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Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution

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ABSTRACT

Meranti (*Philippine mahogany*) sawdust, an inexpensive material, showed strong scavenging behaviour through adsorption for the removal of methylene blue (MB) from aqueous solution. Batch studies were performed to evaluate and optimize the effects of various parameters such as contact time, pH, initial dye concentrations and adsorbent dosage. Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data at different temperatures. The experimental data fitted well with the Langmuir adsorption isotherm, indicating thereby the mono layer adsorption of the dye. The monolayer sorption capacity of meranti sawdust for MB was found to be 120.48, 117.64, 149.25 and 158.73 mg/g at 30, 40, 50 and 60 °C, respectively. Thermodynamic calculations showed that the MB adsorption process is endothermic and spontaneous in nature. Kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model. The results indicated that the meranti sawdust could be an alternative material in place of more costly adsorbents used for dye removal.

1. Introduction

The pollution caused by industrial wastewater has become a common problem for most of the countries. Wastewater from the textile, cosmetics, printing, dying, food coloring, and paper making etc., are polluted by dyes. The number of dyes presently used in textile industry is about 10,000. The annual production of these dyes is over 7×10^5 tons [1]. Effluent discharged from dyeing industries is highly colored and not only is toxic to aquatic life in receiving water but also affects its aesthetic value. Color impedes light penetration affecting plants in the receiving streams, thereby seriously affects the ecosystem of the streams [2]. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria [3]. Many dyes and pigment have toxic as well as carcinogenic, mutagenic and teragenic effects on aquatic life and also on humans [4].

Methylene blue has wider application, which includes coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. [5]. Though methylene blue is not strongly hazardous but on inhalation, it can show various harmful effects. 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 gastric. Accidental large dose creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia [6].

During the last few years new or tighter regulations coupled with increased enforcement concerning wastewater discharges have been established in many countries. There is an increased demand of cheaper methods of pollutant removal [7]. Thus, adsorption process are being employed widely for large-scale biochemical, chemical and environmental recovery and purification applications. The major advantages of a sorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation, no effect by toxic substances, and superior removal of organic waste constituents as compared to the conventional biological treatment processes [8]. Activated carbon as an adsorbent has been widely investigated for the adsorption of basic dyes [9–13], but its high-cost limits its commercial application. In recent years, extensive research has been undertaken to develop alternative and economic adsorbents. An economic sorbent is defined as one which is abundant in nature, or is a by-product or waste from industry and requires little processing [14]. Such alternatives include: chitosan bead [15], oil palm trunk fiber [16], fly ash [8], and dried biomass of Baker's yeast [17], durian (*Durio zibethinus Murray*) peel [18], Guava (*Psidium guajava*) leaf powder [19], chitosan/oil palm ash composite [20], high lime Soma fly ash [21], almond shells [22], pomelo (*Citrus grandis*) peel [23], treated parthenium biomass [24] and broad bean peels [25]. Recently, an extensive list of sorbent literature for dye removal has been compiled by Allen and Koumanova [26].

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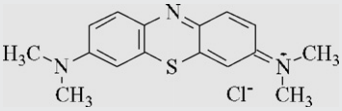
Table 1
Various physical and chemical properties of adsorbate and adsorbent.

Properties	Values	Properties	Values
Chemical structure		Particle size (μm)	100–150
		Surface area (m^2/g)	630
		Pore volume (ml/g)	0.064
Chemical formula	$C_{16}H_{18}N_3ClS$	Pore diameter (Å)	363.4
Wave length	668 (nm)	Bulk density (g/cm^3)	0.27
IUPAC name	3,7-bis(dimethylamino)- phenothiazin-5-ium chloride	Skeletal density (g/cm^3)	3.21
		Wet density (g/cm^3)	2.98
Molecular weight	319.85 (g/mol)	Ash contents (%)	2.20
Type	Basic dye	Moisture contents (%)	6.25
Color	Blue	Water soluble components (inorganic matter) (%)	21.73
Solution pH	6.5		
pH_{ZPC}	6.23	Insoluble components (organic matter) (%)	76.22
Solubility	Soluble in water		

Sawdust has received particular attention as an economical adsorbent for removing basic dyes from wastewater due to its abundance, easy availability and low cost. Further, it will be a step ahead toward exploring the possibility on the use of waste biomass for industrial wastewater pollution management. The studies on the use of meranti sawdust as adsorbent are limited. It is a common tree present all in tropical countries such as Malaysia and Indonesia. Meranti tree is widely used for furniture making and the waste sawdust produced is generally used for heating in the boiler. The main aim of this study was to investigate the potentiality of using meranti sawdust as an adsorbent for the adsorption of methylene blue (MB). The effects of initial dye concentration, contact time, adsorbent dosage and pH on MB adsorption were studied. Adsorption isotherms and kinetics parameters were also calculated and discussed.

2. Materials and methods

2.1. Adsorbent

Meranti wood was bought from market and converted into sawdust in the laboratory. The sawdust was washed with distilled water and then dried in a dryer at 70 °C. The material was ground to a fine powder in a still mill. The resulting material was sieved in the size range of 100–150 μm particle size. To remove water soluble substances, the ground powder was treated with 0.5 M HCl at room temperature for 4 h. After that, the sawdust was filtered out, washed with distilled water until no chloride was released and activated at 70 °C in a oven for 24 h. The material was placed in an airtight container for further use.

