Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.987169

57 (2016) 3741–3749
February

Taylor & Francis
Taylor & Francis Group

Study of the kinetics and thermodynamics of adsorption of Red Bemacid on the cords of *Luffa cylindrica*

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Received 26 February 2014; Accepted 7 November 2014

ABSTRACT

The present study explored the possibility of using *Luffa cylindrica* cords for the removal of dye Red Bemacid CL-BN200 through the adsorption batch process under different experimental conditions. The determination of the concentrations of dye have been performed using an UV–visible spectrophotometer (S6). The kinetics and thermodynamics of adsorption of Red Bemacid by cords of *L. cylindrica* were studied. Experimental data were analyzed by the Langmuir , Freundlich, and Temkin isotherms, and isothermal constants were calculated using a linear regression analysis. The Langmuir isotherm showed the maximum value of adsorption capacity was 12.30 mg/g, and the correlation coefficient (R^2) was 0.997. The pseudo-first- and pseudo-second-order kinetic models were applied to the experimental data. The experimental data fitted very well the pseudo-second-order kinetic model ($R^2 = 0.99$) and also followed the model of intraparticle diffusion (K_{dif} vary from 0.261 to 2.341 mg/(g min$^{1/2}$) for concentrations between 5 and 50 mg/L), whereas diffusion is not the only rate-control step. The thermodynamic parameters were evaluated. The positive value of ΔH° (2.06 kJ/mol) indicated that the adsorption of Red Bemacid on *L. cylindrica* cords was endothermic, the result was supported by the increase in the adsorption of Red Bemacid more and more with temperature. Positive values of entropy ($\Delta S^\circ =$ 11.87 J/mol K) correspond to a good affinity cords *L. cylindrica* molecules Red Bemacid. Negative values of the free enthalpies ($\Delta G^\circ = -1.21$, -1.36, and 1.43 kJ/mol at 277, 290, and 296 K, respectively) for the studied system show that the adsorption process is spontaneous.

Keywords: Adsorption; *Luffa cylindrica* cords; Red Bemacid CL-BN200; Langmuir and Freundlich isotherms; Kinetics; Thermodynamics

1. Introduction

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

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are not likely to diminish, the efforts to control and dispose of wastes are appropriately rising.

Dyes are color organic compounds which can colorize other substances. These substances are usually present in the effluent water of many industries, such as textiles, leather, paper, printing, and cosmetics. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents discharged into water bodies [1].

Dyes are widely used in industries such as the textile, paper, pulp mill, leather, dye synthesis, printing, food, and plastics industries. Since many of the organic dyestuffs are harmful to human beings and toxic to micro-organisms, removal of dyestuffs from wastewater has received considerable attention over the past decades [2,3]. Most of these dyes pose acute problems for the ecological system, as they are toxic and have carcinogenic properties, which make the water contaminated with dyes inhibitory to aquatic life. Textile industries produce significant amounts of wastewater containing dyes. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers, and from the fabric dyeing and finishing steps. In the section for dyeing textile industry, about 1 m^3 of water is used for each 1,000 kg treated clothing [4].

Given the great variety of fibers, dyes, and process aids, these processes generate wastewater of great chemical complexity and diversity [5].

Many types of dyes, such as direct, reactive, acid, and basic dyes, are used in the textile industry [5]. With industrialization, the discharge of industrial wastewater has increased. At the same time, there are environmental concerns, and there is the need to find cheap and efficient methods for the treatment of industrial wastewater prior to disposal into natural waters [6,7]. The most efficient method for the removal of dyes from aqueous effluents is the adsorption process. Efficient and environment-friendly technologies are thus needed to be developed to reduce the dye content in wastewaters from discharge to acceptable level at affordable cost. The search for alternative and innovative wastewater treatment techniques has drawn attention to the use of less expensive materials abundantly [8], such as activated bituminous coal [5], clay [6], neem (*Azadirachta indica*) leaf powder [3], jute fiber carbon [9], Abu-Tartur phosphate rock [10], black stone cherries [11], Jordanian diatomite [12], hazelnut shell [13], spent activated clay [1], bamboo activated carbon [14], coir pith carbon [15], Egyptian rice hull [16], vetiver root activated carbon [17], activated carbon from oil palm wood [18], algae [19], fungi [20], bacteria [21], and yeast [22] for the dyes removal and recovery technologies, and has gained importance during recent years [23].

