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Isotherm and kinetic studies of Burazol Blue ED dye biosorption by dried anaerobic sludge

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ABSTRACT

Biosorption potential of dried anaerobic sludge (DAS) for Burazol Blue ED (BB) was studied with respect to pH, equilibrium time, initial dye concentrations and temperature to determine equilibrium and kinetic models. The most suitable pH, equilibrium time and initial dye concentration were determined as 0.5 ± 0.03, 75 min and 150 mg/L, respectively, at a biomass dosage of 0.4 g/L and $25\,^{\circ}C \pm 1.0$. The equilibrium data was best described by the Langmuir isotherm model. Maximum uptake capacity (q_m) of DAS for the dyestuff (BB) were 118.3, 125.8 and 127.5 mg/g biomass at temperatures of 25, 40 and 50 °C, respectively, indicating that the biosorption process is spontaneous and favored at higher temperatures. The overall biosorption process was best described by pseudo-second-order kinetic model. Gibbs free energy changes were calculated as −356.8, −519.7 and −520.6 J/mol at 25, 40 and 50 °C, respectively.

1. Introduction

Dye molecules have synthetic origin and their structures differ in terms of chemical composition, molecular weight and toxicity. They can be classified as anionic (acid, direct and reactive dyes), cationic (basic dyes) and nonionic (disperse dyes) dyes according to their dissociation in an aqueous solution [1]. They are consumed in a great number of industries such as textile, pesticide, paint, solvent, pharmaceutics, paper and pulp as well as petroleum. Effluents of these industries contain undesired quantities of chemicals and cause a big concern from environmental point of view. Such effluents need to be treated properly before they are released to the receiving waters [2,3].

Conventional dye treatment technologies are based on physicochemical principles and their applications are limited due to various reasons such as high cost and low efficiency. For example, the large-scale applications of activated carbon cited as one of the best available control technologies by the US Environmental Protection Agency are hampered by high operating costs, relatively high price and problems with regeneration [3]. In recent years, many non-conventional low-cost adsorbents of natural material (wood, coconut shell, lignite, coal) [3], biosorbents (bacteria, fungi and algae) [4,5] and waste materials (seeds of *Capsicum annuum*, cotton waste, palm fruit bunch and aquatic plants) from industry and agriculture were proposed [6–8]. They are cheap to produce and carry wide range of binding sites for dyes molecules. This technology, using above biological biomass as adsorbing materials, is named as biosorption. It is based on the property of microbial biomass to sequester toxic molecules such as dyes through interactions between toxic molecules and the functional groups present on the cell wall surface of the biological cells. They are mainly composed of polysaccharides, proteins and lipids [9].

For this reason, it would be interesting to investigate whether dried anaerobic sludge (DAS) constitutes an ideal material to be used as a biosorbent for the removal of Burazol Blue ED (BB) dye or not. The anaerobic sludge is a well known biomass mainly consisting of both bacteria and protozoa, which means that there could be ample amount of binding sites for the dye molecules. It is also cheap, readily available in large quantities and has been previously used to remove some hazardous materials such as Methylene Blue [10], Rhodamine B [11], mono chlorinated phenols [12] and Reactive Black 5 [13].

BB is an anionic dye which is one of the commonly used dyes in textile industry of Turkey. Its removal from contaminated water causes a big concern from environmental point of view. To the

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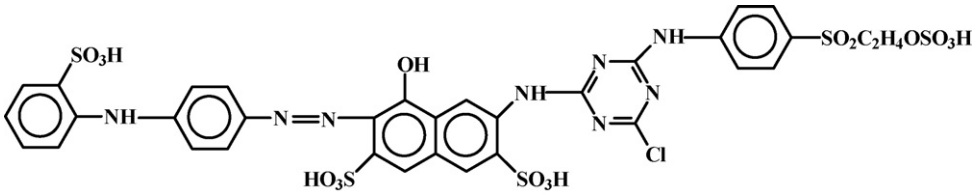

Fig. 1. The chemical structure of Burazol Blue ED dye.

best of our knowledge, BB dye biosorption by DAS is not reported. Therefore, the present work investigates the biosorption potential of DAS for the removal of BB dye from aqueous solutions in a batch study with variation in the parameters of initial pH, contact time and initial dye concentrations. The equilibrium binding has been described in terms of Langmuir and Freundlich isotherms. Kinetic data were evaluated according to the pseudo-first order, pseudo-second-order kinetics and intraparticle diffusion model from which the rate constants of biosorption and equilibrium capacity were determined. The Gibbs free energy values were also calculated at all studied temperatures.

