

Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon

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Abstract

Oil palm fibre, an abundant agricultural by-product in Malaysia, was used to prepare activated carbon by physiochemical activation method. Adsorption isotherm of methylene blue onto the prepared activated carbon was determined by batch tests. The effects of various parameters such as contact time, initial methylene blue concentration and temperature were investigated, at solution pH of 6.5. The adsorption capacity was found to increase with increase in the three parameters studied. Equilibrium data were fitted to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. The equilibrium data were best represented by the Langmuir isotherm, with maximum monolayer adsorption capacity of 277.78 mg/g at 30 °C. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. Various thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) were evaluated. Oil palm fibre-based activated carbon was shown to be a promising material for adsorption of methylene blue from aqueous solutions.

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1. Introduction

Dyes have been extensively used in many industries, such as textile, leather tanning, paper production, food technology, hair colorings, etc. It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tonnes of dye-stuff produced annually [1]. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons [2]. This wastewater contains a variety of organic compounds and toxic substances which are harmful to fish and other aquatic organisms [3]. Methylene blue is the most commonly used substance for dyeing cotton, wood and silk. It 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 [4]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

In general, dyes are poorly biodegradable or resistant to environmental conditions [5]. 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 [6]. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications [7]. 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, especially for application concerning wastewater treatment. Researchers have studied the production of activated carbons from cassava peel [8], bagasse [5], date pits [9], olive stones [10], fir woods and pistachio shells [11] and jute fiber [12].

Oil palm is a major source of edible oil which is extracted from its fruits. One of the significant problems in the palm fruit processing is managing of the wastes generated during the processes. In Malaysia, more than two million tonnes (dry weight) of extracted oil palm fibre are estimated to be generated annually [13]. At present, it is usually used as boiler fuel to produce

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steam in the palm oil mills. To make better use of this cheap and abundant waste, it is proposed to make it into activated carbon. Conversion of oil palm fibre 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.

Therefore, the purpose of this work was to evaluate the adsorption potential of oil palm fibre-based activated carbon for methylene blue dye. The equilibrium, kinetic and thermodynamic data of the adsorption process were then studied to understand the adsorption mechanism of methylene blue molecules onto the prepared activated carbon.

2. Materials and methods

2.1. Methylene blue

Methylene blue (MB) 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 Appendix A.

2.2. Preparation and characterization of activated carbon

Oil palm fibre used for preparation of activated carbon was obtained from United Palm Oil Mill, Nibong Tebal, Malaysia. The precursor was first washed and soaked in *n*-hexane to remove dirt and oil. Then, it was dried and crushed to desired mesh size (1–2 mm). The pre-treated precursor was then carbonized at 700 °C with constant heating rate of 10 °C/min, under purified nitrogen (99.995%) flow of 150 cm³/min for 2 h (first pyrolysis) in a stainless steel vertical tubular reactor placed in a tube furnace. 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, using the same heating rate of 10 °C/min. Once the final temperature was reached, the nitrogen gas flow was switched to carbon dioxide (CO₂) and activation was held for 2 h. The activated product was then cooled to room temperature under nitrogen flow of 150 cm³/min and then washed with hot deionized water and 0.1 M hydrochloric acid until the pH of the washing solution reached 6–7.

Textural characterization of the activated carbon was carried out by N₂ adsorption at 77 K using Autosorb I (Quantachrome Corporation, USA). The Brunauer–Emmett–Teller (BET) is the most common standard procedure used when characterizing an activated carbon [14]. Scanning electron microscopy (SEM) analysis was carried out for the prepared activated carbon to study the surface morphology and to verify the presence of porosity. In addition, the surface functional groups of the

prepared activated carbon were detected by Fourier transform infrared (FTIR) spectroscope (FTIR-2000, Perkin-Elmer). The spectra were recorded from 4000 to 400 cm⁻¹.

