

## EQUILIBRIUM AND KINETIC STUDIES OF METHYLENE BLUE ADSORPTION ON ACTIVATED CARBON PREPARED FROM OIL PALM EMPTY FRUIT BUNCH

I. A. W. Tan, A. L. Ahmad and B. H. Hameed

School of Chemical Engineering, University of Science Malaysia, Engineering Campus,  
14300 Nibong Tebal, Penang, MALAYSIA.

(chbassim@eng.usm.my)

**ABSTRAK :** *Tandan buah kosong kelapa sawit (EFB), sejenis bahan buangan pertanian yang banyak terdapat di Malaysia, telah digunakan untuk menyediakan karbon teraktif dengan kaedah pengaktifan fisiokimia. Bahan mentah yang telah dirawat dikarbonkan di bawah keadaan lengai, diikuti dengan rawatan kimia yang menggunakan potasium hidroksida serta pengaktifan fizikal yang menggunakan karbon dioksida. Analisis mikroskop elektron pengimbasan menunjukkan bahawa karbon teraktif yang disediakan adalah porous dengan liang-liang yang berkembang dengan baik. Isoterma penjerapan metilena biru (MB) pada karbon teraktif ditentukan daripada eksperimen kelompok pada suhu 30°C dengan kepekatan awal MB dari 50 hingga 500 mg/l. Data keseimbangan dimasukkan ke dalam model-model isoterma Langmuir, Freundlich, Temkin dan Dubinin-Radushkevich. Data keseimbangan diwakilkan terbaik oleh model isoterma Langmuir, dengan kapasiti penjerapan ekalapis maksimum sebanyak 303.03 mg/g. Data kinetik telah dianalisis dengan menggunakan model-model 'pseudo-first-order', 'pseudo-second-order' dan 'intraparticle diffusion'. Model 'pseudo-second-order' adalah model yang terbaik menerangkan kinetik penjerapan tersebut, memberikan jumlah perbezaan kuasa dua yang terendah sebanyak 4.77%, serta pemalar-pemalar kinetik bernilai 0.002-2.624 g/mg h. Prestasi penjerapan bagi karbon teraktif yang disediakan daripada EFB ke atas MB adalah setanding dengan karbon teraktif komersial.*

**ABSTRACT :** Oil palm empty fruit bunch, an abundant agricultural waste product in Malaysia, was used to prepare activated carbon by physiochemical activation method. The pre-treated precursor was first carbonized under inert atmosphere, followed by chemical treatment using potassium hydroxide and physical activation using carbon dioxide. Scanning electron microscopy analysis showed that the activated carbon was porous with well developed pores. Adsorption isotherm of methylene blue onto the activated carbon was determined by batch tests at 30°C with initial concentrations of methylene blue ranging from 50 to 500 mg/l. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The equilibrium data were best represented by the Langmuir isotherm model, with maximum monolayer adsorption capacity of 303.03 mg/g. The kinetic data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The pseudo-second-order kinetic model was the best applicable model to describe the adsorption kinetics, giving the lowest sum of squared errors of 4.77%, with kinetic constants of 0.002-2.624 g/mg h. The adsorption performance of the empty fruit bunch-based activated carbon on methylene blue was comparable to commercially available activated carbon.

**KEYWORDS :** Adsorption, empty palm fruit bunch, activated carbon, methylene blue, Langmuir isotherm, pseudo-second-order kinetic model.

## INTRODUCTION

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons (Métivier-Pignon *et al.*, 2003). Industries such as textile, leather, paper and plastics produce dye effluents. It is estimated that more than 100,000 commercially available dyes with over  $7 \times 10^5$  tons of dye-stuff are produced annually (Lee *et al.*, 2006). Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk. MB can cause harmful effects where acute exposure to it will cause increased heart rate, vomiting, shock, Heinz body formation, jaundice, quadriplegia and tissue necrosis in humans (Vasanth Kumar and Kumaran, 2005). Therefore, the treatment of effluent containing such dye is of interest due to its harmful impact on receiving waters.

