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Equilibrium Modeling, Kinetic and Thermodynamic Studies on the Adsorption of Basic Dye by Low-Cost Adsorbent

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ABSTRACT

In this study, the removal of methylene blue (MB) dye from aqueous solutions using low-cost material as adsorbent by a batch system was investigated. Experiments were carried out as a function of contact time, initial concentration (50–300 mg/L), pH (2–12) and temperature (303–323K). The equilibrium adsorption of MB dye on petai (*Parkia speciosa*) seed adsorbent was analyzed by Langmuir and Freundlich models. The results indicate that the Freundlich model provides the best correlation of the experimental data. The adsorption capacities of the petai seed adsorbent for removal of MB dye was determined with the Langmuir equation and found to be 91.74, 94.34 and 100.03 mg/g at 303, 313, and 323 K, respectively. The kinetic data was found to follow closely the pseudo-second-order model. Various thermodynamic parameters such as enthalpy (ΔH^o), entropy (ΔS^o) and free energy (ΔG^o) were evaluated. The positive value of the enthalpy change (17.89 kJ/mol) indicates that the adsorption is endothermic process. The results indicate that petai seed adsorbent is suitable as adsorbent material for adsorption of MB dye from aqueous solutions.

***Keywords*: Adsorption; Methylene blue; Petai (*Parkia speciosa*) seed; Isotherm; Kinetics; Thermodynamic**

1. Introduction

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored (Kadirvelu et al., 2003). Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing and also from food colouring, cosmetics, paper and carpet industries (Sun et al., 2010). Wastewater containing dyes from the textile industry is very difficult to treat using conventional wastewater treatment methods, which are coagulation, ultrafiltration, ozonation, oxidation, sedimentation, reverse osmosis, flotation, precipitation, etc., due to economic considerations (Eren et al., 2010). Adsorption technology has been used extensively in industrial processes for many purposes of separation and purification.

The removal of coloured and colourless organic pollutants from industrial wastewater is considered as an important application of adsorption process using suitable adsorbents

(Moussavi and Khosravi, 2011). The design and efficient operation of adsorption processes require equilibrium adsorption data for use in kinetic and mass transfer models. These models can then be used to predict the performance of the adsorption contact processes under a range of operating conditions.

The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems. The adsorption isotherm is also an invaluable tool for the theoretical evaluation and interpretation of thermodynamic parameters, such as heats of adsorption. An isotherm may fit experimental data accurately under one set of conditions but fail entirely under another. Langmuir, Freundlich are the main requirements for the design of adsorption systems. Basic dyes have been classified as toxic colorants. The most important basic dye is methylene blue, discovered by Caro in 1878. Methylene blue (3, 7-bis (Dimethylamino)-phenazathionium chloride Tetramethylthionine chloride) is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution like electrolytes into methylene blue cation and the chloride ion.

The coloured cation is adsorbed by several adsorbents preferentially to a very great extent (Sastri, 1942). For that reason, methylene blue was selected to be the adsorbate in this research. It may be mutagenic and carcinogenic and can cause severe damage to human beings, such as dysfunction of the kidneys, reproductive system, liver, and brain and central nervous system (Kadirvelu et al., 2003). The use of low-cost adsorbents as a replacement for costly methods of removing dyes from solution has increased during the last years such as rice husk (Vadivelan and Kumar, 2005), bagasse (Tsai et al., 2001), palm ash (Ahmad et al., 2007), coconut bunch waste (Hameed et al., 2008a), pumice powder (Feryal, 2005), wheat straw (Han et al., 2010), pomelo peel (Hameed et al., 2008b), bamboo-based activated carbon (Liu et al., 2010) banana stalk (Hameed et al., 2008c) and peanut hull (Tanyildizi, 2011).

The main purpose of the present study is the removal of methylene blue onto petai (*Parkia speciosa*) seed adsorbent from aqueous solutions under different experimental conditions. The effects of solution pH, dye concentration, contact time and solution temperature were studied for MB removal. The isotherm, kinetics and thermodynamics of MB adsorption were also evaluated.