2.3. Batch equilibrium studies

Adsorption tests were performed in a set of Erlenmeyer flasks (250 ml) where 100 ml of methylene blue 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 μm was added to each flask and kept in an isothermal shaker at 30 °C for 24 h to reach equilibrium. The original pH of the solutions was used, which was around 6.5. Similar procedures were followed for another two sets of Erlenmeyer flask containing the same initial dye concentrations and same amount of activated carbons but were kept under 40 and 50 °C. 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–vis spectrophotometer (Shimadzu, Japan) at 668 nm. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/l) 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).

2.4. Batch kinetic studies

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 methylene blue 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 μm was added to each flask and kept in an isothermal shaker at 30 °C. 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:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 and C_t (mg/l) are the liquid-phase concentrations of dye 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).

3. Results and discussion

3.1. Textural characterization of prepared activated carbon

The BET surface area of the prepared activated carbon was found to be 1354 m²/g, with total pore volume of 0.778 cm³/g.

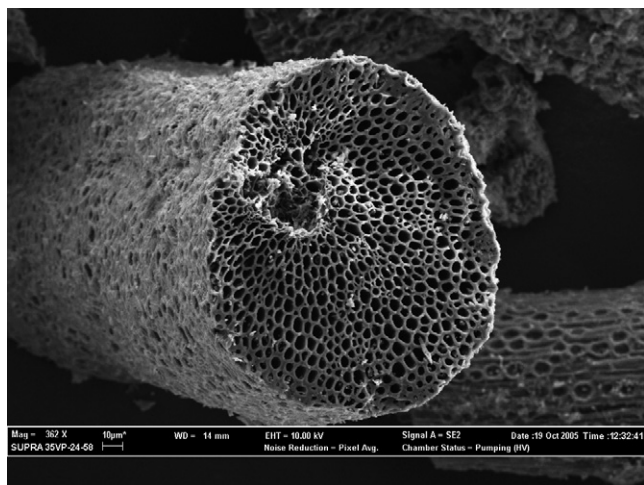


Fig. 1. SEM image of oil palm fibre-based activated carbon ($\times 362$).

The average pore diameter was found to be 2.3 nm. The activated carbon derived from oil palm fibre contained relatively large surface area and total pore volume compared to commercially available activated carbons such as BDH from Merck, F100 and BPL from Calgon Corporation with BET surface area of 1118, 957 and 972 m^2/g as well as total pore volume of 0.618, 0.526 and 0.525 cm^3/g , respectively [15].

The high BET surface area and total pore volume of the prepared activated carbon was due to the activation process used, which involved both chemical and physical activating agents of KOH and CO_2 . Pore development in the char during pyrolysis was also important as this would enhance the BET surface area and pore volume of the activated carbon by promoting the diffusion of KOH and CO_2 molecules into the pores and thereby increasing the KOH-carbon and CO_2 -carbon reactions, which would then create more pores in the activated carbon. Stavropoulos and Zabaniotou [16] stated that KOH is dehydrated to K_2O , which reacts with CO_2 produced by the water-shift reaction, to give K_2CO_3 . Intercalation of metallic potassium appeared to be responsible for the drastic expansion of the carbon material and hence the creation of a large specific surface area and high pore volume.

Fig. 1 shows the SEM image of the derived activated carbon. Many large pores in a honeycomb shape were clearly found on the surface of the activated carbon. The well-developed pores had led to the large surface area and porous structure of the activated carbon. Fig. 2 displays the FTIR spectra obtained for the prepared activated carbon. The spectrum displayed the following bands:

- 3400 cm^{-1} : O–H stretching vibrations;
- 2383 cm^{-1} : $\text{C}\equiv\text{O}$ stretching vibrations;
- 1565 cm^{-1} : $\text{C}=\text{C}$ stretching vibration in aromatic rings;
- 1083 cm^{-1} : C–OH stretching vibrations;
- 800 cm^{-1} : C–H out-of-plane bending in benzene derivatives.

