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Factors Affecting Lanthanum and Cerium Biosorption on *Pinus brutia* Leaf Powder

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The biosorption behavior of lanthanum and cerium ions from aqueous solution by leaf powder of *Pinus brutia* was separately studied in a batch system as a function of initial pH, contact time, initial metal ion concentration, temperature, and adsorbent amount. The uptake of lanthanum and cerium was increased when the initial pH of the solution was increased. Thermodynamic parameters such as standard enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) were calculated and the results indicated that biosorption was endothermic and spontaneous in nature. The biosorption of lanthanum and cerium on powdered leaf of *Pinus brutia* was investigated by the Freundlich, Langmuir, and D-R isotherms. The results show that lanthanum and cerium adsorption can be explained by the Langmuir isotherm model and monolayer capacity was found as $22.94\,\mathrm{mg\,g^{-1}}$ for lanthanum and $17.24\,\mathrm{mg\,g^{-1}}$ for cerium. Desorption of lanthanum and cerium was studied using 0.5 M HNO_3 solution. The results suggested that powdered leaf of *Pinus brutia* may find promising applications for the recovery of lanthanum and cerium from aqueous effluents.

Keywords biosorption; cerium; lanthanum; *Pinus brutia*

INTRODUCTION

Rare earth elements (REEs) are widely used in the field of nuclear energy, chemical engineering, metallurgy, electronics, and computers and the demand for them is expected to correspondingly increase in time (1–3). From the rare earth elements (REEs), lanthanum has received special attention due to its technological importance because of increasing demands for advanced new materials. Current applications of lanthanum as a pure element or in association with other compounds are in super alloys, catalysts, special ceramics, and in organic synthesis (4). Cerium, as the most common and lowest-cost member of the group, has some well-established uses that are quite distinct from the others. However, high purity is usually required for its utilization in industry where it is used, for example, for sulfur control in steels, pyrophoric alloys, ceramic, catalyst support, and polishing powders, etc. Cerium is accompanied by other REEs in its minerals, as well as in the spent nuclear fuel (5). However, increasing use of REEs might couse environmental contamination. Thus, their possible long-term hazardous environmental effects are of concern (6).

Many conventional methods for removing heavy metals, radionuclides, and lanthanides from aqueous solution exist (7). These include adsorption, ion exchange, coagulation, floatation, hyper-filtration, chemical precipitation, and reverse osmosis (1,5,8). All these conventional methods have some advantages as well as disadvantages, such as disposal of chemicals, resins, and adsorbents to nature may themselves be harmful. This has initiated research in new, low-cost materials for possible use as adsorbents (7). Biosorption can be a candidate for the recovery of metals from dilute industrial aqueous solutions, the extraction of radionuclides and lanthanides from mine leachates, and metal recovery or water pollution control applications (9). This novel approach is competitive, effective, economical, and eco-friendly technology in contrast to traditional methods (10,11). Biosorption is a process where metal ions in solution are removed by dead biomass such as seaweed, yeast, bacteria, and fungi. In general, biomass could be an industrial waste or naturally grown and collected material (3).

Plant leaves have also been recommended as a simple and inexpensive biosorbent to remove heavy metals from solutions. They contain various components such as polyphenolics, plant pigments, and protein which would provide active sites for heavy metal binding (12). Several studies were reported regarding the heavy metal removal by using plant leaves. Al-Subu (13) described the removal of lead from aqueous solutions using leaves of three different plant species; cypress (*Cupressus sempervirens*), cinchona (*Eucalyptus longifolio*) and pine (*Pinus halepensis*). Ucun et al. (14), used ovulate cone biomass of *Pinus sylvestris* as a biosorbent for Cr(VI) from artificial wastewaters and studied to determine the constants of the adsorption isotherm relation. Bhattacharyya and Sharma (7) used dry Neem leaf powder, as an adsorbent for the removal

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of toxic heavy metals such as Pb(II). Kumar et al. (10), investigated the potential use of untreated *Tectona grandis* L.f. biomass as metal sorbent for zinc from aqueous solution.

