Journal of Water Sciences & Environment Technologies

Cit this: *JOWSET, **2016** (01), N°02, 32-38*

Equilibrium, kinetics and thermodynamics studies of Methylene blue adsorption from aqueous solutions by biosorbent derived from Algerian date stones

Omar KHELIFI*[1,2], Ikram MEHREZ[2,3]

[1] *Laboratoire d'Analyses Industrielles et Génie des Matériaux, Département de génie des procédés, Faculté des sciences et de la technologie, Université 8 Mai 1945 Guelma, Algérie.*

[2] *Département des sciences de la matière, Faculté des sciences et de la technologie, Université Ahmed Draia Adrar, Algérie.*

[3] *Laboratoire Energie, Environnement et Systèmes d'Information, Faculté des sciences et de la technologie, Université Africaine d'Ahmed Draia - Adrar, Algérie.*

**Corresponding Author: Tel.: +213 662 524 309; fax: +213 37 20 72 68; e-mail: khelifi_omar@yahoo.fr*

In this study, Algerian date stones were evaluated for the preparation of a biosorbent, in order to use them for methylene blue (MB) removal from aqueous solutions. To describe the adsorption equilibrium, the experimental data were analyzed by some isotherm models. The Freundlich model showed better representation of data (R2>0.99). Kinetics study shows that pseudo-second order fitted the adsorption kinetics. Thermodynamic parameters showed that the adsorption process was feasible, spontaneous and exothermic. According to the results, the biosorbent derived from date stones is expected to be an economical product and beneficially low-cost biosorbent for MB removal from aqueous solutions.

Received: 12 November 2016
Accepted: 08 December 2016
Available online: 11 December 2016

Keywords:
Adsorption
Methylene blue
Biosorbent
Date stones

Introduction

Water pollution from industrial waste is a serious problem in many countries. This pollution may cause adverse effects on the environment and on human health [1]. Industrial wastewaters loaded with dyes have been extensively studied in order to deal with prior to discharge into the natural environment. To reduce the harmful effects of these pollutants, many wastewater treatment processes, including physicochemical, are implemented, in particular, the technique of adsorption on different solid materials has been the subject of many works [2]. The adsorption of organic molecules such as dyes on activated carbon has proven to be a very effective processing technology, however in the case of some recalcitrant's dyes; carbon overdoses are required for better efficiency, making the cost of excessive operation [3]. Moreover, the regeneration of activated carbon is also a delicate operation and does not unanimity about its usefulness [4]. Methylene blue (MB) is a cationic dye commonly used for dyeing paper, cotton, wool and silk [5]. The harmful effects of BM include: difficulty breathing, nausea, vomiting, tissue necrosis, profuse sweating, mental confusion, cyanosis and methemoglobinemia [6]. During the last two decades, many researchers have focused on the preparation of some biosorbents from natural waste of fruit trees [7], orange peel [8], coconut coir [9], eggshells [10], wheat shells [11], coir pith [12], neem leaf powder [13], fly ash [14], tamarind fruit shell [15] and cocoa waste [16]. These biosorbents that are available, with a very low returns cost, have proved effective towards organic molecules in laboratory scale. In this context, we proposed to test a biosorbent based on southern Algerian date stones.

In this study, we investigated the using of Algerian date stones powder as low-cost biosorbent for methylene blue (MB)

adsorption from aqueous solutions. As far as we know, there is no report on preparation of biosorbent from Algerian date stones for adsorption of methylene blue (MB) from aqueous solutions. The effect of operating parameters such as initial concentration of methylene blue, contact time and temperature were studied. Thereafter, the adsorption isotherms, kinetic and thermodynamic aspects of the retention process were explored.

Materials and methods

Biosorbent preparation

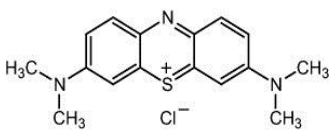
To prepare the biosorbent, we used the date stones of Adrar city (south west of Algeria) as a precursor. Date stones were collected and were scraped with a knife to remove all residual fibers at the surface. Then they were washed with tap water several times and then with distilled water. After washing, they were dried in an oven at 105 °C for 24 h. Then, they are ground and sieved so as to retain a fraction of less than 0.5 mm uniform. The retaining powder was stored in a desiccator. Some physicochemical properties of the prepared biosorbent are presented in Tab. 1.

Tab 1: Physicochemical Properties of the prepared biosorbent.

