

Removal of methylene blue from aqueous solution by chaff in batch mode

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Received 27 January 2006; received in revised form 19 February 2006; accepted 21 February 2006

Available online 4 April 2006

Abstract

A new adsorbent system for removing methylene blue (MB) from aqueous solutions has been investigated. This new adsorbent is cereal chaff, an agriculture product in middle-west region in China. Variables of the system, including biosorption time, chaff dose, pH, salt concentration and initial MB concentration, were adopted to study their effects on MB removal. The results showed that as the dose of chaff increased, the percentage of MB sorption increased accordingly. There was no significant difference in the dye concentration remaining when the pH was increased from 4.0 to 11.0. The salt concentration has negative effect on MB removal. At the experimental range of MB concentration, the amount of MB adsorbed onto per unit mass of chaff (q_e) is direct ratio to MB initial concentration (c_0). The equilibrium data were analyzed using five equilibrium models, the Langmuir, the Freundlich, the Redlich–Peterson, the Koble–Corrigan and the Temkin isotherms. The results of non-linear regressive analysis are that the isotherms of Langmuir, Redlich–Peterson and Koble–Corrigan are better fit than the isotherms of Freundlich and Temkin at different temperatures according to the values of determined coefficients (R^2) and Chi-square statistic (χ^2). The maximum equilibrium capacities of chaff from Langmuir models are 20.3, 25.3 and 26.3 mg g⁻¹ at 298, 318 and 333 K, respectively. Using the equilibrium concentration constants obtained at different temperatures, various thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated. The thermodynamics parameters of MB/chaff system indicate spontaneous and endothermic process. It was concluded that an increase in temperature results in a bigger MB loading per unit weight of the chaff.

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Keywords: Chaff; Biosorption; Methylene blue; Equilibrium; Thermodynamic

1. Introduction

Many industries, such as paper, plastics, food, cosmetics, textile, etc., use dyes in order to color their products. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable. The sorption technique is proved to be an effective and attractive process for the treatment of these dye-bearing wastewaters [1,2]. Currently, the most widely used and effective physical method in industry is activated carbon, although running costs are expensive [3]. In recent years, agricultural by-products such as peat and pith, waste cellulose, apple pomace and wheat straw have been widely studied for dyes removal from wastewater [4–6].

Methylene blue (MB) is selected as a model compound in order to evaluate the capacity of adsorbents for the removal of dye (methylene blue) from its aqueous solutions. MB has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools and coating for paper stock. Previously some researchers had proved several low-cost biomaterials such as giant duckweed [7], rice husk [8], sawdust [9], sewage sludge [10] and neem sawdust [11] for the removal of methylene blue from its aqueous solutions.

Like rice husk, cereal chaff contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl, amidogen, etc., which make biosorption processes possible [12,13]. Chaff is obtained from agriculture as a by-product; furthermore, its yield is vast. Biosorption for lead(II) and copper(II) from aqueous solution by chaff has been studied and the chaff can be used as an adsorbent to remove lead(II) and copper(II) from aqueous solution [13–15]. The aim of this work was to study the possibility of the utilization of chaff for removal of MB from aqueous solutions. The system variables studied

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include adsorptive time, solution pH, chaff dose, salt concentration and the initial MB concentration at different temperatures. The isotherm constants for the Langmuir, the Freundlich, the Redlich–Peterson, the Koble–Corrigan and Temkin isotherms have been calculated. The thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated.

1.1. Adsorption model

The analysis of adsorption process requires equilibrium to better understand the adsorption process. Equilibrium isotherm equations are used to describe the experimental sorption data. Sorption isotherms provide fundamental physicochemical data for evaluating the applicability of sorption process. In the present investigation, the equilibrium data were analyzed using five equilibrium models, the Langmuir, the Freundlich, the Redlich–Peterson, the Koble–Corrigan and the Temkin isotherms for describing solid–liquid sorption systems.

1.1.1. Langmuir isotherm

The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution [16]. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent.

The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (1)$$

where c_e is the equilibrium concentration (mg l^{-1}); q_e is the amount of MB adsorbed onto per unit mass of chaff (mg g^{-1}); q_m is the q_e for a complete monolayer (mg g^{-1}), a constant related to sorption capacity; and K_L is a constant related to the affinity of the binding sites and energy of adsorption (1 mg^{-1}).

