Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (*Cocos nucifera*) bunch waste

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Abstract

In this paper, the ability of coconut bunch waste (CBW), an agricultural waste available in large quantity in Malaysia, to remove basic dye (methylene blue) from aqueous solution by adsorption was studied. Batch mode experiments were conducted at 30 °C to study the effects of pH and initial concentration of methylene blue (MB). Equilibrium adsorption isotherms and kinetics were investigated. The experimental data were analyzed by the Langmuir, Freundlich and Temkin models of adsorption. The adsorption isotherm data were fitted well to Langmuir isotherm and the monolayer adsorption capacity was found to be 70.92 mg/g at 30 °C. The kinetic data obtained at different concentrations have been analyzed using a pseudo-first-order, pseudo-second-order equation and intraparticle diffusion equation. The experimental data fitted very well the pseudo-second-order kinetic model.
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Keywords: Coconut bunch waste; Methylene blue; Adsorption isotherm; Equilibrium; Kinetics

1. Introduction

The textile industry is a growing industry in Malaysia. It contributes about 22% of the total volume of industrial wastewater generated in the country [1]. Synthetic dyestuffs, one group of organic pollutants, are used extensively in textile, paper, printing industries and dyehouses. It is reported that there are over 100,000 commercially available dyes with a production of over 7×10^5 metric tonnes per year [2,3]. Methylene blue is not regarded as acutely toxic, but it can have various harmful effects. 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, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia-like syndromes [4]. Due to large-scale production and extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors [5]. Therefore, removal of dyes from wastewater is most desirable.

Recently, the principal existing and emerging processes for dyes removal has been compiled by Crini [6]. Adsorption on activated carbon has been shown to be very effective for removal of dyes and other pollutants from aqueous solutions. The removal of basic dyes from aqueous solutions has been studied using activated carbons prepared from different precursors [7–11]. Activated carbon is still considered expensive adsorbent and the higher the quality the greater the cost. Both chemical and thermal regeneration of spent carbon is expensive, impractical on a large-scale and produces additional effluent and results in considerable loss of the adsorbent. This has led many workers to search for the use of cheap and efficient alternative materials [12]. These include palm ash [13,14], chitosan/oil palm ash composite beads [15], pomelo (*Citrus grandis*) peel [16], salts-treated beech sawdust [17], waste materials [18], natural *Luffa cylindrica* fibres [19], sunflower seed shells [20], algal biomass based materials [21], wheat bran [22], guava (*Psidium guajava*) leaf powder [23], almond shells [24], dehydrated peanut hull [25] and wheat shells [26].

In this work, we attempt to use coconut bunch waste, an agricultural waste abundantly available in Malaysia as a sor-

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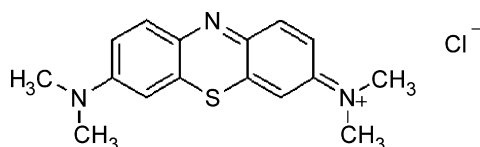
Scheme 1. Chemical structure of methylene blue.

bent to remove methylene blue from aqueous solution. Coconut palm (*Cocos nucifera*) is a member of the family Arecaceae (palm family). The coconut palm is grown throughout the tropical world. This palm sustains the livelihood of millions of people in coastal regions of tropics [27]. It is one of the most important crops in Malaysia. The total area planted of coconut palm increased from 117,000 ha (1998) to 147,000 ha in 2004 [28]. The coconut bunch waste accumulates in the agro-industrial yards, has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Therefore, any attempt to reutilize this waste will be useful.

The objective of this work was to investigate the potential of coconut bunch waste, an agricultural waste, as adsorbent in the removal of the basic dye, methylene blue, from aqueous solutions.

2. Materials and methods

2.1. Adsorbate

Basic dye used in this study was methylene blue (MB) purchased from Sigma–Aldrich. The MB was chosen in this study because of its known strong adsorption onto solids. The maximum absorption wavelength of this dye is 668 nm. The structure of MB is shown is Scheme 1.