Physicochemical properties	Value
pH	6.945
Conductivity (µS cm^{-1})	380.4
Apparent density (g cm^{-1})	0.064
Absolute density	1.367
Humidity (%)	3.661
Ash content (%)	9.946
Particle size (mm)	0.02-0.5

In this study, Methylene blue (MB) was used as adsorbate to determine the effectiveness of prepared biosorbent. The main properties of MB are shown in Tab. 2. A stock solution of MB (500 mg L^{-1}) was prepared by dissolving an appropriate amount of dehydrated MB (analytical grade, Sigma-Aldrich®). Test solutions of desired initial concentrations were obtained by diluting the MB stock solution with distilled water.

Tab 2: Main properties of methylene blue (MB).

Common nomenclature	Methylene blue
Generic nomenclature	Basic Blue 9
Color index	52015
Chemical formula	$C_{16}H_{18}N_3SCl$
Molecular weight	319.85 g/mol
Wavelength (λ_{max})	665 nm
Chemical structure	

Batch mode adsorption studies

In order to determine the adsorption capacity of prepared biosorbent for methylene blue, as well as the effect of initial MB concentration (10-100 mg L^{-1}), contact time (10-120 min) and temperature (25-55 °C) on MB adsorption experiments were carried out in batch mode by mixing 50 ml of MB solution of known concentration with a mass of 1 g of dry biosorbent. The content was agitated with a constant stirring rate at 200 rpm. After shaking, the biosorbent was separated by centrifugation. The solutions were centrifuged at 3000 rpm for 15 min using a centrifuge (SIGMA 2-16P, Germany). The supernatant portion was analyzed using a UV-Vis spectrophotometer (Cary 60, Malaysia) at a wavelength of 665.0 nm. The removal rate R (%) and the equilibrium amount of MB adsorbed per unit mass of biosorbent qe (mg g^{-1}) were, respectively, calculated from the following equations:

$$R = \frac{C_i - C_e}{C_i} \times 100$$

$$q_e = \frac{C_i - C_e}{m} \times V$$

Where C_i (mg L^{-1}) is the initial MB concentration; C_e (mg L^{-1}) is the equilibrium MB concentration; V (L) is the volume of the solution; and m (g) is the mass of biosorbent.

For kinetic studies, 50 ml of 100 mg L^{-1} of MB concentration was mixed with 1 g of prepared biosorbent under a mechanical agitation at room temperature. The samples were collected at different time intervals, and the MB concentration was determined. To investigate the controlling mechanism of adsorption processes, the pseudo-first order and pseudo-second order models were applied to model the kinetics studies of MB adsorption. The amount of MB adsorbed at time t, q_t (mg g^{-1}), was calculated by following equation:

$$q_t = \frac{C_i - C_t}{m} \times V$$

Where C_t (mg L^{-1}) is the concentration of MB solution at time t.

Desorption and biosorbent reuse

To investigate the feasibility of MB desorption and the possibility of biosorbent reuse, desorption and regeneration experiment were also conducted. The used biosorbent was treated with 50 mL of heated water at 60 °C and stirring at 200 rpm. The sample was stirred for 1h. After centrifugation, the concentration of desorbed methylene blue was determined.

Results and discussion

Effect of initial MB concentration

Fig. 1 shows the effect of the initial methylene blue concentration (10-100 mg L^{-1}) on the adsorption capacity of

prepared biosorbent. We note that the adsorption capacity increases with increasing the initial MB concentration. The increasing of adsorption capacity from 0.475 to 4.42 mg g^{-1} could be attributed to the ratio between the active sites available for adsorption and the initial number of MB molecules.

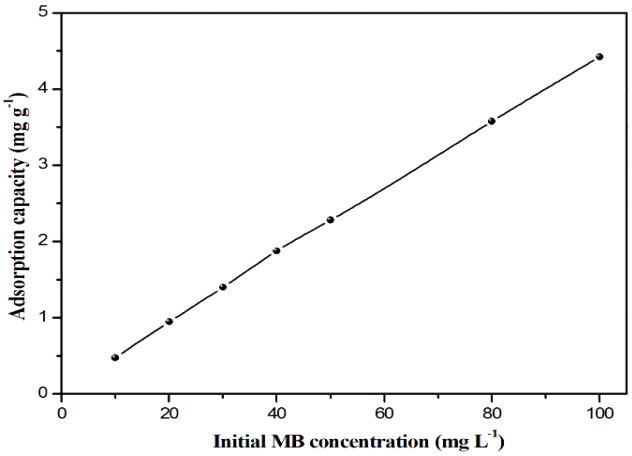


Fig. 1: Effect of initial MB concentration on the adsorption capacity of prepared biosorbent.

