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Biosorption of Acid Red 274 (AR 274) on *Enteromorpha prolifera* in a batch system

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Abstract

The biosorption of Acid Red 274 (AR 274) dye on *Enteromorpha prolifera*, a green algae grown on Mersin costs of the Mediterranean, Turkey, was studied as a function of initial pH, temperature, initial dye and biosorbent concentration. The experiments were conducted in a batch manner. The Langmuir and Freundlich isotherms were used for modelling the biosorption equilibrium. At optimum temperature 30 °C and initial pH 2.0–3.0, the Langmuir isotherm fits best to the experimental equilibrium data with a maximum monolayer coverage of 244 mg/g. The equilibrium AR 274 concentration of the exit stream of a single batch was also obtained by using the experimental equilibrium curve and operating line graphically. The pseudosecond-order kinetic model and Weber–Morris model were applied to the experimental data and it was found that both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process. The biosorption process follows a pseudosecond-order kinetics and activation energy was determined as −4.85 kJ/mol. Thermodynamic studies showed that the biosorption of AR 274 on *E. prolifera* is exothermic and spontaneous in nature.
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Keywords: Biosorption; Acid Red 274; *Enteromorpha prolifera*; Kinetic models; Isotherm models

1. Introduction

Dyes are synthetic aromatic water-soluble dispersible organic colorants, having potential application in various industries such as textiles, leather, paper, plastics, etc. to color their final products [1,2]. The effluents of these industries are highly colored and disposal of these wastes into the environment can be extremely deleterious [3]. Wastewaters containing dye may be toxic and even carcinogenic and this posses a serious hazard to aquatic living organisms [1,3,4]. The presence of dyes in water reduces light penetration and has a derogatory effect on photosynthesis. There are more than 100 000 dyes available commercially, most of which are difficult to decolorize due to their complex structure and synthetic origin [5]. They are specifically designed to resist fading upon exposure to sweat, light, water and oxidizing agents, and as such very stable and difficult to degrade [6]. Of current world production of dyestuffs of 10 mL kg per year between 1 and 2 mL kg of active dye enter the biosphere, either dissolved or suspended in water, every year [7]. It is evident, therefore, that removal of such colored agents from aqueous effluents is of significant environmental, technical and commercial importance [8].

The conventional methods for treating dye-containing wastewaters are coagulation and flocculation, reverse osmosis, electroflotation, membrane filtration, irradiation and ozonation and active carbon adsorption [9,10]. The most popular of these technologies is activated carbon adsorption and widely used but it is expensive. Therefore, there is a growing interest in using low-cost, easily available materials for the adsorption of dye colors.

An alternative inexpensive adsorbent able to reduce the cost of a adsorption system has always been searched. A low cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another

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Nomenclature

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_0	initial dye concentration (mg/L)
E	the activation energy of adsorption (kJ/mol)
ΔG	free energy change (kJ/mol)
ΔH	enthalpy change (kJ/mol)
k_0	the temperature independent factor (g/mg min)
k_2	pseudosecond-order rate constant of sorption (g/mg min)
K	intraparticle rate constant (mg/g min$^{1/2}$)
K_a	a constant related to the energy of adsorption (L/mg)
K_F	adsorption capacity
n	adsorption intensity
q_{eq}	the adsorbed dye amount per unit weight of adsorbent at equilibrium (mg/g)
$q_{eq,cal}$	the calculated value of the adsorbed dye amount per unit weight of adsorbent at equilibrium (mg/g)
q_t	the adsorbed dye amount on the surface of adsorbent at any time t (mg/g)
Q^0	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_L	dimensionless separation factor
R^2	correlation coefficient
ΔS	entropy change (J/mol K)
T	absolute temperature (K)
V_0	solution volume (L)
X_0	biosorbent amount in biosorption solution (g)

industry [11]. A wide variety of microorganisms such as bacteria, fungi, algae either in their living or inactivated form and various materials such as coal, fly ash, wood, silica gel, rice husk, cotton waste, bark, sugar industry mud, palm-fruit brunch, etc. have been investigated to remove dyes from aqueous solutions with varying success for color removal [5,12]. The term 'biosorption' refers to different modes involving a combination of active and passive transport mechanisms to remove unwanted materials by microbial biomass. The use of inactivated biomass is advantageous as the process is free from nutrient supply and moreover there are no toxicity constraints in the organism employed [13]. Microbial cell surface is naturally formed by various chemical groups such as hydroxyl, carboxylate, amino and phosphate which are responsible for the sequestration of unwanted materials from effluents.

Recent investigations by various groups have shown that selected species of seaweeds possess impressive adsorption capacities for a range of heavy metal ions but there is few studies on the color removal [10]. Seaweeds are a widely available source of biomass as over 2 million tonnes are either harvested from the oceans or cultured annually for food or phycocolloid production, especially in the Asia–Pacific region [10]. Aguilera-Morales et al. reported that the main constituents in *Enteromorpha* spp., a kind of seaweeds, were minerals, protein and ether extract and hemicellulose was dominant in the cellular wall of algae [14]. In this study, *Enteromorpha prolifera*, growing on Mediterranean cost, was used as an biosorbent for the removal of Acid Red 274 (AR 274), one of the components of textile industry wastewaters.