2. Materials and methods

2.1. Preparation of anaerobic sludge

A mixed anaerobic sludge (whose suspended solids were 60 g/L and volatile suspended solids 38 g/L) was obtained from the anaerobic digesters of Ankara Municipal Wastewater Treatment Plant, Turkey. It is a complex consortium microorganisms mainly containing archaebacteria (methanogens). The biomass was washed thorougly with distilled water twice, followed by spreading on Petri dishes and dried in an oven at 60 °C overnight. It was then powdered using a mortar and pestle and sieved to select particles of approximately 150 μm for use as a biosorbent.

2.2. Preparation of dye solution

Burazol Blue ED (BB) dye ($C_{38}H_{41}N_8O_{16}S_5Cl$: 1061.54 g/mol) (Fig. 1) was obtained from BURBOYA textile company in Bursa, Turkey and used without further purification. As shown in Fig. 1, BB dye has five sulfonate groups, which have negative charges in aqueous solutions. The tests solutions containing BB dye were prepared by diluting 1.0 g/L of stock solution which was prepared by dissolving an accurate quantity of dye in distilled water.

2.3. Experimental procedure

Laboratory biosorption experiments were optimized at the desired pH value, contact time and different initial BB dye concentrations. The batch experiments were carried out in a stoppered conical flask (250 mL) at an agitation speed of 200 rpm on a magnetic stirrer. Throughout the study, the pH was varied from 0.5 to 6.0, the contact time from 10 to 90 and the BB dye concentration from 25 to 300 mg/L at constant biomass feed of 0.4 g/L. The experiments were repeated at 25, 40 and 50 °C. When the sorption procedure was completed, the solutions were centrifuged at 4500 rpm for 10 min and the supernatants were then analyzed for residual BB dye concentrations using a spectrophotometer, (UV–vis, Cecil 4002) at λ_{max} 594 nm. The solutions involved were diluted to known concentrations, to give absorbancies in the range of 0.1–1.0, before making the measurements.

The biosorption capacity was determined by using the following equation taking into account the concentration difference of the solution at the beginning and at equilibrium:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and the equilibrium dye concentrations (mg/L), V is the volume of solution (L) and m is the amount of biomass used (g).

The negative controls (with no biomass) were prepared and run simultaneously. Experimental data were the mean values from two independent experiments.

3. Results and discussion

3.1. Effect of pH

The pH is an important parameter for biosorption studies and affects not only the biosorption capacity, but also the color and solubility of dye solutions. The maximum biosorption capacities of DAS were plotted against the equilibrium pH using 50 mL of 150 mg/L initial dye solution and 0.02 g biomass dose at 25 °C for a prefixed time period (60 min) in Fig. 2. As shown in this figure, the equilibrium uptake capacity of the biomass decreased from 105.8 to 71.6 mg/g biomass when the solution pH was changed from 0.5 to 1.5. This trend was followed by a sharp decrease up to pH 2.0, which caused the equilibrium uptake capacity to drop from 71.6 mg/g biomass to 3.0 mg/g biomass. The biosorption capacity further decreased to the lowest level of 1.0 mg/g biomass at pH 5. From this study, the optimum pH was determined as 0.5 at which the maximum biosorption capacity of DAS for BB dyes was determined as 105.8 mg/g biomass at 25 °C. This effect was largely related to the anionic characters of BB dye. Weak base groups on the biomass surface were protonated and acquired a net positive charge with diminishing solution pH. This caused a significantly high electrostatic attraction between the surface of DAS and BB dye and as a result, a high biosorption capacity [14].