2.2. Preparation and characterization of adsorbent

The coconut bunch waste (CBW) used was collected from the main fruit market of Nibong Tebal, Penang. It was washed thoroughly with distilled water to remove the surface adhered particles and water-soluble materials. Then it was sliced, spread on trays and oven dried at 70 °C for 48 h. The dried slices were ground and sieved to obtain a particle size range of 1–2 mm and stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

Scanning electron microscopy (SEM) analysis was carried out on the CBW, to study its surface texture before and after MB adsorption. Fourier Transform Infrared (FTIR) (FTIR-2000, Perkin Elmer) analysis was applied on the CBW and dye adsorbed CBW to determine the surface functional groups, where the spectra were recorded from 4000 to 400 cm^{-1}.

2.3. Adsorption studies

The batch sorption experiments were carried out in 250-mL Erlenmeyer flasks where 0.20 g of the adsorbent and 200 mL of the MB solutions (50–500 mg/L) were added. The pH of all solutions in contact with adsorbents was found to be in the range
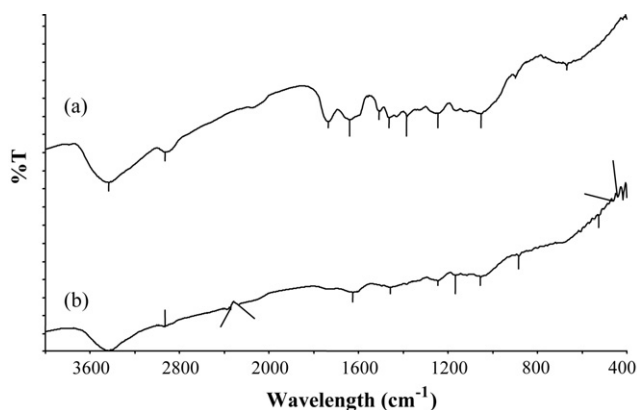

Fig. 1. FT-IR spectrum of (a) CBW (b) MB adsorbed CBW.

6.5–7.5, otherwise indicated. The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at 100 rpm and 30 °C for 5 h and 15 min to achieve equilibration. The concentration of the MB in the solution after equilibrium adsorption was measured by a double beam UV–vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at 668 nm. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

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

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).

To study effect of solution pH, a sample of 0.20 g adsorbent was added to dye solution (200 mL, 100 mg/L) at constant temperature (30 °C). The experiments were carried out at pH 2–12. The Erlenmeyer flasks were subsequently capped and agitated in an isothermal shaker at 100 rpm and 30 °C for 5 h and 15 min. The concentration of the MB in the solution after equilibrium adsorption was measured as above.

Kinetic studies of adsorption were also carried out at various concentrations of the MB wherein the extent of adsorption was investigated as a function of time. The amount of adsorption at time t, q_t (mg/g), was calculated by

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

3. Results and discussion

3.1. Characterization of sorbent

The FTIR spectrum of CBW given in Fig. 1a shows peaks at 3436.56 cm^{-1} (N–H stretch), 2929.92 cm^{-1} (C–H stretch), 1734.82 cm^{-1} (C=O stretch), 1639.25 cm^{-1} (NH$_2$ deformation), 1507.98 cm^{-1} (NH deformation), 1463.34 cm^{-1} (CH$_2$ deformation), 1383.98 cm^{-1} (C–O–H bend), 1245.86 cm^{-1} (Si–C stretch), 1052.17 cm^{-1} (P–H deformation), 898.41 cm^{-1} (C–N stretch) and 668.79 cm^{-1} (C–O–H twist). It is clear that the adsorbent displays a number of absorption peaks, reflecting the complex nature of the adsorbent. Comparing Fig. 1a and b, we can conclude that some of these peaks are shifted or
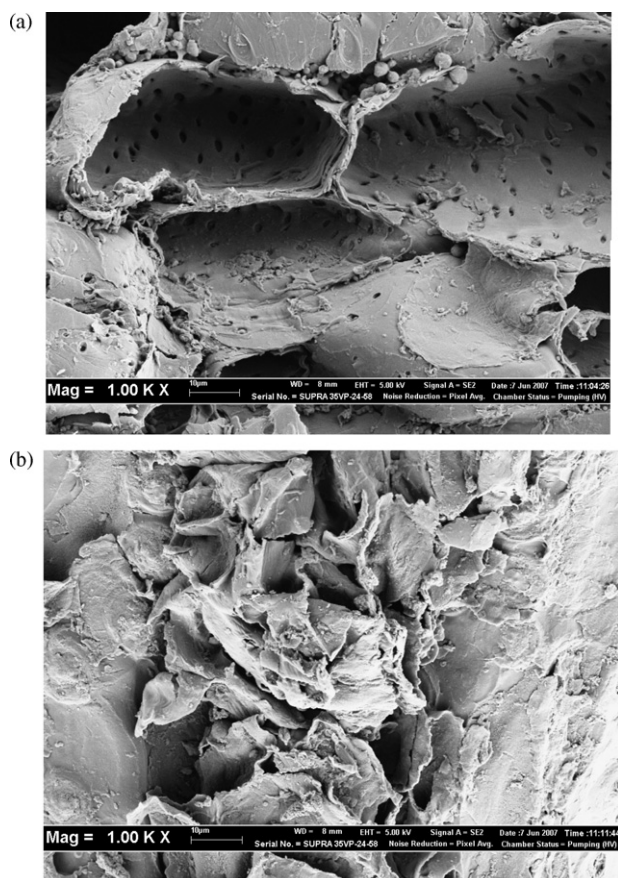
(a)

