Fixed bed adsorption of methylene blue by using palm oil mill effluent waste activated sludge

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ABSTRACT
The waste activated sludge (WAS) discharged during the aerobic treatment of palm oil mill effluent (POME) was used to produce a low cost adsorbent for the removal of methylene blue (MB) from aqueous solution. This study employed a continuous process in a fixed bed column packed with WAS as the adsorbent. The effect of the dye inlet flow rate, height of the packing and inlet dye concentration on adsorption were studied. The adsorption data obtained from these experiments were then fitted into three dynamic adsorption models, Adam's-Bohart model, Thomas model and the Yoon-Nelson model, in which the Thomas and the Yoon-Nelson models gave better fit to the experimental data under various conditions. The highest uptake capacity, q_e, was obtained when a 6 cm bed depth was used at an inlet concentration of 100 mg/L and a flow rate of 0.9 mL/min.
Keywords: Adsorption; Fixed bed; Methylene Blue; POME; Waste activated sludge

INTRODUCTION

Palm oil mill operators use biological treatment systems to treat the palm oil mill effluent (POME). Currently, 85% of all POME treatments are based on biological anaerobic digestion followed by aerobic oxidation in ponds (Vijayaraghavan et al., 2007). However, biological treatment systems generate waste activated sludge (WAS) continuously, which is very expensive to handle and dispose off (Horan, 1990). As a result, the potential for the re-use of WAS should be investigated.

It has been demonstrated that WAS from biological treatment plants have functional groups including -OH, -NH, $-NH_2$, -C=O and C=C (Luo et al., 2006). These functional groups will act as the binders for attachment of an adsorbate (Aksu, 2001). Based on these findings, researchers have exploited the potential of WAS to adsorb various adsorbates (Caner et al., 2009; Gulnaz, 2009).

Currently, activated carbon (AC) is used as the adsorbent in most adsorption systems; however, it is non-sustainable and expensive (Crini, 2006). Therefore, studies have been conducted to identify alternatives to replace the AC in the adsorption process. Low-cost alternatives that have been conducted to date include bamboo (Hameed et al., 2007), and fruit stones and nutshells (Aygun et al., 2003). Even though the costs can be reduced significantly by using the above alternatives, these materials must be converted into AC via high thermal treatment before they can be used as an adsorbent. However, to the best of our knowledge, no studies have been conducted to evaluate the use of WAS from POME treatment plants as an adsorbent. Our preliminary study have shown that the WAS from POME treatment plants could be used as color adsorbent in a batch system. Hence, continuous column studies to evaluate the use of WAS from POME treatment plants as a color adsorbent are warranted.

Unlike previous studies, this study primarily focused on converting WAS from POME treatment plants into an efficient color adsorbent (in a continuous column) without high thermal treatments. Thus, the operational costs will be reduced significantly. Methylene Blue (MB) (textile dye), one of several dyes that can cause harmful effects on living organisms, was used as an adsorbate in this study. The

parameters affecting the adsorption process in columns studies, such as the inlet concentration of MB, bed height, and flow rate of MB, were investigated.

MATERIALS AND METHODS

Preparation of adsorbent

Raw WAS was collected from the Tali Ayer Oil Palm Mill treatment plant, in Bagan Serai, Malaysia. The WAS was then dried in a muffle furnace at 120 °C for 12 hours, after which it was washed with 0.1 M NaOH solution with a mass (WAS) to volume (NaOH) ratio of 1:1 four to five times and then dried at 85 °C for 12 hours in an oven. The chemically activated and dried WAS was removed from the oven and washed with distilled water to remove the remaining chemicals before being dried once again in the oven at 85 °C for 6 hours. After the last drying, the sludge was crushed and sieved to a particle size 0.5 – 2 mm and used as an adsorbent.

