

## Research Article

# Thermodynamics of Biosorption for Removal of Co(II) Ions by an Efficient and Ecofriendly Biosorbent (*Saccharum bengalense*): Kinetics and Isotherm Modeling

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Received 12 May 2012; Revised 1 July 2012; Accepted 2 July 2012

Academic Editor: Mohammad A. Al-Ghouti

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In this research work, a low-cost biomass derived from the pulp of *Saccharum bengalense* (SB) was used as an adsorbent material/biosorbent for the removal of Co(II) ions from aqueous solution. Langmuir, Freundlich, Timken, and Dubinin-Radushkevich (D-R) adsorption isotherms have been applied to further define the mechanism of sorption. From the comparison of different adsorption isotherm models, it was found that biosorption of Co(II) by SB followed Langmuir and Freundlich models. The sorption capacity for cobalt of *Saccharum bengalense* was ( $q_m = 14.7$  mg/g) at 323K. A comparison of kinetic models applied to the adsorption of Co(II) onto *Saccharum bengalense* was evaluated for the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion and Bangham's kinetics models. It was found that the pseudo-second-order mechanism is predominant. Activation parameters evaluated from thermodynamics and kinetic parameters such as free energy change ( $\Delta G^0 = -0.254$ ,  $\Delta G^\# = 84.63$  kJ/mol), enthalpy change ( $\Delta H^0 = +22.24$ ,  $\Delta H^\# = 0.004$  kJ/mol), and entropy change ( $\Delta S^0 = 0.065$ ,  $\Delta S^\# = 0.262$  kJ/mol) revealed the spontaneous, endothermic, and feasible nature of adsorption process. The results of the present investigation suggested that *Saccharum bengalense* (SB) can be used as an environmentally and economically feasible biosorbent for the removal of Co(II) from aqueous solutions.

## 1. Introduction

Cobalt is one of the various metals that is found naturally in the body, but as with all other metals, in excess amounts it becomes toxic and leads to many harmful and potentially permanent side effects. Cobalt present in industrial wastewaters can produce a variety of adverse effects on humans. It may cause interstitial pneumonitis, interstitial fibrosis, myocardial and thyroid disorders, and sensitization of the respiratory tract and skin [1, 2]. Chronic cobalt poisoning may also produce hyperplasia and polycythemia of the bone marrow [3]. Cobalt poisoning also caused cardiomyopathy, hypothyroidism, neuropathy, seizures, blindness, headaches, liver damage, and neurological damage as well as impairing the senses. Acute exposure to cobalt can induce neurotoxicological and genotoxicity disorders in human beings and

in unrelenting cases may cause gastrointestinal troubles and even cancer [4, 5].

The most extensively used methods for removing Co(II) metal ions from wastewaters included adsorption, ion exchange, reverse osmosis, evaporation, membrane filtration and chemical precipitation [6, 7]. Most of these methods suffer from drawbacks such as the disposal of the residual metal sludge; high capital and operational cost; not suitable for small-scale industries [8]. Adsorption, by activated carbons, has the most extensive applications in this regard. It has high adsorption capacity, mesoporous nature, and high-surface area, but it has limited use due to nonregenerable features and high operational cost. For this reason, there is a need for developing ecofriendly and economic alternative methods and materials for waste treatment [9]. Agricultural waste and Natural materials that are accessible in huge quantities may

have potential as alternate and cost effective sorbents. The profusion and accessibility of agricultural by-products make them good sources of raw materials for natural biosorbents [10].

The common name of *Saccharum bengalense* (SB) is “Kana” or “Sarkanda” and is distributed from north and North West India to Pakistan and Afghanistan. A valuable fiber can be extracted from the upper leaf sheaths of the flowering Culm [11]. It can produce large quantities of biomass that may offer a good basis for the selection of SB economic and ecofriendly alternative biosorbent. To the best of our knowledge, no investigations have been reported to explore the biosorption characteristics of this plant for the removal of metal ions such as Co(II). The aim of the present research work is to investigate the biosorption capacity  $q_e$  ( $\text{mgg}^{-1}$ ) of *Saccharum bengalense* to remove Co(II) metal ions from aqueous solution in a batch procedure. Mechanism of adsorption was explained by using two parameters adsorption isotherms. Efficiency of adsorption has been studied in terms of kinetic models. Spontaneity and feasibility of the sorption process is confirmed by determining thermodynamically parameters such as  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$ .

## 2. Methods

**2.1. Collection of Biosorbent.** Large pieces of *Saccharum bengalense* (SB) were collected from the bank of the river Satluj Bahawalpur, Pakistan. SB samples were washed with deionized water to remove any dust or other particles and dried under shade, then the samples were knife-milled. The 60–400  $\mu\text{m}$  particles were collected and washed with deionized water. Finally, the samples were oven dried (at 333 K) to constant mass and stored in air tight plastic bottles and labeled as *Saccharum bengalense* (SB).

**2.2. Characterization of SB.** The biomass SB was characterized by FTIR, elemental analysis, and BET surface area. BET surface area and single-point surface area of SB were determined from the  $\text{N}_2$  adsorption isotherm at 77 K in the range of relative pressure  $10^{-6}$  to 1.0 with a surface area and pore size analyzer (Autosorb 1, Quantachrome Instruments, USA). Before measurement, the sample was degassed at 300°C for 2 h. Elemental analyses were accomplished by (Perkin-Elmer 2400 Series II CHNS/O, USA) elemental analyzer using sulfanilamide as the standard. A potassium bromide (KBr) disc method was used to scan the FTIR spectra in 4000–600  $\text{cm}^{-1}$  range by using FTIR spectrophotometer (Tensor 27, Bruker, Germany).

