Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn.

Handan Ucun [a],[*], Yalcin Kemal Bayhan [a], Yusuf Kaya [b]

[a] *Department of Environmental Engineering, Engineering Faculty, Atatürk University, Erzurum 25240, Turkey*
[b] *Department of Biology, Science and Letters Faculty, Atatürk University, Erzurum 25240, Turkey*

Abstract

Biosorption equilibrium, kinetics and thermodynamics of chromium(VI) ions onto cone biomass were studied in a batch system with respect to temperature and initial metal ion concentration. The biosorption efficiency of chromium ions to the cone biomass decreased as the initial concentration of metal ions was increased. But cone biomass of *Pinus sylvestris* Linn. exhibited the highest Cr(VI) uptake capacity at 45 °C. The biosorption efficiency increased from 67% to 84% with an increase in temperature from 25 to 45 °C at an initial Cr(VI) concentration of 300 mg/L. The Langmuir isotherm model was applied to experimental equilibrium data of Cr(VI) biosorption depending on temperature. According to Langmuir isotherm, the monolayer saturation capacity (Q_{max}) is 238.10 mg/g. The pseudo-first-order and pseudo-second-order kinetic models were applied to test the experimental data for initial Cr(VI). The pseudo-second-order kinetic model provided the best correlation of the used experimental data compared to the pseudo-first-order kinetic model. The activation energy of biosorption (E_a) was determined as 41.74 kJ/mol using the Arrhenius equation. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the thermodynamic constants of biosorption ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were also evaluated.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; Cr(VI); *Pinus sylvestris* Linn.; Kinetic; Thermodynamic

1. Introduction

Chromium is primarily present in the form of hexavalent Cr(VI) as chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$). Chromium(VI) is largely employed in the chemical industry for chrome plating, the manufacture of dyes and pigments, leather tanning, wood preserving, battery, rust and corrosion inhibitors, textiles, rubbers, toner for copying machines and cement-producing plants. Potable waters containing more than 0.05 mg/L chromium are considered to be toxic [1]. In this way, Cr(VI) must be removed from industrial effluents, before being delivered into the environment. The common procedures for Cr(VI) removal from industrial effluents include chemical precipitation, ion-exchange resins, organic groups grafted on textiles and separation by specific membranes [2]. Biosorp-

tion, an alternative process, is competitive, effective and cheap. Biosorption is a term that usually describes the removal of heavy metals through passive binding to biomass from an aqueous solution [3]. Biosorption of metals by biosorbent has been much explored in recent years [4–11].

The removal of heavy metals from contaminated solutions using non-living biomass is a physico-chemical process whose mechanism(s) is not metabolically controlled. The activation energy needed for biosorption is about 10–20 kJ/mol, which is in agreement with the physical nature of the process. Biosorption is usually a very fast process exclusively responsible for metal concentration by non-living biomass. The cell wall constituents play an important role in metal sequestering. The biosorption mechanisms depend on the type of functional groups on the surface of the biomass, the nature of the metal and the characteristics of the matrix around the biosorbent species. Temperature, pH, initial metal concentration, biomass concentration etc. are the environmental influences that are important in the biosorption. Binding is attributed to ion exchange, adsorption, complexation, microprecipitation and crystallization processes occurring

* Corresponding author. Tel.: +90 442 231 48 29; fax: +90 442 236 09 57.
  E-mail addresses: hanucun@atauni.edu.tr,
  hanucun@yahoo.com (H. Ucun).

on the cell wall. The bioadsorption of metals to the biomass surface occurs mainly as a result of either physical binding involving London–Van der Waals forces and electrostatic attraction, or by chemical binding such as ionic or covalent binding between the adsorbent and the adsorbate. However, the exact adsorption mechanism is not well understood yet. Depending on the nature of the biosorption system, the used isotherm model might determine the maximum biosorption capacity and several kinetic and thermodynamic parameters that can be used for a better understanding of the binding mechanism [12,13].

Our previous article [14] studied the chromium(VI) binding capacities of cone biomass of *Pinus sylvestris* Linn. depending on a number of external environmental factors such as; initial pH, initial metal concentrations, contact time except effect of temperature. In this study were investigated Langmuir isotherm, the kinetics of chromium uptake process and the description of the thermal properties of the chromium(VI) biosorption on the cone biomass. The thermodynamic parameters were determined both Langmuir constant and equilibrium constant. The magnitude of the heat effect for the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the metal–biosorbent interaction process. The relative binding affinity of the biosorbent and the main mechanism that could be controlling the biosorption were also discussed.

