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Biosorption of Azo Dye Reactive Black B onto Nonviable Biomass of *Cladosporium cladosporioides* LM1: Thermodynamic, Kinetic and Equilibrium Modeling

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***Abstract*—**This study investigated the biosorption of the azo dye reactive Black B (RBB) from aqueous solution using the nonviable biomass of *Cladosporium cladosporioides* LM1. The biosorption systems were carried out in batch mode considering different conditions of initial pH, contact time, temperature, initial dye concentration and biosorbent dosage. Higher removal rate of RBB was obtained at pH 2. Biosorption data were successfully described by pseudo-second-order kinetic model and Langmuir isotherm model with the maximum monolayer biosorption capacity estimated at 71.43 mg/g. The values of thermodynamic parameters such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated that the biosorption of RBB onto fungal biomass was spontaneous and exothermic in nature. It can be concluded that nonviable biomass of *Cladosporium cladosporioides* LM1 may be an attractive low-cost biosorbent for the removal of azo dye RBB from aqueous solution.

***Keywords*—**Color removal, isotherms and kinetics models, thermodynamic studies, fungus.

I. Introduction

MOST dyes are synthetic chemical compounds having complex aromatic structures [1] and are used in many industries for coloring purposes, such as textile, rubber, tanneries, paper, plastic, paint, cosmetics and pharmaceuticals. It is reported that there are more than 100,000 commercial dyes with an estimated production of 7 x 10^5–1 x 10^6 tons per year [2] and about 15% of the used dyes enter the environment through wastes causing environmental pollution [3]. In aquatic ecosystems, the reduction of light penetration, which is essential for photosynthesis, depletion of dissolved oxygen, and alteration of aesthetic appearance are some impacts from the disposal of colored wastewater [4]. Besides that, many dyes are highly toxic and can cause mutagenic or carcinogenic effects on aquatic life and human beings [5].

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Azo dyes are characterized by one or more chromophore (azo) group (−N=N−) in their chemical structures, and constitute the largest group used in textile dyestuffs, representing about 60-70% in weight [6]. Within the class of azo dyes, the reactives are the most frequently used. These dyes are formed by the combination of azo-based chromophores with different types of reactive groups such as chlorotriazine, vinyl sulfone and trichloropyrimidine [5].

Various physical, chemical and electrical methods such as electrolysis, chemical coagulation, precipitation, ultrafiltration, color irradiation, ozonation, and advanced oxidation have been used for treating dye-containing wastewater [7], [8]. However, there are disadvantages in all these methods such as high operating costs and intensive energy requirements. Biological processes using microorganisms such as anaerobic and activated sludge treatment have also been used to treat textile wastewater [9], [10]. Nevertheless, due to complex and stable aromatic structure of synthetic dyes, toxic, mutagenic and carcinogenic compounds can be formed during microbial biodegradation making the treatment inefficient [11].

Adsorption is an efficient and low cost process to remove contaminants from the water and wastewater [12]. This is attributed to the easy availability and low cost of some adsorbents, simplicity of design and operation and ability to treat wastewater with high concentration of pollutants [13]. In the past decade, the adsorption of dyes onto various types of materials has been studied in detail, such as zeolite [14], cotton plant [15], pine leaves [16], olive stone [17], cashew nut shell [13], water hyacinth leaves [18], and algal [19], yeast [12] and filamentous fungal biomass [11].

Fungal biomass can be used as an inexpensive source of biosorbent once it can be produced cheaply using simple fermentation techniques or obtained as a waste from various industrial fermentation processes [20]. Its pollutant adsorption capacity is due to the chemical characteristics of its cell wall, which contains high amounts of polysaccharides, some proteins and other components. These biomacromolecules have several functional groups such as amino, carboxyl, thiol, sulfhydryl and phosphate groups, which are responsible for binding pollutant molecules [21].

The dye biosorption potential of many different nonviable fungal biomasses has previously been reported, including *Rhizopus arrhizus*, *Trametes versicolor* and *Aspergillus niger*

[20], *Agaricus bisporus* and *Thuja orientalis* [22] and *Panus tigrinus* [23]. The genus *Cladosporium* belongs to Deuteromycetes and has proven to be an efficient biosorbent to remove several hazardous compounds such as heavy metals [24], organochlorine pesticides [25] and metal cyanides [26]. However, biosorption studies on textile dyes using *Cladosporium* biomass may be unsatisfactory, mainly when high chemical diversity of dyes is found.

