Removal of methylene blue from aqueous solution by dehydrated wheat bran carbon

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Abstract

Dyes are usually presents in the effluent water of many industries, such as textiles, leather, paper, printing and cosmetics. The effectiveness of dye adsorption from wastewater has made to get alternative different low cost adsorbent to other expensive treatment methods. The adsorption of methylene blue onto dehydrated wheat bran (DWB) was investigated at temperatures (25–45 °C), initial methylene blue (MB) concentrations (100–500 mg L^{-1}) and adsorbent dosage at the given contact time for the removal of dye. The optimum adsorption conditions were found to be as medium pH of 2.5 and at the temperature of 45 °C for the varying adsorbent dosage. Equilibrium isotherms were analysed by Freundlich, Langmuir and Redlich-Peterson isotherm equations using correlation coefficients. Adsorption data were well described by the Langmuir model, although they could be modelled by the Freundlich and Redlich-Peterson model as well. The pseudo-first order and pseudo-second order kinetic models were applied to test the experimental data. It was concluded that the pseudo-second order kinetic model provided better correlation of the experimental data rather than the pseudo-first order model. The mass transfer model as intraparticle diffusion was applied to the experimental data to examine the mechanisms of rate controlling step. It was found that at the higher initial MB concentration, intraparticle diffusion is becoming significant controlling step. The thermodynamic constants of the adsorption process were also evaluated by using the Langmuir constants related to the equilibrium of adsorption at temperatures varied in the range 25–55 °C.
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Keywords: Methylene blue; Adsorption; Dehydrated wheat bran (DWB); Equilibrium; Kinetic; Thermodynamic parameters

1. Introduction

Many industries, such as cosmetics, leather, paper, printing textile finishing industries use dyes in order to colour their products and also consume a lot of clean water which becomes coloured wastewater poured into the environment. The presence of dyes that resist against light and heat in the effluent water is the major contaminant causing different type of risks. The presence of very small amount of dyes in water is highly visible and undesirable, reducing photosynthetic activity and causing difficulties in the environment. Introducing dyes compounds into the environment also means the bad appearance of colour in the environment [1–3].

Physical and chemical treatments are some of the methods to treat wastewaters including dyes. Most commercial systems use activated carbon as adsorbent to remove dyes in wastewater because of its significant adsorption capacity [4–7]. Although, activated carbon is a preferred adsorbent, its widespread use is restricted due to its cost. In order to decrease the cost of treatment, some attempts have been made to find low cost alternative adsorbents. Recently numerous studies have been done to develop cheaper and effective adsorbents from a variety of starting materials such as waste materials [8–10], mango seed kernel [11], perlite and clay [12–14], sawdust [15], sugarcane [16], jute fiber [17], bagasse pith [18] and carbons from agricultural wastes [19].

Activated carbons have the advantage of exhibiting a high adsorption capacity for colour pollutants due to their high surface area or porous structure. Besides these physical characteristics, the adsorption capacity of a carbon produced from different sources is strongly influenced by the chemical nature of the surface. Although the determination of the number and the nature of the activated carbon groups began earlier, the precise nature of the functional groups is not entirely established. Due to these

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Nomenclature

a_R Redlich-Peterson adsorption constant $((L\,mg^{-1})^\beta)$

C unadsorbed MB concentration in solution at any time $(mg\,L^{-1})$

C_{eq} unadsorbed MB concentration in solution at equilibrium $(mg\,L^{-1})$

C_0 initial MB concentration $(mg\,L^{-1})$

D effective diffusivity $(m^2\,t^{-1})$

q adsorbed MB quantity per gram of adsorbent at any time $(mg\,g^{-1})$

q_{eq} adsorbed MB quantity per gram of adsorbent at equilibrium $(mg\,g^{-1})$

q_{max} maximum amount of MB per unit weight of DBP to form a complete monolayer on the surface $(mg\,g^{-1})$

K Langmuir constant related to adsorption equilibrium $(L\,mg^{-1})$

K_F Freundlich constant $((mg\,g^{-1})\,(mg\,L^{-1})^n)$

K_i intraparticular diffusion rate $(mg\,(g\,min^{-0.5}))$

K_R Redlich-Peterson adsorption constant $(1\,g^{-1})$

n Freundlich adsorption constant

k_1 rate constant of pseudo-first order adsorption (min^{-1})

k_2 rate constant of pseudo-second order adsorption $(g\,mg^{-1}\,min^{-1})$

r_p particle radius (m)

r^2 regression correlation coefficient

t time (min)

T temperature (K, °C)

X adsorbent concentration $(g\,L^{-1})$

ΔG Gibbs free energy change $(kJ\,mol^{-1})$

ΔH Enthalpy change of adsorption $(kJ\,mol^{-1})$

ΔS Entropy change of adsorption $(J\,mol^{-1}\,K^{-1})$

β Redlich-Peterson adsorption constant

functional groups such as carboxyl, hydroxyl, aldehyde, quionen and anhydride, the carbons have an acid–base character. It is now known that the acid or base character of carbon depends on its preparation and treatment conditions at which it was oxidised [20].