2. Materials and methods

2.1. Preparation of biosorbent and chromium solution

Cone biomass was 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, lignin, rosin and tannins in their cell walls [15,16]. *P. sylvestris* Linn., ovulate cones were used in this investigation. They were dried at $80\,^{\circ}\mathrm{C}$ for 24 h, ground in a mortar to a very fine powder and sieved through a 400-mesh copper sieve.

A stock solution of Cr(VI) was obtained by dissolving $K_2Cr_2O_7$ salt in double distilled water and the concentration of Cr(VI) in the stock solution was measured, and the solution was used for further experimental solution preparation.

2.2. Batch biosorption studies

Cr(VI) solutions was prepared by diluting 1.0 g/L stock solution of chromium. The range of concentrations of prepared Cr(VI) solutions varied from 50 to 300 mg/L. Biosorption experiments were carried out in 250 ml Erlenmeyer flasks using 100 ml Cr(VI) solution with 1 g/L of the dried biosorbent. Before mixing with the cone biomass, the pH of each solution was adjusted to 1.0 with HCl. This pH value was determined as the optimum pH value for Cr(VI) biosorption from the previous

study [14]. The biosorption medium was placed in a mechanical platform shaker (Thermolyne ROSİ 1000) and stirred for 2 h at the required temperature and at a fixed agitation speed of 150 rpm. Temperature was maintained at desired values using a temperature-controlled storage unit, where the experiments were conducted. The accuracy of temperature measurements was $\pm 1\,^{\circ}\mathrm{C}$. The samples (5 ml) were taken at definite time intervals and were filtered immediately to remove biomass by filter paper (Whatman GF/A) and the Cr(VI) in the remaining solution was analyzed. The total volume of withdrawn samples never exceeded 5% of the working volume. The biosorption tests were conducted in duplicate under identical conditions. Cr(VI) biosorption equilibrium over a temperature range of $25–45\,^{\circ}\mathrm{C}$ was modeled by using the Langmuir model and kinetic and thermodynamic parameters for the biosorption process were evaluated.

2.3. Chromium analysis

The unadsorbed Cr(VI) in the adsorption medium was determined with a spectrophotometer (Shimadzu UV-160) at a wavelength of 540 nm, using diphenylcarbazide as a complexing agent [17]. The equilibrium concentrations referenced with the calibration curve. In addition to evaluate the possible occurrence of the chemical reduction of Cr(VI) to Cr(III) under acidic conditions was studied. Therefore the extent of biosorption was calculated from the difference between the initial Cr(VI) and final total Cr concentration. The total Cr present in the solution was determined by oxidizing any Cr(III) formed with $KMnO_4$, followed by the same procedures described for the determination of Cr(VI) [17]. The Cr(III) form of Cr(VI) was not determined in the solution.

3. Results and discussion

3.1. Effect of pH

Solution pH influences both cell surface metal binding sites and metal chemistry in water. At pH values below the isoelectric point (<2.7), the overall surface charge on cone biomass will be positive. It is known that the dominant form of chromium(VI) at pH 1.0 is the acid chromate ion species ($HCrO_4^-$) and increasing pH shifts the concentration of $HCrO_4^-$ to other forms [14,18,19]. When Cr(VI) comes in contact with organic substances or reducing agents in an acidic medium, some portions of the originally added Cr(VI) are reduced to the trivalent state. Polyphenolics in the adsorbent such as tannin, however, apparently act as reducing agents for Cr(VI) in acidic solution. It was found that Cr(VI) concentrations were the same as total Cr at pH 1.0–2.0. It is considered that the scales of cone were composed of weak reducing agents for Cr(VI) and therefore, Cr(III) was not found. The binding of chromium(VI) could be occurring either via positively charged ligands on the surface of biosorbent primarily electrostatical in nature or through the reduction of chromium(VI) to chromium(III) under strongly acidic conditions (pH < 2.5) by contact with the electron-donor groups of the biomass, subsequently resulting in the binding of

chromium(III) to the biomass [20–22]. Therefore, Cr(III) was not found. Aoyama et al. [23] reported the effect of initial solution pH on the removal of Cr(VI) by pine leaves. At pH 2.0, 33% of originally added Cr(VI) reduced to the trivalent state. But it was not also determined Cr(III) at pH 2.0 in this study.

3.2. Effect of temperature

The equilibrium uptake of Cr(VI) ions to the cone biomass (q_e) was affected by temperature (T) and increased with increasing temperature up to 45 °C. It was observed that 146 mg Cr(VI) per g of cone biomass was adsorbed at the equilibrium at 45 °C. Chromium(VI) biosorption was endothermic thus the extent of adsorption increased with increasing temperature.