2. Material and methods

2.1. Biosorbent

E. prolifera, a kind of green algae, was obtained from Mediterranean cost in Mersin, Turkey. The algae was washed twice with tap water in order to remove insect larvae, soil, etc. It was dried in sunlight and then in an oven at 105 °C for 24 h until all the moisture evaporated, put in distilled water and blended by using a commercial blender (Waring) to obtain larger surface area. A stock solution of 10 g/L of biosorbent was prepared.

2.2. Adsorbate

The test solutions containing Acid Red 274 dye, commercial name Supranol Red 3BW, were prepared by diluting 1.0 g/L of stock solution of dye which was obtained by dissolving weighed amount of AR 274 in 1 L of distilled water. Necessary dilutions were made from the stock solution to prepare solutions in the range of concentrations 25–1000 mg/L. The pH of each solution was adjusted to the required value with concentrated H_2SO_4 and NaOH solutions before mixing the biosorbent solution.

2.3. Batch biosorption studies

The algae solution (10 mL), except for the studies of biosorbent concentration effect, was mixed with 90 mL of the desired dye concentration and initial pH in Erlenmayer flasks. The flasks were agitated on a shaker at constant temperature for 2 h ample time for adsorption equilibrium. Samples (5 mL) of biosorption medium were taken before mixing the biosorbent suspension and dye bearing solution, then at pre-determined time intervals (0.5, 5, 10, 15, 20, 30, 45, 60 and 120 min) for the residual dye concentration in the solution. Samples were centrifuged at 3500 rev/min for 5 min and the supernatant liquid was analysed.

2.4. Analysis

The concentration of Acid Red 274 remaining in the biosorption medium were measured colorimetrically using a spectrophotometer (Shimadzu UV-160A). The absorbance values were read at 527 nm.

3. Results and discussion

3.1. The determination of optimum biosorption conditions

3.1.1. The effect of the initial pH

pH affects not only the biosorption capacity, but also the color of the dye solution and the solubility of some dyes [5]. Therefore, the pH value of the solution was an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH [9]. The effect of initial pH on AR 274 biosorption by *E. prolifera* is shown in Fig. 1. The maximum uptake value (mg/g) was obtained at 2–3 values of initial pH due to existing a significantly high electrostatic attraction between the positively charged surface of the algae cells and anionic dye, AR 274. Acid dyes are also called anionic dyes because of the negative electrical structure of the chromophore group [15,16]. This kind of dye is composed of ionizable groups such as sulfonates, carboxylates or sulfates to favor their solubilization in water [17]. As the initial pH increases, the number of negatively charged sites on the biosorbent surface increases and the number of positively charged sites decreases. A negative surface charge does not favor the adsorption of dye anions due to the electrostatic repulsion [18]. It was also reported that electrostatic attraction could be the primary mechanism in the biosorption of Acid Blue 29 on *Aspergillus niger* [5]. In general, the acidic dye uptakes are much higher in acidic solutions than those in neutral and alkaline conditions [12]. A similar trend was observed for the biosorption of reactive dyes on inactive *R. arrhizus* [19], the adsorption of Congo red by coir pith carbon [18], the adsorption of reactive dyes [12] and acidic dyes on cross-linked chitosan beads [12].

3.1.2. The effect of the temperature

Investigation of temperature effect on the biosorption of acidic dyes are very important in the real application of biosorption as various textile and other dye effluents are produced at relatively high temperatures [5]. The biosorption of AR 274 on *E. prolifera* was investigated as a function of temperature and maximum uptake value was obtained at 30 °C as can be seen from Fig. 2. An increase in the adsorbed dye amounts with increasing temperature from 20 up to 30 °C deals with an increase in the adsorption capacity of *E. prolifera*. Further increase in temperature from 30 °C may alter the surface activity of *E. prolifera* resulting a decrease in uptake value, indicating that AR 274-*E. prolifera* process is exothermic in nature. The exothermic nature of dye biosorption has also been reported for the biosorption of Remazol Black B by *R. arrhizus* [20].

3.1.3. The effect of the initial dye concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of all molecule between the aqueous and solid phases [21–24]. In this study, the effect of initial dye concentration on biosorption of the AR 274 by *E. prolifera* was investigated at different initial dye concentrations. The equilibrium uptake values increased from 60.3 to 241 mg/g with increasing initial dye concentration from 60.3 to 256 mg/L as a result of the increase in the driving force. However, AR 274 removal yield decreased from 100 to 94.14% with an increase in initial dye concentration from 60.3 to 256 mg/L. At lower dye concentrations, solute concentrations to biosorbent sites ratio is higher, which cause an increase in color removal [25]. At higher concentrations, lower adsorption yield is due to the saturation