**2.3. Adsorption Experiments.** All analytical grade chemical reagents including atomic absorption spectrometric standards were purchased from Fluka Chemicals. Cobalt stock solution (1000 mg/L) was prepared from  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  by dissolving the calculated amount in doubly distilled water. Further dilutions were prepared freshly as per requirement. A Pekin-Elmer 2380 Atomic Absorptions Spectrophotometer with air-acetylene flame was employed for the determination of cobalt concentration. The percentage removal efficiency of

TABLE 1: FTIR, physical and chemical analysis of *Saccharum bengalense*.

Physical analysis		Elemental analysis (%wt.)	
BET surface area ( $\text{m}^2/\text{g}$ )	9.43	C	41.2
Porosity	0.043	H	4.2
Single-point surface area ( $\text{m}^2/\text{g}$ )	5.78	N	0.9
Mean size ( $\mu\text{m}$ )	16.02		
FTIR (wave number)		Assignment	
SB	Co (loaded)		
3356.93	3373.26	OH stretching	
2913.29	2914.05	Stretching vibration of the C–H	
1601.31	1600.51	C–O, C–C stretching	
1425.49	1426.09	C–H bending	
1039.44	1037.39	C–O–C stretching	
899.01	898.65	Ar-bending	
663.84	625.56		

adsorbent (% A), the sorption capacity at time  $t$ ,  $q_t$  ( $\text{mg/g}$ ) and the sorption capacity at equilibrium  $q_e$  ( $\text{mg/g}$ ) were calculated as follows:

$$\% \text{ adsorption} = \frac{C_o - C_e}{C_o} \times 100,$$

$$q_t \text{ (mg/g)} = (C_o - C_t) \times \frac{V}{m}, \quad (1)$$

$$q_e \text{ (mg/g)} = (C_o - C_e) \times \frac{V}{m},$$

where  $C_o$  ( $\text{mg/L}$ ) and  $C_t$  ( $\text{mg/L}$ ) were the liquid-phase concentrations of solutes at the initial and a given time  $t$ , respectively.  $C_e$  ( $\text{mg/L}$ ) was the concentration of Co(II) at equilibrium,  $V$  is the volume of the solution in liter and  $m$  is the mass of the adsorbent in grams.

## 3. Results and Discussion

**3.1. FT-IR, Physicochemical Analysis of the Biosorbent.** SB generally considered as structures built by cellulose molecules and surrounded by hemicellulosic materials (glucmannans, galactans, and arabogalactans), lignin, and pectin. The results of physical analysis, elemental analysis, and FT-IR are shown in Table 1.

In the FT-IR spectrum of SB, the intense peak at 1039.40  $\text{cm}^{-1}$  along with the weak peak at 1240.00  $\text{cm}^{-1}$  and the shoulder at 1159.41  $\text{cm}^{-1}$  are C–O stretching vibration of ethers and alcohols. The band at 1601.3  $\text{cm}^{-1}$  is due to carbonyl groups of aldehydes and ketones. The absorption band at 1730.90  $\text{cm}^{-1}$  is attributed to the vibrations by carbonyl groups of ester and carboxylic acid groups. The single peak at 2913.29  $\text{cm}^{-1}$  is due to C–H stretching vibration of CH,  $\text{CH}_2$ , and  $\text{CH}_3$  groups present in lignin. The broad band centered

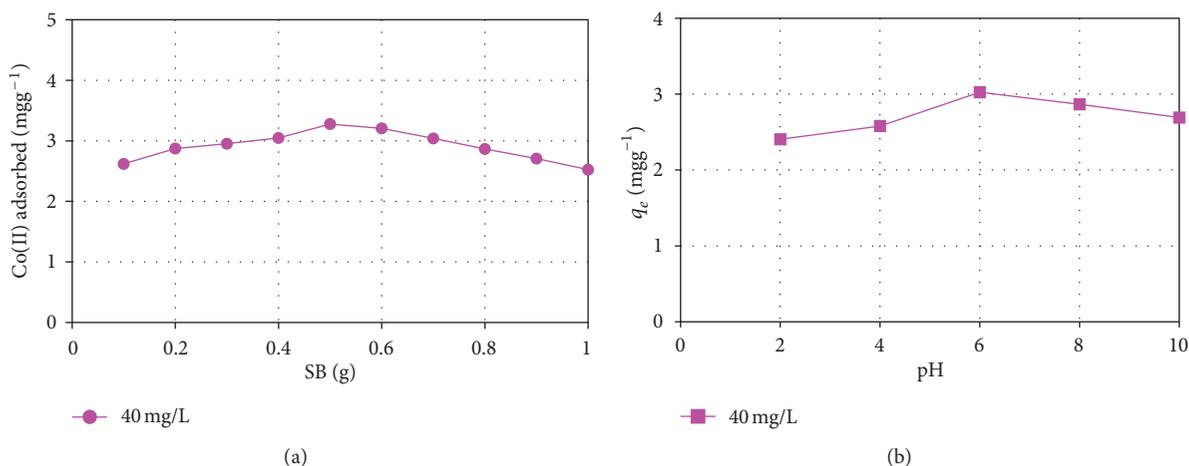


FIGURE 1: (a) Effect of adsorbent dose for sorption of Co(II) ions on SB: pH, 6.0; concentration, 50 mg/L; temperature, 323 K; contact time, 1 h. (b) Effect of pH for sorption of Co(II) ions on SB: Adsorbent dose, 0.5 g/50 mL; concentration, 50 mg/L; temperature, 323 K; contact time, 1 h.

at  $3356.93\text{ cm}^{-1}$  is a characteristic band of O–H stretching vibration. Thus, SB mainly consists of compounds having oxygen-containing functional groups.