In the present work, we are interested in the elimination of acid dye: Red Bemacid CL-BN200 from synthetic aqueous solutions using the cords of *Luffa cylindrica*. These acid dyes are used in SOITEX Tlemcen, Algeria. Why there has been a growing interest in the development of applications using new materials such as ultrafine fibers as intermediate or finished products in sectors as diverse as the industries ? The main advantage of the use of fibers is their increased responsiveness due to the increased surface to volume ratio of the fibers.

The sponge gourd, fruit of *L. cylindrica*, has a ligneous netting system in which the fibrous cords are disposed in a multi-directional array forming a natural mat. This fibrous vascular system is composed of fibrils glued together with natural resinous materials of plant tissue. Gianpietro et al. [24] has reported that the fibers of *L. cylindrica* were composed of 60% cellulose, 30% hemicellulose, and 10% lignin. Recently, the *L. cylindrica* have been used as support of immobilization for the decolorisation of certain solutions [25–33] and dyeing water [28–32]. Indeed, Akhtar et al. [25], [26,27] showed that the *L. cylindrica* gave good results during its use as support to produce a new system of sorption to remove the cadmium, the Chromium III and nickel II ions from the contaminated aqueous mediums.

2. Materials and methods

2.1. Preparation of material

The cords of *L. cylindrica* were washed with boiling distilled water for 30 min. These cords were then placed in a solution of NaOH (12%) for 15 min and washed again with tap water. They are whitened with bleach 12% for 3 h at ambient temperature after which the cords are rinsed with distilled water several times. The cords of *L. cylindrica* were oven dried at 105℃ for 120 min, then crushed and sifted. Samples are ready for adsorption.

2.2. Dye solution preparation

The dye Red Bemacid is an acid ($\lambda_{\max} = 540$ nm), water-soluble dye, due to the presence of sulfonate or carboxylate group. It is often difficult to know the chemical composition of the dye, as confidentiality on the chemical composition is generally preserved.

Currently, the textile industry of Soitex Tlemcen, Algeria, deposited registered trademarks that give no indication of the structure, but characterize the nuance and application processes.

The fiber–dye affinity is the result of ionic bonds between the sulfonic acid portion of the dye and the amino groups of textile fibers. The use of a coloring material must meet a number of criteria:

1. Abrasion resistance,
2. photolytic color stability,
3. resistance to chemical oxidation (including detergents) and to microbial attack.

Stock dye solutions (1,000 mg/L) were prepared by dissolving 1 g of dye in 1 L of distilled water. Experimental solutions of desired concentration were obtained by further dilution.

2.3. Adsorption experiments

The method used for the establishment of the adsorption isotherm method is to put in a water bath fitted with a stirrer, a series of flasks with which we introduce a volume ($V = 300$ mL) solution of the adsorbate (Red Bemacid) known concentration (5, 10, 25, and 50 mg/L) and a mass ($m = 1$ g) of the adsorbent of well-defined size ($0.1 \le d_p(\text{mm}) \le 1$), and specific surface area 22.48 m^2/g at different temperatures (277, 290, and 296 K) with pH 6. For a given contact time corresponding to equilibrium, we recover the filtrate solution for passing the UV–visible spectrophotometer (S6).

