Journal of Hazardous Materials 141 (2007) 156–162

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves

Runping Han *, Weihua Zou, Weihong Yu, Shujian Cheng, Yuanfeng Wang, Jie Shi

Department of Chemistry, Zhengzhou University, No. 75 of Da Xue North Road, Zhengzhou 450052, PR China

Received 16 May 2006; received in revised form 26 June 2006; accepted 27 June 2006
Available online 30 June 2006

Abstract

A new adsorbent, the fallen phoenix tree's leaf, has been investigated in order to remove methylene blue (MB) from aqueous solutions. Variables of the system, including contact time, leaf dose, solution pH, salt concentration and initial MB concentration, were adopted to study their effects on MB biosorption. The results showed that as the dose of leaf increased, the percentage of MB sorption increased accordingly. There was no significant difference about the quantity of MB adsorbed onto leaf as the pH was within the range 4.5–10.0. The salt concentration has negative effect on MB removal. The equilibrium data were analyzed using the Langmuir and the Freundlich isotherms. The results of non-linear regressive analysis are that the Langmuir isotherm is better fit than the Freundlich isotherm at different temperature according to the values of determined coefficients (R^2) and χ^2-statistic (*SS*). The Langmuir monolayer saturation capacities of MB adsorbed onto leaf are 80.9, 83.8, 89.7 mg g^{-1} at 295, 309 and 323 K, respectively. Using the equilibrium concentration contents obtained at different temperatures, various thermodynamic parameters, such as ΔG°, ΔH° and ΔS°, have been calculated. The thermodynamics parameters of MB/leaf system indicate spontaneous and endothermic process. It was concluded that an increase in temperature be advantage to adsorb MB onto leaf.

Keywords: Phoenix tree's leaf; Biosorption; Methylene blue; Equilibrium; Thermodynamic

1. Introduction

Many industries, such as plastics, dyestuffs and textile, use dyes to color their products and also consume substantial volumes of water. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in industrial wastewater. The presence of very small amounts of dyes in water is highly visible and undesirable [1]. Due to increasingly stringent restrictions on pollutant content of industrial effluents, it is necessary to remove dyes from wastewater before it is discharged into environment.

Adsorption techniques are proved to be an effective and attractive process for removal of non-biodegradable pollutants (including dyes) from wastewater [2,3]. Most commercial systems use activated carbon as adsorbent to remove dyes in wastewater because it has excellent adsorption ability. But its widespread use is limited due to high running cost. Many low-cost adsorbents, including natural materials, biosorbents, and waste materials from industry and agriculture, have been proposed by several workers [4–7]. These materials do not require any expensive additional pretreatment step and could be used as adsorbents for removal of dyes from solution.

In China, many cities have planted phoenix tree in main roads, parks and schools. So a lot of phoenix tree's leaves felled in autumn and often are collected as waste by cleaners. Like other plant materials, the phoenix tree leaves contain abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen, etc., which make biosorption processes possible [8]. Thus the research is needed to develop an alternative technology for utilizing these leaves. Several researchers reported plant-leaf used to adsorb heavy metals from solution [9–13], but no research was reported about dye adsorption onto fallen leaves. In the present study the fallen phoenix tree's leaves have been used as an adsorbent for the removal of methylene blue (MB) from its aqueous solutions. MB is selected as a model compound for evaluating the potential of leaves to remove dye from

* Corresponding author. Tel.: +86 371 67763707; fax: +86 371 67763220.
E-mail address: rphan67@zzu.edu.cn (R. Han).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2006.06.107

wastewaters. MB is a thiazine (cationic) dye, which is most commonly used for coloring paper, temporary hair colorant, dyeing cottons, wools, etc. Previously some researchers had proved several low-cost biomaterials such as giant duckweed [14], rice husk [15], cereal chaff [16], sewage sludge [17] and sawdust [18] for the removal of methylene blue from its aqueous solutions. The aim of this work was to study the possibility of the utilization of leaf for removal of MB from aqueous solutions. The system variables studied include contact time, solution pH, leaf dose, salt concentration, and the initial MB concentration at different temperature. The isotherm constants for the Langmuir and the Freundlich model have been obtained using non-linear regressive analysis. The thermodynamic parameters, such as ΔG°, ΔH°, ΔS°, have been calculated.