Comparing and assignments of SB before and after Co(II) sorption are too important to indicate the functional groups responsible for Co(II) binding. Regarding FT-IR for SB after Co(II) uptake, it was found that oxygen containing functional groups like phenolic –OH, carboxy –COOH, and methoxy –OCH<sub>3</sub> groups are affected after uptake process (Figure not shown). This was confirmed by shifts in their position or band intensity from  $3356.93\text{ cm}^{-1}$  to  $3373.26$ ,  $1039.44$  to  $1037.39$ , and from  $1730.99$  to  $1658.26\text{ cm}^{-1}$  [12] as indicated in Table 1.

**3.2. Effect of the Adsorbent Dosage.** Adsorbent quantity is very imperative feature as it determines the extent of removal of metal and may be used to determine the cost of adsorbent per unit volume of solution to be treated.

With increase in the adsorbent dosage, from 0.1 to 2.0 g/50 mL, the amount of adsorbed Co(II) ions increases from 72% to 89.2%. It was noticed that the extent of adsorption increased with the increase in adsorbent dosage (see Figure 1(a)). Adsorbent dosage has a direct effect on adsorbate removal of Co(II) because of the following reasons: (a) it may increase in SB surface, (b) availability of more adsorption sites on SB [13].

It is obvious that the optimum amount of SB for further adsorption experiments was selected as 0.5 g/50 mL. On the other hand, with further increase in adsorbent amount, the adsorption capacity decreases. This may be due to (i) the overlapping or aggregation of adsorption sites of SB resulting a decrease in total adsorbent surface area available to Co(II) ions, (ii) adsorption density increases with the decrease in adsorbent dosage due to higher amount of Co(II) per unit weight of adsorbent, (iii) the time required to reach the equilibrium decreased at higher doses of SB.

**3.3. Effect of pH.** In this present investigation, the biosorption of cobalt was studied at pH range of 2–10 with the adsorbent dose of 0.5 g/50 mL and adsorbate concentration of 50 mg/L. The maximum removal efficiency was 85.4% at pH 6. Acidic conditions are required for metal uptake as it increases the affinity of SB to Co(II) ions. It was observed that pH significantly affects the adsorption process. As the pH of the medium is increased, the competition between positively charged metal ions and H<sup>+</sup> ions decreases, and metal ions become the dominant species to sorb on the biosorbent [14]. This is true as far as the metal ions are present as positively charged species in the solution. So an optimum pH is expected to lie in the acidic region [15]. At lower pH (2–6), H<sup>+</sup> ions compete with Co(II) ions for the available adsorption site whereas at higher pH, adsorption sites are inactive. Above optimum pH, Co(II) ions react with hydroxide ions and precipitate as metal hydroxide (see Figure 1(b)).

**3.4. Adsorption Kinetics.** Adsorption kinetics describes the relationship of solute uptake rate of the adsorption and the adsorption time. In order to clarify the adsorption kinetics in different kinetic models, the pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion and Bangham's models were applied to the sorption data.

**3.4.1. Pseudo-First-Order Model.** The pseudo-first-order model is based on the assumption that the adsorption rate is proportional to the number of available sites [16].

The pseudo-first-order model is expressed by the following equation:

$$\frac{dq_t}{dt} = k_f (q_e - q_t), \quad (2)$$

where  $q_t$  and  $q_e$  (mg/g) are the amount of metal ions adsorbed on per unit weight of adsorbent at time  $t$  and equilibrium, respectively;  $k_f$  ( $\text{min}^{-1}$ ) is the pseudo-first-order rate constant of the sorption process.

By applying the boundary conditions  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$  and integrating, the following equation is obtained:

$$\ln(q_e - q_t) = \ln q_e - k_f t. \quad (3)$$

Linear plots of  $\ln(q_e - q_t)$  versus  $t$  can be plotted to evaluate this kinetic model and to determine  $q_e$  and rate constant from intercept and the slop, respectively.

**3.4.2. Pseudo-Second-Order Model.** It is based on the assumption that adsorption rate is proportional to the square of the number of unoccupied sites

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2, \quad (4)$$

where  $k_s$  ( $\text{gm g}^{-1} \text{min}^{-1}$ ) is the rate constant of the pseudo-second-order model. Integrating the above equation from  $t = 0$  to  $t = t$  and  $q_t = 0$  to  $q_t = q_t$ , the following equation is obtained:

$$q_t = \frac{k_s \cdot q_e^2 \cdot t}{1 + k_s q_e t}. \quad (5)$$

The most often used linearized form is given as [17]

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e}. \quad (6)$$

The parameters  $k_s$  and  $q_e$  can be calculated from the intercept and the slope of the plot  $t/q_t$  versus  $t$ .

**3.4.3. Elovich Model.** Elovich equation is a rate equation based on the adsorption capacity  $q_t$  ( $\text{mg/g}$ ). The kinetic sorption data may also be analyzed using the Elovich equation. Rate equation can be expressed as

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}. \quad (7)$$

This equation can be simplified by assuming  $\alpha\beta \gg t$  and by applying the boundary conditions:  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the linear form obtained is [18]

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t, \quad (8)$$

where  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption ( $\text{g/mg}$ ).  $\alpha$  is the initial sorption rate constant ( $\text{mg/g min}$ ). The constant can be obtained from the slope and intercept of the plot of  $q_t$  versus  $\ln t$ .