2. Materials and methods

2.1. Materials

Methylene blue supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all the solutions and reagents. MB was chosen in this study because of its known strong adsorption onto solids. MB has a molecular mass of 373.9 g/mol, which corresponds to methylene blue hydrochloride with three groups of water. Chemical structure of MB is shown in Fig.1.

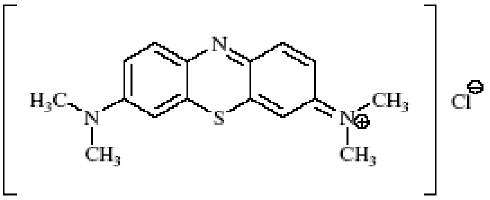

Fig.1. Chemical structure of MB

Petai (*Parkia speciosa*) seed used in this work was obtained locally. The adsorbent was first washed with distilled water for several times to remove all the dirt particles from its surface and then was dried overnight at 105 °C. It was crushed, ground, sieved through a 200-300 µm size sieve and dried in an oven at 60 °C for 12 h before use. The adsorbent was used directly for adsorption experiments without any treatment.

2.2. Analytical measurements

Concentrations of MB were determined by finding out the absorbance at the characteristic wavelength using a UV-Visible spectrophotometer (UV-1601 Shimadzu, Japan). A standard solution of the dye was taken and the absorbance was determined at different wavelengths to obtain a plot of absorbance versus wavelength. The wavelength corresponding to maximum absorbance (λ_{max}) as determined from this plot was 668 nm. This wavelength was used for preparing the calibration curves between absorbance and the concentration of the dye solution.

2.3. Batch equilibrium experiments

The adsorption of MB from aqueous solution onto petai seed was performed using batch equilibrium technique. For the determination of adsorption isotherms, 100 ml of dye solution of known initial concentration (50–300 mg/L) was shaken with a certain amount of the adsorbent (0.3 g) on a shaker. The conical flasks were then sealed and placed in a water bath shaker and shaken at 125 rpm with a required adsorbent time at 303, 313, and 323 K and pH 6.8. The effect of pH was investigated at temperature 303 K and initial concentration 100 mg/L. pH adjustments have been done using solutions of 1.0M NaOH and 1.0M HCl. The initial and equilibrium MB concentrations were determined using a double beam UV-Visible spectrophotometer (UV-1601 Shimadzu, Japan) at 668 nm. The

2.4. Batch kinetic experiments

The procedure of kinetic tests was basically identical to those of equilibrium tests. Adsorption tests were performed in a set of Erlenmeyer flasks (250 mL) where 100 ml of MB solutions with initial concentrations of 50–300 mg/L were placed in these flasks. Equal mass of 0.3 g of the petai (*Parkia speciosa*) seed adsorbent with particle size of 100-200 µm was added to each flask and kept in an isothermal shaker at 303K. The aqueous samples were taken at preset time intervals and the concentrations of MB were similarly measured. Dye concentrations were determined at time zero and at subsequent times using a calibration curve based on absorbance at λ_{max} 668 nm UV-Visible spectrophotometer versus dye concentration in standard MB dye solutions. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{1}$$

where C_o and C_t (mg/L) are the liquid phase concentrations of dyes initially and at time t , respectively.

3. Results and discussion

3.1. Effects of agitation time and concentration of dye on adsorption

Effects of agitation time and dye concentration on removal of MB by petai (*Parkia speciosa*) seed adsorbent at 303K are presented in Fig. 2. The percentage of dye removal is dependent on the initial amount of dye concentration (Mohd Salleh et al., 2011a).

The amount of dye adsorbed (mg/g) increased with increase in agitation time and reached equilibrium after 210 min for the dye concentrations 50, 100, 250, 200 and 300 mg/L used in this study. The adsorption capacity at equilibrium (q_e) increased from 16 to 82 mg/g with an increase in the initial dye concentrations from 50 to 500 mg/L, respectively. It is clear that the removal of dyes depends on the concentration of the dye. When the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher adsorption of MB. Fig. 2 also shows that most of the dye is adsorbed to achieve adsorption equilibrium in about 210 min, although the data were measured for 300 min. The time required to attain this state of equilibrium is termed equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operation conditions.

