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Biosorption of Acid Blue 290 (AB 290) and Acid Blue 324 (AB 324) dyes on *Spirogyra rhizopus*

Ayla Özer[a,*], Gönül Akkaya[a], Meral Turabik[b]

[a] *University of Mersin, Department of Chemical Engineering, 33343 Çiftlikköy-Mersin*
[b] *University of Mersin, Higher Vocational School of Mersin, Chemical Prog., Çiftlikköy-Mersin*

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Abstract

In this study, the biosorption of Acid Blue 290 and Acid Blue 324 on *Spirogyra rhizopus*, a green algae growing on fresh water, was studied with respect to initial pH, temperature, initial dye concentration and biosorbent concentration. The optimum initial pH and temperature values for AB 290 and AB 324 biosorption were found to be 2.0, 30 °C and 3.0, 25 °C, respectively. It was observed that the adsorbed AB 290 and AB 324 amounts increased with increasing the initial dye concentration up to 1500 and 750 mg/L, respectively. The Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models were applied to the experimental equilibrium data and the isotherm constants were determined by using Polymath 4.1 software. The monolayer coverage capacities of *S. rhizopus* for AB 290 and AB 324 dyes were found as 1356.6 mg/g and 367.0 mg/g, respectively. The intraparticle diffusion model and the pseudo-second order kinetic model were applied to the experimental data in order to describe the removal mechanism of these acidic dyes by *S. rhizopus*. The pseudo-second order kinetic model described very well the biosorption kinetics of AB 290 and AB 324 dyes. Thermodynamic studies showed that the biosorption of AB 290 and AB 324 on *S. rhizopus* was exothermic in nature.

Keywords: Acid blue 290; Acid blue 324; *Spirogyra rhizopus*; Biosorption

1. Introduction

Dyes and pigments represent one of the problematic groups; they are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing and also from food colouring, cosmetics, paper and carpet industries [1,2]. The effluents of these industries are highly colored and disposal of these wastes into receiving waters causes damage to the environment as they may significantly affect photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of metals, chlorides, etc., in them [3]. Hence, removal of dyes from such wastewaters is a major environmental problem and complete dye removal is necessary because dyes will be visible even at low concentration [4]. Currently, the major methods of textile wastewater treatment involve physical and/or chemical processes [5–7]. Such methods are often very costly and, although the dyes are removed, accumulation of concentrated sludge creates a disposal problem [6,8]. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use [6].

Activated carbon adsorption is the most popular physicochemical treatment for the removal of dissolved dyes from wastewaters [1,9]; however, its manufacturing and regeneration costs are high [8,10]. An alternative inexpensive adsorbent able to reduce the cost of an adsorption system has always been searched. A wide variety of microorganisms such as bacteria [7], fungi [3,11], algae [12–14] either in their living or inactivated form and various materials such as sepiolite [15], tree fern [16], coir pith [1], cotton [17], dolomitic sorbents [18], chitosan [19], bagasse fly ash [2], apple pomace and wheat straw [20], fly ash and coal [21] and sugarcane dust [22] have been investigated to remove dyes from aqueous solutions with varying success for color removal.

Microorganisms are known to accumulate unwanted materials by two distinct processes: (i) bioaccumulation, an energy-dependent process and (ii) biosorption, an energy independent physical adsorption. The term biosorption implies a

* Corresponding author. Fax: +90 324 361 00 32.
E-mail address: ayozer@mersin.edu.tr (A. Özer).

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Nomenclature

a_{RP}	Redlich-Peterson isotherm constant $(L/mg)^{\beta}$
A	Koble-Corrigan parameter $(L^n\ mg^{1-n}/g)$
B	Koble-Corrigan parameter $(L/mg)^n$
C	the dye concentration at any time t (mg/L)
C_{ad}	the adsorbed dye concentration (mg/L)
$C_{ad,e}$	the adsorbed dye concentration at equilibrium (mg/L)
C_{eq}	unadsorbed dye concentration in solution at equilibrium (mg/L)
C_o	initial dye concentration (mg/L)
ΔG	free energy change (kJ/mol)
ΔH	enthalpy change (kJ/mol)
k_2	pseudo-second order rate constant of sorption (g/mg min)
K_a	constant related to the affinity of the binding sites (L/mg)
K_c	the equilibrium constant
K_F	adsorption capacity $[(mg/g)(mg/L)^{-1/n}]$
K_i	intraparticle rate constant $(mg/g\ min^{1/2})$
K_{RP}	Redlich-Peterson isotherm constant (L/g)
n	adsorption intensity
q	amount of adsorbed dye on the surface of the adsorbent at any time t (mg/g)
q_{eq}	the amount of adsorbed dye per unit weight of biomass at equilibrium (mg/g)
q_{cal}	calculated amount of adsorbed dye per unit weight of biomass at equilibrium (mg/g)
q_{exp}	experimental amount of adsorbed dye per unit weight of biomass at equilibrium (mg/g)
Q^o	maximum amount of the dye per unit weight of biomass to form a complete monolayer on the surface bound at high C_{eq} (mg/g)
R	the universal gas constant, 8.314 (J/mol K)
R^2	correlation coefficient
ΔS	entropy change (kJ/mol K)
T	absolute temperature (K)
X	biosorbent concentration (g/L)
β	exponent in Redlich-Peterson isotherm

