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Removal of eosin Y and eosin B dyes from polluted water through biosorption using Saccharomyces cerevisiae: Isotherm, kinetic and thermodynamic studies

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ABSTRACT

Biosorption of two anionic dyes, eosin Y and eosin B, from aqueous solution using Saccharomyces cerevisiae was investigated in a batch mode. The influence process parameters such as contact time, initial dye concentration, sorbent dosage, pH and temperature of aqueous solution were studied. The maximum adsorption capacities were found to be at 200 and 100 mg g^{-1} for eosin Y and 1 eosin B, respectively. The Langmuir and Temkin model were found to be appropriate for the description of biosorption process of eosin Y and eosin B, respectively. The pseudo-second order kinetic model fitted well in correlation to the experimental results for both dyes. Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) were also investigated. Thermodynamic studies indicated that biosorption of both dyes onto S. cerevisiae was an endothermic process. The negative values of free energy change showed that the biosorption of both dyes was spontaneous at the temperatures under investigation. These results indicate that biomass S. cerevisiae particles with clean surface and high porosity are an interesting alternative for dye removal from the wastewater effluents.

1. Introduction

Many industries, such as textile, paper, plastics and dyestuffs, consume substantial volume of water, and also use chemicals during manufacturing and dyes to color their products. As a result, they generate a considerable amount of polluted wastewater (Crini and Badot. 2008). Color is a visible pollutant and presence of even very minute amount of coloring substance makes it undesirable due to its appearance (Kumara and Porkodi. 2007). Generally, dyes are stable to light, heat and oxidizing agents, and are usually biologically non-degradable (Crini and Badot. 2008). Eosin Y and eosin B coal tar xanthene dye, which used extensively in the printing and dyeing industries was chosen as the model anionic dye to avoid environmental hazards during investigation, as this dye is not specifically listed as toxic by different health agencies (Chatterjee et al. 2005).

The removal of color arising from the presence of the water-soluble reactive dyes is a major problem due to the difficulty in treating such wastewaters by conventional treatment methods (Ghouti et al. 2009). Dye wastewater is usually treated by physical or chemical treatment processes. These include flocculation combined with flotation, electroflocculation, membrane filtration, electrokinetic coagulation, electrochemical destruction, ion-exchange, irradiation, precipitation, ozonation, and katox treatment method involving the use of activated carbon and air mixtures (Srinivasan and Viraraghavan. 2010). Although they can remove dyes partially, their initial investment and operational costs are so high that they can be widely used in dyeing and finishing industries, especially in developing countries (Aksu and Tezer. 2000). Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in wastewater treatment (Gupta and Suhas. 2009). Studies have shown that activated carbons are good materials for the removal of different types of dyes in general but their use is sometimes restricted in view of higher cost. Also, the activated carbons after their use (treatment of wastewater) become exhausted and are no longer capable of further adsorbing the dyes (Gupta and Suhas. 2009). However, because of the cost involved search for alternative adsorbent that could provide an economical solution is very important in developing countries (Ponnusami. 2007). Many studies have been undertaken to investigate the use of low-cost adsorbents such as biosorbent (Aksu. 2003; Crini and Badot. 2008; Fu and Viraraghavan. 2002a; Fu and Viraraghavan. 2002b), fly ash (Gupta. 2000), rice husk (Ponnusami. 2007), tea waste (Hameed. 2009), palm ash (Ahmad. 2007), agricultural waste (Hameed and Daud. 2008). The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials is termed biosorption. In this instance, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing sorbents in order to concentrate and to remove dyes from solutions. These biosorbents and their derivatives contain a variety of functional groups which can complex dyes. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to μg l^{-1} levels. Biosorption is a novel approach, competitive, effective and cheap (Crini. 2006). Among the promising biosorbents for heavy metal and dyes removal which have been researched during the past decades, Saccharomyces cerevisiae has received increasing attention due to the unique nature in spite of its mediocre capacity for metal and dye uptake. Compared with other fungi, S. cerevisiae is widely used in beverage production, is easily cultivated using cheap media, is also a