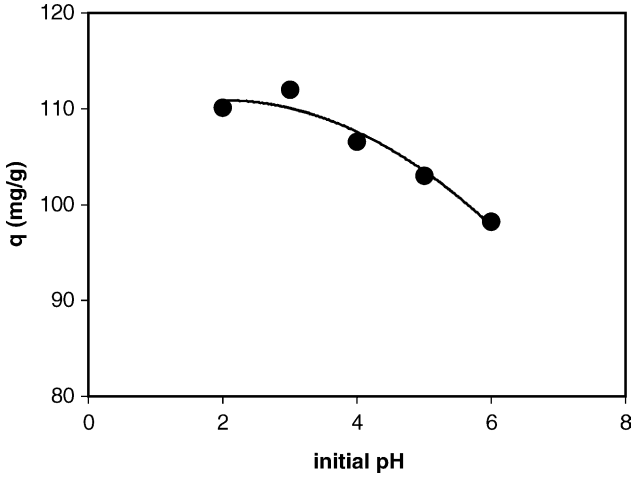

Fig. 1. The effect of initial pH (temperature 30 °C, 250 mg/L initial dye concentration, agitation speed 150 rev/min).

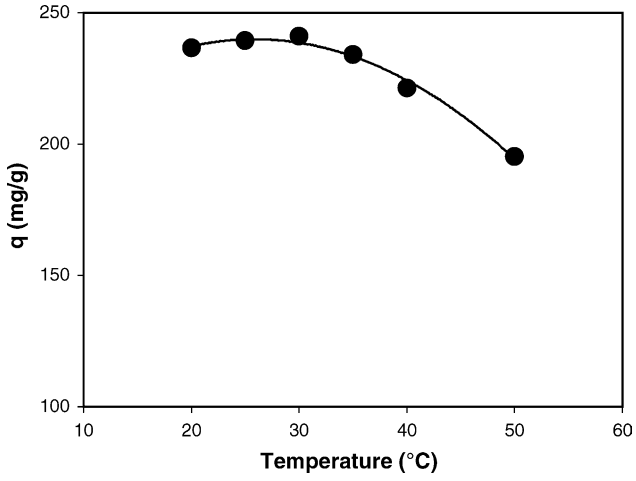

Fig. 2. The effect of temperature (initial pH 3.0, 250 mg/L initial dye concentration, agitation speed 150 rev/min).

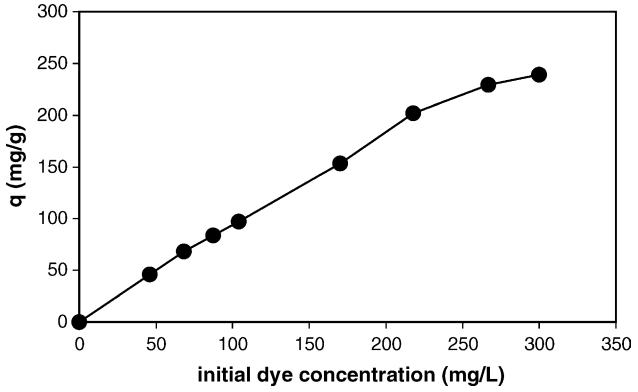

Fig. 3. The effect of initial AR 274 concentration (initial pH 3.0, temperature 30 °C, agitation speed 150 rev/min).

of adsorption sites. A plot of the final uptake values (mg/g) of AR 274 on *E. prolifera* at the end of 120 min versus the initial dye concentrations was also presented in Fig. 3. As seen from Fig. 3, the saturation plateau is reached at 250–300 mg/L and did not change with further increment in initial AR 274 concentration, suggesting that available sites on the biosorbent are the limiting factor for AR 274 biosorption.

3.1.4. The effect of the biosorbent concentration

To investigate the effect of biosorbent concentration, the biosorption of AR 274 onto *E. prolifera* was measured at five different biosorbent concentration at an initial dye concentration of 250 mg/L. The uptake values and adsorbed dye concentrations are given in Fig. 4. It is obvious from Fig. 4 that by increasing the biosorbent concentration the adsorbed dye concentration increases but the amount adsorbed per unit mass decreases. 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 concentration. The decrease in amount of dye adsorbed with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration and the solute concentration in the surface of the adsorbent [25]. Another reason may be due to the particle interaction, such as aggregation, resulted from high biosorbent concentration. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusional path length [26]. Further increment in biosorbent concentration from 3.0 g/L did not cause significant improvement in adsorption. This is due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the dye molecules bound to the sorbent and those remaining unadsorbed in the solution [27].

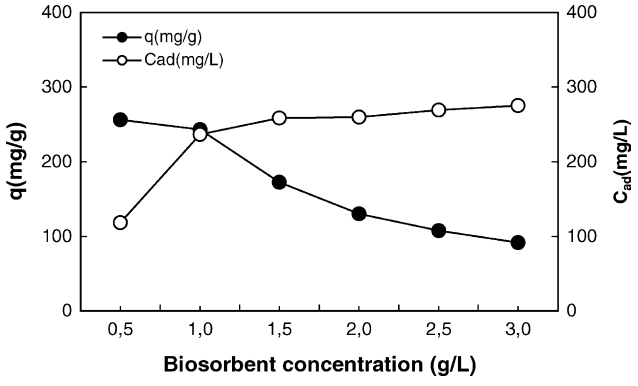

Fig. 4. The effect of biosorbent concentration (initial pH 3.0, temperature 30 °C, initial dye concentration 250 mg/L, agitation speed 150 rev/min).