The main surface functional groups present in the derived activated carbon were quinone and aromatic rings. The $\text{C}\equiv\text{O}$ stretching vibrations found was probably due to the incorpora-

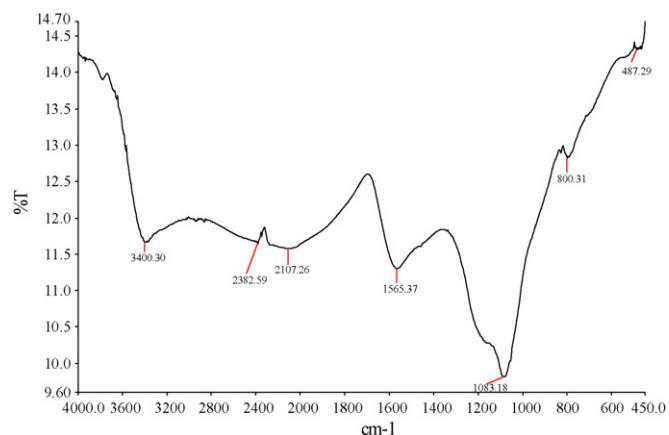


Fig. 2. FTIR spectra of oil palm fibre-based activated carbon.

tion of heteroatoms (in this case, oxygen atom from enriched carbon dioxide atmosphere during the activation process) at the edge of the aromatic sheet or within the carbon matrix [17].

3.2. Effect of contact time and initial dye concentration on adsorption equilibrium

Adsorption isotherms are usually determined under equilibrium conditions. Fig. 3 shows the adsorption capacity 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 to reach equilibrium ranged between 1 and 6 h. For MB solutions with initial concentrations of 300–500 mg/l, equilibrium time of 24 h was required. However, the experimental data were measured at 48 h to make sure that full equilibrium was attained. As can be seen from Fig. 3, 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 solution. At this point, the amount of the dye desorbing from the activated carbon was in a state of dynamic equilibrium with the

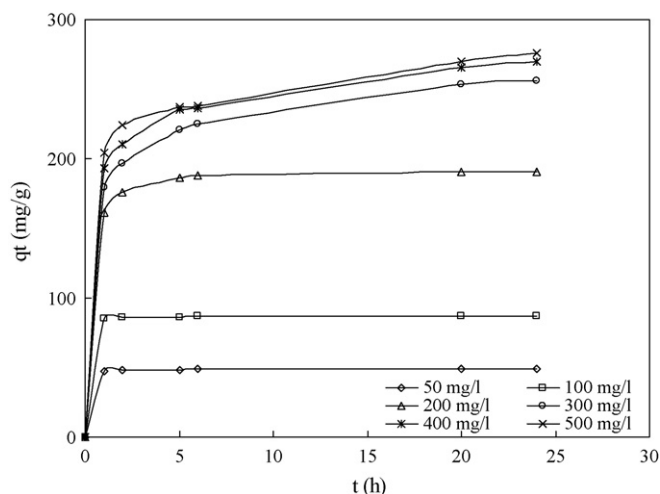


Fig. 3. The variation of adsorption capacity with adsorption time at various initial MB concentrations at 30 °C.

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. The adsorption capacity at equilibrium (q_e) increased from 49 to 276 mg/g with an increase in the initial dye concentrations from 50 to 500 mg/l.

Three consecutive mass transport steps are associated with the adsorption of solute from solution by porous adsorbent [18]. 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 [12].

3.3. Effect of temperature on adsorption equilibrium

Fig. 4 shows the adsorption equilibrium versus the temperature at various initial MB concentrations. It was found that for low MB concentrations, the effect of temperature on the adsorption equilibrium was not significant. However, for higher MB concentrations of 300–500 mg/l, the adsorption equilibrium increased with increase in temperature, indicating the endothermic nature of the adsorption reaction. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of MB molecules into the pores of the activated carbon at higher temperatures [19].