(b)

Fig. 2. Scanning electron microscope of (a) fresh CBW and (b) dye adsorbed CBW.

disappeared (1734.82 cm^{-1} (C=O stretch); 1507.98 cm^{-1} (NH deformation) and 1383.98 cm^{-1} (C–O–H bend)) and new peaks (2346.73 cm^{-1}, 2276.45 cm^{-1} (N–H stretch); 1166.96 cm^{-1} (C–N stretch) and 526.12 cm^{-1} (C–S stretch)) are also detected. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of the CBW in sorption process.

Fig. 2 shows the SEM micrographs of CBW samples before after dye adsorption. The CBW exhibits a caves-like, uneven and rough surface morphology. The surface of dye-loaded adsorbent, however, shows that the surface of CBW is covered with dye molecules.

3.2. Effect of initial dye concentration on dye adsorption

The effect of the initial MB concentration on the intake rate by CBW adsorption at adsorbent dosage of 0.20 g and mixing speed of 100 rpm is shown in Fig. 3. It can be seen that the adsorption at different concentrations is rapid in the initial stages and gradually decreases with the progress of adsorption until the equilibrium is reached. The amount of MB adsorbed at equilibrium (q_e) increased from 30.42 to 65.55 mg/g as the concentration was increased from 50 to 500 mg/L. The initial concentration provides an important driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phases. Hence a higher initial concentration of dye
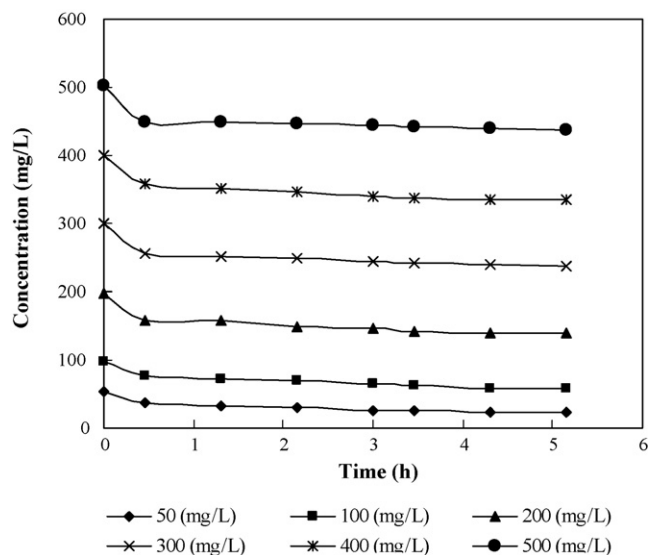

Fig. 3. Effect of initial concentration on removal of MB by CBW (conditions: sorbent dosage, 0.20 g; initial pH, 7.0; temperature, 30 °C).

will enhance the adsorption process. The MB removal decreased from 57% to 13% as the MB concentration was increased from 50 to 500 mg/L. The equilibrium conditions were reached within 3–4 h for low concentrations (less than 100 mg/L) while the rate of adsorption was slower for concentrations ranging from 200 to 500 mg/L (approximately 5 h).