Adsorption kinetic experiments were used to investigate the effect of contact time and determine the kinetic parameters. For these tests, 1-g *L. cylindrica* was added to 300-mL dye solutions with different initial concentrations (5, 10, 25, and 50 mg/L). The mixture was agitated on an electromagnetic stirrer, at 298 K and 400 rpm. At predetermined time intervals (0–200 min), 10- mL samples were taken out and filtered. The same methods were used to determine the residual dye concentration. The adsorption amount at time, t, q_t (mg/g), was calculated by the following equation:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where C_t is the concentration of dye solution at time, t (mg/L), C_0 is the initial concentration of dye, respectively (mg/L). V is the volume of dye solution (L) and m is the weight of adsorbent used (g).

3. Results and discussion

3.1. Adsorption isotherms

Adsorption isotherm models are widely used to describe the adsorption process and investigate mechanisms of adsorption. Adsorption isotherms were calculated based on the well-known Langmuir, Freundlich, and Temkin models.

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, using uniform strategies of adsorption with no transmigration of the adsorbate on the plane of the surface [34]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \tag{2}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_L the Langmuir adsorption constant (L/mg), and q_m is the theoretical maximum adsorption capacity (mg/g).

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [35]. The well-known logarithmic form of the Freundlich isotherm [36] is given by the following equation:

$$\log(q_e) = \log(k_F) + \frac{1}{n_F}\log(C_e) \tag{3}$$

where K_F (mg/g $(\text{L/mg})^{1/\text{n}}$) and $1/n$ are the adsorption constants of Freundlich model generally related to the strength of interaction between adsorbate and sorbent:

Temkin's model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate θ. From q_e plotted as a function of ln, C_e, B_T, and K_T values can be determined.

$$q_e = \frac{RT}{B_T}\ln(K_T . C_e) \tag{4}$$

Where R is the perfect gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and B_T is the variation in energy of adsorption (J/mol); K_T is the constant of Temkin (L/mg).

The plots of $1/q_e$ vs. $1/C_e$ for the adsorption of Red Bemacid at 277, 290, and 296 K according to the linear form of the Langmuir isotherm is shown in Fig. 1.

The adsorption isotherm constants of Red Bemacid adsorption process on the cords of *L. cylindrica* are listed in Table 1. From Table 1, the values of $1/n$ were found to be less than 1. The low value of the linear correlation coefficient, R^2, indicated the unsuitability of Temkin isotherm model. The values of R^2 for Freundlich model (0.963, 0.999, and 0.994 at 277, 290, and 296 K, respectively) were high, indicating that this model can be used to characterize the equilibrium adsorption. However, Freundlich model was not the best model in this study. Langmuir models were fitting well with the isotherm data at various temperatures with highest R^2 values, compared to Temkin and Freundlich models. The Langmuir fit is consistent with strong monolayer sorption onto specific sites.

The results of Langmuir model demonstrated that the homogeneous monolayer Remazol Brilliant Blue R was covered onto *LC* [37] and methylene blue dye onto *Luffa* fibers [30]. The maximum adsorption capacities (q_m) of cords of *L. cylindrica* for Red Bemacid were 4.30, 11.40, and 23.43 mg/g at 277, 290, and 296 K, respectively, are higher than that of other cellulose wastes, such as orange peel and banana peel having 13 and 15 mg/g methylene blue dye adsorption capacities, respectively [38]. The removal of dye by *LC* was found 5.84 mg/g [37]. Based on these properties, we can say that *L. cylindrica* cords can be used efficiently for removing dye from aqueous solution instead of other cellulosic-based adsorbents.