2.2. Adsorbate

Basic dye used in this study was methylene blue (MB) purchased from Sigma–Aldrich (M) Sdn Bhd, Malaysia and used without purification. The MB was chosen in this study because of its known strong adsorption onto solids. The characteristics of the dye are listed in Table 1.

2.3. Scanning electron microscopy, Fourier transform infra red study and surface area analysis

Scanning electron microscopy (Carl-Ziess SMT, Oberkochen, Germany) analysis was carried out on meranti sawdust to study its surface morphology before and after MB adsorption. For the main functional groups that might be involved in dye adsorption, a Fourier Transform Infrared (Nicolet, AVATAR FTIR-360) analysis was done on the plain and dye adsorbed meranti sawdust to determine the surface functional groups, and the spectra were recorded from 4000 to 400 cm^{-1}. The surface area of meranti sawdust was determined using a Micromeritics ASAP 2010 gas adsorption surface analyzer.

2.4. Batch adsorption studies

Batch adsorption studies were carried out by shaking 0.5 g of meranti sawdust with 100 ml of the aqueous solution of MB for the different times using a temperature-controlled shaker. The solution-adsorbent mixtures were stirred at 150 rpm and at the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its concentrations using UV/visible spectrophotometer Shimadzu (UV-1601PC) at 668 nm. The effect of pH of the initial solution on the equilibrium uptake of MB was analyzed over a pH range from 3 to 12. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. The adsorption experiments were also conducted to determine the equilibrium time, the optimum pH and dosage of the adsorbent for maximum adsorption. The percentage of dye adsorption by the adsorbent was computed using the equation:

$$\%\,\text{Adsorption} = \left\{\frac{(C_i - C_e)}{C_i}\right\} 100 \quad (1)$$

where, C_i and C_e are the initial and equilibrium concentrations of dye (mg/L) in the solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent [27]:

$$q = \frac{(C_i - C_e)V}{W} \quad (2)$$

where, q is the adsorption capacity (mg/g), V is the volume of dye solution (L) and W is the weight of the adsorbent (g).

3. Results and discussion

3.1. Characterization of meranti sawdust

The cell walls of meranti sawdust mainly consist of cellulose and lignin and many hydroxyl groups, such as tannins or other phenolic compounds. Lignin is a polymer material built up from the phenyl propane nucleus, an aromatic ring with a three-carbon side chain. Vanillin and syringaldehyde are the two other basic structural units of lignin molecule. Tannins are complex polyhydric phenols, which

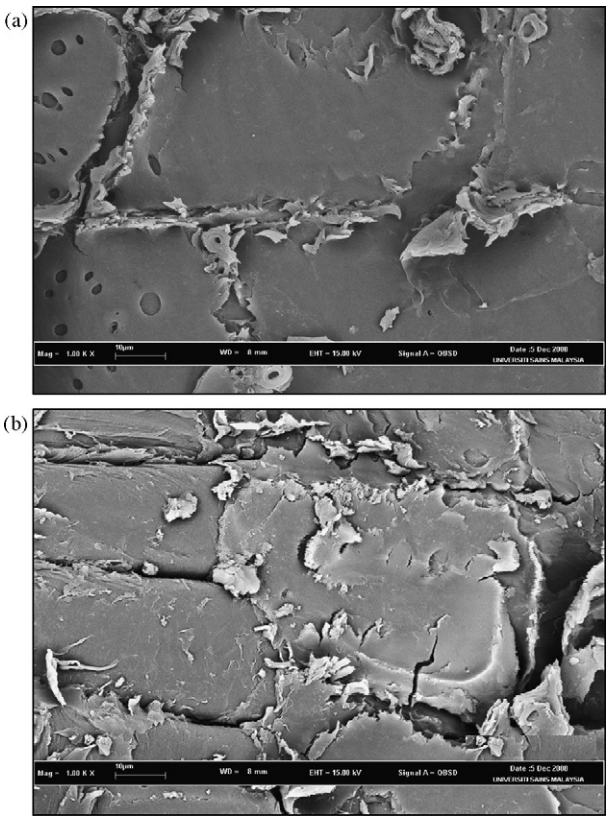


Fig. 1. SEM micrograph of meranti sawdust (magnification: 1000): (a) before MB adsorption (b) after MB adsorption.

are soluble in water and have the property of precipitating protein (gelatin) [28].