1.1.2. Freundlich isotherm

Freundlich studied the sorption of a material onto animal charcoal and found that if the concentration of solute in the solution at equilibrium, c_e , was raised to the power $1/n$, the amount of solute sorbed being q_e , then $c_e^{1/n}/q_e$ was a constant at a given temperature [17].

This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_e = K_F \cdot c_e^{1/n} \quad (2)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively. The Freundlich model is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

1.1.3. Redlich–Peterson isotherm

The three-parameter Redlich–Peterson equation which has a linear dependence on concentration in the numerator and an exponential function in the denominator has been proposed to

improve the fit by the Langmuir or Freundlich equation and is given by Eq. (3) [18]:

$$q_e = \frac{A c_e}{1 + B c_e^g} \quad (3)$$

where A , B and g are the Redlich–Peterson parameters, g lies between 0 and 1. For $g=1$, Eq. (3) converts to the Langmuir form.

1.1.4. Koble–Corrigan isotherm

Koble–Corrigan model is another three-parameter empirical model for representing the equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm type models and is given by Eq. (4) [19]:

$$q_e = \frac{A c_e^n}{1 + B c_e^n} \quad (4)$$

where A , B and n are the Koble–Corrigan parameters.

1.1.5. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm [20]

$$q_e = \frac{RT}{b_t} \ln(a_t c_e) \quad (5)$$

or

$$q_e = A + B \ln c_e \quad (6)$$

where R is the general gas constant, T the absolute temperature (K) and A ($(RT/b_t) \ln a_t$) and B (RT/b_t) represent isotherm constants, respectively.

1.2. Error analysis

As different forms of the equation affected R^2 values more significantly during the linear analysis, the non-linear analysis might be a method of avoiding such errors [21].

In this paper, a non-linear Chi-square of determination test was used. The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The relative mathematical formula is

$$x^2 = \sum \frac{(q_e - q_{e,c})^2}{q_{e,c}} \quad (7)$$

where $q_{e,c}$ is the amount of MB being adsorbed obtained by calculating from relative model (mg g^{-1}) and q_e is the amount of sorbate adsorbed onto per unit mass of chaff obtained from experiment (mg g^{-1}). If data from the model are similar to the experimental data, x^2 will be a small number; if they are different, x^2 will be a large number. In order to confirm the best fit isotherm for the adsorption system, it is necessary to analyze the data using the Chi-square statistic (x^2), combined with the values of determined coefficient (R^2).

2. Materials and methods

2.1. Materials

The cereal chaff used in the present investigation was obtained from local cereal mills. The collected materials were then washed with distilled water for several times to remove all the dirt particles. The washed chaff was dried in an oven at 373 K for a period of 24 h, and then ground and screened through a set of sieves to get different geometrical sizes 0.25–0.42 mm. This produced a uniform material for the complete set of adsorption tests which was stored in an air-tight plastic container for all investigations.

The stock solutions of MB were prepared in distilled water. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration. Both chaff and MB solution were placed in a 125 ml conical flask for adsorptive experiment.

2.2. Methods

The data obtained in batch model studies were used to calculate the equilibrium MB uptake quantity. It was calculated for adsorptive quantity of MB by using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{1000m} \quad (8)$$

where q_e is the biomass adsorption equilibrium MB uptake quantity (mg g^{-1}), V the sample volume (ml), c_0 the initial MB concentration (mg l^{-1}), c_e the equilibrium MB concentration (mg l^{-1}) and m is the dry weight of the biomass (g).

2.2.1. Effect of contacting time on biosorption

Batch biosorption tests were done at different contacting times at the initial concentration of MB 30 mg l^{-1} and chaff dose concentration 8 g l^{-1} in 50 ml solution. The temperature was controlled with a water bath at the temperature of 298 K for all studies except the effect of the MB initial concentration. Agitation was made at a constant agitation speed of 100 rpm. The samples were then collected at 10, 15, 30, 40, 50, 60, 90, 120, 150, 180, 210 and 240 min and were centrifuged. The left out concentration in the supernatant solution was analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance changes at a wavelength of maximum absorbance (668 nm).

2.2.2. Effect of chaff dose on biosorption

Batch biosorption tests were done at the initial concentration of MB 30 mg l^{-1} and the chaff dose $2\text{--}12 \text{ g l}^{-1}$ in 50 ml solution. Agitation was made for 3 h at a constant agitation speed of 100 rpm. The samples were then centrifuged and the left out concentration in the supernatant solution was analyzed as said before.