In the countries producing wheat for floor industry, the wheat bran which constitute protein, fat, fiber and starch [21] is one of the by product to produce carbon for removing waste as heavy metals and dyes [22]. However, there are not yet any reports of methylene blue adsorption by dehydrated wheat bran carbon. The aims of this work were to produce carbon of wheat bran dehydrated with sulphuric acid and to investigate the adsorption of MB on it. The experiments were done in a batch system to evaluate the adsorption capacity of carbon, and MB adsorption was investigated with respect to initial MB concentration, adsorbent dosage and temperature. The equilibrium of adsorption was modelled by using the Langmuir, Freundlich and Redlich-Peterson isotherm models, the kinetic

parameters and intraparticle diffusion were also then determined for the MB-DWB system. Finally thermodynamic parameters were investigated with respect to temperatures.

2. Theoretical

2.1. Methylene blue

Methylene blue was chosen in this study because of its known strong adsorption onto solids. Methylene blue has a molecular weight of 373.9 g mol, which corresponds to methylene blue hydrochloride with three groups of water. The structure of the methylene blue is given below Fig. 1.

Methylene blue, a cationic dye, is not regarded as acutely toxic, but it has 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, diarrhoea, and gastritis [21].

2.2. Equilibrium parameters of DWB

Adsorption is a well-known equilibrium separation process for wastewater treatment containing organics such as colour. Equilibrium study on adsorption has provided information on the capacity of the adsorbent. Also, an adsorption isotherm is characterised by certain constant values that express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. At constant temperature, this kind of adsorption isotherm is generally fitted to the Langmuir or Freundlich model [23,24]. The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The well-known expression of the Langmuir model is given as:

$$q_{eq} = \frac{q_{max}KC_{eq}}{1 + KC_{eq}} \tag{1}$$

where q_{eq} is the MB adsorbed on carbon at equilibrium, C_{eq} is the equilibrium concentration in the solution, q_{max} is the adsorption capacity and K is the adsorption equilibrium constant $(L\,mg^{-1})$ related to energy of adsorption. The linear form of this equation is written as:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Kq_{max}} + \frac{C_{eq}}{q_{max}} \tag{2}$$

A plot of C_{eq}/q_{eq} versus C_{eq} indicates a straight line of slope $1/q_{max}$ and an intercept of $1/Kq_{max}$. The Freundlich model is however an empirical equation based on adsorption on a heterogeneous surface, suggesting that binding sites are not equivalent
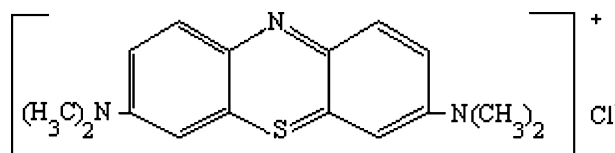

Fig. 1. The structure of methylene blue.

and/or independent. Freundlich equation is expressed as:

$$q_{eq} = K_F C_{eq}^{1/n} \tag{3}$$

where K_F is an indicator of the adsorption capacity and n is an indicator of the adsorption intensity. The logarithmic form of this equation is given by the following equation:

$$\ln q_{eq} = \ln K_F + \frac{1}{n} \ln C_{eq} \tag{4}$$

K_F and $1/n$ can be determined from the plot of $\ln q_{eq}$ versus $\ln C_{eq}$.

A further empirical model has been developed by Redlich-Peterson to improve the fit by the Langmuir or Freundlich equation and this model equation is given as:

$$q_{eq} = \frac{K_R C_{eq}}{1 + a_R C_{eq}^{\beta}} \tag{5}$$

where K_R, a_R and β are the Redlich-Peterson parameters. The β value lies between 0 and 1. Although the two parameters in the Langmuir and Freundlich equation can be graphically determined, Redlich-Peterson constants is not applicable because of the three unknown parameters so the three parameters in the equation are obtained using a quasi-Newton algorithm included in the 'STATISTICA' software.

