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Equilibrium, kinetic and thermodynamic studies of the biosorption of textile dye (Reactive Red 195) onto *Pinus sylvestris* L.

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ABSTRACT

This study investigated the biosorption of Reactive Red 195 (RR 195), an azo dye, from aqueous solution by using cone biomass of *Pinus sylvestris* Linneo. To this end, pH, initial dye concentration, biomass dosage and contact time were studied in a batch biosorption system. Maximum pH for efficient RR 195 biosorption was found to be 1.0 and the initial RR 195 concentration increased with decreasing percentage removal. Biosorption capacity increased from 6.69 mg/g at 20 °C to 7.38 mg/g at 50 °C for 200 mg/L dye concentration. Kinetics of the interactions was tested by pseudo-first-order and pseudo-second-order kinetics, the Elovich equation and intraparticle diffusion mechanism. Pseudo-second-order kinetic model provided a better correlation for the experimental data studied in comparison to the pseudo-first-order kinetic model and intraparticle diffusion mechanism. Moreover, the Elovich equation also showed a good fit to the experimental data. Freundlich and Langmuir adsorption isotherms were used for the mathematical description of the biosorption equilibrium data. The activation energy of biosorption (*Ea*) was found to be 8.904 kJ/mol by using the Arrhenius equation. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the study also evaluated the thermodynamic constants of biosorption (ΔG^o, ΔH^o and ΔS). The results indicate that cone biomass can be used as an effective and low-cost biosorbent to remove reactive dyes from aqueous solution.

1. Introduction

Dyes are extensively used in many industries including textile, leather, pulp and paper, food and plastics. They are classified as acid and reactive dyes, cationic-basic dyes, non-ionic-disperse dyes, and anionic direct dyes [1,2]. Amongst the most commonly used ones are reactive dyes which present medium to high fastness for cellulose fibres [3]. Approximately 700,000 tones and 10,000 different types of dyes and pigments are being produced annually across the world and a significant proportion of these dyes enter the environment in wastewater [4]. There are some reports about the negative effects of these dyes. For example, reactive dyes are toxic for several organisms and constitute a threat to ecosystems mainly because they block out the sunlight and thus reduce photosynthesis and dissolved oxygen concentration [5,6]. Besides, many dyes or their metabolites have carcinogenic, teratogenic and mutagenic effects on humans and other life forms [7,8]. Therefore, removal of dyes before disposal of the wastewater is extremely important. Several methods such as photochemical oxidation, membrane filtration, ozone treatment, activated carbon adsorption, reverse osmosis and coagulation have been developed to remove dyes from wastewater [9–11]. However, they are ineffective, especially for the removal of brightly coloured, water-soluble reactive and acid dyes. In addition, most of these methods require high costs and are difficult to operate particularly on a great scale. Conversely, biosorption has attracted increasing interest owing to its lower cost, its effectiveness in producing less sludge and its environmental friendliness [12–14].

Over the last few decades, there has been an increase in the use of plant waste products for dye removal by biosorption from wastewater because of their natural availability and the high degree of dye removal achieved under laboratory conditions [15]. These alternative biosorbents include *Enteromorpha prolifera* [8], *Azadirachta indica* [12], *Posidonia oceanica* fibres [15], *Eriobotrya japonica* [16], wheat bran [17], *Botrytis cinerea* [18], *Penicillium restrictum* [19] and *Pinus sylvestris* [20].

Cone biomass is a waste itself and a readily available biosorbent. The ovulate cone is the well known cone of the *Pinus* and other conifers. Each cone is composed of an axis upon which are borne, in a spiral fashion, a large number of woody scales. Two megasporangia in ovules develop on the upper surface of each scale. Upon maturity they become seeds; the ovulate cone is, therefore, a seed-bearing cone. The scales of the mature cone are composed of epidermal and sclerenchyma cells which contain cellulose, hemicellulose, lignine, rosin and tannins in their cell walls [21,22].

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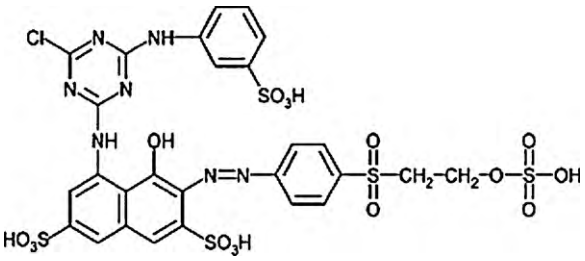

Fig. 1. Chemical structure of Reactive Red 195.