direct interaction between the biosorbent and the dye adsorbate. Biosorption is a promising potential alternative to conventional processes for the removal of dyes. However, these technologies are still being developed and much more work is required [23]. The major advantages of biosorption technology are its effectiveness in reducing the concentration of dyes to very low levels and the use of inexpensive biosorbent material [23]. The use of dead rather than living biomass eliminates the problems of waste toxicity and nutrient requirements. Dyes vary greatly in their chemistries and their interactions with microorganisms depend on the chemistry of a particular dye [19,23]. There is also limited information available on the interactions between biomass and dyes [23]. The precise binding mechanisms may range from physical (i.e. electrostatic or Van der Waals forces) to chemical binding (i.e. ionic and covalent) [23]. Many of the studies to date on metal biosorption by seaweeds have largely been restricted to various species of brown and green seaweeds [24]. On the other hand, the seaweeds and freshwater algae species have not been evaluated the dye biosorption to any great extend. Algae have been found to be potential suitable biosorbents because of their cheap availability both in fresh or saltwater, relatively high surface area and high binding affinity [25,26]. Biosorption on algae has mainly been attributed to the cell wall properties where both elecrostatic attraction and complexation can play a role [27]. Algae cell surface is naturally formed by various chemical groups such as hydroxyl, carboxylate, amino and phosphate which are believed to be responsible for the sequestration of unwanted materials from effluents. Moreover, most of the algal cells are often covered by micilaginous layers characterised by a significant adsorption capacity due to the presence of alginate constituting 14–40% of the dry weight of the biomass [28].

Since little is known on the biosorption of acidic dyes to green algae on growing fresh water, *Spirogyra rhizopus*, the biosorptive properties of the algae for Acid Blue 290 and Acid Blue 324 dyes were investigated in a batch system; the equilibrium, kinetic and thermodynamic parameters were determined.

2. Material and methods

2.1. Algal biomass

The alga was obtained from a fresh water channel in Mersin, Turkey and identified as *Spirogyra rhizopus*. *Spirogyra* species was of isagamous filamentous green algae and appears as an elongated thread or filament composed of cylindrical cells. *Spirogyra* belongs to chlorophyta class having plastide pigment with a starch grain characteristic. Flagellas is absent in *Spirogyra* [29]. *Spirogyra rhizopus* after collecting from the channel was washed twice with tap water in order to remove adhering insect larvae, soil, etc. It was dried in sunlight and then in an oven at 105 °C for 24 h until all the moisture was evaporated, put in distilled water and blended to obtain larger surface area. A stock solution of 10 g/L of biosorbent was prepared.

2.2. Dye solutions

CI Acid Blue 290 (Telon Blue A3GL) and CI Acid Blue 324 (Telon Blue BRL micro) dyes were supplied from DyStar. The test solutions containing Acid Blue 290 and Acid Blue 324 dyes were prepared by diluting 1.0 g/L of stock solution of dyes which were obtained by dissolving weighed amount of AB 290 and AB 324 in 1 L of distilled water. Higher dye concentration in solution was obtained by dissolving weighed amount of each dye. The initial pH of solution was adjusted to the required value with concentrated and diluted H_2SO_4 and NaOH solutions before mixing the biomass suspension.

2.3. Batch studies

The biosorption experiments were conducted in 250 mL Erlenmayer flasks containing 100 mL of biosorption solution.

Ten milliliters of stock biosorbent solution, except for the biosorbent concentration experiments, was contacted with 90 mL of dye solution at known initial dye concentration and initial pH in an Erlenmayer flask and then the flasks were agitated at a constant temperature and shaking rate for 60 min, which is more than ample time for biosorption equilibrium. Samples (5 mL) were taken before mixing the algae solution and dye bearing solution and at pre-determined time intervals (0, 0.5, 5, 10, 15, 20, 30, 45 and 60 min) for the residual dye concentration in the solution. Samples were centrifuged at 3500 rpm for 5 min and the supernatant liquid was analysed. All of the experiments were carried out in duplicates and the average values were used in calculations.

2.4. Dye concentration analysis

The concentration of dye remaining in the solution were measured colourimetrically using a spectrophotometer (JASCOV-530 UV/VIZ). The absorbance values for AB 290 and AB 324 were read at 409 nm and 716 nm, respectively. Then, dye concentration was calculated from a calibration curve of absorbance versus concentration. The adsorbed dye amount at equilibrium, q_{eq} (mg/g), was computed as follows:

$$q_{eq} = \frac{C_o - C_{eq}}{X} \quad (1)$$

where C_o and C_{eq} are the initial and equilibrium dye concentration (mg/L) and X is the biosorbent concentration in solution (g/L).

3. Results and discussion

3.1. Determination of optimum biosorption conditions

3.1.1. The effect of initial pH

Initial pH is one of the most important environmental factors influencing not only site dissociation, but also the solution chemistry of the dyes: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation are strongly influenced by pH and, on the other side, strongly influence the speciation and the adsorption availability of the dyes. Fig. 1 shows the effect of initial pH on the biosorption of AB 290 and AB 324 dyes on *S. rhizopus* at temperature 25 °C, biosorbent concentration of 1.0 g/L and initial dye concentration of 100 mg/L. The optimum initial pH values for AB 290 and AB 324 biosorption were determined to be 2.0 and 3.0, respectively. The adsorbed AB 290 and AB 324 amounts at the optimum initial pH were obtained as 66.40 mg/g and 46.88 mg/g, respectively. This can be explained on the basis of zero point discharge for biomass. For the algal biomass, the isoelectric point would be at a pH of 3.0 [30]. In the aqueous solution, the acid dye is first dissolved and the sulfonate groups of the acid dye (D-SO_3Na) are dissociated and converted to anionic dye ions [2,31]:

$$\text{D-SO}_3\text{Na} \xrightarrow{\text{H}_2\text{O}} \text{D-SO}_3^- + \text{Na}^+ \quad (2)$$