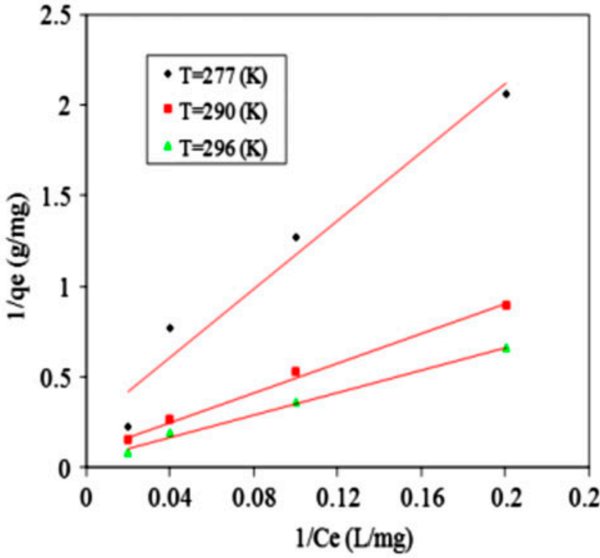

Fig. 1. Linearization of the Langmuir equation for adsorbing Red Bemacid/cords *LC:* pH 6, C_0 = 50 mg/L, V = 300 mL, and m = 1 g.

Table 1
Parameters of different adsorption models for Red Bemacid/cords (*LC*)

Model parameters	System T (K) C_0(mg/L)	Red Bemacid/cords (*LC*) 277 50	 290	 296
Freundlich	K_F	0.10	0.32	0.34
	$1/n_F$	0.91	0.77	0.88
	R^2	0.963	0.999	0.994
Langmuir	q_m	4.30	11.40	23.43
	K_L	0.025	0.021	0.014
	R^2	0.979	0.998	0.997
Temkin	K_T (L/g)	1.52	0.993	3.20
	B_T	2.7	1.66	0.0558
	R^2	0.805	0.946	0.881

3.2. Adsorption kinetics

Three kinetic models, pseudo-first-order, pseudo-second-order, and intraparticle diffusion, were applied to the experimental data to analyze the adsorption kinetics of Red Bemacid dye.

The pseudo-first-order equation can be expressed as [39]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{5}$$

where q_e and q_t are the amounts adsorbed at equilibrium and at time, t (mg/g), and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}).

The pseudo-second-order kinetic model can be represented in the following form [40]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{6}$$

where k_2 is the rate constant of the pseudo-second-order adsorption (g/mg min).

The kinetics of adsorption of the adsorbate on the adsorbent was verified at different initial concentrations (5, 10, 25, and 50 mg/L).

The validity of each model was determined by the sum of squared errors (SSE %), given by

$$\text{SSE} = \frac{1}{N}\sqrt{\sum_N (q_{e,\text{exp}} - q_{e,\text{cal}})^2} \tag{7}$$

where N is the number of trials. Low value indicates a better SSE smoothing.

The kinetic parameters for adsorption of Red Bemacid presented in Table 2 were calculated from plots of log (q_e−q_t) vs. t (Fig. 2) and the plots of t/q_t vs. t (Fig. 3). For the first-order kinetic model, the obtained R^2 values were relatively low, ranging from 0.90 to 0.993, and the calculated q_e(cal) were much larger than the experimental q_e(exp). For the second-order kinetic model, the obtained R^2 values were between 0.996 and 0.998. Moreover, the experimental q_e(exp) values agree well with the calculated ones. These results indicate that the adsorption system of dye obeyed a pseudo-second-order kinetic model. The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism.

Most adsorption reactions take place through multi-step mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion, and (iii) interaction between adsorbate and active site. Since the first step is excluded by shaking the solution, the rate-determining step is one of the other two steps. Weber and Morris [41] described the intraparticle uptake of the adsorption process to be proportional to the half-power of time:

$$q_t = K_{\text{dif}}\, t^{1/2} \tag{8}$$

where K_{dif} is the intraparticle diffusion rate constant (mg/g min$^{1/2}$).

For the system studied (Red Bemacid/cords (*LC*)), we have two distinct phases. One is attributed to the diffusion in the mesopores or macropores, the second part, in the absence of micropores systems tend towards equilibrium. The values of the diffusion rate constants (K_{dif}) are calculated by the linearization of the first phase described by Eq. (6). According to (Fig. 4), the curves (linear) do not pass through the origin. This shows the dual nature of the adsorption phenomenon. The intercept is due to the presence of an external resistance transfer material which gives the thickness of the boundary layer. The results obtained are given in Table 3.

