Adsorption Isotherms, Kinetics, Thermodynamics and Desorption Studies of Basic Dye on Activated Carbon Derived from Oil Palm Empty Fruit Bunch

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Abstract: The adsorption characteristics of basic dye (methylene blue, MB) on activated carbon prepared from oil palm Empty Fruit Bunch (EFB) were evaluated. The effects of dye initial concentration, agitation time, solution pH and temperature on MB adsorption were investigated. The adsorption uptake was found to increase with increase in initial concentration, agitation time and solution temperature. The adsorption equilibrium data were best represented by the Langmuir isotherm. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. The mechanism of the adsorption process was determined from the intraparticle diffusion model. Boyd plot revealed that the adsorption of MB on the activated carbon was mainly governed by external mass transport where particle diffusion was the rate limiting step. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), standard free energy (ΔG°) and activation energy were determined. The regeneration efficiency of the spent activated carbon was acceptably high, with MB desorption of 71%.

Key words: Oil palm empty fruit bunch, methylene blue, adsorption isotherms, intraparticle diffusion, desorption

INTRODUCTION

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons (Métivier-Pignon et al., 2003). Methylene blue (MB) is the most commonly used substance for dying cotton, wood and silk. MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia (Ghosh and Bhattacharyya, 2002). Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

Colour removal from industrial wastewaters by adsorption techniques has been of growing importance due to the chemical and biological stability of dyestuffs to conventional water treatment methods and the growing need for high quality treatment (Başar, 2006). However, commercially available activated carbons are still considered as expensive materials due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications (Attia et al., 2008). Therefore, in recent years, this has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural by-products, such as apricot shell (Karagözoglu et al., 2007), male flower of coconut tree (Senthilkumara et al., 2006), jute fiber (Senthilkumara et al., 2005), rubber wood sawdust (Kalavathy et al., 2005), corn cob (Tseng et al., 2006), bamboo (Hameed et al., 2007) and oil palm fibre (Tan et al., 2007).

At present, Malaysia is one of the largest exporters of palm oil in the international market. One of the significant problems in the palm fruit processing is managing of the wastes generated during the processes. Approximately 15 million tons of EFB waste is generated annually throughout Malaysia by palm oil mills (Rahman et al., 2007). In practice this biomass is burnt in incinerator by palm oil mills which creates environmental pollution problems in nearby localities and also offers limited value to the industry. To make better use of this
abundant waste, it is proposed to convert it into activated carbon. Conversion of coconut husk to activated carbon will serve a double purpose. First, unwanted agricultural waste is converted to useful, value added adsorbents and second, the use of agricultural by products represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problem in Malaysia. From our previous study, EFB-based activated carbon was found to be an effective adsorbent for removing chlorophenol from aqueous solutions (Tan et al., 2009).

The present study aims to evaluate the potentiality of EFB-based activated carbon to remove MB from aqueous solutions. The experimental data of the adsorption process were analyzed to study the adsorption isotherms, kinetics, thermodynamics and mechanism of MB on the EFB-based activated carbon. The feasibility of regenerating the spent activated carbon using ethanol desorption was then determined.

MATERIALS AND METHODS

Preparation of activated carbon: EFB used for preparation of activated carbon in this study was obtained from a local palm oil mill. The activated carbon preparation procedure was referred to our previous study (Tan et al., 2008) where the pre-treated EFB was loaded in a stainless steel vertical tubular reactor placed in a tube furnace and the carbonization of the precursor was carried out by ramping the temperature from room temperature to 700°C with heating rate of 10°C min⁻¹ and hold for 2 h. Throughout the carbonization process, purified nitrogen (99.995%) was flowed through at flow rate of 150 cm³ min⁻¹. The activated carbon was prepared using physiochemical activation method consisting of potassium hydroxide (KOH) treatment followed by carbon dioxide (CO₂) gasification by applying the optimum operating conditions obtained from our earlier study (Tan, 2008). The char produced from the carbonization process was mixed with KOH pallets with KOH:char Impregnation Ratio (IR) of 2.9:1. The dried mixture was then activated under the same condition as carbonization, but to a final temperature of 844°C. Once the final temperature was reached, the nitrogen gas flow was switched to CO₂ and activation was held for 1.8 h. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1 M HCl until the pH of the washing solution reached 6-7.

Batch equilibrium and kinetic studies: MB supplied by Sigma-Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. Deionized water was used to prepare all the solutions and reagents. MB has a chemical formula of C₉H₉N₃SCl, with molecular weight of 319.86 g mol⁻¹.

