Equilibrium, Kinetic and Thermodynamic Studies of the Biosorption of Textile Dye (Yellow Bemacid) onto *Brahea edulis*

G. Henini, Y. Laidani, F. Souahi, A. Labbaci, S. Hanini

Abstract—Environmental contamination is a major problem being faced by the society today. Industrial, agricultural, and domestic wastes, due to the rapid development in the technology, are discharged in the several receivers. Generally, this discharge is directed to the nearest water sources such as rivers, lakes, and seas. While the rates of development and waste production are not likely to diminish, efforts to control and dispose of wastes are appropriately rising. Wastewaters from textile industries represent a serious problem all over the world. They contain different types of synthetic dyes which are known to be a major source of environmental pollution in terms of both the volume of dye discharged and the effluent composition. From an environmental point of view, the removal of synthetic dyes is of great concern. Among several chemical and physical methods, adsorption is a promising technique due to the ease of use and low cost compared to other applications in the process of discoloration, especially if the adsorbent is inexpensive and readily available. The focus of the present study was to assess the potentiality of *Brahea edulis* (BE) for the removal of synthetic dye Yellow bemacid (YB) from aqueous solutions. The results obtained here may transfer to other dyes with a similar chemical structure. Biosorption studies were carried out under various parameters such as mass adsorbent particle, pH, contact time, initial dye concentration, and temperature. The biosorption kinetic data of the material (BE) was tested by the pseudo first-order and the pseudo-second-order kinetic models. Thermodynamic parameters including the Gibbs free energy ΔG, enthalpy ΔH, and entropy ΔS have revealed that the adsorption of YB on the BE is feasible, spontaneous, and endothermic. The equilibrium data were analyzed by using Langmuir, Freundlich, Elovich, and Temkin isotherm models. The experimental results show that the percentage of biosorption increases with an increase in the biosorbent mass (0.25 g: 12 mg/g; 1.5 g: 47.44 mg/g). The maximum biosorption occurred at around pH value of 2 for the YB. The equilibrium uptake was increased with an increase in the initial dye concentration in solution (C_o = 120 mg/l; q = 35.97 mg/g). Biosorption kinetic data were properly fitted with the pseudo-second-order kinetic model. The best fit was obtained by the Langmuir model with high correlation coefficient ($R^2 > 0.998$) and a maximum monolayer adsorption capacity of 35.97 mg/g for YB.

Keywords—Adsorption, *Brahea edulis*, isotherm, yellow bemacid.

G. Henini and A. Labbaci are with the Process Engineering Department and Laboratory Environment-Water, University of Chlef, Algeria (phone: +213 774970103; e-mail: g.henini@gmail.com, ablabbaci@yahoo.fr).

Y. Laidani is with the Chemistry Department and Laboratory Chemical Plant-Water–Energy, University of Chlef, Algeria (e-mail: laidaniykh@yahool.fr).

F. Souahi is with the Chemical Engineering Department, National Polytechnic School, Algeria (e-mail: fsouahi@yahoo.fr).

S. Hanini is with the Process Engineering Department, University of Medea, Algeria (e-mail: s_hanini2002@yahoo.fr).

I. INTRODUCTION

MANY industries give rise to dye-bearing effluents in their production processes. Textile industries, particularly, are major consumers of water and release a fair amount of color in their effluents [1]. Over 100,000 commercially available dyes exist, and more than 7×10^5 tons are produced annually, with a considerable fraction being discharged directly in aqueous effluent [2]. Dyes are a kind of organic compound with a complex aromatic molecular structure that can bring bright and firm color to other materials. However, the complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade [3]. The most efficient method for the removal of synthetic dyes from aqueous effluents is the adsorption procedure [4]–[7]. This process transfers the dye species from the water effluent to a solid phase thereby keeping the effluent volume to a minimum [7], [8]. Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment [7], [8].

Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. Activated carbon is regarded as an effective but expensive adsorbent due to its high costs of manufacturing and regeneration. In addition to activated carbon, some adsorbents including peat [9], chitin [10], chitosan [11], silica [12], perlite [13], natural phosphate [14], hydroxyapatite [15], Titania [16], and some agricultural wastes [17]-[20] have also been reported. However, the adsorption capacities of the above-mentioned adsorbents are not very high. In order to improve the efficiency of the adsorption processes, it is necessary to develop cheaper and easily available adsorbents with high adsorption capacities. The use of natural biomaterials is a promising alternative due to their relative abundance and their low commercial value. BE is a very ornamental palm, a cheap, plentiful, and easily available plant in the Mediterranean countries. There is currently no research regarding the biosorption potential of this biomaterial.

This paper reports on the ability of BE to remove YB from aqueous solution. BE has already been shown to have a high adsorption capacity. YB has been used as a model compound because of its strong adsorption study on solids and its use in characterizing adsorptive materials. This dye has been identified as the most problematic dye in the effluents because it is resistant to fading from exposure to light, water, and chemicals due to their complex chemical structure.

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For the present study, a batch-contact-time method was used, and the equilibrium of YB adsorption on to BE was investigated with attempts to fit the data to Langmuir, Freundlich, Elovich, and Temkin equations. The uptake of YB on BE was examined as a function of temperature, initial dye concentration, mass adsorbent particle, pH, and contact time. Kinetic and thermodynamic studies were conducted to evaluate the adsorption capacity of BE.

II. MATERIALS AND METHODS

A. Preparation of the Biosorbent

The BE was obtained in Chlef - Algeria. The cords of BE were repeatedly washed with distilled water to remove dirt particles and was then boil in the water for 30 min. The crude material was dried in the open air before being washed with bleach (12%) for 3 hours and then dried in a stove at 105 °C for 24 h, before being ground and sieved to remove the fraction of particles of diameter between 80 and 630 μm.

B. Dye Solution Preparation

YB (ET-IL) (λmax = 390 nm) is an industrial synthetic dye for dyeing polyamide textile chemical nature that was provided by the Soitex Tlemcen-Algeria. The dye used in this research belongs to the group E which is distinguished by a high level of light fastness, good migration power, good coverage streaking kinetic origin, good combinability, quick exhaustion even low temperature and rapid fixation with the saturated steam. Dye solutions (1000 mg/l) were prepared by dissolving 1 g of dye in 1 L of double distilled water. Experimental solutions of the desired concentration were obtained by further dilution.

C. Adsorption Studies

Adsorption studies for the evaluation of the BE adsorbent for the removal of YB dye from aqueous solutions were carried out by using the batch contact adsorption. For these experiments, fixed amount of adsorbent 1 g were placed in a 500 ml glass Erlenmeyer flasks containing 300 ml of dye solutions 50, 100, and 120 ml, which were agitated for a suitable time 160 min from 293 to 313 K at pH 6.2. Subsequently, in order to separate the adsorbent from the aqueous solutions, the flasks were centrifuged at 350 rpm for 10 min, and aliquots of 2 ml of the supernatant were properly diluted with water. The final concentrations of the dye remaining in the solutions were determined by UV / visible (S6) to the spectrophotometry.

Absorbance measurements were made at the maximum wavelength of YB which was 390 nm. The amount of the dye uptake of the removal of dye by the adsorbents was calculated by applying (1):

$$q_t = \frac{C_0 - C_t}{m} V \qquad (1)$$

where q_t is the amount of dye taken up by the adsorbent (mg/g); C_0 is the initial YB concentration put in contact with the adsorbent (mg/dm^3), C_t is the dye concentration (mg/dm^3)

after the batch adsorption procedure, V is the volume of dye solution (dm^3) put in contact with the adsorbent, and m is the mass (g) of the adsorbent.