Characteristics of the adsorbent such as surface area, pore volume, pore diameter, density, moisture content, ash content, and solubility in water (inorganic and organic matter) were determined. The results are summarized in Table 1. Fig. 1 shows the SEM micrograph of meranti sawdust before and after dye adsorption. It is clear that meranti sawdust has considerable layers of pores where there is a good possibility for dye to be adsorbed. The surface of dye loaded adsorbent is different from the surface of plain adsorbent. The FTIR spectrum of meranti sawdust shows that some peaks were shifted (Fig. 2 and Table 2). There is a strong peak at 3445 cm^{-1} representing the –OH stretching of phenol group of cellulose and lignin, and the peak at 2927 cm^{-1} indicates the presence of $–CH_2$ stretching of aliphatic compound. The appearance of peaks at 1735 cm^{-1} and 1633 cm^{-1} indicate the presence of C=O stretching of aldehyde group and C=C stretching of phenol group, respectively. Where as the peaks between at 1508 cm^{-1} and 1372 cm^{-1} in the spectrum of meranti sawdust can be due to C=C of aromatic ring. Peaks at 1243 cm^{-1} and 1041 cm^{-1} in the FTIR spectrum of meranti sawdust can be due to C–O stretching of phenolic group and six member cyclic ether group of cellulose, respectively. These changes observed in the spectrum indicated the possible involvement of those functional groups on the surface of meranti sawdust in adsorption process.

Table 2
FTIR of meranti sawdust.

S. No.	Frequency (cm^{-1})		Differences	Assignment
	Before adsorption	After adsorption		
1	3445	3442	3	OH stretching
2	2927	2921	6	CH_2 stretching
3	2359	2360	−1	NH stretching
4	1735	1735	–	C=O stretching
5	1633	1627	6	C=C stretching
6	1508	1507	1	C=C of aromatic ring
7	1459	1458	1	CH_2 deformation
8	–	1424	–	OH Bending
9	1372	1384	−12	C–O–H bending
10	1243	–	–	C–O stretching
11	1041	1058	−17	Six member cyclic ether

Pore sizes are classified in accordance with the classification adopted by the International Union of Pure and Applied Chemistry (IUPAC), that is, micropores (diameter (d) < 20 Å), mesopores (20 Å < d < 500 Å), and macropores (d > 500 Å). The average pore diameter determined by Barrett–Joiner–Halenda (BJH) method was 363.4 Å, suggesting that meranti sawdust consists of mesopores.

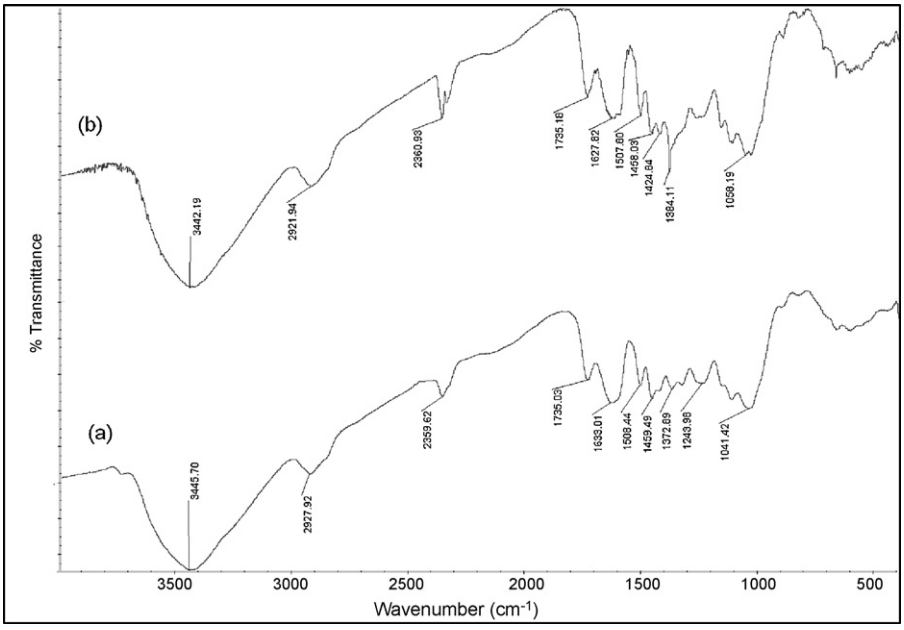


Fig. 2. FTIR spectra of meranti sawdust: (a) before MB adsorption (b) after MB adsorption.

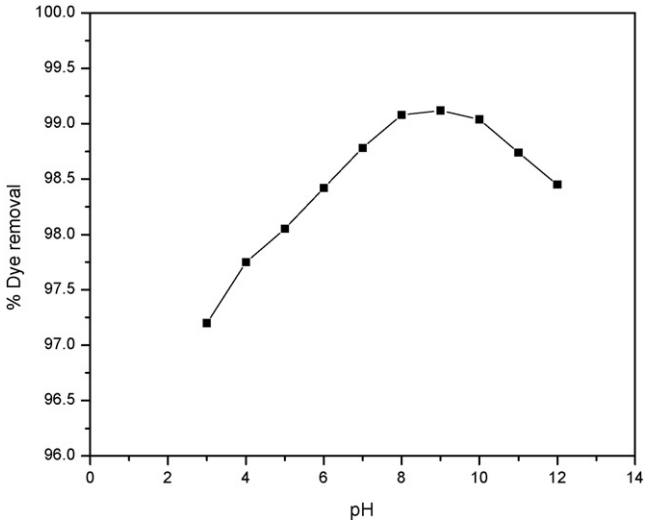


Fig. 3. Effect of the solution pH on MB adsorption.