2.2.3. Effect of solution pH on biosorption

The effect of pH on the amount of MB removal was analyzed over the pH range from 2 to 11. The pH was adjusted using

0.1 mol l^{-1} NaOH and 0.1 mol l^{-1} HCl solutions. In this study 50 ml of dye solution of 30 mg l^{-1} was agitated with 8 g l^{-1} of chaff. Agitation was made for 180 min at a constant agitation speed and the samples were treated as before. The pH of original solution was near 7 and it was not adjusted.

2.2.4. Effect of NaCl and CaCl₂ concentrations on biosorption

The effect of salt concentration (ionic strength) on the amount of MB adsorbed or removed by chaff was analyzed over the NaCl or CaCl₂ concentration range from 0 to 0.20 mol l^{-1} .

2.2.5. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.4 g of chaff particles with 50 ml of MB solution of different initial dye concentrations, $20\text{--}200 \text{ mg l}^{-1}$. A series of such conical flasks was then shaken at a constant speed of 100 rpm in a shaking water bath with temperatures 298, 318 and 333 K, respectively. The samples were then centrifuged and the left out concentration in the supernatant solution was analyzed for MB absorbance.

3. Results and discussion

3.1. The effect of contacting time on biosorption

The results of biosorption quantity per gram chaff (q_t) and percent removal efficiency (p) at different shaking times are shown in Fig. 1.

From Fig. 1, a two-stage kinetic behavior is evident: a very rapid initial adsorption over a few minutes, followed by a longer period of much slower uptake. As can be seen from Fig. 1, with the beginning of adsorption the adsorbed quantity of MB onto per unit mass of chaff (q_e) increased quickly, then after 60 min, the change became slow. So the adsorption of MB on chaff was speedy, and within 60 min, the reaction of sorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed MB did not significantly change with time. Also the adsorption capacity of MB is about 3.60 mg g^{-1} after

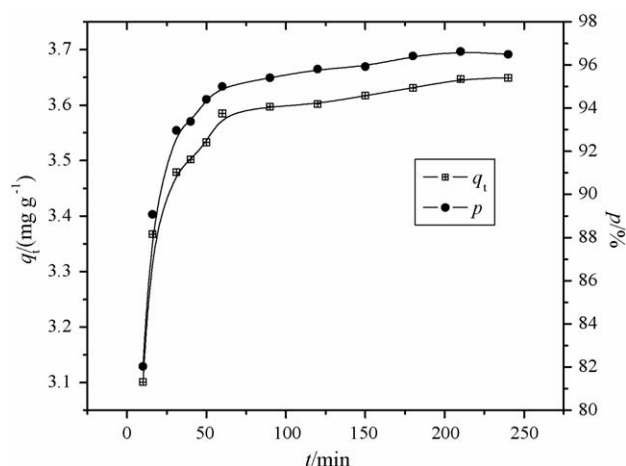


Fig. 1. The effect of contacting time on biosorption and removal efficiency.

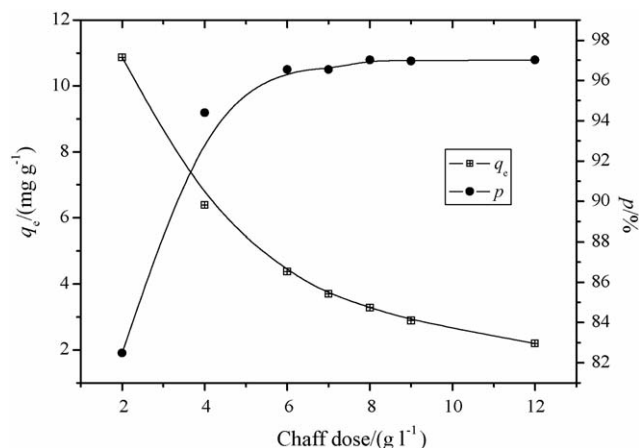


Fig. 2. The effect of chaff dose on biosorption.

60 min of contact. According to the results of the experiments, the agitation time was fixed at 180 min for the rest of the batch experiments to make sure that equilibrium was reached.

Also from Fig. 1, the change of the removal efficiency with sorption time increasing is similar to the change of adsorbed quantity. Up to 60 min, the removal efficiency is 95%.

