

Biosorption of neodymium(III) and cerium(III) ions by Loquat leaves (*Eriobotrya japonica*) kinetics and thermodynamic studies

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ABSTRACT

Loquat leaves as biosorbent have been proven for removal of neodymium(III) and cerium(III) ions from aqueous solution through batch contact technique as a function of biosorbent dosage, temperature, initial metal concentration and contact time. Loquat leaves properties were determined by elemental analysis, Fourier-transform infrared spectroscopy and thermogravimetric analysis. The percent uptakes of neodymium(III) and cerium(III) ions by Loquat leaves were 50% and 70% respectively at 25°C. The pseudo-second-order equation most accurately describes the sorption process. While thermodynamic studies showed that the biosorption process is spontaneous and endothermic. Langmuir model fits the sorption isotherm with maximum capacities of 42 and 54 mg/g for neodymium(III) and cerium(III) ions respectively. Desorption studies using 0.1 M HNO₃ indicate that the highest percent recovery was achieved for neodymium(III) (~70%) than for cerium(III) ions (~60%).

Keywords: Biosorption; Loquat leaves; Neodymium(III); Cerium(III); Kinetics; Thermodynamics

1. Introduction

Neodymium and cerium are rare earth (RE) elements extracted from monazite and bastnasite with an average abundance of 41 and 66 µg/g respectively in the earth's crust [1]. Neodymium is found in permanent magnets, lasers, and glass additives [2]. Whereas cerium is found in color televisions, fluorescent lamps, microwave devices, lasers and nickel and chromium alloy [3]. Therefore, the demand for (RE) oxides increased from 75,500 tons in 2000 to 123,100 tons in 2016 [4].

The increase in applications of neodymium and cerium lead to their release into the environment mainly to rivers and coastal areas due to the disposal of e-waste and mining activities. Sneller et al. [5] reported that the maximum permissible concentration for rare earth elements (REEs) [5] for Ce(III) is 22.1 µg/L and for Nd(III) is 1.8 µg/L in fresh surface water. Rim et al. [6] reviewed the toxicological results

of rare earth compounds on the health of workers. So, separation and purification of (RE) elements are necessary for economic, environmental and pollution control.

Several techniques were applied to retake (RE) elements from aqueous solution, such as chemical precipitation [7], ion exchange [8], and adsorption [9]. Biosorption is considered as a promising green technology [10] because it covers adsorption, ion exchange and micro precipitation onto functional groups and surface of biological origin [11].

Sorption of metals on the surface of the biosorbent generally occurs through complicated mechanisms which include one or more of the processes such as ion-exchange, chelation, complexation, electrostatic interaction, physical adsorption and micro-precipitation (Fig. 1) [12].

Loquat leaves (LL) have several medical purposes such as anti-inflammatory, antioxidant, anti-mutagenic and anti-tumor activities because they possess phenolic, terpenoid, triterpenses and megastigmane glycosides [13].

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Several review articles summarize researches about biosorption of (RE) elements by different biological materials [14,15]. Different biosorbents (ginkgo, osmanthus, banyan, magnolia, holly leaves, walnut shell, and grapefruit peel) have previously removed (RE) elements from aqueous solution and showed good capacities [16]. The *Pinus brutia* leaves and the modified form with citric acid were used for removal of the trivalent ions of lanthanum and cerium from aqueous solution [17]. The Langmuir model fits well with a monolayer capacity (q_m) of 17.24 mg/g using unmodified leaf powder, while the capacity increase to 62.1 mg/g for the modified form. Loquat leaves were used for cadmium(II) recovery from diluted solution with a 98% removal [18] and the modified Loquat leaves with sodium hydroxide were used for removal of copper(II) and lead(II) ions [19]. Also, they were used to remove malachite green (MG) dye [20].