Despite their strategic and economic importance, only in the last few years some investigations have been published related to the recovery of REEs by biomaterials. Sert et al. (15), used leaf powder of *Platanus orientalis* for the biosorption of La and Ce (III). Texier et al. (16) investigated the selective sorption of three trivalent lanthanide (La, Eu, and Yb) ions by biomass from *P. aeruginosa*. Palmieri et al. (17), worked on to develop a study on neodymium biosorption from acidic solution utilizing different types of biomass in batch experiments. Diniz and Volesky (3) investigated the biosorption of La, Eu, and Yb using *Sargassum* biomass. This study focuses on exploring the biosorption potential in the recovery of a light (La), intermediate (Eu), and a heavy (Yb) rare earth elements using *Sargassum* biomass in single- and multi-component metal systems.

Pinus brutia is one of the important forest trees of the Mediterranean region, reaches its greatest distribution in southern Turkey where it has become one of Turkey's most valuable commercial trees (18). Previously, *Pinus brutia* saw dust and *P. brutia* pine bark were used for Cu and Pb(II) adsorption, respectively (19,20)

Thus, in this work finely ground *Pinus brutia* leaf powder was tested as a biosorbent for the removal of lanthanum and cerium from aqueous solutions. The effects of initial solution pH, contact time, initial metal concentration, temperature, and the adsorbent amount on the biosorption were discussed. Thermodynamic parameters and isotherm studies related with the process were performed.

MATERIALS AND METHODS

Chemicals and Reagents

All chemicals and reagents used in this study were of analytical grade. Lanthanum and cerium stock solutions ($1\,gL^{-1}$) were individually prepared by dissolving $La(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (Merck) in deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. 0.1 g of dry biomass was contacted with 0.025 L of known concentration solutions.

Biosorbent Preparation

P. brutia leaves were collected from a number of trees at Ege University Campus, Izmir, Turkey. The leaves were washed repeatedly with deionized water to remove dust and soluble impurities and dried in an oven at 80°C for 24 h, ground in a mortar to a very fine powder and sieved through a 125 μm copper sieve, and stored in a desiccator before use. The dried leaves were used as biosorbent without any chemical treatment to avoid extra expenditure.

Batch Biosorption Experiments

Biosorption tests were carried out by a batch technique in order to determine the optimum conditions for the system. Solutions containing the metals were individually prepared by diluting the stock solutions to appropriate volumes using de-ionized water. The pH values of these solutions were adjusted with $1\,mol\,L^{-1}$ NH_3 and $1\,mol\,L^{-1}$ HNO_3 solution by using Metrohm 654 pH meter with a combined pH electrode. Batch biosorption experiments were performed by a thermostatically controlled shaker (GFL-1083 model). In the experiments, powdered leaf of *P. brutia* was separately shaken with 25 mL of Lanthanum and Cerium solutions at varying experimental conditions in 50 mL erlenmeyer flasks at a speed of 100 rpm. The supernatants were filtered through a filter paper (Whatman No. 41) and the concentration of La and Ce(III) in the solution were measured before and after equilibrium by a Perkin-Elmer Optima 2000DV ICP OES. All the experiments were carried out in duplicate and the mean value was used in all cases.

The amount of metal adsorbed by *P. brutia* leaves was calculated using the following equation:

$$q = (C_0 - C_e) \times V/M \qquad (\text{mg g}^{-1}) \qquad (1)$$

where q is the metal uptake ($mg\,g^{-1}$), C_0 and C_e are the initial and equilibrium metal concentrations in the solution ($mg\,L^{-1}$), respectively, V is the solution volume (L), and M is the mass of biosorbent (g).

The distribution coefficient (K_d) of metal ions between the aqueous and the solid phase can be directly obtained as:

$$K_d = \frac{C_0 - C_e}{C_e} x \frac{V}{m} \qquad (\text{mL g}^{-1}) \qquad (2)$$

where C_0 ($g\,L^{-1}$) and C_e ($g\,L^{-1}$) are initial and equilibrium lanthanum or cerium concentrations, respectively, V/m is the ratio of the volume of the metal solution (mL) to the amount of adsorbent (g) in a batch.