3.3. Effect of solution pH on dye adsorption

Effect of pH on adsorption was studied using 100 mg/L dye concentration, pH 2–12 at 30 °C as given in Fig. 4. The dye adsorption was significantly changed over the pH value of 2–10. The dye adsorption was constant at pH 10–12. The lowest dye adsorption was recorded at pH 2 (13 mg/g). The equilibrium adsorption (q_e) was found to increase with increasing pH. The q_e increases from 13 to 85 mg/g for an increase in pH from 2 to 12. Wang et al. [29] reported that MB adsorption usually increases as the pH is increased. Lower adsorption of MB at acidic pH is probably due to the presence of excess H$^+$ ions competing with the cation groups on the dye for adsorption sites. At higher pH, the surface of CBW particles may get negatively charged, which enhances the positively charged dye cations through electrostatic
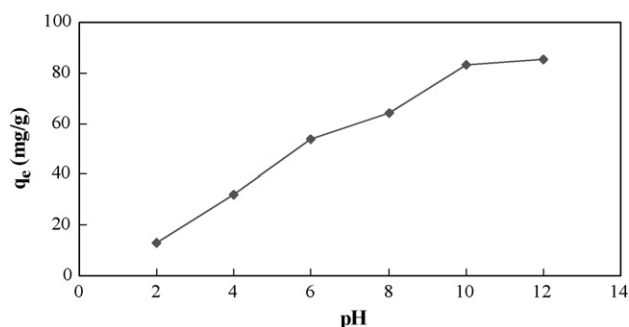

Fig. 4. Effect of the solution pH on the adsorption of methylene blue on CBW (C_0 = 100 mg/L, temperature 30 °C, stirring rate 100 rpm and W = 0.2 g).
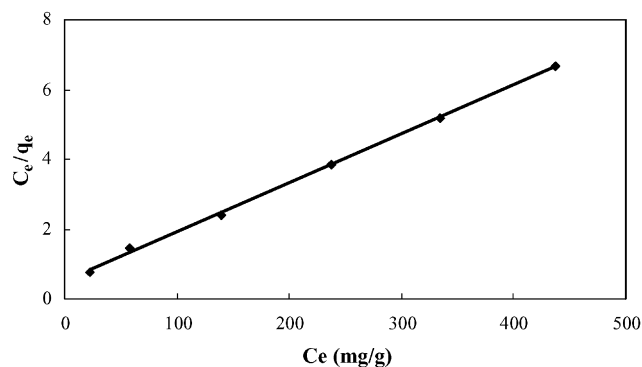
Fig. 5. Langmuir isotherm for MB sorption onto CBW at 30 °C.

Table 1
Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of MB onto CBW

Isotherm	Parameters
Langmuir	
Q_0 (mg/g)	70.92
b (L/mg)	0.029
R^2	0.999
Freundlich	
K_F	13.45
n	3.66
R^2	0.953
Temkin	
A	0.484
B	12.773
R^2	0.966

forces of attraction. The complex nature of the adsorbent as shown in Fig. 1 may indicate the possible involvement of some functional groups on the surface of CBW in sorption process.

3.4. Adsorption isotherms

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [30]. The isotherm results were analyzed using the Langmuir, Freundlich and Temkin isotherms. The Langmuir adsorption model [30] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions [6–8]. The expression of the Langmuir model is given by Eq. (3)

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

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed dye per unit mass of sorbent and unadsorbed dye concentration in solution at equilibrium, respectively. Q_0 is the maximum amount of the dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e, and b is a constant related to the affinity of the binding sites (L/mg). The Langmuir equation can be described by the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{4}$$

The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Fig. 5) shows that the adsorption obeys the Langmuir model. The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [31]:

$$R_L = \frac{1}{(1 + b C_0)} \tag{5}$$

where C_0 is the highest initial concentration of adsorbate (mg/L), and b (L/mg) is Langmuir constant. The value of R_L indicates

the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. The value of R_L in the present investigation was found to be 0.70 at 30 °C indicating that the adsorption of MB on CBW is favorable.