Loquat tree, which is found a lot all over Jordan, is a green one all year long and sheds large amount of leaves as agricultural waste. The low cost, reusability, availability and stability of those leaves are important to control

process efficiency. This encourages us to test the efficiency of Loquat leaves in removing Nd(III) and Ce(III) ions from aqueous solution under changing biosorbent dosage, temperature, initial metal concentration and time. Therefore, for the first time Loquat leaves are significant and have a remarkable potential for the removal of Nd(III) and Ce(III) ions from aqueous solution. Table 1 indicates the biosorption capacities of Loquat leaves for neodymium and cerium are higher than most of those reported.

2. Materials and methods

2.1. Chemicals

All reagents were analytical grade. Hydrochloric acid (HCl) 37%, nitric acid (HNO₃) 69% and glacial acetic acid from Tedia (United States), sodium hydroxide pellets (NaOH) from SDS vorte partenaire chimie (Peypin, France), neodymium(III) chloride hexahydrate from Aldrich (United States), cerium(III) nitrate hexahydrate

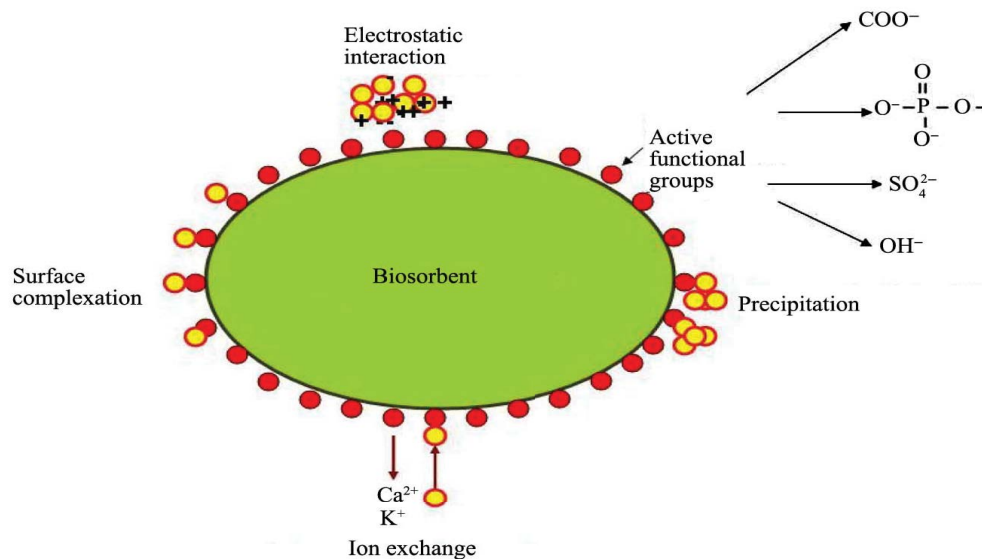


Fig. 1. Various mechanisms of biosorption of REEs.

Table 1
Comparison between various adsorbents for removal of neodymium and cerium from aqueous solution

Adsorbent	Neodymium q_m (mg/g)	Cerium q_m (mg/g)	References
<i>Pinus brutia</i> leaf powder	–	17.24	[17]
<i>Platanus orientalis</i> leaf powder	–	32.05	[21]
Nano modified activated carbon	–	15.04	[22]
Chitosan benzoyl thiourea derivatives	20.86	–	[23]
EDTA- β -cyclodextrin	–	50.16	[24]
Silica-based urea–formaldehyde (SiO ₂ /UF) composite	4.95	–	[25]
Bone powder	10.75	–	[26]
Alfalfa biomass	34.25	–	[27]
Sodium alginate-coated magnetite (Alg-Fe ₃ O ₄) nanoparticles	–	31.83	[28]
Loquat leaves	42.00	54.00	Present work

from Fluka AG (Switzerland). Arsenazo(III) indicator from Janseen chimica (Gardena, California).

2.2. Preparation of biosorbent

Loquat leaves were collected from a farm in north of Amman, Jordan. They were washed with double distilled water to remove soluble and insoluble impurities. Afterward, they were air-dried and then oven-dried at 70°C for 48 h to remove moisture. Then, leaves were grounded using a grinding mill and sieved to 150 μm particle size and kept in a desiccator. Loquat leaves were characterized by elemental analysis, Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Also, treatment of LL by dilute acid and base show stability with no effect.