Fig. 1 shows the biosorption kinetics of chromium(VI) ion removal at 25, 35 and 45 °C by plotting the chromium(VI) uptake capacity, q_e (mg/g), versus time, t (min). The biosorption capacity increased with increasing contact time and temperature. A larger amount of chromium(VI) uptake was removed in the first 30 min of contact time. Equilibrium was established in 120 min at the end of a rapid biosorption for all the temperatures studied. After an equilibrium time of 120 min, no more Cr(VI) was adsorbed. The increase in Cr(VI) uptake may also be due to creation of some new sorption sites on the sorbent surface or the increased rate of intraparticle diffusion of sorbate ions the pores of adsorbent at higher temperature, as diffusion is an endothermic process. Since diffusion is an endothermic process, greater biosorption will be observed at higher temperature [24].

3.3. Effect of initial chromium(VI) concentration on temperature-dependent biosorption

The initial concentration provides an important driving force to overcome all mass transfer resistance of chromium(VI) between the aqueous and solid phases. The initial concentration of Cr(VI) in the solution remarkably influenced the equilibrium uptake of Cr(VI) at all the temperature studied (25–45 °C). It was noted that, as the initial concentration increased the sorption of Cr(VI) increased as is generally expected due to equilibrium process. The equilibrium sorption capacity of biomass
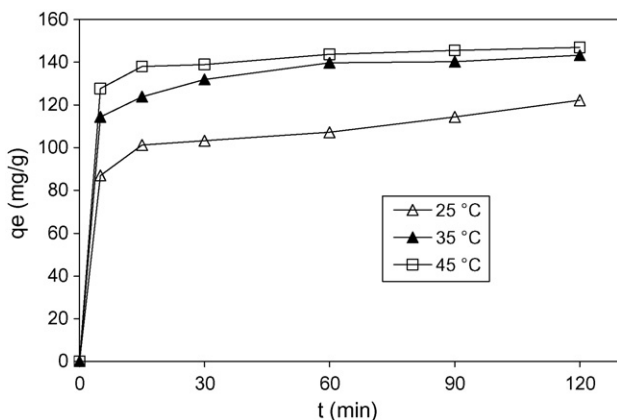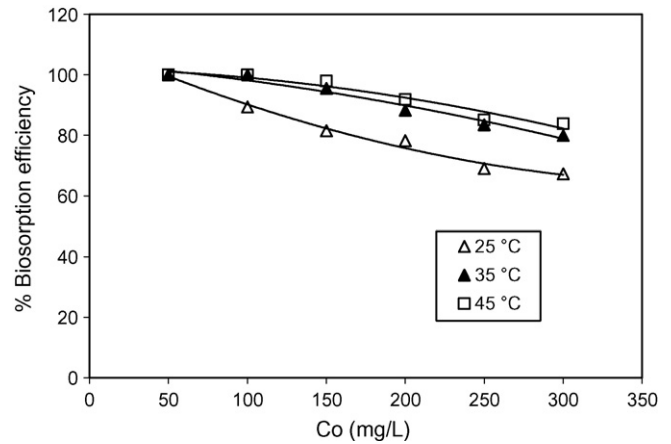

Fig. 2. The effect of initial chromium(VI) concentration and temperature on the biosorption efficiency of chromium ions to *Pinus sylvestris* (*m* 1 g/L).

increased with both increasing initial chromium(VI) ion concentration up to 300 mg/L and increasing temperature up to 45 °C. The biosorption efficiency of chromium ions to the cone biomass decreased as the initial concentration of metal ions was increased. This may be due to the increase in the number of Cr(VI) ions competing for the available binding sites in the biomass and due to the lack of binding sites for complexation of Cr(VI) ions at higher concentration levels. But it increased with increasing temperature (Fig. 2). The increase in metal uptake at increased temperature is due to either the higher affinity of sites for metal or an increase in binding sites on the biomass. At higher temperatures the energy of the system seems to facilitate Cr(VI) attachment onto the cell surface. This trend is in agreement with the earlier work on sorption of Cr(VI) [11,25,26].