III. RESULTS AND DISCUSSION

A. Effect of the Mass of the Adsorbent

The influence of the mass of adsorbent was studied in the range 0. 25 to 1.5 g. The curve of Fig. 1 shows an increase in adsorption of YB as function the mass of BE. The increase of the dye reduction rate with increasing the adsorbent mass is due to the availability of a large active surface site. This deduction is reported by different authors.
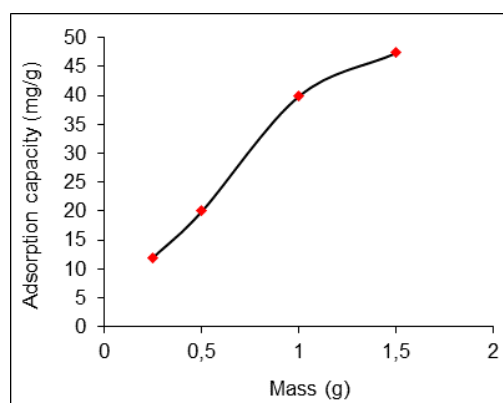

Fig. 1 Effect of the mass of the adsorbent on the adsorption of dye YB: particle size 80 μm <dp <0.630 mm, T = 313 K, C_0 = 120 mg/L, m = 1 g/L, pH = 6.20, and V = 300 ml

B. Effect of pH on the Removal of Dye

Many studies suggest that pH is an important factor in the adsorption process [21]. Some experiments were therefore performed at 313 K with 120 mg/L solutions to study the YB adsorption on BE as a function of solution pH. The results for the study of the effect of pH on dye adsorption are shown in Fig. 2, actually shows that acid pH but less than 2, the adsorption of YB on the material (BE) is adsorbed to the pH decrease greater than 3 up to the limit of the study pH = 12. This dye adsorption behavior can be explained by the fact that during the pH adjustment (concentrated acid or base) of the solution containing the dye; the BE ((pH) between 5 and 7) undergo accordingly possible alteration of the ionic character of their surfaces and the aggregation state of the dye. For the dye YB (pH = 6.20), it is noticed that at pH lower than 2, the solution changes from dark yellow; as well as pH greater than 10, the original YB, changes color. That is why the pH study with the dye was carried out at pH between 2 and 10. The maximum absorption is obtained at pH around 2 because of the very low solubility at pH < 2. It is obvious that the maximum absorption is YB to pH=2 and below. At pH=2, a considerable high electrostatic attraction exists between the positively charged surface of the adsorbent and dye anions, due to the ionization of functional groups of adsorbent and negatively charged anionic dye molecules. As the pH of the system increases, the number of negatively charged sites increases. A negatively charged site on the adsorbent does not

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favor the adsorption of anionic dyes due to the electrostatic repulsion.
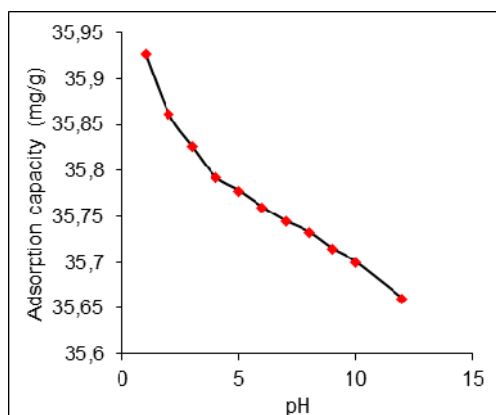
Fig. 2 Effect of pH on the adsorption of the dye YB: T = 313 K,
C_0 = 120 mg/L, m = 1 g/L, pH = 6.20, and V = 300 ml

C. Effect of Contact Time

The contact time necessary to reach the equilibrium depends on the initial dye concentration. It has been shown that the adsorption capacity increases with this concentration by other authors [22]. The effect of contact time on the adsorption of YB onto BE is illustrated in Fig. 3. Hence, it appears that a rapid initial uptake occurs, with equilibrium reached than 150 min for an adsorption capacity value of 35.97 mg/g. The fast uptake of the dye molecules is due to solute transfer, as there are only sorbate and sorbent interactions with negligible interference from solute–solute interactions. The initial rate of adsorption was therefore greater for the high initial YB concentrations, the resistance to the dye uptake diminishing as the mass transfer driving force increased.
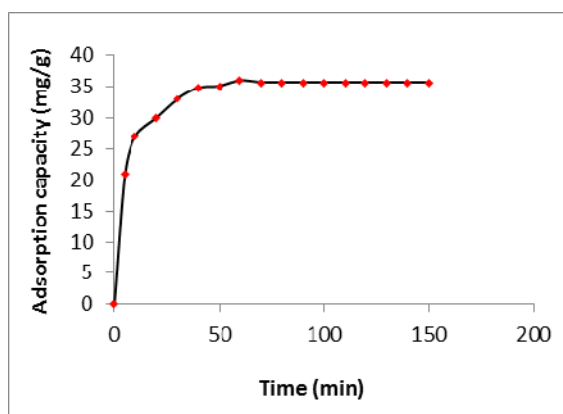