The current study investigated the biosorption of Reactive Red 195 (RR 195) ions from aqueous solution by using cone biomass of *P. sylvestris* L. This dye is largely used for textile dying in Turkish cloth industry. To investigate the mechanisms of RR 195 biosorption, the characteristic constants of biosorption were determined using a pseudo first- and second-order equation, the Elovich equation and intraparticle diffusion equation, respectively. The Langmuir and Freundlich isotherms were used to describe equilibrium isotherms. The biosorption mechanisms of RR 195 onto cone biomass were also evaluated in terms of thermodynamics and kinetics. The magnitude of the heat effect for the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the dye–biosorbent interaction process. The relative binding affinity of the biosorbent and the main mechanism for biosorption are also discussed.

2. Materials and methods

2.1. Materials

The biosorbent used in this study, *P. sylvestris* cones, was collected in July 2007. The cones were washed repeatedly with deionized water to remove the adhering dirt and soluble impurities, dried at 80 °C for 24 h and crushed. The dried biomass was ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve. The powdered biosorbent was stored in glass bottles prior to use.

The textile dye, Reactive Red 195 (RR 195), was obtained from Dystar, Turkey and used without further purification. Its chemical composition is shown in Fig. 1. By dissolving RR195 in deionized water, the dye containing stock solution (1000 mg/L) was obtained. The other required concentrations (50–200 mg/L) were prepared by diluting the stock solution of RR 195. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to desired values with dilute HCl or NaOH.

2.2. Batch biosorption studies

The experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL of dye solutions. The effect of biomass concentration on RR 195 biosorption was determined using biomass sampling amounts ranging from 5.0 to 40 g/L. To determine the effect of initial dye concentration of RR 195, dye concentrations ranging from 50 to 200 mg/L were prepared and used. The batch experiments were performed under shaking at 200 rpm at 20 °C, pH 4.0 for 180 min. The effect of temperature on RR 195 biosorption was increased from 20 to 50 °C. The effect of pH on the biosorption process was determined at different pH values ranging from 1.0 to 6.0.

After the biosorption process, the solution was centrifuged for 5 min at 4500 rpm and supernatants were analyzed for remaining dye concentration using a spectrophotometer (540 nm) (Shimadzu UV-160A).

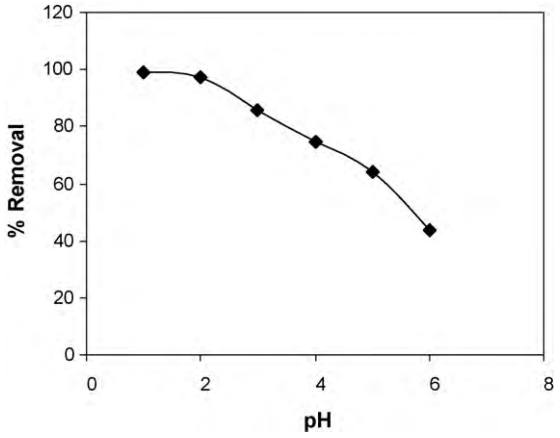

Fig. 2. Effect of pH on % Removal of *P. sylvestris* for RR 195 (C_0 = 100 mg/L; T = 25 °C; m = 20 g/L).

3. Results and Discussion

3.1. Effect of initial pH

pH is an important parameter for biosorption studies and affects not only the biosorption capacity, but also the colour and solubility of dye solutions [19]. The effect of initial solution pH on the biosorption amount of cone biomass was investigated in the pH range between 1-6 (which was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards) at a constant temperature of 20 °C and 100 mg/L initial Reactive Red 195 concentration. It was observed that the solution pH affects the amount of dye biosorbed.