Desorption of Lanthanum and Cerium from Leaves

Desorption experiments were carried out using 0.1 g of biomass previously loaded with lanthanum and cerium separately at optimum conditions as described above. The loaded biomass was contacted with 25 mL of 0.5 M HNO_3 solution at 30°C for 1 h (15,21).

RESULTS AND DISCUSSION

Effect of Initial pH

pH is an important factor controlling the process of adsorption. The pH affects not only the surface charge of the biosorbent, but also the degree of ionization and speciation of the heavy metal in solution (22). 25 mL of 100 mg L^{-1} lanthanum and cerium(III) were treated separately with 0.1 g of powdered leaf of *P. brutia* at different pHs, in a thermostatically controlled shaker at 30°C for 2 h. Figure 1 shows that the biosorption increased with the increase in pH. The highest biosorption efficiency was obtained at pH 5.0 for both La and Ce(III). Similar results were reported by Texier et al. (16) for biosorption of La by *Pseudomonas aeruginosa*. Therefore, the following experimental runs were performed at pH 5.0. Lanthanum and cerium biosorption at pH higher than 6.0 was not considered due to the precipitation, indicating the hydrolysis of the metal ion with the formation of the corresponding insoluble hydroxide (4).

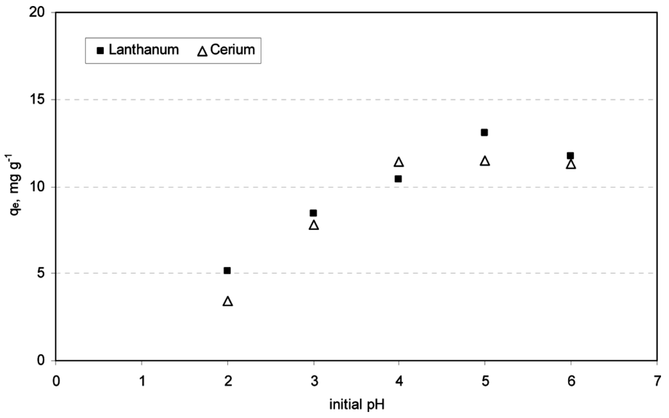

FIG. 1. Effect of initial pH on lanthanum and cerium biosorption on leaf powder of *P. brutia* (Initial lanthanum and cerium concentrations: 100 mg L^{-1}; contact time: 120 min, temperature: 30°C; biosorbent amount: 0.1 g).

Effect of Contact Time

Biosorption experiments were carried out with contact times varying from 1 to 480 minutes with a biosorbent amount of 0.1 g at pH 5.0. The results are presented in Fig. 2. At the start, the ions adsorbed and occupied selectively the active sites on the adsorbents. As the contact time increased the active sites on the adsorbents were filled. The rate of biosorption became gradually slower and reached a plateau. Therefore, the following experiments were carried out at 30 minutes and 15 minutes for La and Ce(III), respectively.

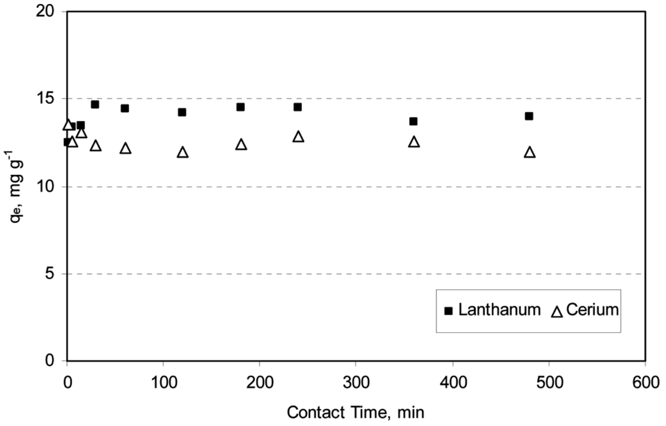

FIG. 2. Effect of contact time on lanthanum and cerium biosorption on leaf powder of *P. brutia* (Initial lanthanum and cerium concentrations: 100 mg L^{-1}; pH 5, temperature: 30°C, biosorbent amount: 0.1 g).