In this work, RBB, an anionic azo dye used widely in the textile industry was used as a model dye. The main purpose was to explore the capability of nonviable biomass of *Cladosporium cladosporioides* LM1 as biosorbent to remove RBB from aqueous solution under different experimental conditions. Thereby, effects of initial pH, contact time, dye concentration and biosorbent dosage were evaluated. In addition, kinetic, equilibrium and thermodynamic studies on the removal of dye were also done to understand the overall biosorption mechanisms.

II. Materials and Methods

A. Dye and Chemicals

The anionic textile dye C.I. RBB (empirical formula $C_{26}H_{21}O_{19}N_5S_6Na_4$; molecular weight = 991.82) was purchased from a textile industry in Brazil and it was used without any further purification. The RBB chemical structure is shown in Fig. 1. The maximum absorbance (λ_{max} = 597) of the RBB was determined by a UV-Visible spectrophotometer (Hach DR6000). Stock solutions of the dye were prepared by dissolving the powdered dyestuff in distilled water (1.0 g/L) and the other concentrations were obtained by diluting this stock dye solution. The pH of solution was adjusted by the addition of 0.1 M NaOH or 0.1 M HCl solutions. Culture media were purchase from Himedia Labs and all other chemicals used were of analytical grade.

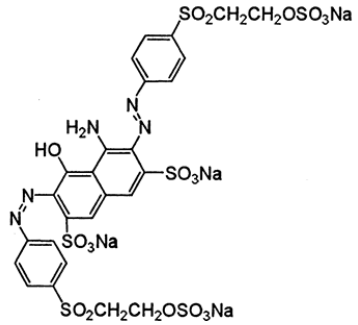

Fig. 1 Chemical structure of RBB

B. Fungus

The filamentous fungus *Cladosporium cladosporioides* LM1 was obtained from Culture Collection of Department of Sanitary and Environmental Engineering of the Federal University of Mato Grosso, Brazil. The fungus stock culture was maintained by periodic subculture on Potato Dextrose Agar (PDA) slants at 4 °C. PDA consisted of (g/L) infusion of potatoes 200.0, dextrose 20.0, agar 15.0, pH 5.6 ± 0.2.

For identification of fungus, DNA was extracted from mycelium with Axygen Biosciences kits according to the manufacturer's recommendations. The ITS1 and ITS4 primers were used for amplification of the ITS region [27]. Amplicons were purified using ExoSap-IT PCR Product Cleanup Reagent (GE Healthcare) and sequenced by the Sanger method. MEGA 7 software [28] was used to obtain the consensus sequence obtained from primers ITS1 and ITS4 and this sequence was compared with the known sequences available at GenBank database through the nBLAST tool (http://www.ncbi.nlm.nih.gov). The sequence that shared 97% or more of similarities was identified as the same specie [29]. The sequence has been deposited in GenBank under accession number MH475346.

C. Preparation of Biosorbent

The fungus was grown in Potato Dextrose Broth (g/L: infusion of potatoes 200.0, dextrose 20.0, pH 5.1 ± 0.2) at 28 ± 2 ºC in static condition. When the sporulation occurred after 6-8 days, the biomass was autoclaved (121 °C, 30 min) and nonviable biomass was washed several times thoroughly with distilled water followed by oven drying at 80 ºC. Thereafter, the dry biomass was powdered and sieved through ASTM Standard sieve to obtain a homogeneous material (particle smaller than 150 μm) and then it was stored in desiccators for further use.

D. Biosorption Experiments

Dye biosorption experiments were conducted in 150 mL Erlenmeyer flasks containing 50 mL of the dye aqueous solution. The flasks were agitated on a rotary shaker at 150 rpm. The effects of different physicochemical variables such as pH (2, 4, 6, 8 and 10), initial dye concentration (50, 75, 100, 150, 200 and 250 mg/L), biosorbent dosage (0.75, 1.0, 1.25, 1.5, 1.75, 2.0 and 3.0 g/L) and temperature (25, 35 and 45 °C), on the biosorption efficiency were evaluated. At the end of each equilibrium experiment, the biosorbent was removed by filtration (filter membrane Ø 0.45 μm) and the residual dye in the solution was measured quantitatively by UV–Vis spectrophotometer (Hach DR6000) at λ_{max} = 597 nm. All biosorption experiments were performed in triplicates. Dye removal efficiency, R (%), and biosorption capacity of the fungal biomass at equilibrium, q_e (mg/g), were calculated using (1) and (2) respectively:

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

$$q_e = \frac{(C_i - C_e)}{B} \quad (2)$$

where C_i (mg/L) and C_e (mg/L) are the initial and the equilibrium dye concentrations and B is the biosorbent dosage in solution (g/L).