As seen in Fig. 2, the biosorption of RR 195 was at its maximum amount at the initial pH of 1.0, but decreased with pH up to 6.0. The biosorption capacity for RR 195 onto cone biomass increased from 43.59% to 98.80% when the solution pH decreased from 6.0 to 1.0. A similar observation has been reported in the literature, suggesting that reactive dye biosorption decreases with increasing pH [23,24]. Reactive dyes are also called anionic dyes because of the negative electrical structure of the chromophore group [8]. The increase in OH^- ions with increasing pH also results in a competition with dye anions for biosorption sites, leading to a decrease in biosorption. As pH decreases, the number of positively charged sites on the biosorbent surface increases; as a result, dye biosorption also increases due to the electrostatic attractions between negatively charged dyes anions and positively charged biosorbent surface [25]. In the initial experiments, the optimum pH value was obtained at pH 1.0. However, in the following experiments, the pH value was fixed at 4.0, which was the native pH value of solution.

3.2. Effect of biosorbent dosage

The influence of initial biosorbent concentration on the biosorption capacity of cone biomass was studied for a dye concentration of 100 mg/L and a biosorbent content of 5–40 g/L at 20 °C temperature (figure not shown). The increase in biosorbent dose resulted in an increase in biosorption efficiency. Biosorption efficiency increased from 57.78% to 74.67% as the biosorbent dose increased from 5 to 20 g/L. Further increases in biosorbent dosage reduced the maximum removal of RR 195. This can be explained by aggregate formation during biosorption, which takes place at high biosorbent concentrations causing a decrease in the effective biosorption area. The increase in the percentage of dye removal with biosorbent dosage could be attributed to an increase in the biosorbent surface areas, augmenting the number of biosorption sites avail-

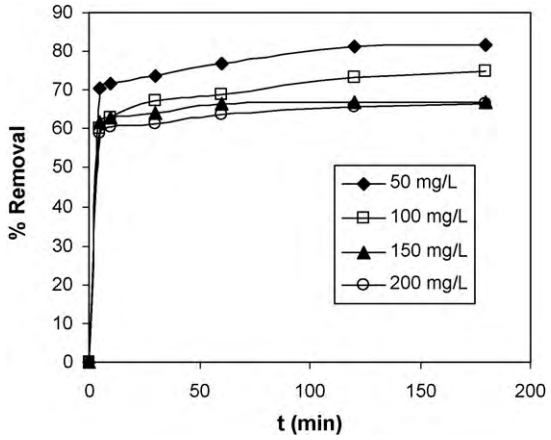

Fig. 3. Effect of contact time on % Removal of *P. sylvestris* for RR 195 (m = 20 g/L; T = 25 °C; pH 4.0).

able for biosorption, as already reported [26,27]. Similar behaviour for the effect of biosorbent dosage on RR 195 biosorption capacity was observed and discussed in the literature for different types of biosorbents [17]. Therefore, in the following experiments, the biosorbent dosage was fixed at 20 g/L.

3.3. Effect of contact time

Contact time is one of the important parameters for successful deployment of the biosorbents for practical application [18]. The effect of contact time under different initial dye concentrations (50 to 200 mg/L) on the biosorption of RR 195 onto cone biomass is presented in Fig. 3. RR 195 showed a fast rate of biosorption during the first 30 min. of the dye-biosorbent contact. The equilibrium was achieved within 180 min. After this equilibrium period, the amount of biosorbed dye did not show time-dependent change.

3.4. Effect of initial dye concentration and temperature

The effect of the initial RR 195 concentration in the solutions on biosorption is shown in Fig. 4. Biosorption experiments were carried out at a fixed biosorbent dose of 20 g/L and with RR 195 concentrations ranging from 50-200 mg/L for different temperatures (20-50 °C). As seen in Fig. 4, equilibrium uptake increased simultaneously with the increase in initial RR 195 concentrations in the range of experimental concentrations. Under the same conditions,

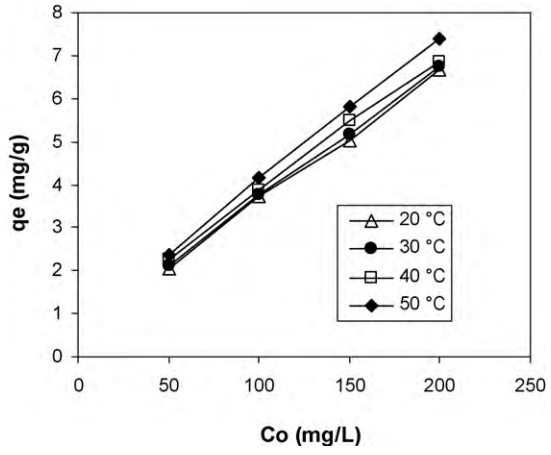

Fig. 4. Effect of initial RR 195 concentration and temperature on biosorption capacity (m = 20 g/L; pH 4.0).