3.4. 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

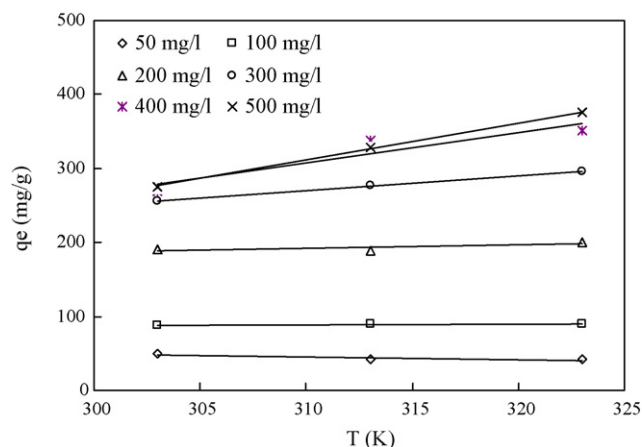


Fig. 4. Effect of temperature on adsorption equilibrium at various initial MB concentrations.

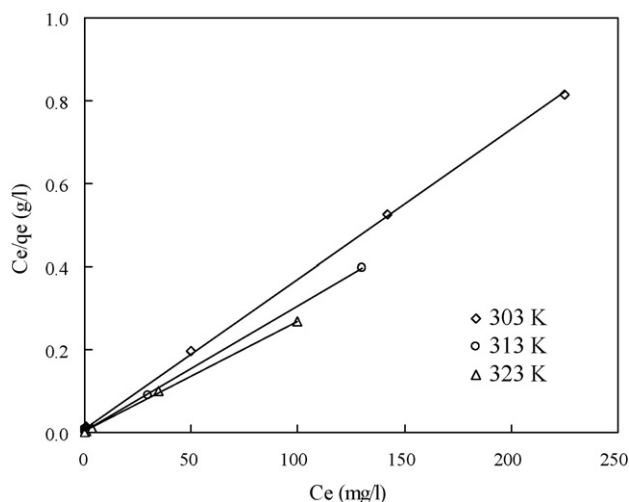


Fig. 5. Langmuir adsorption isotherm of MB onto activated carbon at 30, 40 and 50 °C.

used for design purposes [20]. 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 compared by judging the correlation coefficients, R^2 values.

3.4.1. 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 [21]. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (3)$$

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 (mg/g), Q_0 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 $1/Q_0$ was obtained, as shown in Fig. 5. The R^2 value of 0.999 indicated that the adsorption data of MB onto the activated carbon at all the three temperatures studied were best fitted to the Langmuir isotherm model. The Langmuir constants b and Q_0 were calculated from Eq. (3) and their values are shown in Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) [21], which is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant and C_0 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

Table 1
Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm model constants and correlation coefficients for adsorption of MB onto prepared activated carbon

Isotherms	Solution temperature (K)	Constants		R^2
		Q_0 (mg/g)	b (l/mg)	
Langmuir: $\frac{C_e}{Q_0 + C_e} = \frac{q_e}{Q_0}$	303	277.78	0.40	0.999
	313	333.33	1.67	0.999
	323	384.62	0.58	0.999
Freundlich: $\log q_e = \log K_F + (1/n) \log C_e$	Solution temperature (K)	K_F (mg/g (l/mg) ^{1/n})	$1/n$	R^2
	303	91.85	0.23	0.729
	313	138.10	0.23	0.525
323	132.28	0.26	0.564	
Temkin: $q_e = (RT/b) \ln(AC_e)$	Solution temperature (K)	A (l/g)	B	R^2
	303	24.03	33.91	0.853
	313	88.52	39.51	0.696
323	35.44	48.60	0.775	
Dubinin–Radushkevich: $q_e = q_s \exp(-B\epsilon^2)$	Solution temperature (K)	q_s (mg/g)	E	R^2
	303	273.09	1290.99	0.995
	313	366.79	2236.07	0.833
323	293.42	2357.02	0.424	

($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.005 at 30 °C, and this again confirmed that the Langmuir isotherm model was favorable for adsorption of MB onto the oil palm fibre-based activated carbon under the conditions used in this study.