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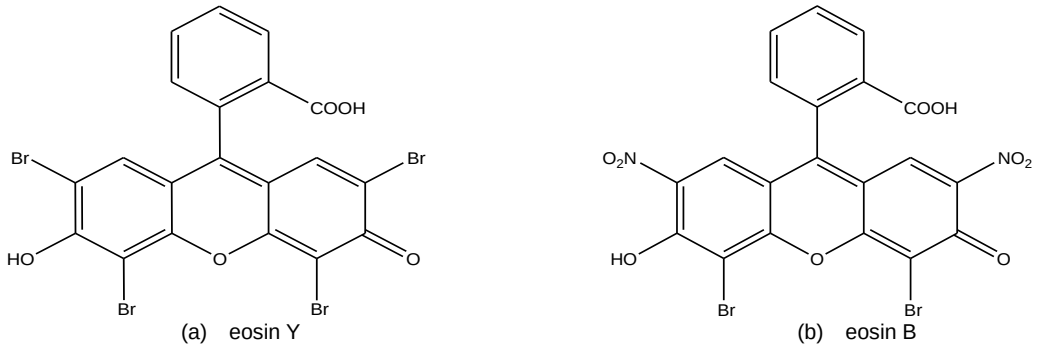
by-product in large quantity as a waste of the fermentation industry, and is easily manipulated at molecular level (Wang and Chen. 2006).

In the present study, biosorption techniques are employed for removal of eosin Y and B by S. cerevisiae yeast from aqueous solution. The effects of temperature, pH, initial dye concentration and sorbent dosage on biosorption were investigated. Moreover, the biosorption isotherms, kinetics and thermodynamic were also explored.

2. Materials and methods

2.1. Materials

The anionic dyes used in this study were eosin Y and eosin B that molecule structure of the dye is shown in Fig. 1. The dye eosin Y and eosin B were obtained from Merck, Germany. Stock dye solutions were prepared by dissolving 1.00 g of dyes in 1 L of double distilled water. All working solutions were prepared from the stock solutions by further dilution. The NaOH pellets and HCl solution used for adjusting of pH were obtained from Merck, Germany.



(a) eosin Y (b) eosin B

Fig.1. Structure of (a) eosin Y (b) eosin B.

2.2. Preparation of the biosorbent

S. cerevisiae was provided from Research and Technology Department of Ministry of Sciences (Persian Type Culture Collection) in the form of freeze dry, and then cultured in sterilized medium. The composition of growth medium was (grams per liter): glucose, 15; $(NH4)_2SO_4$, 9; $MgSO_4$, 2.5; yeast extract, 1; KH_2PO_4, 1; K_2HPO_4, 0.2. The medium was sterilized by autoclaving at a pressure of 1.5 atm and temperature of 121 ºC for 20 min. The yeast cells were grown for 16 h and then filtered. Yeast biomass was deactivated by heating in an oven at 80 ºC for 24 h. The dried yeast was ground and screened through a sieve with 100 mesh. The pretreatment of the biosorbent was carried out with nonviable yeast cells in 700 g L^{-1} ethanol solution 20 min at room temperature. Then, it was centrifuged at 3600 rpm for 10 min and the ethanol solution was discarded. The ethanol washed biomass was rinsed several times with de-ionized water to remove excess ethanol and adsorbed nutrient ions. The rinsed yeast was again centrifuged and remaining biomass was dried at 70 ºC for 12 h. The dried cells were ground and screened as mentioned above. The purpose of grinding dried yeast was to make a homogenized yeast biomass in order to destroy biomass aggregates and increase uptake capacity (Ghorbani. 2008). The ground biomass was stocked in the refrigerator for use in biosorption studies.

2.3. Biosorption studies

Batch biosorption experiments were carried out in 250 ml glass stoppered and Erlenmeyer flasks with 150 ml of dye solution. Necessary amount of adsorbent was then added to the solution. The flasks were agitated at a constant speed of 170 rpm for 3 h in an incubator shaker (JalTajhiz,TSL20, Iran) for different time intervals at room temperature (25 °C).The influence of pH (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0), contact time (10, 15, 25, 35, 60, 90, 120, 150 and 180 min), initial dye concentration (50, 100, 150, 200 and 250 mg L^{-1}), biosorbent dosage (0.30, 0.50, 1.00, 2.00 and 3.00 g L^{-1} for eosin Y and 0.07, 0.10, 0.30, 0.50,0.75 and 1.00 g L^{-1} for eosin B) and temperature (15, 25, 35 and 45 ºC) was evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual dye concentration in the solution. Then the supernatant was centrifuged at 5000 rpm for 5 min to remove particulates. The residual amount of dye in each flask was investigated using UV-Vis spectrophotometer (GBC, Cintra 20, Australia) at an absorbance wavelength of 510 nm and 505 nm for eosin Y and eosin B, respectively. The pH of the solution was adjusted with HCl and NaOH solutions and measured using a pH meter (Jenway-3510). The amount of dye sorbed onto unit weight of biosorbent and color removal were calculated using the following equations 1 and 2, respectively:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

$$R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where, q_e is the amount of dye adsorbed onto the unit amount of the biomass (mg g^{-1}), C_o and C_e (mg L^{-1}) are the liquid phase concentrations of dye at initial and equilibrium solution, respectively, V (L) is the volume of the solution and W (g) is the mass of dry sorbent used.