III. Results and Discussion

A. Effect of pH

Studies have demonstrated that solution pH significantly influences the dye biosorption because it affects the adsorbate solubility and ionizing functional groups of the adsorbent

surface [19]. Fig. 2 illustrates the effect of different initial pH on the removal of RBB by nonviable biomass of *Cladosporium cladosporioides* LM1 at a dye concentration of 50 mg/L, for 120 min, 25 ºC and 1.0 g biomass/L. At pH 2, the highest dye biosorption was achieved (77%), while in other pH (4, 6, 8 and 10), the dye removal was less than 10%. This could be attributed to deprotonation of functional groups on biosorbent surface when pH increased, decreasing electrostatic interaction with anionic molecules of dye and/or the presence of excess of OH^- ions competing with RBB molecules [17]. Similar pH trends were reported by other researchers for fungal biomass [1], [11], [22]. Since the greatest removal efficiency was observed at pH 2, this pH was used in subsequent experiments.

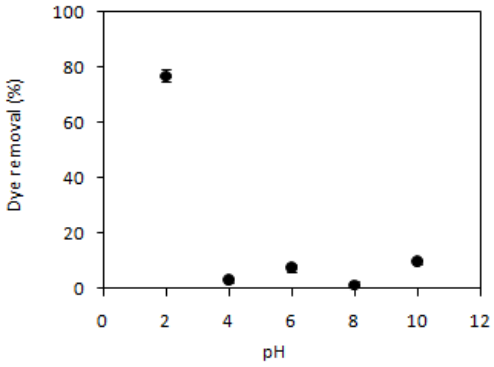

Fig. 2 Effect of pH on RBB removal efficiency of *Cladosporium cladosporioides* LM1 (biosorbent dosage = 1.0 g/L, [RBB] = 50 mg/L, contact time = 120 min, temperature = 25 ºC)

B. Effect of Biosorbent Dosage

The effect of biosorbent dosage on the RBB biosorption was evaluated at a dye concentration of 50 mg/L, for 120 min and at 25 ºC. Fig. 3 shows that the RBB removal increased when the biosorbent dosage increased, reaching >99% at biomass concentration of 2.0 and 3.0 g/L. This was already expected because the surface area and consequently the number of available adsorption sites were raised with an increase in biosorbent amount, thereby increasing the amount of adsorbed dye. On the order hand, the higher biosorption capacity, 39.7 mg/g, was obtained when 1.0 g/L biosorbent was used and decreased to 17.1 mg/g at 3.0 g/L biomass. The reduction in biosorption capacity with increasing biosorbent concentration could be explained by biosorption sites that remained unsaturated during the adsorption reaction [1].

C. Contact Time as a Function of Temperature

Contact time is an important parameter to evaluate the efficiency of biosorbent. Ideal biosorption materials should be capable of quickly adsorbing high concentrations of dye from liquid phase and reach equilibrium [1], [19]. As illustrated in Fig. 4, a rapid biosorption of dye occurred during the first 10 min for three temperatures and was gradually slowed down until equilibrium was nearly reached after 75 min. This could be attributed to the abundant availability of active sites on the biosorbent surface at the beginning of biosorption process, which became less efficient when these functional groups were occupied. Also, it can be seen that the equilibrium biosorption capacity of fungal biomass decreased from 39.7 to 35.7 mg/L when the temperature was increased from 25 to 45 °C. A decrease in RBB removal capacity of the biosorbent with the increase in temperature indicates the biosorption of dye on *Cladosporium cladosporioides* LM1 biomass is kinetically controlled by an exothermic process.