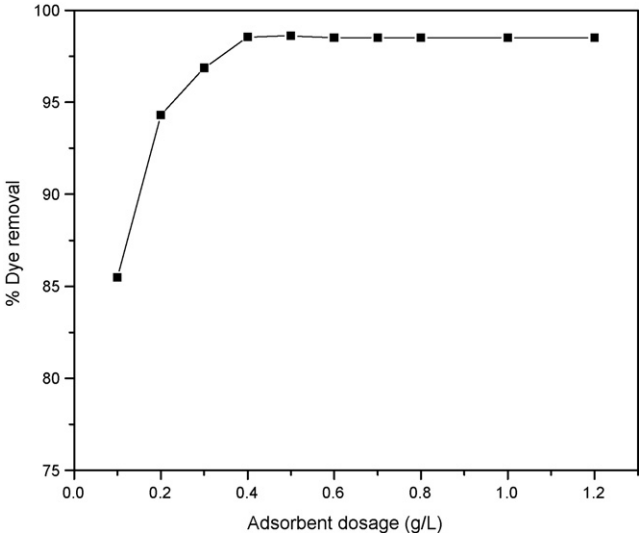


Fig. 4. Effect of adsorbent dosage on MB adsorption.

3.2. pH_{ZPC} and effect of pH

The determination of pH_{ZPC} of meranti sawdust was performed according to the solid addition method [29]: 50 mL of 0.01 M KNO_3 solution was placed in conical flasks. The initial pH of the solutions was adjusted to a value between 3 and 12 by adding 0.1 M HCl or NaOH solutions. Then, 1 g of meranti sawdust was added to each flask, strirred and the final pH of the solutions was measured after 24 h. The value of pH_{ZPC} can be determined from the curve that cuts the pH_0 line of the plot ΔpH vs pH_0. The pH_{ZPC} of an adsorbent is a very important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution. The value of pH_{ZPC} is close to the value of pH of aqueous slurry which is 6.23 (Table 1).

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. The effect of pH on the adsorption of MB on meranti sawdust is presented in Fig. 3. It shows that the adsorption of the dye in the pH range of 3–12 varies between 97% and 99%. The percentage removal of MB was minimum at the pH 3 and increased with further increase in pH. However, at higher pH values of 9–12 the dye adsorption decreased. Hamdaoui [3] in a study of the sorption of methylene blue onto cedar sawdust and crushed brick reported that as pH of the system decreased and the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. Also, lower adsorption of methylene blue at acidic pH is due to the presence of excess H^+ ions competing with dye cations for the adsorption sites. Moreover, the decrease in adsorption at high pH values might be due to hydrolysis, of sawdust itself which creates positively charged sites. A similar phenomenon was observed for the adsorption of MB onto pomelo (*C. grandis*) peel [23] and broad bean peels [25]. Therefore, pH 9 was selected to be the optimum pH for further studies.

3.3. Effect of adsorbent dosage

Fig. 4 shows the removal of MB by meranti sawdust at different dosage of adsorbent (0.1–1.2 g) at initial concentration of 100 mg/L dye solution and 30 °C. From the figure it was observed that, the percentage of dye removal increased from 85.0 to 98.5% with an increase in adsorbent mass from 0.1 to 0.5 g. The percentage removal increased with the sawdust dosage up to a certain limit and then it reached a constant value. The increase in adsorption of dyes with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites. A similar behaviour was reported for the adsorption of MB on papaya (*Carica Papaya L.*) seeds [30] and jackfruit (*Artocarpus heterophyllus L.*) peel [31].

3.4. Effect of contact time and initial dye concentration

The effect of contact time on the removal of MB by meranti sawdust at initial concentrations 50–200 mg/L at 30 °C is shown in Fig. 5. The time curve shows that the removal of adsorbate is rapid but it gradually slows down until it reaches the equilibrium. This is due to the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. The equilibrium was attained after shaking for 3 h. Once equilibrium was attained, the percentage sorption of methylene blue did not change with further increases of time. So,

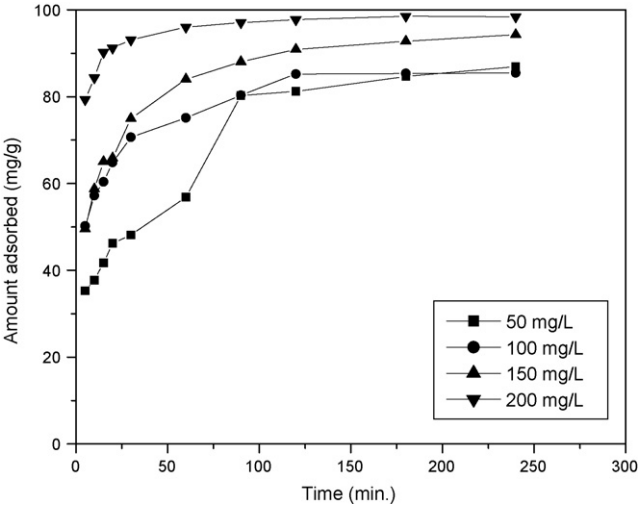


Fig. 5. Effect of contact time and initial concentration on MB adsorption.

it was assumed that longer treatment might not have further effect to change the properties of the adsorbent. In batch type of adsorption systems, the rate of removal of adsorbate species from aqueous solution is controlled primarily by the rate of transport of the adsorbate species from the exterior/outer sites to the interior sites of the adsorbent particles [32]. A similar trend was also observed for MB adsorption onto hazelnut shells [33] and beech wood sawdust [34].