if RR 195 concentration in the solution was higher, the active sites of cone biomass were surrounded by a greater number of RR 195 ions, resulting in a more sufficient biosorption process [26]. Therefore, the values of q_e increased with an increase in initial RR 195 concentrations. A larger biosorption capacity of RR 195 was also observed in a higher temperature range. The biosorption capacity increased from 6.69 mg/g at 20 °C to 7.38 mg/g at 50 °C for 200 mg/L dye concentration. The increase in biosorption capacity at increasing temperatures is either due to the higher affinity of sites for dye or to an increase in binding sites onto the biomass. Similar results were reported for various dye adsorptions by other biosorbents [12,15,17]

3.5. Biosorption kinetics

Different kinetic models were used to describe the experimental data of biosorption [28,29]. The pseudo-first-order rate Lagergren model is:

$$dq/dt = k_1(q_e - q_t) \quad (1)$$

where q_t (mg/g) is the amount of adsorbed dye on the biosorbent at time t and k_1 (1/min) is the rate constant of first-order adsorption. The integrated form of Eq. (1) is

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (2)$$

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (3)$$

A straight line of $\log(q_e - q_t)$ versus t suggests the applicability of this kinetic model. q_e and k_1 can be determined from the intercept and slope of the plot, respectively. The pseudo-second-order kinetic model (Ho equation) is expressed as:

$$dq/dt = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption. Eq. (4) can be rearranged and linearized to obtain:

$$q_t = (k_2 t\, q_e^2)/(1 + k_2 t q_e) \quad (5)$$

$$t/q_t = 1/(k_2(q_e)^2) + t/q_e \quad (6)$$

The plot t/q_t versus t should give a straight line if the pseudo-second-order kinetics are applicable, and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

$$h = k_2(q_e)^2 \quad (7)$$

where h is the initial sorption rate (mg/g min) [29].

For evaluating the biosorption kinetics of RR 195 ions, the pseudo-first-order and pseudo-second-order kinetic were used to fit the experimental data. The biomass was contacted with the RR 195 solution (100 mg/L) at various temperatures depending on contact time. The equilibrium uptake of RR 195 ions onto cone biomass was affected by temperature and increased with increasing temperature up to 50 °C. The equilibrium was established in 180 min for all the temperatures studied. Similar observations were reported in the literature. For example, the adsorption capacity of the wheat bran for RR 195 dye increased with an increase in temperature [17].

Using Eqs. (3) and (6) the pseudo-first-order and pseudo-second-order kinetic constants and q_e values were determined from the plots (Fig. 5a-b). The linear fits were observed for all temperatures. A comparison of the pseudo-first-order and pseudo-second-order biosorption rate constant at different temperatures is presented in Table 1. It is important to note that for a pseudo-first-order model, the correlation coefficient is less than the pseudo-second-order coefficient. The values of correlation coefficient for Ho equation are very high (R^2 = 0.999) and the theoretical $q_{e,cal}$ values are closer to the experimental $q_{e,exp}$ values. The values for the product h representing the rate of initial biosorption, k_2

