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Methylene blue adsorption from aqueous solution by dehydrated peanut hull

Dursun Özer, Gülbeyi Dursun *, Ahmet Özer

Department of Chemical Engineering, Firat University, 23279 Elazig, Turkey

Abstract

Dyes are colour organic compounds which can colorize the other substances. These substances usually presents in the effluent water of many industries, such as textiles, leather, paper, printing and cosmetics. To observe the potential feasibility of removing colour, peanut hull as an agricultural by-product was dehydrated with sulphuric acid (DPH) and used for adsorption of methylene blue (MB) from aqueous solution. The effects of various parameters such as initial methylene blue concentrations, temperatures and particle sizes were examined and optimal experimental conditions were determined. Adsorption data were well described by the Langmuir model, although they could be modelled by the Freundlich model as well. The adsorption process followed the pseudo-second order kinetic 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 different temperatures. The results in this study indicated that dehydrated peanut hull was a good adsorbent for removing methylene blue.
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1. Introduction

Dyes are colour organic compounds which can colorize the other substances. These substances usually presents in the effluent water of many industries, such as textiles, leather, paper, printing and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies. The extensive use of dyes causes environmental problem in the ecosystem. This not only prevents sunlight penetration into water and reduces photosynthetic activity and causing difficulties in the environment. Introducing dyes compounds into the environment also means the bad appearance of colour in the environment [1–4].

There are several methods to remove dyes such as physical and chemical processes to treat wastewaters including organic pollutant and dyes. Also most commercial systems use activated carbon as adsorbent to remove dyes in wastewater because of its high adsorption ability [5–8]. Although, activated carbon is a preferred adsorbent, its widespread use is restricted due to its high cost. In order to decrease the cost of treatment, some attempts have been made to find low cost alternative adsorbents. Recently numerous approach have been done to develop cheaper and effective adsorbents to remove dyes from a variety of starting materials such as waste materials [9–11], mango seed kernel [12], perlite and clay [13–15], saw dust [16], sugarcane [17], jute fibre [18], bagasse pith [19], carbons from agricultural wastes [20], wheat bran [21] and peanut hull [22–24].

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 with different ways 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 polar functional groups such as carboxyl, hydroxyl, aldehyde, ketones and anhydrides, the carbons have an acid–base character. It is now known that the acid or

* Corresponding author.
E-mail address: gdursun@firat.edu.tr (G. Dursun).

Nomenclature

C unadsorbed MB concentration in solution at any time (mg dm^{-3})

C_{eq} unadsorbed MB concentration in solution at equilibrium (mg dm^{-3})

C_0 initial MB concentration (mg dm^{-3})

D effective diffusivity

$\Delta G°$ Gibbs free energy change (kJ mol^{-1})

$\Delta H°$ enthalpy change of adsorption (kJ mol^{-1})

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})

K Langmuir constant related to adsorption equilibrium (dm^3 mg^{-1})

K_F Freundlich constant ((mg g^{-1}) (mg dm^{-3})^n)

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

n Freundlich adsorption constant

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 DPH to form a complete monolayer on the surface (mg g^{-1})

r_p particle radius (m)

r^2 regression correlation coefficient

$\Delta S°$ entropy change of adsorption (kJ mol^{-1} K^{-1})

t time (min)

T temperature (K, °C)

X adsorbent concentration (g dm^{-3})

base character of carbon depends on its preparation and treatment conditions at which it was oxidised with in acid or inert atmosphere [25].

In the countries producing peanut for the related industry, the peanut hull is one of the waste material which has no economic value other than producing adsorbent. This waste material has been used to produce partially carbonized material for removing waste as heavy metals [26–28], organic pollutant such as phenol [29] and dyes [30,31]. However, there are no reports of methylene blue adsorption by peanut hull dehydrated with sulphuric acid. The aim of this work was to produce a new adsorbent from peanut hull by dehydrating with sulphuric acid, to characterize the adsorbent and to investigate the adsorption of methylene blue on it. The experiments were done in a batch system to evaluate the adsorption capacity of adsorbent, and the adsorption of MB was studied with respect to initial MB concentration, adsorbent dosage, particle size and temperature. The equilibrium of adsorption was modelled by using the Langmuir and Freundlich isotherm models, the kinetic parameters and intraparticle diffusion were also then determined for the MB-DPH 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, which corresponds to methylene blue hydrochloride with three groups of water. The structure of the methylene blue is given as below.
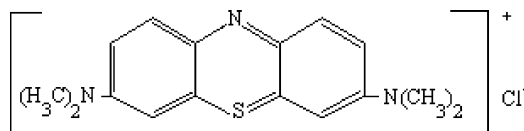
Methylene blue, a cationic dye, is not regarded as acutely toxic, but it has various harmful effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting and gastritis problems [32].