3.2. Application of the pseudosecond-order kinetic model

Information on the kinetics of dye uptake is required for selecting optimum operating conditions for full-scale batch dye removal processes [10]. 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 [10]. The two important aspects for parameter evaluation of the adsorption study are the kinetics and equilibrium of adsorption. Several models can be used in order to investigate the mechanism of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes. Ho and McKay have conducted a literature review containing the use of sorbents and biosorbents to treat polluted aqueous effluents containing dyes/organics or metal ions and they noted that the highest correlation coefficients were obtained by using the pseudosecond-order kinetic model for different metal ion-sorbent system [28]. If the rate of sorption follows a second-order mechanism, the pseudosecond-order kinetic model is expressed as [28,29]:

$$dq/dt = k_2(q_{eq} - q_t)^2 \quad (1)$$

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

$$t/q_t = 1/k_2 q_{eq}^2 + t/q_{eq} \quad (2)$$

If the pseudosecond-order kinetics is applicable, the plot of t/q_t against t of Eq. (2) should give a linear relationship, from which $q_{eq,cal}$ and k_2 can be determined from the slope and intercept of the plot.

In this part, the pseudosecond-order kinetic model was applied to the experimental data in order to investigate the biosorption mechanism of Acid Red 274 and potential rate controlling steps such as mass transport and chemical reaction processes. Figs. 5 and 6 show the plots of the experimental and predicted q_t (mg/g) values from the pseudosecond-order kinetic model for the biosorption of AR 274 on *E. prolifera* at different temperatures and initial dye concentrations, respectively. The values of the k_2, experimental and calculated q_{eq} values and correlation coefficients are presented in Table 1. The experimental and calculated q_{eq} and k_2

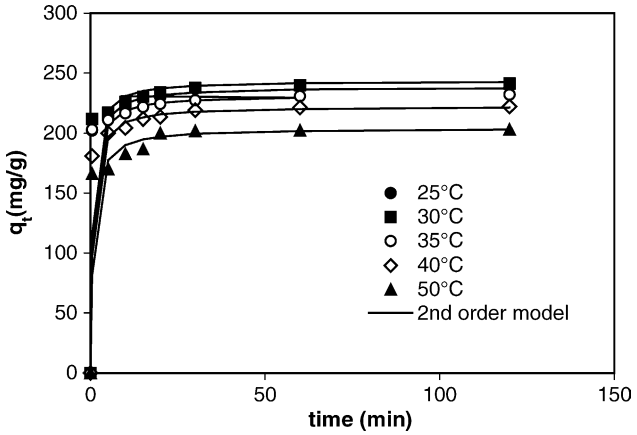

Fig. 5. Comparison of experimental q_t and predicted q_t from the pseudosecond-order kinetic model for different temperatures.

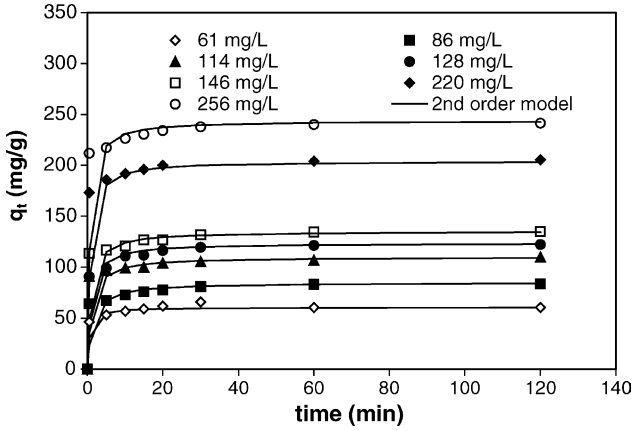

Fig. 6. Comparison of experimental q_t and predicted q_t from the pseudosecond-order kinetic model for different initial dye concentrations.

Table 1
A comparison of the pseudosecond-order rate constants, experimental and calculated q_{eq} values and correlation coefficients obtained at the different initial AR 274 concentrations and temperatures (initial pH 3.0, agitation speed 150 rev/min)

C_0 (mg/L)	q_{eq} (mg/g)	$q_{eq,cal}$ (mg/g)	k_2 (g/mg min)	R^2
61	60.26	60.6	0.0336	1.0000
85.7	83.08	84.74	0.0091	0.9998
114.6	109.78	109.89	0.0088	0.9998
128.8	121.56	123.45	0.0086	0.9999
146	134.56	135.14	0.0083	0.9999
219	204.03	204.08	0.0075	0.9999
256	241.32	243.9	0.0073	1.0000
Temperature (°C)	q_{eq} (mg/g)	$q_{eq,cal}$ (mg/g)	k_2 (g/mg min)	R^2
25	238.10	238.87	0.00678	1.0000
30	241.32	243.9	0.0073	1.0000
35	230.91	232.55	0.00712	1.0000
40	221.29	222.23	0.00698	1.0000
50	203.00	204.08	0.00648	0.9999