Fig. 3 Effect of contact time on the adsorption of YB into BE,
C_0 = 120 mg/L, T =313 K, m = 1g/L, pH= 6.20, and V = 300 ml

D. Effect of Initial Concentration

The effect of initial dye concentration on dye removal was studied. Experiments were done at different dye concentrations (50, 100, and 120 g/L) (BE: 1 g/L, pH 6.20, and 300 mL dye solution). The dye removal decreases by increasing the initial dye concentration as shown in Fig. 4.

These curves show that the adsorption rate is fast at the beginning of the process and becomes slower during the stirring time to reach equilibrium. The adsorption equilibrium time of these three concentrations is 60 min. The adsorption capacity of the adsorbent for YB increased with increasing initial dye concentration. The results may be ascribed to the following facts. The momentum of the mass transfer would increase with increasing initial concentration, thus bringing on a greater uptake of YB. The higher the initial concentration is, the greater the driving force to overcome mass transfer resistance at the solid-liquid surface is.
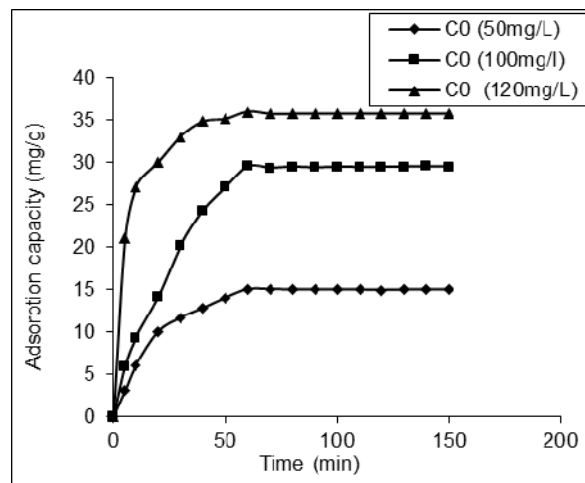

Fig. 4 Effect of initial dye concentration on the adsorption into BE, T = 313 K, m = 1g/L, pH= 6.20, and V=300 ml

E. Effect of Temperature

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution. In addition, changing the temperature alters the equilibrium capacity of the adsorbent for a particular adsorbate. A study of the temperature dependence of the adsorption processes therefore gives valuable information about the enthalpy and entropy changes accompanying adsorption

The adsorption studies were carried out at different temperatures 293, 303, and 313 K (Fig. 5). The adsorption capacity increases with the increasing temperature, indicating that the adsorption is an endothermic process. This may be a result of increase in the mobility of the dye with the increasing temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the BE large dye molecule to penetrate further.
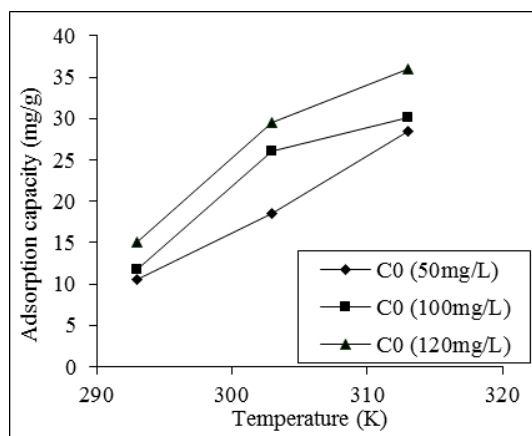
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Fig. 5 Effect of temperature on the adsorption of YB by BE, m = 1g/L, pH = 6.20, and V=300 ml

