



## Biosorption of palladium(II) from aqueous solution by moss (*Racomitrium lanuginosum*) biomass: Equilibrium, kinetic and thermodynamic studies

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### ABSTRACT

The biosorption potential of *Racomitrium lanuginosum* as aquatic moss biosorbent for the removal of Pd(II) from aqueous solution was investigated. The effects of pH, biomass dosage, contact time, and temperature on the biosorption processes were systematically studied. Experimental data were modeled by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. Langmuir isotherm model ( $R^2 = 0.994$ ) fitted the equilibrium data better than the Freundlich isotherm model ( $R^2 = 0.935$ ). The monolayer biosorption capacity of *R. lanuginosum* biomass for Pd(II) was found to be 37.2 mg/g at pH 5. The mean free energy was calculated as 9.2 kJ/mol using the D–R isotherm model ( $R^2 = 0.996$ ). This result indicated that the biosorption of Pd(II) was taken place by chemical ion-exchange. The calculated thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed that the biosorption of Pd(II) on *R. lanuginosum* biomass was feasible, spontaneous and exothermic under examined conditions. Experimental data were also tested using the biosorption kinetic models. The results showed that the biosorption processes of Pd(II) on *R. lanuginosum* followed well pseudo-second-order kinetics at 20–50 °C ( $R^2 = 0.999$ ).

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### 1. Introduction

With the rapid increase in global industrial activities, heavy metal pollution has become serious. Release of heavy metals from various industrial activities such as mining, ore processing, smelting, metal plating and textile dyeing creates metal pollution and causes hazardous effects on humans and animals.

Platinum group elements (PGEs), platinum, palladium and rhodium is available at low concentration in the earth crust. However, the increasing uses of PGEs in vehicle exhaust catalysts, in addition to some other applications (e.g. industry, jewellery and anticancer drugs) cause their anthropogenic emission and spread in the environment [1–3]. Recently,  $^{103}\text{Pd}$  has been used in the treatment of cancer [4]. The demand and the production of Pd have recently increased rapidly, although a decreasing tendency has been observed since 2000 [5]. WHO reported that for the general population, dental alloys contribute considerably to the total Pd intake ( $<1.5\text{--}15\ \mu\text{g person}^{-1}$ ), and skin contact with Pd-containing jewellery is an important route of exposure [4]. Palladium exposure through inhalation of Pd from automobile catalyst emissions is expected to be low (about  $2.2\ \text{ng person}^{-1}\ \text{day}^{-1}$ ). However, if the worst case air pollution scenario of  $57\ \text{ng m}^{-3}$  is considered, the

average daily intake would reach  $1254\ \text{ng person}^{-1}$  [4]. The increasing demand for palladium metal (Pd(II)) in industry has prompted the research into new methods for its recovery from wastage due to the importance in terms of environment and health mentioned above [6–8].

The toxic effects of heavy metals on living tissues and environment directed the research to develop alternative technologies for wastewater purification systems [9]. Conventional separation techniques used for the treatment of industrial effluents include ion exchange, chemical precipitation, reverse osmosis, membrane filtration, purification technique and adsorption biological treatment [10]. Most of these methods are not suitable for small-scale industries due to some drawbacks such as high capital and operational cost or the disposal of the residual metal sludge [11]. Biosorption plays an important role in elimination of metal ions from aqueous solutions [12,13]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic [14]. Various sorbents have been used to remove Pd(II) ions from aqueous solution [15–21].

Mosses are cryptogamic organisms which occur in almost all terrestrial ecosystems and by virtue of their ability to tolerate long periods of drought may even colonize areas with extreme environmental conditions [22]. Mosses show a high capacity for

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assimilating nutrients, toxic organics and heavy metals, leading to a concentration inside the plants several times higher than in the surrounding environment [23,24]. Various types of them have also been used for removing different heavy metals from aqueous solution [25,26]. As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Pd(II) by *Racomitrium lanuginosum*. In addition, this new material was chosen as biosorbent in this study due to being of its natural, abundantly available and thus low-cost biomass.