values increased up to 30 °C and then decreased with further increase in temperature indicating the exothermic nature of AR 274 biosorption. The temperature optima obtained from the pseudosecond-order kinetic model confirmed the experimental optimum temperature (Fig. 2). As can be seen from Fig. 6, the adsorption of AR 274 on *E. prolifera* occurred very fast and the short contact time owing to the large difference in concentration between the biosorbent surface and solution at low initial dye concentrations. A similar trend was observed for the adsorption of anionic dyes on chemically cross-linked chitosan beads [12]. As seen from Table 1, the values of rate constant decreased with a increase in the initial dye concentration. There are many factors which can contribute to this sorbate concentration effect on rate of adsorption: increasing the solute concentration in solution seems to reduce the diffusion of solute in the boundary layer and to enhance the diffusion in the solid [30]. Also, the experimental equilibrium data for AR 274 are in good agreement with those calculated using the pseudosecond-order kinetic model (Table 1). The correlation coefficients obtained from the pseudosecond-order kinetic model were greater than 0.99 for all the initial dye concentrations and temperatures for contact times of 120 min. This indicates that the biosorption of AR 274 on *E. prolifera* follows the pseudosecond-order kinetic model.

3.3. The determination of the activation energy

The pseudosecond-order rate constant is expressed as a function of temperature by the following Arrhenius type relationship [28,29]:

$$k_2 = k_0 \exp[-E/RT] \quad (3)$$

where k_0 is the temperature independent factor (g/mg min), E the activation energy of sorption (kJ/mol), R the universal gas constant (8.314 kJ mol^{-1} K^{-1}) and T the absolute temperature (K). The activation energy of AR 274 on *E. prolifera* was calculated by using pseudosecond-order kinetic constants, by calculating the slope of the plot of ln k_2 versus 1/T (Fig. 7). The activation energy in the range of 30–50 °C was found to be −4.85 kJ/mol (R^2 = 0.9981). The observed activation energy values for the biosorption of AR 274 were of the same magnitude as the heat of physical adsorption.

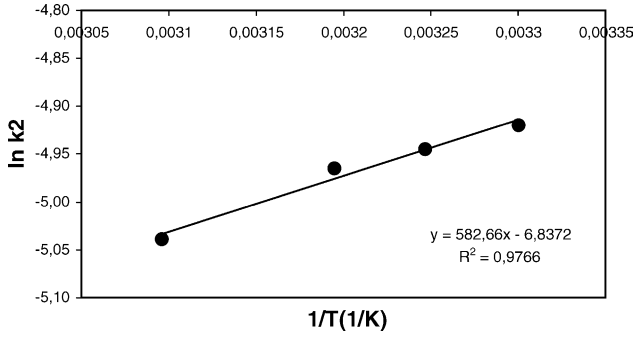

Fig. 7. The determination of the activation energy.

3.4. Weber–Morris model (intraparticle diffusion)

In order to investigate the contribution of intraparticle diffusion, which is accepted to be rate controlling step, on the adsorption of AR 274 on inactivated *E. prolifera*, the equation described by Weber and Morris can be used to assess this opinion [9,24,30,31]:

$$q_t = Kt^{1/2} \quad (4)$$

where q_t (mg/g) is the amount of dye adsorbed at time t, K the intraparticle rate constant (mg/g min$^{1/2}$). According to this model, the plot of uptake (q_t) 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 plateu to the equilibrium.

Weber–Morris model was applied to the biosorption of AR 274 on *E. prolifera* as a function of the biosorbent concentration and the variation of q versus $t^{1/2}$ was given in Fig. 8. The linear portions of the curves do not pass through the origin indicating that the mechanism of AR 274 removal on *E. prolifera* is complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process. For the different biosorbent concentrations, the intraparticle rate constant values calculated from the slopes of the linear portions of the plots of q versus $t^{1/2}$ were found as 10.36, 7.02, 2.35, 1.39, 1.45 and 1.02 mg/g min$^{1/2}$ for 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 g/L, respectively. At low biosorbent concentrations, increase in K was due to the decrease in the intraparticle diffusion resistance. Also, this may be explain why the maximum biosorption capacity (mg/g) of *E. prolifera* was obtained at 0.5 g/L of biosorbent concentration.

3.5. Equilibrium modelling

The equilibrium sorption isotherm is fundamentally important in the design of sorption system [32]. Equilibrium studies in sorption give the capacity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium [32]. By plotting solid phase concentration (mg/g) against liquid phase concentration (mg/L) graphically it is possible to depict the equilibrium adsorption isotherms (Fig. 9).

The Langmuir model is valid for monolayer adsorption onto a surface with a finite number of identical sites. The well-known expression of the Langmuir model is given by Eq. (5)

$$q_{eq} = (Q^0 K_a C_{eq})/(1 + K_a C_{eq}) \quad (5)$$

Eq. (5) can be rearranged to the following linear form:

$$1/q_{eq} = 1/Q^0 + 1/(K_a Q^0) \cdot 1/C_{eq} \quad (6)$$

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^0 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^0 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 sorbent did not reach its full saturation in experiments.