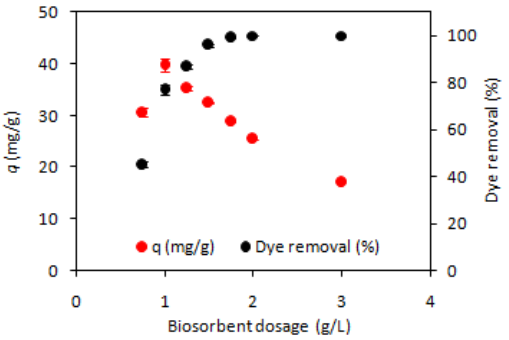

Fig. 3 Effect of biosorbent dosage on RBB removal efficiency of *Cladosporium cladosporioides* LM1 (pH = 2, [RBB] = 50 mg/L, contact time = 120 min, temperature = 25 ºC)

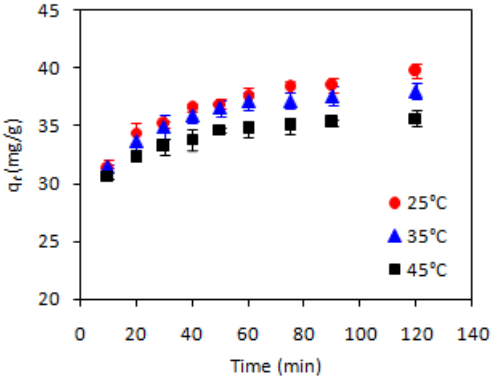

Fig. 4 Effect of contact time on RBB removal efficiency of *Cladosporium cladosporioides* LM1 at different temperatures (pH = 2, biosorbent dosage = 1.0 g/L, [RBB] = 50 mg/L)

D. Effect of Initial Concentration of Dye

In this study, the effect of initial concentration of RBB on removal capacity of the fungal biomass was investigated using solutions of dye that ranged from 50 to 250 mg/L, pH 2, and 25 °C. The results given in Fig. 5 indicated that the dye removal efficiency decreased with the increase in the initial dye concentration. On the other hand, it is found that the higher the concentration of RBB, the higher is the biosorption capacity, which reached at 250 mg/L the maximum value of 66.8 mg/g. This effect can be explained on the basis of the dye/biosorbent ratio. At low dye/biosorbent ratios, there are several sorption sites in the fungal biomass structure. As the dye/biosorbent ratio increases, sorption sites become saturated, resulting in a decline in the sorption efficiency [30]. Similar results have been reported for sorption of RBB from aqueous solution onto cotton plant waste [15] and biomass of *Penicillium restrictum* [1].

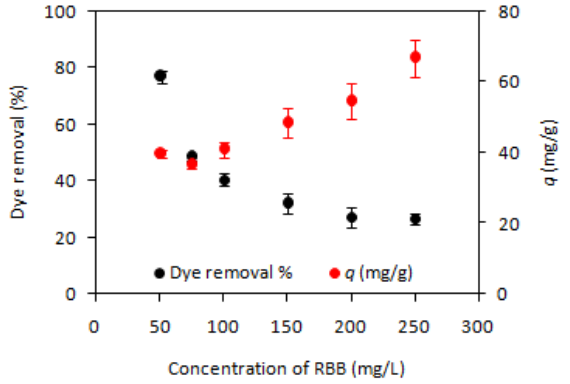

Fig. 5 Effect of initial dye concentration on RBB removal efficiency of *Cladosporium cladosporioides* LM1 (biosorbent dosage = 1.0 g/L, pH = 2, [RBB] = 50 mg/L, temperature = 25 °C)

E. Kinetic Studies

Kinetic studies provide useful information on the mechanism of the adsorption process and feasibility of scale-up operation [16]. In this study, kinetics studies on RBB removal were conducted using aqueous dye solution (50 mg/L), at various contact time (10-120 min), and temperature (25, 35 and 45 ºC). Several kinetic models are available to describe the sorption kinetics. Mostly used models including the pseudo-first order [31], pseudo-second order [32] and intraparticle diffusion [33] were applied to the dynamical experimental data to evaluate the kinetics of RBB biosorption by the biomass of *Cladosporium cladosporioides* LM1.

The linear form of the pseudo-first order model can be defined by (3):

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (3)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of RBB dye biosorbed at the equilibrium and at time t (min), respectively. K_1 (1/min) is the pseudo-first order rate constant. To calculate the values of K_1 and the predicted q_e, the plot of log (q_e–q_t) against t was used.