The objective of the present work is to investigate the biosorption potential of *R. lanuginosum* biomass for removing Pd(II) from aqueous solution. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. Kinetic and thermodynamic parameters were also calculated to describe the biosorption mechanism of Pd(II) on *R. lanuginosum* biomass.

## 2. Experimental procedures

### 2.1. Biomass preparation

The moss (*R. lanuginosum*) biomass was used as biosorbent for the biosorption of Pd(II) ions. Samples of the biomass were collected from the East Black Sea region of Turkey. Samples were washed with deionized water and inactivated by heating in an oven at 70 °C for 48 h. The inactivated dried moss biomass was ground and sieved through different sizes and 180–300 μm fraction was used in all experiments.

### 2.2. Reagents and equipments

In this work, all chemical reagents were in analytical grade (Meck Company, Germany) and they were used without further purification. Double deionized water (Milli-Q Millipore 18.2 MΩ cm<sup>-1</sup> conductivity) was used through out experimental work.

Phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to obtain a solution of pH 2. Acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to obtain solutions of pH 4–6. Ammonium buffer solution (0.1 mol/L) was prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to obtain solutions of pH 8.

A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. A PerkinElmer Analyst 700 (Norwalk, CT, USA) flame atomic absorption spectrometer with deuterium background corrector was used. The operating parameters for working elements were set as recommended by the manufacturer. Fourier Transform Infrared (FT-IR) spectra of dried unloaded biomass and Pd(II)-loaded biomass were taken using KBr discs at 400–4000 cm<sup>-1</sup> using a FT-IR (JASCO-430 model, US) spectrometer.

### 2.3. Batch biosorption procedure

Experimental conditions were optimized by studying the contact time from 5 to 60 min, the pH from 2 to 8, the initial metal concentration from 25 to 300 mg/L, the biosorbent dosage from 1 to 16 g/L, and temperature from 20 to 50 °C. Biosorption experiments were carried out at optimum conditions: pH 5, 30 min contact time and 0.1 g biomass in a 250 mL stoppered conical flask containing 25 mL of test solution. Initial solutions with different concentration of Pd(II) were prepared by proper dilution of stock 1000 mg/L Pd(II) standards.

0.1 g biomass was then added and contents in the flask were shaken for 30 min using electrically thermostatic reciprocating shaker at 120 rpm. After equilibrium time (30 min), the contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by flame AAS. The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption (\%)} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_f$  are the initial and final metal ion concentrations, respectively.

## 3. Results and discussion

### 3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible interactions between the functional groups of *R. lanuginosum* biomass and the metal ions. The FT-IR spectra of dried unloaded biomass and Pd(II)-loaded biomass are shown in Fig. 1. The broad and strong bands at 3205–3251 cm<sup>-1</sup> were due to the overlapping of –OH and –NH<sub>2</sub> stretching vibration. The peaks at 1637–1646 cm<sup>-1</sup> were attributed to stretching vibration of carboxyl group (–C=O). The bands observed at 1031–1058 cm<sup>-1</sup> were assigned to C–O stretching of alcohols and carboxylic acids. The peaks observed at 2917 cm<sup>-1</sup> can be assigned to the C–H group.

The stretching vibration peaks at 3205, 1637, and 1031 cm<sup>-1</sup> were shifted to 3251, 1646, and 1058 cm<sup>-1</sup>, after biosorption of Pd(II), respectively. The results indicated that the biosorption could be carried out by ion-exchange between the Pd(II) ions and the hydrogen atoms of –OH, –NH<sub>2</sub> and –COOH groups of the biomass. The same mechanism was reported for the biosorption of Cd and Zn ions on aquatic moss, *Fontinalis antipyretica* [27]. It was reported in another study that the same functional groups of terrestrial moss, *Pleurozium schreberi* was responsible for metal-binding capacity [28].