It is also evident from Fig. 5 that the amount of dye adsorbed (mg/g) increased with increased dye concentration and remained constant after equilibrium time. The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process. The equilibrium adsorption capacity of meranti sawdust increased with an increase in initial dye concentration, while the percent removal of dye showed the opposite trend. When the initial dye concentration increased from 50 to 200 mg/L, the loading capacity of meranti sawdust increased from 35.29 to 98.40 mg/g, and the percentage removal decreased from 98 to 86 %. At high concentrations the fractional sorption is low. It can be seen that the initial concentration of dyes had only a small influence on the time of contact necessary to reach equilibrium. However, for low concentrations the initial uptake of dye is rapid, indicating a rapid surface reaction. Consequently, the concentration of dye will greatly affect the extent and rate of dye uptake on sawdust. A similar phenomenon was observed for the adsorption of MB onto pomelo (*C. grandis*) peel [23] and castor seed shell [35].

3.5. Adsorption behavior of sawdust (isotherm studies)

The adsorption isotherms revealed the specific relation between the concentration of the adsorbate and its adsorption degree onto adsorbent surface at a constant temperature. To quantify the adsorption capacity of meranti sawdust for the removal of MB from aqueous solution, the Langmuir, Freundlich and Temkin isotherm models were used.

3.5.1. Langmuir model

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes [36]. The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hint towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect of adsorption phenomenon.

The data of the equilibrium studies for adsorption of MB onto meranti sawdust may follow the following form of Langmuir model:

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

where C_e is the equilibrium concentration (mg/L) and q_e is the amount adsorbed per specified amount of adsorbent (mg/g), Q_0 is the Langmuir equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/q_e vs C_e (Fig. 6) should be a straight line with a slope $(1/Q_0)$ and an intercept as $(1/bQ_0)$. The values of constants Q_0 and b were calculated and reported in Table 3. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L [37], also known as the separation factor, given by:

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

The value of R_L lies between 0 and 1 for favourable adsorption, while $R_L > 1$ represents unfavourable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L = 0$.

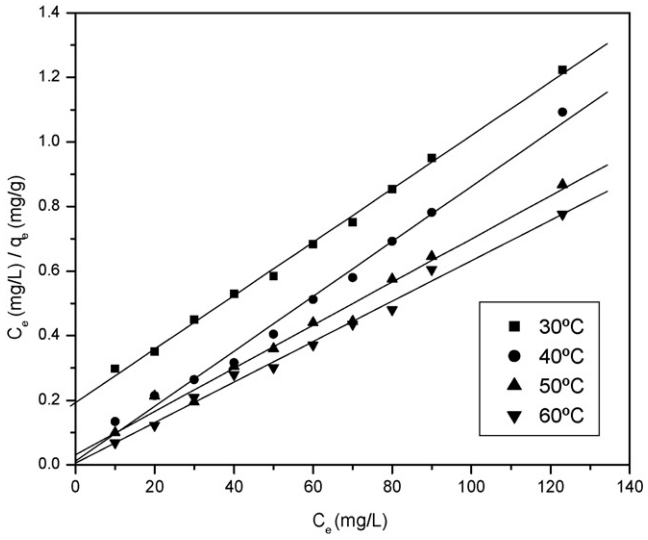


Fig. 6. Langmuir isotherm plots for MB adsorption at different temperatures.

The isotherm data have been linearized using Langmuir isotherm as shown in Fig. 6, the high values of correlation coefficient (R^2 = 0.991 to 0.997) indicate a good agreement between the parameters and confirms the monolayer adsorption of MB onto meranti sawdust surface. The dimensionless parameter R_L remained among 0.010 to 0.189 ($0 < R_L < 1$) consistent with the requirement for a favourable adsorption process.

3.5.2. Freundlich model

The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption [38]. According to this model:

$$q_e = (K_F)(C_e^{1/n}) \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \quad (6)$$

where, K_F is Freundlich equilibrium constant, n is an empirical constant and rest of the terms have the usual significance. Thus, a plot of $\ln q_e$ vs $\ln C_e$ (Fig. 7) should be a straight line with a slope $1/n$ and an intercept of $\ln K_F$. This model deals with the multilayer adsorption of the substance on the adsorbent. The related parameters were calculated and reported in Table 3. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent and thus is responsible for multilayer adsorp-

Table 3
The related parameters for the adsorption of MB on meranti sawdust at different temperatures.