**3.4.4. The Intraparticle Diffusion Equation.** The intraparticle diffusion equation [19] can be written as follows:

$$q_t = K_{id} \sqrt{t} + C, \quad (9)$$

where  $k_{id}$  is the intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ), and  $C$  is the intercept.

By using this model, the plot of  $q_t$  ( $\text{mg g}^{-1}$ ) versus the square root of time ( $t^{1/2}$ ) should be linear if the intraparticle diffusion is involved in the adsorption process, and if these lines pass through the origin, then the intraparticle diffusion is the rate-controlling step [20].

**3.4.5. Bangham's Equation.** Kinetic data were further used to know about the controlling step occurring in the present adsorption system using Bangham's equation [21]

$$\log\left(\frac{C_o}{C_o - q_t \cdot m}\right) = \log\left(\frac{k_B}{2.303 \cdot V}\right) + [\alpha] \ln(t), \quad (10)$$

where  $\alpha$  ( $<1$ ) and  $k_B$  are constants,  $C_o$  is the initial concentration of adsorbate in solution ( $\text{mg/L}$ ),  $V$  is the volume of solution ( $\text{L}$ ),  $m$  is the weight of adsorbent per liter of solution ( $\text{g/L}$ ),  $q_t$  ( $\text{mg/g}$ ) is the amount of adsorbate retained at time  $t$ .

Here are two indicators for pseudo-first-order and pseudo-second-order kinetic models to decide whether the system follows them or not, that is,  $R^2$  value and comparison of experimental and calculated  $q_e$  values.

The kinetic parameters for the adsorption of Co(II) ions onto (S.B) are summarized in Table 2 and shown in Figures 2(a)–2(e).

These results show that the adsorption of Co(II) on SB followed the pseudo-second-order kinetic model at all-time intervals. The calculated  $q_e$  values agree with experimental  $q_e$  values, and the correlation coefficient values for the pseudo-second-order kinetic plots were high as shown in Figure 2(b). But in case of pseudo-first-order model, calculated  $q_e$  values did not agree well with experimental  $q_e$  values, and the value of correlation coefficients was low.

The correlation coefficient  $R^2$  value obtained from Figure 2(d) was (0.855) indicating that the Elovich expression could not fit properly those experimental data.

The correlation coefficients for the intraparticle diffusion model are lower than that of the pseudo-second-order kinetic model, whereas this model indicates that the adsorption of Co(II) ions on SB also followed the intra-particle diffusion model as shown in Figure 2(c). As the plots of  $q_t$  ( $\text{mg g}^{-1}$ ) versus the square root of time ( $t^{1/2}$ ) did not pass through the origin, this is indicative of some degree of boundary layer control, and this further shows that the intra-particle diffusion is not the only rate-limiting step, but also other kinetic models may direct the rate of adsorption [22].

Kinetic data can further be used to verify whether pore diffusion was the only rate-controlling step or not in the adsorption system using Bangham's equation. The correlation coefficient,  $R^2$ , value obtained was 0.906 indicating that that pore diffusion was not solely the rate limiting and the Bangham's expression could not as well fit properly those experimental data.

**3.5. Equilibrium Parameters of Biosorption.** The equilibrium adsorption isotherms are considered one of the most important aspects in understanding the mechanism of the adsorption. The results obtained were analyzed using different