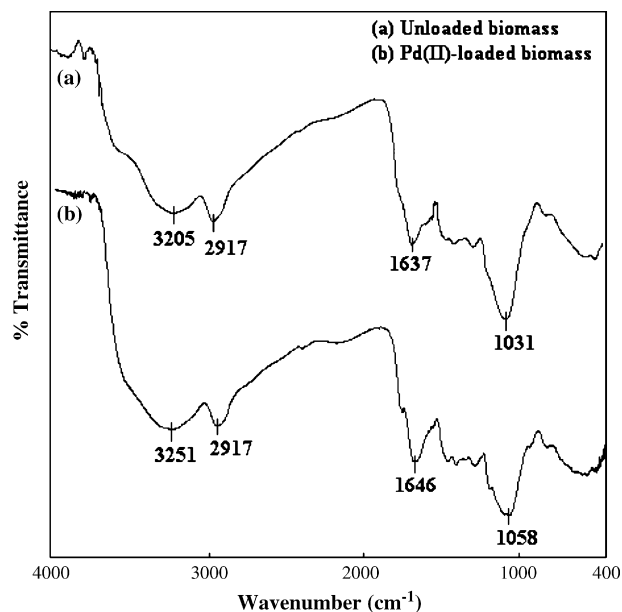


Fig. 1. FT-IR spectrum of dried unloaded biomass, Pd(II)-loaded biomass.

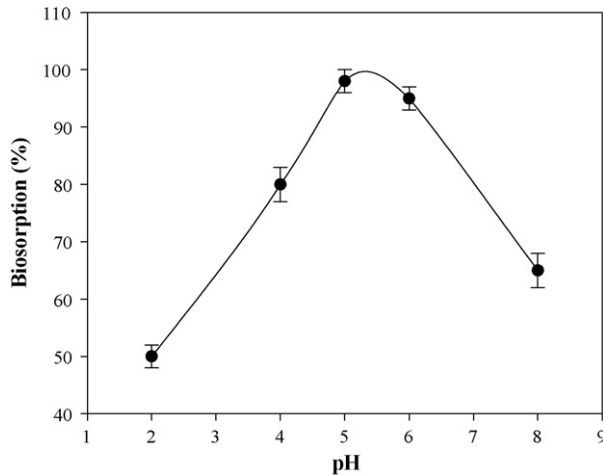


Fig. 2. Effect of pH on the biosorption of Pd(II) on *R. lanuginosum* biomass (metal concentration: 25 mg/L; temperature: 20 °C).

### 3.2. Effect of pH

The pH of solution has been identified as one of the most important parameters affecting metal ion sorption. This is partly because hydrogen ions themselves are strongly competing with sorbate. The biosorption of Pd(II) as a function of hydrogen ion concentration was examined over a pH range of 2–8 and the results were presented in Fig. 2. The biosorption yield was found to be 50 and 80% at pH 2 and pH 4, respectively. The maximum biosorption yield was found to be 98% at pH 5. Therefore, all the biosorption experiments were carried out at pH 5. At high pH values (pH > 5), the biosorption yield was dramatically decreased. The effect of pH can be explained considering the surface charge on the biosorbent. At low pH value (pH 2), due to high positive charge (protons) density on the surface sites, electrostatic repulsion will be high during the biosorption of metal ions resulting in lower biosorption yield. Electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase metal biosorption. When the pH values increased, biosorbent surfaces were more negatively charged and the biosorption of the metal ion with positive charge (Pd<sup>2+</sup>) process was reached maximum around pH 5. Decrease in biosorption at higher pH (pH > 5) is due to the formation of soluble complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease again. The maximum biosorption capacity was determined using *F. antipyretica* (aquatic moss) for Cd and Zn at pH 5 [27] and using terrestrial moss, *P. schreberi* for Cu(II) at pH 5.5 [28].