In general, dyes are poorly biodegradable or resistant to environmental conditions (Tsai *et al.*, 2001). Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design. However, commercially available activated carbons are still considered expensive (Sourja *et al.*, 2005). This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications (Martin *et al.*, 2003). 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 cassava peel (Rajeshwarisivaraj *et al.*, 2001), bagasse (Tsai *et al.*, 2001), date pits (Girgis and El-Hendawy, 2002), maize cob (Kadirvelu *et al.*, 2003) and jute fiber (Senthilkumaar *et al.*, 2005).

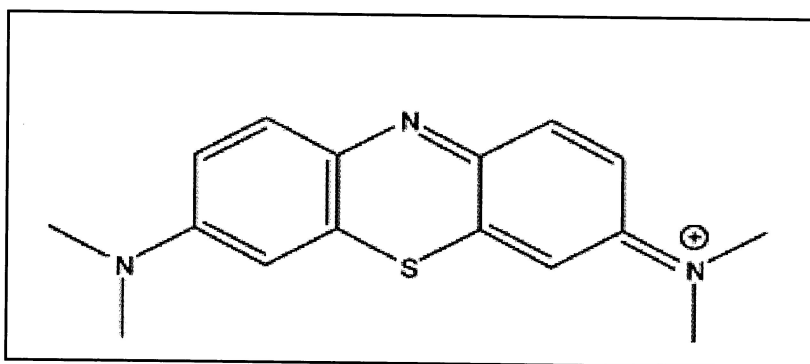
At present, Malaysia is the largest exporter of palm oil in the international market. One of the significant problems in the palm fruit processing is managing of the wastes generated during the processes. Approximately 15 million tons of oil palm empty fruit bunch (EFB) biomass waste is generated annually throughout Malaysia by palm oil mills (Rahman *et al.*, 2006). In practice this biomass is burned 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 make it into activated carbon. Not many studies have been done on converting EFB into activated carbon. Conversion of EFB 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. The focus of this research was to evaluate the adsorption potential of EFB-based activated carbon on MB dye. The surface morphology of the prepared activated carbon was examined. The equilibrium and kinetic data of the adsorption process were then studied to understand the adsorption mechanism of MB molecules onto the prepared activated carbon.

## MATERIALS AND METHODS

### Methylene blue

Methylene blue (MB) which corresponds to methylene blue hydrochloride with three groups of water, with molecular weight of 373.9 g/mol, was used as an adsorbate and was not purified prior to use. Deionized water was used to prepare all the solutions and reagents. Chemical structure of MB is shown in Figure 1.



**Figure 1.** Chemical structure of methylene blue dye

### Preparation and characterization of activated carbon

EFB used for preparation of activated carbon was obtained from a local palm oil mill. The precursor was first washed and soaked in n-hexane to remove dirt and oil. Then, it was dried and cut into the size of 1-2 mm. The pre-treated precursor was then carbonized at 700°C under purified nitrogen (99.995%) flow of 150 cm<sup>3</sup>/min for 2 h (first pyrolysis) in a stainless steel vertical tubular reactor placed in a tube furnace. The schematic diagram of the experimental setup is shown in Figure 2. The char produced was then soaked in potassium hydroxide (KOH) solution with an impregnation ratio of 1:1. The mixture was then dehydrated in an oven overnight at 105°C and then activated under the same condition as carbonization, but to a final temperature of 850°C. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide (CO<sub>2</sub>) and activation was held for 2 h. The activated product was then cooled to room temperature and washed with hot deionized water and hydrochloric acid of 0.1 molar until the pH of the washing solution reached 6-7. Scanning electron microscopy (SEM) analysis was carried out on the prepared activated carbon to study the surface morphology and to verify the presence of porosity.