Effect of contact time

The effect of contact time on the MB removal was studied on a range of 10 to 120 min, and the adsorption capacity variation is shown in Fig. 2. The obtained results show that the removal rate increases rapidly during the first 40 minutes and then slowly increased to 60 minutes and then remains almost constant. Fig. 2 shows that the MB removal rate was reached 98.8 % at 60 min, equivalent to 4.9 mg g^{-1} of adsorption capacity. The increased removal rate in the first part could be due to external mass transfer is fast. Then, the slow increase of methylene blue removal rate until equilibrium time is 60 min. This means that there is a transfer of internal mass of the biosorbent, this generally corresponds to a diffusion phenomenon in the internal porosity of the adsorbent.

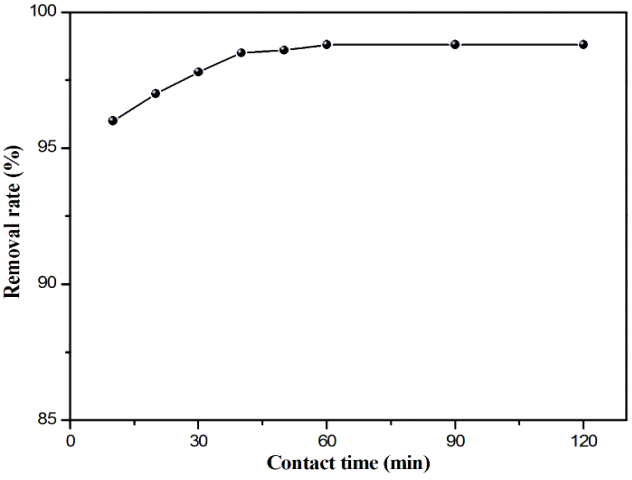


Fig. 2: Effect of contact time on the removal rate of MB.

Effect of temperature

The effect of temperature was investigated in the interval 25-55 °C and the results are shown in Fig. 3. The experiments were performed by mixing 1 g of the prepared biosorbent with MB solution (50 ml, 100 mg L^{-1} and initial pH). Fig. 3 illustrates a decrease in MB adsorption capacity depending on the increase of temperature; it decreases from 4.4 to 4.29 mg g^{-1} at the studied temperature range. The temperature elevation disadvantages the course of the adsorption phenomenon [17]. Therefore the best results are obtained in the area of the room temperature. The effect of temperature on the MB adsorption capacity is in agreement with the results found by the use of a biomaterial based on Cactus [1].

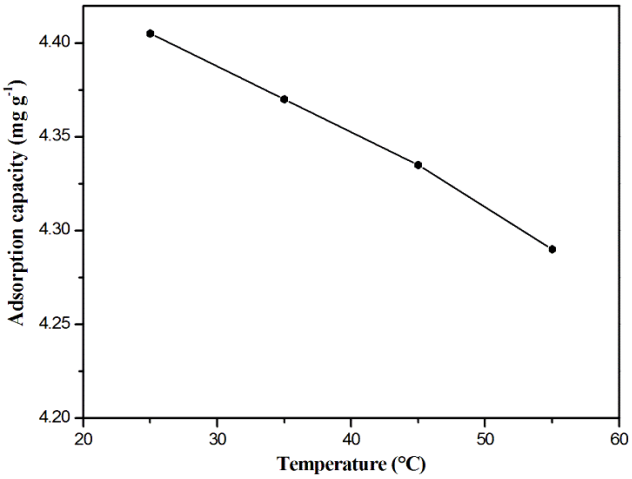


Fig. 3: Effect of temperature on the adsorption capacity of MB by prepared biosorbent.

Adsorption Equilibrium Study

For adsorption equilibrium study: Langmuir, Freundlich and Temkin adsorption isotherms have been tested and were applied to describe the adsorption process of our experimental results. Linear form of the Langmuir isotherm equation can be expressed as follows [18]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}}$$

Where K_L (L mg^{-1}) is the Langmuir constant, Q_{max} (mg g^{-1}) represents the maximum adsorption capacity under the experimental conditions. Q_{max} and K_L are determined from the slope and intercept of plotting C_e/q_e versus C_e, respectively.