2.4. Biosorption equilibrium

Equilibrium experiments were carried out by taking known amount of yeast in 250 ml flasks containing 150 ml of different initial concentrations (50–250 mg L^{-1}) of dye solution in optimum pH and temperature of 25 ºC. The mixture was shaken in an incubator shaker at 170 rpm for 180 min, which is sufficient time to reach the equilibrium. The samples were then centrifuged and analysis was performed as previously mentioned.

2.5. Biosorption kinetics

Sorption kinetics experiments were carried out at different initial dye concentrations. Kinetic experiments were performed by mixing 2.00 g L^{-1} of sorbent for eosin Y and 0.10 g L^{-1} for eosin B with 150 ml dye solution (100 mg L^{-1}). The suspensions were shaken for 180 min with constant temperature of 25°C. The samples were taken at different time intervals, centrifuged and analyzed for remaining dye concentrations as described before.

3. Results and discussion

3.1. Effect of pH on dye adsorption

The ionic forms of the dye in solution and the surface electrical charge of the biomass depend on solution pH. Therefore, solution pH influences both the fungal biomass surface dye binding sites and the dye chemistry in the medium (Srinivasan and Viraraghavan. 2010). The effect of pH on the percentage both of dyes adsorption by S. cerevisiae was shown in Fig. 2. For an initial dye concentration of 100 mg L^{-1} the biosorption uptake of S. cerevisiae particles decreased with the increase of the solution pH. The maximum removal percentage for eosin Y and eosin B dyes were found to be 91.72 and 97.11, at the pH of 4.0 and 2.0, respectively. In fact, the eosin is a dipolar molecule at low pH, as shown in Fig.1 with a decrease in the pH of the dye

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solution, more dye molecules are protonated and are suitable to interact with negatively charged groups in biomass. On the other hand, the outer layer of the cell wall of S. cerevisiae consists on a coat protein that can develop a charge by dissociation of ionizable side groups of the constituent amino acids. The ionic state of ligands such as carboxyl, phosphate, imidazole and amino groups will be to promote reaction with the positively dye ions. At lower pH, cell wall ligands were closely associated with the hydronium ions [H_3O^+] and restricted the approach of dye cations as a result of the repulsive force. Electrostatic attraction to negatively charged functional groups may be one of the specific biosorption mechanisms (Özer and Özer. 2003; Wang and Chen. 2006).

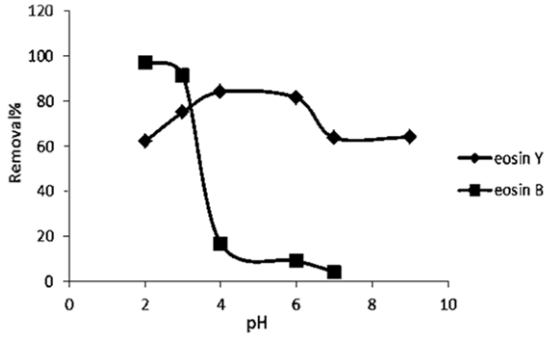

Fig. 2. Effect of pH on the percentage biosorption of the eosin Y and eosin B dye by S. cerevisiae. (T = 25 ° C, biosorbent dosage = 2.0 for eosin Y and 0.1 g L^{-1} for eosin B, C_0 = 100 mg L^{-1}, t = 3h).