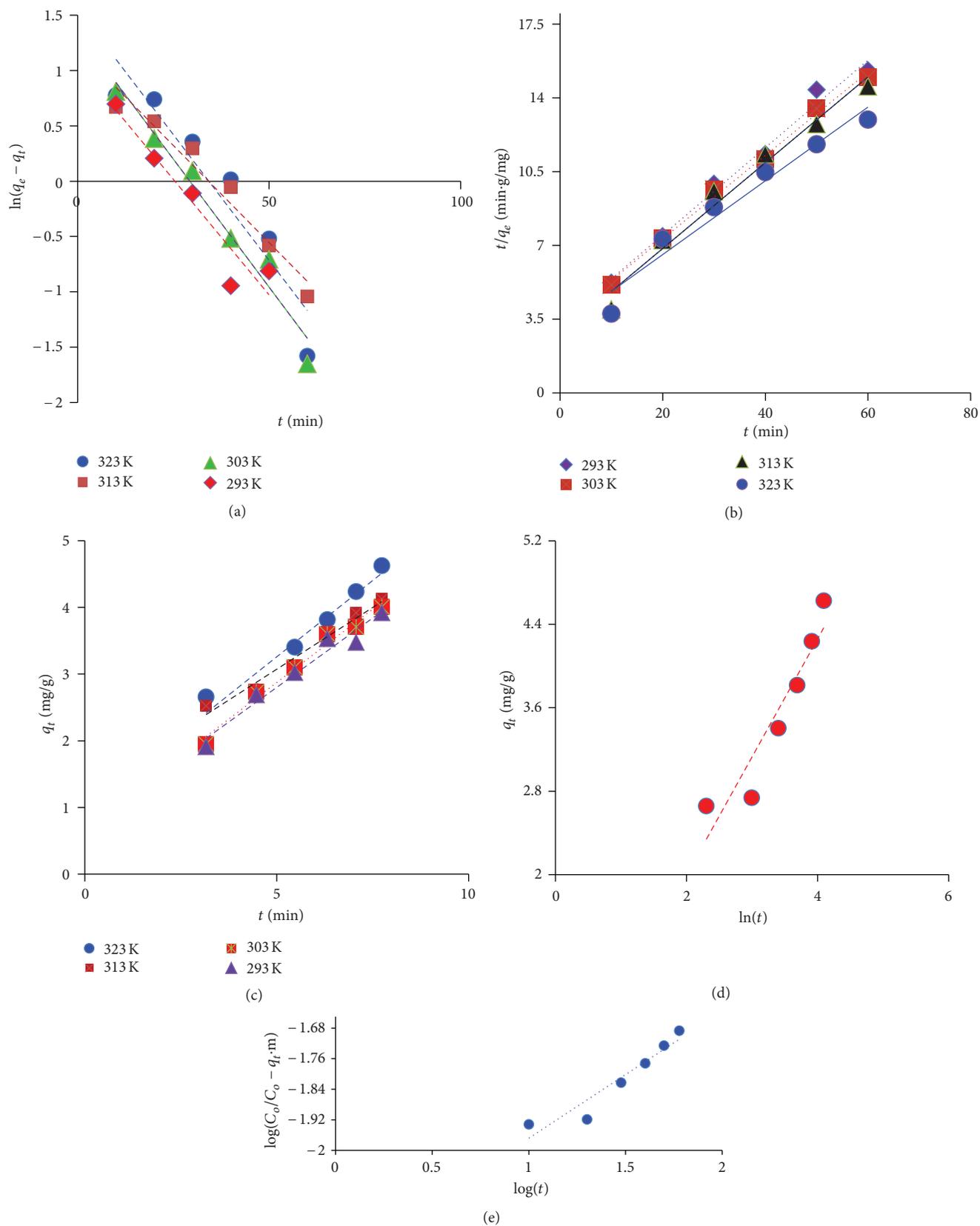


FIGURE 2: (a) Pseudo-first-order kinetics model, (b) pseudo-second-order kinetics model, (c) intra-particle diffusion kinetic model, (d) Elovich kinetic model, and (e) Bangham kinetic model for sorption of Co(II) ions on SB: pH, 6.0; concentration, 50 mg/L; adsorbent dose, 0.5 g/50 mL.

TABLE 2: Kinetics parameters for sorption of Co(II) on SB.

Kinetics model	Constants parameters		$q_e$ (Exp)	$R^2$
Pseudo-first-order model	$q_e$ (Cal.)	$K_f$ ( $\text{min}^{-1}$ )	4.62	0.895
	4.73	0.0454		
Pseudo-second-order model	$T$	$q_e$ (Cal.)	4.62	0.903
	293 K	$K_s$ ( $\text{g mg}^{-1} \text{min}^{-1}$ )		
	303 K	0.0184		
	313 K	0.0202		
	323 K	4.62	0.0226	
		4.62	0.024	
Intra-particle diffusion model	$C$	$k_{id}$ ( $\text{mg g}^{-1} \text{min}^{-1/2}$ )	4.62	0.710
	1.59	0.327		
Elovich model	$\alpha$ ( $\text{mg/g min}$ )	$\beta$ ( $\text{g/mg}$ )	4.62	0.885
	0.11	0.884		
Bangham model	$\alpha$	$k_B$	4.62	0.906
	0.332	$5.7 \times 10^{-4}$		

isotherm equations (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm equations).

**3.5.1. Langmuir Adsorption Isotherm.** The Langmuir adsorption isotherm model assumes that adsorption takes place at specific homogeneous sites within the adsorbent [23]

$$q_e = \frac{K_L \cdot q_m \cdot C_e}{1 + K_L \cdot C_e} \quad (11)$$

The different linear forms of the Langmuir isotherm model [24] are

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (12)$$

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot C_e} + \frac{1}{q_m} \quad (13)$$

$$\frac{q_e}{C_e} = K_L \cdot q_m - K_L \cdot q_e \quad (14)$$

$$q_e = q_m - \frac{q_e}{K_L C_e} \quad (15)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is the adsorption capacity at equilibrium;  $C_e$  ( $\text{mg/L}$ ) is the concentration of Co(II) at equilibrium;  $q_m$  is the monolayer adsorption capacity of the adsorbent ( $\text{mg g}^{-1}$ );  $K_L$  is the Langmuir constant ( $\text{L mg}^{-1}$ ) related to the free energy of adsorption. Equations (13) and (14) are commonly applied to biosorption process.

**Klotz Equation.** It is multiplied inverse of (13), a plot of  $1/q_e$  versus  $1/C_e$  for the Klotz method for Langmuir adsorption gives a straight line of slope  $1/(K_L \cdot q_m)$  and intercept  $1/q_m$ . The values for these parameters are calculated from Figure 3(a) and are given in Table 3.

**3.5.2. Freundlich Isotherm.** The linear equation of the Freundlich adsorption model is [25]

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (16)$$

where  $K_F$  ( $\text{dm}^3 \text{g}^{-1}$ ) and  $n$  (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity, respectively. The plot of  $\ln C_e$  versus  $\ln q_e$  for the adsorption was employed to generate the intercept value of  $K_F$  and the slope value of  $n$ , respectively, as shown in Figure 3(b).

The “ $n$ ” value provides information about the process to be favorable or unfavorable under studied conditions. The value of “ $n$ ” was “1.33” for SB. This shows that the adsorption onto the heterogeneous systems is quite favorable. The  $R^2$  value is 0.98; thus, the sorption of Co(II) by SB followed Freundlich model, and the sorption is favorable under the specific set of conditions.