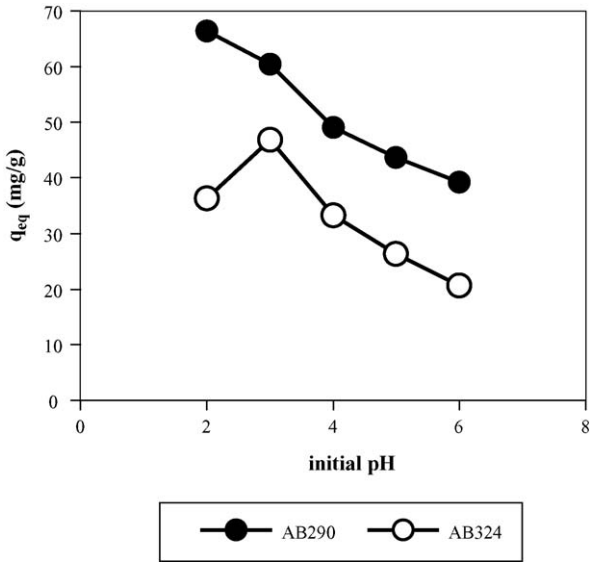

Fig. 1. The effect of initial pH on the equilibrium uptake capacity of *S. rhizopus* for AB 290 and AB 324 (X = 1.0 g/L, temperature 25 °C, agitation rate 150 rpm, C_o = 100 mg/L).

At the isoelectric point, electrostatic repulsion between adsorbed molecules is at a minimum. These molecules have higher structural stability, and therefore a smaller tendency to spread at the interface resulting maximum adsorption at isoelectric point. However, several investigators observed that maximum adsorption occurred at pHs below this point. At lower pH below the isoelectric point, the surface of algae may acquire a positive charge leading to increased anionic dye (direct, acidic, reactive) uptake due to the electrostatic force of attraction, as was observed for the biosorption of AB 290 dye on *S. rhizopus*. As the pH of the system increases, the number of negatively charged sites increases. A negatively charged surface site on the biosorbent does not favour the adsorption of dye anions due to the electrostatic repulsion [32]. The decrease in uptake amount of AB 324 on *S. rhizopus* below the isoelectric point can be explained by the increase in conformational size of molecules and the lateral electrostatic repulsions between adjacent adsorbed molecules [33].

3.1.2. The effect of the temperature

The equilibrium uptakes as a function of temperature at optimum initial pH values, biosorbent concentration of 1.0 g/L and initial dye concentration 100 mg/L are given in Fig. 2 for the studied dyes. The equilibrium uptakes increased with increasing temperature up to 30 °C for AB 290 and 25 °C for AB 324 and then decreased. An increase of the equilibrium uptake up to 30 °C for AB 290 and 25 °C for AB 324 deals with an increase in the biosorption capacity of *S. rhizopus* at equilibrium. The decrease of the equilibrium uptakes with further increase in temperature means that the dye biosorption process is exothermic. If adsorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in adsorption capacity. Temperature could influence the desorption step and consequently the reversibility of the adsorption equilibrium [34]. In general, an increase in temperature is followed by an

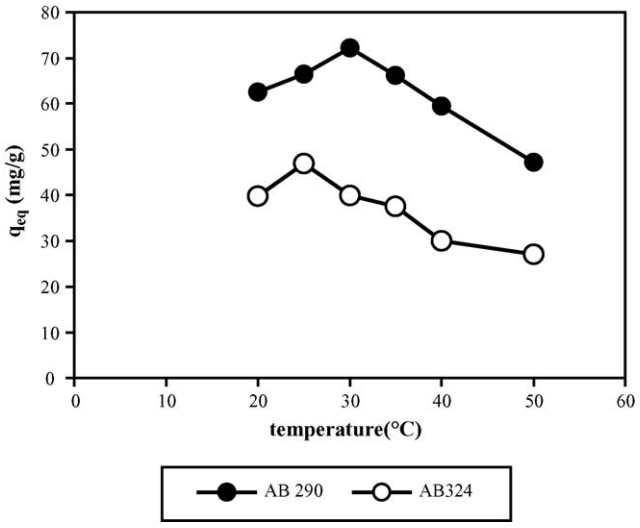

Fig. 2. The effect of temperature on the equilibrium uptake capacity of *S. rhizopus* for AB 290 and AB 324 (initial pH 2.0 for AB 290 initial pH 3.0 for AB 324, $X = 1.0$ g/L, $C_o = 100$ mg/L, agitation rate 150 rpm).

increase in the diffusivity of the ion, and consequently by an increase in the adsorption rate if diffusion is the rate controlling step [34].

3.1.3. The effect of the initial dye concentration

The effect of initial dye concentration on AB 290 and AB 324 biosorption by *S. rhizopus* was investigated in the range of 20–3000 mg/L of the initial dye concentrations at biosorbent concentration of 1.0 g/L, temperature of 25 and 30 °C, and initial pH 2.0 and 3.0 for AB 290 and AB324, respectively. The variation of the uptake values with initial dye concentrations were depicted in Fig. 3. The uptake amounts increased with increasing initial dye concentrations up to 1500 mg/L for AB 290 and 750 mg/L for AB 324 and then was not changed by further increase in initial dye concentrations suggesting that available sites on the biosorbent are the limiting factor for dye biosorption. The biosorption yields [$Y\% = ((C_o - C)/C_o) \times 100$] of AB 290 and AB 324 dyes on *S. rhizopus* decreased from 71.0% to 45.0% and from 45.4% to 41.9%, respectively, while the adsorbed AB 290 and AB 324 amounts increased from 212 to 670 mg/g and from 139.8 to 318.0 mg/g, respectively, with increasing initial dye concentration from 300 to 1500 mg/L.