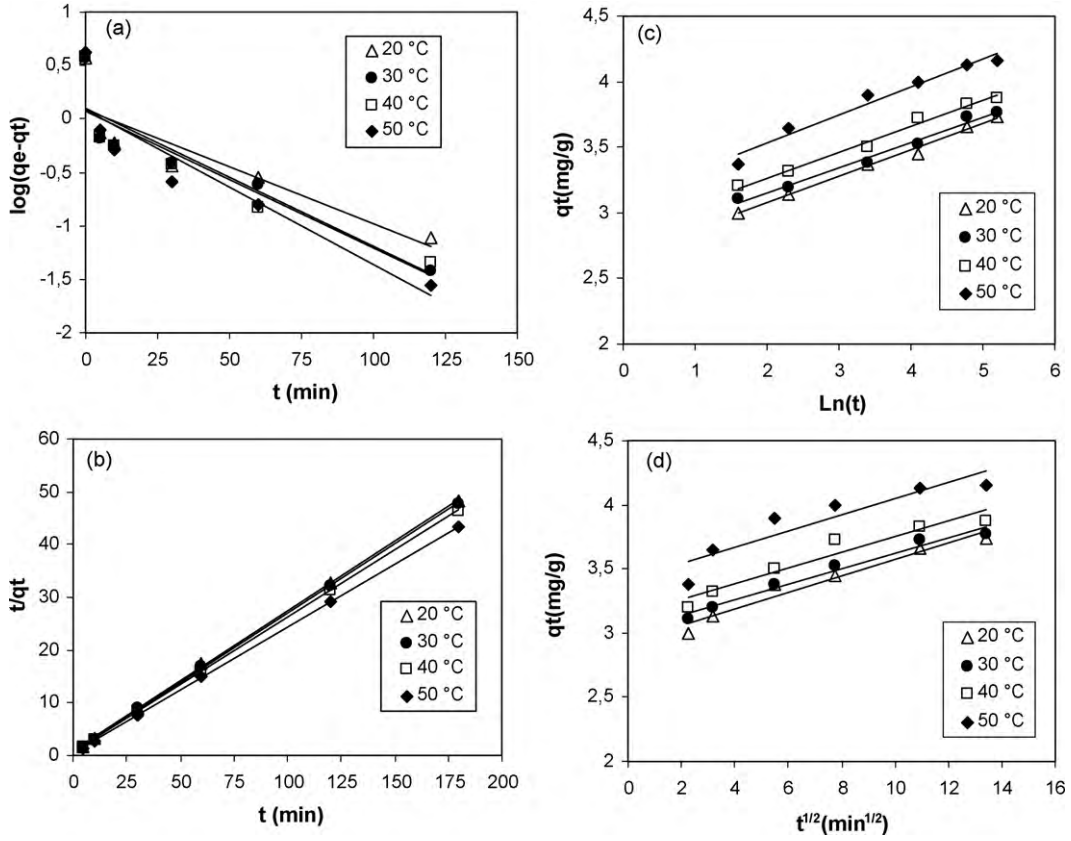

Fig. 5. Plots biosorption kinetic equations, (a) the pseudo first-order and (b) the pseudo second-order biosorption kinetics (c) the Elovich equation and (d) the intrapaticle diffusion kinetic of of *P. sylvestris* for RR 195 at different temperatures (C_0 = 100 mg/L; m = 20 g/L; pH 4.0).

and q_e increased with the rise in temperature. In the view of these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the biosorption of RR 195 onto cone biomass at different temperatures.

The biosorption data were further analyzed using the Elovich and intra-particle diffusion models. The Elovich equation is given as follows:

$$dq_t/dt = \alpha \exp(-\beta q_t) \quad (8)$$

where α is the initial adsorption rate (mg/g min), and the parameter β is desorption constant (g/mg). These coefficients are computed from the plots of q_t vs. ln t. The integrated form of Eq. (8) is

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t) \quad (9)$$

When the adsorbate ions and the surface sites interact chemically through a second-order mechanism, the application of the Elovich equation may be more appropriate [30]. Fig. 5c shows a plot of q_t versus ln t for the Elovich equation at different temperatures. The parameters of the Elovich equation are shown in Table 1. When the temperature of the solution increased, the constant α was observed to increase. As the temperature increases (from 20 to 50 °C), the values of α increase from 1.10×10^5 to 5.08×10^5. The Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, but the equation does not propose any definite mechanism for adsorbate-adsorbent interaction. The coefficients are significantly depending on the amount of adsorbent with a being much more sensitive [30].

Most adsorption reactions take place through multi step mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion and (iii) interaction between adsorbate and active site. Since the first step is excluded by shaking the solution, the rate-determining step is one of the other two steps.

Weber and Morris [31] described the intraparticle uptake of the adsorption process to be proportional to the half-power of time:

$$q_t = k_i(t)^{1/2} + C \quad (10)$$

where k_i is the intraparticle diffusion rate constant (mg/g min$^{1/2}$). The k_i is the slope of strait-line portions of the plot of q_t versus $t^{1/2}$. The plots are shown in Fig. 5d. The external surface biosorption (stage 1) is absent because of completion before 5 min. The second portion (stage 2, up to 5 min) describes

Table 1
Kinetic parameters for RR 195 biosorption onto *P. sylvestris* L.