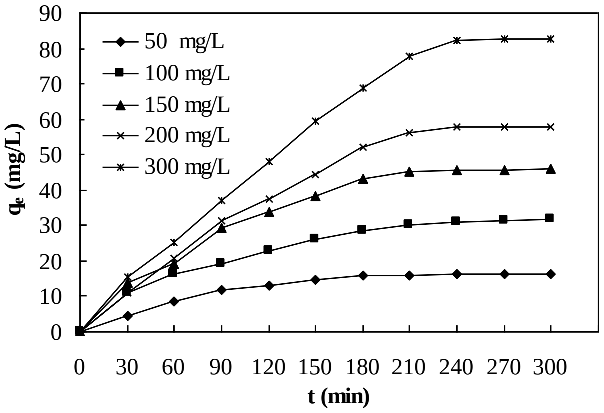

Fig.2. The variation of adsorption capacity with adsorption time at various initial MB concentrations at 303 K (pH 6.8, W = 0.3 g, V = 100 mL)

3.2. Effect of pH on adsorption

Dependence of dye adsorption on pH is shown in Fig. 3. Dye adsorption efficiency is affected by pH variation. The adsorption of MB increased with an increase pH. The optimum pH for the adsorption of MB was found to be in the range 6–10. This can be explained by considering the electrostatic attraction that exists between the negatively charged surface of the adsorbent and MB, a cationic dye. Lower adsorption at acid pH was probably due to the presence of excess of H^+ ions competing with the dye cations for adsorption sites. At alkaline pH, the numbers of positively charged sites decrease and the number of negatively charged sites increase which favors the removal of the cationic dye. Similar trends were observed for the adsorption of methylene blue onto Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2005), malachite green onto agro-industry waste (Garg et al., 2004) and methylene blue onto various carbons (Kannan and Sundaram, 2001).

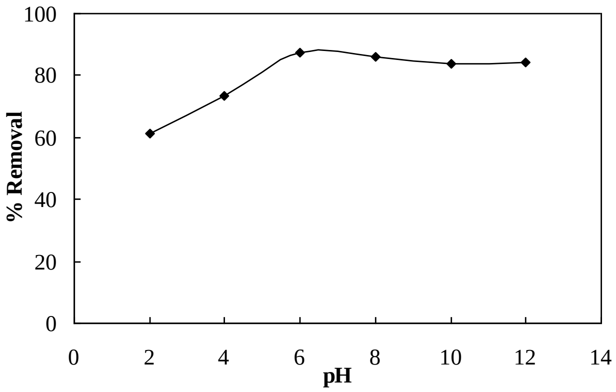

Fig.3. Effect of pH on the adsorption of MB onto petai (*Parkia speciosa*) seed adsorbent (T = 303 K, C_o = 100 mg/L, W= 0.3 g, V = 100 mL, contact time = 200 min).

3.3. Effect of temperature

The effect of temperature on adsorption of MB on the petai (*Parkia speciosa*) seed adsorbent was investigated by varying the adsorption temperature at 303, 313 and 323 K. An increase in the temperature from 303 to 323 K leads to an increase in the adsorption capacity from 91.74 to 100.03 mg/g at an equilibrium time, indicating the endothermic nature of the adsorption reaction. This causes the amount of material to be adsorbed on the surface to increase. Increase in temperature also decreases the activation energy barrier there by increasing the rate of adsorption (Shukla et al., 2002). The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbate and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of MB molecules into adsorbent at higher temperatures (Karthikeyan et al., 2005).

3.4. Adsorption isotherms

In order to optimize the design of an adsorption system to remove basic dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. In this respect, the equilibrium experimental data for adsorbed MB on petai (*Parkia* *speciosa*) seed adsorbent was compared using two most commonly used equilibrium relations are Freundlich and Langmuir isotherm equations.