3.4.2. Freundlich isotherm

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage [21]. 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 (mg/g), K_F and n are Freundlich constants with n giving an indication of how favorable the adsorption process and K_F (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 [22]. A value for $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption [23]. The plot of $\log q_e$ versus $\log C_e$ gave a straight line with slope of $1/n$ with value of 0.23–0.26 (Fig. 6), indicating a normal Langmuir isotherm. Fre-

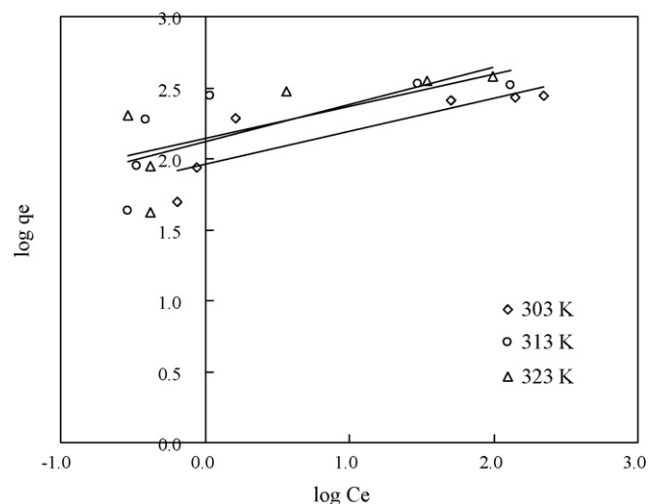


Fig. 6. Freundlich adsorption isotherm of MB onto activated carbon at 30, 40 and 50 °C.

undlich constants K_F and n were also calculated and are listed in Table 1.

3.4.3. 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 [24]. The Temkin isotherm has been used in the form as follows:

$$q_e = \left(\frac{RT}{b} \right) \ln(AC_e) \quad (6)$$

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

3.4.4. Dubinin–Radushkevich isotherm

Another popular equation for the analysis of isotherms of a high degree of rectangularity is Dubinin–Radushkevich

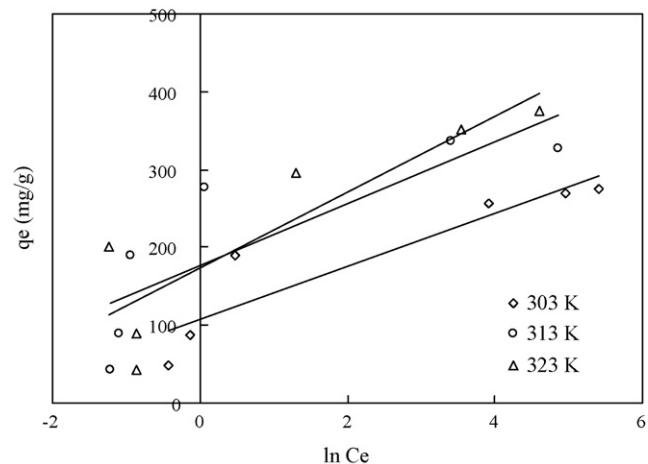


Fig. 7. Temkin adsorption isotherm of MB onto activated carbon at 30, 40 and 50 °C.

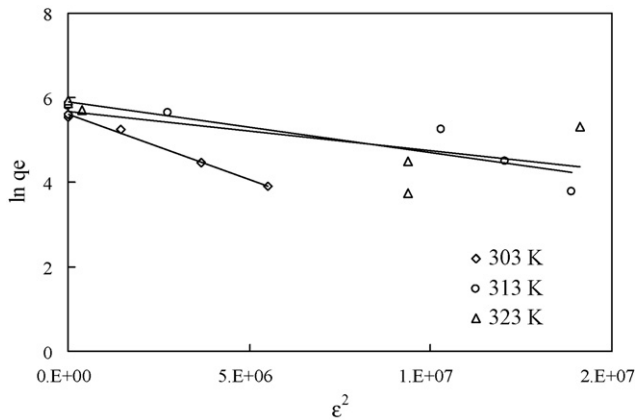


Fig. 8. Dubinin–Radushkevich adsorption isotherm of MB onto activated carbon at 30, 40 and 50 °C.