Kinetics of Biosorption

Kinetic studies were performed to determine the best fitting rate equations and rate constants of biosorption. According to the experimental results, biosorption kinetics of lanthanum and cerium on powdered *P. brutia* leaves is well described by the pseudo-second-order rate equation. If the rate of sorption is a second-order mechanism, the pseudo-second-order (23) chemisorption kinetic rate equation is expressed as:

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

where k_2 (g mg^{-1} h^{-1}) is the rate constant for the pseudo-second-order adsorption processes, q_t (mg/g) is the amount adsorbed at time t and q_e (mg/g) is the amount adsorbed at equilibrium. After integration and rearrangement of the above equation, the following equation is obtained with a linear form

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

The plot of t/q_t versus t gives a straight line with slope of $1/q_e$ and intercept of $1/k_2 q_e^2$. So the amount of cation sorbed per gram of sorbent at equilibrium q_e and sorption rate constant k_2 could be evaluated from the slope and intercept, respectively. The results obtained are shown in Table 1 and in Fig. 3.

It is apparent from q_e values that lanthanum ions are sorbed slightly more than cerium ions and the rate constant values show that cerium is slightly rapidly adsorbed by leaf

TABLE 1
Kinetic parameters for the biosorption of lanthanum and cerium onto powdered *P. brutia* leaf

	Pseudo-second-order		
	K_2 (g mg^{-1} h^{-1})	q_e (mg g^{-1})	R^2
Lanthanum	2.35	13.91	0.99
Cerium	3.52	12.22	0.99

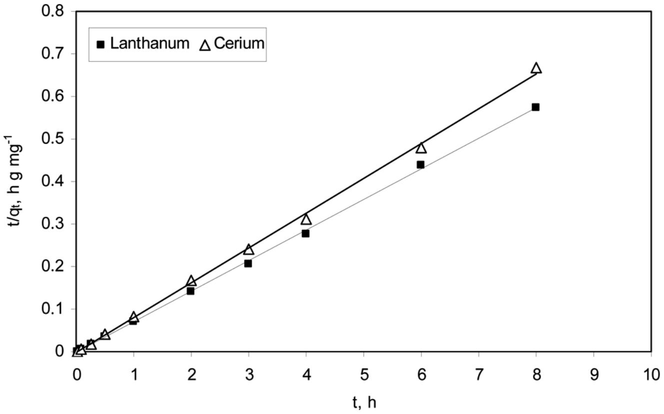

FIG. 3. Pseudo-second-order kinetic plots for the biosorption of lanthanum and cerium onto leaf powder of *P. brutia*.

powders. The correlation coefficients of the pseudo-second-order rate equation for the linear plot suggest that the kinetics of adsorption can be described by the pseudo-second-order rate equation very well.

Effect of Initial Metal Ion Concentration

Figure 4 shows the effect of initial metal ion concentration on the biosorption of La and Ce(III) by leaf powder of *P. brutia*. The biosorption was carried out at different initial metal ion concentrations ranging from 25 to 300 mg L^{-1} while the pH kept constant as 5. The data show that the biosorption efficiency decreases by the increase in the metal ion concentration. This may be attributed to a lack of sufficient surface area to accommodate much more metal available in the solution. At lower concentrations, metal ions present in solution could interact with the binding sites and thus the percentage of the biosorption was higher than those at higher metal ion concentrations. At higher concentrations, a lower adsorption percentage is due to the saturation of adsorption sites.