The Langmuir adsorption, which is the monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance, and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The Langmuir equation is given in the following equation (Langmuir, 1918):

$$q_e = \frac{q_o K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), q_o the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg/g), C_e the concentration of adsorbate at equilibrium (mg/L) and K_L is the Langmuir constant (L/mg). Eq. (3) can be rearranged to a linear form:

$$C_e / q_e = 1 / K_L q_o + C_e / q_o \tag{3}$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (as shown in Fig. 4). It was observed that the equilibrium adsorption data followed Langmuir's isotherm. Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of petai (*Parkia speciosa*) seed surface, i.e. each dye molecule/ petai seed adsorption has equal adsorption activation energy and demonstrates the formation of monolayer coverage of dye molecule on the outer surface of petai seed adsorbent. From Table 1 the R^2 value ≥ 0.94 indicated that the adsorption data of MB onto the petai seed adsorbent at all the three temperatures studied were good fitted to the Langmuir isotherm model. The maximum monolayer adsorption capacity of MB onto the petai adsorbent increased from 91.74 to 100.03 mg/g with increase in solution temperature from 303 to 323 K, respectively. The q_o values show that the adsorption capacity of petai seed adsorbent was highly comparable to the adsorption capacities of some other low-cost adsorbent materials for MB. Langmuir parameters calculated from Eq. (4) are listed in Table 1.

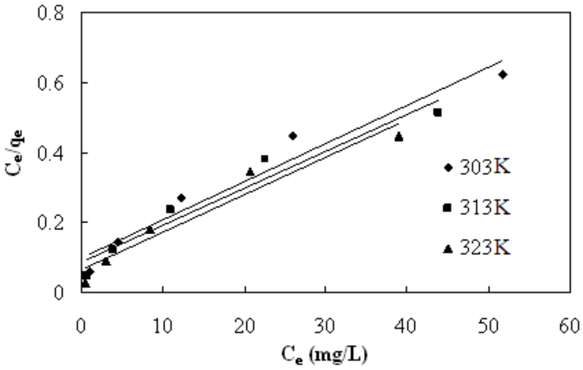

Fig.4. Langmuir isotherms for MB dye adsorption onto petai (*Parkia speciosa*) seed adsorbent at different temperatures

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, R_L, given by Weber, and Chakkravorti (1974):

$$R_L = \frac{1}{1+K_L C_o} \tag{4}$$

The parameter R_L indicated the shape of isotherm as follows:

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0<R_L <1$	Favorable
$R_L = 0$	Irreversible

The calculated R_L values at different initial MB concentrations are shown in Fig. 5. From Fig. 5 it was observed that adsorption was found to be more favorable at higher concentrations. Values of R_L were found to be 0.031, 0.025 and 0.021 at 303, 313 and 323 K, respectively and confirmed that the petai (*Parkia speciosa*) seed adsorbent is favorable for adsorption of MB dye under conditions used in this study.

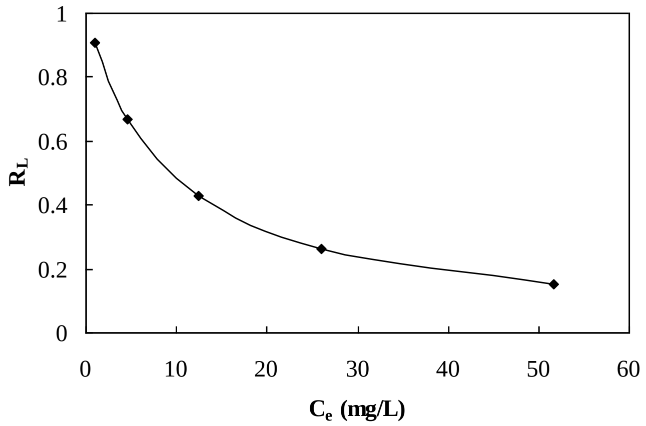

Fig.5. Separation factor for MB onto petai (*Parkia speciosa*) seed adsorbent at 303K

The Freundlich equation is an empirical equation employed to describe heterogeneous systems, characterized by the heterogeneity factor 1/n, describes reversible adsorption, and is not restricted to the formation of the monolayer. This isotherm is suitable for a highly heterogeneous surface. Hence, the empirical equation can be written (Freundlich, 1906):

$$q_e = K_F C_e^{1/n} \tag{5}$$

Where q_e is the solid phase adsorbate concentration in equilibrium (mg/g), C_e the equilibrium liquid phase concentration (mg/L), K_F the Freundlich constant (mg/g)(L/mg)$^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of Eq.5:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

Therefore, the plots of $\ln q_e$ vs $\ln C_e$ for the adsorption of MB onto petai seed adsorbent as shown in Fig. 6 were employed to generate the intercept value of K_F and the slope of 1/n.