3.1.4. The effect of the biosorbent concentration

The effect of biosorbent concentration on the dye uptake capacity of *S. rhizopus* was investigated for five different biosorbent concentrations in the range of 0.5–3.0 g/L and the adsorbed AB 290 and AB 324 amounts on *S. rhizopus* were given in Fig. 4, at initial dye concentration of 100 mg/L, temperature of 25 and 30 °C, and initial pH 2.0 and 3.0 for AB 290 and AB324, respectively. The adsorbed AB 290 concentration increased from 42.22 to 87.13 mg/L, while the adsorbed AB 290 amount per unit biomass weight decreased from 84.44 to 29.04 mg/g by increasing the biosorbent concentration from 0.5 to 3.0 g/L. The same trend was also observed for AB 324 biosorption. It is readily understood that the number of available adsorption sites increases with an increase in biosorbent concentration and it, therefore results in the increase of adsorbed dye concentration. In fact, in the presence of a high biomass concentration there is a very fast superficial adsorption onto the cells that produces a lower dye concentration in solution than when the cell concentration is lower [30]. The decrease in the q_{eq} values at high biosorbent concentrations can be explained that the dye molecules will prefer to attach themselves on the biosorbent particles on their flat face, as this orientation requires the minimum energy while the high uptake values (q_{eq}) at low biosorbent concentrations could be attributed to adsorption of dye perpendicular to the solid surface [35]. As a result, a purification process involving low biosorbent concentration may be suggested for the desired purification since higher uptake values were obtained at low biosorbent concentrations.

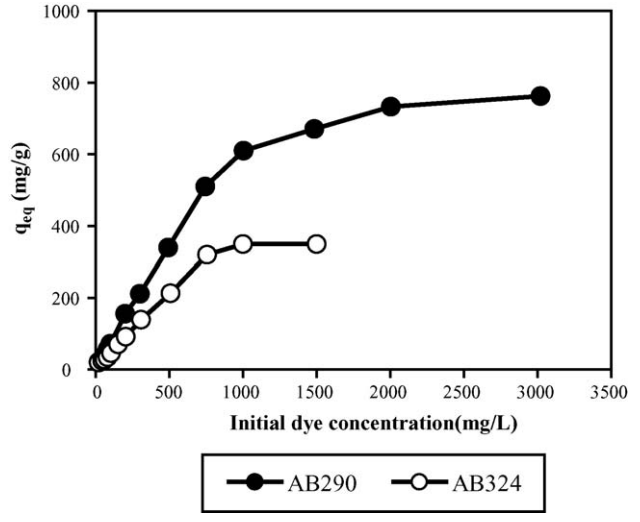

Fig. 3. The effect of initial AB 290 and AB 324 concentration on the equilibrium uptake capacity of *S. rhizopus* (initial pH 2.0 and temperature 30 °C for AB 290, initial pH 3.0 and temperature 25 °C for AB 324, $X = 1.0$ g/L, agitation rate 150 rpm).

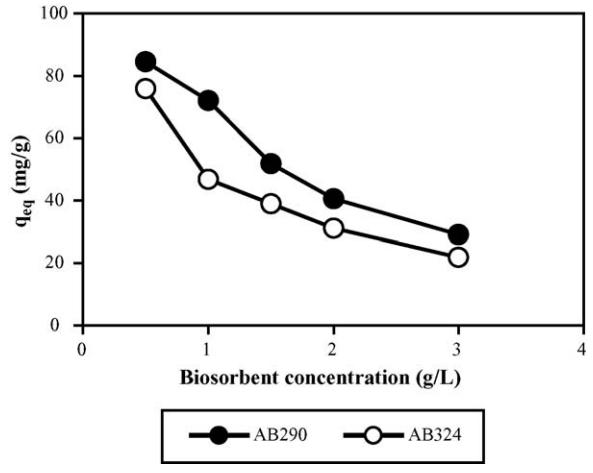

Fig. 4. Effect of biosorbent concentration on the equilibrium uptake capacity of *S. rhizopus* for AB 290 and AB 324 (initial pH 2.0 and temperature 30 °C for AB 290, initial pH 3.0 and temperature 25 °C for AB 324, $C_o = 100$ mg/L, agitation rate 150 rpm).

3.2. Equilibrium modelling

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption system [36]. Equilibrium studies in adsorption give the capacity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium [36]. By plotting solid phase concentration (mg/g) against liquid phase concentration (mg/L) graphically it is possible to depict the equilibrium adsorption isotherms.

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation and the well-known expression of the Langmuir model is given by Eq. (3):

$$q_{eq} = \frac{Q^o K_a C_{eq}}{1 + K_a C_{eq}} \quad (3)$$

where q_{eq} (mg/g) and C_{eq} (mg/L) are the amount of adsorbed dye per unit weight of biomass and unadsorbed dye concentration in solution at equilibrium, respectively. Q^o is the maximum amount of the dye per unit weight of biomass to form a complete monolayer on the surface bound at high C_{eq} (mg/L) and K_a is a constant related to the energy of adsorption (L/mg). Q^o represents a practical limiting adsorption capacity when the surface is fully covered with dye molecules and it assists in the comparison of adsorption performance, particularly in cases where the adsorbent did not reach its full saturation in experiments.

The Freundlich expression (Eq. (4)) is an exponential equation:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (4)$$

In this equation, K_F and $1/n$ are the Freundlich constants indicating adsorption capacity and intensity, respectively.

The three parameter Redlich-Peterson equation has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by Eq. (5).

$$q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^{\beta}} \quad (5)$$

where K_{RP}, a_{RP} and β are the Redlich-Peterson parameters. β lies between 0 and 1. For $\beta = 1$ Eq. (5) converts to the Langmuir form [3,37]. The three parameter Redlich-Peterson isotherm was evaluated using non-linear least squares method.