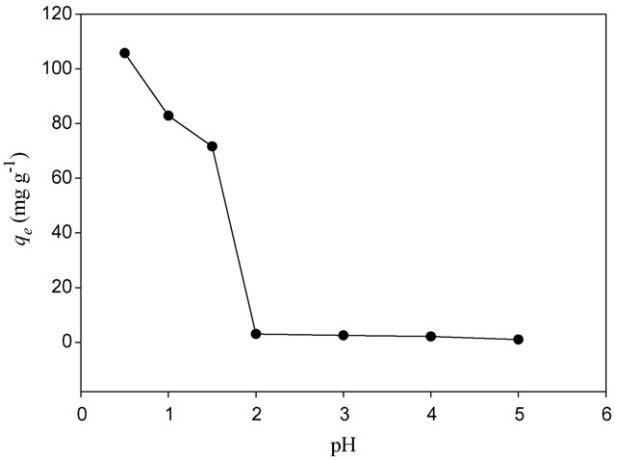

Fig. 2. Effect of pH for the biosorption of BB dye onto DAS at 25 °C (dye concentration: 50 mL of 150 g/L; biosorbent dose: 0.4 g/L; contact time: 60 min).

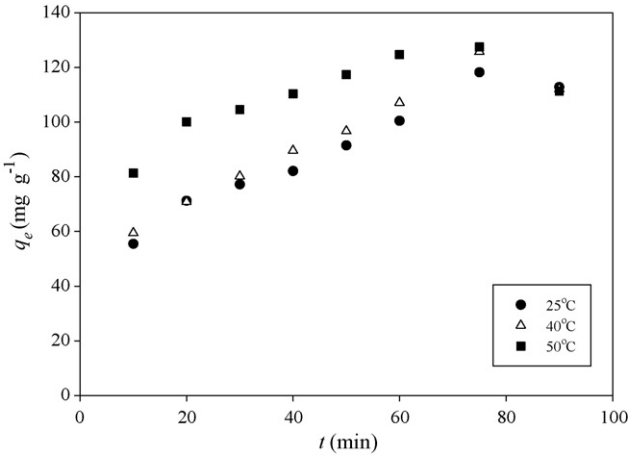

Fig. 3. The effects of equilibrium time for biosorption of BB dye onto DAS at temperatures of 25, 40 and 50 °C (dye concentration: 50 mL of 150 g/L; biosorbent dose: 0.4 g/L; pH 0.5).

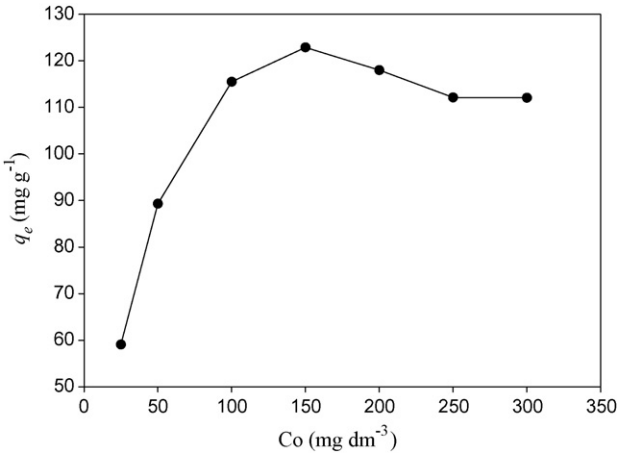

Fig. 4. The effects of initial BB dye concentration for biosorption of BB dye onto DAS at 25 °C (biosorbent dose: 0.4 g/L; contact time: 75 min; pH 0.5; temperature: 25 °C).

Similar result was also mentioned by Won et al. who investigated the biosorption of Reactive Orange 16 by using sewage sludges [15].