The Freundlich isotherm [32] is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed as:

$$q_e = K_F C_e^{1/n} \tag{6}$$

where K_F and n are Freundlich constants with K_F (mg/g (L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favourable adsorption condition [33,34,35]. To determine the constants K_F and n, the linear form of the equation may be used to produce a graph of $\ln(q_e)$ against $\ln(C_e)$ (Fig. 6):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{7}$$

Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 6).

Temkin and Pyzhev considered the effects of some indirect sorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with
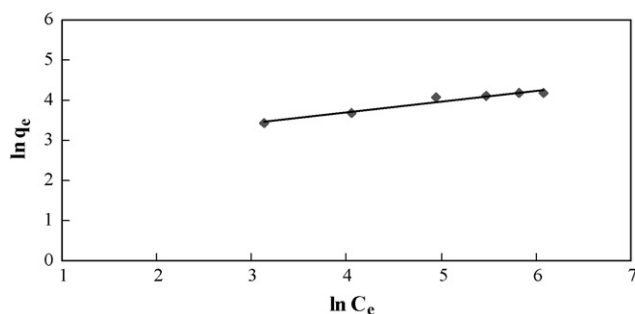

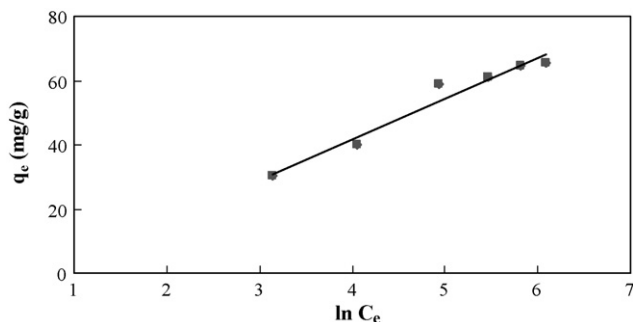Fig. 6. Freundlich isotherm for MB sorption onto CBW at 30 °C.

Fig. 7. Temkin isotherm for MB sorption onto CBW at 30 °C.

Table 2
Comparison of adsorption capacities of various adsorbents for MB

Adsorbents	Q_0 (mg/g)	T (°C)	Reference
CBW	70.92	30	This study
Yellow passion fruit waste	44.70	25	[38]
Fallen phoenix tree's leaves	83.8 ± 7.6	36	[39]
Wheat shells	16.56	30	[40]
Olive pomace	42.3	25	[41]
Charcoal	62.7	25	[41]
Ground hazelnut shells	76.9	20	[42]
Walnut sawdust	59.17	20	[42]
Cherry sawdust	39.84	20	[42]
Oak sawdust	29.94	20	[42]
Pitch-pine sawdust	27.78	20	[42]
Posidonia oceanica (L.) fibres	5.56	30 ± 2	[43]
Glass wool	2.2436	35	[44]

coverage [36]. The Temkin isotherm has been generally applied in the following form:

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \tag{8}$$

and can be linearized as:

$$q_e = B \ln A + B \ln C_e \tag{9}$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K). Therefore, by plotting q_e versus $\ln C_e$ enables one to determine the constants A and b as shown in Fig. 7. The constants A and B are listed in Table 1.

As seen in Table 1, the Langmuir isotherm fits quite well with the experimental data (correlation coefficient $R^2 > 0.99$), whereas, the low correlation coefficients ($R^2 < 0.96$) show poor agreement of Freundlich and Temkin isotherms with the experimental data. The monolayer adsorption capacity according to this model was 70.92 mg/g at 30 °C. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto CBW surface, since the Langmuir equation assumes that the surface is homogenous. This finding was similar to other studies on the sorption of MB on different sorbents. For example, Langmuir isotherm was found to fit well with the experimental data in the adsorption of

methylene on oil palm fibre activated carbon [7], palm kernel fibre [37] and algal biomass [21].

Table 2 compares the adsorption capacity of different types of adsorbents used for removal of MB. The most important parameter to compare is the Langmuir Q_0 value since it is a measure of adsorption capacity of the adsorbent. The value of Q_0 in this study is larger than those in most of previous works. This suggests that MB could be easily adsorbed on CBW.