2.3. Kinetic parameters of DWB

In order to investigate the mechanism of adsorption on DWB, kinetic model has been used to identify the possible mechanisms of such adsorption process. In this study, pseudo-first and pseudo-second order kinetic models have been proposed as follows to elucidate the mechanism of adsorption depending on the characteristics of the adsorbent.

2.3.1. Lagergren model

Lagergren [25] proposed a pseudo-first order kinetic model as below. The integrated form of the model is:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303} t \tag{6}$$

where q is the amount of MB adsorbed at time t (min), q_{eq} is the amount of MB adsorbed at equilibrium and k_1 is the rate constant of pseudo-first order adsorption.

2.3.2. Pseudo-second order model

The adsorption kinetics can also be given by a pseudo-second order reaction [26]. The integrated linearised form of this model is:

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} t \tag{7}$$

where k_2 is the pseudo-second order rate constant of MB adsorption. The plot of t/q versus t of Eq. (7) should give a linear relationship, from which q_{eq} and k_2 can be determined from the slope and intercept of the plot, if second order kinetic equation is applicable.

Since the models mentioned above cannot identify a diffusion mechanism, the intraparticle diffusion model is also tested to find the rate controlling step. This model refers to the theory proposed by Weber and Morris [27]. In the model, the rate of intraparticular diffusion is a function of $t^{1/2}$, which can be defined below and calculated by linearization of the given curve of the second stage ranged from 120 to 360 min which is obtained by the plot of q_e versus $t^{1/2}$.

$$q = f\left(\frac{Dt}{r_p^2}\right)^{1/2} = K_i t^{1/2} \tag{8}$$

where r_p is the particle radius, D is the effective diffusivity of MB within the particle and K_i is the intraparticular diffusion rate.

2.4. Determination of thermodynamic parameters

The thermodynamic parameters, namely free energy (ΔG), enthalpy (ΔH) and entropy (ΔS), have an important role to determine spontaneity and heat change for the adsorption process. Equilibrium constant can be used to evaluate the thermodynamic parameters [28].

The van't Hoff equation is used to determine the value of the equilibrium constant with temperature changes. The equation is given as:

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2} \tag{9}$$

Integrated form of this equation can be represented as follows:

$$-\ln K = \frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + C \tag{10}$$

If C is written as: $C = (\Delta S/R)$ then, $\ln K$ can be obtained as below:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R}\left(\frac{1}{T}\right) \tag{11}$$

The enthalpy and entropy changes of the process can be determined from the slope and intercept of line obtained by plotting $\ln K$ versus $1/T$.

If the equation $\Delta G = -RT \ln K$ is combined with the Eq. (11), equation free energy is then obtained as:

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

3. Materials and methods

3.1. Preparation of dehydrated wheat bran

The wheat bran used in this study is almost a waste material of wheat factory in Turkey. Dehydrated wheat bran was prepared by mixing one part of wheat bran and two parts of concentrated sulphuric acid. The mixture was manually stirred at the beginning to contact wheat bran well with acid and left for 24 h. At the end of the dehydration process, sufficient distilled water was

added to the mixture before filtering by using a water pump. This process was repeated until the final pH of the filtrate was about 2.5. The dehydrated material rinsed with distilled water was dried for 24 h in oven at 80 °C. Finally, dehydrated wheat bran carbon was grounded and screened through 50 mesh sieve, and stored in a closed bottle to be used in adsorption studies later.

3.2. Chemicals

Stock solution was prepared by dissolving 1.178 g of methylene blue hydrochloride three hydrate of analytical reagent grade in 1 L of double-distilled water. The test solutions were prepared by diluting of stock solution to the desired concentrations. The concentrations of solution varied in the range 100–500 mg L^{-1}.

3.3. Adsorption studies

This method involved agitating (150 rpm) Erlenmeyer flasks of 1 L containing different amount of DWB (0.5–2 g) and 0.5 L of MB solutions at the desired concentration, a constant temperature and pH. Samples of 10 cm^3 were taken from mixture during stirring at pre-determined time intervals for determining the residual colour concentration in the medium. Before analysis, samples were centrifuged and supernatant liquid was analysed for the remaining colour. All the experiments were carried out in duplicates and average values were used for further calculations. For isotherm studies, a series of flasks containing 0.1 L MB solution in the range of 150–500 mg L^{-1} were prepared. The weighed amount of 0.2 g DWB was added to each flask and then the mixtures were agitated at constant temperature of 25, 35 and 45 °C. These experiments were carried out at a constant pH of 2.5 for 72 h.