3.2. Effect of equilibrium time

Rapid sorption is among desirable parameters for successful deployment of the biomass for practical application. Fig. 3 indicates the BB dye uptake by the biomass as a function of time at pH 0.5 and different temperatures of 25, 40 and 50 °C. An uptake capacity of 55.5 mg/g biomass observed within 10 min and then the sorption capacity was increased constantly with increasing time. The equilibrium time was reached in 75 min at which the uptake capacity was 118.3 mg/g biomass at 25 °C. Beyond the equilibrium time, there was a steady decrease observed on the uptake capacity. A similar trend was observed at 40 and 50 °C at which the maximum uptake capacities were determined as 125.8 and 127.5 mg/g biomass in 75 min, respectively. Therefore 75 min was fixed as the optimum equilibrium time for studies carried out at 25, 40 and 50 °C. The increase observed on the uptake capacity with increasing contact time was due to availability of biosorption sites on the biomass surface. A decrease observed on the uptake capacity after equilibrium time could be related to the desorption of dye molecules from the biomass surfaces. This was probably caused by repulsive forces between dye molecules at adjacent sites on the biomass surfaces [14].

The optimum equilibrium time determined in our study was consistent with a study reported by Wang et al. [11]. They investigated the biosorption of an anionic dye, Eosin Y, by anaerobic sludge and reported the optimum equilibrium time as 75 min.

3.3. Effect of initial dye concentration

The parameter, initial concentration, provides an important driving force to overcome resistances encountered when all molecules were transferred between the aqueous and solid phases [16]. In this study, BB dye uptake capacity of DAS was investigated at biomass concentration of 0.4 g/L, pH 0.5 and 25 °C and the results (mg/g biomass) were given in Fig. 4. The uptake capacity increased from 59.1 to 115.5 mg/g biomass as the initial dye concentration increased from 25 to 100 mg/L. This was followed by a small increase reaching 122.9 mg/g biomass at an initial concentration of 150 mg/L which is the maximum dye uptake value at 25 °C. Further increase at initial concentrations from 200 to 300 mg/L resulted in a decrease to a value of 112.1 mg/g biomass. This effect could be explained as follows: At lower initial dye concentrations, all dye molecules could interact with the binding sites on the biomass surface and high sorption rates occur. At high initial dye concentrations, binding sites on the biomass surface were saturated and no further biosorption occurs. A decrease observed on the biosorption capacity is mainly due to the repulsive forces between dye molecules at adjacent sites on the cell surface. This results in removal of some dye molecules from the surface [14].

3.4. Effect of temperature

The temperature has two main effects on the sorption processes. Firstly, increasing temperature is known to increase the diffusion rate of the adsorbate molecules within the pores as a result of decreasing solution viscosity. Secondly, it will also modify the equilibrium capacity of the adsorbent for a particular adsorbate [17]. To investigate the effect of temperature, the equilibrium biosorption capacity of BB dye onto DAS was studied at constant temperatures of 25, 40 and 50 °C (Fig. 3). As seen in Fig. 3, an increase in the temperature from 25 to 40 °C showed a slight increase on the uptake capacity of DAS for the dye molecules from 118.3 to 125.8 mg/g biomass under optimum conditions of pH and equilibrium time. The same trend was observed when temperature was increased

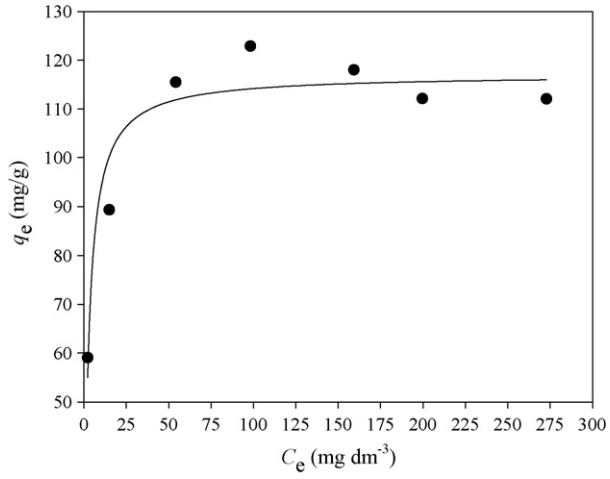

Fig. 5. Langmuir plot for biosorption of BB dye onto DAS at 25 °C.