T (°C)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model				Elovich			Intraparticle diffusion		
		k_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e,cal}$ (mg/g)	h (mg/g min)	R^2	β (g/mg)	α (x10^5 mg/g min)	R^2	k_i (mg/g min$^{1/2}$)	C	R^2
20	3.73	0.024	1.20	0.768	0.092	3.77	1.297	0.999	4.943	1.10	0.992	0.063	2.94	0.956
30	3.76	0.030	1.27	0.840	0.097	3.81	1.407	0.999	5.192	3.29	0.986	0.061	3.01	0.970
40	3.88	0.029	1.19	0.822	0.111	3.92	1.704	0.999	5.061	4.04	0.987	0.061	3.14	0.932
50	4.16	0.034	1.23	0.843	0.128	4.19	2.243	0.999	4.721	5.08	0.966	0.063	3.41	0.842

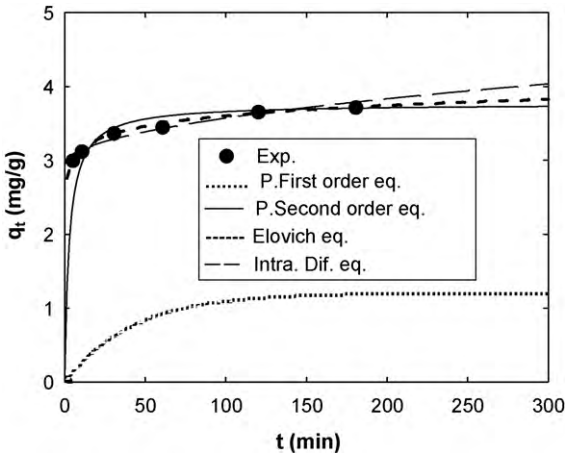

Fig. 6. Comparison between the measured and modeled time profiles for RR 195 onto *P. sylvestris* at 25 °C (C_0 = 100 mg/L; m = 20 g/L; pH 4.0).

the gradual adsorption stage, where intraparticle diffusion is rate limiting. The second linear portion (stage 2) followed by a plateau (stage 3) is attributed to the final equilibrium stage. k_i values are determined from the slope of second linear portion of this plot. Fig. 5d shows that the straight-line portion does not pass through the origin. The large intercept suggest that the process was largely of surface biosorption. Values of C and k_i, are given in Table 1 for all temperatures.

A comparison of the calculated and measured results at 20 °C is shown in Fig. 6. As can be seen, the pseudo second-order, and the Elovich chemisorption models are suitably fitted, whereas the intraparticle equation also fits the experimental data well. The pseudo first-order equation does not give a good fit to the experimental data for the biosorption of RR 195. This suggests that the biosorption systems studied belong to the second-order kinetic model, based on the assumption that the rate-limiting step may be chemical adsorption.

Activation energy was determined according to the Arrhenius equation;

$$\ln k = (-E_a/RT) + \ln A \tag{11}$$

where E_a is activation energy, T the temperature in Kelvin, R the gas constant (8.314 J/mol K) and A is a constant called the frequency factor. Value of E_a can be determined from the slope of ln k versus $1/T$ plot (Fig. 7). The magnitude of activation energy may give an idea about the type of adsorption. Two main types of adsorption may occur, physical and chemical. In physisorption,

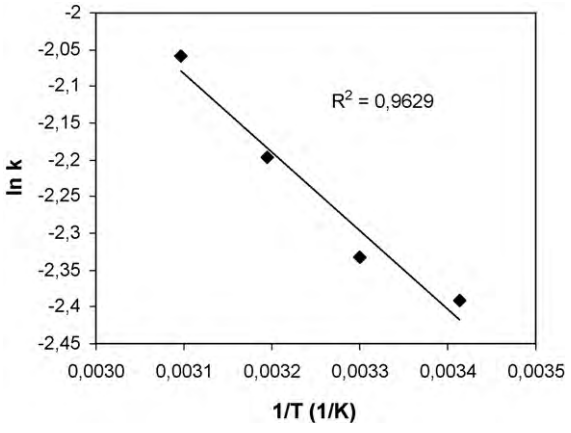

Fig. 7. Arrhenius plot.

the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The activation energy for physisorption is usually no more than 4.2 kJ/mol since the forces involved in physisorption are weak. Chemisorption is specific and involves forces much stronger than in physisorption on. Therefore, the activation energy for chemisorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemisorption are encountered, activated and, less frequently, nonactivated. Activated chemisorption means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, in some systems the chemisorption occurs very rapidly, suggesting the activation energy is near zero. This is termed as a nonactivated chemisorption [32].