3.5. Adsorption kinetics

A linear form of pseudo-first-order model was described by Lagergren [45] in the form:

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \tag{10}$$

A linear plot of $\log(q_e - q_t)$ against time allows one to obtain the rate constant (Fig. 8). If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to MB sorption on CBW. So, the adsorption process is a pseudo-first-order process [45,46]. The Lagergren's first-order rate constant (k_1) and q_e determined from the model are presented in Table 3 along with the corresponding correlation coefficients. It was observed that the pseudo-first-order model did not fit well. It was found that the calculated q_e values do not agree with the experimental q_e values (Table 3). This suggests that the adsorption of MB does not follow first-order kinetics.

The pseudo-second-order kinetics may be expressed in a linear form as [35,47]:

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

where the equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg h) can be determined experimentally from the slope and intercept of plot t/q_t versus t (Fig. 9). The k_2 and q_e determined from the model are presented in Table 3 along with the corresponding correlation coefficients. The values of the calculated and experimental q_e are represented in Table 3. It can be seen from Table 3 that there is an agreement between q_e experimental and q_e calculated values for the
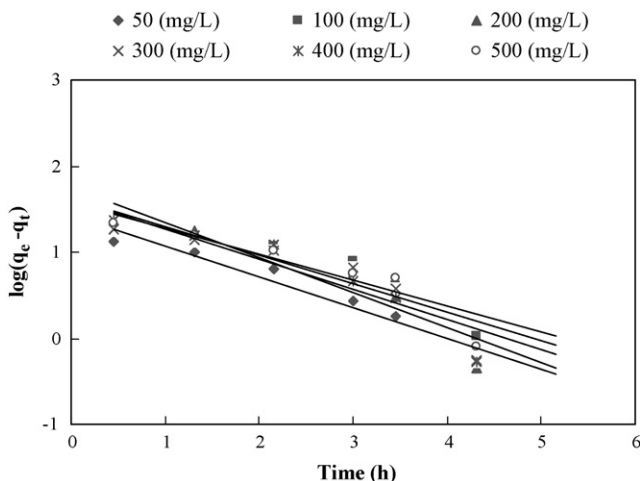

Fig. 8. Pseudo-first-order sorption kinetics of MB onto CBW.

Table 3
Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained at different initial MB concentrations

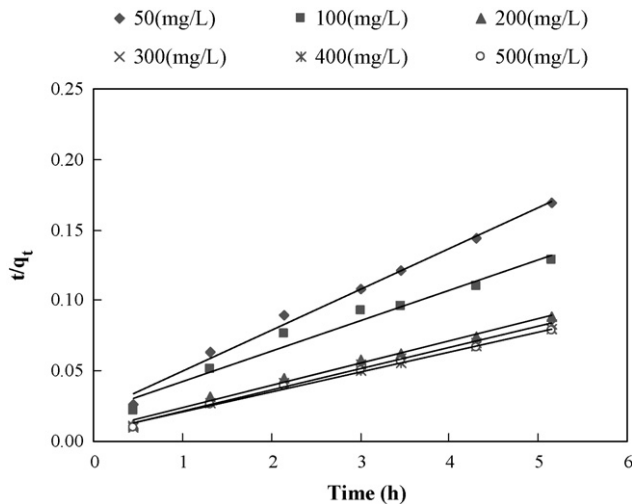| Initial conc. (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
		k_1 (1/h)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg h)	$q_{e,cal}$ (mg/g)	R^2
50	30.415	0.831	27.24	0.937	0.041	34.36	0.991
100	40.142	0.695	37.91	0.846	0.022	46.51	0.968
200	58.315	0.897	50.16	0.830	0.028	64.10	0.990
300	62.065	0.812	41.73	0.816	0.034	66.23	0.993
400	64.645	0.928	54.83	0.899	0.027	70.92	0.994
500	65.55	0.767	43.17	0.862	0.030	70.42	0.994

Fig. 9. Pseudo-second-order sorption kinetics of MB on CBW.

pseudo-second-order model. Hence, the pseudo-second-order model better represented the adsorption kinetics.

Similar phenomenon has been observed in the adsorption of methylene blue by hazelnut shells and wood sawdust [42], activated carbon prepared from rattan sawdust [8] and bamboo-based activated carbon [6].