isotherm [25] which is as follow:

$$q_e = q_s \exp(-B\varepsilon^2) \quad (7)$$

where ε can be correlated:

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

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:

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

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

From Table 1, the Langmuir isotherm model yielded the best fit with the highest R^2 value at all temperatures compared to the other three models. Conformation of the experimental data into Langmuir isotherm equation indicated the homogeneous nature of oil palm fibre-based activated carbon surface, i.e., each dye molecule/oil palm fibre carbon adsorption had equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of dye molecule at the outer surface of oil palm fibre-based activated carbon. Similar observation was

reported by the adsorption of MB onto activated carbon prepared from jute fiber [12] and olive-seed waste residue [16].

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 277.78 mg/g if compared to some data obtained from the literature.

3.5. Adsorption kinetics

Three simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the pseudo-first-order equation given by Lagergren and Svenska [26] as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

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 at 30 °C were calculated from the plots of $\ln(q_e - q_t)$ versus t (figure not shown) for different initial concentrations of MB. The R^2 values obtained were relatively small and the experimental q_e values did not agree with the calculated values obtained from the linear plots (Table 3).

On the other hand, the pseudo-second-order equation based on equilibrium adsorption [27] 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 at 30 °C, as shown in Fig. 9, yielded R^2 values that were greater than 0.999 for all MB concentrations. It also showed a good agreement between the experimental and the calculated q_e values (Table 3), indicating 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 [28] was tested to identify the diffusion mechanism. According to this theory:

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

where k_p ($\text{mg/g h}^{1/2}$), the intraparticle diffusion rate constant, is obtained from the slope of the straight line of q_t versus $t^{1/2}$

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

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
Palm fiber-based activated carbon	277.78	This work
Bamboo dust-based activated carbon	143.20	[33]
Coconut shell-based activated carbon	277.90	[33]
Groundnut shell-based activated carbon	164.90	[33]
Jute processing waste	22.47	[34]
Mango seed kernel powder	142.86	[30]
Jute fiber-based activated carbon	225.64	[12]
Olive-seed waste residue-based activated carbon	190.00–263.00	[16]
^a Filtrisorb F300	240.00	[16]

^a Commercial activated carbon.

Table 3
Comparison of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models for different initial MB concentrations at 30 °C

Initial MB concentration (mg/l)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model			
		$q_{e,cal}$ (mg/g)	k_1 (h^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg h)	R^2	$q_{e,cal}$ (mg/g)	k_p (mg/g $h^{1/2}$)	R^2	SSE (%)
50	49.06	9.14	0.75	0.55	49.26	0.59	0.999	50.81	0.75	0.83	1.76
100	87.02	14.74	0.86	0.60	86.96	0.66	1.000	89.08	0.91	0.90	2.07
200	190.52	95.94	0.70	0.87	196.08	0.02	1.000	232.78	17.53	0.94	42.26
300	256.25	158.62	0.34	0.76	238.10	0.01	0.999	304.54	31.73	0.99	48.30
400	269.84	163.02	0.35	0.76	250.00	0.01	0.999	314.02	30.47	0.98	44.18
500	275.73	151.00	0.32	0.65	243.90	0.02	1.000	292.73	21.45	0.91	17.00