### 3.3. Biosorption isotherm models

The biosorption equilibrium data were fitted for the linear Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms

The Langmuir model represents one of the first theoretical treatments of nonlinear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules [29]. This model can be written as follows

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

where  $q_e$  is the equilibrium metal ion concentration on the adsorbent (mg/g),  $C_e$  is the equilibrium metal ion concentration in the solution (mg/L),  $q_m$  is the monolayer biosorption capacity of the

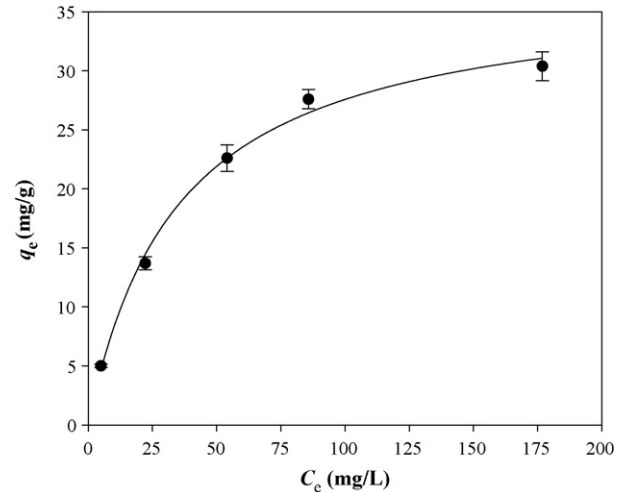


Fig. 3. Langmuir isotherm plots for the biosorption of Pd(II) on *R. lanuginosum* biomass (biomass dosage: 4 g/L; contact time: 30 min; pH: 5; temperature: 20 °C).

adsorbent (mg/g), and  $K_L$  is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

Fig. 3 indicates the non-linear relationship between the amount (mg) of Pd(II) sorbed per unit mass (g) of *R. lanuginosum* biomass against the concentration of Pd(II) unsorbed in solution (mg/L). The coefficient of determination ( $R^2$ ) was found to be 0.994, indicating that the biosorption of the Pd(II) on *R. lanuginosum* biomass fitted well with the Langmuir model. In other words, the sorption of Pd(II) ions on *R. lanuginosum* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. The maximum biosorption capacity ( $q_m$ ) of *R. lanuginosum* biomass was found to be 37.2 mg/g for Pd(II). Moreover, the  $K_L$  constant value was found as 0.03 L/mg.

On the other hand, Table 1 presents the comparison of sorption capacity,  $q_m$  of *R. lanuginosum* biomass for Pd(II) with that of different sorbents in literature. From this table, it can be resulted that the *R. lanuginosum* has considerable biosorption potential for Pd(II) from aqueous solution when compared with that of the other sorbents.

The Freundlich isotherm is the most widely non-linear sorption model used. This model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. The Freundlich model [30] is

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

Table 1

Comparison of sorption capacity of *R. lanuginosum* biomass for Pd(II) with that of different sorbents

Sorbent	Sorption capacity (mg/g)	Reference
Bayberry tannin immobilized collagen fiber membrane	33.4	[15]
Thiol cotton fiber	32.0–42.0 <sup>a</sup>	[16]
Fe <sub>3</sub> O <sub>4</sub> nano-particles	11.0	[8]
EN-Lignin	22.7	[17]
PA-Lignin	40.4	[18]
Amberlite IRC 718	58.5	[19]
Amberlite XAD-16	33.6	[20]
Lysine modified crosslinked chitosan resin	109.5	[21]
<i>Racomitrium lanuginosum</i>	37.2	Present study

<sup>a</sup> Sorption capacity range for ten batch experiments.

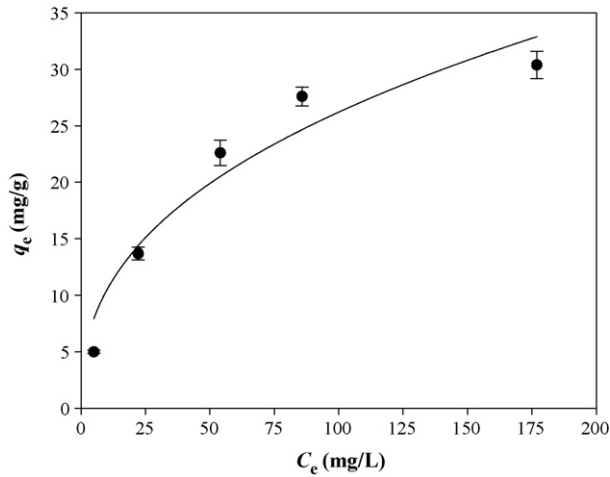


Fig. 4. Freundlich isotherm plots for the biosorption of Pd(II) on *R. lanuginosum* biomass (biomass dosage: 4 g/L; contact time: 30 min; pH: 5; temperature: 20 °C).