3.4. Biosorption kinetics

Different kinetic models were used to describe the experimental data of heavy metals adsorption on biomass [25,27,28]. The pseudo-first-order rate Lagergren model is

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{1}$$

where q_t (mg/g) is the amount of adsorbed chromium 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

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

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
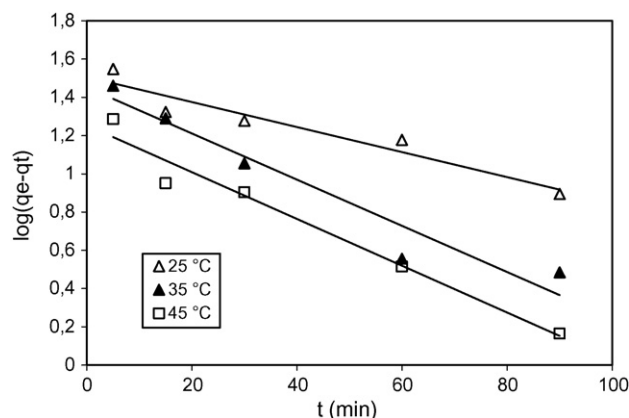
$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Fig. 1. The biosorption curves of Cr(VI) ions obtained at different temperatures (for initial Cr(VI) concentration (C_0) 150 mg/L, biosorbent dosage (*m*) 1 g/L).

Fig. 3. First-order kinetics plot for biosorption of Cr(VI) on *P. sylvestris*.

Fig. 4. Second-order reaction kinetics plot for biosorption of Cr(VI) on *P. sylvestris*.

where k_2 (g/mg min) is the rate constant of second-order adsorption. Eq. (3) can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \tag{4}$$

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

$$h = k_2(q_e)^2 \tag{5}$$

where h is the initial sorption rate (mg/g min) [28].

For evaluating the biosorption kinetics of Cr(VI) ions, the pseudo-first-order and pseudo-second-order kinetics were used to fit the experimental data. The biomass was contacted with Cr(VI) solution (150 mg/L) for different periods of time. Using Eq. (2), a $\log(q_e-q_t)$ versus t was plotted at the different temperatures. Fig. 3 is shown these plots. Approximately, linear fits were observed for all temperatures. It was observed that Cr(VI) sorption followed pseudo-second-order kinetics at all the temperatures studied. By plotting t/q_t against t straight line is obtained in all cases and using Eq. (4) the second-order rate constant (k_2) and q_e values were determined from the plots (Fig. 4). A comparison of the pseudo-first-order and pseudo-second-order adsorption rate constant at different temperatures is presented in Table 1. The Lagergren first-order rate constant (k_1) and $q_{e,cal}$ determined from the model are not in good agreement with the experimental values of $q_{e,exp}$. It is important to note that for a pseudo-first-order model, the correlation coefficient is less than pseudo-second-order coefficient. The values of correlation coefficient for Ho equation were very high ($R^2 > 0.990$) and the theoretical $q_{e,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 1). The values for the product h that represents the
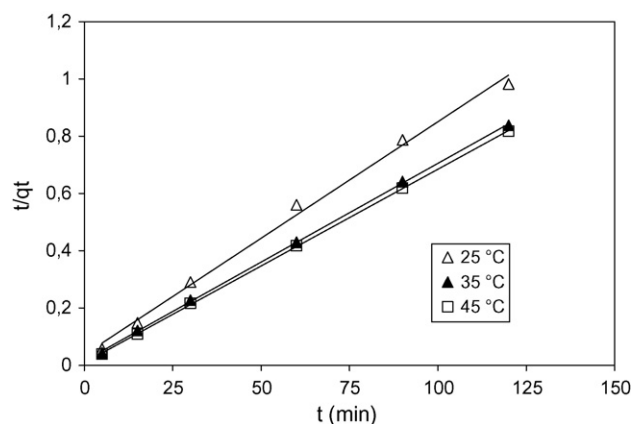
rate of initial sorption, the values of k_2 and q_e increased with the rise in temperature. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cr(VI) onto cone biomass at different temperatures in contrast to the pseudo-first-order model. Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Cr(VI) onto cone biomass of *P. sylvestris*.

3.5. Activation energy of Cr(VI) sorption

Activation energy is determined according to the Arrhenius equation:

$$\ln k = \frac{-E_a}{RT} + \ln A \tag{6}$$

where E_a is activation energy, T the temperature in Kelvin, R the gas constant (8.314 J/mol K) and A is constant called the frequency factor. Value of E_a can be determined from the slope of $\ln k$ versus $1/T$ plot (Fig. 5). The magnitude of activation energy may give an idea about the type of sorption. Two main types of adsorption may occur, physical and chemical. In physical adsorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The activation energy for physical adsorption is usually not more than 4.2 kJ/mol, since the forces involved in physical adsorption are weak. Chemical adsorption is specific and involves forces much stronger than in physical adsorption. Therefore, the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions. Two kinds of chemical adsorption are encountered, activated and, less frequently, nonactivated. Activated chemical adsorption means that the rate varies with