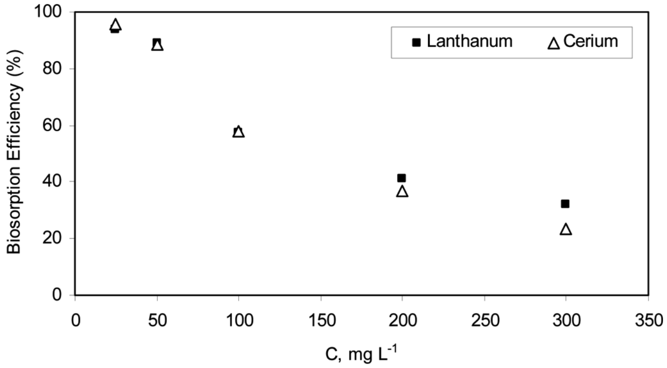

FIG. 4. Effect of initial concentration on lanthanum and cerium adsorption on leaf powder of *P. brutia* (Initial pH: 5, temperature: 30°C, contact time: 30 min for lanthanum, 15 min for cerium, adsorbent amount: 0.1 g).

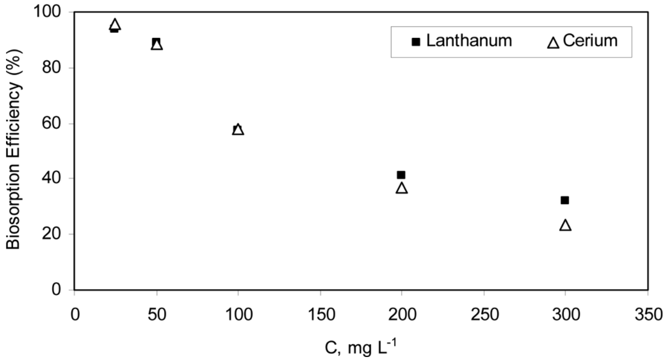

FIG. 5. Effect of adsorbent amount on the lanthanum and cerium adsorption on leaf powder of *P. brutia* (Initial metal ion concentration: 25 mg L^{-1}; initial pH: 5; contact time: 30 min for lanthanum, 15 min for cerium; temperature: 30°C).

Effect of Biosorbent Dose

The results of the dependence of lanthanum and cerium biosorption on biosorbent dose are shown in Fig. 5. The volume of solution (25 mL) was kept constant while the dose of adsorbents varied from 0.05 to 0.45 g. The amount of La and Ce (III) adsorbed on the biomass (mg g^{-1}) increased with the increasing sorbent concentration. This is expected because increasing sorbent particles in the solution causes more ions interact to these particles.

Effect of Temperature

The experiments were carried out at 20, 30, 40, and 50°C, while the other parameters were kept constant. La and Ce(III) solutions were shaken with 0.1 g *P. brutia* at pH 5 for 30 and 15 minutes, respectively. Figure 6 shows that the uptake of lanthanum and cerium slightly increases with increasing temperature.

The adsorption enthalpy was measured using the method based on the Van't Hoff plot. The values of $\Delta H°$

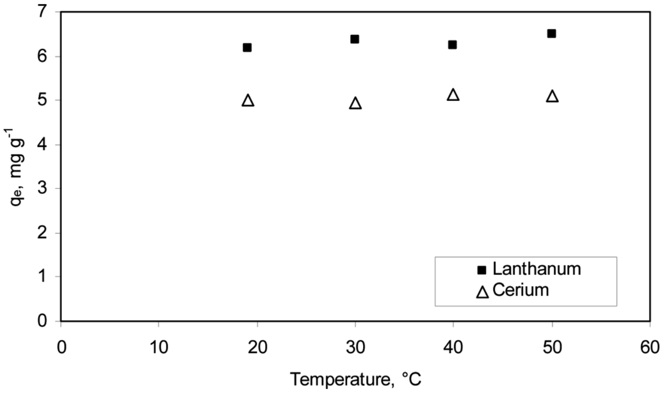

FIG. 6. Effect of temperature on the lanthanum and cerium biosorption on *P. brutia* leaf powder (Initial metal ion concentration: 25 mg L^{-1}; Initial pH: 5; contact time: 30 min for lanthanum, 15 min for cerium; biosorbent amount: 0.1 g).