where  $K_f$  is a constant relating the biosorption capacity and  $1/n$  is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material.

Fig. 4 shows the non-linear Freundlich isotherms for the biosorption of Pd(II) on *R. lanuginosum* biomass.  $K_f$  and  $1/n$  were found to be 4.2 and 0.39.  $1/n$  value between 0 and 1 indicates that the biosorption was favourable at studied conditions. The  $R^2$  value was found to be 0.935. This result indicates that the Freundlich model was not able to adequately describe the relationship between the sorbed amount of Pd(II) and its equilibrium concentration in the solution. However, the Langmuir isotherm model best fitted with the equilibrium data since it presents higher  $R^2$  value.

Another equation that has been used to determine the possible biosorption mechanism is the Dubinin–Radushkevich equation, which assumes a constant sorption potential. The linear form of the D–R isotherm equation [31] is:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

where  $q_e$  is the amount of metal ions adsorbed on per unit weight of biomass (mol/L),  $q_m$  is the maximum biosorption capacity (mol/g),  $\beta$  is the activity coefficient related to biosorption mean free energy ( $\text{mol}^2/\text{J}^2$ ) and  $\varepsilon$  is the Polanyi potential ( $\varepsilon = RT \ln(1 + 1/C_e)$ ).

The D–R isotherm model well fitted the equilibrium data since the  $R^2$  value was found to be 0.996 for Pd(II) biosorption (Fig. 5). From the intercept of the plots the  $q_m$  value was found to be  $5.5 \times 10^{-4}$  mol/g. The biosorption mean free energy ( $E$ ; kJ/mol) is as follow:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The biosorption mean free energy gives information about biosorption mechanism. If  $E$  value lies between 8 and 16 kJ/mol, the biosorption process takes place by chemical ion-exchange while

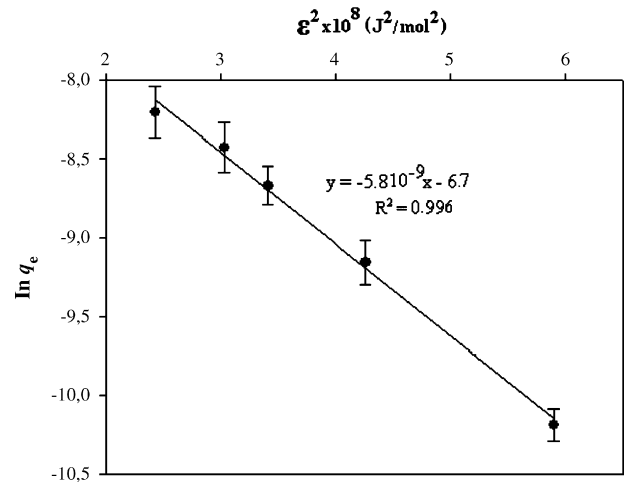


Fig. 5. D–R isotherm plots for the biosorption of Pd(II) on *R. lanuginosum* biomass (pH: 5; adsorbent dosage: 4 g/L; contact time: 30 min; temperature: 20 °C).

$E < 8$  kJ/mol, the biosorption process is carried out physically [32]. The mean biosorption energy was calculated as 9.2 kJ/mol. This value indicated that biosorption of Pd(II) on *R. lanuginosum* mainly proceeds by chemical ion-exchange.