Table 1
Kinetic parameters for biosorption of Cr(VI) on *P. sylvestris*

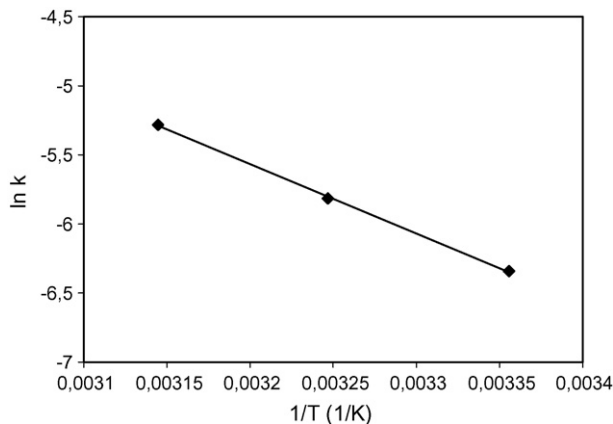| T (°C)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model			
		k_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	k_2 ($\times 10^3$) (g/mg min)	$q_{e,cal}$ (mg/g)	h (mg/g min)	R^2
25	122	0.0150	32.07	0.9177	1.764	123.46	26.88	0.9954
35	143	0.0279	28.33	0.9342	2.976	144.93	62.50	0.9997
45	146	0.0281	17.90	0.9686	5.081	147.06	109.89	0.9999

Fig. 5. Arrhenius plot.

temperature according to a finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation (high E_a). However, in some systems chemisorption occurs very rapidly, suggesting the activation energy is near zero. This is termed nonactivated chemisorption [29].

Fig. 5 shows the corresponding linear plot of $\ln k$ against $1/T$ with a high correlation coefficient of 0.9995. The activation energy for the sorption of Cr(VI) on *P. sylvestris* was calculated and its value was found to be 41.74 kJ/mol. This value is of the same magnitude as the activation energy of activated chemisorption. Some authors have reported similar results [30–35]. Lazaridis and Asouhido [31], who when studying Cr(IV) sorption on calcined Mg–Al–CO$_3$ hydrotalcite, reported a value for E_a of 39.8 kJ/mol. Hsu et al. [35] found high value of energy for the adsorption of Cr(VI) on LDH (Li/Al layered double hydroxide) at different temperatures ranging from 10 to 90 °C. The E_a value of Cr(VI) on LDH was 41.5 kJ/mol. *P. sylvestris* has the higher activation energy. To track for the sorption mechanism, Ho et al. [36] argues that for diffusion-controlled processes the activation energy of adsorption is less than 25–30 kJ/mol. The E_a value of Cr(VI) on *P. sylvestris* provides evidence that reaction kinetics is the control mechanism. In the case of chemisorption, the rate of sorption is generally controlled by the kinetics of bond formation [37].

Tewari et al. [26] have reported that values of E_a for Cr(VI) sorption on *Mucor hiemalis* at different temperature was 4.0 kJ/mol. This appears that the sorption of Cr(VI) on *M. hiemalis* is physical adsorption process. From the value of activation energy it appears that the sorption of Cr(VI) on *P. sylvestris* is endothermic and involves chemical adsorption process. However, it is difficult to decide which mechanism is effective on biosorption of heavy metal ions on sorbent, only taking activation energies into consideration. 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 study of biosorption

Langmuir isotherm equation is based on monolayer sorption onto a surface with finite number of identical sites, which are homogeneously distributed over the sorbent surface and is given

Table 2
Isotherm parameters for Cr(VI) biosorption on *P. sylvestris*

T (°C)	Q_{max} (mg/g)	b (L/mg)	R^2
25	238.10	0.04502	0.9797
35	263.16	0.11656	0.9816
45	256.41	0.21667	0.9754

by Eq. (7) [38]:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \qquad (7)$$

where Q_{max} and b are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively. These constants can be determined from the C_e/q_e versus C_e. The values of Q_{max} and b constants and the correlation coefficient for the Langmuir isotherm are presented in Table 2. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by Hall et al. [39] as

$$R_L = \frac{1}{1 + b C_0} \qquad (8)$$

where C_0 is the initial Cr(VI) concentration (mg/L) and b is the Langmuir adsorption equilibrium constant (L/g). The value of R_L indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). R_L values are 0.18, 0.11, and 0.076 while initial Cr(VI) concentrations are 100, 200 and 300 mg/L, respectively. All R_L values obtained using Eq. (8) for Cr(VI) biosorption are greater than zero and less than unity showing favorable biosorption of Cr(VI) 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, $\Delta G°$ is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, 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 $\Delta G°$ is a negative quantity. Value of $\Delta G°$ can be determined from the following equation:

$$\Delta G° = -RT \ln b \qquad (9)$$

where R is gas constant, b the Langmuir constant and T is absolute temperature. Relation between $\Delta G°$, $\Delta H°$ (enthalpy) and $\Delta S°$ (entropy) can be expressed by the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (10)$$