The initial adsorption rates h (mg/g min) can be calculated from the pseudo-second-order model by the following equation:

$$h_{o,2} = k_2 q_e^2 \qquad (12)$$

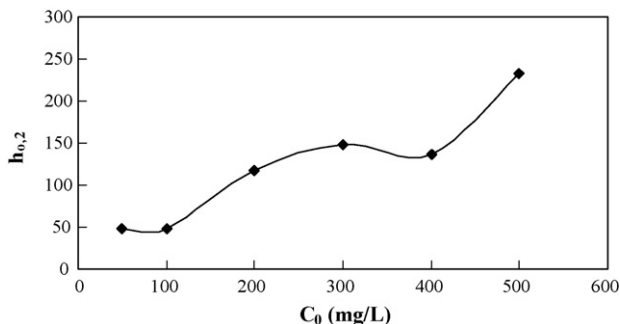and the results are plotted in Fig. 10. It was found that the initial rate of adsorption increases with increasing the initial MB concentration, which would be expected due to the increase in driving force at higher concentration.

3.6. Sorption mechanism

In order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were fitted to the Weber's intraparticle diffusion [48]. The kinetic results were analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism, which model is expressed as:

$$q_t = k_{id} t^{1/2} + C \qquad (13)$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g h$^{1/2}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ [48] as shown in Fig. 11. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate controlling step. The calculated intraparticle diffusion coefficient k_{id} values are listed in Table 4. If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. However, the linear plots at each concentration did not pass through the origin. This indicates that the intraparticle diffusion was not only rate controlling step.
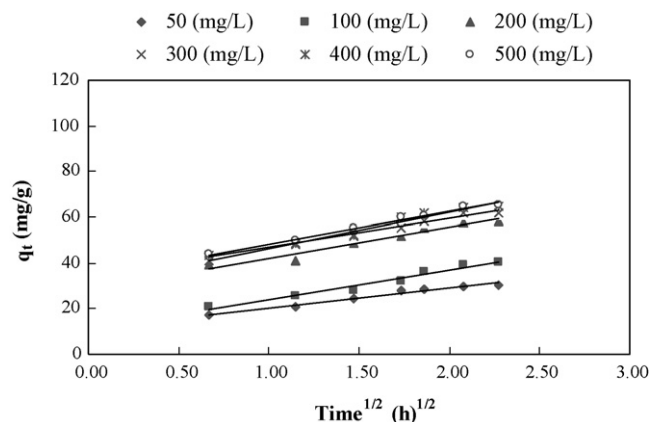

Fig. 10. The variation of the initial rate of adsorption with the initial MB concentration.

Fig. 11. Plots for evaluating intraparticle diffusion rate constant for sorption of MB onto CBW.

Fig. 12. A single-stage batch adsorber.

Fig. 13. Adsorbent mass (W) against volume of effluent (V) treated for different percentages of MB removal ($C_0 = 50$ mg/L).
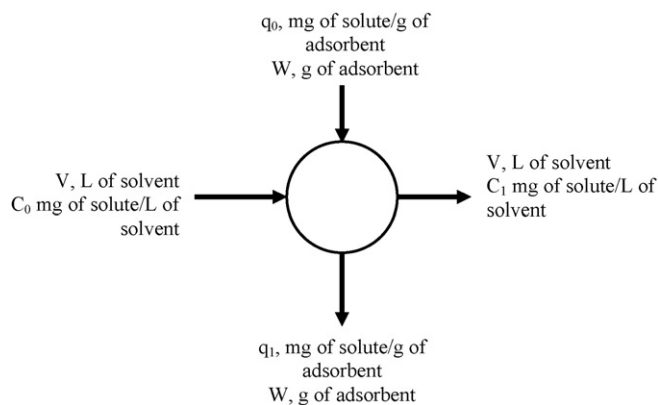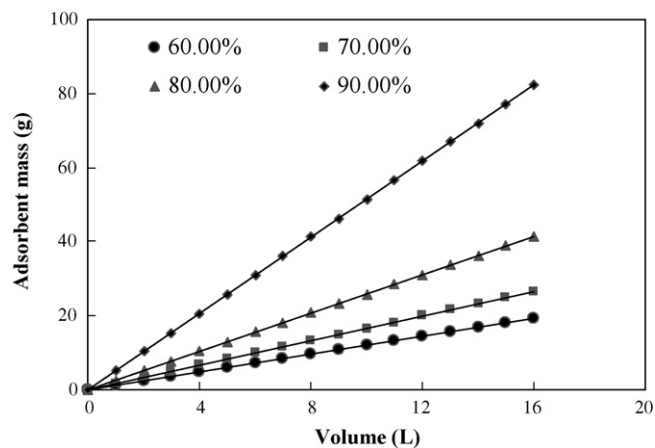
3.7. Design of batch sorption from isotherm data