**3.5.3. Dubinin-Radushkevich (D-R) Isotherm.** The linear form of (D-R) isotherm model [26] is

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (17)$$

where  $\beta$  is a constant connected with the mean free energy of adsorption per mole of the adsorbate ( $\text{mol}^2 \text{kJ}^{-2}$ ),  $q_m$  is the theoretical saturation capacity ( $\text{mg g}^{-1}$ ), and  $\varepsilon$  is the Polanyi potential [27], which is equal to

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (18)$$

where  $R$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) is the gas constant, and  $T$  (K) is the absolute temperature. Hence, by plotting  $\ln q_e$  versus  $\varepsilon^2$ , it is possible to generate the value of  $q_m$  from the intercept and the value of  $\beta$  from the slope. The description of the sorption of Co(II) on SB by the Dubinin-Radushkevich (D-R) equation is a pointer to the heterogeneity of the surface of the SB [28]. The biosorption mean free energy  $E_s$  ( $\text{kJ/mol}$ ) is as follows [29]:

$$E_s = \frac{1}{\sqrt{2\beta}} \quad (19)$$

The (D-R) constants for Co(II) were calculated from Figure 3(c), and results are given in Table 3.

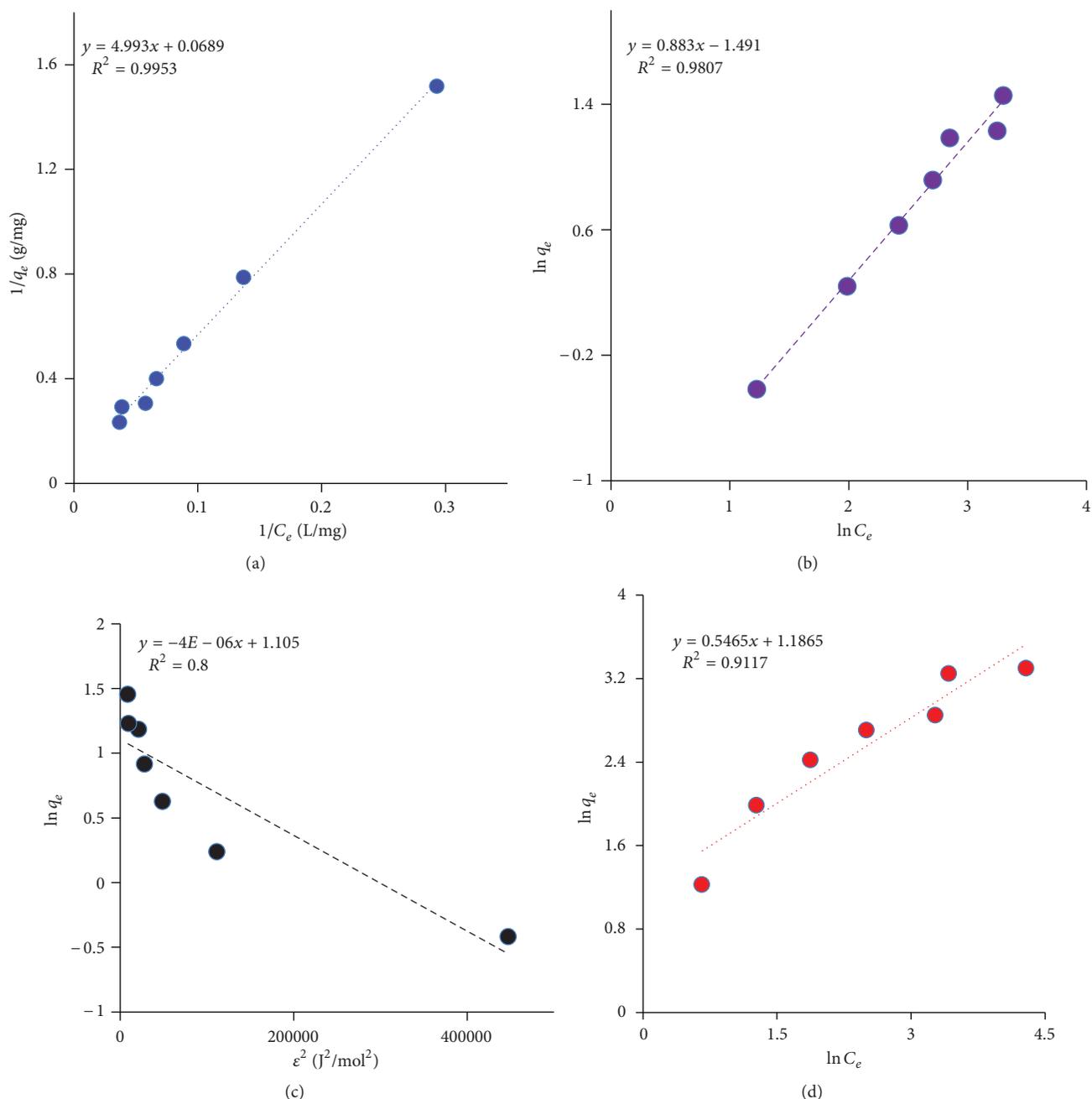


FIGURE 3: (a) Langmuir adsorption isotherm at different temperatures, (b) Freundlich isotherm, (c) Dubinin-Radushkevich (D-R) adsorption isotherm, (d) Temkin adsorption isotherm for sorption of Co(II) ions on SB: pH, 6.0; temperature, 323 K; adsorbent dose, 0.5 g/50 mL.

Here are two indicators for D-R model to decide whether the system follows it or not, that is,  $R^2$  value and comparison of calculated and experimental  $q_m$  values. The calculated  $q_m$  value for SB is 3.01 mg/g which is not comparable with experimental  $q_m$  value (2.5 mg/g). The  $R^2$  values were less than 0.98; hence, it is indicated that the adsorption of cobalt onto SB did not follow the Dubinin-Radushkevich isotherm.