### 3.4. Biosorption kinetics

Biosorption kinetics depends on the biosorbate–biosorbent interaction and operating condition and examined for their suitability for practical applications in water pollution control. In order to clarify the biosorption kinetics of Pd(II) on *R. lanuginosum* biomass two kinetic models, which are Lagergren’s pseudo-first-order and pseudo-second-order model were applied to the experimental data.

The linear form of the pseudo-first-order rate equation by Lagergren [33] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where  $q_t$  and  $q_e$  (mg/g) are the amounts of the metal ions sorbed at equilibrium (mg/g) and  $t$  (min), respectively, and  $k_1$  is the rate constant of the equation ( $\text{min}^{-1}$ ). The biosorption rate constants ( $k_1$ ) can be determined experimentally by plotting of  $\ln(q_e - q_t)$  vs  $t$ . The plots of  $\ln(q_e - q_t)$  vs  $t$  for the pseudo-first-order model were not shown as figure because the  $R^2$  values for this model at studied temperatures is low ( $R^2 = 0.960$ – $0.972$ , as seen in Table 2). The  $R^2$  values show that the biosorption mechanisms of Pd(II) on *R. lanuginosum* biomass does not follow the pseudo-first-order kinetic model.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [34]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \tag{7}$$

Table 2  
Pseudo-first-order and pseudo-second-order parameters calculated for the of Pd(II) biosorption using *R. lanuginosum* biomass at 20–50 °C.

Temperature (°C)	Pseudo-first-order			Pseudo-second-order		
	$k_1$ (1/min)	$q_e$ (mg/g)	$R^2$	$k_2$ (g/mg min)	$q_e$ (mg/g)	$R^2$
20	0.10	1.1	0.960	0.12	1.3	0.995
30	0.09	0.7	0.972	0.11	1.2	0.995
40	0.08	0.5	0.961	0.10	1.1	0.999
50	0.07	0.3	0.969	0.08	1.0	0.999

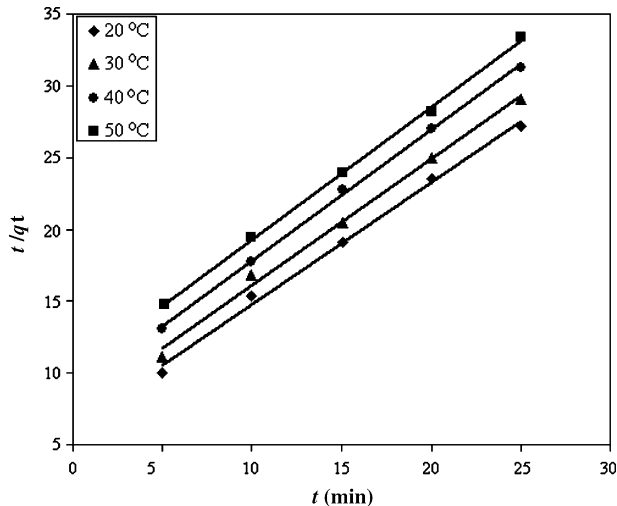


Fig. 6. Pseudo-second-order kinetic plots at different temperatures for the biosorption of Pd(II) on *R. lanuginosum* biomass.

where  $k_2$  (g/mg min) is the rate constant of the second-order equation,  $q_t$  (mg/g) is the amount of biosorption time  $t$  (min) and  $q_e$  is the amount of biosorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step [35]. The linear plots of  $t/q_t$  vs  $t$  for the pseudo-second-order model for the biosorption of Pd(II) ions on *R. lanuginosum* biomass at 20–50 °C were shown in Fig. 6. The rate constants ( $k_2$ ), the  $R^2$  and the  $q_e$  values are given in Table 2. The  $R^2$  values are in the range, 0.995–0.999, indicating that the biosorption of Pd(II) on *R. lanuginosum* biomass follows well the pseudo-second-order kinetic model.