Preparation of adsorbate

MB, a cationic dye, was purchased from Sigma Aldrich (M) Sdn. Bhd, Malaysia in powder form and used as received without further purification. All working solutions (20 mg/L, 50 mg/L, and 100 mg/L) were prepared by diluting the powdered MB with distilled water to the desired concentrations. In addition, MB with concentrations of 5 mg/L and 30 mg/L were also prepared to obtain a calibration curve for spectrophotometry analysis.

Experimental setup

Continuous flow adsorption experiments were conducted in a transparent cylindrical plastic column (1.5 cm internal diameter and 30 cm height). A 0.5 mm stainless sieve was attached to the bottom of the column. A known quantity of adsorbent was then placed in the column to yield the desired bed height (3 cm, 6 cm and 9 cm) of the adsorbent. MB solution of known concentration (20 mg/L, 50 mg/L and 100 mg/L) was channeled into the column using a peristaltic pump (BT-100-2J Longer Pump) at the desired flow rate (0.3 mL/min, 0.6 mL/min and 0.9 mL/min). Samples were collected from the exit of the column at different time intervals and analyzed for MB using a UV-Vis Spectrophotometer (UV-Vis Aquamate 171501) by monitoring the changes in absorbance at a wavelength of maximum absorbance of 664.5 nm. Operation of the column was stopped when the effluent MB concentration exceeded 99.5% of its initial concentration.

Analysis of column data

The operation and behavior of the continuous column adsorption can be determined by using the time to reach breakthrough and the shape of the breakthrough curve. The breakthrough curves show the loading behavior of a dye in a continuous column (Uddin et al., 2009) and are usually expressed in terms of normalized concentration defined as the ratio of the outlet concentration (C_t) to the inlet concentration (C_o) as a function of time (in minutes).

The uptake capacity (q_e) of MB in WAS is shown in Equation 1.

$$q_e = \frac{m_{ad}}{M} \quad (1)$$

where q_e is the dye uptake capacity (mg/g), m_{ad} is the dye mass adsorbed (mg) and M is the adsorbent mass (g).

The total amount of MB (m_{total}) sent through the column is calculated by Equation 2.

$$m_{total} = \frac{(C_o)(F)(t_e)}{1000} \quad (2)$$

where C_o is the inlet concentration of MB (mg/L), F is the flow rate of MB (mL/min), and t_e is the exhaustion time (minutes).

The total removal percent of MB (column performance) is calculated by Equation 3.

$$Total\ \ Removal\,(\%) = \frac{m_{ad}}{m_{total}}\, x\, 100\% \quad (3)$$

Data Modeling

Thomas Model

Thomas (Thomas, 1944) developed a model for adsorption processes in which external and internal diffusion limitations are not present. The linearized form of the Thomas model can be expressed as in Equation 4 (Ahmad and Hameed, 2010):

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{Th} q_e W}{Q} - k_{Th} C_o (t) \quad (4)$$

where k_{Th} is the Thomas rate constant (mL/min.mg), q_e is the equilibrium of MB uptake (mg/g), C_o is the inlet MB concentration (mg/L), C_t is the effluent MB concentration at time t (mg/L), W is the mass of adsorbent (g), Q is the inlet flow rate (mL/min) and t is the flow time (min). The value of C_o/C_t is the ratio of inlet to outlet MB concentrations. A linear plot of ln $[(C_o/C_t) - 1]$ against time (t) was drawn to determine the values of q_e and k_{Th} from the interception point and slope of the plot, respectively.

The Adam's - Bohart Model

Generally, the Adam's–Bohart model (Bohart and Adams, 1920) is used to describe the initial part of the breakthrough curve. The expression is given in Equation 5.

$$\ln\left(\frac{C_t}{C_o}\right) = k_{AB} C_o (t) - \frac{k_{AB} N_o Z}{L} \quad (5)$$

where, C_o is the inlet dye concentration (mg/L), C_t is the effluent dye concentration (mg/L), k_{AB} is the kinetic constant (mL/mg.min), L is the linear velocity (flow rate / column section area, cm/min), Z is the bed depth of the column (cm) and N_o is the saturation concentration (mg/mL). A linear plot of ln (C_t/C_o) against time (t) was drawn and values of k_{AB} and N_o were determined from the slope and interception point of the plot, respectively.