2.2. Equilibrium parameters of DPH

Equilibrium study on adsorption has provided information on the capacity of the adsorbent. Adsorption isotherm is characterized by certain constant values which 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. This kind of adsorption isotherm is generally fitted to the Langmuir or Freundlich model at given constant temperature [33,34]. 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

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

where q_{eq} is the amount of MB adsorbed on adsorbent at equilibrium, C_{eq} the equilibrium concentration in the solution, q_{max} the maximum adsorption capacity and K is the adsorption equilibrium constant. The linear form of this equation is written as

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

A plot of C_{eq}/q_{eq} versus C_{eq} indicates a straight line of slope $1/q_{max}$ and an intercept of $1/K q_{max}$. However, the Freundlich model is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent 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 that of the adsorption intensity, respectively. The logarithmic form of this equation is given by the following equation:

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

From the plot of $\ln q_{eq}$ versus $\ln C_{eq}$, K_F and $1/n$ values can be obtained.

2.3. Kinetic parameters of DPH

Kinetic models have been proposed to determine the mechanism. The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent as well as on the mass transport process. In order to determine the mechanism of MB onto DPH, 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 [35] proposed a pseudo-first order kinetic model as below. The integrated form of the model is

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \tag{5}$$

where q is the amount of MB adsorbed at time t (min), q_{eq} 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 [36]. The integrated linear form of this model is

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \tag{6}$$

where k_2 is the pseudo-second order rate constant of MB adsorption. The plot of t/q versus t of Eq. (6) 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 [37]. In the model, the rate of intraparticular diffusion is a function of $t^{1/2}$ and can be defined below and calculated by linearization of the given curve:

$$q = f\left(\frac{Dt}{r_p^2}\right)^{1/2} = K_i t^{1/2} \tag{7}$$

where r_p is the particle radius, D 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 [38]. The very useful relationship between standard free energy change and equilibrium constant is given by the following equation:

$$\Delta G^\circ = -RT \ln K \tag{8}$$

where K is the adsorption equilibrium constant obtained from Langmuir isotherms, ΔG° the free energy change, R the universal gas constant, 8.314 J/mol K and T is the absolute temperature. The equilibrium constant can be expressed in terms of enthalpy change of adsorption (ΔH°) and entropy change of adsorption (ΔS°) as a function of temperature. The relation between K and temperature is given by the van't Hoff equation:

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

Integrated and rearranged final form of this equation can be represented as follows:

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

ΔH° and ΔS° can be obtained from the slope and intercept of a van't Hoff plot of $\ln K$ versus $1/T$.

3. Materials and methods

3.1. Preparation of dehydrated peanut hull

The peanut hull used in this study, which grounded and sieved below 50 mesh size, is almost a waste material of peanut in Turkey. Dehydrated peanut hull was prepared by mixing one part of peanut hull and two parts concentrated sulphuric acid (w/w, 98%). The mixture was manually stirred at the beginning to contact peanut hull 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 3.5. The dehydrated material rinsed with distilled water was dried for 24 h in an oven at 80 °C. Finally, dehydrated peanut hull (DPH) was grounded and screened through 50 mesh sieve and stored in a closed bottle to use 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 dm^3 of double-distilled water. The test solutions were prepared by dilution to the desired concentrations, ranging from 100 to 400 mg dm^{-3}.

3.3. Adsorption studies

The experiments were conducted in 1 dm^3 Erlenmeyer flasks containing different amount of DPH (0.5–1.0 g) and 0.5 dm^3 of MB solutions at the desired concentration and the constant temperature. The flasks were agitated on a shaker at 150 rpm constant shaking rate. Samples (10 cm^3) were taken from mixture during stirring at pre-determined time intervals for determining the residual colour concentration in the medium. The 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 $0.1\,dm^3$ MB solution in the range of $100–400\,mg\,dm^{-3}$ were prepared. The weighed amount of 0.1 g DPH was added to each flask and then the mixtures were agitated at constant temperature of 25, 30, 40 and $50\,°C$. These experiments were carried out at a constant pH of 3.5 for duration of 24 h.

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

$$q_{eq} = \frac{C_0 - C_{eq}}{X} \tag{11}$$

$$\text{adsorption percent}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{12}$$

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

3.4. Analysis

The concentration of residual colour of methylene blue (MB) in the adsorption media was determined spectrophotometrically. The absorbance of the colour was read at 660 nm [39].

The BET surface area was determined from adsorption isotherms using a Micromeritics ASAP 2020 Surface Area Analyzer. The BET surface area of DPH was measured as $1.85\,m^2\,g^{-1}$.