F. Kinetics Studies

The adsorption kinetics of YB on BE are already apparent in Fig. 3 at the initial concentrations of 120 mg/L (at 313 K). The data were analyzed by applying pseudo first- order (2) [23], pseudo-second-order (3) [24] models in order to gain a better understanding of the adsorption process.

$$Log(q_e - q_t) = Log q_e - \frac{k_1}{2.303}t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (3)$$

q_e (mg/L) and q_t (mg/L) are the amounts of *YB* adsorbed at equilibrium and at any contact time of adsorption *t* (h), respectively; k_1 (1/h), k_2 (g/mg. h), are the pseudo-first-order, pseudo-second-order, respectively.

According to (2), The slope of the linear fit of $ln(q_e - q_t)$ versus *t*, allows to determine the value of (- $k_1/2.203$). The intercept of the straight line gives the value of Log q_e.

According to (3), linear plots of t/q_t versus t at different dye concentration values (50, 100 and 120 mg/L) for the adsorption of dye onto *BE* are shown in Fig. 6. The pseudo-second-order rate constant k_2 and the corresponding linear regression correlation coefficient values, *R*, are given in Table I. The applicability of the kinetic model is compared by judging the correlation coefficients R^2 and the agreement between the calculated and the experimental q_e values. In a view of these both considerations, we may conclude that the pseudo second-order mechanism is predominant R^2 (0.995–0999). Similar results have been observed in the adsorption of organic pollutants onto rods of dates [22].
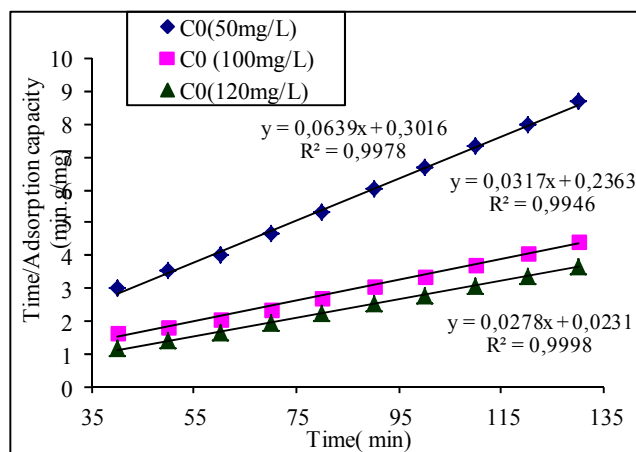

Fig. 6 Pseudo-second-order plots for the adsorption of YB onto BE at various concentrations

TABLE I
RESULTS OF APPLICATION OF ADSORPTION MODELS FOR THE SYSTEM (YB/BE)

		YB system / BE	
	T(K)	313	
	C_0 (mg/L)	50	120
Pseudo first- order	q_e, exp (mg/g)	15	35.97
	q_e, cal (mg/g)	14.53	33.34
	K_1 (1/min)	0.13	0.14
	R^2	0.991	0.995
Pseudo-second-order	q_e, cal (mg/g)	15.06	35.97
	K_2 (g/mg min)	0.041	0.042
	R^2	0.995	0.999

G. Adsorption Isotherms

To optimize the design of an adsorption system for the adsorption of adsorbate, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations such as Langmuir, Freundlich, Elovich, and Temkin adsorption isotherms were studied.

The analysis of the isotherm data by seeing how well they can be accommodated by different models is an important step in establishing a model that can be successfully used for the design purposes [25]. The equilibrium adsorption isotherm is vital to the design of adsorption systems, and its shape provides information about the homogeneity and heterogeneity of the adsorbent surface [26]. Moreover, the correlation of the equilibrium data with either theoretical or empirical equations is essential for practical operation [27]. The Langmuir [28] and Freundlich [29] models are commonly used to describe the adsorption isotherm, and their constants afford significant parameters for predicting adsorption capacities [30]. The Freundlich equation, which is essentially empirical, is the earliest known relationship describing the adsorption process. The isotherm assumes that the adsorbent surface sites have a spectrum of different binding energies. The Langmuir expression and its linearized form are represented by (4) and (5) [27]:

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$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \tag{4}$$

$$\frac{C_e}{q_e} = \frac{1}{K_L \, q_m} + \frac{C_e}{q_m} \tag{5}$$

where C_e, K_L and q_m are the equilibrium concentration of dye solution (mg/L), the Langmuir constant (L/mg) and the maximum adsorption capacity (mg/g), respectively.