The mean free energy of biosorption ( $E_s$ ) was found to be 0.353 kJ/mol for SB. This value showed that the adsorption was physical in nature. Since D-R model is not being followed by this system, this  $E_s$  value provides only an estimation of the nature of the biosorption processes.

**3.5.4. Temkin Isotherm.** Temkin isotherm assumes that heat of adsorption decreases linearly with the adsorption onto the surface at a particular temperature, and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is expressed in linear form by the following equation [30, 31]:

$$q_e = B \ln K_T + B \ln C_e, \quad (20)$$

where  $B = RT/b$  is related to the heat of adsorption,  $T$  (K) is the absolute temperature,  $R$  is the universal gas constant (8.3143 J/mol),  $b$  indicates the adsorption potential of the adsorbent (J/mol), and  $K_T$  is the equilibrium binding

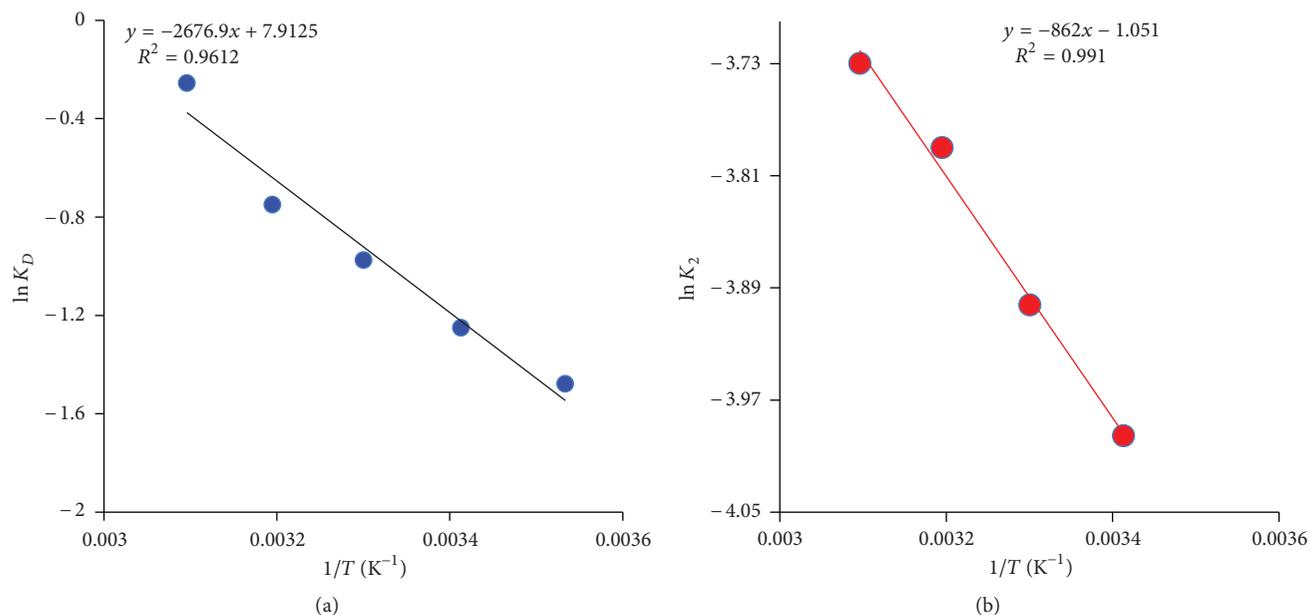


FIGURE 4: (a) Thermodynamics parameters, (b) activation energy by Arrhenius plot, (c) activation parameters for sorption of Co(II) ions on SB: pH, 6.0; Concentration, 50 mg/L; adsorbent dose, 0.5 g/50 mL.

constant (L/mg). The parameters for the Temkin model are obtained from the plot of  $q_e$  versus  $\ln C_e$  (Figure 3(d)). The values for these parameters are given in Table 3. The  $R^2$  values indicated that the adsorption of Co(II) on SB did not follow Temkin model.

From the comparison of different adsorption isotherm models, it was found that biosorption of Co(II) by SB followed Langmuir and Freundlich models. The  $R^2$  values were quite close for other adsorption models.

#### 4. Thermodynamic Parameters of Adsorption

Thermodynamic parameters for adsorption of Co(II) onto SB were calculated using the following relations [27, 41, 42]:

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0, \\ \Delta G^0 &= -RT \ln K_D, \\ \ln K_D &= \frac{-\Delta G^0}{RT} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \\ K_D &= \frac{q_e}{C_e}, \end{aligned} \quad (21)$$

where  $R$  is the universal gas constant (8.314 J/mol K),  $T$  the temperature (K), and  $K_D$  ( $C_s/C_e$ ) is the distribution coefficient.  $q_e$  is the adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  (mg/L) is the concentration of Co(II) at equilibrium ( $\text{mg L}^{-1}$ ). The Gibbs free energy indicates the degree of spontaneity of the sorption process, and the higher negative value reflects a more energetically favorable sorption. The negative values of  $\Delta G^0$  confirm the thermodynamic feasibility of the process and spontaneous nature of adsorption on SB [43]. The

positive value of  $\Delta H^0$  indicated the endothermic nature of the adsorption, while the positive values of  $\Delta S^0$  reflected the increase in randomness for solid-solution interface and affinity of the adsorbent material [44]. The values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  were calculated from Figure 4(a), and results were discussed in Table 4.