Table 1
Isotherm constants for the biosorption of BB dye onto DAS at 25 °C.

t (°C)	Langmuir			Freundlich		
	q_{max} (mg/g)	K_L (L/mg)	R_L^2	n	K_F (L/mg)	R_F^2
25	117.1	0.398	0.915	8.51	64.03	0.782

Table 2
Comparison of BB dye biosorption by DAS and previous studies.

Biosorbent	Dye	Operating conditions					Reference
		pH	t (°C)	Biosorbent dosage (g/L)	Biosorption capacity (mg/g)	C_0 (mg/L)	
Dried anaerobic sludge	Burazol Blue ED	0.5	25	0.4	117	150	This study
Sewage sludge	Methylene Blue	2	25	10	21	200	[10]
Anaerobic sludge	Eosin Y	7	38	3	2.4	–	[11]
Dried activated sludge	Reactive Black 5	2	20	1	117	200	[13]
Waterworks sludge	Reactive Orange 16	2	25	10	47	500	[15]
Sewage sludge	Reactive Orange 16	2	25	10	115	500	[15]
Powdered activated sludge	Direct Yellow 12	–	25	4	110	200	[28]

C_0: Initial concentration.

from 40 to 50 °C. The biosorption capacity was then increased from 125.8 to 127.5 mg/g biomass. The increase in the uptake capacity with increasing temperature could be explained by the availability of more binding sites. Since the process is endothermic, another reason could be due to the increasing number of molecules acquiring sufficient energy to undergo particles interactions.

After equilibrium time, a steady decrease was observed. This could be related to the desorption of dye molecules from the biomass surfaces. It was probably caused by repulsive forces between dye molecules at adjacent sites on the biomass surfaces [18]. This result indicated that, though the BB dye biosorption process onto DAS was favored at higher temperatures, the increase observed in the biosorption capacity was not worth the additional cost of the heating.

3.5. Biosorption isotherms

The Langmuir isotherm model is valid for monolayer biosorption process onto a surface with a finite number of energetically equivalent identical sites. The Langmuir isotherm equation [19] can be represented by the following expression:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

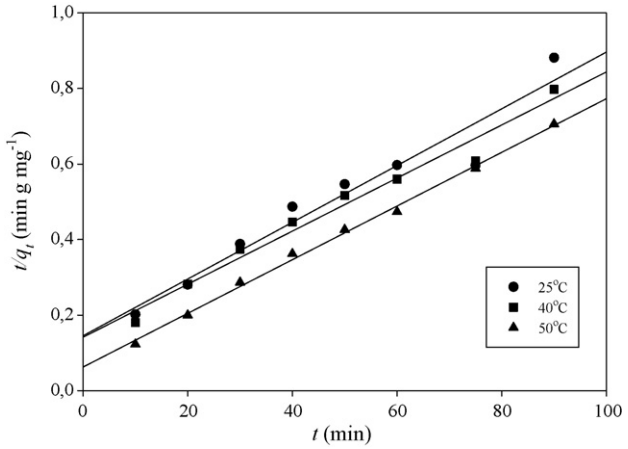

Fig. 6. Pseudo-second-order kinetic plots for biosorption of BB dye onto DAS at temperatures of 25, 40 and 50 °C.

where q_m is the maximum amount of adsorption (mg/g), q_e (mg/g) and C_e (mg/L) are the equilibrium BB dye and solution concentrations at equilibrium and K_L is the Langmuir adsorption constant (L/mg) related to the free energy of adsorption.

The Freundlich isotherm model assumes that adsorption takes place on heterogeneous surfaces and the sorption capacity depends on the concentration of BB dye at equilibrium. The Freundlich isotherm equation [20] is shown as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F and n are the Freundlich isotherm constants (L/g). The constant K_F and n are defined as a sorption coefficient representing the amount of dye molecules for a unit equilibrium concentration and a measure of the sorption intensity or surface heterogeneity, respectively. $1/n = 0$ value shows that the partition between two phases does not depend on the concentration, $1/n < 1$ value corresponds to a normal L-type Langmuir isotherm while $1/n > 1$ indicates a cooperative sorption involving strong interactions between the molecules of adsorbate [21].