The amount of adsorption at equilibrium, q_{eq} (mg g^{-1}) and the percent adsorption (%) was computed as follows:

$$q_{eq} = \frac{(C_0 - C_{eq})}{X} \tag{13}$$

$$\text{Percent adsorption } \% = \frac{C_0 - C}{C_0} \times 100 \tag{14}$$

where C_0 and C_{eq} are the initial and equilibrium concentrations, X is the weight of DWB in one liter and C is the solution concentration at the end of adsorption.

3.4. Analysis

The concentration of residual colour of MB in the adsorption media was determined spectrophotometrically. The absorbance of the colour was read at 660 nm [29].

The BET surface area was determined from adsorption isotherms using a Micromeritics ASAP 2020 Surface Area Analyzer. The BET surface area of DWB was measured as 9.5 m^2 g^{-1}.

The infrared spectrum of wheat bran and dehydrated wheat bran were obtained with a Mattson 1000 FTIR spectrometer with a pellet of powdered potassium bromide and sample.
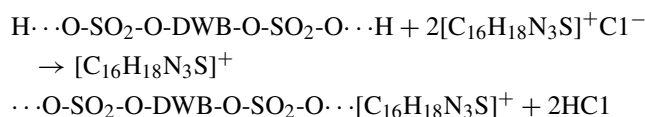
4. Results and discussion

Adsorption of MB onto DWB was investigated as a function of initial MB concentration and adsorbent dosage. The results are given as the units of adsorbed MB quantity per gram of adsorbent at any time (q, mg g^{-1}) and at equilibrium (q_{eq}, mg g^{-1}), respectively, and that of unadsorbed MB concentration in solution at any time (C, mg L^{-1}) and at equilibrium (C_{eq}, mg L^{-1}), respectively.

4.1. Effect of initial pH of methylene blue adsorption

It was observed that there is no significant effect of pH on methylene blue adsorption by DWB at the pre-experiments carried out at different pH. For that reason, results related to the effect of pH were not given. Wheat bran (WB) is rich in proteins, carbohydrates, minerals and fats [22]. MB is a cationic dye; its adsorption mechanisms by DWB can be explained on the basis of anionic groups formed during dehydration of wheat bran by sulphuric acid. It is probable that sulphuric acid reacts with hydroxyl groups in the carbohydrate to form sulphuric esters having a cation-exchanger functional group as depicted below. The sulphuric ester groups may be formed as a result of reacting of sulphuric acid with double bonds that may be present at hydrophobic end of fats in the wheat bran. It is possible that the sulphonic acid functional groups may be formed as a result of similar mechanisms during treatment of WB with sulphuric acid.

OH-WB-OH + H$_2$SO$_4$

    → H···O-SO$_2$-O-DWB-O-SO$_2$-O···H + H$_2$O
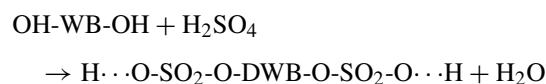
The following process can be proposed to explain the adsorption of methylene blue on DWB.

H···O-SO$_2$-O-DWB-O-SO$_2$-O···H + 2[C$_{16}$H$_{18}$N$_3$S]$^+$Cl$^-$

    → [C$_{16}$H$_{18}$N$_3$S]$^+$

···O-SO$_2$-O-DWB-O-SO$_2$-O···[C$_{16}$H$_{18}$N$_3$S]$^+$ + 2HCl

The presence of functional groups depends on the treatment procedure of the sample. The IR spectra of raw material and adsorbent treated with acid were obtained and shown in Fig. 2. It can be deduced that the broad mixed stretching vibration adsorption band of hydroxyl and amino groups at 3390 cm^{-1} was reduced considerably with the acid treatment. Fig. 2 also shows that esterification brought the reduction of stretching vibration adsorption band of carboxyl group at 1700 cm^{-1}. The decreasing intensity of adsorption band of carboxyl groups at 1700 cm^{-1} may be attributed to the destruction of carboxyl groups during the treatment of wheat bran with sulphuric acid.

4.2. Effect of initial methylene blue concentration on temperature dependent adsorption

To determine the effect of initial MB concentration on the equilibrium uptake, the initial MB concentration was varied from 150 to 500 mg L^{-1} at 25, 35 and 45 °C. The equilibrium
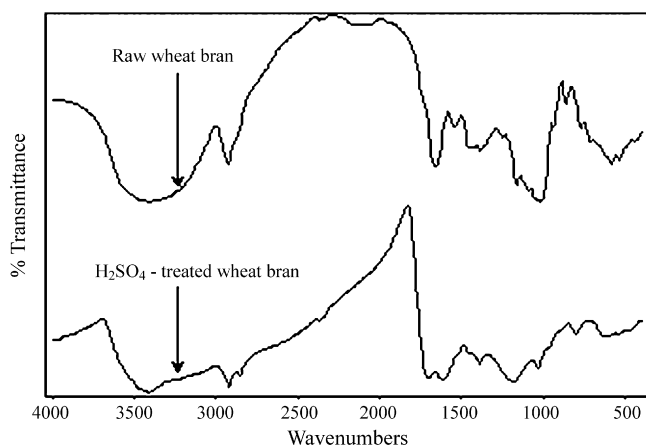
Fig. 2. The IR spectrum of raw and chemically modified adsorbent.