2.3. Biosorption experimental procedures

Kinetic study was done by shaking 10 mg of LL with 25.0 mL of 30 ppm of Nd(III) and Ce(III) solution at pH 4.0 in a plastic bottle at time intervals of 15–1,440 min. The mixture was filtered and the amount of Nd(III) and Ce(III) ions remaining in the filtrate solution was determined by vis-spectrophotometer using Arsenazo(III) indicator at $\lambda_{\text{max}} = 653.0$ nm within 1 h of the sample preparation [29,30].

In spectrophotometric method the neodymium(III) and cerium(III) ions react with Arsenazo(III) at pH 4.0 to form a colored chelate absorbing at λ_{max} of 653 nm. Beer's law is obeyed over the range of 10–40 ppm, with a molar absorptivity of (4.99×10^4) L mol⁻¹ cm⁻¹ and the correlation coefficients (R^2) are 0.9912 and 0.9904 for Nd(III) and Ce(III) ions respectively. Sandell's sensitivity index is 0.02 $\mu\text{g}/\text{mL}$ with a relative error of 0.0%–0.2% and a relative standard deviation of 0.0%–2.1% [31].

The sorption isotherms of Nd(III) and Ce(III) ions onto Loquat leaves were carried out by shaking 10 mg of LL

with 25.0 mL of metal ion solution of different concentrations ranging from 10–40 ppm at pH 4.0 for 24 h and temperatures (25°C, 35°C and 45°C).

Desorption was done by contacting 0.2 g of LL with 10.0 mL of 30 ppm of Nd(III) and Ce(III) in 20.0 mL centrifuge tube and mixed for 24 h. Then centrifuged, decanted and washed with deionized water. Desorption was carried using 0.1 M nitric acid. Vis-spectrophotometer was used to measure the amount of Nd(III) and Ce(III) ions in the collected elutes.

3. Results and discussion

3.1. Characterization of Loquat leaves

3.1.1. Elemental analysis

Elemental analysis shows 45.81% carbon, 6.19% hydrogen and 1.40% nitrogen and the rest (about 46.6%) is mainly oxygen, which agrees with the analysis of some medicinal plants, such as: Neem, Kalmeg and Tulsi [32], because they contain different phenolic compounds and triterpenoid acids [33].

3.1.2. Fourier-transform infrared spectroscopy

Loquat leaves were analyzed by FTIR spectroscopy for the qualitative analysis of major functional groups present. Fig. 2 illustrates the FTIR spectra over the range 400–4,000 cm⁻¹ and specific bands are found in Table 2 [34,35]. Fig. 2 shows major peaks, such as: broad peak at 3,421 cm⁻¹ refer to the stretching of the NH and -OH group, C-H stretching vibrations of -CH₃ and -CH₂ functional groups at 2,924 cm⁻¹ and C=O group of carboxylic acids at 1,726 cm⁻¹. However, the peak at 1,066 cm⁻¹ is referring to the C-O stretching bond and the peak at 887 cm⁻¹ is caused by C-N bonding in amines. The abundance of hydroxyl, amine and carboxyl groups are responsible for