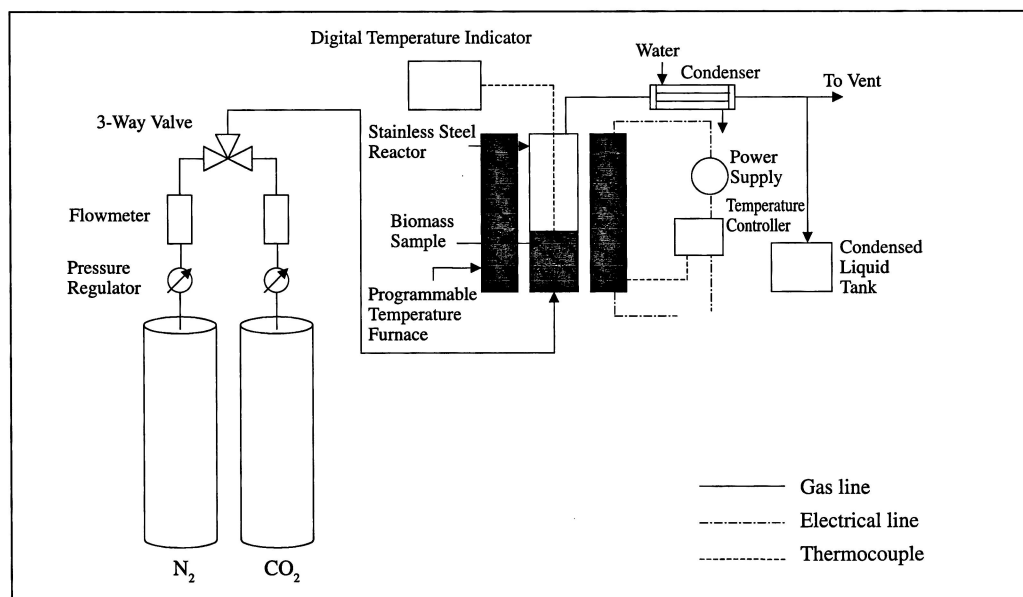


Figure 2. Schematic diagram of the experimental setup

### Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 ml) where 100 ml of MB solutions with initial concentrations of 50-500 mg/l were placed in these flasks. Equal mass of 0.1 g of the prepared activated carbon with particle size of 200  $\mu\text{m}$  was added to each flask and kept in an isothermal shaker of 120 rpm at 30°C for 48 h to reach equilibrium. The pH of the solutions was around 6.5 without any pH adjustment. Aqueous samples were taken from the solutions and the concentrations were analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. Each experiment was duplicated under identical conditions. The concentrations of MB in the supernatant solutions before and after adsorption were determined using a double beam UV spectrophotometer (Shimadzu, Japan) at 668 nm. The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by :

$$q_e = \frac{(C_o - C_e) V}{W} \quad (1)$$

where  $C_o$  and  $C_e$  (mg/l) are the liquid-phase concentrations of MB at initial and equilibrium, respectively.  $V$  is the volume of the solution (l) and  $W$  is the mass of dry adsorbent used (g).

## **Batch kinetic studies**

The procedure of kinetic tests was basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of MB were similarly measured. The amount of adsorption at time  $t$ ,  $q_t$  (mg/g), was calculated by :

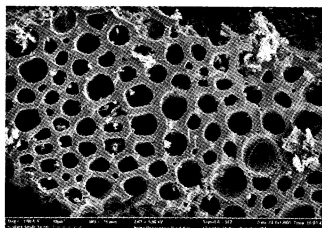
$$q_t = \frac{(C_o - C_t)V}{W} \quad (2)$$

where  $C_o$  and  $C_t$  (mg/l) are the liquid-phase concentrations of MB at initial and at any time  $t$ , respectively.  $V$  is the volume of the solution (l) and  $W$  is the mass of dry adsorbent used (g).

