K_F ) [(mg/g (L.mg)^b)]</td>
<td>114806.1</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.999</td>
<td>( R^2 )</td>
<td>0.7244</td>
</tr>
<tr>
<td>( R_L )</td>
<td>0.017</td>
<td>( R^2 )</td>
<td>0.7244</td>
</tr>
</tbody>
</table>

The Freundlich model in Fig.5 produces a correlation factor, \( R^2 \) of 0.7244 which shows it does not fit well into the model. By comparing the Langmuir and Freundlich models of correlation factors in Table 1, the Langmuir gives a better fit of 0.999. The value for \( 1/n \) is 4.053 which show that the adsorption of methylene blue is a favorable adsorption process (Fytianos et al., 2000).
3.4 Adsorption Kinetics

Two types of rate constant adsorption which are taken into account to identify the adsorption isotherm are the pseudo first order equation and pseudo second order equation by Langergen and Svenska (Langergren & Svenska, 1898). The pseudo first order equation is determined by

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

Where \( q_e \) is the amount of methylene blue adsorbed (mg/g) at equilibrium and \( q_t \) are the amount methylene blue adsorbed at time \( t \) (mg/g). \( k_1 \) is the rate constant of the adsorption process (h\(^{-1}\)). The data on \( \ln(q_e - q_t) \) versus time, \( t \) in Figure 6 were plotted to obtain the values of \( k_1 \). The correlation factors (\( R^2 \)) are from the range of 0.9100 to 0.9856 for different concentrations of methylene blue. These values are not agreeable to the experimental results and therefore do not follow the first order kinetics of pseudo order model.
Therefore a second order kinetics of pseudo order model was implemented to verify the suitability of the experimental data with the adsorption kinetics. The pseudo second order kinetics model is given by:

\[
\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t
\]  

(7)

Where \( q_e \) and \( q_t \) are the amounts of methylene blue adsorbed at equilibrium and at time \( t \) (mg/g). \( k_2 \) is the rate constant of the pseudo second order kinetics model which values can be obtained by plotting \( t/q \) versus \( t \) in Figure 7. The values of calculated \( q_e \) in Table 2 are comparable with the experimental data for second order pseudo order isotherm compared to the first order pseudo isotherm. Other than that the values for correlation coefficients (\( R^2 \)) are in the range of 0.9940 to 0.9997 which shows that the kinetic chosen is at good agreement with the experimental data. The values for the coefficients factor are also greater than 0.99 showing that the adsorption kinetics of EFB char follows the second order pseudo kinetic model.
Fig. 7 Pseudo-second-order kinetics for adsorption of EFB char with methylene blue char.

Table 2 Comparison of the rate constants of first and second pseudo order, calculated and experimental $q_e$ values at different dye concentration.

<table>
<thead>
<tr>
<th>Initial Concentration (mg l$^{-1}$)</th>
<th>$q_{e,exp}$ (mg/g)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$R^2$</th>
<th>$k_1$ (h$^{-1}$)</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$k_2$ [g(mg.h$^{-1}$)]</th>
<th>$q_{e,cal}$ (mg/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>23.8125</td>
<td>13.04</td>
<td>0.9298</td>
<td>0.032</td>
<td>13.04</td>
<td>24.038</td>
<td>0.9997</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>43.6775</td>
<td>25.54</td>
<td>0.9081</td>
<td>0.011</td>
<td>25.54</td>
<td>45.045</td>
<td>0.9973</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>51.2175</td>
<td>32.87</td>
<td>0.932</td>
<td>0.012</td>
<td>32.87</td>
<td>52.91</td>
<td>0.9967</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>54.3875</td>
<td>51.8</td>
<td>0.9521</td>
<td>0.037</td>
<td>51.8</td>
<td>55.25</td>
<td>0.994</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 shows the adsorption capacity of the potential EFB char as compared to other treated char samples that have been activated physically or chemically. Therefore by activating the raw char sample by acid or base treatment, the adsorption capacity will increase tremendously and the sample is possible to be applied in the industry.
Table 3 Adsorption capacity of different char and carbon samples on different sorption components.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatments</th>
<th>Sorption components</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit</td>
<td>Commercial AC</td>
<td>Methylene Blue</td>
<td>276</td>
<td>32</td>
</tr>
<tr>
<td>Coconut Shell char</td>
<td>NaOH-activated</td>
<td>Methylene Blue</td>
<td>916.26</td>
<td>33</td>
</tr>
<tr>
<td>Oil palm fiber</td>
<td>Chemical &amp; physical activation</td>
<td>Methylene Blue</td>
<td>277.78</td>
<td>34</td>
</tr>
<tr>
<td>Raw EFB</td>
<td>-</td>
<td>Methylene Blue</td>
<td>50.76</td>
<td>35</td>
</tr>
<tr>
<td>EFB char</td>
<td>-</td>
<td>Methylene Blue</td>
<td>55.25</td>
<td>This study</td>
</tr>
</tbody>
</table>

4. Conclusion

The study performed showed that EFB char has the potential to be used as activated carbon in the textile industry. It is shown that the char has the ability to remove methylene blue dye at several concentrations. The adsorption behavior follows the Langmuir isotherm which indicates a homogeneous adsorption process at the surface of the char. The maximum adsorption capacity, Q₀, of the untreated EFB char is 55.25 mg/g. This value shows the EFB char has the potential to be used as adsorbent as it has comparable adsorption capacity as compared to other carbon materials.

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