2. Materials and methods

2.1. Materials

The fallen phoenix tree's leaves used in the present investigation was obtained from Zhengzhou city in autumn. The collected materials were washed with distilled water for several times to remove all the dirt particles. The washed leaf 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 40–60 mesh. 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 leaf and MB solution were placed in a 50 ml conical flask for adsorptive experiment. Fresh dilutions were used for each adsorption study.

2.2. Methods

Batch sorption experiments were carried out by shaking the flasks at 100 rpm for a period of time using a water bath shaker. Following a systematic process, the biosorption uptake capacity of MB in batch system was studied in the present work.

2.2.1. Effect of contact time on biosorption

Batch biosorption tests were done at different contact time at the initial concentration of MB 130 mg l^{-1} and leaf dose concentration 2 g l^{-1} in 10 ml solution in each flask. The temperature was controlled with a water bath at the temperature of 295 K for all studies except the effect of the MB initial concentration. The flasks were then taken out at some intervals and the samples were centrifuged. The left out solution was used to determine the MB concentration. The concentration of MB in solution was analyzed using a UV spectrophotometer (Shimadzu Brand UV-3000) by monitoring the absorbance at a wavelength of maximum absorbance (668 nm).

2.2.2. Effect of leaf dose on biosorption

Batch biosorption tests were done at the initial concentration of MB 70 mg l^{-1} and the leaf dose 1–8 g l^{-1} in 10 ml solution. Agitation was made for 3 h. 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 adsorbed onto leaf was investigated over the pH range from 2.5 to 10. The pH was adjusted using 0.1 mol l^{-1} NaOH or 0.1 mol l^{-1} HCl solutions. In this study, 10 ml of MB solution of 130 mg l^{-1} was agitated with 2 g l^{-1} of leaf. Agitation was made for 180 min and the adsorption mixture was centrifuged to separate the leaf from the solution. The pH of original solution was near 7 and it was not adjusted in other experiments.

2.2.4. Effect of NaCl and $CaCl_2$ concentration on biosorption

The effect of salt concentration (ionic strength) on the amount of MB adsorbed or removed by leaf was analyzed over the NaCl or $CaCl_2$ concentration range from 0 to 0.20 mol l^{-1}. MB solution of 110 mg l^{-1} (10 ml) was agitated with 2 g l^{-1} of leaf. The agitation was 180 min.

2.2.5. Effect of initial MB concentration on temperature-dependent biosorption

Equilibrium experiments were carried out by mixing 2 g l^{-1} of leaf particles with 10 ml of MB solution of different initial dye concentration, 30–180 mg l^{-1}. A series of such conical flasks was then shaken in a shaking water bath with temperatures 295, 309 and 323 K, respectively. After 180 min, the samples were then centrifuged and the left out concentration in the supernatant solution was analyzed for MB absorbance.

The amount of adsorbed MB per gram leaf (q_e) was obtained using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{1000m} \quad (1)$$

where q_e is the equilibrium uptake value (the amount of MB adsorbed onto per unit mass of leaf) (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 leaf (g).

3. Results and discussion

3.1. The effect of contact time on biosorption

The results of biosorption quantity per gram leaf (q_t) at different contact time were shown in Fig. 1.

From Fig. 1, a two-stage kinetic behavior is evident: a rapid initial adsorption over 30 min, followed by a longer period of much slower uptake. As shown in Fig. 1, with the beginning of adsorption the values of q_t increased quickly, then 150 min later, the change became slow. So within 150 min, the reaction of adsorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed MB did not significantly change with time. According to the results of the experiments,

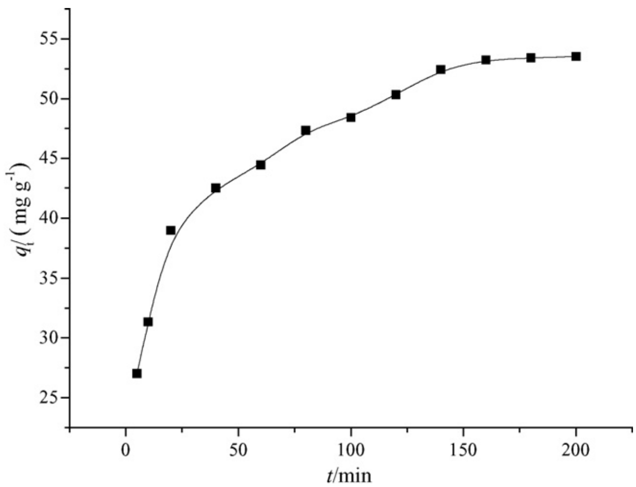


Fig. 1. The effect of contact time on biosorption (c_0 = 130 mg l^{-1}, leaf dose = 2 gl^{-1}).