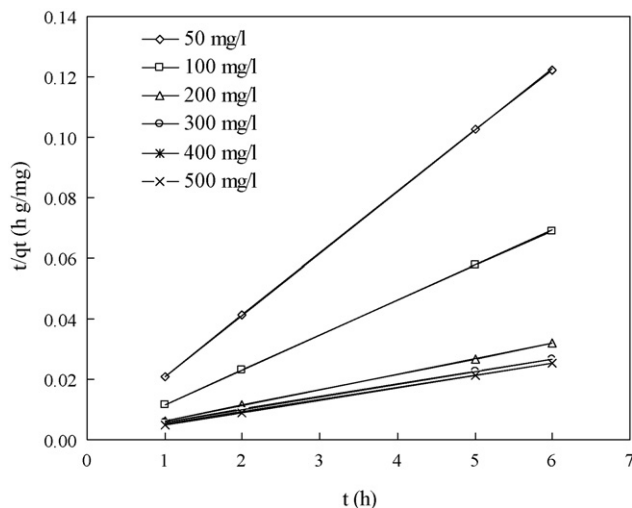


Fig. 9. Pseudo-second-order kinetics for adsorption of MB adsorption onto activated carbon at 30 °C.

(Fig. 10). 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 low adsorbate concentrations left in the solutions [11]. As can be seen from Fig. 10, 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 [29].

3.6. Validity of kinetic models

The adsorption kinetics of MB onto the prepared activated carbon was verified at different initial concentrations. The validity of each model was determined by the sum of squared errors

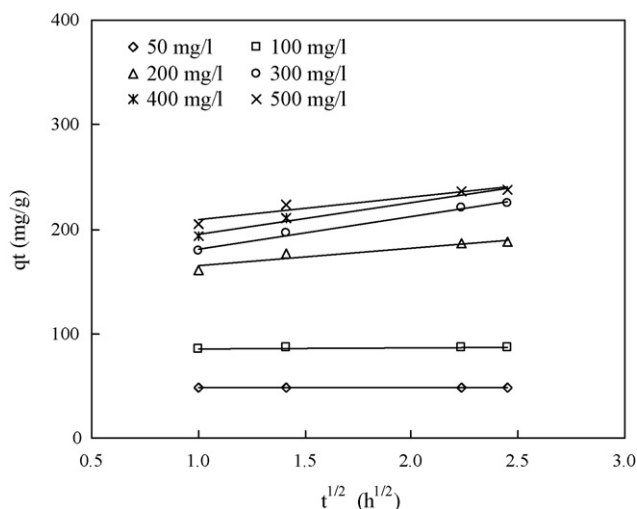


Fig. 10. Intraparticle diffusion model for adsorption of MB adsorption onto activated carbon at 30 °C.

Table 4
Thermodynamic parameters for adsorption of MB onto prepared activated carbon

Initial concentration (mg/l)	ΔH° (J/mol)	ΔS° (J/mol K)	ΔG° (J/mol)		
			303 K	313 K	323 K
50	11691.98	75.92	-10892.10	-12963.20	-12353.30
100	31359.58	143.33	-11587.10	-14528.60	-14388.00
200	72617.80	280.65	-12009.50	-16100.10	-17566.70
300	114724.90	398.89	-4110.27	-14447.40	-11811.80
400	68832.44	234.97	-1617.74	-6305.74	-6215.41
500	45670.46	152.81	-513.65	-2406.78	-3553.94

(SSE, %) given by:

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

where N is the number of data points.

The lower the value of SSE indicates the better a fit is. Table 3 lists the SSE values obtained for the three kinetic models studied. It was found that the pseudo-second-order kinetic model yielded the lowest SSE values. This agrees with the R^2 values obtained earlier and proves that the adsorption of MB onto the oil palm fibre-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 behavior over the whole range of studies, strongly supporting the validity and agrees with chemisorption being rate-controlling [30].

3.7. Adsorption thermodynamics

The concept of thermodynamic assumes that in an isolated system where energy cannot be gained or lost, the entropy change is the driving force [31]. The thermodynamic parameters that must be considered to determine the process are changes in standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) due to transfer of unit mole of solute from solution onto the solid–liquid interface. The value of ΔH° and ΔS° were computed using the following equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

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

$$K_d = \frac{C_{Ae}}{C_e} \quad (15)$$

where C_{Ae} (mg/l) is the amount adsorbed on solid at equilibrium and C_e (mg/l) is the equilibrium concentration.