**4.1. Activation Energy.** The kinetic parameters at different temperatures were plotted in terms of the Arrhenius Equation [45] as

$$\ln k_2 = \ln k_0 - \frac{E_a}{RT}, \quad (22)$$

where  $k_2$  is the pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{ min}^{-1}$ ),  $k_0$  is the independent temperature factor ( $\text{g mg}^{-1} \text{ min}^{-1}$ ),  $R$  is the gas constant ( $\text{J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the solution temperature (K). A plot of  $\ln k_2$  versus  $1/T$  gives a straight line, and the corresponding activation energy was determined from the slope of linear plot shown in Figure 4(b). The activation energy for the biosorption of Co(II) on SB is given in Table 4. The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. Low activation energies ( $5\text{--}50 \text{ kJ mol}^{-1}$ ) are characteristics for physical adsorption process, while higher activation energies ( $60\text{--}800 \text{ kJ mol}^{-1}$ ) suggest chemical adsorption process [46].

**4.2. Determination of Activation Parameters.** Activation parameters such as enthalpy ( $\Delta H^\#$ ), entropy ( $\Delta S^\#$ ), and free

TABLE 3: Equilibrium isotherm parameters of biosorption of Co(II) on SB.

Adsorption isotherm	Linear form	Constant parameters		
Langmuir isotherm	$\frac{1}{q_e} = [1/K_L \cdot q_m] \cdot \frac{1}{C_e} + \frac{1}{q_m}$	$q_m$ (mg/g)	$K_L$	$R^2$
		14.51	0.013	0.995
Freundlich isotherm	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$K_F$	$n$	$R^2$
		0.225	1.131	0.980
(D-R) isotherm	$\ln q_e = \ln q_m - \beta \epsilon^2$	$\beta$	$q_m$	$R^2$ $E_s$ (kJ/mol)
		$-4 \times 10^{-6}$	3.01	0.800    0.353
Temkin isotherm	$q_e = \beta \ln \alpha + \beta \ln C_e$	$B$	$K_T$ (L/mg)	$R^2$
		0.546	8.77	0.911

TABLE 4: Thermodynamical and activation parameters for sorption of Co(II) on SB.

Thermodynamically Activated Parameters	Parameters values kJ mol <sup>-1</sup>	Conclusion
$\Delta G^0$	-0.254	Spontaneous and feasible process
$\Delta H^0$	+22.24	Endothermic process
$\Delta S^0$	+0.065	Increase in randomness at solid/solution interface
$\Delta G^\#$	+84.63	Energy requirement for sorption process
$\Delta H^\#$	+0.004	Endothermic process
$\Delta S^\#$	-0.262	Associated mechanism
$E_a$	0.007	Physical adsorption

TABLE 5: Comparison of adsorption potential of various adsorbents for cobalt removal from aqueous solution.

Adsorbent	$q_{max}$ (mg/g)	Reference
(1) Kaolinite	0.919	[32]
(2) Granular activated carbon	1.193	[33]
(3) Alginate-chitosan hybrid gel beads	3.12	[34]
(4) Palygorskite	8.88	[35]
(5) Arca green hull biomass	11.53	[36]
(6) Coir pith	12.82	[37]
(7) Neutral zeolite	14.38	[38]
(8) <i>Saccharum bengalense</i>	14.51	[Present Study]
(9) <i>Sargassum wightii</i>	20.63	[39]
(10) AMT metal removing agent	35	[40]

energy ( $\Delta G^\#$ ) can be calculated from the Eyring equation [47]:

$$\ln\left(\frac{k_2}{T}\right) = \left[\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\#}{R}\right] - \frac{\Delta H^\#}{RT}, \quad (23)$$

where  $k_B$  is the Boltzmann constant ( $1.3807 \times 10^{-23}$  J K<sup>-1</sup>),  $h$  is Planck's constant ( $6.6261 \times 10^{-34}$  J s), and  $k_2$  is the pseudo-second-order rate constant. The plot of  $\ln(k_2/T)$  against  $1/T$  is shown in Figure 4(c).

Gibbs energy of activation can be calculated as

$$\Delta G^\# = \Delta H^\# - T\Delta S^\#. \quad (24)$$

The change of activation Gibbs energy ( $\Delta G^\#$ ) for adsorption of Co(II) ions on SB was calculated as +84.61 kJ mol<sup>-1</sup> at 323K. It indicates that adsorption reactions require energy to convert reactants into products. The  $\Delta G^\#$  value determines the rate of the reaction; rate increases as  $\Delta G^\#$  decreases, and as the energy requirement is fulfilled, the reaction proceeds [48]. The positive value of  $\Delta H^\#$  confirms the endothermic process, demonstrating that the reaction consumes energy [49]. The negative value of  $\Delta S^\#$  suggests that adsorption of Co(II) on SB surface is an associated mechanism [50, 51].

4.3. Comparison of Adsorption Capacity of SB with Different Adsorbents. SB has been compared with various adsorbents in terms of adsorption capacity (mg/g). Table 5 shows such a comparison. It can be easily observed that the adsorption capacity of SB is high as compared to a number of other materials.

## 5. Conclusion

It can be concluded that *Saccharum bengalense* is an effective biosorbent for the removal of Co(II) ions from aqueous water. The biosorption of Co(II) by SB followed Langmuir and Freundlich models. The rate constant increased with increase in temperature indicating endothermic nature of adsorption. The values of  $\Delta G^\#$ ,  $\Delta H^\#$ ,  $\Delta S^\#$ , and  $E_a$  predicting the adsorption of Co(II) onto SB were diffusion controlled and an associative mechanism. The adsorption capacity increased with the rise in temperature was indicating that the adsorption was a spontaneous, feasible, and endothermic process.

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