Fig. 3. Effect of adsorbent dosage on the adsorption of MB ($C_0 = 100$ mg L^{-1}; $T = 25$ °C; pH 2.5; RPM = 150).

adsorption capacity of the DWB increased with increasing initial MB concentration up to 500 mg L^{-1} because the initial MB concentration provides an important driving force to overcome all mass transfer resistance. The increase of loading capacity of DWB with increasing initial MB concentration may also be due to higher interaction between MB and adsorbent. As DWB offer a finite number of surface binding sites, MB adsorption showed a saturation trend at higher initial colour concentration.

The maximum adsorption yields were determined as 95%, 99.4% and 99.8% at 200 mg L^{-1} initial MB concentration for 25, 35 and 45 °C, respectively. The adsorption yield showed a decreasing trend as the initial MB concentration was increased. At lower concentrations, all MB present in the adsorption medium could interact with the binding sites so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites.

The equilibrium uptake of MB by DWB was also affected by temperature. The effects of temperature on the equilibrium adsorption capacities of DWB were also studied. It can be deduced that MB adsorption capacity increased with increasing temperature from 25 to 45 °C. Similar results were observed for MB adsorption yields of DWB and the adsorption yields were increased with increasing temperature. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the sorption of MB onto DWB is endothermic in nature and may involve not only physical but also chemical sorption. This effect may be attributed to the enlargement of pore size or creation of some new active sites on the adsorbent surface due to bond rupture [30,31].

Acemioglu investigated the adsorption of MB onto perlite. They found equilibrium uptake between 28 and 94 mg g^{-1} for various initial dye concentrations [12]. Senthilkumaar et al. investigated also the adsorption of MB onto jute fiber carbon. They found equilibrium uptake of MB from 45 to 74 mg g^{-1} as the MB concentration increased from 50 to 200 mg L^{-1} [17]. Batch adsorption of MB on various carbons was performed by Kannan & Sundaram [19] and equilibrium adsorption capacities varied from 9.7 to 298 mg g^{-1} at 30 °C were determined. In the present work, adsorption capacity of DWB was obtained

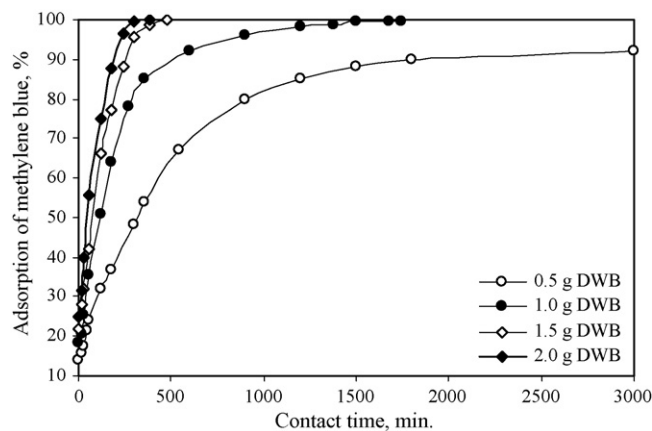as 99.84 mg g^{-1} for initial MB concentration of 200 mg L^{-1} at 45 °C.

4.3. Effect of the adsorbent dosage

To determine the effect of adsorbent dosage on the amount of adsorption, the adsorbent concentration was varied from 1 to 4 g L^{-1}, while initial MB concentration was held constant at 100 mg L^{-1} at the temperature of 25 °C. As expected, the percentage of MB removal increased with increasing DWB dosage at the same initial dye concentration. As seen from Fig. 3, the removal yield increased from 48 to 99.5% for the given adsorbent dosage at the duration of adsorption of 300 min. The increase in MB removal with the adsorbent dose can be attributed to increased surface area and the sorption sites. However, the decrease in adsorption capacity can be explained with the reduction in the effective surface area.

4.4. Determination of equilibrium parameters

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. The most widely used isotherms equation for modelling of the adsorption data are the Langmuir, Freundlich and Redlich-Peterson equations.