3.2. Effect of biosorbent dosage on dye adsorption

Biosorbent dosage is a significant factor to be considered for effective pollutant removal as it determines sorbent–sorbate equilibrium of the system (Iftikhara. 2009). The effect of biosorbent dosage on the removal both of dyes were studied for an initial dye concentration of 100 mg L^{-1}, by varying the dosage, keeping all other parameters constant. The effect of biosorbent dosage on equilibrium uptake, q_e (mg g^{-1}) and % removal against biomass dosage (g L^{-1}) was shown in Fig. 3. It was observed that the amount of dye adsorbed onto unit weight of biosorbent gets decreased with increasing biomass concentration for both of dyes. For eosin Y dye uptake decreased from 275.10 to 27.84 mg g^{-1} for an increase in biomass dosage from 0.30 to 3.00 g L^{-1} and for eosin B dye uptake decreased from 908.58 to 58.23 mg g^{-1} for an increase in biomass concentration from 0.07 to 1.00 gL-1. Higher uptake was obtained when the dosage was low. This is due to the fact that the active sites could be effectively utilized when the dosage was low. When the adsorbent dosage is higher, biosorption sites remain unsaturated during adsorption reaction (Ponnusami et al. 2009). Whereas at equilibrium time the removal increases from 85.1 to 94.7% and 71.26 to 96.22% for an increase in biosorbent dosage from 0.3 to 3.0 g L^{-1} and 0.07 to 1.0 g L^{-1} for eosin Y and eosin B, respectively. The effective amounts of biomass were found to be 2.00 and 0.10 g L^{-1} for eosin Y and eosin B, respectively. The increase in color removal was due to the increase of the available sorption surface and availability of more adsorption sites (Bennani et al. 2009).

3.3. Effect of initial dye concentration and contact time

Dye concentration also affects the efficiency of color removal. Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye may enhance the adsorption process (Aksu. 2005). The experimental results of adsorption of eosin Y and eosin B onto S. cerevisiae at various concentrations with different contact time were shown in Fig. 4. It can be seen that the actual amount adsorbed per unit mass of S. cerevisiae increased with the increase for both of dyes concentration. The amount of eosin Y and eosin B adsorbed at equilibrium (q_e) increased from 18.67 to 82.92 mg g^{-1} and 451.90 to 622.40 mg g^{-1},respectively as the initial concentration was increased from 50 to 200 mg L^{-1}.This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye (Gurses et al. 2006).Moreover, the initial rate of adsorption was greater for higher initial dye concentration because the resistance to the dye uptake decreased as the mass transfer driving force increased (Karima et al. 2009).The percentage of dye removal decreases with the increase in the initial dye concentration. This may be due to the saturation of the sorption sites on the biosorbent as the concentration of the dye increases (Farah et al., 2007). It can be seen from Fig. 4, the process was found to be initially very rapid, and a large fraction of the total amount of dye was removed within approximately 15 min for eosin Y and 30 min for eosin B. The rapid uptake of the dye indicates that the sorption process could be ionic in nature where the dye molecules bind to the various negatively charged organic functional groups present on the surface of the biomass (Farah et al. 2007). From the results, it was obvious that the adsorption occurred quickly and reached equilibrium within 3 h.

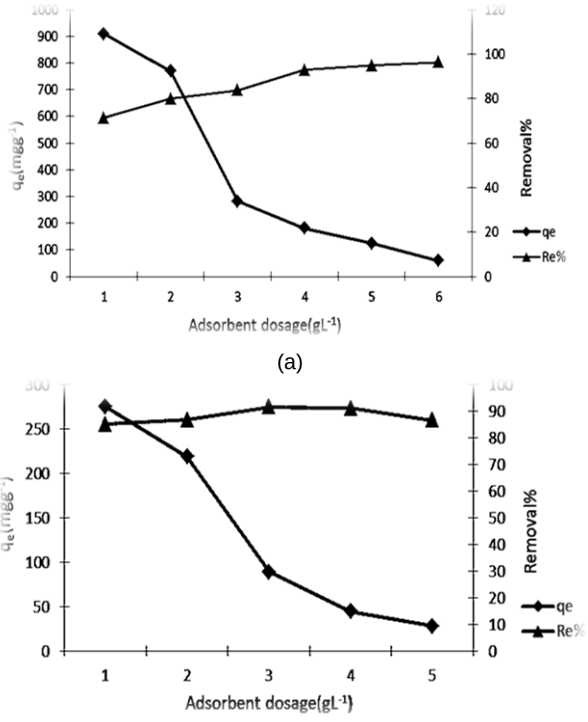

Fig.3. Effect of biosorbent dosage on the biosorption of (a) eosin Y and (b) eosin B dye by S. cerevisiae. (T = 25 °C, pH = 4 and 2 for eosin Y and eosin B, respectively, C_o = 100 mg L^{-1}, t = 3h).