Adsorption isotherms and its constants	Temperatures (°C)			
	30	40	50	60
Langmuir adsorption isotherm constants				
Q_0 (mg/g)	120.48	117.64	149.25	158.73
b (L/mg)	0.042	0.726	0.210	0.984
R^2	0.997	0.991	0.985	0.992
R_L	0.189	0.013	0.045	0.010
Freundlich adsorption isotherm constants				
K_F (mg/g) (L/mg)$^{1/n}$	12.14	11.35	11.25	12.05
n	1.441	1.371	1.348	1.366
R^2	0.895	0.928	0.944	0.987
Temkin adsorption isotherm constants				
K_T (L/mg)	39.62	21.46	37.29	25.53
B	6.927	7.355	7.125	7.413
R^2	0.977	0.975	0.983	0.971

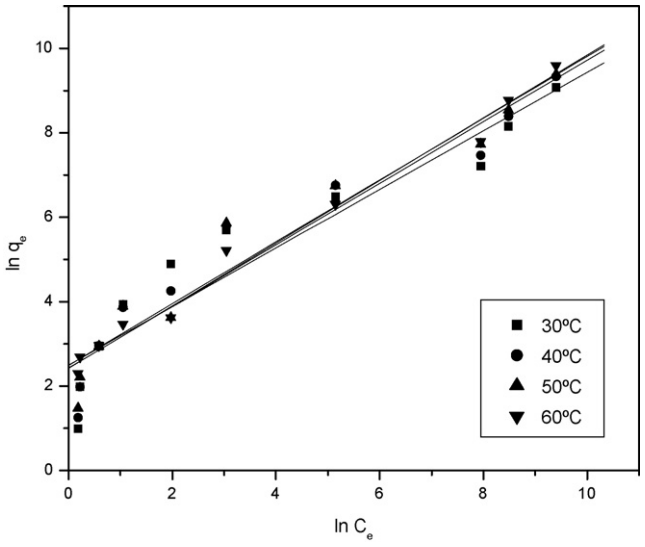


Fig. 7. Freundlich isotherm plots for MB adsorption at different temperatures.

tion due to the presence of energetically heterogenous adsorption sites.

3.5.3. Temkin model

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

$$q_e = \left(\frac{RT}{b}\right) \ln(K_T C_e) \quad (7)$$

Eq. (7) can be expressed in its linear form as

$$q_e = B \ln K_T + B \ln C_e \quad (8)$$

where,

$$B = \left(\frac{RT}{b}\right) \quad (9)$$

The adsorption data were analyzed according to Eq. (8). A plot of q_e vs $\ln C_e$ yielded a linear line, as shown in Fig. 8 enables the determination of the isotherm constants K_T and B. K_T is the Temkin

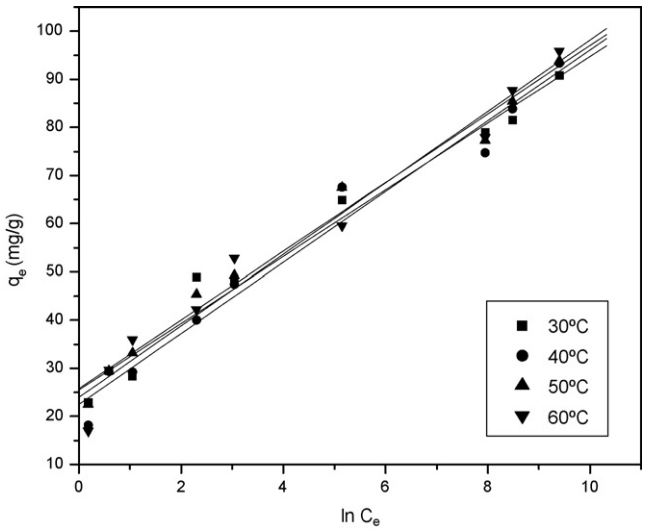


Fig. 8. Temkin isotherm plots for MB adsorption at different temperatures.

Table 4
Comparison of adsorption capacities of various adsorbents for MB.

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
Meranti sawdust	120.48	This work
Raw beech sawdust	9.78	[40]
Cedar sawdust	142.36	[3]
Coffee husks	90.09	[41]
Fallen phoenix tree's leaves	83.8 ± 7.6	[42]
Rice husks	40.50	[43]
Date pits	80.31	[44]
Wheat shells	16.56	[45]
Yellow passion fruit waste	44.70	[46]
Crushed brick	96.61	[3]

equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant B is related to heat of adsorption. The constants K_T and B together with the R^2 values are shown in Table 3.

From Table 3, the Langmuir adsorption isotherm model yielded best fit as indicated by the highest R^2 values at all temperatures compared to the other two models. Table 4 lists a comparison of maximum monolayer adsorption capacity of MB on various adsorbents. Meranti sawdust is found to have a relatively large adsorption capacity of 120.48 mg/g and this indicates that it could be considered a promising material for the removal of MB from aqueous solution.

3.6. Thermodynamic study of adsorption

In order to evaluate the thermodynamic parameters for the adsorption of MB onto meranti sawdust, the adsorption studies were carried out at different temperatures 303, 313, 323 and 333 K. The standard free energy change (ΔG°) is the fundamental criterion of spontaneity of a process and can be determined using equilibrium constant as shown below:

$$\Delta G^\circ = -RT \ln K \quad (10)$$

where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature and K is the equilibrium constant. Since Langmuir adsorption isotherm is the best fit so value of b was used in place of K in the calculations of all thermodynamic parameters.