## **RESULTS AND DISCUSSION**

### **Characterization of prepared activated carbon**

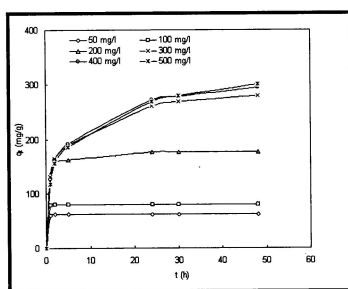
Figure 3 shows the SEM image of the derived activated carbon. Many large and well-developed pores in a honeycomb shape were clearly found on the surface of the activated carbon. This might be due to the activation process used, which involved both chemical and physical activating agents of KOH and CO<sub>2</sub>. Pore development in the char during pyrolysis was also important as this would enhance the surface area and pore volume of the activated carbon by promoting the diffusion of KOH and CO<sub>2</sub> molecules into the pores, thereby increasing the KOH-carbon and CO<sub>2</sub>-carbon reactions, which would then create more pores in the activated carbon. Stavropoulos and Zabaniotou (2005) stated that KOH is dehydrated to K<sub>2</sub>O, which reacts with CO<sub>2</sub> produced by the water-shift reaction, to give K<sub>2</sub>CO<sub>3</sub>. Intercalation of metallic potassium appeared to be responsible for the drastic expansion of the carbon material and hence the creation of a large surface area and high pore volume.



**Figure 3.** SEM image of EFB-based activated carbon (x1000)

### Effect of contact time and initial dye concentration on adsorption equilibrium

Figure 4 shows the adsorption capacity versus the adsorption time at various initial MB concentrations at 30°C. It indicated the contact time needed for MB solutions with initial concentrations of 50-200 mg/l to reach equilibrium ranged between 1-5 h. For MB solutions with initial concentrations of 300-500 mg/l, equilibrium time of 24 h was required. As can be seen from Figure 4, the amount of MB adsorbed onto the activated carbon increased with time and, at some point in time, it reached a constant value beyond which no more MB was further removed from the solutions. At this point, the amount of the dye desorbing from the activated carbon was in a state of dynamic equilibrium with the amount of the dye being adsorbed onto 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 ( $q_e$ ) increased from 62 to 300 mg/g with an increase in the initial dye concentrations from 50 to 500 mg/l.



**Figure 4.** The variation of adsorption capacity with adsorption time at various initial MB concentrations

Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent (Faust and Aly, 1983). First, the adsorbate migrates through the solution, i.e., film diffusion, followed by solute movement from particle surface into interior site by pore diffusion and finally the adsorbate is adsorbed into the active sites at the interior of the adsorbent particle. This phenomenon takes relatively long contact time. A similar phenomenon was observed for the adsorption of methylene blue from aqueous solution on jute fiber carbon and the equilibrium time was 250 min (Senthilkumaar *et al.*, 2005).

### Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The

analysis of the isotherm data by fitting them to 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 : the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The applicability of the isotherm models to the adsorption study done was judged by the correlation coefficients,  $R^2$  value of each plot. The higher the  $R^2$  value, the better the fit.

### **Langmuir isotherm**

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Weber and Chakkravorti, 1974). The linear form of Langmuir isotherm equation is given as :

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \quad (3)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg/l),  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $Q_o$  and  $b$  are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When  $C_e/q_e$  was plotted against  $C_e$ , a straight line with slope of  $1/Q_o$  was obtained, as shown in Figure 5. The Langmuir constants  $b$  and  $Q_o$  were calculated from Eq. (3) and their values are shown in Table 1, together with the  $R^2$  value. The  $R^2$  value of 0.999 indicated that the adsorption data of MB onto the prepared activated carbon was well fitted to the Langmuir isotherm model.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ( $R_L$ ) (Weber and Chakkravorti, 1974), which is defined by :

$$R_L = \frac{1}{1 + bC_o} \quad (4)$$

where  $b$  is the Langmuir constant and  $C_o$  is the highest dye concentration (mg/l). The value of  $R_L$  indicates the type of the isotherm to be either favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ) or irreversible ( $R_L = 0$ ). The value of  $R_L$  was found to be 0.002 and this again confirmed that the Langmuir isotherm model was favorable for adsorption of MB onto the EFB-based activated carbon under the conditions used in this study.