Koble-Corrigan model is another three-parameter empricial model for the representing equilibrium biosorption data. It is a combination of the Langmuir and Freundlich isotherm type models and is given by:

$$q_{eq} = \frac{A\, C_{eq}^n}{1 + B\, C_{eq}^n} \quad (6)$$

where A, B and n are the Koble-Corrigan parameters. This model is valid when $n > 1$ [38].

Generally, the Langmuir isotherm model is applied to experimental adsorption data in order to investigate the maximum monolayer adsorption capacity of adsorbent/biosorbent while Freundlich isotherm model described better the adsorption from aqueous solutions [31]. Redlich-Peterson and Koble-Corrigan isotherm models are applied to improve the fit for a wide range of initial adsorbate concentration.

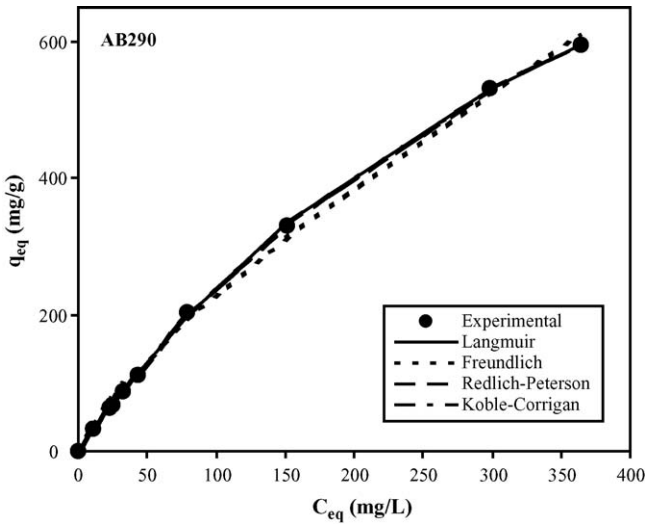

Fig. 5. Comparison of the experimental and predicted isotherms for AB 290 biosorption (initial pH 2.0, temperature 30 °C, agitation rate 150 rpm).

In this study, The Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models were applied to the equilibrium data of the biosorption of AB 290 and AB 324 dyes on *S. rhizopus* at optimum initial pH and temperature values. The experimental and predicted isotherms for AB 290 and AB 324 biosorption were given in Figs. 5 and 6, respectively. The isotherm constants were determined using nonlinear regression programme of Polymath 4.1 software which uses Levenberg-Marquardt algorithm for finding the parameter values which minimize the sum of the squares of the errors (ERRSQ) and were presented in Table 1. As can be seen from Table 1, Q^o values of *S. rhizopus* were determined to be 1356.6 and 367.0 mg/g for AB 290 and AB 324 dyes, respectively. It was observed that the uptake capacity of *S. rhizopus* for AB 290 was higher

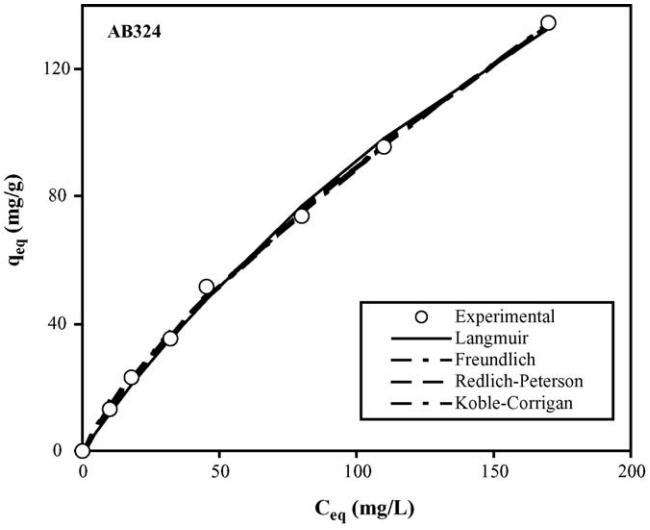

Fig. 6. Comparison of the experimental and predicted isotherms for AB 324 biosorption (initial pH 3.0, temperature 25 °C, agitation rate 150 rpm).

Table 1
The parameters obtained from the isotherm models for AB 290 and AB 324 biosorption

	Langmuir			
	Q^o (mg/g)	b (L/mg)		ERRSQ
AB 290	1356.60	0.00125		61.92
AB 324	367.00	0.00332		44.05
	Freundlich			
	K_F (mg/g)/(mg/L)$^{1/n}$	n		ERRSQ
AB 290	6.78	1.31		1172.70
AB 324	2.47	1.29		20.45
	Redlich-Peterson			
	$K_{R\text{-}P}$ (L/mg)	$a_{R\text{-}P}$ (L/mg)$^{\beta}$	β	ERRSQ
AB 290	2.94	0.0024	0.998	61.74
AB 324	2.55	0.3540	0.358	18.51
	Koble-Corrigan			
	A (L^n mg^{1-n}/g)	B (L/mg)^n	n	ERRSQ
AB 290	2.938	0.00215	0.998	0.6188
AB 324	2.245	0.0012	0.810	19.63

than AB 324, resulting in structural differences of this two dyes. q_{eq} values were found to be smaller than Q^o indicating that the biosorption of AB 290 and AB 324 dyes on *S. rhizopus* is by a monolayer type adsorption. The magnitude of K_F and n shows easy separation of AB 290 and AB 324 dyes from aqueous solutions with high adsorptive capacity of *S. rhizopus*. Regarding that ERRSQ is a criterion of how experimental data fits theoretical isotherms, one can say that Koble-Corrigan isotherm model for the biosorption of AB 290 and Redlich-Peterson isotherm model for the biosorption of AB 324 defined best with respect to other isotherm models, where the lowest values of ERRSQ were obtained for both dye–biomass systems studied.