To determine the equilibrium isotherms for each equation, initial MB concentrations were varied from 150 to 500 mg L^{-1} while the adsorbent concentration was kept constant (2 g L^{-1}) at 25, 35 and 45 °C. The linearised isotherms plots are presented in Figs. 4 and 5 for the Freundlich and Langmuir equations, respectively, but adsorption constants of Redlich-Peterson were calculated by using a quasi-Newton algorithm included in the 'STATISTICA' software. As seen from Table 1, although correlation coefficients of three equations are considerably well obtained, the Langmuir model exhibited best fit to the adsorption data than the other models.

The Langmuir equation is based on a monolayer adsorption by the adsorbent with the same energy of active sites. The surface of this carbon material was expected to have nearly homogeneous sites for adsorption, so a much better fit was obtained.

Table 1
Isotherms constants for MB adsorption on DWB

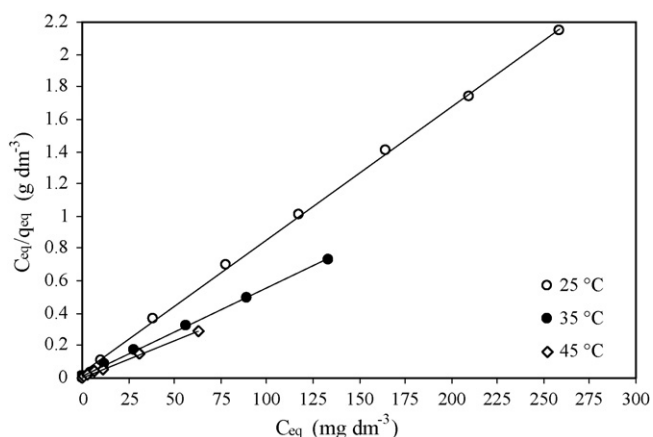| T (°C)	Langmuir constants			Freundlich constants			Redlich-Peterson constants			
	q_{max} (mg g^{-1})	K (mg L^{-1})	r^2	K_F	n	r^2	K_R (L mg^{-1})	a_R (L mg^{-1})$^\beta$	β	r^2
25	122.0	0.245	0.999	79.6	13.0	0.999	13296	0.004	1.00	1.00
35	185.2	0.425	0.999	96.6	7.0	0.999	1771	0.042	1.00	0.99
45	222.2	0.978	0.999	122.0	6.2	0.999	1200	0.237	0.98	0.98

Fig. 4. The linearised Langmuir adsorption isotherm of MB on DWB (0.1 L MB solution; pH 2.5; adsorbent dosage = 2 g L^{-1}; equilibrium time = 72 h.).
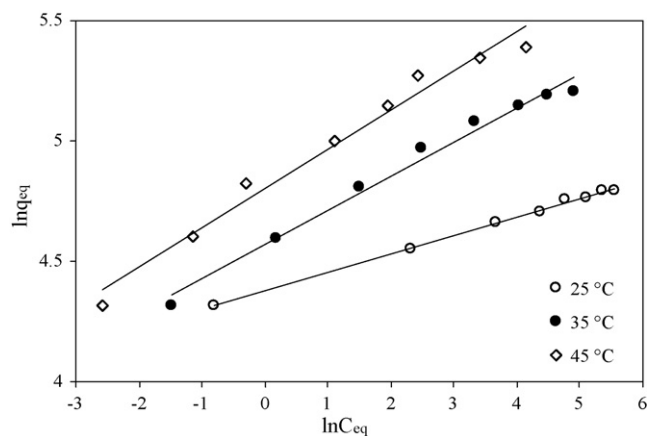

Fig. 5. The linearised Freundlich adsorption isotherm of MB on DWB (0.1 L MB solution; pH 2.5; adsorbent dosage = 2 g L^{-1}; equilibrium time = 72 h).

The values of Freundlich constant, K_F, increased with increasing temperature and showed easy uptake of MB by the adsorbent. The highest K_F value was reported as 122 at 45 °C. All n values were found high enough for adsorption (>1.0). Values of q_{max}
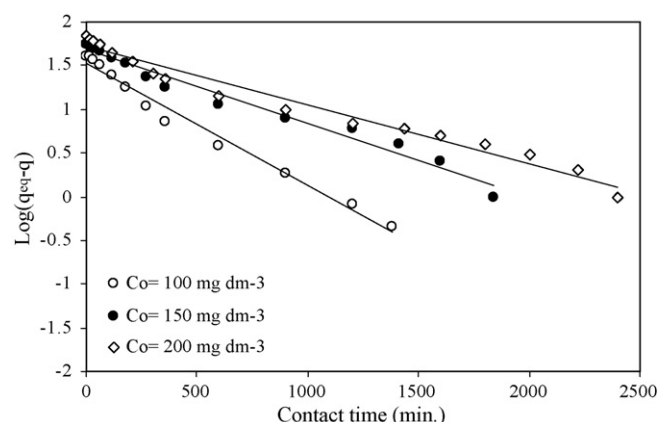