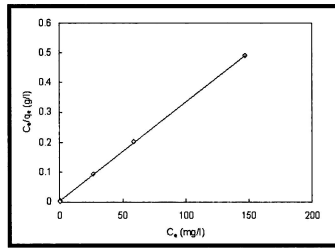


Figure 5. Langmuir adsorption isotherm of MB onto activated carbon

### Freundlich isotherm

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (Weber and Chakkravorti, 1974). The well-known logarithmic form of Freundlich isotherm is given by the following equation :

$$\log q_e = \log K_F + (1/n)\log C_e \quad (5)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg/l),  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g),  $K_F$  and  $n$  are Freundlich constants with  $n$  giving an indication of how favorable the adsorption process and  $K_F$  ( $\text{mg/g (l/mg)}^{1/n}$ ) is the adsorption capacity of the adsorbent.  $K_F$  can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon for a unit equilibrium concentration. The slope of  $1/n$  ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu, 1998). A value for  $1/n$  below one indicates a normal Langmuir isotherm while  $1/n$  above one is indicative of cooperative adsorption (Fytianos *et al.*, 2000). The plot of  $\log q_e$  versus  $\log C_e$  gave a straight line with slope of  $1/n$  with value of 0.21 (Figure 6), indicating a normal Langmuir isotherm. Freundlich constants  $K_F$  and  $n$  were also calculated and are listed in Table 1.

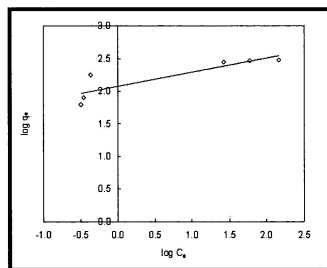


Figure 6. Freundlich adsorption isotherm of MB onto activated carbon



**Table 1.** Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm model constants and correlation coefficients for adsorption of MB onto prepared activated carbon at 30°C

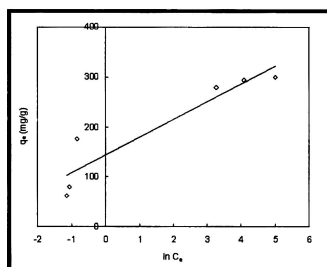
Isotherms	Constants		Correlation Coefficients, R <sup>2</sup>
Langmuir	Q <sub>o</sub> 303.03 mg/g	b 0.83 l/mg	0.999
Freundlich	K <sub>F</sub> 119.43 mg/g (l/mg) <sup>1/n</sup>	1/n 0.21	0.770
Temkin	A 55.18 l/g	B 35.69	0.881
Dubinin-Radushkevich	q <sub>s</sub> 302.60 mg/g	E 2236.07	0.899

### Temkin Isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions (Hosseini *et al.*, 2003). The Temkin isotherm has been used in the following form :

$$q_e = (RT/b) \ln(AC_e) \quad (6)$$

where  $RT/b = B$ . A plot of  $q_e$  versus  $\ln C_e$  yielded a linear line, as shown in Figure 7. The constants A and B together with the R<sup>2</sup> value are shown in Table 1.



**Figure 7.** Temkin adsorption isotherm of MB onto activated carbon

### Dubinin-Radushkevich Isotherm

Another popular equation for the analysis of isotherms of a high degree of rectangularity is Dubinin-Radushkevich isotherm (Rengaraj *et al.*, 2004) which is as follows :

$$q_e = q_s \exp(-B\varepsilon^2) \tag{7}$$

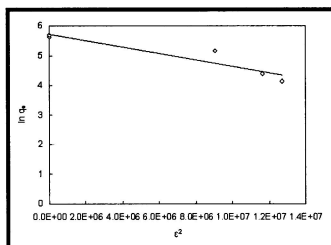
where  $\varepsilon$  can be correlated :

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \tag{8}$$

The constant B gives the mean free energy E of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship :

$$E = \left[ \frac{1}{\sqrt{2B}} \right] \tag{9}$$

where R is the gas constant (8.31 J/mol K) and T is the absolute temperature. A plot of  $\ln q_e$  versus  $\varepsilon^2$  (Figure 8) enables the constants  $q_s$  and E to be determined (Table 1).



**Figure 8.** Dubinin-Radushkevich adsorption isotherm of MB onto activated carbon

From Table 1, the Langmuir isotherm model yielded the best fit with the highest  $R^2$  value compared to the other three models. Conformation of the experimental data into Langmuir isotherm equation indicated the homogeneous nature of EFB-based activated carbon surface, i.e., each dye molecule/EFB 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 prepared activated carbon. Similar observation was reported by the adsorption of MB onto activated carbon prepared from jute fiber (Senthilkumar *et al.*, 2005) and olive-seed waste residue (Stavropoulos and Zabaniotou, 2005).