The plot of Langmuir biosorption isotherms of BB dye by DAS obtained at 25 °C is illustrated in Fig. 5 and the isotherm model parameters are tabulated in Table 1. It is apparent from these data that Langmuir isotherm represents the equilibrium data reasonably well with regression coefficient value (R^2) of 0.915. However, the Freundlich isotherm model did not fit well to the experimental data with showing the R^2 values of 0.784 at the same temperature. These mean that the surface of DAS contains homogeneous biosorption patches.

The comparison of BB dye biosorption capacity by DAS with that of literature studies was presented in Table 2. The value of K_L in the Langmuir model of the present study, which is an indicator of biosorption uptake capacity, was found to be higher than those in most of previous work.

3.6. Biosorption kinetic

The kinetic studies were carried out to determine the efficiency of BB dye biosorption onto DAS. The pseudo-first-order rate equation can be written as follow [22]:

$$\frac{1}{q_t} = \frac{1}{q_1} + \frac{k_1}{q_1 t} \quad (4)$$

where q_1 and q_t are the amounts of BB dye biosorbed at equilibrium and at time t, in mg g^{-1}, and k_1 is the pseudo-first-order rate constant (1/min) of biosorption.

Table 3
Kinetic parameters for the biosorption of BB dye onto DAS at temperatures of 25, 40 and 50 °C.

t (°C)	Intraparticle diffusion			Pseudo-second-order			
	C (mg/g)	k_P (mg/g min$^{1/2}$)	R^2	k_2 (g/mg min)	q_2 (mg/g)	q_{exp} (mg/g)	R^2
25	24.48	9.80	0.958	3.389×10^{-4}	139.22	118.25	0.966
40	27.20	10.01	0.926	5.178×10^{-4}	129.27	125.75	0.948
50				1.480×10^{-3}	128.15	127.50	0.986

The pseudo-second-order kinetic model is expressed as [23]:

$$\frac{t}{q_t} = \frac{1}{kq_2^2} + \frac{1}{q_2}t \quad (5)$$

where q_2 is the maximum biosorption capacity (mg/g) for the pseudo-second-order sorption, q_t is the amount of BB dye biosorbed at time t (mg/g), k_2 is the equilibrium rate constant of pseudo-second-order sorption (mg/g min). An adequate pseudo-second-order kinetic model should show a linear plot of t/q_t against t with a reasonable magnitude of R^2. Values of q_2 and k_2 can be easily deduced from the slope and intercept of the plot of t/q_t versus t (Fig. 6), respectively.

The pseudo-second-order kinetic parameters for the biosorption of BB dye onto DAS are presented in Table 3. The results show that the pseudo-second-order rate constants (k_2) indicated a steady increase with increasing solution temperatures. They were determined as 3.39×10^{-4} at 25 °C, 5.18×10^{-4} at 40 °C and 1.48×10^{-3} g/mg min at 50 °C. The correlation coefficients (R^2) for the pseudo-second kinetic model were 0.966, 0.948 and 0.986 at 25, 40 and 50 °C, respectively. They were higher than those of pseudo-first-order one ($R^2 < 0.90$; not given in Table 3). The theoretical values of q_e also agreed reasonably well with the experimental data.

The kinetic analysis and the constants calculated from the experimental data forms a base study for BB dye biosorption kinetics since there are no reported data on kinetics of BB dye biosorption by DAS. However, our results were compared with dyes of similar chemical structure reported in the literature. These include Acid Red 57 by dried *Neurospora crassa* [8] and Reactive Black 5 by dried activated sludge [18]. Their biosorption process followed the pseudo-second-order kinetics.