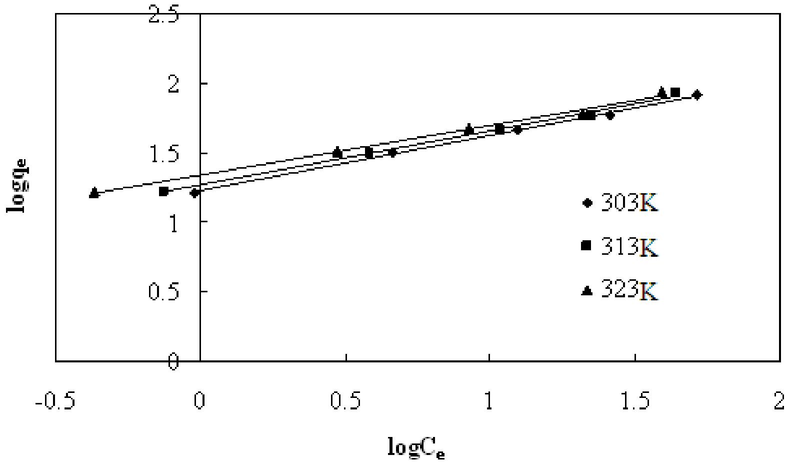

Fig.6. Freundlich isotherm for MB dye adsorption onto petai (*Parkia speciosa*) seed adsorbent at different temperatures

The values of the Freundlich constants (K_F) and (n), the correlation coefficients (R^2) are given in Table 1. It can be seen that the Freundlich model yields a much better fit than the Langmuir model when the R^2 values are compared in Table 1. From Table 1, the values of K_F are 16.79, 18.37 and 22.02 at 303,313 and323 K, respectively. Furthermore, the values of n are greater than 1, reflecting the favorable adsorption.

Table 1: Isotherm parameters for removal of MB by petai (*Parkia speciosa*) seed adsorbent different emperatures

Isotherms	Parameters	Temperature (K)		
		303	313	323
Langmuir	q_o (mg/g)	91.74	94.34	100.03
	K_L (L /mg)	0.107	0.123	0.155
	R^2	0.956	0.944	0.947
	R_L	0.031	0.025	.021
Freundlich	K_F (mg/g (L/mg)$^{1/n}$)	16.79	18.37	22.02
	N	2.52	2.54	2.81
	R^2	0.992	0.995	0.997

The Langmuir and Freundlich parameters for the adsorption of MB are listed in Table 1. It is evident from these data that the surface of petai (*Parkia speciosa*) seed adsorbent is made up of heterogeneous adsorption patches. In other words, Freundlich isotherm model fits very well when the R^2 values are compared (Table 1).

2.5. Adsorption kinetics

In order to investigate the mechanism of adsorption, the pseudo-first-order kinetics model, the pseudo-second-order kinetics model and the intraparticle diffusion model were used to test dynamical experimental data. The pseudo-first-order model was presented by Lagergren (Lagergren, 1898).

The Lagergren's first-order reaction model is expressed as follows by Yalçin et al. (2004):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{7}$$

After integrating and applying the boundary condition (t = 0 and q_t =0 to t = t and q_e = q_t), Eq.7 takes the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

Where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant adsorption. Values of k_1 at 303 K were calculated from the plots of $\ln(q_e-q_t)$ versus t (Fig.7) for different initial concentrations of MB. The k_1 values, the correlation coefficients, R^2 and the q_e values are given in Table 2.