The Yoon–Nelson model

Yoon and Nelson (Yoon and Nelson, 1984) developed a model to describe the adsorption behavior in the continuous column adsorption. The linearized form of the Yoon-Nelson model is given in Equation 6.

$$\ln \frac{C_t}{C_o - C_t} = k_{YN} (t) - k_{YN} \tau \quad (6)$$

where, k_{YN} is the rate velocity constant (L/min) and τ is the time in (min) required for 50% adsorbate breakthrough. A linear plot of ln $[C_t / (C_o - C_t)]$ against sampling time (t) was used to determine the values of k_{YN} and τ from the slope and intercept of the plot. The validity of the adsorption model was further determined by using normalized standard deviation (ε %). The calculated τ (using Equation 6)

was compared to the τ value obtained from the experiment. Smaller percentage of deviation will indicate that the Yoon-Nelson model is applicable for this adsorption. The normalized standard deviation (ε %) is given by Equation 7 :

$$\varepsilon\% = \left[\sqrt{\frac{[(q_{e,\exp} - q_{e,cal}) / q_{e,\exp}]^2}{N-1}} \right] \times 100\% \quad (7)$$

where $q_{e,exp}$ and $q_{e,cal}$ are the adsorption equilibriums obtained from experimental work and calculated values, respectively, and N is the number of data points.

Bed depth service time (BDST) model

According to (Han et al., 2007), BDST model is used to predict the bed capacity by utilizing the different breakthrough values. The modified version of the equation used in this evaluation is given in Equation 8.

$$t = \frac{N_a}{C_o F} Z + \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \quad (8)$$

where t is the time (mins), N_a is the adsorption capacity (mg/L), C_o is the inlet concentration of MB (mg/L), F is the linear velocity of MB across the column (cm/min), Z is the bed depth (cm), K_a is the rate constant in BDST model (L/mg.min) and C_t is the effluent concentration of the MB (mg/L). A plot of t versus Z is expected to yield a linear curve in which N_o and K_a could be evaluated, from the slope and y-axis intersection point, respectively.

RESULTS AND DISCUSSION

Effect of initial concentration

The effects of the three initial MB concentrations (20 mg/L, 50 mg/L and 100 mg/L) on the adsorption process at a constant flow rate of 0.9 mL/min and fixed bed height of 6 cm are shown in Figure 1(a). It can be deduced that, at a lower inlet concentrations, a slower breakthrough curve and the highest treated volume will be obtained. The breakthrough point (C_t/C_o = 0.05) for the 20 mg/L, 50 mg/L and 100 mg/L MB inlet concentrations occurred after 15 hours, 7.5 hours and 4.25 hours, respectively. The highest dye removal (76.6%) was recorded for the inlet MB concentration of 50 mg/L. The slow transport of MB onto WAS was due to the lower concentration gradient and resulted in a slower breakthrough curve (Uddin et al., 2009). Conversely, a higher concentration of MB has been shown to lead to a higher driving force for the MB ions to overcome the mass transfer resistance in the liquid phase (Ahmad and Hameed, 2010). Consequently, quick saturation of the available binding sites for MB has caused the breakthrough time to decrease with the increasing inlet MB concentration. Apart from achieving a quicker breakthrough curve, the adsorption capacity of the bed also increased simultaneously with the increasing initial MB concentration. The highest bed capacity achieved was 20.16 mg/g (at 100 mg/L MB, 0.9 mL/min and a bed height of 6 cm). As the inlet concentration of the feed increases, the loading rate of MB on the bed and the driving force to overcome the mass transfer resistance increases (Goel et al., 2005).