Eq. (10) can be written as

$$\ln b = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (11)$$

Table 3
Thermodynamic parameters for the sorption of Cr(VI) on *P. sylvestris*

T (°C)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)
25	−19.22		
35	−22.30	62.02	272.99
45	−24.67		

Table 4
Previously reported $\Delta G°$ (kJ/mol) for the adsorption Cr(VI) on various adsorbents

Adsorbent	T (°C)	$\Delta G°$ (kJ/mol)	References
TAC	22	−12.33	[25]
	30	−12.92	
	38	−13.86	
SPC	22	−1.17	[25]
	30	−3.30	
	38	−4.35	
CAC	22	−2.37	[25]
	30	−4.35	
	38	−6.94	
CKW	25	−10.72	[32]
	33	−11.64	
	40	−12.53	
Acticarbone	25	−7.24	[32]
	33	−8.14	
	40	−8.71	
Thujua oriantalis	16	−11.89	[33]
	42	−18.30	
	60	−22.70	
Mucor hiemalis	27	−18.40	[26]
	40	−20.20	
	50	−21.30	
Alternanthera philoxeroides	4	−22.63	[43]
	20	−24.74	
	40	−26.46	
Tea factory waste	25	−0.29	[44]
	45	−0.60	
	60	−1.70	

where values of $\Delta H°$ and $\Delta S°$ can be determined from the slope and the intercept of the plot between $\ln b$ versus $1/T$ [40]. The value of $\Delta G°$, $\Delta H°$ and $\Delta S°$ for the sorption of Cr(VI) on *P. sylvestris* at different temperature is given in Table 3.

The magnitude of $\Delta G°$ increased with the rise in temperature. The negative value confirms the feasibility of the process and the spontaneous nature of sorption of Cr(VI) on *P. sylvestris*. The value of $\Delta H°$ was positive, indicating that the biosorption reaction is endothermic. This is also supported by the increase in value of uptake capacity of the sorbent with the rise in temperature. The positive value of $\Delta S°$ reflects the affinity of Cr(VI) for sorbent used. In addition, positive value of $\Delta S°$ shows the increasing randomness at the solid/liquid interface during the sorption of Cr(VI) on selected biosorbent. The thermodynamic parameters were also calculated using equilibrium constant, K_c:

$$K_c = \frac{C_s}{C_e} \qquad (12)$$

where C_s is the amount of Cr(VI) adsorbed by per biomass (mmol/g) and C_e is the Cr(VI) concentration in solution at equilibrium (mmol/ml) [25,41,42]. The adsorption standard free energy changes $\Delta G°$ can be calculated according to Eq. (9) ($\ln K_c$ used instead of $\ln b$). $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of van't Hoff plots of $\ln K_c$ versus $1/T$ (Fig. 6):

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (13)$$

The values of $\Delta G°$ obtained −22.22, −25.40 and −27.89 kJ/mol at 25, 35 and 45 °C, respectively. The values of $\Delta H°$ and $\Delta S°$ obtained 62.35 kJ/mol and 284.19 J/mol K. The values of $\Delta H°$ and $\Delta S°$ by using equilibrium constant and Langmuir constants are positive and almost equal. A comparison of
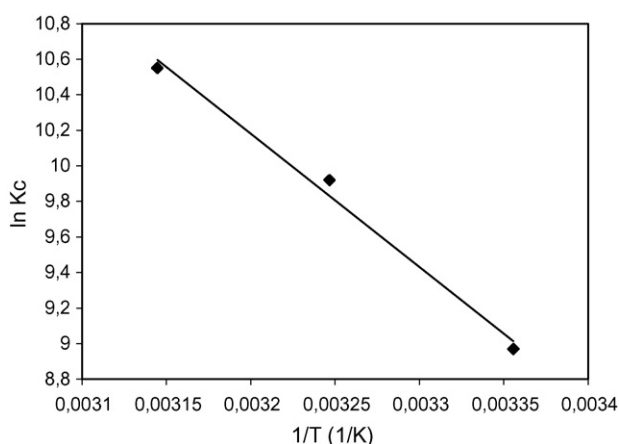
$\Delta G°$ (kJ/mol) for the adsorption Cr(VI) on various adsorbents is given in Table 4.