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

3.2. Effect of leaf dose on biosorption

The values of q_e and percentage removal efficiency of MB (p) at different doses of leaf were shown in Fig. 2. It was observed that the percent removal efficiency of MB increased from 68% to 95% when the adsorbent dose increased from 1 to 8 g l^{-1}. On the other hand, the plot of adsorption amount versus adsorbent dose showed that with increasing leaf dose from 1 to 8 g l^{-1}, the values of q_e decreased from 43.3 to 8.3 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. As the value of p is 88% at leaf dose 2 g l^{-1}, this dose was chosed in present study.

At higher leaf concentration, there is a very fast superficial adsorption onto the leaf surface that produces a lower solute concentration in the solution than when leaf dose is lower. Thus with increasing adsorbent dose, the amount of MB adsorbed per unit mass of leaf reduced, thus causing a decrease in q_e value. A similar effect was previously reported [14,15,19].

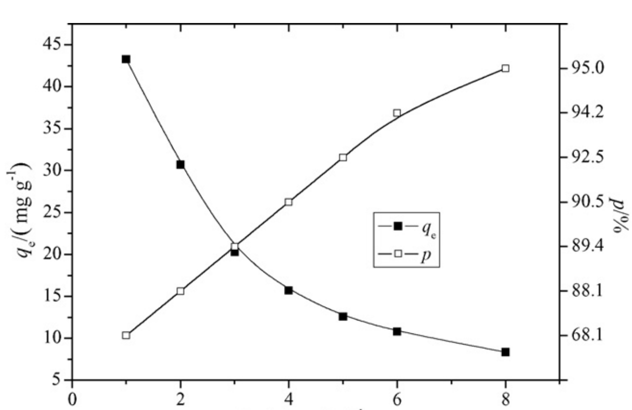


Fig. 2. The effect of leaf dose on biosorption and removal efficiency (c_0 = 70 mg l^{-1}).

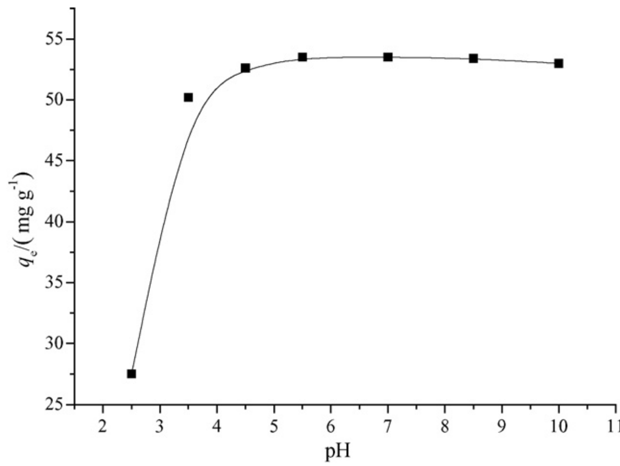


Fig. 3. The effect of solution pH on biosorption (c_0 = 130 mg l^{-1}, leaf dose = 2 g l^{-1}).

3.3. Effect of solution pH on biosorption

Fig. 3 shows the effect of solution pH on values of q_e at the initial concentration of MB 130 mg l^{-1}.

From Fig. 3, it was observed that the solution pH affected the values of q_e. It was observed that the values of q_e were increased with the pH value increasing at the range of 2.5–4.5. While, when the value of pH was from 4.5 to 10, the adsorption quantity was approximately no change. Several reasons may be attributed to MB adsorption behavior of the sorbent relative to solution pH. The surface of leaf 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 leaf 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 [14,16].