The adsorption capacity of *S. rhizopus* was relatively high when compared with other adsorbents/biosorbents used for the anionic dyes in the literature. For example, Acid orange 7 removal capacity of spent brewery grains was determined as 30.47 mg/g [39], the maximum uptake value of Basic green 4 on sugarcane dust was determined as 20.6 mg/g [40], the maximum monolayer coverage capacities of *E. prolifera* for Acid Red 324 and Acid Red 337 biosorption were found as 210.87 and 160.59 mg/g, respectively [41]. Differences between dye uptake values are due to the properties of adsorbent such as structure, functional groups, surface area and solution chemistry.

3.3. Biosorption mechanism

If the movement of dye from the bulk liquid to the liquid film surrounding the adsorbent is ignored, the adsorption process in porous solids can be separated into three stages: the first stage is diffusion through the solution to the external surface of the adsorbent and also called film mass transfer or boundary layer diffusion of solute molecules. The second stage is diffusion within the pores or capillaries of the adsorbent internal structure to the sorption sites where the third stage of rapid uptake occurs [41]. The last step is assumed to be rapid while steps 1 and 2 are the rate determining steps, either singly or in combination. In order to investigate the mechanism of dye biosorption and potential rate-controlling steps such as external mass transfer, intraparticle diffusion and adsorption processes and also for design purposes, mass transfer model (Weber-Morris model) and kinetic model (the pseudo-second order kinetic model) have been used to test the experimental data.

3.3.1. Intraparticle diffusion model (Weber-Morris model)

In a diffusion controlled adsorption process, the adsorbed amount of the solute varies almost proportionately with a function of retention time, $t^{1/2}$ as early mentioned by Weber and Morris:

$$q = K_i t^{1/2} \tag{7}$$

According to this model, the plot of uptake (q) versus the square root of time should be linear if intraparticular diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. In many cases, an initial steep-sloped portion indicating external mass transfer is followed by a linear portion to the intraparticle diffusion and plateau which represents the final equilibrium stage where the intraparticular diffusion starts to slow down due to exteremely low solute concentration in the solution and surface.

In this part of study, Weber-Morris model was applied to the biosorption of AB 290 and AB 324 on *S. rhizopus* as a function of the initial dye concentration and the variations of q versus $t^{1/2}$ were given in Fig. 7 for AB 290 and Fig. 8 for AB 324. The linear portions of the curves do not pass through the origin indicating that the mechanism of AB 290 and AB 324 biosorption on *S. rhizopus* is complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process. The deviation of straight lines from the origin can

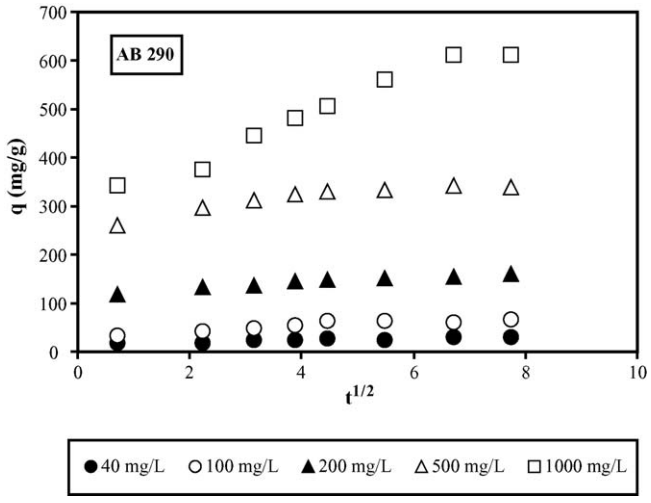

Fig. 7. Plots for the intraparticle diffusion for the biosorption of AB 290 at different initial dye concentrations (initial pH 2.0, temperature 30 °C, agitation rate 150 rpm).

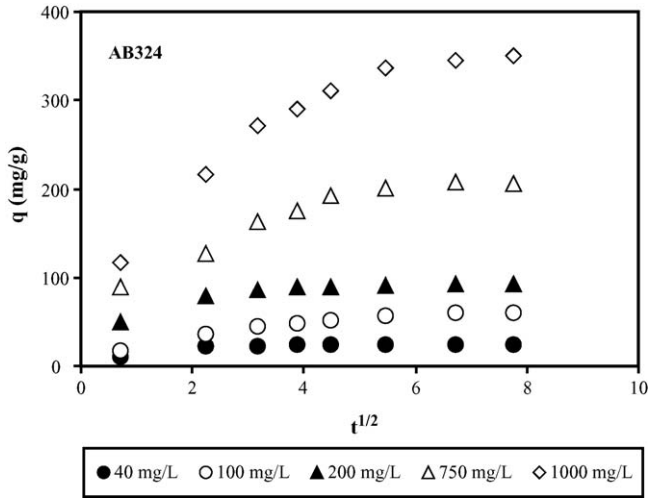

Fig. 8. Plots for the intraparticle diffusion for the biosorption of AB 324 at different initial dye concentrations (initial pH 3.0, temperature 25 °C, agitation rate 150 rpm).