Fig. 7 shows the corresponding linear plot of ln k against $1/T$ with correlation coefficient of 0.963. The activation energy for the biosorption of RR 195 onto *P. sylvestris* was calculated and its value was found to be as 8.904 kJ/mol. This value is of the same magnitude as the activation energy of activated chemisorption. Dogan et al., [33], who when studying methyl violet and methylene blue dyes biosorption onto sepiolite, reported a value for E_a of 4.2 and 17.3 kJ/mol, respectively. The second-order rate constants have increased with the increase in temperature. Gad and El-Sayed [34], reported a value for E_a of 62.03 kJ/mol for the removal of Rhodamine-B onto Activated carbon, this finding shows that dye adsorption process by BPH activated carbon is chemisorptions and endothermic process. From the value of activation energy, it appears that the biosorption of RR 195 onto cone biomass is endothermic and involves chemical adsorption process. With respect to the magnitude of heat of biosorption, the dominant adsorption mechanism in the whole biosorption process can also be proposed.

3.6. Equilibrium biosorption models

To examine the relationship between biosorbed and aqueous concentrations (C_e) at the equilibrium, isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich isotherms are the most widely used. The result of biosorption studies of RR 195 at various temperatures and different concentrations ranging from 50 to 200 mg/L onto a fixed amount of *P. sylvestris* biosorbent are expressed by two of Freundlich and Langmuir isotherms. The Langmuir isotherm assumes that biosorption occur at specific homogeneous sites on adsorbent and is used successfully in many monolayer biosorption processes. This model can be written as follows:

$$q_e = (Q_{max} b C_e)/(1 + bC_e) \tag{12}$$

where Q_{max} and b are Langmuir constants denoting maximum adsorption capacity and the affinity of binding sites, respectively. These constants can be determined from the linear plot of $1/q_e$ versus $1/C_e$.

On the other hand, the empirical Freundlich isotherm model based on a heterogeneous surface is given below:

$$q_e = K_f C_e^{1/n} \tag{13}$$

where K_f and n are Freundlich constants characteristic of the system. K_f and n are the indicators of adsorption capacity and intensity, respectively. These constants can be determined from the linear plot of log q_e versus log C_e.

The Langmuir and Freundlich constants along with the correlation coefficients (R^2) were calculated from the corresponding plots for the biosorption of RR 195 at different temperatures and the results are presented in Table 2. A comparison of the calculated and measured results is shown in Fig. 8. The Freundlich isotherm

Table 2
Isotherm parameters for RR 195 biosorption onto *P. sylvestris* L.

T (°C)	Freundlich isotherm			Langmuir isotherm		
	K_f	n	R^2	Q_{max} (mg/g)	b (L/g)	R^2
20	0.573	1.741	0.990	8.425	0.035	0.989
30	0.678	1.856	0.994	7.788	0.046	0.982
40	1.177	2.417	0.982	6.398	0.120	0.943
50	1.626	2.743	0.980	6.386	0.228	0.936

provides the best correlation for the biosorption process, whereas the Langmuir isotherm does not give a good fit to the experimental data for the biosorption of RR 195.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter. R_L that is defined by Hall et al. [35], as:

$$R_L = 1/(1 + bC_o) \quad (14)$$

The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$). linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values are 0.37 and 0.125 while initial RR 195 concentrations are 50 and 200 mg/L, (20 °C) respectively. All the R_L values obtained using Eq. (14) for RR 195 biosorption are greater than zero and less than unity showing favourable biosorption of RR 195 onto cone biomass.