3.2. Effect of chaff dose on biosorption

The adsorption amount (mg g^{-1}) and percentage adsorption of MB at different doses of chaff are shown in Fig. 2. It was observed that the percent removal efficiency of MB increased from 82.5 to 97.0% when the adsorbent load increased from 2 to 12 g l^{-1} . On the other hand, the plot of adsorption amount versus adsorbent dose reveals that with increasing chaff dosage from 2 to 12 g l^{-1} , the values of q_e decreased from 10.9 to 2.2 mg g^{-1} . The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

At higher chaff concentration, there is a very fast superficial adsorption onto the chaff surface that produces a lower solute concentration in the solution than when chaff dose is lower. Thus, with increasing adsorbent dose, the amount of MB adsorbed per unit mass of chaff reduced, thus causing a decrease in q_e value. A similar effect was previously reported [3,7,8].

3.3. Effect of solution pH on biosorption

Fig. 3 shows the effect of solution pH on amount of MB adsorbed onto chaff and percent MB removal efficiency at various initial solution pH for an initial dye concentration of 30 mg l^{-1} and chaff dose of 8 g l^{-1} .

From Fig. 3, it was observed that the solution pH affects the values of q_e and percent removal efficiency (P). It was observed that the values of q_e were increased with the pH value increasing at the range of 2–4, while, when the value of pH was increased from 4 to 11, the adsorption quantity was approximately constant. Several reasons may be attributed to MB adsorption behavior of the sorbent relative to solution pH. The surface of chaff

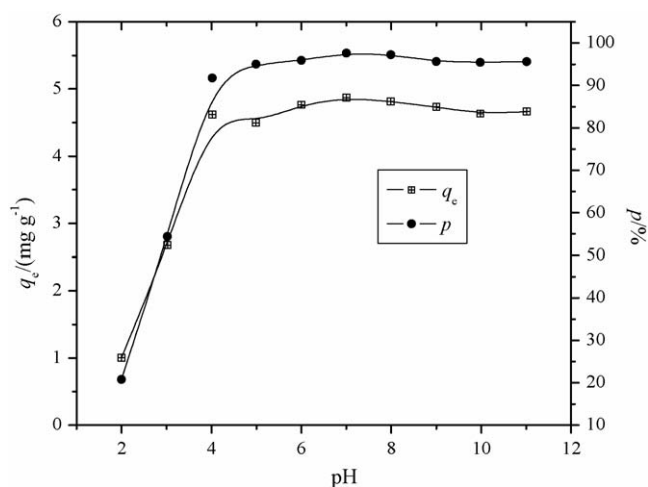


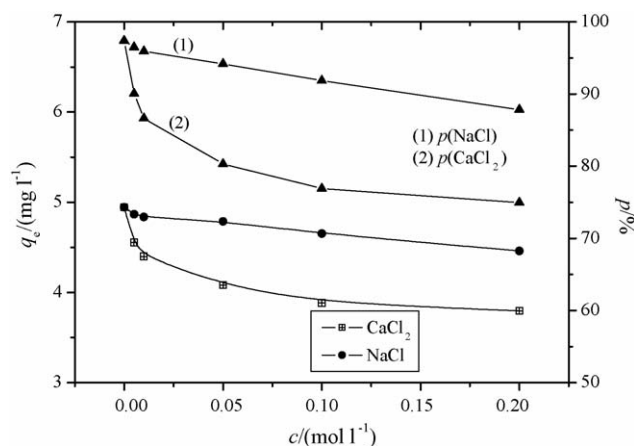
Fig. 3. The effect of solution pH on biosorption.

may contain a large number of active sites and the solute (MB ions) uptake can be related to the active sites and also to the chemistry of the solute in the solution. At lower pH values, the surface of adsorbent would also be surrounded by the hydrogen ions which compete with MB ions binding the sites of the sorbent. At higher pH the surface of chaff particles may get negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction. Other adsorbent, such as giant duckweed, has the same results about the pH effect on MB adsorption [7].

The structure of chaff is cellulose based, and the surface of cellulose in contact with water is negatively charged. Dissolved MB ions are positively charged and will undergo attraction on approaching the anionic chaff structure. On this basis, it is expected that a MB will have a strong sorption affinity for chaff.