Table 2 lists the comparison of maximum monolayer adsorption capacity of MB onto various adsorbents. The activated carbon prepared in this work had a relatively large adsorption capacity of 303.03 mg/g compared to some other adsorbents reported in earlier studies (Kannan and Sundaram, 2001; Chakraborty *et al.*, 2002; Senthilkumaar *et al.*, 2005; Vasanth Kumar and Kumaran, 2005; Banerjee and Dastidar, 2005), including commercial activated carbon, F300 (Stavropoulos and Zabaniotou, 2005).

**Table 2.** Comparison of the maximum monolayer adsorption of MB onto various adsorbents

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
Oil palm empty fruit bunch-based activated carbon	303.03	This work
Bamboo dust-based activated carbon	143.20	Kannan and Sundaram, 2001
Coconut shell-based activated carbon	277.90	Kannan and Sundaram, 2001
Groundnut shell-based activated carbon	164.90	Kannan and Sundaram, 2001
Saw dust	133.87	Chakraborty <i>et al.</i> , 2002
Jute fiber-based activated carbon	225.64	Senthilkumaar <i>et al.</i> , 2005
Mango seed kernel powder	142.86	Vasanth Kumar and Kumaran, 2005
Jute processing wastes	22.47	Banerjee and Dastidar, 2005
Olive-seed waste residue-based activated carbon	190.00-263.00	Stavropoulos and Zabaniotou, 2005.
*Filtrisorb F300	240.00	Stavropoulos and Zabaniotou, 2005.

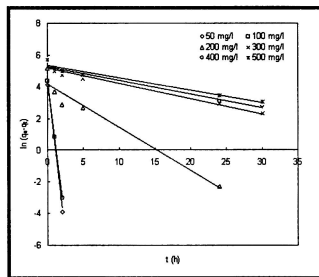
\* Commercial activated carbon

### Adsorption kinetics

The kinetic data of adsorption was analyzed by the pseudo-first-order equation given by Langergren and Svenska (1898) as :

$$\ln (q_e - q_t) = \ln q_e - k_t t \quad (10)$$

where  $q_e$  and  $q_t$  are the amounts of MB adsorbed (mg/g) at equilibrium and at time  $t$  (h), respectively and  $k_1$  ( $h^{-1}$ ) is the rate constant adsorption. Values of  $k_1$  were calculated from the plots of  $\ln(q_e - q_t)$  versus  $t$  (Figure 9) for different initial concentrations of MB. The  $R^2$  values obtained for all MB concentrations were relatively high ( $>0.95$ ), however the deviations of the calculated  $q_e$  values from the experimental  $q_e$  values were relatively large (3.50-110.91 mg/g) indicating that this model was not applicable to the kinetic data.



**Figure 9.** Pseudo-first-order kinetics for adsorption of MB onto activated carbon

On the other hand, the pseudo-second-order equation (Ho and McKay, 1998) based on equilibrium adsorption is expressed as :

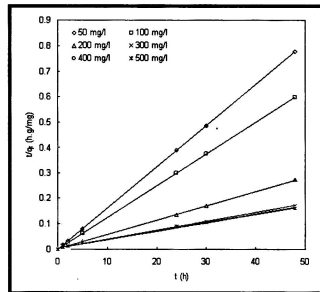
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

where  $k_2$  (g/mg h) is the rate constant of second-order adsorption. The linear plot of  $t/q_t$  versus  $t$ , as shown in Figure 10, yielded  $R^2$  values that were greater than 0.99 for all MB concentrations. It also showed a good agreement between the experimental and the calculated  $q_e$  values, with  $\Delta q_e$  of 0.02-8.61 mg/g, showing the applicability of this model to describe the adsorption process of MB onto the prepared activated carbon.