The Freundlich expression (Eq. (7)) is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. Theoretically using this expression, an infinite amount of adsorption can occur

$$q_{eq} = K_F C_{eq}^{1/n} \quad (7)$$

or, in its linear form

$$\ln q_{eq} = \ln K_F + 1/n \ln C_{eq} \quad (8)$$

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

The Langmuir and Freundlich isotherm models were applied to the equilibrium data of AR 274 dye on *E. prolifera* at different temperatures and their linear forms were

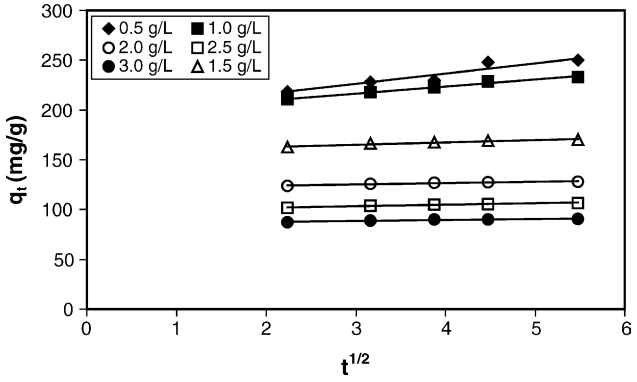

Fig. 8. . Weber–Morris model plots for biosorbent concentrations.

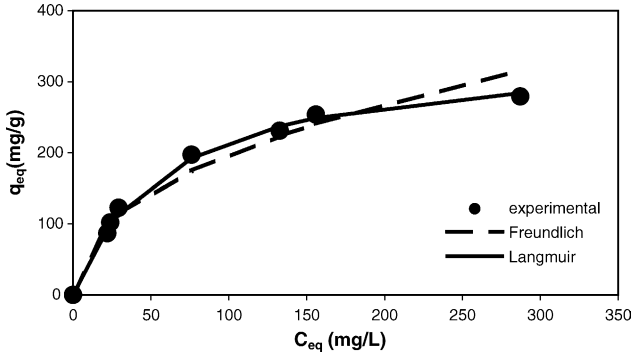

Fig. 9. The graphical comparison of the experimental and calculated equilibrium data.

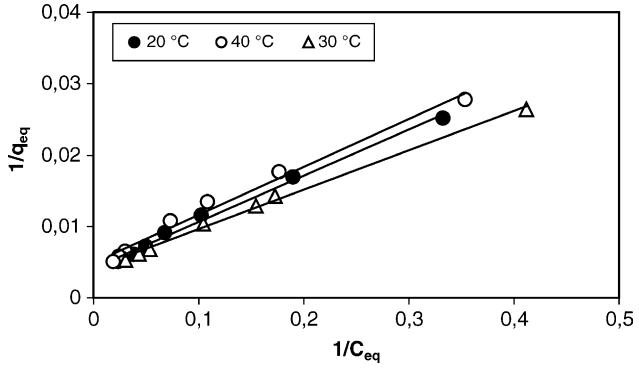

Fig. 10. The linearized Langmuir isotherms obtained at different temperature values (initial pH 3.0).

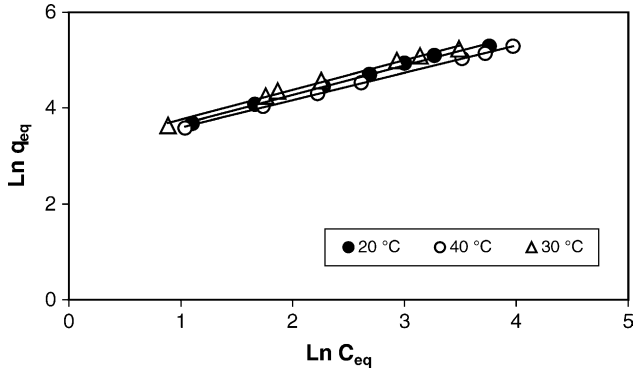

Fig. 11. The linearized Freundlich isotherms obtained at different temperature values (initial pH 3.0).

given in Figs. 10 and 11, respectively. The isotherm constants were determined by using linear regression analysis and were presented in Table 2.

As can be seen from Table 2, Q^0 of *E. prolifera* was determined to be 244 mg/g at 30 °C and initial pH 3.0, as was previously mentioned on determination of optimum conditions. q_{eq} was found to be smaller than Q^0 indicating that the biosorption of AR 274 dye on *E. prolifera* is by a monolayer type adsorption. For AR 274 biosorption, the values of n calculated from Freundlich isotherms at different temperatures were found to be very close to each other, indicating that the adsorption intensity was not affected by changing the temperature of adsorption medium. The magnitude of K_F and n shows easy separation of AR 274 from aqueous solutions with high adsorptive capacity of *E. prolifera,* especially at 30 °C and initial pH 3.0.