The linearized Freundlich isotherm equation is represented by the following equation [19]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where K_F (mg g^{-1}) (L g^{-1})$^{1/n}$ is the Freundlich constant related to the bonding energy and n is the heterogeneity factor. K_F and n

are, respectively, determined from the intercept and slope of plotting ln qe versus ln Ce.

The Temkin isotherm equation assumes that the fall in the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy [20]. The Temkin isotherm has been applied in the following form:

$$q_e = \left(\frac{RT}{B}\right) \ln A + \left(\frac{RT}{B}\right) \ln C_e$$

Where A (L g^{-1}) and B (J mol^{-1}) are the Temkin constants. T is the absolute temperature and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A and B are determined from the intercept and slope of plotting qe versus ln Ce, respectively.

Tab. 3: Isotherms parameters for MB adsorption by prepared biosorbent.

Langmuir Model	Q_{MAX} (mg g^{-1})	K_L (L mg^{-1})	R^2
	6.7010	0.1417	0.9624
Freundlich Model	K_F (mg g^{-1}) (L $g^{-1})^{1/N}$	1/n	R^2
	0.8816	0.6556	0.9999
Temkin Model	A (L g^{-1})	B (kJ mol^{-1})	R^2
	2.3368	2.1546	0.9489

The values of isotherm constants are presented in Tab. 3. The results indicate that the MB adsorption onto prepared biosorbent by date stones was well correlated with the Freundlich isotherm. It could be seen from the results, that the linear correlation coefficients (R^2) for the Freundlich isotherm model has highest value of regression coefficient compared to the Langmuir and Temkin isotherm, which indicate that this model describe very well the adsorption process and suggests that the adsorption on the surface of prepared biosorbent was a multilayer adsorption. The maximum adsorption capacity (Q_{max}) of MB founds in the present study was compared with that of other biosorbent reported in the literature and are presented in Tab. 4.

Tab 4: Maximum adsorption capacities for MB removal by various biosorbents.

Biosorbents	**Qmax (mg g^{-1})**	**References**
Orange peel	18.60	[8]
Coconut coir	15.59	[9]
Wheat shells	16.56	[11]
Coir pith	5.87	[12]
Neem leaf powder	3.67	[13]
Fly ash	1.91	[14]
Tamarind fruit shell	1.72	[15]
Cocoa waste	1.21	[16]
Date stones	6.70	Present study

The maximum adsorption capacity of prepared biosorbent was compared with other biosorbents. From Table 4, the value of adsorption capacity of prepared biosorbent is lower than that of orange peel [8], coconut coir [9] and wheat shell [11]. On the other hand, this value is higher or considerably greater than other reported biosorbents [12-16]. The different performances of MB adsorption could be explained in term of the following factors: (i) the heterogeneous nature and composition of biosorbent; (ii) the textural and surface properties of each biosorbent such as structure, functional groups and their surface area.

Adsorption Kinetics Studies

According to literature, several models can be used to express the kinetics and to explain the mechanism of the adsorption processes, e.g. pseudo-first order, pseudo-second order models.

A pseudo-first-order reaction model was applied to our experimental data. The linear form of the pseudo-first order of Lagergren is given by the following equation [21]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first order. k_1 and q_e were calculated from the slope and intercept of the plot of $\ln(q_e - q_t)$ versus t, respectively.

On the other hand, the pseudo-second order equation based on equilibrium adsorption is expressed as follows [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order. The following expression denotes the initial adsorption rate h (mg g^{-1} min^{-1}):

$$h = k_2 q_e^2$$

The plot of (t/q_t) against t represents a linear relationship from which qe and k_2 were determined from the slope and intercept of the plot, respectively.

The experimental results relating to the adsorption kinetics were compared to kinetic models, which allow the determination of these models parameters (Tab. 5). The analysis of correlation coefficients shows that the pseudo-second order kinetic model gives the best adjustments compared to the pseudo-first order model and fits best since its highest value ($R^2 > 0.99$). Indeed, the value of the calculated adsorption capacity by the pseudo-second order is close to that determined by the experimental data. Pseudo-second order kinetic model implies that the predominant process here is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the biosorbent [23].

These results are in agreement with the majority of published research work.

Tab 5: Kinetics parameters of both models MB adsorbed by prepared biosorbent.