3.4. Effect of NaCl and $CaCl_2$ concentration on biosorption

Fig. 4 shows the effect of various concentration of NaCl and $CaCl_2$ solution on the values of q_e and p for an initial MB concentration of 110 mg l^{-1} and leaf dose of 2 g l^{-1}.

The wastewater containing dye has commonly higher salt concentration, and effects of ionic strength are of some importance in the study of dye adsorption onto adsorbents. From Fig. 4, NaCl and $CaCl_2$ existed in solution affected the MB adsorption onto leaf. It was seen that the increase in the salt concentration resulted in a decrease of values of q_e and percent removal efficiency (p). This trend indicated that the adsorbing efficiency decreased when NaCl and $CaCl_2$ concentration 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 from 0 to

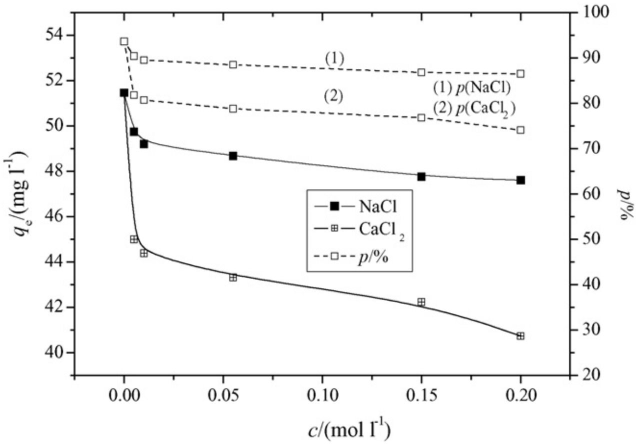


Fig. 4. The effect of NaCl and $CaCl_2$ concentration on biosorption and percent removal efficiency ($c_0 = 110\,mg\,l^{-1}$, leaf dose $= 2\,g\,l^{-1}$).

$0.20\,mol\,l^{-1}$, the values of q_e decreased from 51.5 to 47.5 and $40.7\,mg\,l^{-1}$ for NaCl and $CaCl_2$ while the values of p decreased from 93.5% to 86.5% and 74.0% for NaCl and $CaCl_2$, respectively. Another reason is that ionic strength increase, the activity (effective concentration) of MB and the active sites decrease, so the adsorptive capacity of MB onto adsorbents decreases. As Ca^{2+} has more contribution to ionic strength and more positive charge than Na^+, the effect of Ca^{2+} on adsorption is more serious than Na^+ in the same mole concentration [16]. But even at $0.20\,mol\,l^{-1}$ of salt, the leaf still has bigger percent removal efficiency and the leaf 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 effect of the initial concentration of MB in the solutions on biosorption was shown in Fig. 5.

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 from the concentration gradient. In the same conditions, if the concentration of MB in solution was bigger, the active sites of leaf were surround by much more MB ions, the process of adsorption would carry out more sufficient. So the values of q_e increased with the increasing of initial MB concentrations.

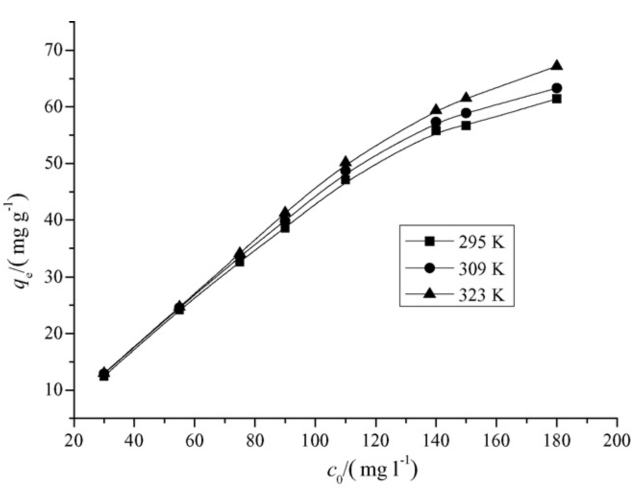


Fig. 5. Equilibrium adsorption quantities of MB at different initial concentrations with different temperature (leaf dose $= 2\,g\,l^{-1}$).

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 increased temperature indicated that the adsorption of MB ions onto leaf is endothermic in nature. So the adsorptive process may be chemical process. Other studies have the same results about the initial MB concentration on adsorption capacity [14–17].