The infrared spectrum of peanut hull and dehydrated peanut hull were obtained with a Mattson 1000 FTIR spectrometer with a pellet of powdered potassium bromide and sample.

4. Results and discussion

4.1. Effect of initial pH of methylene blue adsorption

It was observed that there is no significant effect of pH on adsorption methylene blue by DPH at the pre-experiments carried out at different pH. For that reason, it was not given the results related to the effect of pH. Peanut hull (PH) is rich in fibre, cellulose, lignin and protein [31]. The adsorption mechanisms of methylene blue which is a cationic dye by DPH can be explained on the base of anionic groups formed during dehydration of peanut hull by sulphuric acid. It is probably that sulphuric acid react with hydroxyl groups in the carbohydrate to form sulphuric esters have a cation exchanger functional group and considered as anion active agent, as depicted below. The sulphuric ester groups may be formed as a result of reacting of sulphuric acid with double bonds may be present at hydrophobic end of fats in the peanut hull.

$$\text{OH–PH–OH} + H_2SO_4$$
$$\rightarrow \text{H}\cdots\text{O–SO}_2\text{–O–DPH–O–SO}_2\text{–O}\cdots\text{H} + H_2O$$
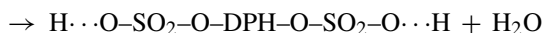
It is possible that the sulphonic acid functional groups may be formed as a result of similar mechanisms during treatment of
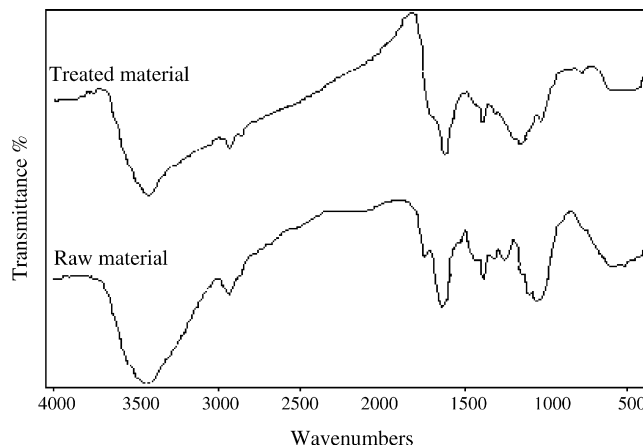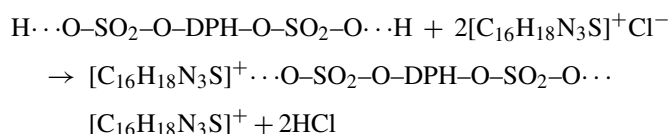

Fig. 1. The IR spectrum of raw and chemically modified adsorbent.

peanut hull with sulphuric acid. The following process can be proposed to explain the adsorption of methylene blue on DPH.

$$\text{H}\cdots\text{O–SO}_2\text{–O–DPH–O–SO}_2\text{–O}\cdots\text{H} + 2[C_{16}H_{18}N_3S]^+Cl^-$$
$$\rightarrow [C_{16}H_{18}N_3S]^+\cdots\text{O–SO}_2\text{–O–DPH–O–SO}_2\text{–O}\cdots$$
$$[C_{16}H_{18}N_3S]^+ + 2HCl$$

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. 1. 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. 1 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 peanut hull with sulphuric acid.

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

To investigate the effect of initial methylene blue (MB) concentration on the equilibrium uptake, the initial MB concentration was varied from 100 to $400\,mg\,dm^{-3}$ at 25, 30, 40 and $50\,°C$ as shown in Table 1. The equilibrium uptake capacities of the DPH increased with increasing initial MB concentration up to $400\,mg\,dm^{-3}$ because the initial MB concentration provides an important driving force to overcome all mass transfer resistance. The increase of loading capacity of DPH with increasing initial MB concentration may also be due to higher interaction between MB and adsorbent. MB adsorption showed a saturation trend at higher initial colour concentration while DPH offer a finite number of surface binding sites.

The removal yields were found to be 92.0%, 95.0%, 97.5% and 98.6% at $100\,mg\,dm^{-3}$ initial MB concentration for 25, 30, 40 and $50\,°C$, respectively (Table 1). The removal yield showed a decreasing trend as the initial MB concentration was increased as shown in Fig. 2. At lower concentrations, all MB present in the adsorption medium could interact with the binding sites

Table 1
The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures (conditions: 0.1 dm^3 MB solution, pH 3.5, DPH dosage: 1 g dm^{-3})