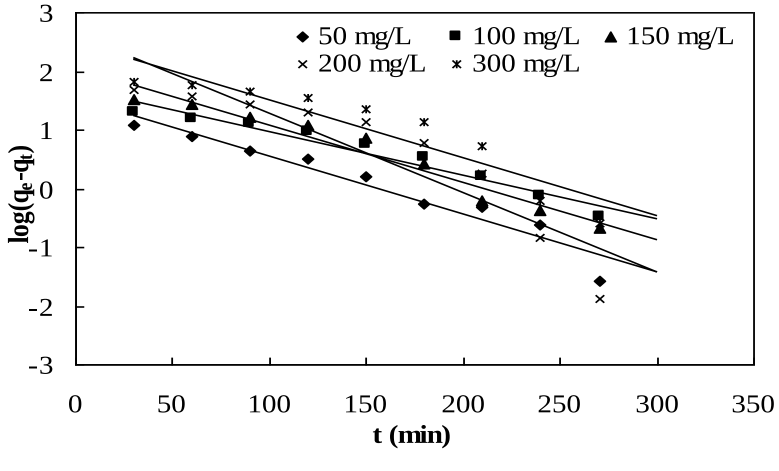

Fig.7. Pseudo-first-order kinetics for adsorption of MB dye onto petai (*Parkia speciosa*) seed adsorbent at 303K

Table 2: Comparison of the pseudo-first-order and pseudo-second-order models for different initial MB concentrations at 303K

C_o mg/L	First-order kinetic model			Second-order kinetic model			
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	$k_2 \times 10^{-3}$ (g/mg min)	H (mg/g min)	R^2
50	35.03	0.023	0.93	22.32	1.87	0.093	0.97
100	52.29	0.017	0.95	42.91	2.12	0.390	0.99
150	112.56	0.022	0.95	67.567	2.41	1.100	0.98
200	116.86	0.031	0.82	117.64	0.839	1.161	0.95
300	123.66	0.042	0.86	200.03	0.3713	1.485	0.96

The adsorption data was also analyzed in terms of pseudo-second-order mechanism, described by Tseng et al., (2003) and Wu et al., (2003):

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \tag{9}$$

Where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min). After integrating and applying boundary conditions (t=0 and q_t =0 to t = t and q_e = q_t), Eq. 9 becomes:

$$q_t = \frac{t}{\frac{1}{k_2 q_e^{\ 2}} + \frac{t}{q_e}} \tag{10}$$

This has linear form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\ 2}} + \frac{1}{q_e} t \tag{11}$$

According to Gundogan et al., (2004), if initial adsorption rate is:

$$h = k_2 q_e^{\ 2} \tag{12}$$

Then Eqs. (11) and (12) become:

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \tag{13}$$

And

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{14}$$

Thus the rate constant k_2, initial sorption rate h, and predicted q_e can be calculated from the plot of t/q versus time t using Eq.14.

Fig. 8 shows the plot between t/q versus time t. The initial sorption rate h, pseudo-second-order-rate constant k_2, amount of dye adsorbed at equilibrium q_e.