3.4. Effect of NaCl and CaCl₂ concentrations on biosorption

Fig. 4 shows the effect of various concentrations of NaCl and CaCl₂ solutions on the amount of MB adsorbed onto per unit

Fig. 4. The effect of NaCl and CaCl₂ concentrations on biosorption.

mass of chaff and percent removal efficiency for an initial MB concentration of 30 mg l^{-1} and chaff dose of 8 g l^{-1} .

The wastewater containing dye has commonly higher salt concentration, and ionic strength effects are of some importance in the study of dye adsorption onto adsorbents. From Fig. 4, NaCl and CaCl₂ existing in solution affected the MB adsorption onto chaff. It was seen that the increase in the salt concentration resulted in a decrease of MB adsorption onto chaff and percent removal efficiency. This trend indicated that the adsorbing efficiency decreased when NaCl and CaCl₂ concentrations increased in the MB solution, which could be attributed to the competitive effect between MB ions and cations from the salt for the sites available for the sorption process. As the concentration of salt is increased from 0 to 0.20 mol l^{-1} , the amount of MB adsorbed onto chaff (q_e) decreased from 4.94 to 4.46 and 3.80 mg l^{-1} for NaCl and CaCl₂, respectively, while the percent removal efficiency decreased from 97.4 to 87.8 and 75.0% for NaCl and CaCl₂. Another reason is that ionic strength increases, the activity of MB and the active sites decreases, so the adsorptive capacity of MB decreases. As Ca²⁺ has more contribution to ionic strength and more positive charge than Na⁺, the effect of Ca²⁺ on adsorption is more serious than Na⁺. But even at 0.20 mol l^{-1} of salt, the chaff still has bigger percent removal efficiency and the chaff has been used to efficiently remove MB from aqueous solution with higher salt concentration.

3.5. The effect of initial MB concentration on temperature-dependent biosorption

The influence of the initial concentration of MB in the solutions on the values of q_e and percent removal efficiency is shown in Figs. 5 and 6, respectively.

As seen from Fig. 5, equilibrium uptake increased with the increasing of initial MB concentrations at the range of experimental concentration. This is a result of the increase in the driving force concentration gradient, as an increase in the initial MB concentrations. In the same conditions, if the

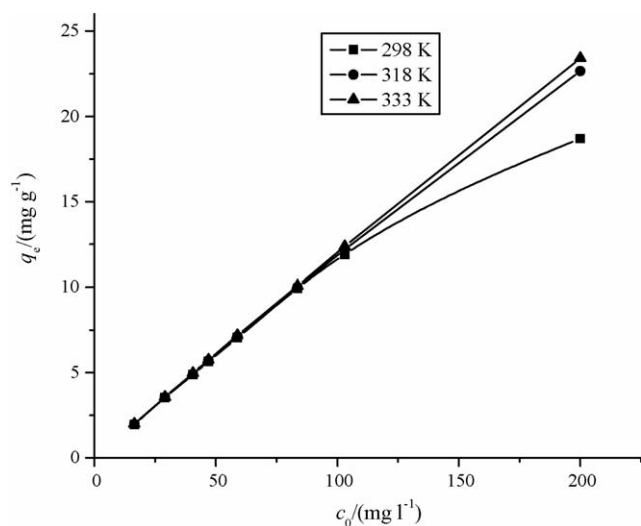


Fig. 5. Equilibrium quantities of MB at different initial concentrations with different temperatures.

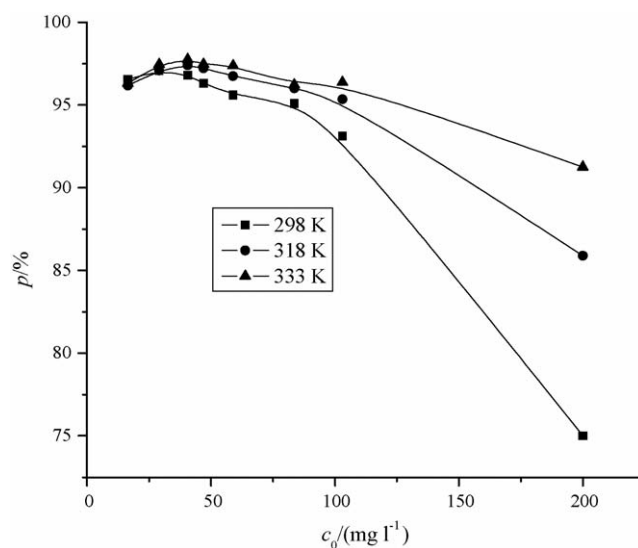


Fig. 6. Percent removal efficiency of MB at different initial MB concentrations with different temperatures.

concentration of MB in solution was bigger, the active sites of chaff were surrounded by much more MB ions, the reaction of adsorption would carry out more sufficiently. So the adsorption quantity for MB increased with the increasing of initial MB concentrations.