3.7. Thermodynamic parameters

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG^o is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. In addition, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG^o is a negative quantity. The value of ΔG^o can be determined from the following equation

$$\Delta G^o = -RT \ln K_c \quad (15)$$

where K_c the adsorption equilibrium constant and T is is absolute temperature. Relation between ΔG^o. ΔH^o (entalpy) and ΔS^o (entropy) can be expressed by the following equations:

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

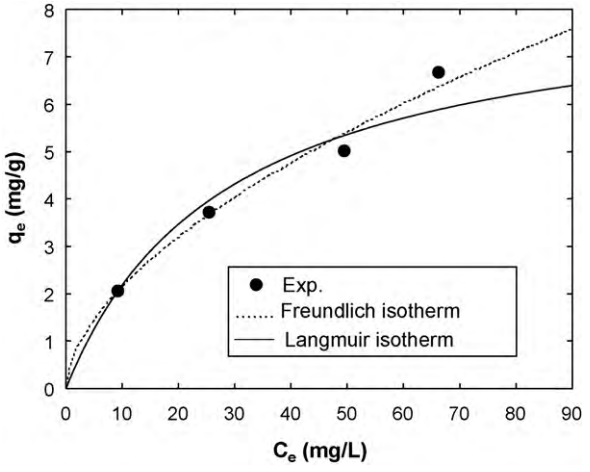

Fig. 8. Comparison between the measured and isotherms profiles for RR 195 biosorption onto *P. sylvestris* at 25 °C.

Table 3
Thermodynamic parameters for RR 195 biosorption onto *P. sylvestris* L.

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)
20	−13.253	29.422	144.672
30	−14.022		
40	−15.723		
50	−17.555		

Eq. (16) can be written as

$$\ln K_c = \Delta S^o/R - \Delta H^o/(RT) \quad (17)$$

where the values of ΔH^o and ΔS^o can be determined from the slope and intercept of the plot between $\ln K_c$ versus $1/T$ (figure not shown). The values of ΔG^o, ΔH^o and ΔS^o for the biosorption of RR 195 onto cone biomass at different temperatures are given in Table 3. The negative values of Gibb's free energy changes approve a spontaneous in nature of biosorption. The value of enthalpy change was positive, indicating the biosorption process is endothermic. The positive value of ΔS^o suggests increased randomness at the solid/solution interface during the biosorption of RR 195 onto *P. sylvestris*.

Cicek et al. [17] have reported that the values of ΔG^o for the adsorption of reactive dyes onto wheat bran were found to be -28.4, -31.1 and -34.4 kJ/mol for RB 19, -26.5, -28.8 and -31.0 kJ/mol for RR 195, -27.7, -29.7 and -31.7 kJ/mol for RY 145 at 20, 40 and 60 °C. The values of ΔH^o for the removal of RB 19, RR 195 and RY 145 have been determined to be 19.69, 6.72 and 1.37 kJ/mol, respectively and the values of ΔS^o were found to be 162.3, 113.2 and 99.3 J/mol K, respectively, which is a quite comparable result obtained in this study.

4. Conclusions

In the present study, the biosorption of R.R. 195 onto *P. sylvestris* L. was studied. Freundlich and Langmuir adsorption isotherm models were applied for the mathematical description of the biosorption equilibrium data. The Freundlich isotherm provided the best correlation for the biosorption process. The biosorption capacity was observed to increase with increasing solute concentrations and temperatures. The maximum biosorption capacity was found to be 7.38 mg/g for 200 mg/L at 50 °C. The kinetic studies showed that pseudo-second-order rate equations were able to provide a realistic description of the biosorption kinetics of RR 195. Moreover, the Elovich equation also fitted the experimental data well. The value of adsorption energy, E_a, gives an idea about the nature of biosorption. From the value of the activation energy of the process, it was concluded that the biosorption of RR 195 by *P. sylvestris* cone is chemical sorption. The biosorption dependence of RR 195 on temperature was investigated and the thermodynamic parameters (ΔG^o, ΔH^o and ΔS^o) were calculated. The results revealed an endothermic heat of the biosorption and a negative free energy value, indicating that the process of RR 195 biosorption is favoured at high temperatures. In the light of these experimental results, it can be concluded that cone biomass has a potential for use as an alternative biosorbent material for the removal of RR 195 dye from aqueous solutions since it has the advantages of easy supply, low cost, high biosorption capacity and reasonable rapid biosorption rate. Although cone biomass was tested only for RR 195 in synthetic dye solutions in this work, previous experiments [20,28,36] have shown that cone biomass could adsorb different hazardous materials such as Cu, Zn, Cr and Pb when using synthetic solutions containing only metal. Therefore, it is assumed that this biosorbent can potentially be used for real wastewater containing dyes, bleaching agents, metals and salts. In order to confirm such assumption, the effect of competition among different contami-

nants for biomass adorption sites on the final removal efficiency shall be investigated using a real wastewater

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