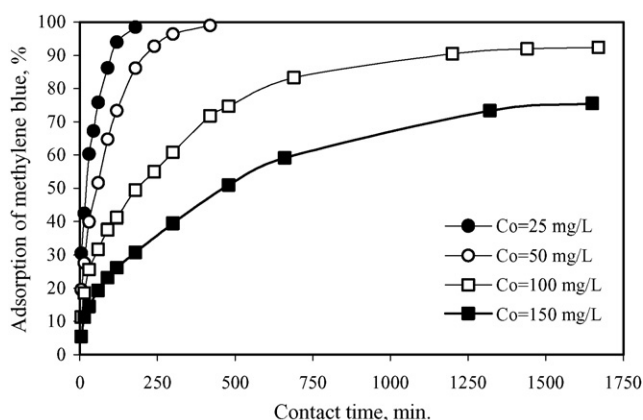| C_0 (mg dm^{-3})	25 °C		30 °C		40 °C		50 °C	
	q_{eq} (mg g^{-1})	Adsorption (%)	q_{eq} (mg g^{-1})	Adsorption (%)	q_{eq} (mg g^{-1})	Adsorption (%)	q_{eq} (mg g^{-1})	Adsorption (%)
100	92.0	92.0	95.0	95.0	97.5	97.5	98.6	98.6
150	93.3	62.2	108.3	72.2	122.7	81.8	126.8	84.5
200	96.0	48.0	110.2	55.1	136.4	68.2	143.0	71.5
250	102.0	40.8	115.8	46.3	141.5	56.6	153.0	61.2
300	103.5	34.5	117.3	39.1	143.1	47.7	159.0	53.0
350	105.0	30.0	120.1	34.3	145.2	41.5	157.5	45.0
400	108.0	27.0	122.0	30.5	148.0	37.0	158.1	39.5

Fig. 2. Effect of initial MB concentration on the adsorption of MB (T = 25 °C; pH 3.5; adsorbent dosage = 1 g dm^{-3}; and RPM = 150).

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 values of MB by DPH were also affected by temperatures. The effect of temperature on the equilibrium adsorption capacities of DPH were also presented in Table 1. As observed from Table 1 that adsorption capacity increased with increasing temperature from 25 to 50 °C as shown in Fig. 3. It was observed that the adsorption yields were increased with increasing temperature. The increase of the
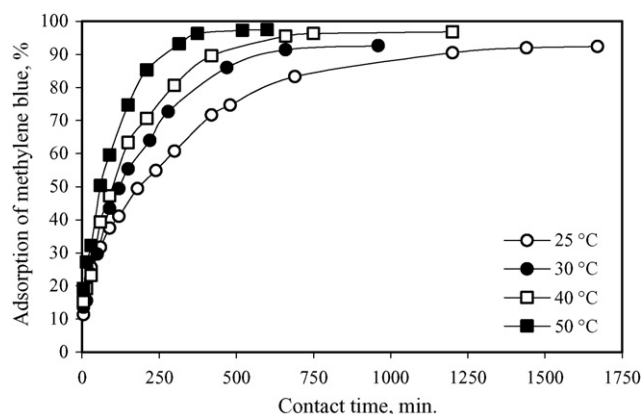

Fig. 3. Temperature effect on the adsorption of MB (C_0 = 100 mg dm^{-3}; pH 3.5; adsorbent dosage = 1 g dm^{-3}; and RPM = 150).

adsorption yield and adsorption capacity at increased temperature indicated that the sorption of MB onto DPH 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 rupture of bond [40,41].

In this work, adsorption capacity of DPH was obtained as 92 and 98.6 mg g^{-1} for initial MB concentration of 100 mg dm^{-3} at 25 and 50 °C, respectively. The adsorption of MB onto the different materials such as perlite was investigated from other researchers. The results of equilibrium uptake were found as between 28 and 94 mg g^{-1} for various initial dye concentrations [13]. Senthilkumaar et al. investigated also the adsorption of MB onto jute fibre carbon. They found equilibrium uptake values of MB changing from 45 to 74 mg g^{-1} as the MB concentration increased from 50 to 200 mg dm^{-3} [18]. Batch adsorption of MB on various carbons was performed by Kannan and Sundaram [20] and equilibrium adsorption capacities varied from 9.7 to 298 mg g^{-1} at 30 °C were determined. The adsorption capacity of Neem leaf powder was also obtained as 8.76 mg g^{-1} [42].

4.3. Effect of the adsorbent dosage

The effect of adsorbent dosage on the adsorption rate of the methylene blue was studied, while other experimental conditions were kept constant as the adsorbent concentration was varied from 1 to 2 g dm^{-3}. Results obtained for the adsorption of methylene blue are shown in Fig. 4. It is clear that an increase in the mass of DPH resulted in a decrease in q_{max} values despite the fact that MB uptake increased. As seen from the figure, the removal yield decreased from 84% to 49.85% for the given adsorbent dosage at the duration of adsorption of 720 min. The increase in the uptake of MB with the adsorbent dose can be attributed to increased surface area and the sorption sites. Since the particle size range constant, the surface area will be directly proportional to the mass of adsorbent in the solution. However, the decrease in adsorption capacity can be explained with the reduction in the effective surface area.