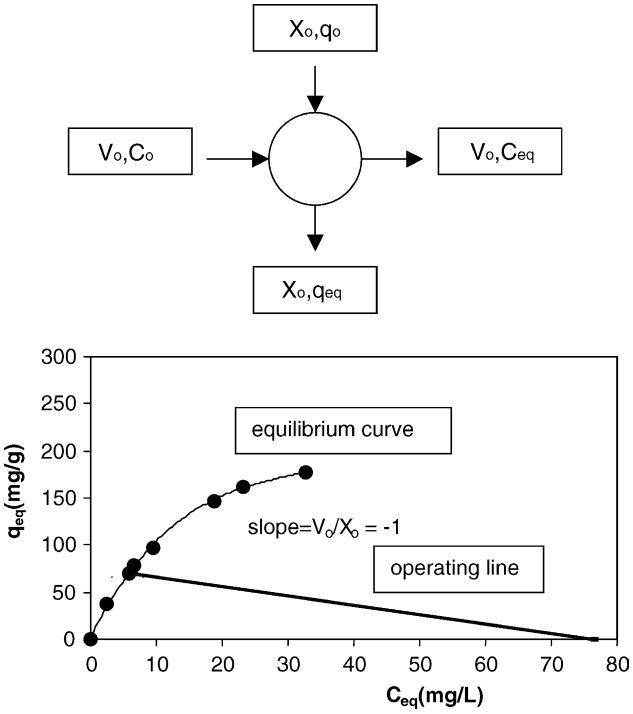

Fig. 12. AR 274 adsorption in a single stage batch reactor by inactivated *E. prolifera*.

The adsorption capacity of *E. prolifera* was relatively high when compared with other adsorbents used for the anionic dyes in the literature. For example, Sulfur Black 5 removal capacity of *Tremella fuciformis* was determined as 92 mg/g sorbent while maximum sorption capacity of *A. niger* was found to be 6.63 mg/g. Ragajuru et al. studied for the removal of direct red dye using four bacterial strains and reported that the maximum removal capacity was 112 mg/g as reported by Fu and Viraraghavan [5]. Differences between dye uptake values are due to the properties of each adsorbent such as structure, functional groups and surface area.

The adsorption in a batch stirred reactor can be considered as a single stage equilibrium. The same quantity of solution (V_0) is treated at the single stage by a given amount of adsorbent (X_0) to reduce the dye concentration of solution from C_0 to C_{eq} (Fig. 12). The mass balance for the dye in the single stage is given by

$$V_0C_0 + X_0q_0 = V_0C_{eq} + X_0q_{eq} \quad (9)$$

$$-V_0/X_0 = (q_{eq} - q_0)/(C_{eq} - C_0) \quad (10)$$

Table 2
Comparison of the adsorption constants obtained from the Langmuir and Freundlich adsorption isotherms at different temperatures for AR 274 dye (initial pH 3.0, agitation speed 150 rev/min)

Temperature (°C)	Langmuir model			Freundlich model		
	Q^0 (mg/g)	K_a (L/mg)	R^2	K_F	$1/n$	R^2
20	238.1	0.0649	0.9933	20.92	0.6166	0.9945
30	244.0	0.0741	0.9963	23.28	0.6187	0.9932
40	204.1	0.0729	0.9850	20.44	0.5740	0.9992

The amount of dye adsorbed per unit mass of biosorbent at the beginning in a batch reactor (q_0) is equal to 0.0. Eq. (10) will provide the operating line passing through (C_0, q_0) and (C_{eq}, q_{eq}) for the single stage. The equilibrium AR 274 concentrations can also be obtained by using the experimental equilibrium curve and operating line. The equilibrium curve and operating line for AR 274 at 30 °C and initial pH 3.0 are given in Fig. 12. To determine the equilibrium AR 274 concentration in solution leaving the reactor, the initial dye concentration located at the proper point on the ordinate (C_0 = 76 mg/L, q_0 = 0.0 mg/g), the operating line passing through (C_0, q_0) with a slope of $V_0/X_0 = -1.0$. The absisca (C_{eq}) and ordinate (q_{eq}) values for the intersection of coordinates of the operating line and the equilibrium curve gives C_{eq} = 5.1 mg/L and 69.9 mg/g, respectively while the experimental C_{eq} and q_{eq} values were obtained 5.8 mg/L and 70.2 mg/g, respectively.

Substituting the Freundlich and Langmuir equations for q_{eq} in Eq. (10) and rearranging give for a single stage

$$C_0 = C_{eq} + (X_0/V_0)\, K_F C_{eq}^{1/n} \quad (11)$$

$$K_a C_{eq}^2 + [1 - K_a C_0 + Q^0(X_0/V_0)K_a]C_{eq} - C_0 = 0 \quad (12)$$

The experimental K_F, n, Q^0 and K_a values obtained under the optimum biosorption conditions were used to calculate the C_{eq} values in the stream leaving the single batch system from Eqs. (11) and (12). For 76 mg/L initial AR 274 concentration at 30 °C and initial pH 3.0, Eq. (11) is solved for the C_{eq} by a trial and error computation and was found as 5.94 mg/L. The positive root obtained from analytical solution of Eq. (12) gives the equilibrium dye concentration as 5.49 mg/L. The experimental equilibrium data for Acid Red 274 are in good agreement with those obtained by both isotherm models and graphical method. On the other hand, the isotherm constants, K_F, $1/n$, Q^0 and K_a, or the operating lines obtained from the experimental equilibrium data can be used to find the stage number and/or the final concentration of the exit stream for the desired purification without any experiments. As a result, the removal of a given amount of solute can be accomplished with greater economy of adsorbent if the solution is treated with separate small batches of adsorbent rather than in single batch, with filtration between each stage [22].