The linear form of the pseudo-second order model is given by (4):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

where q_e and q_t are the amounts of dye adsorbed by biosorbent (mg/g) at the equilibrium and at time t (min), respectively, and K_2 is the pseudo-second order rate constant (g/mg min). From the plot of t/q_t versus t, the values of K_2 and q_e were obtained.

The intraparticle diffusion model permits to identify the diffusion mechanisms and can be expressed by (5):

$$q_t = K_{id} t^{0.5} + C \quad (5)$$

where C (mg/g) is the intercept and K_{id} is the intraparticle diffusion rate constant (mg/g min$^{0.5}$). By plotting q_t versus $t^{0.5}$, the models parameters K_{id} and C were determined.

TABLE I
KINETIC PARAMETERS FOR THE BIOSORPTION OF RRB ONTO *CLADOSPORIUM CLADOSPORIOIDES* LM1 AT DIFFERENT TEMPERATURES

T (°C)	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	k_1 (1/min)	q_1 (mg/g)	R^2	k_2 (g/mg min)	q_2 (mg/g)	R^2	k_{id} (mg/g min$^{0.5}$)	C (mg/g)	R^2
25	0.0241	9.32	0.979	0.0058	40.66	0.999	1.0011	29.44	0.930
35	0.0339	8.45	0.980	0.0085	38.91	0.999	0.8095	30.12	0.889
45	0.0311	6.21	0.981	0.0111	36.23	0.999	0.6223	29.55	0.900

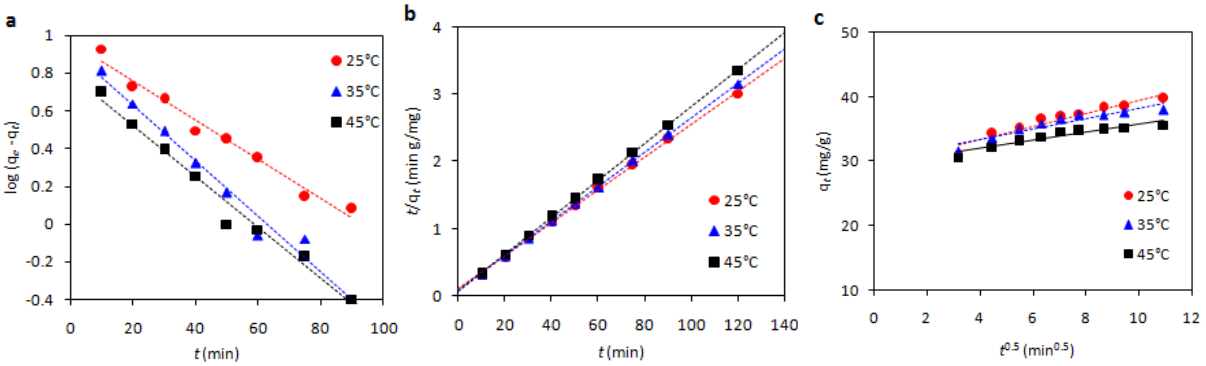

Fig. 6 Pseudo-first order (a), pseudo-second order (b) and intraparticle diffusion (c) models for the biosorption of RBB onto biomass of *Cladosporium cladosporioides* LM1, at different temperatures

The kinetic parameters for the RBB biosorption for different temperatures are given in Table I. Although pseudo-first order model generated good fits (R^2 > 0.979, Fig. 6 (a)), the calculated q_1 values (9.32, 8.45, 6.21 mg/g at 25, 35 and 45 °C) did not agree with the experimental ones (39.7, 38,0, 35.7 mg/g at 25, 35 and 45 °C). The pseudo-second order model, on the order hand, generated the best fits (R^2 = 0.999 for all temperatures studied, Fig. 6 (b)) and the biosorption capacities (q_2) estimated were also close to those acquired by experiments (Table I). In the case of intraparticle diffusion

model, the regression coefficients varied between 0.889 and 0.930 and the values of C were different from zero indicating that intraparticle diffusion is not the only rate-limiting step (Fig. 6 (c)). These results suggest that biosorption of RBB by *Cladosporium cladosporioides* LM1 is complex and likely controlled by both surface and intraparticle diffusion processes.