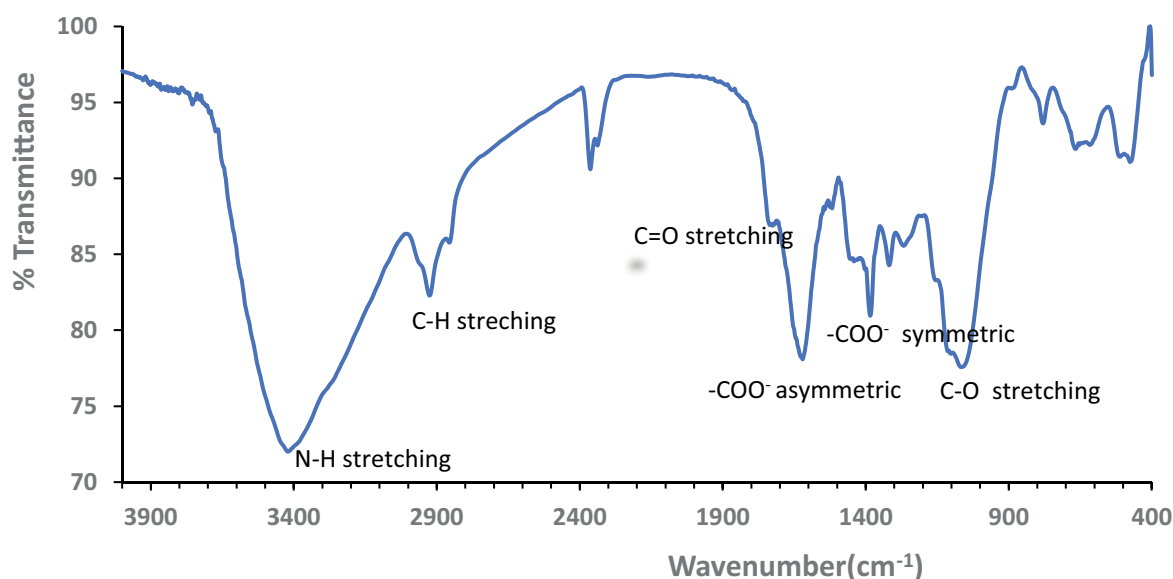


Fig. 2. FTIR spectra for Loquat leaves.

bonding Nd(III) and Ce(III) ions with LL through electrostatic or chelation attractions [36].

3.1.3. Thermogravimetric analysis

Fig. 3 shows three main regions during the thermal decomposition of LL. The first region of weight loss at ($T < 150^{\circ}\text{C}$) was 4.58%, and mainly corresponds to evaporation of water, and some small volatile organic molecules like oils, dyes, etc. The second region corresponds to the decomposition of LL biomass at a temperature between 150°C and 500°C with 59.43% weight loss, and the third decomposition step corresponds to the oxidation of the charred residue at $T > 500^{\circ}\text{C}$ with 12.3% weight loss, so Loquat leaves show excellent thermal stability up to 150°C . This is similar to what has been found for agricultural biomass from olive trees [37] and Laurel shrub leaves [38].

3.2. Batch biosorption of Nd(III) and Ce(III) ions

3.2.1. Biosorbent dosage

The percentage uptake of Nd(III) and Ce(III) ions increased with mass (Fig. 4), due to the availability of

more binding sites for Nd(III) and Ce(III) ions. The highest capacity (q_e) found was 42 for Nd(III) and 54 mg/g for Ce(III) ions for 10 mg LL, which was used in all the experiments [39]. The percentage uptake was constant for a mass of more than 0.15 g because all the active sites on the surface have been saturated with Nd(III) and Ce(III) ions.

The biosorption process was done at pH 4 since it is the optimum pH for the adsorption of Nd(III) and Ce(III) ions and to avoid their hydrolysis. Similar results was found by Rusnadi et al. [40] using modified alginate beads, modified sodium alginate with magnetite nanoparticles [28] and magnetite nanoparticles [41].

3.2.2. Temperature

The percentage uptake of Nd(III) and Ce(III) ions by LL increased with temperature (25°C , 35°C , and 45°C) as shown in Fig. 5, which indicates that the biosorption mechanism is energy dependent and endothermic [42]. This agrees with the biosorption of lanthanum and cerium ions by *Pinus brutia* leaf powder [17].

3.2.3. Initial concentration of Nd(III) and Ce(III) ions

Fig. 6 shows the effect of initial metal concentration with the percentage uptake of Nd(III) and Ce(III) ions by LL. The biosorption was carried out at different initial metal ion concentrations ranging from 10 to 40 mg/L at pH 4. The data show that the percentage uptake of metal ions decreases as initial metal concentration increases due to saturation of adsorption sites at low initial concentration [17]. A similar result was reported for the effect of initial neodymium ion concentration by *Chlorella vulgaris* [43].