The values of ΔH° and ΔS° were calculated from the slope and intercept of plot between $\ln K_d$ versus $1/T$ (Fig. 11). ΔG° can be calculated using the relation below:

$$\Delta G^\circ = -RT \ln K_d \quad (16)$$

The calculated values of ΔH° , ΔS° and ΔG° are listed in Table 4. The positive value of ΔH° indicated the endothermic

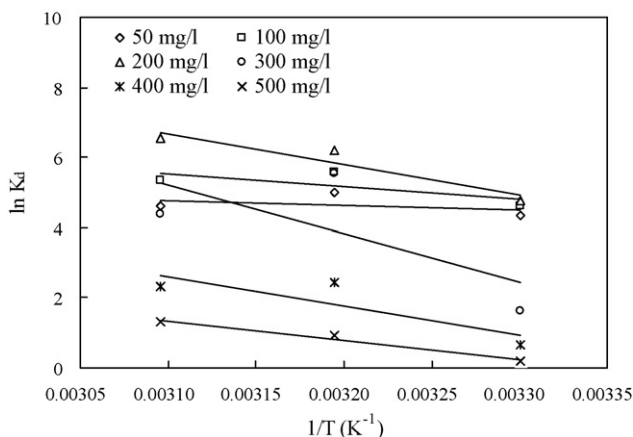


Fig. 11. Plot of $\ln K_d$ versus $1/T$ at various initial MB concentrations.

nature of the adsorption interaction. From Table 1, the maximum monolayer adsorption capacity of MB onto the prepared activated carbon increased from 277.78 to 384.62 mg/g with increase in solution temperature from 30 to 50 °C. This further confirmed the endothermic nature of the adsorption process. The positive value of ΔS° showed the affinity of the oil palm fibre-based activated carbon for MB and the increasing randomness at the solid–solution interface during the adsorption process. The negative value of ΔG° indicated the feasibility of the process and the spontaneous nature of the adsorption with a high preference of MB onto the prepared activated carbon. Similar observations were reported for adsorption of arsenic onto coconut husk carbon [32] and adsorption of MB onto mango seed kernel powder [30].

4. Conclusion

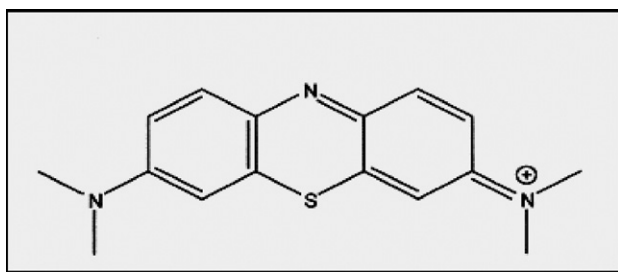
The present investigation showed that oil palm fibre was a promising precursor to be used in the preparation of activated carbon for the removal of methylene blue dye from aqueous solutions over a wide range of concentrations. The BET surface area of the prepared activated carbon was 1354 m²/g. SEM study showed that the activated carbon was porous with well-developed pores. The main surface functional groups present in the derived activated carbon were quinone and aromatic rings. Methylene blue was found to adsorb strongly onto the surface of the oil palm fibre-based activated carbon. 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 277.78 mg/g at 30 °C. The kinetics of the adsorption process was found to follow the pseudo-second-order kinetic model. The positive ΔH° value indicated the endothermic nature of the adsorption interaction whereas the positive ΔS° value showed the increased randomness at the solid–solution interface during the adsorption process. The negative value of ΔG° indicated the feasibility and the spontaneous nature of the adsorption of MB onto the prepared activated carbon. The adsorption potential of the oil palm fibre-based activated carbon was comparable to commercial activated carbon and some other adsorbents reported in earlier studies.

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Appendix A. Chemical structure of methylene blue dye



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