3.6. Determination of isotherm adsorption model constants about MB/leaf system

The analysis of adsorption process requires equilibrium to better understand the adsorption process. Equilibrium isotherm equations are used to describe the experimental sorption data. Adsorption isotherms also provide fundamental physicochemical data for evaluating the applicability of sorption process. Analysis of the equilibrium data is important to develop an equation which accurately represents the results and which could be used for design purposes. An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent and can also be used to find the adsorptive capacity of biomass. Langmuir and Freundlich equilibrium model have been applied in this paper.

The Langmuir adsorption 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 [20]. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \quad (2)$$

where q_m is the q_e for a complete monolayer ($mg\,g^{-1}$), a constant related to adsorption capacity, and K_L is a constant related to the affinity of the binding sites and energy of adsorption ($l\,mg^{-1}$).

Freundlich model is one fairly satisfactory empirical isotherm and can be used for non-ideal sorption [21]. It is expressed by the following equation:

$$q_e = K_F c_e^{1/n} \quad (3)$$

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 also more widely used, but it does not provide information of maximum adsorption capacity.

As different forms of the equation affected more significantly determined coefficient (R^2) during the linear analysis, the non-

Table 1
Langmuir and Freundlich isotherm constants for MB biosorption onto leaf at different temperatures using non-linear regressive method

Model	295 K	309 K	323 K
Langmuir			
K_L ($l\,mg^{-1}$)	0.0676 ± 0.0152	0.0669 ± 0.0150	0.0621 ± 0.0135
q_m ($mg\,g^{-1}$)	80.9 ± 7.3	83.8 ± 7.6	89.7 ± 8.1
R^2	0.945	0.946	0.952
SS[a]	19.1	20.3	20.7
Freundlich			
K_F [$mg\,g^{-1}$ $(l\,mg^{-1})^{1/n}$]	10.1 ± 3.1	12.3 ± 3.2	12.5 ± 3.1
$1/n$	0.427 ± 0.076	0.4287 ± 0.0765	0.445 ± 0.075
R^2	0.862	0.863	0.876
SS[a]	47.9	51.3	52.9

[a] $SS = \sqrt{\sum (q_e - q_c)^2 / N}$, q_e and q_c are the experimental value and calculated value according the model, respectively; N is the number of the experimental point.

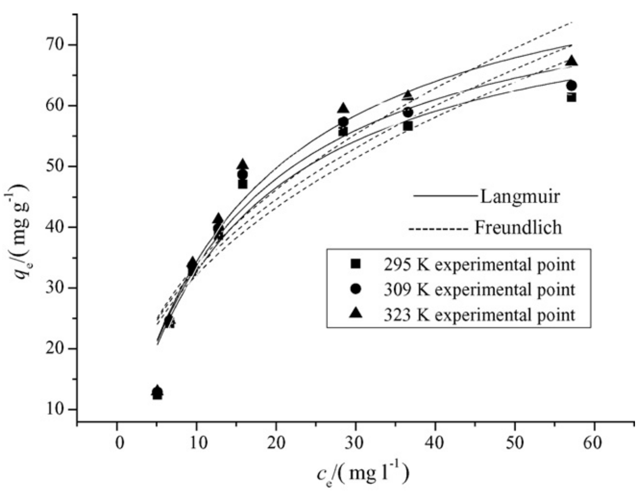


Fig. 6. The experimental points and non-linear fitted curve with Langmuir and Freundlich models.

linear analysis might be a method of avoiding such errors [22]. In this paper, a non-linear χ^2-statistic (SS) of determination test were used. The Langmuir and Freundlich adsorption constants evaluated from the isotherms at different temperatures and the values of R^2 and SS are presented in Table 1 according to Eqs. (2) and (3) using non-linear regressive analysis. The uncertainties of the relative parameters are also listed in Table 1. The non-linear fitted curve with different adsorption models and experimental points were shown in Fig. 6 at 295, 309, 323 K, respectively.

A high K_L value indicates a high affinity. From Table 2, the biosorption capacity of leaf (q_m) increased slightly on increasing the temperature while the values of K_L decreased during temperature rising. The values of q_m obtained at 295, 309, 323 K are 80.9, 83.8, 89.7 $mg\,g^{-1}$, respectively. So an increase in temperature is advantage to adsorb MB onto leaf, but the increment of q_m is about 11% as the temperature form 295 to 323 K.