3.4. Effect of temperature

Most textile and other dye effluents are produced at relatively high temperatures and hence temperature will be an important factor in real application of biosorption in future (Srinivasan and Viraraghavan, 2010). Increasing the temperature is known to increase the diffusion rate of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, the change temperature affects the equilibrium uptake of the adsorbent for a particular adsorbate (Farah et al. 2007). The effect of temperature on the dyes biosorption experiments was investigated with initial concentration of 200 mg L^{-1} at temperatures 15, 25, 35 and 45 ºC. As seen from Fig. 5, the maximum equilibrium uptakes were found to be at 45 ºC. The equilibrium biosorption uptake of both dyes increased sharply with increase in temperature. The increase in equilibrium biosorption uptake indicates that higher temperature favor eosin Y and eosin B removal therefore this system is endothermic. This may be due to a higher temperature would lead to higher affinity of sites for dye or binding sites on the yeast. The energy of the system facilitates dyes attachment on the cell surface to some extent (Wang and Chen. 2006). It may also be due to the fact that at higher temperatures, an increase in free volume occurs due to increased movement of the solute (Ho and McKay. 2003). Thus, an increasing the temperature of

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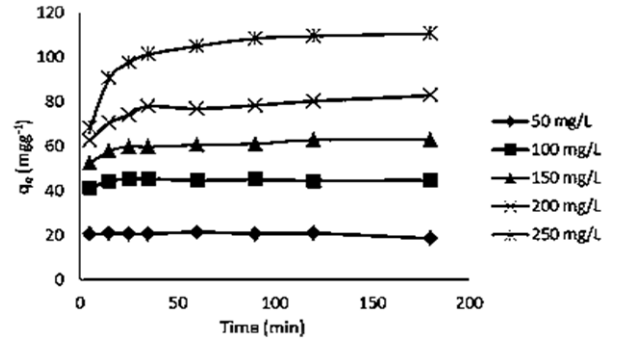
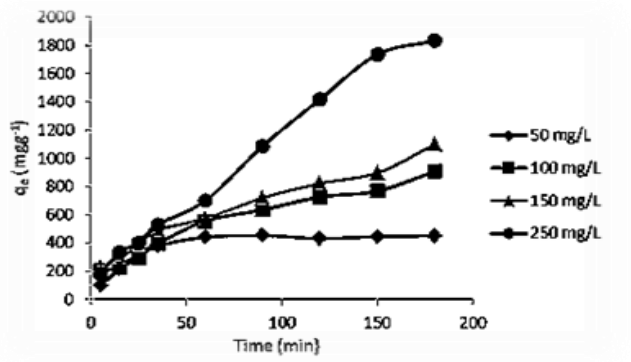
the reaction from 15 to 45 ºC, the equilibrium uptake of the dye increased from 142.40 to 202.84 mg g^{-1} for eosin Y and 451.80 to 1454.52 mg g^{-1} for eosin B.



(a)



(b)

Fig.4. Effect of the initial concentration and contact time for the biosorption of (a) eosin Y and (b) eosin B by S. cerevisiae. (T = 25 °C, pH = 4 and 2, biosorbent dosage = 2.0 and 0.1 g L^{-1} for eosin Y and eosin B, respectively, t = 3h).

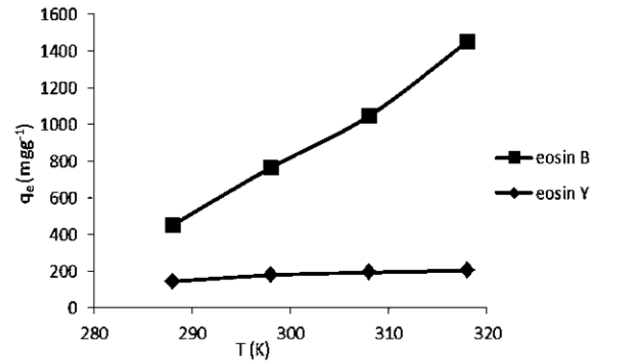


Fig. 5. Effect of temperature on the biosorptin uptake of eosin Y and eosin B by S. cerevisiae. (pH = 4 and 2, biosorbent dosage = 2.0 and 0.1 g L^{-1} for eosin Y and eosin B, respectively, C_o= 200 mg L^{-1},t = 3h).

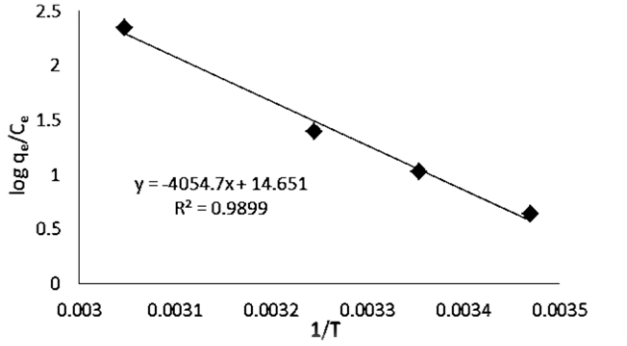
3.4.1. Thermodynamic parameters

Thermodynamic parameters such as changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for this biosorption process have been determined using the following equations 3 and 4:

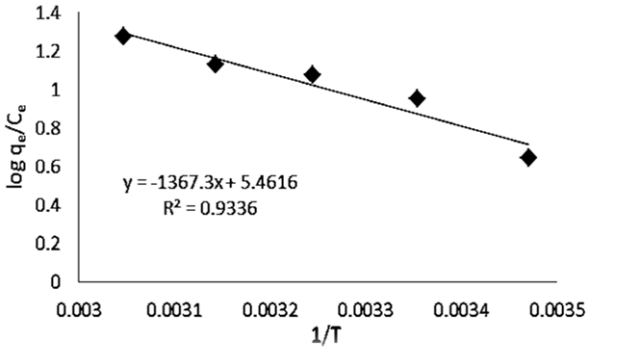
$$\Delta G^o = \Delta H^o - \Delta S^o \quad (3)$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^o}{2.303R} + \frac{-\Delta H^o}{2.303RT} \quad (4)$$

where q_e is the maximum amount of dye adsorbed per unit weight of the S. cerevisiae (mg g^{-1}), C_e is equilibrium concentration (mg L^{-1}) and T is temperature in Kelvin and R is the universal gas constant, 8.314 J mol^{-1} K^{-1}. The values of ΔH° and ΔS° were determined from the slope and intercept of the linear plot of log (q_e/C_e) versus 1/T, respectively (Fig. 6). The value of Gibbs free energy (ΔG°) is then calculated from Eq. (3). The obtained values of ΔH°, ΔS, and ΔG° are given in Table 1 for the initial dye concentration of 200 mg L^{-1}. The positive value of ΔH° for eosin Y and eosin B removal with S. cerevisiae biomass indicated that the dye biosorption process was endothermic in nature and adsorption process is favorable at higher temperatures and possible strong bonding between dye and each sorbent. The negative values of ΔG° confirm the feasibility of the processes and spontaneous nature of adsorptions at different temperature with a high degree of affinity of the dye molecules for each sorbent surface (Aksu et al. 2008). The positive value of ΔS° suggests increased randomness during biosorption at the solid–solution interface during the adsorption of dye onto biomass (Karima et al. 2009). Generally, the value of ΔG_{ads} for chemical adsorption is more than −4.7 Kcal mol^{-1}. The value of ΔG_{ads} for this case is less than −4.7 K $calmol^{-1}$ suggesting that the process is controlled by chemical adsorption (Özer and Özer. 2003). It is a chemisorption mechanism where there is an increase in the number of molecules acquiring sufficient energy to undergo chemical reaction with increasing temperature (Farah et al. 2007).



(a)



(b)

Fig. 6. Van't Hoff plot for the biosorption of (a) eosin Y and (b) eosin B dye by S. cerevisiae.

3.5. Biosorption isotherm

Analysis of equilibrium data is important to develop an equation which accurately represents the results and could be used for the

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design of biosorption systems used for the removal of organic pollutants. The empirical models for single solute systems used to describe the biosorption equilibrium are Langmuir, Freundlich and Temkin models. These models can provide information of dye-uptake capacities and differences in dye uptake between various species.

3.5.1. Langmuir isotherm

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation, based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface, these binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between adsorbed molecules is given by the following equation (Langmuir. 1918):

$$q_e = \frac{q_e b C_e}{1+bC_e} \quad (5)$$

where, C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of metal ion adsorbed (mg g^{-1}), q_m and b are the Langmuir constants related to maximum biosorption capacity describing a complete mono-layer adsorption (mg g^{-1}) and bonding energy of adsorption (L mg^{-1}), respectively.

Table 1. Thermodynamic parameters for biosorption of eosin Y and eosin B dye by S. cerevisiae.

Type of dye	ΔH°, kJ mol^{-1}	ΔS°, J $mol^{-1}K^{-1}$	$-\Delta G^\circ$, kJ mol^{-1}				
Eosin Y	26.174	104.56	288	298	308	318	328
Eosin B	77.62	280.51	39.55	50.01	60.26	70.62	81.34
			73.02	75.83	78.64	81.44	-

The values of various Langmuir constants were calculated from this isotherm and their values are listed in Table 2.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given by Eq. (4) (Hall. 1966):

$$R_L = \frac{1}{1+bC_o} \quad (6)$$

where, C_o is the critical concentration (mg L^{-1}) and b is the Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. In this study, the value of R_L was obtained to be in the range of 0–1, telling that the biosorption process is favorable for the both of dyes (Hameed. 2009).