4.4. Effect of the particle size

Adsorption process is related with surface area of adsorbent directly because it determines the time required for transport
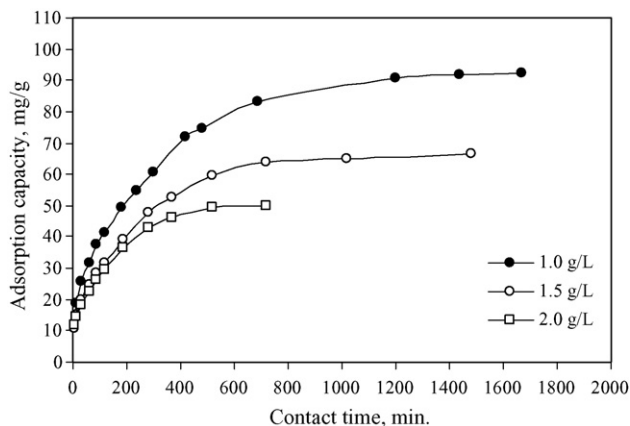
Fig. 4. Effect of adsorbent dosage on the adsorption of MB ($C_0 = 100\,\mathrm{mg\,dm^{-3}}$; $T = 25\,^{\circ}\mathrm{C}$).

within the pore to adsorption sites so particle size is very important factors affecting adsorption capacity. As can be observed from Fig. 5, adsorption capacity of DPH increased from 30.8% to 98% within 300 min with decreasing particle size from 30 meshes to below 100 meshes relatively. This situation was explained by larger total surface area of smaller particles for the same amount of adsorbent.

4.5. Determination of equilibrium parameters

The most widely used isotherms equation for the design of adsorption systems are the Langmuir and Freundlich equations. To determine the equilibrium isotherms for both equations; initial MB concentrations were varied from 100 to 400 mg dm^{-3} while the adsorbent concentration was kept constant (1 g dm^{-3}) at 25, 30, 40 and 50 °C. The linear form of isotherms plots are presented in Figs. 6 and 7. The isotherm constants and correlation coefficients are tabulated in Table 2. As observed from the table, although the equilibrium data fitted well to both of the adsorption models. The Langmuir model exhibited a slightly better fit to the adsorption data than the Freundlich model. The Langmuir equation is based on a monolayer adsorption by the adsorbent with the same energy of active sites. The surface of
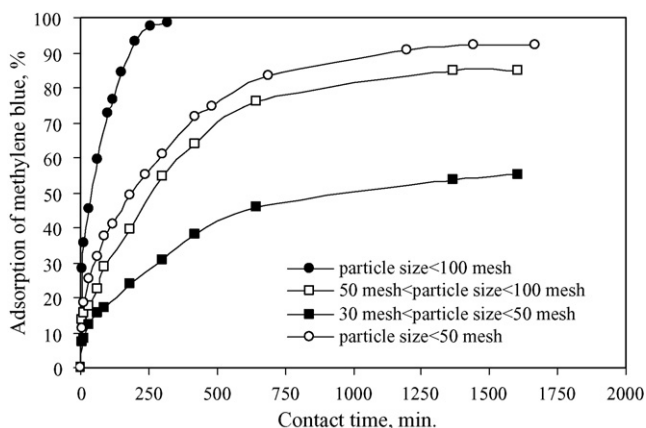

Fig. 5. Effect of particle sizes on the adsorption of MB ($C_0 = 100\,\mathrm{mg\,dm^{-3}}$; $T = 25\,^{\circ}\mathrm{C}$; pH 3.5; adsorbent dosage = 1 g dm^{-3} and RPM = 150).
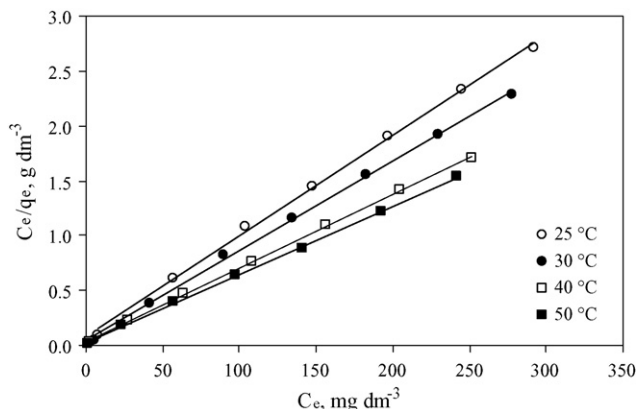