Fig. 6. Pseudo-first order adsorption kinetics of MB (0.5 L MB solution; pH 2.5; T = 25 °C; adsorbent dosage = 2 g L^{-1}; RPM = 150).

and K at different temperatures are shown in Table 1. In the Redlich-Peterson equations, the magnitude of K_R, a_R and β of the isotherm constants were given in Table 1 as well. The maximum capacity of these equations, q_{max}, defined the total capacity of DWB for MB adsorption and increased with increasing temperature. Its maximum value was determined as 222.2 mg g^{-1} at 45 °C. When the adsorption is endothermic, an increase in T results in an increase in K. This indicated a shift of the adsorption equilibrium to the adsorption direction.

4.5. Kinetic parameters of adsorption

The plots of linearised form of the pseudo-first order equation are shown in Fig. 6. The values of k_1, q_{eq} and correlation coefficients are compared in Table 2. The results showed that the correlation coefficient for the first order kinetic model obtained at 25 °C was low, and they decreased with increasing temperature. The theoretical $q_{eq,cal}$ values found from this model did not give reasonable values, so pseudo-first order model did not describe the adsorption results of MB onto DWB.

Fig. 7 shows the linearised form of the pseudo-second order model. The values of correlation coefficient were very high and

Table 2
Change of the pseudo-first and second order reaction rate constants with temperature

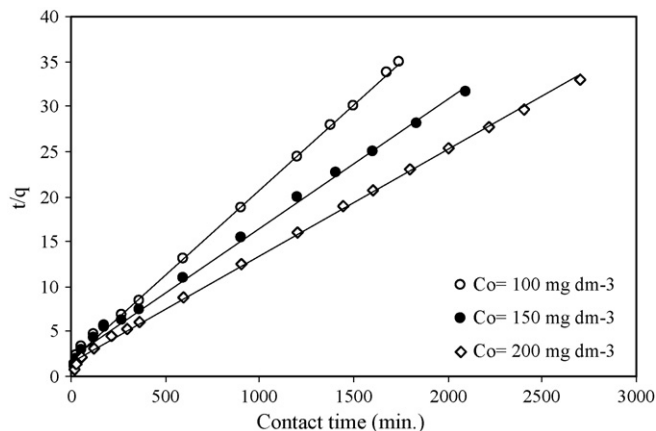| T (°C)	$q_{eq,exp}$ (mg g^{-1})	First order kinetic model			Second order kinetic model		
		k_1 (dm^{-3} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	r^2	k_2 (g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	r^2
25	49.86	0.0032	34.33	0.984	0.00019	52.90	0.999
35	66.50	0.0018	48.20	0.976	0.00010	69.90	0.997
45	82.00	0.0016	52.00	0.972	0.00009	84.70	0.999

Fig. 7. Pseudo-second order adsorption kinetics of MB (0.5 L MB solution; pH 2.5; $T = 25\,°C$; adsorbent dosage = $2\,g\,L^{-1}$; RPM = 150).

the theoretical $q_{eq,cal}$ values were much closed to the experimental q_{eq} values in Table 2. In view of these results, it can be said that the pseudo-second order kinetic model, in contrast to the pseudo-first order model, provided a good correlation for the adsorption of MB onto DWB.