In order to study the effect of MB initial concentration and contact time on the adsorption uptake, adsorption tests were performed in a set of 43 Erlenmeyer flasks (250 mL) where 100 mL of MB solutions with initial concentrations of 50-500 mg L⁻¹ were placed in these flasks. Equal mass of 0.1 g of the prepared activated carbon with particle size of 200 μm was added to each flask and kept in an isothermal shaker of 120 rpm at 30°C for 30 h to reach equilibrium. The pH of the solutions was original without any pH adjustment. Similar procedures were followed for another two sets of Erlenmeyer flask containing the same initial dye concentrations and same activated carbons dosage, but were kept under 40 and 50°C for thermodynamic studies. Aqueous samples were taken from each of the MB solutions at preset time intervals using disposable filtered syringes and the concentrations were then analyzed. The concentrations of MB in the supernatant solution before and after adsorption were determined using a double beam UV-Visible spectrophotometer (UV-1601 Shimadzu, Japan) at 668 nm wavelength. The amount of adsorption at equilibrium, qₑ (mg g⁻¹), was calculated by:

\[ qₑ = \frac{(C₀-Cₑ)V}{W} \]  (1)

where \(C₀\) and \(Cₑ\) (mg L⁻¹) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. \(V\) is the volume of the solution (L) and \(W\) is the mass of dry adsorbent used (g).

The equilibrium data were then fitted using four different isotherm models, namely the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. For kinetic studies, the amount of adsorption at time t, \(qₜ\) (mg g⁻¹), was calculated by:

\[ qₜ = \frac{(C₀-Cₜ)V}{W} \]  (2)

where \(Cₜ\) (mg L⁻¹) is the liquid-phase concentrations of dye at time, t.

The kinetic data were then fitted using the pseudo-first-order, pseudo-second-order and intraparticle diffusion models.

Regeneration of spent activated carbon: The feasibility of regenerating the spent activated carbon saturated with MB was evaluated using ethanol desorption technique (Tanthapanichakoon et al., 2005). Initially, batch
equilibrium tests were performed on the fresh activated carbons prepared where 100 mL of MB solution with initial concentration of 400 mg L⁻¹ were placed in 250 mL Erlenmeyer flasks. 0.1 g of the fresh EFB-based activated carbon was added into the flask and placed in an isothermal water bath shaker at 30°C, with rotation speed of 120 rpm, agitated for 48 h until complete equilibrium was attained. The solution pH was kept original without any pH adjustment. The concentrations were similarly measured using UV-visible spectrophotometer and the concentration of adsorbate adsorbed at equilibrium, \( C_{eq} \) (mg L⁻¹) was calculated as the difference between the initial and equilibrium concentration (\( C_0 - C_a \)).

The spent activated carbon was then separated from the solution and washed with deionized water to remove any unabsorbed MB. The sample was then dried at 110°C in an oven and then added into Erlenmeyer flask containing 100 mL of 95 vol% ethanol for desorption of the MB. The flask was kept in the isothermal water bath shaker at the same temperature for the same time duration as the adsorption tests. After desorption, the concentrations of MB desorbed, \( C_{des} \) (mg L⁻¹) was similarly measured using the UV-visible spectrophotometer. The percent desorption was calculated using Eq. 3:

\[
\text{Desorption} \% = \frac{C_{des}}{C_{eq}} \times 100 \tag{3}
\]

RESULTS AND DISCUSSION

Effect of MB initial concentration and agitation time on adsorption equilibrium: Figure 1 shows the adsorption uptake versus the adsorption time at various initial MB concentrations at 30°C. It indicated that the contact time needed for MB solutions with initial concentrations of 50-200 mg L⁻¹ to reach equilibrium was around 2 h. However, for MB solutions with higher initial concentrations of 300-500 mg L⁻¹, equilibrium times of around 24 h were required. This observation could be explained by the theory that in the process of dye adsorption, initially the dye molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent (Senthilkumar et al., 2005). Therefore, MB solutions of higher initial concentrations will take relatively longer contact time to attain equilibrium due to higher amount of dye molecules (Fig. 1). The amount of MB adsorbed on the activated carbon increases with time and at some point in time, it reaches a constant value beyond which no more MB is further removed from the solution. At this point, the amount of the dye desorbing from the activated carbon is in a state of dynamic equilibrium with the amount of the dye being adsorbed on the activated carbon. The amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. In this study, the adsorption capacity at equilibrium (qₑ) was found to increase from 41.11 to 384.57 mg g⁻¹ with an increase in the initial dye concentrations from 50 to 500 mg L⁻¹. When the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher adsorption of MB.