The effect of isotherm shape can be used to predict whether a sorption system is 'favorable' or 'unfavorable'. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by the following relationship [33,34]:

$$R_L = 1/(1 + K_a C_0) \quad (13)$$

where R_L is a dimensionless separation factor, indicating the shape of the isotherm. The isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, the isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$.

The R_L values at 30 °C and initial pH 3.0 for the studied system were found in the range of 0.213–0.0512 for 50–250 mg/L initial dye concentrations. As a result, it can be said that the isotherm shape of AR 274 adsorption on *E. prolifera* is favorable type.

3.6. 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:

$$\Delta G = -RT \ln K_c \quad (14)$$

where ΔG is free energy change, J/mol; R the universal gas constant, 8.314 J/mol K and T the 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 [35,36]. The equilibrium constant of biosorption is defined as $K_c = C_{ad,e}/C_{eq}$ [22]. Where $C_{ad,e}$ is the amount of dye (mg) 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 [37]. For the AR 274 biosorption on *E. prolifera*, the K_c values were calculated at different temperatures for 250 mg/L initial dye concentration, 3.0 initial pH and 1.0 g/L biosorbent concentration and were found to be 8.217, 5.75, 4.87 and 2.74 L/g for 30, 35, 40 and 50 °C, respectively. The K_c value decreased with increasing temperature resulting a shift of the adsorption equilibrium to the left [35].

According to the Van't Hoff equation

$$\ln K_c = -(\Delta H/R)(1/T) + \Delta S/R \quad (15)$$

According to Eq. (15), the $\ln K_c$ versus $1/T$ plots for the biosorption of AR 274 onto *E. prolifera* were given in Fig. 13. ΔH and ΔS values in the range of 30–50 °C were obtained as −42.58 kJ/mol and −123.08 J/mol K at initial pH 3.0 and initial AR 274 concentration 250 mg/L, respectively. The effect

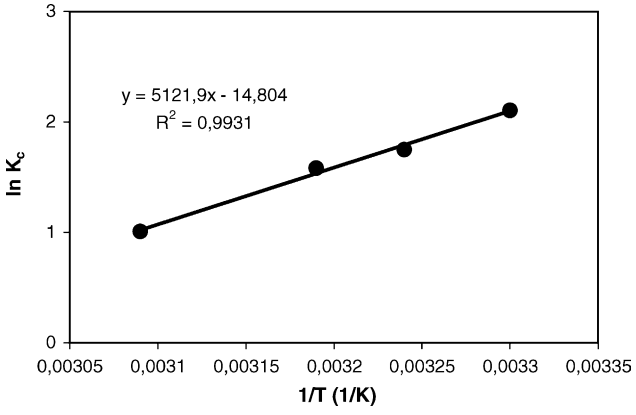

Fig. 13. The determination of the biosorption enthalpy.

of temperature on the equilibrium constant K_c is determined by the sign of ΔH. The negative value of ΔH in the range of 30–50 °C shows that the biosorption of AR 274 on *E. prolifera* 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 sorption of dye on biosorbent while low value of ΔS indicates that no remarkable change on entropy occurs.

The change with temperature of the free energy change and the equilibrium constant can be represented as follows:

$$\Delta G = \Delta H - T\Delta S \quad (16)$$

Eq. (16) shows clearly that the adsorption process is composed of two contributions-enthalpic and entropic, which characterize whether the reaction is spontaneous or not [36]. The free energy changes for the AR 274 biosorption on *E. prolifera* were determined by using the experimental equilibrium constants and were found to be −5.28, −4.67, −4.06 and −2.83 kJ/mol for 30, 35, 40 and 50 °C, respectively. The negative values of ΔG confirm the feasibility of the process and the spontaneous nature of biosorption with a high preference of AR 274 on *E. prolifera*. However, the entropic contribution is even larger than the free energy of adsorption ($\Delta G = \Delta H - T\Delta S < 0$).

4. Conclusion

Based on this investigation, it can be said that optimum conditions for the biosorption of AR 274 on *E. prolifera* a green algae grown on Mersin costs of the Mediterranean, Turkey, were determined as 30 °C temperature, initial pH 3.0, initial dye concentration 300 mg/L and 0.5 g/L of biosorbent concentration. The biosorption equilibrium was best defined by the Langmuir isotherm model at these optimum conditions. *E. prolifera* can be employed as an effective and low-cost biosorbent for the removal of AR 274 dye from wastewaters with its relatively high sorption capacity of 244 mg/g. Kinetic studies were done and it is concluded that the biosorption process follows a pseudosecond-order kinetics and activation energy was determined as −4.85 kJ/mol. According to Weber–Morris model, the mechanism of AR 274 removal on *E. prolifera* is complex and both the surface adsorption as well as intraparticle diffusion contribute to the actual adsorption process. Both the values of the separation factor R_L and ΔG value indicated that this biosorption process was favorable. Thermodynamic studies also showed that the biosorption of AR 274 on *E. prolifera* was exotermic in nature.

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