The bigger adsorptive capacity of MB was also observed in the higher temperature range. This was due to the increasing tendency of adsorbate ions to adsorb from the solution to the interface with increasing temperature. The increase of the equilibrium adsorption with increasing temperature indicated that the adsorption of MB ions onto chaff is endothermic in nature. The percent removal efficiency also increased at higher temperature. But the percent removal efficiency decreased with the initial MB concentration increasing at constant temperature. Other studies have the same results about the initial MB concentration on adsorption capacity and percent removal rate [7,8,10].

Using linear regressive method, the correlation of q_e and c_0 at different temperatures is listed in Table 1. R^2 is determined coefficient of linear regressive analysis.

From 298 to 333 K, the change in the slope of the regressive line is small, and the difference of the lines from 298 to 318 K is bigger than the difference from 318 to 333 K, which shows that within lower temperature, increasing the temperature can lead to more increase in capacity of MB adsorbed onto chaff.

Furthermore, the quantity of MB onto chaff is linear to MB initial concentration within the range of experimental concentration with higher R^2 .

Table 1

The relation between the amount of MB adsorbed onto per unit mass of chaff (q_e) and MB initial concentration (c_0)

T (K)	Adsorption equation	R^2
298	$q_e = 0.1031c_0$	0.954
318	$q_e = 0.1158c_0$	0.998
333	$q_e = 0.1186c_0$	0.999

4. Determination of equilibrium model constants about MB/chaff system

Analysis of the equilibrium data is important to develop an equation which accurately represents the results and which could be used for design purposes. Five of these have been applied in this study, Freundlich, Langmuir, Redlich–Peterson, Koble–Corrigan and Temkin isotherms.

An adsorption isotherm is characterized by certain constants whose values express the surface properties and affinity of the sorbent and can also be used to find the biosorptive capacity of biomass. The Langmuir, Freundlich, Redlich–Peterson, Koble–Corrigan and Temkin adsorption constants evaluated from the isotherms at different temperatures and the values of R^2 and χ^2 are presented in Table 2 according to Eqs. (1)–(4) and (6) using non-linear regressive methods. The uncertainties of the relative parameters are also listed in Table 2. The non-linear fitted curve with different adsorption models are shown in Fig. 7 at 298, 318 and 333 K, respectively.

Langmuir constant, q_m , represents the monolayer saturation at equilibrium. The other mono-component Langmuir constant, K_L , indicates the affinity for the binding of MB. A high K_L value indicates a high affinity. From Table 2, the biosorption capacity of chaff (q_m) increased slightly on increasing the temperature while the values of K_L decreased during temperature

Table 2
Isotherm constants for MB sorption onto chaff at different temperatures using non-linear regressive method

	T (K)		
	298	318	333
Langmuir			
K_L (1 mg^{-1})	0.218 ± 0.014	0.153 ± 0.013	0.176 ± 0.018
q_m (mg g^{-1})	20.3 ± 0.5	25.3 ± 0.1	30.7 ± 1.5
R^2	0.994	0.993	0.991
χ^2	0.180	0.381	0.477
Freundlich			
K_F	4.92 ± 0.61	4.79 ± 0.49	4.81 ± 0.48
$1/n$	0.353 ± 0.040	0.404 ± 0.032	0.411 ± 0.031
R^2	0.925	0.964	0.968
χ^2	2.56	1.81	1.77
Redlich–Peterson			
A	4.70 ± 0.54	5.06 ± 0.70	5.14 ± 0.73
B	0.262 ± 0.080	0.344 ± 0.117	0.353 ± 0.122
g	0.968 ± 0.050	0.865 ± 0.051	0.854 ± 0.051
R^2	0.995	0.997	0.997
χ^2	0.199	0.205	0.211
Koble–Corrigan			
n	0.968 ± 0.070	0.850 ± 0.073	0.951 ± 0.126
A	4.51 ± 0.32	4.36 ± 0.31	5.50 ± 0.42
B	0.219 ± 0.016	0.157 ± 0.011	0.171 ± 0.025
R^2	0.995	0.996	0.992
χ^2	0.208	0.251	0.555
Temkin			
A	3.84 ± 0.21	3.50 ± 0.30	3.48 ± 0.34
B	3.88 ± 0.12	4.72 ± 0.18	4.89 ± 0.20
R^2	0.994	0.996	0.989
χ^2	0.458	0.428	0.562