Adsorption isotherms: The analysis of the adsorption equilibrium data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design purposes (El-Guendi, 1991). Adsorption isotherm is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. Adsorption isotherm study was carried out on four isotherm models, namely the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients, \( R^2 \) values. For the Langmuir isotherm, when \( C_e / q_e \) is plotted against \( C_e \), a straight line with slope of \( 1/q_m \) and intercept of \( 1/q_m K_f \) is obtained. For the Freundlich isotherm, the plot of \( \log q_e \) versus \( \log C_e \) gives a straight line with slope of \( 1/n \) and intercept of \( \log K_f \). A plot of \( \log q_e \) versus \( \ln C_e \) for the Temkin isotherm yields a linear line with slope of \( B \) and intercept of \( (B \ln A) \). For Dubinin-Radushkevich isotherm, a plot of \( \ln q_e \) versus \( e^2 \) enables the constants \( q_m \) and \( E \) to be determined (Tan et al., 2009).
Table 1 shows the four isotherm models used, together with all the constants and R² values obtained from each plot. The Langmuir model yielded the best fit with R² value equal or higher than 0.98, as compared to the other three models. Conformation of the experimental data into Langmuir isotherm indicated the homogeneous nature of EFB-based activated carbon surface, i.e., each dye molecule/EFB-based carbon adsorption had equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of dye molecule at the outer surface of the activated carbon. Similar observations were reported by the adsorption of MB on activated carbons prepared from olive-seed waste residue (Stavropoulos and Zabaniotou, 2005) and corn cob (Tseng et al., 2006). The activated carbon prepared in this work had relatively large adsorption capacity (357.14 - 416.67 mg g⁻¹) if compared to some adsorbents reported in the literature.

**Adsorption kinetic studies:** The rate constant of adsorption is determined from the pseudo-first-order equation given by Lagergren and Svenska (1898) as:

\[
\ln(q_e - q(t)) = \ln q_e - k_1 t \tag{4}
\]

where \(k_1\) is the first-order adsorption rate constant (1 h⁻¹).

The pseudo-second-order equation (Ho and McKay, 1999) based on equilibrium adsorption is expressed as:

\[
\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} \times \frac{1}{q_e} - t \tag{5}
\]

where \(k_2\) (g mg⁻¹ h) is the rate constant of second-order adsorption.

The constants and R² values obtained from the two linear plots are summarized in Table 2. It was found that for pseudo-first-order equation, the R² values were relatively small and the experimental \(q_e\) values did not agree with the calculated values, indicating that the adsorption of MB on the activated carbon did not follow this model. However, for pseudo-second-order model, there was a good agreement between the experimental and the calculated \(q_e\) values. Besides, the R² values obtained for this model were greater than 0.99 for all MB concentrations, indicating the applicability of the second-order kinetic model to describe the adsorption process of MB on the EFB-based activated carbon. Based on the higher R² and the smaller deviation values between the experimental and calculated \(q_e\), the pseudo-second-order model was more suitable to describe the adsorption kinetics of MB on the EFB-based activated carbon. This suggested that the overall rate of the adsorption process was controlled by chemisorption which involved valency forces through sharing or exchange of electrons between the sorbent and sorbate (Ho and McKay, 1999).

**Adsorption mechanism:** As the above kinetic models were not able to identify the diffusion mechanism, thus intraparticle diffusion model based on the theory proposed by Weber and Morris (1962) was tested. It is an empirically found functional relationship, common to the most adsorption processes, where uptake varies almost proportionally with \(t^{1/2}\) rather than with the contact time \(t\). According to this theory:

\[
q_t = k_3 t^{1/2} + C_i \tag{6}
\]
where, $k_p$ (mg g$^{-1}$ h$^{-1}$), the rate parameter of stage 1, is obtained from the slope of the straight line of $q_t$ versus $t^{rac{1}{2}}$, as shown in Fig. 2. $C_r$, the intercept of stage 1, gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect. If intraparticle diffusion occurs, then $q_t$ versus $t^{rac{1}{2}}$ will be linear and if the plot passes through the origin, then the rate limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved. As can be seen from Fig. 2, the linear lines of the second and third stages did not pass through the origin and this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption (Mohanty et al., 2005). It shows that intraparticle diffusion was not the only rate limiting mechanism in the adsorption process.