Fig. 6. The linearised Langmuir adsorption isotherm of MB on DPH (0.1 dm^3 MB solution; pH 3.5; adsorbent dosage = 1 g dm^{-3}; equilibrium time = 500 min).
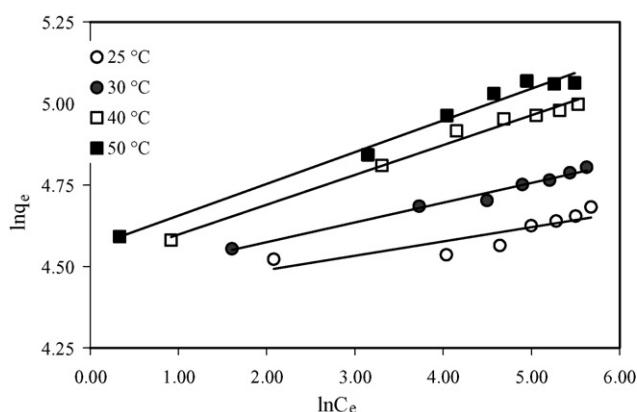

Fig. 7. The linearised Freundlich adsorption isotherm of MB on DPH (0.1 dm^3 MB solution; pH 3.5; adsorbent dosage = 1 g dm^{-3}; equilibrium time = 500 min).

this material was expected to have nearly homogeneous sites for adsorption, so a much better fit was obtained. 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 95.4 at 50 °C. All n values were found high enough for adsorption (>1.0). Values of q_{max} and K at different temperatures are also tabulated in Table 2. The maximum adsorption capacity, q_{max} defined the total capacity of DPH for MB adsorption and increased with increasing temperature. Its maximum value was determined as 161.3 mg g^{-1} at 50 °C. When the adsorption is endothermic, an increase in T results in an increase in K. This indicates a shift of the adsorption equilibrium to the adsorption direction.

Table 2
Isotherms constants for the adsorption of MB on DPH

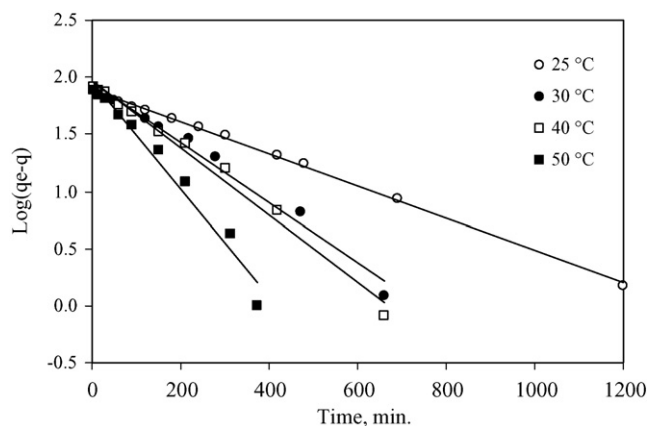| T (°C)	Langmuir constants			Freundlich constants		
	q_{max} (mg g^{-1})	K (mg dm^{-3})	r^2	K_F	n	r^2
25	108.6	0.121	0.998	81.6	22.3	0.762
30	123.5	0.162	0.999	85.8	16.5	0.983
40	149.2	0.209	0.999	90.6	10.9	0.987
50	161.3	0.232	0.999	95.4	10.2	0.983

Fig. 8. Pseudo-first order adsorption kinetics of MB (0.5 dm³ MB solution; pH 3.5; $T = 25\,^\circ C$; adsorbent dosage = 1 g dm⁻³ and RPM = 150).
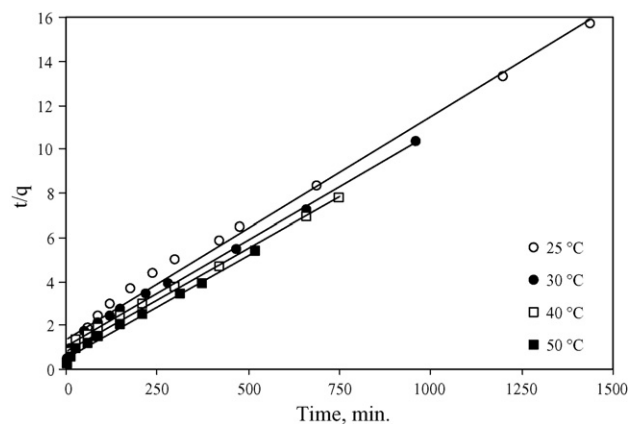

Fig. 9. Pseudo-second order adsorption kinetics of MB (0.5 dm³ MB solution; pH 3.5; $T = 25\,^\circ C$; adsorbent dosage = 1 g dm⁻³ and RPM = 150).