be explained by the difference between the rate of mass transfer in the initial and final stages of adsorption [2]. In this state, Weber-Morris equation can be written as $q = K_i t^{1/2} + I$. It shows clearly that the uptake values are composed of two contributions, intraparticle and external diffusion. The intercepts (I) and the intraparticle rate constant values calculated from the slopes of the linear portions of the plots of Figs. 7 and 8 were presented in Table 2 for AB 290 and Table 3 for AB 324. As can be seen from these tables, the K_i values and intercepts increased with increasing initial dye concentrations and the R^2 values are close to unity indicating the applicability of this model. The increasing trend of intraparticle rate constant values with initial dye concentrations was reported before by various investigators [1,10]. The observed increase in K_i values with increasing initial dye concentration can be explained by the growing effect of driving force, the concentration gradient. Values of intercept give an idea about the thickness of the boundary layer, i.e., the larger intercept the greater is the boundary layer effect [2]. As can be seen from Tables 2 and 3, K_i values obtained for AB 324-*S. rhizopus* biosorption system were greater than those obtained for AB 290-*S. rhizopus* biosorption system suggesting that intraparticle diffusion is more effective on the biosorption mechanism of AB 290 on *S. rhizopus*. Additionally, diffusion rate of AB 324 in biosorbent is faster than that of AB 290, and this means that AB 324 is more easily diffused and transported into pore of biosorbent. Contrary to the intraparticle rate constant values, the intercept values for AB 290 were higher than those obtained for AB 324 indicating that the effect of the external mass transfer resistance on the AB 290 biosorption was low. It is clear that the external mass transfer resistance cannot be neglected,

Table 2
The parameters obtained from the pseudo-second order kinetic model and intraparticle difusion model (W&M) for AB 290 biosorption

C_o (mg/L)	Pseudo-second order kinetic model				Weber-Morris model		
	q_{exp} (mg/g)	q_{cal} (mg/g)	k_2 (g/mg min)	R^2	K_i (mg/g min$^{1/2}$)	Intercept (I)	R^2
40	29.05	29.94	0.0137	0.994	3.29	12.41	0.959
100	66.40	67.11	0.0066	0.993	8.72	22.89	0.959
200	161.67	161.29	0.0045	0.999	8.65	110.61	0.986
500	338.20	344.83	0.0042	0.999	15.21	263.33	0.984
1000	644.28	666.67	0.000351	0.991	49.41	288.20	0.997

Table 3
The parameters obtained from the pseudo-second order kinetic model and intraparticle diffusion model (W&M) for AB 324 biosorption

C_o (mg/L)	Pseudo-second order kinetic model				Weber-Morris model		
	q_{exp} (mg/g)	q_{cal} (mg/g)	k_2 (g/mg min)	R^2	K_i (mg/g min$^{1/2}$)	Intercept (I)	R^2
40	24.15	24.04	0.1408	0.999	7.83	4.88	1.000
100	59.92	63.29	0.0045	0.997	11.00	10.28	0.999
200	93.20	94.34	0.01306	0.999	15.44	40.37	0.952
750	207.36	217.39	0.00084	0.999	27.77	69.02	0.993
1000	350.10	370.37	0.00089	0.998	52.11	90.11	0.975

although this resistance is only significant for the initial period of biosorption time.

3.3.2. Pseudo-second order kinetic model

Information on the kinetics of dye uptake is required for selecting optimum operating conditions for full-scale batch dye removal processes [42]. Mathematical models that can describe the behaviour of a batch biosorption process operated under different experimental conditions are very useful for scale-up studies or process optimisation [42]. The mechanism involved in the dye removal is assumed basically, to be complexation and ion exchange. The simplest way to describe the kinetics of dye removal, in the absence of stoichiometric data, can be represented as:

$$\text{Dye} + X \Leftrightarrow \text{dye} \ldots X \tag{8}$$

where dye represents the dissolved dye concentration, X is the available surface sites and dye $\ldots X$ is the adsorbed state. If the rate of sorption is a second-order mechanism, the pseudo-second order kinetic model is expressed as [43,44]:

$$\frac{dq}{dt} = k_2(q_{eq} - q_t)^2 \tag{9}$$

where k_2 is the pseudo-second order biosorption rate constant (g mg^{-1} min^{-1}), q_{eq} and q_t are the adsorbed amount per unit mass at equilibrium and any time, respectively. For the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$ the integrated and linear form of Eq. (9) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{10}$$

If pseudo-second order kinetics are applicable, the plot of t/q_t against t of Eq. (10) should give a linear relationship, from which q_{cal} and k_2 can be determined from the slope and intercept of the plot.

The pseudo-second order kinetic model was applied to the biosorption data of AB 290 and AB 324 on *S. rhizopus* at the different initial dye concentrations and the rate constants, the experimental and calculated q_{eq} values and correlation coefficients were given in Table 2 for AB 290 and Table 3 for AB324. As can be seen from Tables 2 and 3, the pseudo-second order rate constant values decreased with increasing initial dye concentration and the correlation coefficients of all concentrations studied were also found very high. The variations of experimental and predicted q_t values with time were given in Fig. 9 for AB 290 and Fig. 10 for AB 324. The adequate fitting of calculated (q_{cal}) and experimental (q_{exp}) values for the whole studied range of the initial dye concentration suggest the applicability of pseudo-second order kinetic model to these biosorption systems.

3.4. Determination of thermodynamic parameters

Thermodynamic parameters such as enthalpy change (ΔH), free energy change (ΔG) and entropy change (ΔS) can be estimated using equilibrium constants changing with temperature. The free energy change of the sorption reaction is given by the following equation:

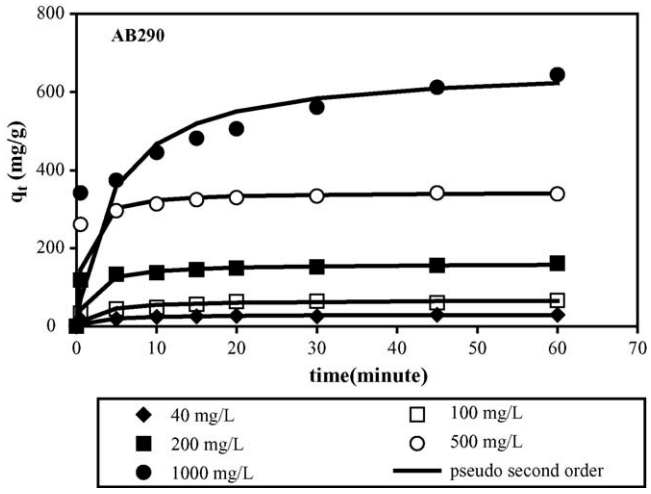

Fig. 9. AB 290 uptake by *S. rhizopus* according to the pseudo-second order kinetic model at different initial dye concentrations (initial pH 2.0, temperature 30 °C, agitation rate 150 rpm).