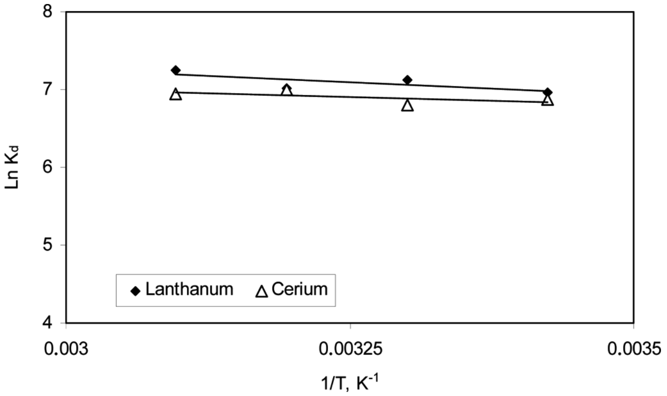

FIG. 7. Plots of $\ln K_d$ vs. $1/T$ for the lanthanum and cerium biosorption on leaf powder of *P. brutia*.

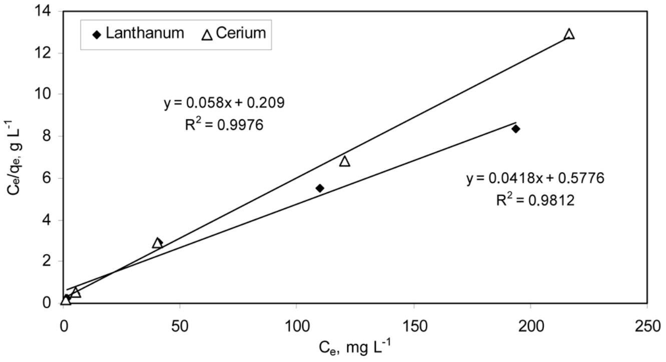

FIG. 8. Langmuir plots for the biosorption of lanthanum and cerium on leaf powder of *P. brutia*.

and ΔS° were calculated from the slope and intercept of the linear variation of $\ln K_d$ with reciprocal temperature, $1/T$, Fig. 7, using the relation:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{3}$$

where ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption, respectively. The free energy of specific adsorption ΔG° is calculated using the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

The values of ΔH°, ΔS°, and ΔG° were given in Table 2 for La and Ce(III) biosorption on leaf powder of *P. brutia*. Positive values of ΔH° and decrease in the value of ΔG° with rise in temperature show that the adsorption is endothermic and is more favourable at high temperature. Negative values of ΔG° indicate the spontaneous nature of the reaction. In addition, the values of ΔS° were found to be positive due to the exchange of the metal ions with more mobile ions present on the exchanger, which would cause increase in the entropy, during the adsorption process.

Adsorption Isotherms

In order to understand the adsorption characteristics of the adsorbents, the equilibrium data were evaluated according to the Freundlich, Langmuir, and D-R isotherms.

The Langmuir equation (24), which has been successfully applied to many adsorptions, is given by

$$\frac{C_e}{q_e} = \frac{1}{bn_m} + \frac{C_e}{n_m} \tag{5}$$

where, C_e is the equilibrium concentration ($\mathrm{mg\,L^{-1}}$), q_e is the amount absorbed at equilibrium ($\mathrm{mg\ g^{-1}}$), n_m ($\mathrm{mg\,g^{-1}}$) and b ($\mathrm{L\,mg^{-1}}$) is the Langmuir constants related to monolayer capacity and energy of adsorption. A linearized plot of C_e/q_e versus C_e is obtained for adsorbent as shown in Fig. 8.

The Freundlich equation, which was applied for the biosorption of lanthanum and cerium, is given as

$$q_e = KC_e^{1/n} \tag{6}$$

Equation (6) can be rearranged to linear form

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{7}$$

where q_e is the amount of solute adsorbed per mass unit adsorbent, C_e is the equilibrium concentration, K and n are the Freundlich constants characteristic of a particular adsorption isotherm and can be evaluated from the intercept and slope of the linear plot of log q versus log C_e (Fig. 9).