Table 2

Characteristic FTIR peaks for LL

Assignment	Loquat leaves peak (cm^{-1})
N–H stretching	3,421
C–H stretching	2,924
C=O stretching	1,726
–COO [−] asymmetric	1,620
–COO [−] symmetric	1,384
C–O stretching	1,066
C–N stretching	887

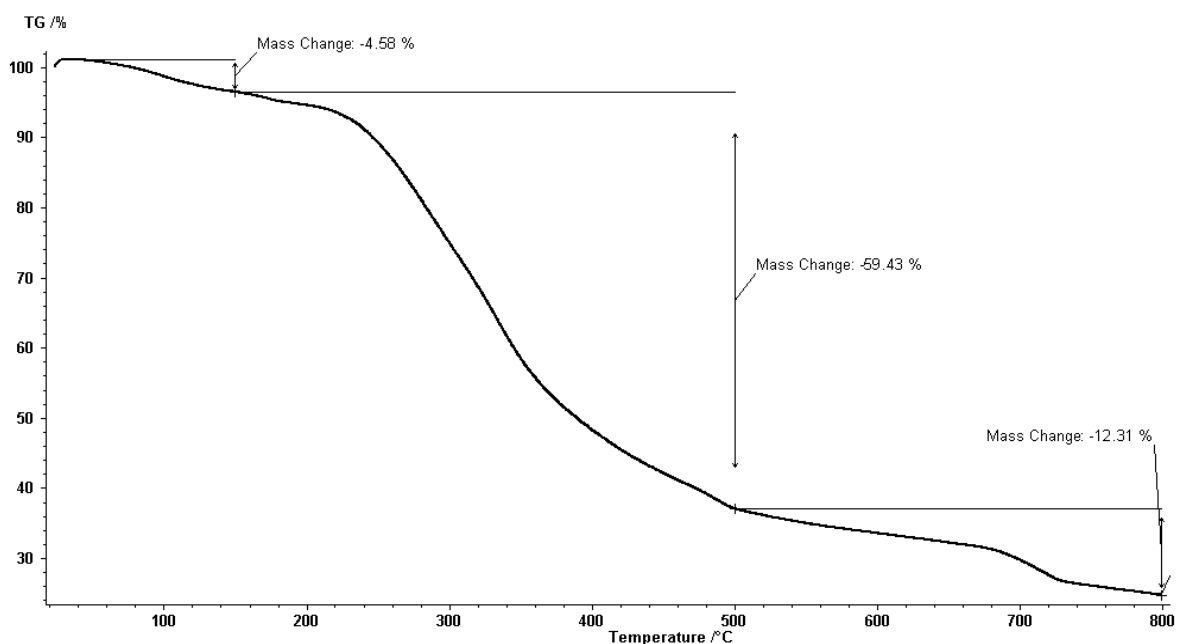


Fig. 3. TGA for Loquat leaves.

3.2.4. Kinetic study

The percentage uptake of Nd(III) and Ce(III) ions and the sorption capacity (q_e) have been calculated using the following equations:

$$\% \text{uptake} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 is the initial metal ions concentration (mg/L), C_e the remaining metal ions concentration in solution at equilibrium, V the volume of Nd(III) and Ce(III) solution (L) and m the mass of LL (g).

Kinetic investigations for biosorption of Nd(III) and Ce(III) ions by LL were tested using the following models:

- Pseudo-first-order

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

- Pseudo-second-order

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

where q_e and q_t (mg/g) are the amount of metal ions adsorbed at equilibrium and at time t (min) respectively. k_1 (min^{-1}) is the rate constant for the pseudo-first-order and k_2 is the rate constant for the pseudo-second-order (g/mg min) adsorption process [44].