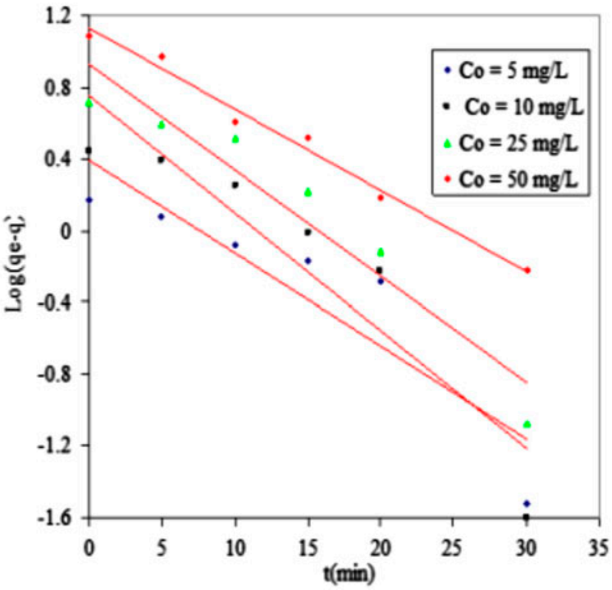

Fig. 2. Linearization of the kinetic model of pseudo-first-order, at T = 296 K.

We observe that the diffusion rate constants increase in the same direction as the initial concentration of Red Bemacid Table 3. Indeed for initial concentrations between 5 and 50 mg/L, the values of K_{dif} vary from 0.261 to 2.341 mg/(g min$^{1/2}$) for the Red Bemacid/cords (*LC*) system. According to the study of

Table 2
Pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of Red Bemacid onto *L. cylindrica*

Model parameters	System	Red Bemacid/cords (*LC*)			
	T (K)	296			
Pseudo-first-order	C_0 (mg/L)	5	10	25	50
	$q_{e,\text{exp}}$ (mg/g)	1.5	2.77	5.26	12.30
	$q_{e,\text{cal}}$ (mg/g)	2.40	3.75	6.34	13.36
	K_1 (min^{-1})	0.19	0.16	0.136	0.104
	R^2	0.90	0.92	0.959	0.993
	SSE (%)	51.9	57.5	62.30	61.20
Pseudo-second-order	$q_{e,\text{cal}}$ (mg/g)	1.63	3.14	5.63	12.92
	K_2 (g/mg min)	0.048	0.02	0.019	0.011
	R^2	0.996	0.98	0.997	0.998
	SSE (%)	7.37	21.31	21.34	35.78

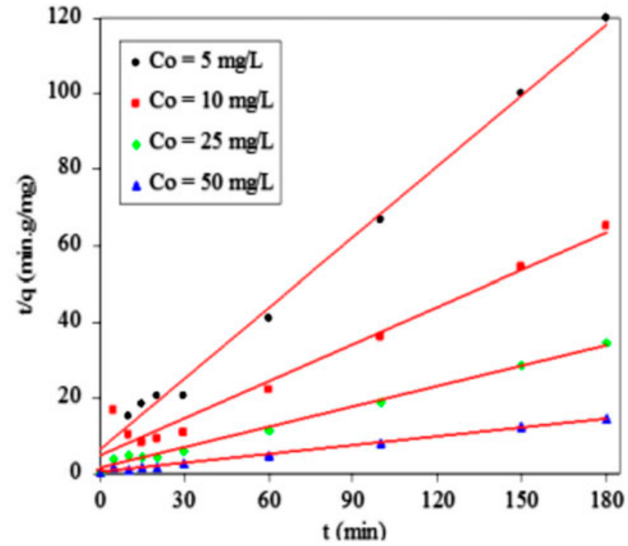

Fig. 3. Linearization of the kinetic model of the pseudo-second-order for the system Red Bemacid cords (*LC*), at *T* = 296 K.