The intraparticle diffusion equation can be written as follows [24]:

$$q_t = k_p t^{1/2} + C \quad (6)$$

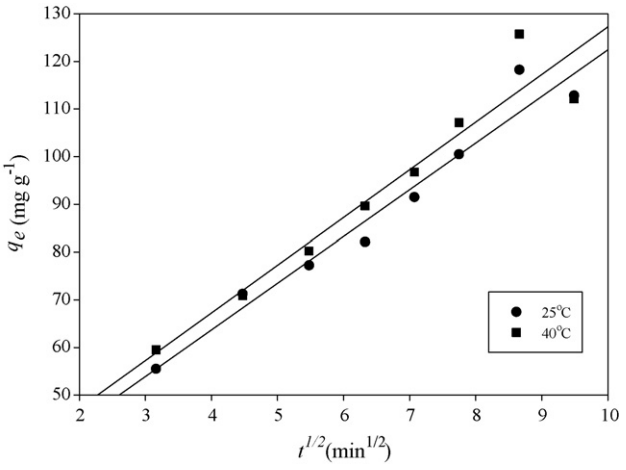

Fig. 7. Intraparticle diffusion kinetic plots for biosorption of BB dye onto DAS at temperatures of 25 and 40 °C.

where C is the intercept, and k_p is the intraparticle diffusion rate constant (mg/g min$^{1/2}$). According to this model, the plot of uptake, q_t, versus the square root of time ($t^{1/2}$) (Fig. 7) should be linear if intraparticle diffusion is involved in the biosorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step [25]. When the plots do not pass through the origin, the intraparticle diffusion is not the only rate-limiting step, but also other kinetic models may control the rate of biosorption, all of which may be operating simultaneously. The intraparticle diffusion model parameters are given in Table 3. As seen in this table, the R^2 values for the plots were found to be 0.958 at 25 °C, 0.926 at 40 °C and 0.711 at 50 °C. This indicated that the biosorption of BB dye by DAS may be followed by an intraparticle diffusion model up to 75 min at 25 and 40 °C, but not at 50 °C. However, the intraparticle diffusion model cannot be accepted as the only rate controlling step for the biosorption process due to the deviation (C value in Table 3) of the plots from the origin.

3.7. Gibbs free energy

Gibbs free energies of the biosorption process (ΔG) at temperatures of 25, 40 and 50 °C were determined by using the following equation [26]:

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

where K_C is the equilibrium constant (q_e/C_e), R is the gas constant and T is the temperature in K. The ΔG value indicates the degree of spontaneity of the biosorption process and higher negative value reflects a more energetically favorable process. In this study, the ΔG values were found to be −356.8, −519.7 and −520.6 J/mol at 25, 40 and 50 °C, respectively. These results indicated that the biosorption process is spontaneous at 25 °C and favored at higher temperatures.

Some researchers have also obtained similar results for ΔG in the biosorption of anionic dyes on other biosorbents. For example, the biosorption of acid orange 7 dye onto spent brewery grains had $\Delta G = -22.8$ kJ/mol [27].

4. Conclusions

Following conclusions were drawn from the present study.

(1) The optimal operating parameters, solution pH, equilibrium time and initial dye concentration were selected as pH 0.5, 75 min and 150 mg/L at biomass dosage (0.4 g/L) and 25 °C. The maximum uptake capacities for BB dye were found to be 118.3, 125.8 and 127.5 mg/g biomass under optimum conditions at 25, 40 and 50 °C, respectively.
(2) The Langmuir isotherm model represented the experimental data well.
(3) By applying the kinetic models to the experimental data, it was concluded that the biosorption process follows the pseudo second-order rate kinetics at temperatures of 25, 40 and 50 °C.
(4) The negative ΔG° value of −356.8 J/mol indicated that the biosorption process was feasible and spontaneous at 25 °C and favored at higher temperatures.

(5) Lastly, it can be concluded that DAS has a potential as a biosorbent for the removal of BB dye from aqueous solutions due to its low cost, high biosorption capacity with low biomass dosage (0.4 g/L), reasonable rapid biosorption rate (75 min) and obtainable easily in large quantities.

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