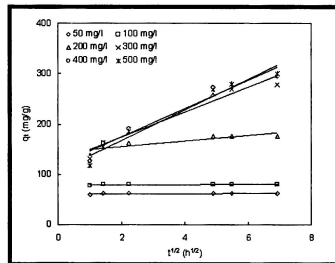
Intraparticle diffusion model based on the theory proposed by Weber and Morris (1962) was tested to identify the diffusion mechanism. According to this theory :

$$q_e = k_p t^{1/2} \quad (12)$$

where  $k_p$  (mg/g  $h^{1/2}$ ), the intraparticle diffusion rate constant, is obtained from the slope of the straight line of  $q_t$  versus  $t^{1/2}$  (Figure 11). The first, sharper portion is the instantaneous adsorption or external surface adsorption. The second portion is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third portion exists, which is the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely



**Figure 10.** Pseudo-second-order kinetics for adsorption of MB onto activated carbon



**Figure 11.** Intraparticle diffusion model for adsorption of MB onto activated carbon

low adsorbate concentrations left in the solutions (Wu *et al.*, 2005). As can be seen from Figure 11, the linear line 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). The  $R^2$  values obtained from intraparticle diffusion model was relatively low (0.30-0.96), showing that this model was not suitable to represent the adsorption process.

### Validity of kinetic models

The adsorption kinetics of MB onto the prepared activated carbon was verified at different initial concentrations. The validity of the three kinetic models was determined by judging the sum of squared errors (SSE, %) given by :

$$SSE = \sqrt{\frac{\sum (q_{e, \text{exp.}} - q_{e, \text{cal.}})^2}{N}} \quad (13)$$

where  $N$  is the number of data points.

The lower the value of SSE indicates the better a fit is. It was found that the pseudo-second-order kinetic model yielded the lowest SSE value of 4.77%, compared to pseudo-first-order kinetic model and intraparticle diffusion model with SSE value of 83.94% and 12.64%, respectively. This agrees with the  $R^2$  values obtained earlier and proves that the adsorption of MB onto the EFB-based activated carbon could be best described by the pseudo-second-order kinetic model which is based on the equilibrium chemical adsorption, that predicts the behaviour over the whole range of studies, strongly supporting the validity and agrees with chemisorption being rate-controlling (Tseng and Tseng, 2005).

## CONCLUSION

The present investigation showed that oil palm empty fruit bunch was a promising precursor to be used in the preparation of activated carbon for the removal of methylene blue dye from aqueous solutions over a wide range of concentrations. MB was found to adsorb strongly onto the surface of the activated carbon. SEM study showed that the prepared activated carbon was porous with well developed pores. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms and the equilibrium data were best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 303.03 mg/g. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model. The adsorption potential of the EFB-based activated carbon on MB was comparable to commercial activated carbon and some other adsorbents reported in earlier studies.

## ACKNOWLEDGMENT

The authors acknowledge the research grant provided by the Ministry of Science, Technology and Innovation (MOSTI), Malaysia under long term IRPA grant (Project No: 08-02-05-1021 EA001).

## REFERENCES

- Banerjee, S. and Dastidar, M.G. (2005). Use of jute processing wastes for treatment of wastewater contaminated with dye and other organics. *Bioresour. Technol.* **96**: pp 1919-1928.
- Chakraborty, S., De, S., Dasgupta, S. and Basu, J.K. (2002). *Removal of dyes from aqueous solution using a low cost adsorbent*. Water and Wastewater Perspectives of Developing Countries, Proceedings of International Conference, New Delhi, India. International Water Association, pp 1089-1096.

El-Guendi, M. (1991). Homogeneous surface diffusion model of basic dyestuffs onto natural clay in batch adsorbers. *Adsorpt. Sci. Technol.* **8** (2): pp 217-225.

Faust, D.S. and Aly, M.O. (1983). *Chemistry of Wastewater Treatment*, Butterworths, Boston.  
Fytianos, K., Voudrias, E. and Kokkalis, E. (2000). Sorption-desorption behavior of 2,4-dichlorophenol by marine sediments. *Chemosphere* **40**: pp 3-6.

Girgis, B.S. and El-Hendawy, A.A. (2002). Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid. *Microporous Mesoporous Mater.* **52**: pp 105-117.