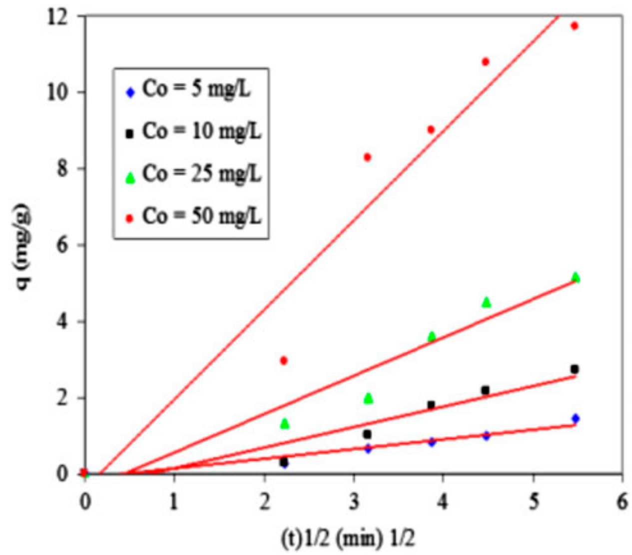

Fig. 4. Application of simplified model intraparticle diffusion for the adsorption of Red Bemacid on cords (*LC*), *T* = 296 K.

Demir et al. [30] on the diffusion intraparticle for the methylene blue/*LC* system, the value of K_{dif} is equal 0.08 mg/(g min$^{1/2}$).

So we note that the coefficient K_{dif} (0.536 mg/(g min$^{1/2}$)) is 6.7 times greater than that of K_{dif}, found by Demir et al. [30] to the concentration C_0 = 10 mg/L.

Table 3
Results of application of the model intraparticle diffusion for system Red Bemacid/cords (*LC*)

System	Red Bemacid/cords *(LC)*			
T (K)	296			
C_0 (mg/L)	5	10	25	50
q_e (mg/g)	1.5	2.77	5.26	12.30
K_{dif} (mg/g min$^{1/2}$)	0.261	0.536	1.004	2.341
$\pm K_{dif}$	0.032	0.090	0.126	0.297
R^2	0.971	0.969	0.970	0.948

3.3. Thermodynamic parameters

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG°, is an indication of spontaneity of a chemical reaction, and therefore is an important criterion for spontaneity. In addition, both enthalpy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The value of ΔG° can be determined from the following equation:

$$\Delta G^\circ = -RT\ \ln(k) \tag{9}$$

where *K* the adsorption equilibrium constant, *R* is the universal gas constant (8.314 J/mol K), and *T* is absolute temperature. Relation between ΔG°, ΔH° (enthalpy), and ΔS° (entropy) can be expressed by the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

Eq. (10) can be written as

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{(RT)} \tag{11}$$

where the values of ΔH° and ΔS° can be determined from the slope and intercept of the plot between ln (*K*) vs. (1/*T*) (Fig. 5). The values of ΔG°, ΔH°, and ΔS° for the biosorption of Red Bemacid onto *L. cylindrica* at different temperatures (277, 290, and 296 K) are given in Table 4. The negative values of Gibb's free energy changes approve a spontaneous nature of biosorption. The value of enthalpy change was positive (ΔH° = 2.06 kJ/mol), indicating that the biosorption process is