It is clear from this table that all the values of $\Delta G°$ are negative suggesting that the adsorption process involved is spontaneous with high preference to Cr(VI). On the other hand, the change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures. Tewari et al. [26] have reported that value of $\Delta H°$ for the sorption of Cr(VI) on *M. hiemalis* was found to be 19.60 kJ/mol while $\Delta S°$ was 127 J/mol K. However, Sağ and Kutsal [45] have reported that values of $\Delta H°$ for Cr(VI) sorption on *Z. ramigera* and *R. arrhizus* were found 16.00 and 83.20 kJ/mol, respectively. Oguz [33] has reported that values of $\Delta H°$ and $\Delta S°$ for Cr(VI) sorption on *Thujua oriantalis* were 59.2 kJ/mol and 240 J/mol K which are quite comparable to the results obtained in this study.

4. Conclusions

In the present study, the thermodynamic and kinetic investigations of Cr(VI) adsorption on the *P. sylvestris* were studied. Biosorption process followed Langmuir isotherm model. The sorption capacity was found to increase with increase of solute concentration and temperature. The maximum sorption capacity was found to be 251 mg/g at 45 °C. The kinetic studies showed

Fig. 6. $\ln K_c$ vs. $1/T$ plot.

that pseudo-second-order rate equations were able to provide a realistic description of adsorption kinetics of Cr(VI). The value of adsorption energy, E_a, gives an idea of the nature of adsorption. The activation energy of the Cr(VI) adsorption was calculated using Arrhenius equation. From the value of activation energy of the process it is suggested that biosorption of Cr(VI) by *P. sylvestris* is chemical sorption. The adsorption dependence of Cr(VI) on temperature was investigated and the thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated. The results show an endothermic heat of adsorption and negative free energy value, indicating that the process of Cr(VI) adsorption is favored at high temperatures.

References

[1] Toxicological Profile for Chromium, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, 2000.

[2] J.L. Brasil, R.E. Ricardo, C.D. Milcharek, L.C. Martins, F.A. Pavan Jr., A.A. Santos, S.L.P. Dias, J. Dupont, C.P.Z. Norena, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to Cr(VI) biosorption on *Araucaria angustifolia* wastes, J. Hazard. Mater. B133 (2006) 143–153.

[3] B. Volesky, Detoxification of metal-bearing effluents. Biosorption for the next century, Hydrometallurgy 59 (2001) 203–216.

[4] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of lead (II) from aqueous solution by cone biomass of *Pinus sylvestris*, Desalination 154 (2003) 233–238.

[5] Y. Nuhoglu, E. Oguz, Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of *Thuja orientalis*, Process Biochem. 38 (2003) 1627–1631.

[6] R. Say, N. Yilmaz, A. Denizli, Removal of chromium(VI) ions from synthetic solution by the fungus *Penicillium purpurogenum*, Eng. Life Sci. 4 (3) (2004) 276–280.

[7] E. Malkoc, Ni(II) removal from aqueous solutions using cone biomass of *Thuja orientalis*, J. Hazard. Mater. B137 (2006) 899–908.

[8] S. Tunali, A. Çabuk, T. Akar, Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil, Chem. Eng. J. 115 (2006) 203–211.

[9] G.Q. Chen, G.M. Zeng, X. Tu, C.G. Niu, G.H. Huanga, W. Jiang, Application of a by-product of *Lentinus edodes* to the bioremediation of chromate contaminated water, J. Hazard. Mater. B135 (2006) 249–255.

[10] F. Ekmekyapar, A. Aslan, Y.K. Bayhan, A. Cakici, Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis* hoffm, J. Hazard. Mater. B137 (2006) 293–298.

[11] M. Zhou, Y. Liu, G. Zeng, X. Li, W. Xu, T. Fan, Kinetic and equilibrium studies of Cr(VI) biosorption by dead *Bacillus licheniformis* biomass, World J. Microbiol. Biotechnol. 23 (2007) 43–48.

[12] M.F. Sawalha, J.P. Peralta-Videa, J. Romero-Gonzalez, J.L. Gardea-Torresdey, Biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (*Atriplex canescens*) biomass: thermodynamic and isotherm studies, J. Colloid Interf. Sci. 300 (2006) 100–104.

[13] B. Godlewska-Zylkiewicz, Microorganisms in inorganic chemical analysis, Anal. Bioanal. Chem. 384 (2006) 114–123.

[14] H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici, O.F. Algur, Biosorption of chromium (VI) from aqueous solution by cone biomass of *Pinus sylvestris*, Bioresour. Technol. 85 (2) (2002) 537–539.

[15] W.W. Robbins, T.E. Weier, C.R. Stocking, Botany An Introduction to plant Science, 2nd ed., John Wiley and Sons Inc., New York, 1957, pp. 495–496.