### 3.5. Biosorption thermodynamics

Thermodynamic behavior of the biosorption of Pd(II) ions on *R. lanuginosum* biomass was evaluated by the thermodynamic parameters including the change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ). These parameters were calculated from following equations

$$\Delta G^\circ = -RT \ln K_D \quad (8)$$

where,  $R$  is the universal gas constant (8.314 J/mol K),  $T$  is temperature (K) and  $K_D$  ( $q_e/C_e$ ) is the distribution coefficient [21].

The enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) parameters were estimated from the following equation

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

According to Eq. (9), the  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters can be calculated from the slope and intercept of the plot of  $\ln K_D$  vs  $1/T$  yields, respectively (Fig. 7).

Gibbs free energy change ( $\Delta G^\circ$ ) was calculated to be  $-20.2$ ,  $-18.9$ ,  $-18.1$ , and  $-17.0$  kJ/mol for Pd(II) biosorption at 20, 30, 40, and 50 °C, respectively. The negative  $\Delta G^\circ$  values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in  $\Delta G^\circ$  values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The  $\Delta H^\circ$  parameter was found to be  $-50.8$  kJ/mol. The negative  $\Delta H^\circ$  is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The enthalpy or heat of biosorption, ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol) corresponds

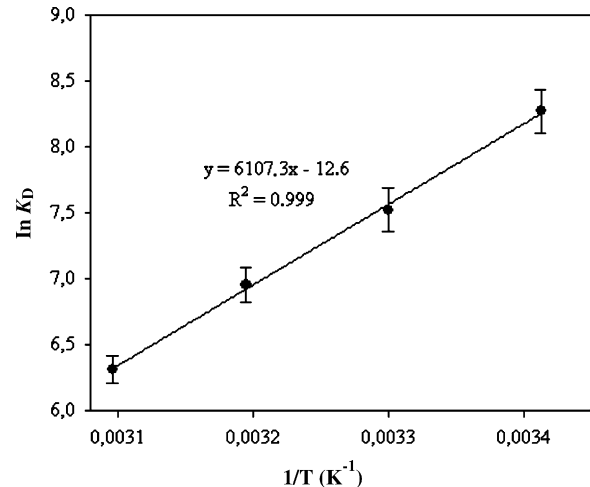


Fig. 7. Plot of  $\ln K_D$  vs  $1/T$  for the estimation of thermodynamic parameters for the biosorption of Pd(II) on *R. lanuginosum* biomass.

a physical sorption as it ranges from 20.9 to 418.4 kJ/mol in case of a chemical sorption [36,37]. The biosorption heat of Pd(II) are in the heat range of chemisorption. Therefore, the  $\Delta H^\circ$  values showed that the biosorption processes of Pd(II) on *R. lanuginosum* were taken place via chemisorption. The mean biosorption energy values obtained from the D–R model also confirm this result. The  $\Delta S^\circ$  parameter was found to be  $-104.8$  J/mol K for Pd(II) biosorption. The negative  $\Delta S^\circ$  value suggests a decrease in the randomness at the solid/solution interface during the biosorption process

## 4. Conclusions

The present study focuses on biosorption of Pd(II) from aqueous solution using the *R. lanuginosum* as a low cost biosorbent. The biosorption characteristic has been examined with the variations in the parameters of pH, biomass dosage, contact time and temperature. The maximum biosorption capacity of *R. lanuginosum* for Pd(II) was determined to be 37.2 mg/g. The experimental data were evaluated by Langmuir, Freundlich and D–R isotherms. The biosorption mean free energy was determined from the D–R isotherm model to be 9.2 kJ/mol, suggesting that the biosorption of Pd(II) on *R. lanuginosum* biomass was taken place by chemical ion-exchange. The interactions between metal ions and the functional groups on the biomass surface were estimated by FT-IR spectroscopy analysis. Kinetic evaluation of the equilibrium data showed that the biosorption of Pd(II) on *R. lanuginosum* followed well the pseudo-second-order kinetic model. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the biosorption process at 20–50 °C. Based on all results, it can be also concluded that the *R. lanuginosum* is an effective and alternative biomass for removing Pd(II) from aqueous solution because of its high biosorption capacity, being natural and low-cost biomass.

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