A schematic diagram of a batch sorption process is shown in Fig. 12 where the effluent contains V (L) of water and an initial MB concentration C_0, which is to be reduced to C_1 in the adsorption process. In the treatment stage W (g) CBW (dye-free) is added to solution and the dye concentration on the solid changes from $q_0 = 0$ (initially) to q_1. The mass balance for the dye in the single-stage is given by

$$V(C_0 - C_1) = W(q_0 - q_1) \qquad (14)$$

Under equilibrium conditions,

$$C_1 \rightarrow C_e \quad \text{and} \quad q_1 \rightarrow q_e$$

$$VC_0 + Wq_0 = VC_e + Wq_e \qquad (15)$$

For the adsorption of MB on CBW, the Langmuir isotherm gives the best fit to experimental data. Consequently equation can be best substituted for q_1 in the rearranged form of Eq. (15) giving adsorbent/solution ratios for this particular system,

$$\frac{W}{V} = \frac{(C_0 - C_1)}{q_e} = \frac{C_0 - C_e}{Q_0 b C_e / (1 + b C_e)} \qquad (16)$$

Fig. 13 shows a series of plots (50, 60, 70, 80 and 90% dye removal at different solution volumes, i.e., 1, 2, 3, 4, 5, 6, 7 and 8 L) derived from Eq. (16) for the adsorption of MB on CBW at initial concentration of 50 mg/L. The amount of CBW required for the 90% removal of MB solution of concentration 50 mg/L was 5.1, 10.3, 15.4 and 20.6 g for dye solution volumes of 1, 2, 3 and 4 L, respectively.

3.8. Cost-estimation of coconut bunch waste sorbent

The coconut bunch waste accumulates in the agro-industrial yards, has no significant industrial and commercial uses, but becomes an issue and contributes to serious environmental problems. Hence, the utilization of such agriculture solid waste for wastewater treatment is most desirable. The cost of this waste as a dye sorbent is only associated with the transport and process expenses which are approximately US$ 50/ton whereas the average price of activated carbon used in Malaysia is US$ 1000–1100/ton. Thus the proposed CBW sorbent is more than 20 times cheaper than activated carbon. Although the adsorption capacity of CBW may be lower than commercial activated carbons, the adsorbent is renewable material, abundantly available and, therefore, low-cost adsorbent. The CBW would be an economical alternative for the commercially available activated carbon in removal of basic dye from aqueous solutions.

4. Conclusions

In this work, the ability of CBW sorbent to remove MB from aqueous solution was investigated. Experimental results show CBW was effective for the removal of MB from aqueous solution. Since CBW used in this work is freely, abundantly and locally available, the resulting sorbent is expected to be economically viable for removal of basic dye from aqueous solution. Results obtained were modeled using three isotherm models: Langmuir, Freundlich and Temkin. Equilibrium isotherms were well described by the Langmuir equation, giving maximum adsorption capacity of 70.92 mg/g at 30 °C. The adsorption kinetics can be well described by the pseudo-second-order model equation. The coconut bunch waste appeared to be suitable for the removal of MB from aqueous solutions.

Table 4
Intraparticle diffusion constants for different initial MB concentrations at 30 °C

Initial conc. (mg/L)	$q_{e,cal}$ (mg/g)	k_i (mg/g h$^{1/2}$)	C	R^2
50	31.814	9.05	10.97	0.977
100	40.309	12.83	11.19	0.972
200	60.076	13.69	28.26	0.952
300	61.913	12.42	33.52	0.985
400	66.718	15.91	30.61	0.973
500	64.731	14.36	34.81	0.991

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