The essential characteristic of a Langmuir isotherm, related to the isotherm shape, can be expressed in terms of a dimensionless constant separation factor, also called the equilibrium parameter [31], R_L, defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

The value of R_L indicates the type of the isotherm to be (i) unfavorable ($R_L > 1$), (ii) linear ($R_L = 1$), (iii) favorable ($0 < R_L < 1$), or (iv) irreversible ($R_L = 0$) [32].
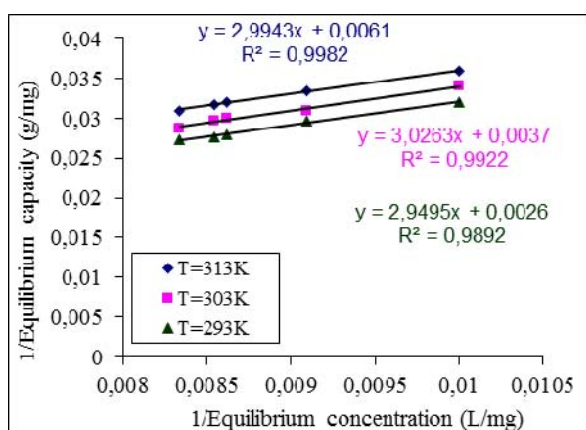

Fig. 7 Linearization of the Langmuir equation for adsorbing YB/BE: pH = 6.2, C_0 = 120 mg/L, V = 300 ml, and m = 1 g

TABLE II
PARAMETERS OF DIFFERENT ADSORPTION MODELS FOR YB/BE

Model parameters	Parameters	YB/BE		
	T (K)	293	303	313
	C_0 (mg/L)		120	
Freundlich [29]	K_F	1.17	3.68	5.27
	$1/n_F$	0.14	0.15	0.12
	R^2	0.98	0.994	0.997
Langmuir [28]	q_m (mg/g)	384.61	270.27	163.93
	K_L (L/mg)	0.0008	0.0012	0.002
	R^2	0.989	0.992	0.998
	R_L	0.912	0.87	0.81
Elovich [34]	α_{El} (mg/g.min)	1.85	4.49	4.05
	β_{El} (g/mg)	0.16	0.143	0.144
	R^2	0.983	0.991	0.995.
Temkin [35]	K_T (L/g)	0.016	0.017	0.0182
	B_T	56.04	52	52.13
	R^2	0.982	0.992	0.993

Fig. 7 shows the Langmuir plot for the adsorption of YB onto BE at 293, 303, and 313 K, as reproduced by the linearized Langmuir (5), and the best straight lines representing the fitted points. Hence, it is evident that the equilibrium data are accommodated well by the Langmuir model, with high correlation coefficients, as shown in Table II. Such coefficients are indicative of monolayer coverage of the YB at the outer surface of the BE particles, and with maximum adsorption capacity (Table II). The results of Table II also show that an increase in temperature from 293 to 313 K promoted an increase in the adsorption capacity. Similar results were found for the adsorption of RC onto Rods Dates [22]. According to the R_L values, all the systems correspond to favorable adsorption processes (Table II). The values tended toward zero, representing the ideal irreversible case, rather than toward unity, representing the completely reversible case [33].