Haghseresht, F. and Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy Fuels* **12**: pp 1100-1107.

Ho, Y.S. and McKay, G. (1998). Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* **70**: pp 115-124.

Hosseini, M., Mertens, S.F.L., Ghorbani, M. and Arshadi, M.R. (2003). Asymmetrical Schiff Bases as Inhibitors of Mild Steel Corrosion in Sulphuric Acid Media. *Mater. Chem. Phys.* **78**: pp 800.

Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N. and Pattabhi, S. (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour. Technol.* **87**: pp 129-132.

Kannan, N. and Sundaram, M.M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-a comparative study. *Dyes and Pigments* **51**: pp 25-40.

Langergren, S. and Svenska, B.K. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. *Veternskapsakad Handlingar* **24** (4): pp 1-39.

Lee, J.W., Choi, S.P., Thiruvengkatachari, R., Shim, W.G. and Moon, H. (2006). Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes. *Dyes Pigments* **69**: pp 196-203.

Martin, M.J., Artola, A., Balaguer, M.D. and Rigola, M. (2003). Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. *Chem. Eng. J.* **94**: pp 231-239.

Métivier-Pignon, H., Faur-Brasquet, C. and Cloirec, P.L. (2003). Adsorption of dyes onto activated carbon cloths: approach of adsorption mechanisms and coupling of ACC with ultrafiltration to treat coloured wastewaters. *Sep. Purif. Technol.* **31**: pp 3-11.

Mohanty, K., Das, D. and Biswas, M.N. (2005). Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by  $ZnCl_2$  activation. *Chem. Eng. J.* **115**: pp 121-131.

Rahman, S.H.A., Choudhury, J.P. and Ahmad, A.L. (2006). Production of xylose from oil palm empty fruit bunch fiber using sulfuric acid. *Biochem. Eng. J.* **30** (1): pp 97-103.

Rajeshwarisivaraj, Sivakumar, S., Senthilkumar, P. and Subburam, V. (2001). Carbon from Cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from aqueous solution. *Bioresour. Technol.* **80**: pp 233-235.

Rengaraj, S., Kim, Y., Joo, C.K., Choi, K. and Yi, J. (2004). Batch adsorptive removal of copper ions in aqueous solutions by ion exchange resins: 1200H and IRN97H. *Korean J. Chem. Eng.* **21** (1): pp 187-194.

Senthilkumaar, S., Varadarajan, P.R., Porkodi, K. and Subbhuraam, C.V. (2005). Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies. *J. Colloid Interface Sci.* **284**: pp 78-82.

Sourja, C., Sirshendu, D., Sunando, D. and Jayanta, K.B. (2005). Adsorption study for the removal of basic dye: experimental and modeling. *Chemosphere* **58**: pp 1079-1086.

Stavropoulos, G.G. and Zabaniotou, A.A. (2005). Production and characterization of activated carbons from olive-seed waste residue. *Microporous Mesoporous Mater.* **82**: pp 79-85.

Tsai, W.T., Chang, C.Y., Lin, M.C., Chien, S.F., Sun, H.F. and Hsieh, M.F. (2001). Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by  $ZnCl_2$  activation. *Chemosphere* **45**: pp 51-58.

Tseng, R.L. and Tseng, S.K. (2005). Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob. *J. Colloid Interface Sci.* **287**: pp 428-437.

Vasanth Kumar, K. and Kumaran, A. (2005). Removal of methylene blue by mango seed kernel powder. *Biochemical Engineering Journal* **27**: pp 83-93.

Weber, T.W. and Chakkravorti, R.K. (1974). Pore and solid diffusion models for fixed-bed adsorbers. *AIChE J.* **20**: pp 228.



Weber, W.J. and Morris, J.C., in: Proc. Int. Conf. Water Pollution Symposium, vol. 2, Pergamon, Oxford, 1962, pp 231-266.

Wu, F.C., Tseng, R.L. and Juang, R.S. (2005). Comparisons of porous and adsorption properties of carbons activated by steam and KOH. *J. Colloid Interface Sci.* **283**: pp 49-56.