$$\Delta G = -\text{RT ln } K_c \tag{11}$$

where ΔG is free energy change, J/mol; R is universal gas constant, 8.314 J/mol K and T is absolute temperature, K. The free energy change indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [45]. The equilibrium constant of biosorption is defined as:

$$K_c = \frac{C_{ad,e}}{C_{eq}} \tag{12}$$

where $C_{ad,e}$ is the amount of dye adsorbed on the adsorbent per liter of the solution at equilibrium (mg/L), C_{eq} is the equilibrium concentration. If biosorbent concentration is 1.0 g/L, $C_{ad,e}$ is equal to q_{eq} at a given temperature. The K_c values for the

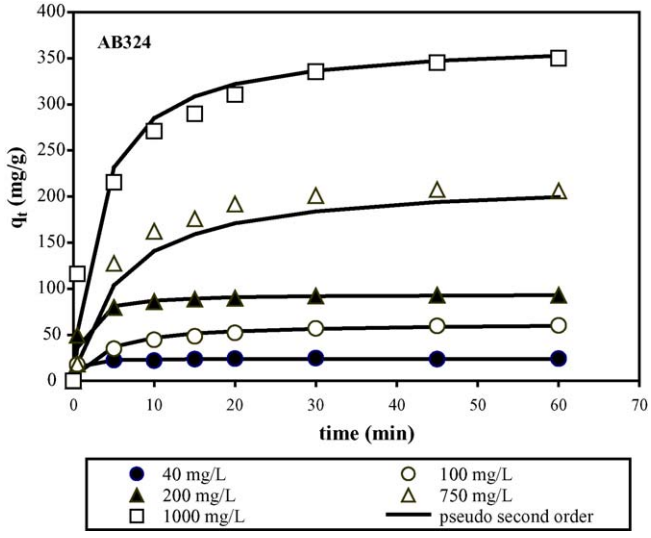

Fig. 10. AB 324 uptake by *S. rhizopus* according to the pseudo-second order kinetic model at different initial dye concentrations (initial pH 3.0, temperature 25 °C, agitation rate 150 rpm).

biosorption of AB 290 and AB 324 dyes on *S. rhizopus* were found as 1.83, 1.32, 1.06 and 0.77 at 30, 35, 40 and 50 °C and 1.144, 0.734, 0.547, 0.414 and 0.310 at 25, 30, 35, 40 and 50 °C at 100 mg/L of the initial dye concentration, respectively. The K_c values decreased with increasing temperature resulting a shift of the adsorption equilibrium to the left for both biosorption systems. The free energy change can be represented as follows:

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

According to Eq. (13), a plot of free energy change versus temperature (K) is linear and the enthalpy and entropy change values are determined from the slope and intercept of the plot [40]. The enthalpy and entropy change values for the biosorption of AB 290 and AB 324 dyes on *S. rhizopus* were found to be −33.9 kJ/mol, −107.4 J/mol K ($R^2 = 0.98$) and −40.8 kJ/mol, −136.9 J/mol K ($R^2 = 0.97$), respectively. The effect of temperature on the equilibrium constant K_c is determined by the sign of ΔH. The negative value of ΔH shows that the biosorption of AB 290 and AB 324 dyes on *S. rhizopus* is exothermic in nature, an increase in T causes a decrease in K_c. The negative ΔS value corresponds to a decrease in randomness at the solid/liquid interface during the adsorption of dye on biosorbent while low value of ΔS indicates that no remarkable change on entropy occurs. The free energy changes for AB 290 and AB 324 biosorption processes were obtained as −1.36 and −0.0038 kJ/mol at optimum biosorption temperatures, respectively. Generally, the change of free energy for the physical and chemical adsorption are in the range of 0 to −20 kJ/mol and −80 to −400 kJ/mol, respectively [35]. As a result, it can be said that the biosorption of AB 290 and AB 324 on *S. rhizopus* occurred by the physical adsorption.

4. Conclusion

The equilibrium and kinetic analysis of the biosorption of two acidic dyes AB 290 and AB 324 on *S. rhizopus* has been investigated. *S. rhizopus* appeared to be effective for the removal of these acidic dyes from aqueous solutions. The optimum biosorption conditions were determined as the initial pH 2.0 and temperature 30 °C for AB 290 and the initial pH 3.0 and temperature 25 °C for AB 324 at the initial dye concentration 100 mg/L, biosorbent concentration 0.5 g/L. The Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models were applied to the equilibrium data. The monolayer adsorption capacity of *S. rhizopus* was obtained as 1356.6 for AB 290 and 367.0 mg/g for AB 324 dyes. It was observed that the biosorption data of AB 290 and AB 324 dyes fitted well to Koble-Corrigan and the Redlich-Peterson models than the other isotherm models according to ERRSQ analysis. Weber-Morris model equation was applied to the experimental data for initial dye concentrations for the two dyes. It was observed that K_i values decreased with increasing initial dye concentrations. The pseudo-second order kinetic model describes the biosorption process with a good fitting. Determination of thermodynamic parameters such as enthalpy, entropy and Gibb's free energy changes showed the reversible and exhotermic nature of the biosorption of AB 290 and AB 324 by *S. rhizopus*.

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