4.6. Kinetic parameters of adsorption

In order to investigate the adsorption process of MB onto DPH, pseudo-first order, pseudo-second order and intraparticle diffusion model were used. The plots of linearised form of the pseudo-first order equation are shown in Fig. 8. The values of k_1, q_{eq} and correlation coefficients are compared in Table 3. The results showed that the correlation coefficients obtained at different temperatures for the first order kinetic model were at the range of 0.998–0.974 and they decreased slightly with increasing temperature. The theoretical $q_{eq,cal}$ values found from this model did not give reasonable values especially at low temperature so pseudo-first order model could not describe the adsorption results of MB onto DPH.

The linearised form of the pseudo-second order model is presented in Fig. 9. The values of correlation coefficient of the model were very high and the theoretical $q_{eq,cal}$ values were much closed to the experimental q_{eq} values given in Table 3. In the view of these results, it can be said that the pseudo-second order kinetic model compared to the pseudo-first order model, provided a better correlation for the adsorption of MB onto DPH.

The adsorption of MB onto DPH follows generally three consecutive steps of external diffusion, intraparticle diffusion and adsorption. One or more of these steps can control the adsorption kinetics altogether or individually. 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 [37], it is assumed that the first sharper linear stage being a rapid
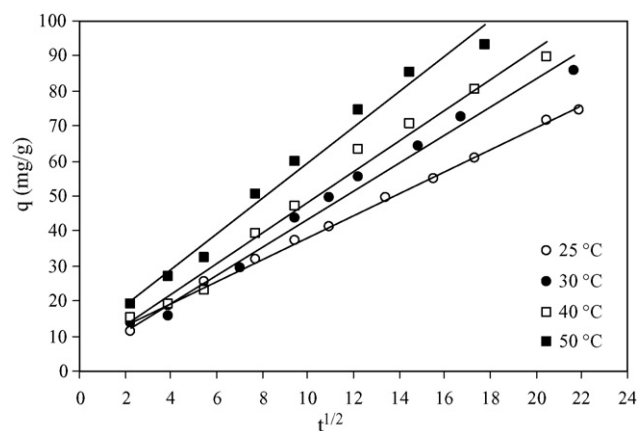

Fig. 10. Intraparticle diffusion at various initial concentrations (0.5 dm³ MB solution; $C_0 = 100$ mg dm⁻³; $T = 25\,^\circ C$; pH 3.5; adsorbent dosage = 1 g dm⁻³ and RPM = 150).

external diffusion and surface adsorption which is neglected, the second linear stage being a gradual adsorption stage where the intraparticle diffusion is rate limited, and the final stage being equilibrium stage. The intraparticle diffusion parameter, K_i, for this region was determined from the slope of the plots of q versus $t^{1/2}$ with varying temperature. At a certain time limit for the intraparticle diffusion as illustrated in Fig. 10 (between 10 and 400 min at given temperatures) the curves reveals linear characteristics. 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. As can be obtained from Fig. 10, diffusion rate, K_i, was in the range of

Table 3
Change of the pseudo-first and second-order reaction rate constants with temperature

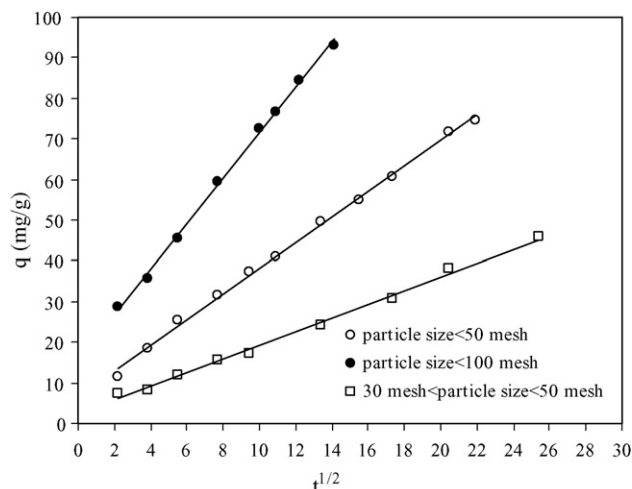| T (°C)	$q_{eq,exp}$ (mg g⁻¹)	First order kinetic model			Second order kinetic model		
		k_1 (dm⁻³ min⁻¹)	$q_{eq,cal}$ (mg g⁻¹)	r^2	k_2 (g mg⁻¹ min⁻¹)	$q_{eq,cal}$ (mg g⁻¹)	r^2
25	92.0	0.00322	77.3	0.998	0.000076	99.0	0.989
30	92.6	0.00599	89.7	0.984	0.000093	103.1	0.991
40	96.3	0.00668	92.5	0.987	0.000103	107.5	0.991
50	97.3	0.01080	93.8	0.974	0.000164	108.7	0.992

Fig. 11. Effect of particle sizes to the intraparticle diffusion on the adsorption of MB (0.5 dm^3 MB solution; pH 3.5; adsorbent dosage = 1 g dm^{-3}; T = 25 °C and RPM = 150).