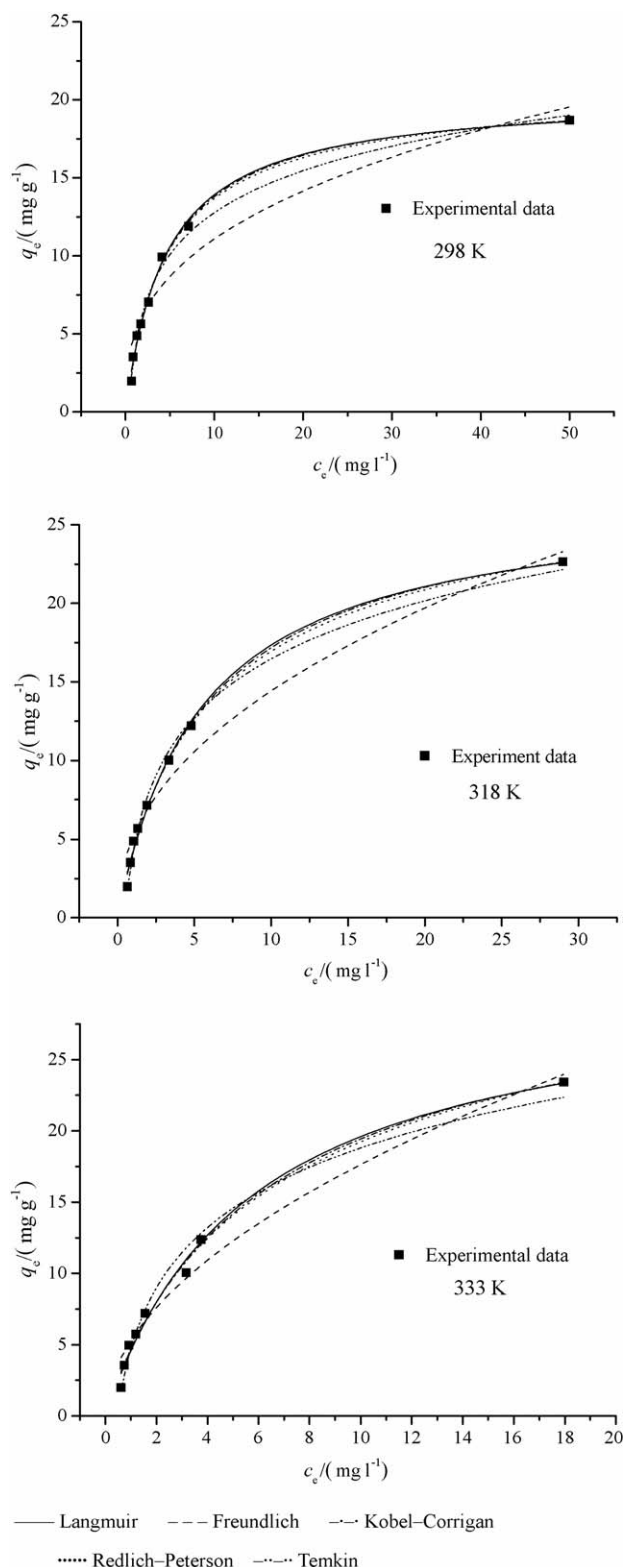


Fig. 7. The non-linear fitted curve with different models at 298, 318 and 333 K, respectively.

rising. The values of q_m obtained at 298, 318 and 333 K are 20.3, 25.3 and 26.3 mg g^{-1} , respectively. Also it can be found that at lower temperature, increasing temperature can result in more increment for adsorptive capacity. The q_m values show that the

Table 3
MB sorption by biosorbents: a selection of the Langmuir constant, q_m , of various related substances from the literature

q_m (mg/g)	Biosorbent	References
20.3	Natural chaff	This paper
32.3	Modified sawdust	[22]
40.6	Rice husk	[8]
119	Giant duckweed	[7]
185	Water hyacinth root	[23]

sorption capacity of cereal chaff particles was highly comparable to the sorption capacities of some other low-cost adsorbent materials for MB. The values q_m about some biosorbent binding MB from the Langmuir constant are listed in Table 3. Compared to other biosorbents listed in Table 3, the value of q_m about chaff for MB is lower, but as agricultural by-product, it is vast and cheap, so chaff can be used to remove MB from solution.