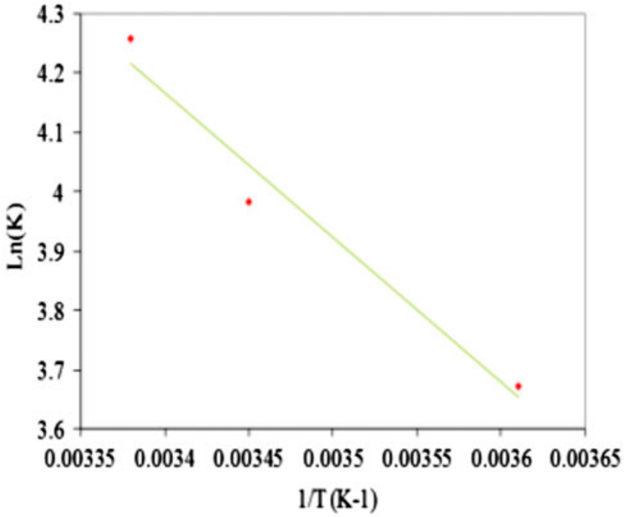

Fig. 5. Application of vant'Hoff balance for determining the enthalpy of adsorption on Red Bemacid cords (*LC*); $C_0 = 50$ mg/L.

endothermic. The positive values of ΔS° (11.87 J/mol K) correspond to good affinity during the biosorption of Red Bemacid onto *L. cylindrica*.

The increase in adsorption Red Bemacid with increasing temperature shows that the adsorption is endothermic. The growth temperature promotes mobility ions and dye produce a swelling effect of the internal structure of the cords (*LC*). It will also allow the dye molecules to penetrate further. Therefore, the adsorption capacity will depend largely on the chemical interaction between functional groups on the adsorbent surface and the adsorbed molecules (which should increase with increasing temperature). This can be explained by an increase in the rate of diffusion of the adsorbate in the pores.

Demir et al. [30] have reported that the values of ΔG° for the adsorption of reactive dye onto *L. cylindrica* were found to be −38, −38.6 kJ/mol for methylene blue at 293 and 303 K, respectively. These values are 28 times greater than ΔG° for this study at the temperature T = 296 and 293 K. The adsorption of both systems process is spontaneous.The value of ΔH° for the removal of methylene blue was determined to be −20 kJ/mol, and the value of ΔS° was found to be 61.5 J/mol K, respectively, which is a slightly different result obtained in this study. ΔS° is 5 times greater and ΔH° is 10 times less than ΔS° and ΔH° of this study.

Table 4
Thermodynamic parameters of the adsorption of Red Bemacid onto *L. cylindrica* at different temperatures

System	Red Bemacid/cords *(LC)*		
C_0 (mg/L)	50		
T (*K*)	277	290	296
$-\Delta G^\circ$ (kJ/mol)	1.21	1.36	1.43
ΔS° (J/(mol K))	11.87		
ΔH° (kJ/mol)	2.06		

4. Conclusion

This study shows that *Luffa*, an abundant natural source, can be used effectively and efficiently for the removal of synthetic dye (Red Bemacid) from aqueous solutions.

Equilibrium data were fitted to Langmuir, Freundlich, and Temkin isotherms, and the equilibrium data were best described by the Langmuir isotherm model (R^2 = 0.997), with a maximum monolayer adsorption capacity of 12.30 mg/g, at 30 min. The adsorption kinetics is best described by the pseudo-second-order (R^2 = 0.99).

The thermodynamic parameters for the adsorption of Red Bemacid onto *L. cylindrica* cords were also determined. The negative sign of ΔG° confirms the spontaneous nature of the adsorption process. The positive sign of ΔS° shows the increased randomness at the solid–solution interface during adsorption, and the positive sign of ΔH° indicates that the adsorption process is endothermic.

Therefore, the potential use of *Luffa* cords for industrial wastewater treatment is real and represents interesting prospects to investigate, particularly for solutions containing organic species at very low concentrations. However, some fundamental points remain obscure, particularly the hydrodynamic behavior of the *Luffa*, and the dynamic adsorption and the interaction of these cords with other chemical solutions other than Red Bemacid.

Abbreviations

LC	—	*Luffa cylindrica*
MB	—	methylene blue
SEE	—	sum of squared errors
RBBR	—	Remazol brilliant blue R

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