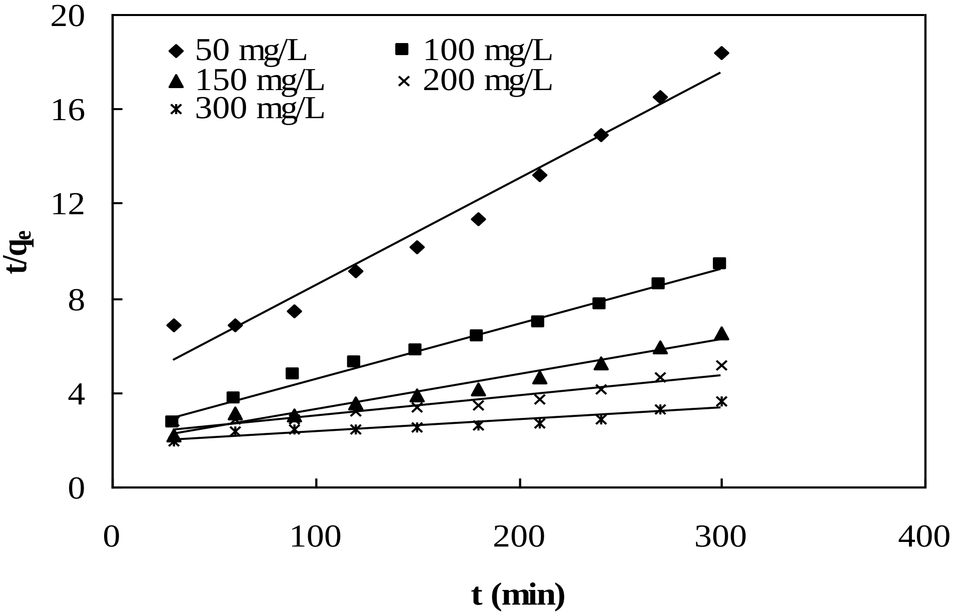

Fig.8. Pseudo-second-order kinetics for adsorption of MB adsorption onto petai (*Parkia speciosa*) seed adsorbent at 303K

The corresponding linear regression correlation coefficient R^2 values are given in Table 2. The kinetic parameters of MB under different conditions were calculated from these plots and are given in Table 2. The correlation coefficients (R^2), for the first-order kinetic model are between 0.82 and 0.95 and the correlation coefficients (R^2), for the pseudo-second-order kinetic model are between 0.94 and 0.99. It is probable, therefore, that this adsorption system is not a pseudo-first-order reaction, it fits the pseudo-second-order kinetic model (Mohd Salleh et al., 2011b).

A similar phenomenon has been observed in the adsorption of methylene blue onto rice husk (Vadivelan and Kumar, 2005), and methylene blue onto activated carbon prepared from rattan sawdust (Hameed et al., 2007).

The Intraparticle diffusion can be described by three consecutive steps (Ugurlu et al., 2005):

(i) The transport of adsorbate from bulk solution to outer surface of the adsorbent by molecular diffusion, known as external (or) film diffusion.

(ii) Internal diffusion, the transport of adsorbate from the particles surface into interior sites.

(iii) The adsorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the adsorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and adsorbent. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris, 1963

is used. The rate constants, for intraparticle diffusion (K_i) are determined using equation given by Weber and Morris, (1963):

$$q_t = k_{diff.} t^{1/2} + C \tag{15}$$

Where k_i and C are the intraparticle diffusion rate constant (mg/g min$^{1/2}$) and intercept , respectively. The k_i is the slope of straight-line portions of plot of q_t versus $t^{0.5}$ as shown in Fig. 9.

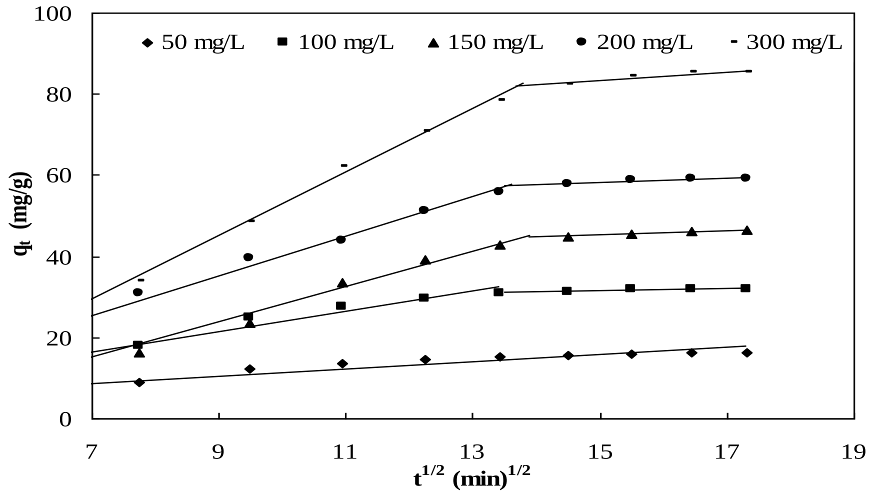

Fig.9. Weber and Morris intra-particle diffusion plots for removal of MB, at different initial dye concentrations, pH 6.8, and temperature 303K.