Table 2. Langmuir, Freundlich and Temkin biosorption isotherm constant for the biosorption of eosin Y and eosin B by S. cerevisiae.

Type of dye	Langmuir				Freundlich			Temkin		
	q_m, mg g^{-1}	b, L mg^{-1}	R_L	R_2	K_F, (mg g^{-1})(mg L^{-1})n	n	R_2	A, L mg^{-1}	B, J mol^{-1}	R_2
Eosin Y	200	0.0203	0.330	0.271	2.616	0.754	0.896	4.01	71.17	0.959
Eosin B	1000	0.166	0.057	0.982	418.79	3.436	0.635	2.85	277.2	0.555

3.5.2. Freundlich isotherm

The Freundlich isotherm (Freundlich. 1906) is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces, where the sorption energy distribution decreases exponentially. This equation is also applicable to multilayer adsorption (Padmavathy. 2008). The Freundlich equation has the general form:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

where, K_F and n are the Freundlich's constants related to the adsorption capacity and adsorption intensity of the sorbent characteristics of the system, respectively. The value of n indicates whether the biosorption process is favorable or not and the high values of K_F showed ready uptake of the dye from wastewater with high adsorptive capacities of these biosorbents (Aksu and Karabayır. 2008). The value of K_F, correlation coefficient and n of both dyes are presented in Table 2.

3.5.3. Temkin isotherm

The Temkin model considered the effects of some indirect adsorbent/adsorbate interactions on adsorption isotherms. Its main assumption is the uniformity in the distribution of binding energies up to some maximum binding energy and also because of these interactions the heat of adsorption of all the molecules in the layer would decreases linearly with coverage. The linear form of Temkin isotherm can be written as (Temkin. 1941):

$$q_e = B \ln A + B \ln C_e \quad (8)$$

Where B=RT/b, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is related to the heat of adsorption. The values of the parameters are given in Table 2. Based on the correlation coefficients, the applicability of the isotherms was compared (Table 2). The experimental results indicate that sorption of eosin B onto S. cerevisiae follows the Langmuir model. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto adsorbent surface. On the other hand, according to Table 2, it was found that R_2 of Temkin model were close to 1.0 for eosin Y. These strongly suggest that Temkin isotherm model was slightly better for describing the biosorption equilibrium than Langmuir and Freundlich model. The results indicated that the surface of S. cerevisiae is heterogeneous in nature and did possess equal distribution of binding energies on the available binding sites.

3.6. Biosorption kinetics

An ideal adsorbent for wastewater pollution control must not only have a large adsorbate capacity but also a fast adsorption rate. Therefore, the adsorption rate is another important factor for the selection of the material and adsorption kinetics must be taken into account since they explain how fast the chemical reaction occurs and also provides information on the factors affecting the reaction rate (Chatterjee et al. 2005). Thus, in the removal of dyes from wastewater, it is necessary to know the rate of adsorption for process design, operation control and adsorbent evaluation. In order to investigate the mechanism of adsorption at different initial concentrations characteristic constants of adsorption rate were determined by using a pseudo first-order equation of Lagergren based on solid capacity, and pseudo second-order equation based on solid phase adsorption (Aksu. 2005).

3.6.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model considers the rate of occupation of the adsorption sites to be proportional to the number of

unoccupied sites. The pseudo- first order rate expression based on solid capacity is generally expressed as follows (Aksu and Donmez. 2003):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

where, q_e and q_t are the amounts of eosin dyes (mg g^{-1}) adsorbed on the sorbent at equilibrium, and time t, respectively, and k_1 is the rate constant (min^{-1}). The plot of log (q_e-q_t) versus t of Eq. (7) should give a linear relationship from which q_e and k_1 can be determined from the slope and intercept of the plot, respectively. The values of rate constant k_1, q_e were calculated. q_e experimental and $R_2$of eosin Y and eosin B are presented in Table 3. This table showed that the q_e calculated is not equal to q_e experimental. Mostly, the first-order kinetic model is not fitted well for whole data range of contact time and can be applied for preliminary stage of biosorption mechanism (Safa and Bhatti. 2011). However, the biosorption of eosin Y and eosin B is not likely to follow the pseudo-first-order kinetic model.