The experimental data were fitted using the Dubinin-Radushkevich (D-R) equation in order to understand the adsorption type.

TABLE 2
Thermodynamic parameters for the lanthanum and cerium biosorption on leaf powder of *P. brutia*

			ΔG° ($\mathrm{kj\,mol^{-1}}$)			
	ΔH° ($\mathrm{kJ\,mol^{-1}}$)	ΔS° ($\mathrm{kJ\,mol^{-1}\,K^{-1}}$)	292 K	303 K	313 K	323 K
Lanthanum	5.650	0.077	−16.93	−17.78	−18.55	−19.33
Cerium	3.325	0.068	−16.59	−17.34	−18.02	−18.70

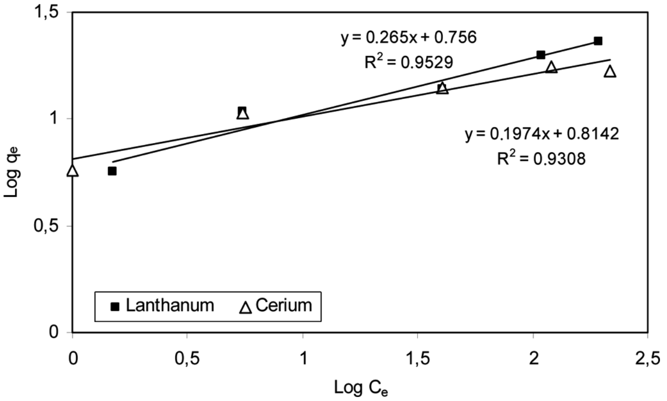

FIG. 9. Freundlich plots for the biosorption of lanthanum and cerium on leaf powder of *P. brutia*.

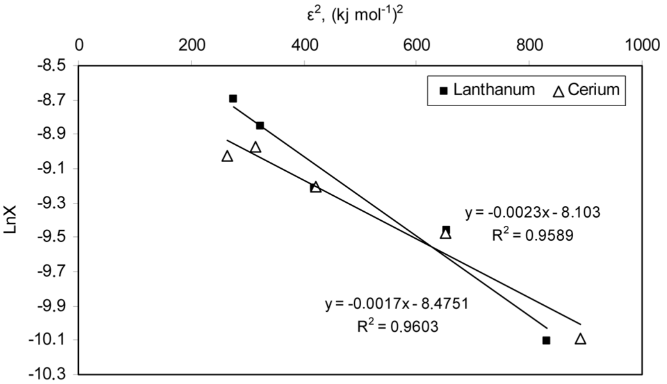

FIG. 10. D-R plots for the biosorption of lanthanum and cerium on leaf powder of *P. brutia*.

The linearized D-R equation can be written as

$$\ln X = \ln X_m - K\varepsilon^2 \tag{9}$$

where ε is Polanyi potential and is equal to

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

X is the amount of metal adsorbed per unit mass of adsorbent ($\mathrm{mol\,g^{-1}}$), X_m is the theoretical adsorption capacity ($\mathrm{mol\,g^{-1}}$), C_e is the equilibrium concentration of adsorbate, K is the constant related to adsorption energy ($\mathrm{mol^2\,kj^{-2}}$), R is the universal gas constant, and T is the temperature in Kelvin.

Figure 10 shows the plot of ln X against ε^2. D-R isotherm constants K and X_m were evaluated from the slope and intercept of the plot, respectively. The mean free energy of adsorption (E_{DR}) is the free energy change when one mole of a solute is transferred to the surface of the adsorbent from infinity in the solution, and that has been calculated by the equation Eq. (11).

$$E_{DR} = (-2K)^{-1/2} \tag{11}$$

The magnitude of E_{DR} ($\mathrm{kJ\,mol^{-1}}$) is useful for estimating the type of adsorption reaction, and if it ranged between 8.0 and 16.0 the adsorption should be taken place by ion exchange reaction. The D-R parameters and mean free energies evaluated are shown in Table 3. In the present case, the E_{DR} value obtained 15.1 $\mathrm{kj\,mol^{-1}}$ for lanthanum, which indicates ion exchange mechanism. The mean free energy of adsorption was found as 17.1 $\mathrm{kJ\,mol^{-1}}$ for cerium. The mechanism is explained by particle diffusion.