H. Thermodynamic Studies

The thermodynamic parameters are important for a better understanding of the effect of temperature on adsorption [21]. Since the K_L Langmuir constant is essentially an equilibrium constant, the variation of K_L with temperature (Table II) can be used to estimate the enthalpy change accompanying adsorption, ΔH^o, i.e., the standard enthalpy changes of adsorption at a fixed surface coverage [36]. The thermodynamic parameters ΔH^o, ΔS^o, and ΔG^o associated with the adsorption process can be determined by using the following equations. The standard Gibbs' free energy change of adsorption, ΔG^o, can be related to the equilibrium Langmuir constant, K_L, by (7)

$$\Delta G^0 = -R \, T \, Ln(K_L) \tag{7}$$

where R is the gas constant (R = 8.314 J/mol.K). A convenient form of the van't Hoff equation [21] then relates K_L to the standard enthalpy and entropy changes of adsorption, ΔH^o and ΔS^o, respectively, viz.

$$Ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{(RT)} \tag{8}$$

On the basis of a plot of $\ln K_L$ versus $1/T$ (8), ΔH^o can be estimated from the slope and ΔS^o from the intercept of what should be a straight line passing through the points. Fig. 8 shows just such a plot with a correlation coefficient of 0.999. The ΔH^o and ΔS^o values are thus found to be +0.854 kJ/mol and +0.024 KJ/mol. K, respectively, while the ΔG^o values are −6.178, −6.418, and −6.658 kJ/mol (at 293, 303, and 313 K, respectively).

The positive value of ΔH^o confirms the endothermic nature of the adsorption process, as has been found in most cases [36], [37]. This feature may be an indication of the occurrence of monolayer adsorption [21]. The positive value of ΔS^o corresponds to an increased degree of freedom in the system as a result of adsorption of the YB molecules. There are

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various possible explanations. One is that it reflects the release of hydrated inorganic cations from the BE causing an overall increase in entropy analogous, for example, to the dissolution of solid sodium chloride [36]-[38]. Another is that structural changes take place as a result of interactions of YB molecules with active groups in the BE surface. Whatever the explanation for the positive entropy change, this is the factor leading overall to a negative free energy change. Adsorption processes with ΔG^o values in the -20 to 0 kJ/mol range correspond to spontaneous physical processes, while those with values in the -80 to -400 k/Jmol range correspond to chemisorption [21]. As ΔG^o changed from -6.178 to -6.658 kJ/mol when the temperature increased from 293, 303, and 313 K, it can be concluded that the adsorption mechanism is dominated by physisorption, in keeping with the finding that the adsorption is rapid and more spontaneous at higher temperature. Spontaneous adsorption processes are a common feature of many other studies of this sort [39].
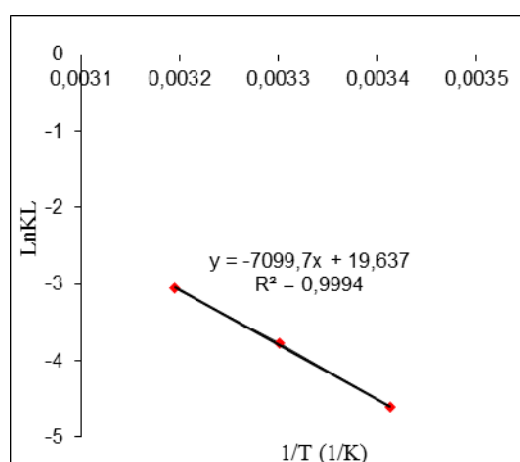

Fig. 8 Plot of ln K_L versus 1/T: estimation of thermodynamic parameters for the adsorption of YB onto BE

IV. CONCLUSION

Kinetic, equilibrium, and thermodynamic studies were done for the adsorption of YB from aqueous solutions onto BE. Results of adsorption showed that BE can be effectively used as a biosorbent for the removal of dye. The kinetics studies of dye on BE indicated that the adsorption kinetics of dye on BE followed the pseudo-second order at different concentration values. The equilibrium data have been analyzed. The results showed that the YB followed Langmuir isotherm. Thermodynamic studies indicated that the dye adsorption onto BE was a spontaneous, endothermic, and physical reaction. Based on the data of present study, BE, an inexpensive and easily available material, can be an alternative for costlier adsorbents used for dye removal in wastewater treatment processes.

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