The Freundlich model does not describe the saturation behavior of the biosorbent as well as Langmuir model. From Table 2, all measured values of K_F showed easy uptake of MB with high adsorptive capacity of chaff and significant differences in sorption capacities due to temperature. The obtained values of $1/n$ ($0.1 < 1/n < 1$) indicated a higher adsorb ability of MB at all temperatures studied [24]. The results also indicated that with the temperature increasing, the ability of biosorption increased.

Relevant adsorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson and Koble–Corrigan at different temperatures. Examination of the data shows that the two isotherms are appropriate descriptions of the data for MB biosorption over the concentration ranges studied. The constants g and n are near to 1, and these indicate the isotherms are approaching the Langmuir form.

The corresponding Temkin parameters of A and B for different temperatures are also given in Table 2 for MB–chaff system.

Based on the values of R^2 and χ^2 , and from Fig. 3, the non-linear forms of the Langmuir, Redlich–Peterson and Koble–Corrigan isotherms appear to produce a better model for adsorption in MB/chaff systems, while the non-linear forms of the Freundlich and Temkin isotherms appear to produce a reasonable model for adsorption in MB/chaff systems at three different temperatures.

5. Thermodynamic parameters of biosorption

To estimate the effect of temperature on the adsorption of MB on chaff, the free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined. The adsorption process can be summarized which represents a heterogeneous equilibrium. The apparent equilibrium constant (K'_c) of the biosorption is defined as [15,24,25]:

$$K'_c = \frac{c_{ad,e}}{c_e} \quad (9)$$

where $c_{ad,e}$ is the concentration of MB on the adsorbent at equilibrium (mg l^{-1}). The value of K'_c in the lowest experimental

Table 4
Thermodynamic parameters of MB biosorption on chaff

	T (K)		
	298	318	333
ΔG^0 (kJ mol $^{-1}$)	−7.83	−8.51	−9.03
ΔH^0 (kJ mol $^{-1}$)		2.41	
ΔS^0 (kJ mol $^{-1}$ K $^{-1}$)		−0.0344	

MB concentration can be obtained [25]. The K'_c value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG^0):

$$\Delta G^0 = -RT \ln K'_c \quad (10)$$

The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a van't Hoff equation of ΔG^0 versus T

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (11)$$

where ΔG^0 is standard Gibbs free energy change (J), R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is absolute temperature (K).

Values of the standard Gibbs free energy change for the biosorption process obtained from Eq. (10) are listed in Table 4.

The negative ΔG^0 values of MB at various temperatures are due to the fact that the adsorption processes are spontaneous with a high preference of MB on chaff and the negative value of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of MB is inversely proportional to the temperature.

The standard enthalpy and entropy changes of biosorption determined from Eq. (11) were 2.41 kJ mol^{-1} and $-0.0344 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. The positive value of ΔH^0 confirms the endothermic character of biosorption on MB–chaff system, whereas the negative ΔS^0 values confirm the decreased randomness at the solid–solute interface during biosorption. The low value of ΔS^0 also indicates that no remarkable change on entropy occurs.

6. Conclusion

The removal of MB from aqueous solution using cereal chaff has been investigated under different experimental conditions in batch mode. The value of q_e about MB adsorbed onto chaff was dependent on solution pH, chaff dose, adsorptive time, salt concentration and MB initial concentration. The amount of 95% total MB was removed within 60 min of the start of experiment at the initial MB concentration 30 mg l^{-1} and the temperature 298 K. The pH had no effect on MB removal as pH increased from 4 to 11. The value of q_e was direct ratio to initial concentration at different temperatures. The equilibrium data were found to be better represented by the Langmuir, the Redlich–Peterson and the Koble–Corrigan isotherms according to the non-linear regressive analysis. The thermodynamics parameters indicate spontaneous and endothermic process.

Acknowledgments

The authors express their sincere gratitude to Henan Science and Technology Department and the Education Department of Henan Province in China for the financial support of this study.

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