The q_m values showed that the adsorption capacity of leaf particles was highly comparable to that of some other low-cost adsorbent materials for MB. The values q_m about some biosorbent binding MB from the Langmuir constant were listed in Table 2. Compared to other biosorbents listed in Table 2, the value of q_m about MB adsorption onto leaf is higher. As waste, it is so cheap, so the leaf can be used to remove MB from solution.

As shown in Table 1, all measured values of K_F showed easy adsorption of MB with high adsorptive capacity of leaf and insignificant differences in sorption capacities due to temperature. The obtained values of $1/n$ ($0.1 < 1/n < 1$) indicated favorable adsorption of MB at all temperatures studied [25]. The results also indicated that with the temperature increasing, the ability of biosorption increased.

Based on the values of R^2, SS and Fig. 6, the non-linear forms of the Langmuir isotherm appears to be a better model for adsorption in MB/leaf system, while the non-linear forms of the Langmuir isotherm is a reasonable model for adsorption in MB/leaf systems at three different temperature. The conformity of the adsorption data to the Freundlich isotherm ($R^2 > 0.86$) could be interpreted as indicating a complex adsorption process, leading to multilayer, interactive or multiple site type binding.

Table 2
MB adsorption by biosorbents: q_m of various related substances from the Langmuir constant

q_m ($mg\,g^{-1}$)	Biosorbent	References
80.9	Phoenix tree leaves	This study
20.3	Cereal chaff	[16]
32.3	Modified sawdust	[23]
40.6	Rice husk	[15]
119	Giant duckweed	[14]
185	Water hyacinth root	[24]

3.7. Thermodynamic parameters of MB biosorption onto leaf

To estimate the effect of temperature on the adsorption of MB on leaf, the free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) 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 [25–27]:

$$K'_c = \frac{c_{ad,e}}{c_e} \tag{4}$$

Table 3
Thermodynamic parameters of MB biosorption on leaf

	T (K)		
	295	309	323
K'_c	4.89	6.05	6.45
ΔG° (kJ mol^{-1})	−3.89	−4.62	−5.01
ΔH° (kJ mol^{-1})		7.77	
ΔS° (kJ mol^{-1} K^{-1})		−0.040	

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 MB concentration can be obtained [26]. The K'_c value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG°)

$$\Delta G^\circ = -RT \ln K'_c \tag{5}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{6}$$

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

Values of the standard Gibbs free energy change for the biosorption process obtained from Eq. (5) are listed in Table 3.

The negative ΔG° values of MB at various temperatures is due to the fact that the adsorption processes are spontaneous with a high preference of MB on leaf and the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of MB are inversely proportional to the temperature [25].

The standard enthalpy and entropy changes of biosorption determined from the Eq. (6) were 7.77 kJ mol^{-1} and −0.040 kJ mol^{-1} K^{-1}, respectively. The positive value of ΔH° confirms the endothermic character of biosorption on MB–leaf system, whereas, the negative ΔS° value confirms the decreased randomness at the solid–solute interface during biosorption. The low value of ΔS° also indicates that no remarkable change on entropy occurs.

4. Conclusion

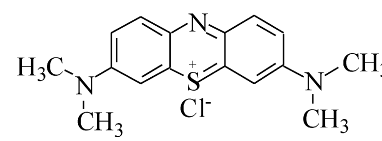
The biosorption of MB from aqueous solution using phoenix tree's leaves as adsorbent has been investigated under different experimental conditions in batch mode. The values of q_e about MB adsorbed onto leaf were dependent on solution pH, leaf dose, contact time, salt concentration and MB initial concentration. The equilibrium data were found to be better represented by the Langmuir isotherm model according to the non-linear regressive analysis. The Langmuir monolayer saturation sorption capacity of MB onto leaf was 80.9 mg g^{-1} at 295 K. 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.

Appendix A

Methylene blue (MB, C.I. no. 52015) has a molecular weight of 373.9 g mol^{-1}, which corresponds to methylene blue hydrochloride with three groups of water. The structure of MB is following:



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