Similarly, the standard enthalpy change ΔH° from 303 K to 333 K was computed from the following equation,

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

Thus a Plot of $\ln K$ vs $1/T$ should be straight line as shown in Fig. 9. ΔH° and ΔS° values were obtained from the slope and intercept of this plot, respectively. The standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°), were obtained from the Eqs. (10) and (11) and its values associated with the adsorption of MB onto meranti sawdust are listed in Table 5. Negative values of ΔG° indicate the feasibility of the process and spontaneous nature of the adsorption with a high performance of MB for meranti sawdust. Positive value of ΔH° indicates the endothermic nature of the process, while positive value of ΔS°

Table 5
Values of thermodynamic parameters for MB adsorption onto meranti sawdust.

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	R^2
303	−6.990	86.62	0.308	0.998
313	−12.83			
323	−13.13			
333	−16.35			

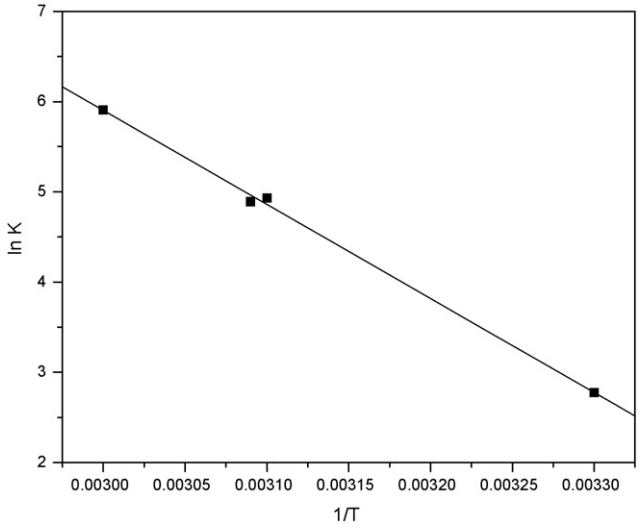


Fig. 9. Plot of ln K vs $1/T$ for MB adsorption onto meranti sawdust.

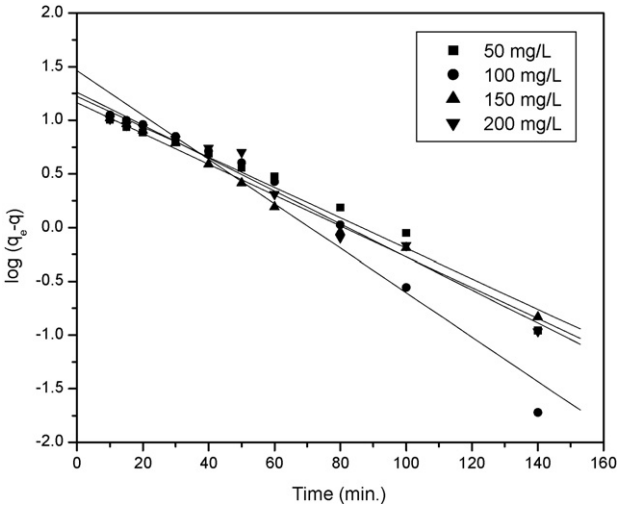


Fig. 10. Pseudo-first-order kinetic plots for MB adsorption onto meranti sawdust.

reflects the affinity of the adsorbents for the MB and suggests some structural changes in adsorbate and adsorbent [45,47].

3.7. Kinetic studies

Kinetics of the adsorption process has been evaluated for this work. This study describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid–liquid interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbents. In order to determine the adsorption kinetics of MB, the pseudo-first order, pseudo-second order and Weber–Morris diffusion models were checked. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

3.7.1. Pseudo-first-order model

The pseudo-first order rate model of Lagergren [48] is based on solid capacity and generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{12}$$

where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q is the amount of solute adsorbed at any time (mg/g) and k_1 is the adsorption constant. Eq. (12) is integrated for the boundary conditions $t = 0$ to $t > 0$ ($q = 0$ to $q > 0$) and then rearranged to obtain the following linear time dependent function:

$$\log(q_e - q) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \tag{13}$$

This is the most popular form of pseudo-first-order kinetic model. Fig. 10 shows an example for these plots. Constant k_1 and correlation coefficients have been calculated and summarized in Table 6.

3.7.2. Pseudo-second-order model

The kinetic data were further analyzed using the pseudo-second-order model [49] which, can be expressed as:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{14}$$

Integrating Eq. (14) for the boundary conditions $t = 0$ to $t > 0$ and $q = 0$ to $q > 0$ and rearranging to obtain the linearized form which is shown as follows:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \tag{15}$$

$$h = k_2 q_e^2 \tag{16}$$

where, h is the initial sorption rate (mg/g min). The plot of t/q vs t of Eq. (15) should give a linear relationship, from which, q_e and k_2 can be determined from the slope and intercept of the plot (Fig. 11). The correlation coefficient (R^2) values for this model (Table 6) are higher than that of the pseudo-first order rate model. Hence it can be assumed that the adsorption of MB perfectly follows the pseudo second order kinetic model.

3.7.3. Weber–Morris diffusion model

The possibility of intra particle diffusion was examined using the intraparticle diffusion Weber–Morris model [50], taking into account that during the course of adsorption the adsorbed amount is proportional to the square root of contact time,

$$q_t = kpt^{1/2} + C \tag{17}$$

where, q_t is the amount adsorbed (mg/g) at time t (min.). In a batch reactor with rapid stirring, there is also a possibility that the transport of MB from the solution into the pores of the adsorbent is the rate-controlling step [32]. This possibility was tested in terms of a graphical relationship between the amount of MB adsorbed

Table 6
Pseudo-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption of MB onto meranti sawdust.