F. Biosorption Isotherms

The equilibrium distribution of RBB between the liquid phase and fungal biomass was expressed in terms of RBB biosorption isotherm. The equilibrium experiments were performed with different initial dye concentrations (50-250 mg/L), using 1.0 g biosorbent/L at 25 °C. The most widely used isotherm equations, Langmuir [34] and Freundlich [35] models, were applied to adsorption data.

The Langmuir isotherm model is based on the monolayer adsorption of adsorbate over a homogeneous adsorbent surface. The linearized form of the Langmuir isotherm is given by (6):

$$\frac{C_e}{q_e} = \frac{1}{K_L\, q_{max}} + \frac{C_e}{q_{max}} \tag{6}$$

where C_e (mg/L) is the dye concentration in the solution at the equilibrium, q_e (mg/g) is the amount of dye adsorbed by the biosorbent at the equilibrium, q_{max} (mg/g) is the maximum capacity corresponding to complete monolayer coverage, and K_L (L/mg) is the Langmuir constant. The parameters q_{max} and K_L was determined from the slope and intercept of the plot between C_e/q_e and C_e (Fig. 7 (a)).

The Freundlich isotherm is an empirical equation based on adsorption on heterogeneous surface and (7) represents its linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where K_f ((mg/g)(mg/L)$^{-1/n}$) is the Freundlich constant and n (dimensionless) is related to the adsorption intensity. K_f and n were determined by plotting $\ln q_e$ and $\ln C_e$ (Fig. 7 (b)).

The Langmuir and Freundlich constants and regression coefficients for the RRB biosorption onto biomass of *Cladosporium cladosporioides* LM1 are listed in Table II. The regression coefficients (R^2) show that the equilibrium data could be better interpreted by the Langmuir isotherm (R^2 = 0.936) than the Freundlich isotherm (R^2 = 0.652). This suggests that the biosorption process of RBB by biomass of *Cladosporium cladosporioides* LM1 assumes a monolayer adsorption, and the maximum biosorption capacity was 71.43 mg/g. The maximum adsorption capacities of RBB onto various adsorbents reported in the literature are presented in Table III. The adsorption capacity of *Cladosporium cladosporioides* LM1 obtained for RBB in this investigation is higher than those obtained for many other adsorbents.

The essential characteristics of the Langmuir isotherm could be expressed in terms of a dimensionless constant (R_L, separation factor) [36], which is defined as (8):

$$R_L = \frac{1}{1+K_L C_0} \tag{8}$$

where C_0 is the initial concentration of RBB (mg/L). R_L is used to interpret the biosorption process as follows: favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$) or linear ($R_L = 1$). R_L value found was 0.1133 indicating that the sorption process is favorable.

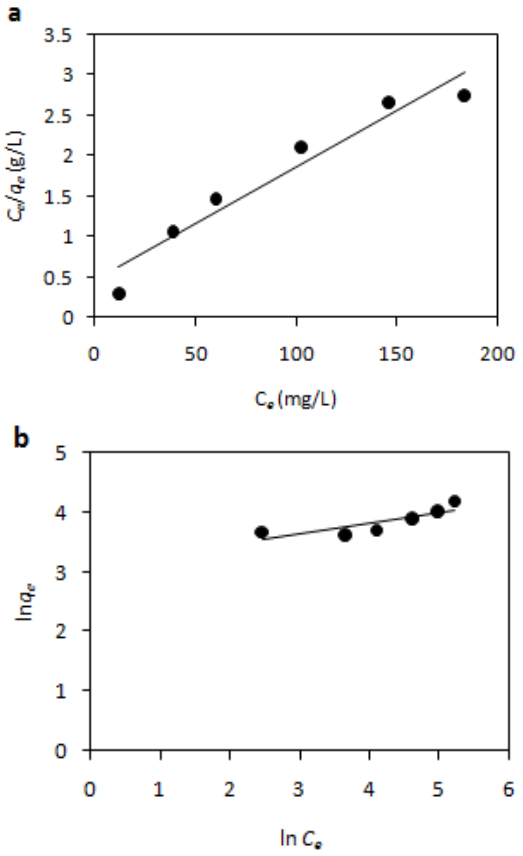

Fig. 7 Langmuir (a) and Freundlich (b) isotherms for the biosorption of RBB onto *Cladosporium cladosporioides* LM1

G. Thermodynamic Studies

The thermodynamic parameters reflect the feasibility and spontaneous nature of the process [20]. Thus, standard changes of free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were calculated by (9) and (10):

$$\Delta G° = -RT \ln K_D \tag{9}$$

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

The combination of (9) and (10) gives:

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{R} x \frac{1}{T} \tag{11}$$

where K_D (q_e/C_e) is the distribution coefficient, T (K) is the absolute temperature and R is the universal gas constant (8.314 J/K mol). By plotting $\ln K_D$ versus $1/T$, the values of $\Delta H°$ and $\Delta S°$ were determined from the slope and intercept (Fig. 8).