The corresponding Freundlich, Langmuir, and D-R parameters with correlation coefficients are reported in Table 3. The results show that, lanthanum and cerium adsorption can be explained by Langmuir isotherm model (correlation coefficients are 0.98 and 0.99, respectively). Monolayer capacity was found as 22.94 $\mathrm{mg\,g^{-1}}$ for lanthanum and 17.24 $\mathrm{mg\,g^{-1}}$ for cerium. Kazy et al. (21) studied lanthanum biosorption by a *Pseudomonas sp*. and reported the Langmuir parameter b is 0.0027 $\mathrm{L\,mg^{-1}}$ and n_m is 1,923 $\mathrm{mg\ g^{-1}}$ with a correlation coefficient of 0.94. Cerium biosorption on *P. orientalis* leaves was reported by Sert et al. (15). In this study the monolayer capacity was found 32.05 $\mathrm{mg\,g^{-1}}$ (correlation coefficient is 0.99).

Desorption/recovery of sorbed metal is one of the most important aspects of any successful biosorption-process development (21). In this study, HNO_3 was used as a reagent for desorption. Desorption studies were conducted immediately after the adsorption of respective La and Ce(III) by leaf powder of *P. brutia*. The loaded biosorbent was drained to remove all La and Ce(III) solution and subsequently resuspended in 25 mL of nitric acid (0.5 $\mathrm{mol\,L^{-1}}$)

TABLE 3
Adsorption isotherm constants for the biosorption of lanthanum and cerium on leaf powder of *P. brutia*

	Freundlich			Langmuir			Dubinin-Radushkevich			
	R^2	n	K	R^2	n_m (mg/g)	b (L/mg)	R^2	K ($\mathrm{mol^2kj^{-2}}$)	X_m (mol/g)	E_{DR} (kj/mol)
Lanthanum	0.9529	4.00	5.79	0.9812	22.94	0.068	0.9589	2.3×10^{-3}	3.03×10^{-4}	15.1
Cerium	0.9308	5.07	6.52	0.9976	17.241	0.278	0.9603	1.7×10^{-3}	2.08×10^{-4}	17.1

at 30°C for 1 h. The desorption percentages of La and Ce(III) are 96% and 78%, respectively. Kazy et al. (21) investigated the desorption process by different reagents. They found 90% La desorption capacity by using 1 M HNO_3.

CONCLUSIONS

In the present study the potential of using leaf powder of *P. brutia* for the removal of lanthanum and cerium was demonstrated. The leaf powder exhibited high biosorption capacity for both metals. The initial pH of the aqueous phase strongly affected the uptake of the ions, with the highest capacity achieved at pH 5.0. Kinetic studies indicated that adsorption behaviors of cations obey pseudo second order rate law. The Langmuir, Freundlich, and D-R adsorption models were used for mathematical description of the biosorption of the La and Ce(III) ions onto leaf powder of *P. brutia*. Cation sorption data were interpreted in terms of Langmuir equation which assumes monolayer adsorption. Consequently, monolayer capacity was found as $22.94\,\mathrm{mg\,g^{-1}}$ for lanthanum and $17.24\,\mathrm{mg\,g^{-1}}$ for cerium. Thermodynamic parameters $\Delta H°$, $\Delta S°$, and $\Delta G°$ were estimated and these parameters show that adsorption is more favorable at high temperature and the process is spontaneous. As the results suggest, biosorption onto leaf powder of *Pinus brutia* showed an alternative and low-cost method for lanthanum and cerium recovery from solutions.

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