Effect of bed height

The adsorption of MB in the packed bed column is largely dependent on the bed height, which is directly proportional to the quantity of WAS in the column. To produce 3, 6 and 9 cm of bed height, 1.17 g, 2.21 g and 2.85 g of WAS were used, respectively. The adsorption breakthrough curves

obtained by varying the bed heights at a flow rate of 0.9 mL/min and an inlet MB concentration of 50 mg/L. The breakthrough curve is presented in Figure 1(b). Faster breakthrough curves were observed for a bed height of 3 cm, while the slowest breakthrough curve was observed at a bed height of 9 cm. The bed capacity (q_e) increased from 10.74 to 12.5 mg/g when the bed height increased from 3 to 9 cm. Higher beds contain more adsorbent; therefore, more binding sites will be available for the MB to attach (Zulfadhly et al., 2001), which will eventually lead to the attainment of a higher bed capacity. Additionally, an increased bed height resulted in more contact time being available for the MB to interact with the adsorbent (Han et al., 2009). This phenomena has allowed the MB molecules to diffuse deeper into the adsorbent. Subsequently, the percentage of dye removal increased when the bed height was increased.

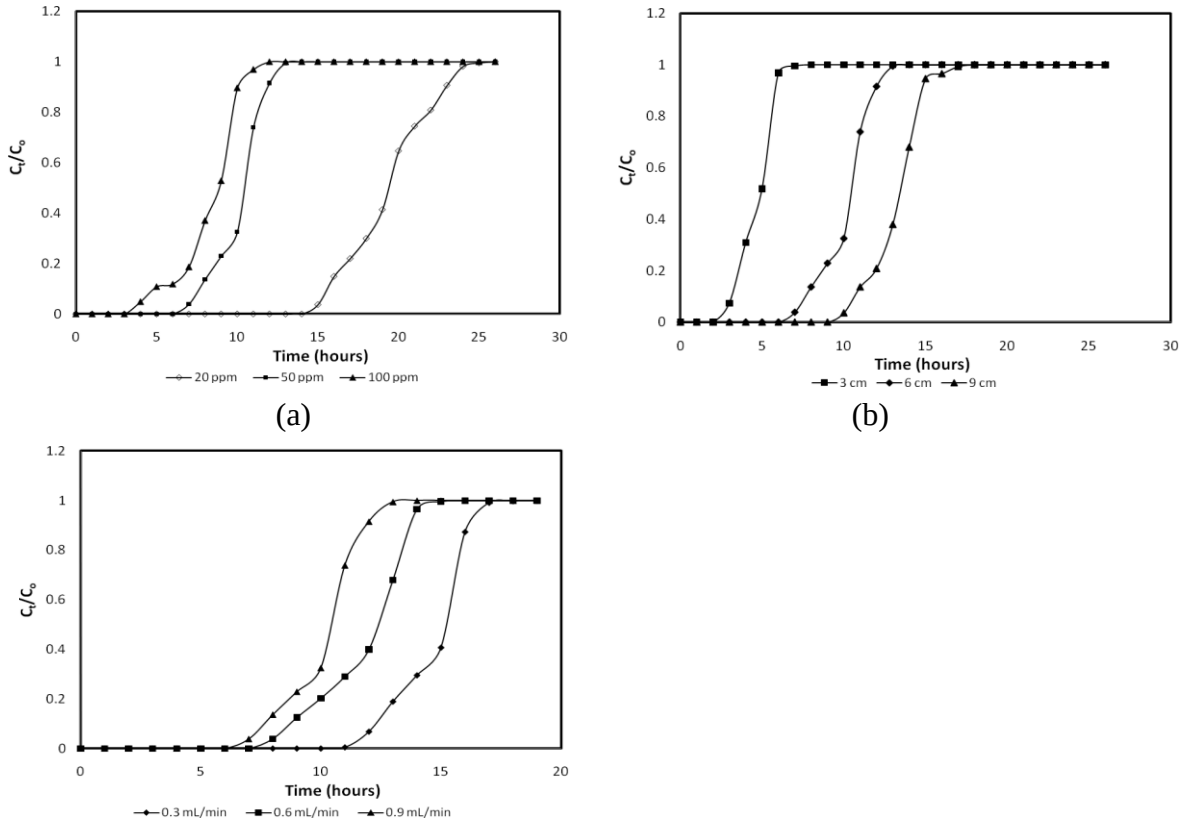

Figure 1 : Breakthrough curve for WAS at (a) Different inlet concentration (Q = 0.9 mL/min and H = 6 cm) (b) Different bed height (C_o = 50 mg/L and Q = 0.9 mL/min) and (c) Different flow rate (C_o = 50 mg/L and H = 6 cm)

Effect of flow rate

The effect of flow rate on MB adsorption by WAS was investigated by varying the flow rate of the MB inlet solution from 0.3 to 0.9 mL/min while maintaining the initial MB concentration and bed depth at 50 mg/L and 6 cm, respectively. A plot of the MB concentration versus time at various flow rates is shown in Figure 1(c), which indicates that a quicker breakthrough was achieved for higher flow rates of MB solution and the slowest breakthrough curve was observed for the slowest flow rate (0.3 mL/min) of MB solution. The highest dye removal (82%) was recorded when the flow rate is 0.3 mL/min. When the inlet flow rate increased from 0.3 mL/min to 0.9 mL/min, the bed capacity decreased from 15.00 to