The adsorption of MB onto DWB follows generally three consecutive steps of external diffusion, intraparticle diffusion and adsorption. One or more of these steps can control the adsorption kinetics. In a well-agitated batch system, the external diffusion resistance is much reduced. Hence, intraparticular diffusion with the adsorption is more likely to be rate-controlling step. In the simplified model studies, to elucidate the adsorption mechanisms developed by Weber and Morris [27], it is assumed that the first sharper linear stage is being a rapid external diffusion and surface adsorption which is neglected, the second linear stage is being a gradual adsorption stage where the intraparticle diffusion is rate limited, and the final stage is being equilibrium stage. The adsorption capacity, q, was plotted against square root of time with various initial MB concentrations. At a certain time limit for the intraparticle diffusion as illustrated in Fig. 8 (between 120 and 360 min at given initial MB concentration), the curves reveals linear characteristics. However, the linear plots at each concentration did not pass through the origin.
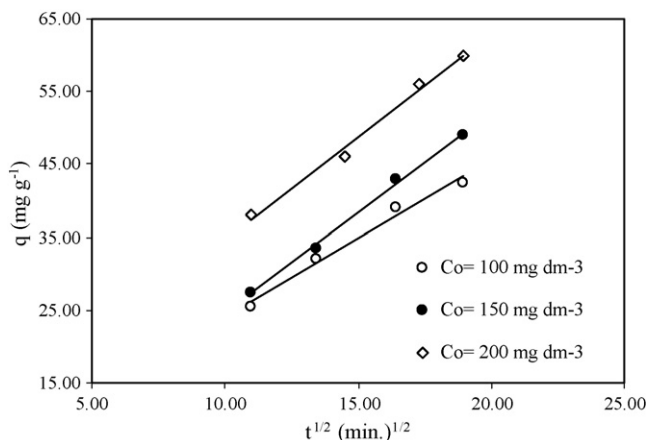

Fig. 8. Intraparticle diffusion at various initial concentrations (0.5 L MB solution; pH 2.5; adsorbent dosage = $2\,g\,L^{-1}$; $T = 25\,°C$; RPM = 150).
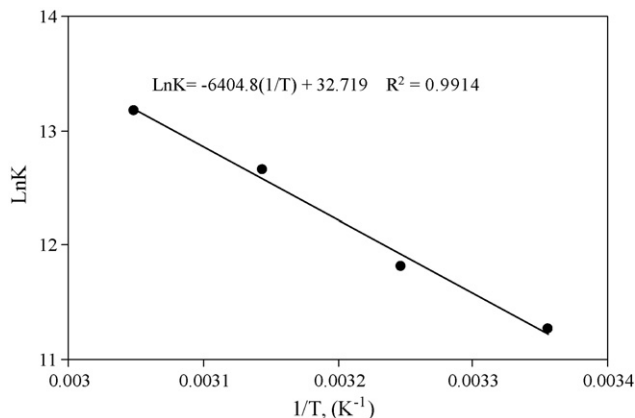

Fig. 9. Plot of ln K vs. $1/T$.

This indicates that the intraparticle diffusion was not only rate controlling step. As can be obtained from Fig. 8, diffusion rate, K_i, was in the range of $2.81–2.14\,mg\,g^{-1}\,min^{-0.5}$ ($r^2 = 0.99$). It was found that the values of K_i increased with the increasing initial MB concentration due to a greater driving force.

4.6. Determination of thermodynamic parameters

The equilibrium constants obtained from Langmuir model at 25, 35, 45 and 55 °C were used to determine the Gibbs free energy changes. Gibbs free energy values for the adsorption process were obtained as -27.8, -30.5, -33.3 and $-36.0\,kJ\,mol^{-1}$ for the temperatures of 25, 35, 45 and 55 °C, respectively. The negative value of ΔG indicates the spontaneous nature of MB adsorption onto DWB. The enthalpy and the entropy changes were determined as $53.24\,kJ\,mol^{-1}$ and $272\,J\,mol^{-1}\,K^{-1}$ from the ln K versus $1/T$ plots in Fig. 9, respectively. The positive value of ΔH suggests the endothermic nature of adsorption while the positive values of ΔS shows the increasing randomness at the DWB and adsorption medium interface during the adsorption.

5. Conclusions

In this study, the ability of DWB to bind MB was investigated using equilibrium, kinetic and thermodynamic aspects. The results indicated that, adsorption capacity of the adsorbent was considerably affected by preparation of carbon, temperature and initial MB concentration. Changing medium of pH value did not affect the adsorption process considerably. It is also reported that MB adsorption increased with both temperature up to 45 °C and initial MB concentration up to $500\,g\,L^{-1}$.

The Langmuir, Freundlich and Redlich-Peterson adsorption models were used to express the sorption phenomenon of the MB. The equilibrium data were well described by the Langmuir model.

The kinetics of MB adsorption onto DWB was studied using the pseudo-first and pseudo-second order kinetic models. The results indicated that the pseudo-second order equation provided the better correlation of the adsorption data. It was also seen that the intraparticle diffusion kinetics can also be one of the rate determining steps as well as pseudo-second order kinetics.

The thermodynamic constants of adsorption were also evaluated. The negative value of ΔG confirms the spontaneous nature adsorption process. The positive value of ΔS showed the increased randomness at the solid-solution interface during adsorption and the positive value of ΔH indicated the adsorption process was endothermic.

It can be concluded that the dehydrated product from wheat bran is an efficient adsorbent for the removal of MB from aqueous solution.

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