The values of constants, k_i and C, for intraparticle diffusion kinetics and pore diffusion coefficients have been given in Table 3. These plots have generally the double nature, i.e. initial curve portions and final linear portions. It is explained by the fact that the initial curved portions are boundary layer diffusion effects. The final linear portions are a result of intraparticle diffusion effects. An extrapolation of the linear portions of the plots back to the axis yield intercepts C which is proportional to the extent of boundary layer thickness (Markovska et al., 2001).

Table 3: Intra-particle diffusion constants for different initial MB dye concentrations at 303K

C_o (mg/L)	Intra-particle diffusion $K_{i,1}$	C	R^2	$K_{i,2}$	C	R^2
50	0.889	2.457	0.89	-	-	-
100	2.528	6.275	0.96	0.261	27.631	0.78
150	4.344	15.299	0.98	0.521	37.267	0.96
200	4.925	19.127	0.99	0.743	51.647	0.82
300	7.792	25.034	0.99	1.016	68.219	0.87

3.6. Activation parameters

The rate constant k_2 at different temperatures listed in Table 2 were then applied to estimate the activation energy of the adsorption of MB onto petai (*Parkia speciosa*) seed adsorbent by the Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT} \tag{16}$$

Where E_a, R and A refer to the Arrhenius activation energy, the gas constant and the Arrhenius factor, respectively. The slope of the plot of $\ln k_2$ versus 1/T (figure not shown) was used to evaluate E_a as listed in Table 4.

Table 4: Thermodynamic parameters of MB dye adsorption on petai (*Parkia speciosa*) seed adsorbent

Temperature (K)	$-\Delta G^o$ (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol K)	Activation energy, E (kJ/mol)
303	27.59	17.89	91.139	26.789
313	28.42			
323	29.42			

The enthalpy (ΔH^o), entropy (ΔS^o) and free energy (ΔG^o) of activation was also calculated using:

$$\ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{17}$$

Where R (8.314 J/mol K) is the universal gas constant, T (K) the absolute solution temperature and K_c is the distribution coefficient which can be calculated as:

$$K_C = \frac{C_{Ae}}{C_e} \tag{18}$$

Where K_C is the equilibrium constant; C_{Ae} (mg/L) is the amount of dye adsorbed on the adsorbent of the solution at equilibrium and C_e (mg/L) is the equilibrium concentration of the dye in the solution.

The values of ΔH^o and ΔS^o were calculated from the slope and intercept of plot between ln K_c versus 1/T. ΔG^o can be calculated using the relation below:

$$\Delta G^o{}_{ads} = \Delta H^o{}_{ads} - T\Delta S^o{}_{ads} \text{----} \qquad (19)$$

The calculated values of ΔH^o, ΔS^o and ΔG^o are listed in Table 5. The positive value of ΔH^o indicated the endothermic nature of the adsorption interaction. The positive value of ΔS^o showed the affinity of the petai (*Parkia speciosa*) seed adsorbent for MB and the increasing randomness at the solid–solution interface during the adsorption process. The negative value of ΔG^o was calculated at 303, 313 and 333 K for different initial MB concentration by using Eq. (20) and these values are listed in Table 4. Similar observations were reported for adsorption of arsenic onto coconut husk carbon (Manju et al., 1998) adsorption of methylene blue onto mango seed kernel powder (Tseng and Tseng, 2005) and adsorption of methylene blue onto oil palm fibre activated carbon (Tan et al., 2007).

4. Conclusions

The results of this study indicate that petai seed adsorbent can be successfully used for the adsorption of MB dye from aqueous solutions. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 91.74, 94.34 and 100.03 mg/g at 303, 313, and 323 K, respectively. The R_L values showed that petai (*Parkia speciosa*) seed adsorbent was favorable for the adsorption of MB dye. Freundlich isotherm best-fit the equilibrium data for adsorption of MB dye. Three kinetic models, pseudo-firstorder, pseudo-second-order, and intra-particle diffusion were tested to investigate the adsorption mechanism. The pseudo-second-order kinetic model fits very well with the dynamical adsorption behavior of MB dye. The negative values of ΔG^o and positive ΔH^o obtained indicated that the MB dye adsorption process is a spontaneous and an endothermic.

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