12.40 mg/g. At lower flow rates of MB solution, the contact time between MB ions and adsorbent is greater (Han et al., 2009), which results in a slower breakthrough curve. Conversely, for the higher flowrate, the MB solution will leave the bed before the equilibrium can be reached. This will result in a decreasing amount of MB being adsorbed. Biosorption of 2,4-dichlorophenol in a fixed bed (Wu and Yu, 2008) exhibited a similar trend as was observed in the present study.

Adsorption analysis

Thomas Model

The data obtained from the experiment were fitted to the Thomas model using Equation 4. From the analysis, it can be deduced that all of the factors (the inlet MB concentration, flow rate and bed height) affect the Thomas rate constant (k_{TH}) and the equilibrium of MB uptake (q_e). The inlet MB concentration and bed height influnce the k_{TH} and q_e in a similar pattern. When the inlet MB concentration increased from 20 mg/l to 100 mg/l, the k_{TH} decreased from 0.65 to 0.17 mL/min.mg while the q_e increased from 9.61 to 19.7 mg/g. Whereas, when the bed height increased from 3 cm to 9 cm, the k_{TH} decreased from 0.64 to 0.4 mL/min.mg and the q_e increased from 10.7 to 12.59 mg/g. Similarly, when the flow rate increased from 0.3 ml/min to 0.9 mL/min, k_{TH} value decreased from 0.48 to 0.4 mL/min.mg and the q_e increased from 5.94 to 12.11 mg/g. These findings could be attributed to the higher driving force of the higher inlet MB concentration (Padmesh et al., 2005). The R^2 values were greater than 0.892, which validates the use of Thomas model to predict the maximum adsorption capacity of the bed. As such, the Langmuir isotherm is applicable to explain the adsorption of MB by WAS in a continuous column (Rao and Viraraghavan, 2002).

Adam's - Bohart Model

A plot of ln (C_t/C_o) against time (t) (Equation 5) was used to calculate the values of N_o and k_{AB}. The results indicate that N_o had no definite pattern when the inlet MB concentration, flow rate and bed height were increased, while the k_{AB} values decreased from 0.70 to 0.13 mL/min.mg when the inlet MB concentrations increased from 20 to 100 mg/L. Hence, it can be concluded that the overall kinetics in the initial part of the adsorption process were dominated by external mass transfer (Aksu and Gönen, 2004). As for the R^2, the values show distribution between 0.787 and 0.948. Nevertheless, most of the R^2 are less than 0.9, which indicates that the data does not fit into the model perfectly. As a result, it can be confirmed that the Adam's – Bohart model is unsuitable to explain the overall adsorption kinetics in the column.