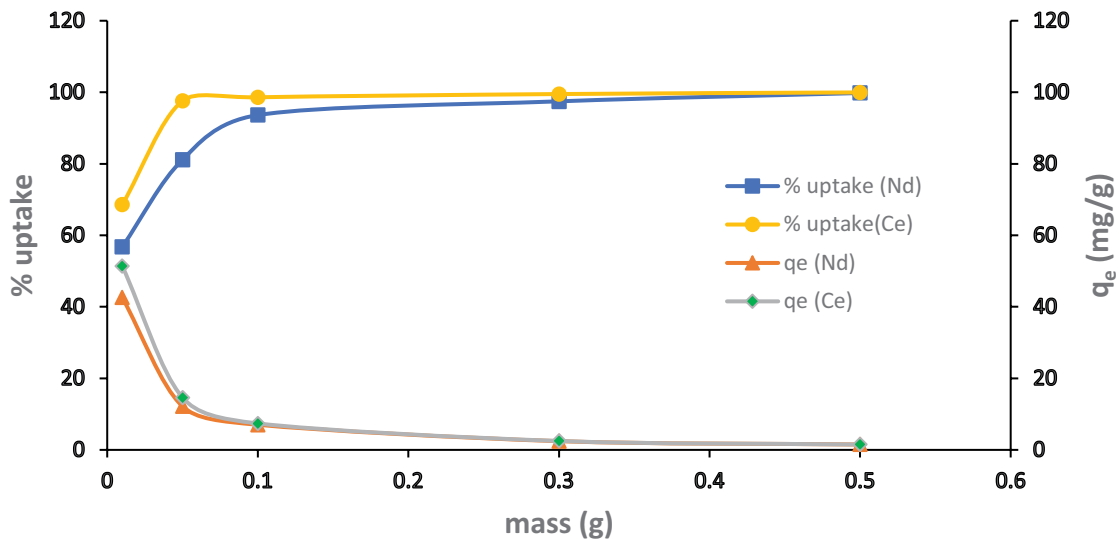


Fig. 4. Loquat leaves dosage effect on the biosorption capacity (q_e) and % uptake of Nd(III) and Ce(III) ions (initial concentration: 30 ppm; pH 4; 25.0°C).

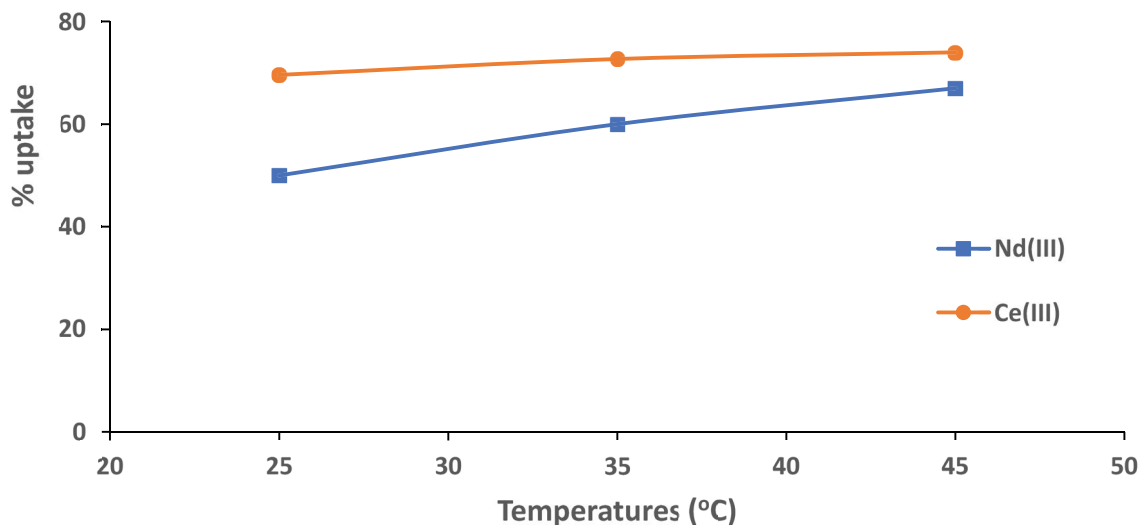


Fig. 5. Percentage uptake of metal ions by Loquat leaves at different temperatures (initial concentration: 30 ppm; 10 mg LL; pH 4).