[16] H. Sakagami, M. Takeda, Y. Kawazoe, K. Nagata, A. Ishihama, M. Ueda, S. Yamazaki, Anti-influenza virus activity of a lignin fraction from cone of *Pinus parviflora*, Sieb. Et zucc., In Vivo, Athens, Greece 6, 1992, pp. 491–495.

[17] APHA (American Public Health Association), Standart Methods for Examination of Water and Wastewater, 16th ed., American Public Health Association, Washington, DC, 1986, pp. 201–300.

[18] L.D. Benefield, J.F.J.R. Judkins, B.L. Weand, Process Chemistry for Water and Wastewater Treatment, Englewood Cliffs, New Jersey, 1982, pp. 433–435.

[19] A. Bingol, H. Ucun, Y.K. Bayhan, A. Karagunduz, A. Cakici, B. Keskinler, Removal of chromate anions from aqueous stream by a cationic surfactant-modified yeast, Bioresour. Technol. 94 (2004) 245–249.

[20] D. Park, Y.-S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, Water Res. 39 (2005) 533–540.

[21] J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass, J. Hazard. Mater. 80 (2000) 175–188.

[22] G. Cimino, A. Passerini, G. Toscano, Removal of toxic cation and Cr(VI) from aqueous solution by hazelnut shell, Water Res. 34 (2000) 2955–2962.

[23] M. Aoyama, T. Sugiyama, S. Doi, N.-S. Cho, H.-E. Kim, Removal hexavalent chromium from dilute aqueous solution by coniferous leaves, Holzforschung 53 (1999) 365–368.

[24] G.S. Agarwal, H.G. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (2006) 949–956.

[25] N.K. Hamadi, X.D. Chen, M.M. Farid, M.G.Q. Lu, Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust, Chem. Eng. J. 84 (2001) 95–105.

[26] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, Biochem. Eng. J. 23 (2005) 185–192.

[27] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (4) (1898) 1–39.

[28] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[29] J.M. Smith, Chemical Engineering Kinetics, 3rd ed., McGraw-Hill, New York, 1981, pp. 310–322.

[30] Y. Sağ, T. Kutsal, Determination of the biosorption activation energies of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*, Process Biochem. 35 (2000) 801–807.

[31] N.K. Lazaridis, D.D. Asouhidou, Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO_3 hydrotalcite, Water Res. 37 (2003) 2875–2882.

[32] L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, J. Hazard. Mater. B123 (2005) 223–231.

[33] E. Oguz, Adsorption characteristics and the kinetics of the Cr(VI) on the *Thuja oriantalis*, Colloids Surf. A: Physicochem. Eng. Aspects 252 (2005) 121–128.

[34] S.S. Baral, S.N. Dasa, P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, Biochem. Eng. J. 31 (2006) 216–222.

[35] L.C. Hsu, S.L. Wang, Y.M. Tzou, C.F. Lin, J.H. Chen, The removal and recovery of Cr(VI) by Li/Al layered double hydroxide (LDH), J. Hazard. Mater. 142 (2007) 242–249.

[36] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: review, Sep. Purif. Methods 29 (2) (2000) 189–232.

[37] M.D. LeVan, G. Carta, C.M. Yon, Adsorption and ion exchange, in: D.W. Green (Ed.), Perry's Chemical Engineers' Handbook, 7th ed., McGraw-Hill, New York, 1997.

[38] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (11) (1916) 2221–2295.

[39] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (1966) 212–223.

[40] K.K. Panday, G. Prasad, V.N. Singh, Copper(II) removal from aqueous solution by fly ash, Water Res. 19 (7) (1985) 869–873.

[41] R. Niwas, U. Gupta, A.A. Khan, K.G. Varshney, The adsorption of phosphamidon on the surface of styrene supported zirconium tungstophosphate:

a thermodynamic study, Colloids Surf. A: Physicochem. Eng. Aspects 164 (2000) 115–119.

[42] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto *Chlorella vulgaris*, Process Biochem. 38 (2002) 89–99.

[43] X.S. Wang, Y. Qin, Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by *Alternanthera philoxeroides* biomass, J. Hazard. Mater. B138 (2006) 582–588.

[44] E. Malkoc, Y. Nuhoglu, Potential of tea factory waste for chromium(VI) removal from aqueous solutions: thermodynamic and kinetic studies, Sep. Purif. Technol. 54 (2007) 291–298.

[45] Y. Sağ, T. Kutsal, Determination of the biosorption heats of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*, Biochem. Eng. J. 6 (2000) 145–151.