Yoon-Nelson Model

Equation 6 was used to determine the rate velocity constant (k_{YN}) and time required to achieve 50% breakthrough (τ). The results indicate that the k_{YN} value decreased from 0.032 to 0.020 l/min and the τ value increased from 278.19 to 797.50 min when the bed height was increased from 3 cm to 9 cm. The linear regression coefficient (R^2) was greater than 0.892 for all of the fitted values in this model, which indicates that this model can be utilized to explain the overall kinetics in the column for the MB adsorption. Moreover, the normalized standard deviation (ε %) shows that the highest deviation of τ from the experiment is only 1.97%. It shows that the Yoon-Nelson model is apt to describe the dynamics of the adsorption in the column. Additionally, these results indicate that the rate of decrease in the adsorption probability of MB onto WAS is directly proportional to the MB adsorption and MB breakthrough on the WAS (Ahmad and Hameed, 2010).

Bed Depth Service Time (BDST)

BDST analysis was done and the linear plot of this model is given in Figure 2. From the graph, the value of N_a and K_a value could be determined. The values obtained from the graph are presented in Table 1. From the Table 1, the trend of the N_a and K_a value could be determined. As the C_t/C_o value increased, the N_a and K_a value increased. Besides that, the correlation coefficient value (R^2) shows this model is applicable as all the values are above (0.96). The constants obtained from this model could be utilized to scaling up process of this fixed bed column (Han et al., 2007).

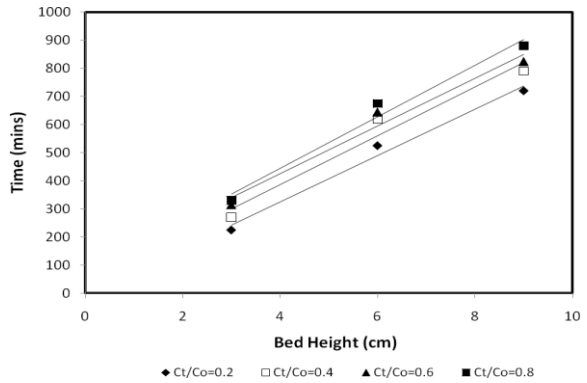

Figure 2 : Bed depth service time of column at different bed height (C_o = 50 mg/l and Q = 0.9 ml/min)

Table 1 : Bed depth service time (BDST) constants for the column at different bed height

C_t/C_o	N_a (mg/l)	K_a (l/mg.min)	F (cm/min)	R^2
0.2	2103.75	-0.005550	0.51	0.9852
0.4	2210.09	0.000203	0.51	0.9616
0.6	2167.50	-0.000095	0.51	0.9720
0.8	2337.59	-0.000350	0.51	0.9789

CONCLUSION

Based on the analysis conducted in this study, the WAS from POME treatment plants can be used as an adsorbent in a continuous column to remove MB. Experimental data confirmed that the bed height (based on initial weight of the adsorbent loaded), inlet MB concentration and flow rate have a significant influence on MB adsorption by WAS. The main outcomes of this study are:

- Both breakthrough time and exhaustion time increases with increasing bed height, but decreases with increasing MB inlet concentration. Additionally, the breakthrough curve became steeper when the flow rate increased. The breakpoint time and exhaustion time decreases with increasing flow rate.
- The highest uptake capacity was obtained when a 6 cm bed depth was used at an inlet concentration of 100 mg/L and a flow rate of 0.9 mL/min, but the dye removal was only about 70%.
- In this column study, an optimal flow rate of 0.3 mL/min with a packing height of 6 cm (C_o = 50 mg/L) was found to be the most effective combination, which removed 82% of the MB.
- The experimental data showed a better fit to the Thomas and Yoon-Nelson adsorption model. Hence, these models can be used to describe the behavior of the adsorption of MB in a continuous column using WAS. Besides that, the BDST model is apt to describe the adsorption of MB by WAS inside this column.

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