Kinetic model	Parameters	Values
Pseudo-first order	q_e (exp.) (mg g^{-1})	4.9755
	q_e (cal.) (mg g^{-1})	0.0357
	k_1 (min^{-1})	0.0805
	R^2	0.9683
Pseudo-second order	q_e (exp.) (mg g^{-1})	4.9755
	q_e (cal.) (mg g^{-1})	4.9800
	k_2 (g mg^{-1} min^{-1})	2.1405
	h (mg g^{-1} min^{-1})	53.085
	R^2	0.9999
Intra-particle diffusion model	k_{id1} (mg g^{-1} $min^{-1/2}$)	0.0395
	C_1 (mg g^{-1})	4.6744
	R_1^2	0.9998
	k_{id2} (mg g^{-1} $min^{-1/2}$)	0.0019
	C_2 (mg g^{-1})	4.9208
	R_2^2	0.6632

Adsorption mechanism

It is always important to predict the rate-limiting step in an adsorption process to understand the mechanism associated with the phenomena [24]. For a solid liquid adsorption process, to analyze the rate controlling steps such as mass transport and chemical reaction processes is very beneficial for elaborating the adsorption mechanism. The adsorption reaction is usually divided into the following steps [25, 26]:

- Metal ion from the bulk liquid to the liquid film or boundary layer surrounding the adsorbent.
- Transport of solute ions from the boundary film to the external surface of the adsorbent (film diffusion).
- Transfer of ions from the surface to the intra-particular active sites (particle diffusion).
- Adsorption of ions by the active sites of adsorbent.

Because the first step is not involved with biosorbent and the fourth step is a very rapid process, they do not belong to the rate controlling steps. Therefore, the rate controlling steps mainly depend on either film diffusion or particle diffusion [27]. The intra-particle diffusion model proposed by Weber and Morris [28] is described by the following:

$$q_t = k_{id} t^{0.5} + C_i$$

Where q_t is the amount of adsorbate on the surface of the biosorbent at time t (mg g^{-1}), K_{id} is the intra-particle rate constant (mg $g^{-1}min^{-0.5}$), t is the time (min) and C_i is the intercept at stage i. The value of C_i is related to the thickness of the boundary layer. The plots of q_t vs. $t^{0.5}$ show multi-linearity characterizations (Fig. 8), indicating the existed of two different steps occurred in the adsorption process.

The first sharp section is the external surface adsorption is attributed to the instantaneous utilization of the most readily available adsorption sites on the biosorbent surface. The second portion describes the gradual layer adsorption stage, where intra-particle diffusion is rate-controlled. Tab 5 lists the corresponding model parameters based on the equation above. The larger slopes of the first sharp sections indicate that the rate of methylene blue removal is higher in the beginning stage due to the instantaneous availability of large surface area and active adsorption sites. The lower slopes of the second subdued portion are due to that the decreased concentration gradients make MB diffusion in the micropores of biosorbent take long time, thus leading to a low removal rate. After the adsorbed material formed a thick layer (caused by the inter-ionic attraction and molecular association), the capacity of adsorbent got exhausted and the uptake rate was controlled by the rate at which the adsorbate was transported from the exterior to the interior sites of the biosorbent particles. We can seen that none of the plots passed through the origin (Fig. 4), which revealed that the intra-particle diffusion was part of the adsorption but was not the only rate-controlling step. Some other mechanisms such as complexes or ion-exchange may also control the rate of adsorption [30].

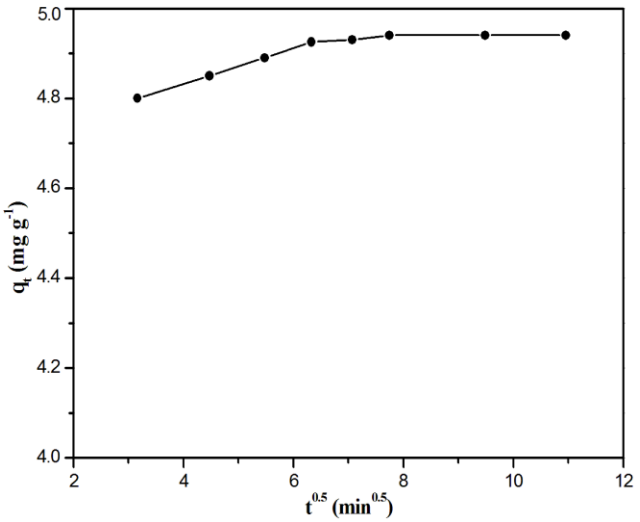


Fig. 4: Intra-particle diffusion model for the adsorption of methylene blue onto prepared biosorbent.