Kinetic data as obtained by the batch method has been treated by the expressions given by Boyd et al. (1947), which is in accordance with the observations of Reichenberg (1953). The three sequential steps in the adsorption are:

- Film diffusion, where adsorbate ions travel towards the external surface of the adsorbent
- Particle diffusion, where adsorbate ions travel within the pores of the adsorbent excluding a small amount of adsorption that occurs on the exterior surface of the adsorbent
- Adsorption of the adsorbate ions on the interior surface of the adsorbent

The third step is considered to be very fast thus it cannot be treated as rate limiting step. If external transport > internal transport, rate is governed by particle diffusion. If external transport < internal transport, rate is governed by film diffusion and if external transport = internal transport, the transport of adsorbate ions to the boundary may not be possible at a significant rate thus, formation of a liquid film surrounding the adsorbent particles takes place through the proper concentration gradient (Mittal et al., 2008).

In order to predict the actual slow step involved in the adsorption process, the kinetic data were further analyzed using the Boyd model given by Eq. 7:

$$B = -0.4977 - \ln(1 - F)$$  \hspace{1cm} (7)

$F$ represents the fraction of solute adsorbed at any time, t (h), as calculated using Eq. 8:

$$F = q_t / q_0$$  \hspace{1cm} (8)

The calculated $B$ values were plotted against time t (h), as shown in Fig. 3. The linear lines for all MB initial concentrations did not pass through the origin and the points were scattered. This indicated that the adsorption of MB on the EFB-based activated carbon was mainly governed by external mass transport where particle diffusion was the rate limiting step (Kalavathy et al., 2005).

**Adsorption thermodynamics:** The value of changes in standard enthalpy ($\Delta H^0$) and standard entropy ($\Delta S^0$) were computed using the following equation:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$  \hspace{1cm} (9)
Table 3: Thermodynamic parameters for adsorption of MB on EFB-based activated carbon

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^o$ (J mol$^{-1}$)</th>
<th>$\Delta S^o$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$\Delta G^o$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.07</td>
<td>113.39</td>
<td>1.89</td>
<td>0.19</td>
</tr>
<tr>
<td>313 K</td>
<td></td>
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<td>0.35</td>
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<tr>
<td>323 K</td>
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where, $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ (K) is the absolute solution temperature and $K_d$ is the distribution coefficient.

The standard free energy ($\Delta G^o$) can be calculated using the relation below:

$$\Delta G^o = -RT\ln K_d$$ (10)

The values of $\Delta H^o$ and $\Delta S^o$ were calculated from the slope and intercept of plot between $\ln K_d$ versus $1/T$ for MB initial concentration of 500 mg L$^{-1}$. The calculated values of $\Delta H^o$, $\Delta S^o$ and $\Delta G^o$ are listed in Table 3. The positive value of $\Delta H^o$ indicated the endothermic nature of the adsorption interaction. The adsorption reaction for the endothermic processes could be due to the increase in temperature increased the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution (Wang and Zhu, 2007). The positive value of $\Delta S^o$ showed the affinity of the EFB-based activated carbon for MB and the increasing randomness at the solid-solution interface during the adsorption process. The negative value of $\Delta G^o$ indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of MB on the activated carbon. The results showed that the adsorption process was more favorable at higher temperature (50°C), due to the endothermic nature of the adsorption system.

**Regeneration of spent activated carbon:** The feasibility of regenerating the spent activated carbon saturated with MB was evaluated using ethanol desorption technique. The MB desorption of 71% obtained in this work was considered relatively high. It was reported in the literature that by using ethanol desorption, the regeneration efficiency of waste tires-based activated carbons for phenol and Red 31 dye were, respectively 35-45 and 30-40 (Tanapapanichakoon et al., 2005). Thus, ethanol desorption technique was shown to be a promising way to regenerate the spent activated carbon prepared in this study as 71% of the adsorption sites could be recovered from the regenerated activated carbon.

**CONCLUSION**

The present investigation showed that EFB-based activated carbon was a promising adsorbent for the removal of MB dye from aqueous solutions over a wide range of concentrations. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the equilibrium data were best described by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 357.14 to 416.67 mg g$^{-1}$ with increase of solution temperature from 30 to 50°C. The adsorption kinetics was found to follow closely the pseudo-second-order kinetic model whereas the adsorption process was mainly governed by external mass transport where particle diffusion was the rate limiting step. The positive $\Delta H^o$ value confirmed the endothermic nature of the adsorption interaction. Ethanol desorption technique was efficient in regenerating the spent activated carbon, giving MB desorption of 71%.

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