TABLE II
BIOSORPTION ISOTHERM CONSTANTS FOR THE BIOSORPTION OF RBB ONTO *CLADOSPORIUM CLADOSPORIOIDES* LM1

Langmuir			Freundlich		
q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g) (mg/L)$^{-1/n}$	n	R^2
71.43	0.0313	0.936	21.867	5.4945	0.652

TABLE III
COMPARISON OF ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS USED FOR RBB REMOVAL

Adsorbent	T (°C)	pH	q_{max} (mg/g)	Reference
Pumice	30	5.0	2.25	[37]
Walnut wood activated carbon	30	5.0	5.42	[37]
Surfactant-modified zeolite	30	5.0	12.93	[14]
Canola stalks	25	2.5	32.79	[38]
Cotton plant stalk	25	1.0	35.70	[15]
Cotton plant hull	25	1.0	50.90	[15]
Activated carbon-immobilized-cationic surfactant	30	2.0	71.42	[39]
Cladosporium cladosporioides LM1	25	2.0	71.43	This study
Acid-treated biomass of brown seaweed *Laminaria* sp.	25	1.0	92.30	[40]
Yeast slurry from brewery	30	2.0	162.73	[12]

The calculated thermodynamic parameters are listed in Table IV. The negative values of $\Delta G°$ indicate that the RRB biosorption onto *Cladosporium cladosporioides* LM1 is spontaneous and feasible at all the studied temperatures (25, 35 and 45 °C). The change in the standard enthalpy ($\Delta H°$) was -11.99 kJ mol^{-1}. The negative value of $\Delta H°$ suggests that the biosorption is exothermic in nature. The $\Delta S°$ parameter was also found to be negative revealing the decreased randomness at the solid/solution interface and no structural modification in fungal biomass during the adsorption of dye.

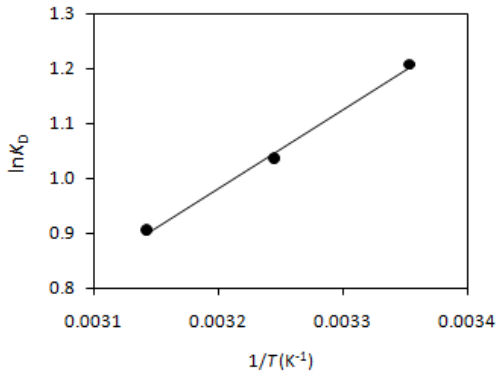

Fig. 8 Plot of lnK_D versus 1/T for estimation of thermodynamic parameters

TABLE IV
THERMODYNAMIC PARAMETERS ESTIMATED FOR MG BIOSORPTION ONTO MALT BAGASSE

T (°C)	K_D	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
25	3.35	–2.98	–11.99	–30.22
35	2.81	–2.68		
45	2.47	–2.38		

IV. CONCLUSION

In this study, nonviable biomass of *Cladosporium cladosporioides* LMI was tested as biosorbent for removal of RBB, an azo textile dye, from aqueous solution. The biosorption process proved to be dependent on the initial pH of the solution, temperature, contact time, initial dye concentration and biosorbent dosage. Maximum biosorption rate was obtained at pH 2. The kinetics of the biosorption process followed the pseudo-second-order model. Experimental equilibrium data provided best fit with the Langmuir isotherm model and the maximum biosorption capacity was estimated to be 71.43 mg/g (at 25 °C). Thermodynamics parameters, $\Delta G°$ and $\Delta H°$, indicated that the MG biosorption onto fungal biomass is spontaneous and exothermic. In conclusion, nonviable biomass of *Cladosporium cladosporioides* LMI may be an economic and effective option for the removal of the azo dye RBB from aqueous media.

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