Adsorption thermodynamic Studies

Thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) for the MB adsorption on the prepared biosorbent was determined to evaluate the feasibility and nature of the adsorption process. The standard Gibbs free energy change ΔG^0 (kJ mol^{-1}) of the adsorption reaction can be determined from the following equation:

$$\Delta G^0 = - R T \ln K_c$$

Where K_c is the thermodynamic equilibrium constant. The K_c value was calculated using the following equation:

$$K_c = \frac{C_a}{C_e}$$

Where C_a (mg L^{-1}) and C_e (mg L^{-1}) are the equilibrium concentrations of MB on the biosorbent and in the solution, respectively. Relation between ΔG^0, ΔH^0 and ΔS^0 can be expressed by the following equations:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\ln K_c = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

Where ΔH^0 is the standard change in enthalpy (kJ mol^{-1}), ΔS^0 is the standard change in entropy (kJ mol^{-1} K^{-1}). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot of ln K_c versus 1/T, respectively (Fig. 5).

The values of calculated thermodynamic adsorption parameters are given in Tab 6. The negative value of ΔG^0 indicates that the adsorption process of MB on prepared biosorbent is feasible and spontaneous. The negative value of ΔH^0 showed that the sorption process was exothermic in nature and positive value of ΔS^0 shows the increasing randomness at solid/liquid interface during the adsorption process.

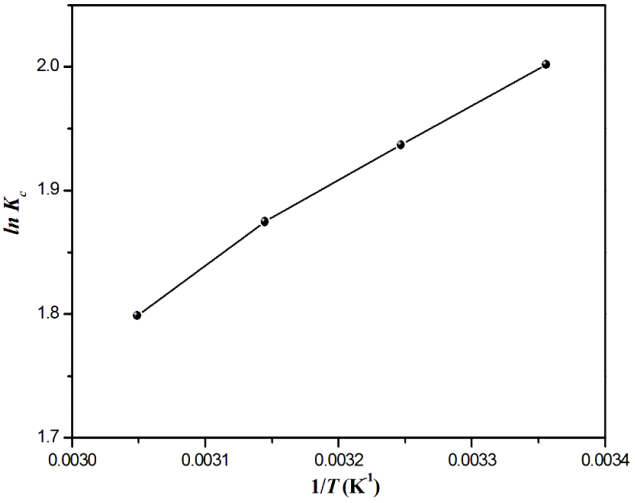


Fig. 5: Thermodynamic plot for MB adsorption on prepared biosorbent.

Generally, the ΔG^0 for physi-sorption is between - 20 and 0 kJ mol^{-1} while chemi-sorption has a range between - 80 and - 400 kJ mol^{-1} [30]. Our results were between -5.9284 kJ mol^{-1} and -5.9766 kJ mol^{-1} (Tab 6). These results indicated that the adsorption of methylene blue onto prepared biosorbent was physi-sorption and thermodynamically spontaneous.

Tab 6: Thermodynamic parameters of MB adsorption on prepared biosorbent.

Thermodynamic parameters	Temperature (K)			
	298	308	318	328
ΔG^0 (kJ mol^{-1})	-5.9284	-5.9444	-5.9605	-5.9766
ΔH^0 (kJ mol^{-1})	-5.4487			
ΔS^0 (J mol^{-1} K^{-1})	1.6079			

Desorption and regeneration

Desorption study help to regenerate the used biosorbent, as to well as recover MB from the spent biosorbent apart from protecting the environment from solid waste disposal problems [31]. Regeneration of biosorbent saturated with MB was performed with heated water and the regeneration efficiency was almost 87 %. The fact that the regeneration efficiency reaches this value indicates that that physic-sorption and ion-exchange mechanisms are operative in the adsorption process.

Conclusions

The biosorption of MB from aqueous solution using date stones as low-cost biosorbent has been investigated under different experimental conditions in batch mode. Equilibrium isotherm data were in good agreement with Freundlich than Langmuir and Temkin isotherms models. The maximum monolayer adsorption capacity, Q_{max}, of MB was found to be 6.7 mg g^{-1} at 25 °C. It was shown that the pseudo-second order kinetic model better described the biosorption data; this suggests that the rate-limiting step may be chemical adsorption rather than diffusion. The thermodynamics parameters indicate spontaneous and exothermic process. Desorption study indicates that physic-sorption and ion-exchange mechanisms are operative in the adsorption process. Based on the obtained results, it can be concluded that the date stones is an easily, locally available and low-cost biosorbent; it may be treated as a cost effective biosorbent for the removal of MB from aqueous solutions.

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