Kinetic models and its parameters	Initial concentrations (mg/L)			
	50	100	150	200
Pseudo-first-order kinetic				
q_e (mg/g)	16.71	28.94	14.54	18.24
k_1 (min^{-1})	0.032	0.047	0.033	0.035
R^2	0.970	0.959	0.991	0.972
Pseudo-second-order kinetic				
q_e (mg/g)	19.53	23.04	24.27	22.27
k_2 (g mg^{-1} min^{-1})	0.060	0.063	0.088	0.076
h (mg g^{-1} min^{-1})	23.15	33.60	52.07	37.94
R^2	0.993	0.991	0.995	0.987
Intraparticle diffusion				
kp (min$^{1/2}$)	1.198	1.430	1.243	2.797
C	7.247	8.605	11.75	6.032
R^2	0.955	0.922	0.876	0.981

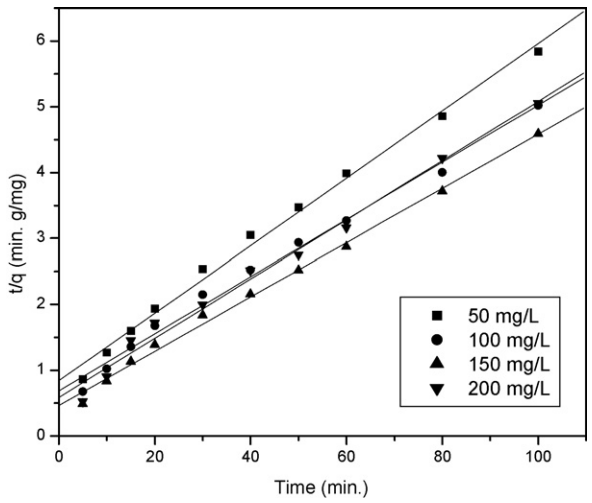


Fig. 11. Pseudo-second-order kinetic plots for MB adsorption onto meranti sawdust.

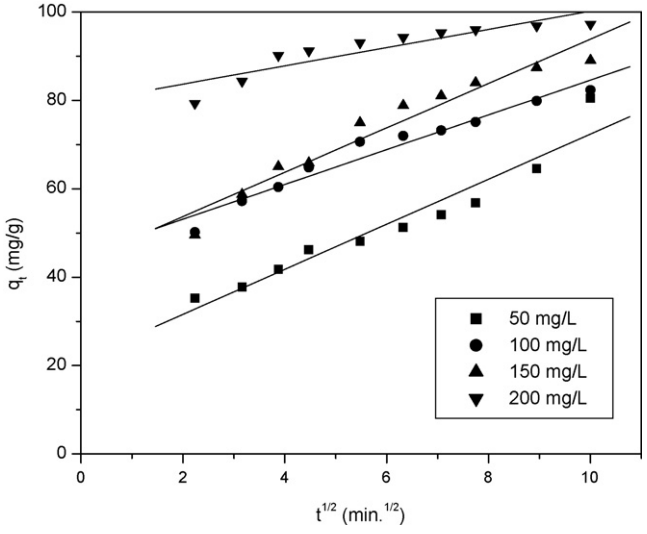


Fig. 12. Intraparticle diffusion constants for different initial MB concentrations.

(mg g^{-1}) and the square root of time (min) and the results are shown in Fig. 12 for different initial concentrations onto meranti sawdust. It is clear from this figure that these plots gave straight lines for each adsorbent but did not pass through the origin showing that the intraparticle diffusion is not the sole rate limiting factor for the adsorption of MB [51]. It is obvious from the figure that there can be distinguished three stages for the adsorption of dye. The first stage is an instantaneous adsorption and is probably due to a strong electrostatic attraction between dye and the external surface of adsorbent. The second stage is a gradual adsorption stage, which can be attributed to intraparticle diffusion of dye molecules through the pores of adsorbent. The *kp* values should be calculated based on the data corresponding to this stage. The final stage corresponds to the equilibrium adsorption when dye molecules occupy all active sites of the adsorbent. The rate constant for intraparticle diffusion *kp*, of MB was determined from the slopes of the respective plots and the values are listed in Table 6.

4. Conclusions

The present study shows that meranti sawdust, an agro-based waste biomass, can be used as an adsorbent for the removal of MB dye from aqueous solutions. The amount of dye uptake (mg/g) was found to increase with increase in contact time, and in initial dye concentration, and percent removal was found to increase with increase in adsorbent dosage. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of methylene blue onto meranti sawdust with a monolayer adsorption capacity of 120.48 mg/g. The dimensionless separation factor (R_L) showed that meranti sawdust could be used for removal of MB from aqueous solutions. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic parameters such as ΔG°, ΔH°, and ΔS° of adsorption. The results indicate that MB adsorption onto meranti sawdust is endothermic and spontaneous in nature. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation. Taking into consideration of the above results, it can be concluded that the meranti sawdust can be an alternative material for more costly adsorbents used for dye removal in wastewater treatment processes.

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