3.6.2. Pseudo-second-order kinetic model

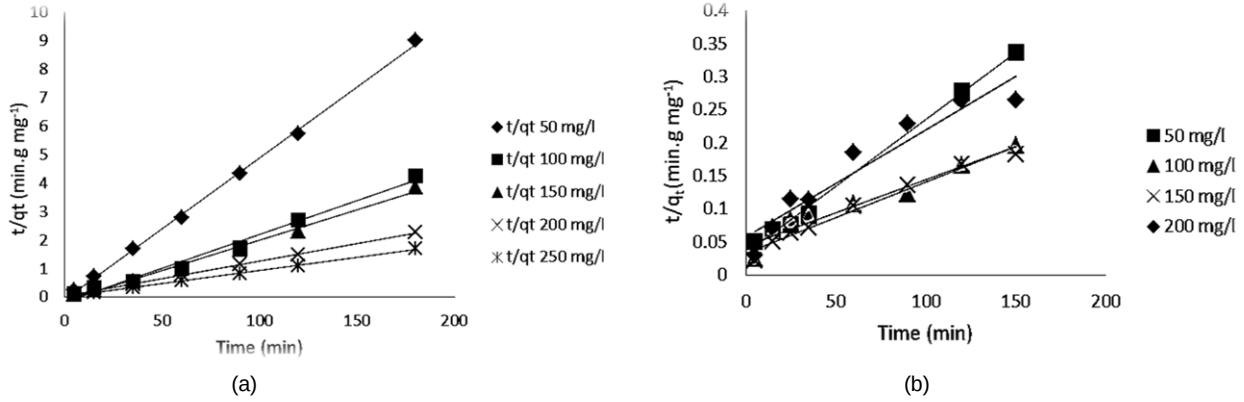
The pseudo-second order kinetic model assumes that the rate limiting step may be biosorption involving valence forces through sharing or exchange of electrons between the biosorbent and sorbate (Aksu et al. 2008; Iftikhara et al. 2009). The pseudo-order equation is also based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism and is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

where, k_2 (g $mg^{-1}min^{-1}$) is pseudo-second order biosorption rate constant, and q_e values were determined from the slope and intercept of the plot of t/q_t versus t (Fig. 6). The values of the rate constants are shown in Table 3 for both of dyes. As can be seen from Table 3, for the both of dye the correlation coefficients for the second-order kinetic model were close to 1.0 for all concentrations studied and the theoretical values of q_e also agreed well with the experimental values. These results indicate that the adsorption system studied belongs to the second-order kinetic model.

Table 3. Comparison study of kinetic parameters for the biosorption of eosin Y and eosin B by S. cerevisiae.

dye	C_0, mgL-1	q_e exp., mg g^{-1}	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			q_e, mg g^{-1}	K_1, min^{-1}	R_2	q_e, mg g^{-1}	K_2 x 10^{-5}, g $mg^{-1}min^{-1}$	R_2
Eosin Y	50	19.31	-	-	-	20.83	0.043	0.999
	100	44.81	0.52	0.046	0.102	45.45	0.097	0.999
	150	63.1	57.54	0.001	0.385	62.5	0.015	0.999
	200	82.92	16.71	0.016	0.946	83.3	0.051	0.999
Eosin B	50	451.9	212.32	0.023	0.744	500	0.138	0.992
	100	907.28	758.57	0.011	0.941	1000	2.300	0.946
	150	897.5	724.43	0.011	0.965	1000	3.125	0.976
	200	622.4	539.51	0.011	0.885	1000	1.750	0.916



(a) (b)

Fig. 7. Pseudo second-order kinetic model data for the biosortion of eosin Y and eosin B on S. cerevisiae.

4. Conclusion

In the present investigation it has been clearly shown that S. cerevisiae could be effectively used as a low cost adsorbent for the removal dyes from aqueous effluents. The results showed that the biosorption uptake was optimal under acidic conditions. Increase in concentration and decrease in adsorbent dosage resulted in increase in equilibrium dye uptake. The equilibrium data were fitted to non-linear models of Langmuir, Freundlich and Temkin, and the equilibrium data were best described by the Langmuir isotherm model for eosin B dye, with maximum monolayer adsorption capacity of 1000 mg g^{-1} of S. cerevisiae. The Temkin isotherm was found to be the most suitable for eosin Y adsorption by S. cerevisiae. Furthermore, the biosorption followed pseudo-second order adsorption kinetics, suggesting that the adsorption process was controlled by chemisorption. Thermodynamic parameters such as change in free energy, enthalpy, and entropy were also determined for each sorbent–dye system indicating the spontaneous, endothermic and irregular nature of sorption in each case. Therefore, the adsorbent is expected to be economically feasible for removal of dye from aqueous solutions.

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