3.15–5.10 mg g^{-1} min$^{-0.5}$ (r^2 = 0.99). It was found that the values of K_i increased with the increasing temperature.

The intraparticle diffusion parameter for the varying particle sizes was also determined from the slope of the plots of q versus $t^{0.5}$. The same trend for the K_i was also observed ranging from 1.69 to 5.61 mg g^{-1} min$^{-0.5}$ (r^2 = 0.99) with the changing particle sizes as shown in Fig. 11. At smaller particle sizes of the adsorbent, increase in K was due to the decrease in the intraparticle diffusion resistance.

4.7. Determination of thermodynamic parameters

Thermodynamic parameters such as free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) can be estimated by using equilibrium constants changing with temperature. The equilibrium constants obtained from Langmuir model at 25, 30, 40 and 50 °C were used to determine the Gibbs free energy changes. Gibbs free energy values for the adsorption process were obtained as −26.17, −27.35, −28.91 and
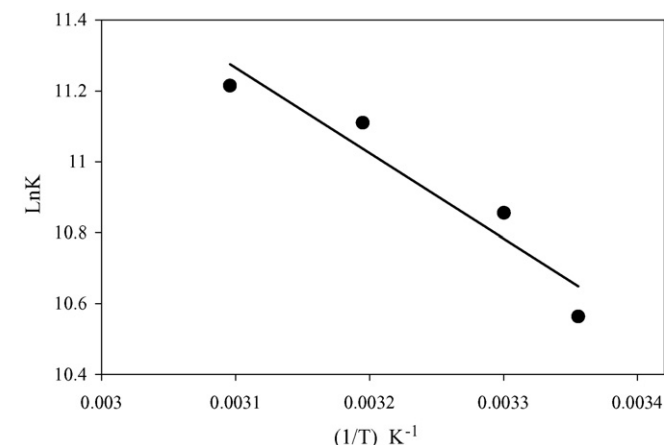
−30.12 kJ mol^{-1} for the temperatures of 25, 30, 40 and 50 °C, respectively. The K values increased with increasing temperature which resulting a shift of adsorption equilibrium to the right. The negative value of $\Delta G°$ indicates the spontaneous nature of MB adsorption onto DPH. According to the van't Hoff equation, the standard enthalpy and the entropy values in the range of 25–50 °C were obtained as 20.05 kJ mol^{-1} and 0.155 kJ mol^{-1} K^{-1} at initial pH 3.5 and initial MB concentration 100 mg dm^{-3}, respectively. As can be deduced from Fig. 12, the positive value of $\Delta H°$ suggests the endothermic nature of adsorption while the positive values of $\Delta S°$ shows the increasing randomness at the DPH-solution and adsorption medium interface during the adsorption.

5. Conclusions

In this study, the ability of DPH obtained by dehydrating with sulphuric acid to bind MB was investigated using equilibrium, kinetic and thermodynamic aspects. The results indicated that, adsorption capacity of the adsorbent considerably affected by preparation of DPH, temperature, particle size and initial MB concentration. Changing medium of pH value did not affect the adsorption process, ruling out charging of the DPH surface and indicating that the nature of the surface sites rather than the pH of the medium. It is also reported that MB adsorption increased with temperature up to 50 °C, initial MB concentration up to 400 g dm^{-3} and changing particle sizes from over 50 meshes to below 100 meshes.

The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon of the MB. The adsorption equilibrium was best defined by the Langmuir isotherm model at these optimum conditions. The DPH can be used as an effective low-cost agricultural waste adsorbent for the removal of MB with its adsorption capacity of 161.3 mg g^{-1} at 50 °C.

The kinetics of MB adsorption onto DPH 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 and reaction rate constant of this equation was obtained as about 0.00016 g mg^{-1} min^{-1} at 50 °C. It was also seen that the intraparticle diffusion kinetics can also be one of the effective controlling steps contributing with the adsorption process.

The thermodynamic constants of adsorption were also evaluated. The negative value of $\Delta G°$ confirms the spontaneous nature adsorption process. The positive value of $\Delta S°$ showed the increased randomness at the solid–solution interface during adsorption and the positive value of $\Delta H°$ indicated the adsorption process was endothermic.

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

Fig. 12. Plot of ln K vs. 1/T for the enthalpy change of the adsorption process.

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