Fig. 7 shows that the percent uptake of Nd(III) and Ce(III) ions by Loquat leaves increased with increasing contact time and reach equilibrium after 60 min and did not significantly increase after that. This was because the LL surface had been covered up with Nd(III) and Ce(III) ions so the adsorbent could not adsorb more. The percentage uptake of Ce(III) ion by LL is higher than that for Nd(III) ions as shown in Fig. 7 at 25°C. Similar results (Table 1) was found for biosorption of lanthanum and cerium by *Platanus orientalis* leaf powder [21] but Loquat leaves give higher capacity.

Therefore, the following experiments were carried out at pH 4.0 and 60 min.

The sorption process of Nd(III) and Ce(III) ions by Loquat leaves (LL) followed pseudo-second-order kinetic model ($R^2 > 0.99$) (Table 3 and Fig. 8) since q_e (mg/g) calculated is equal to q_e (mg/g) experimental and that chemisorption process is the rate-controlling step [45]. Similar results

were found for biosorption of neodymium onto *Chlorella vulgaris* [43] and for cerium ions by *Spirulina* biomass [46].

3.3. Biosorption isotherm

Langmuir [47], Freundlich [48] and Dubinin–Radushkevich [49] isotherm models were used to test the sorption of Nd(III) and Ce(III) by LL:

- Langmuir equation (Form I)

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (5)$$

- Freundlich equation

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

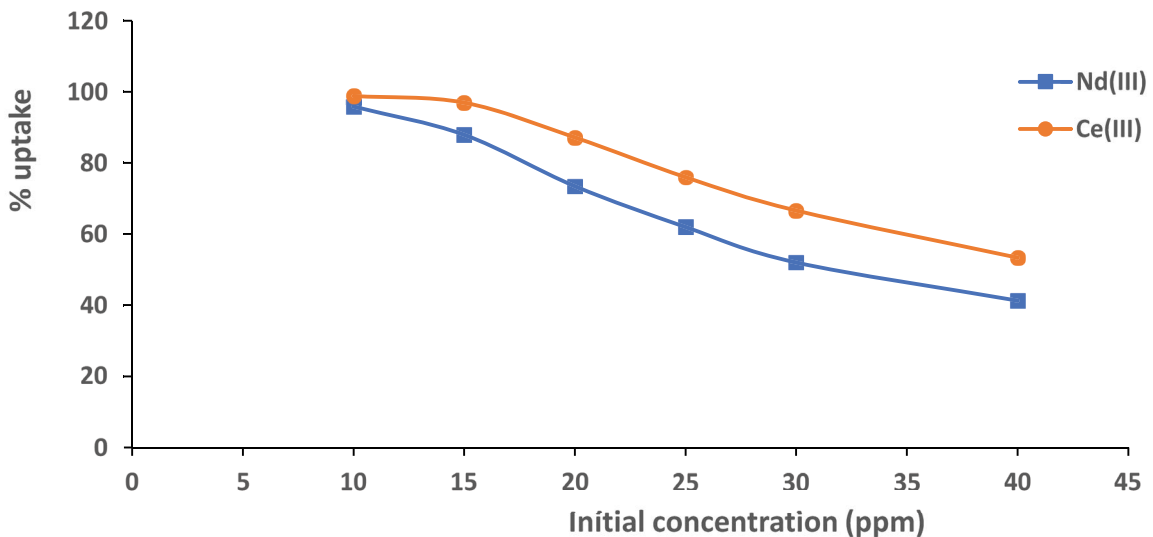


Fig. 6. Initial concentration effect on the percentage uptake of metal ions (10 mg LL; pH 4; 25°C).

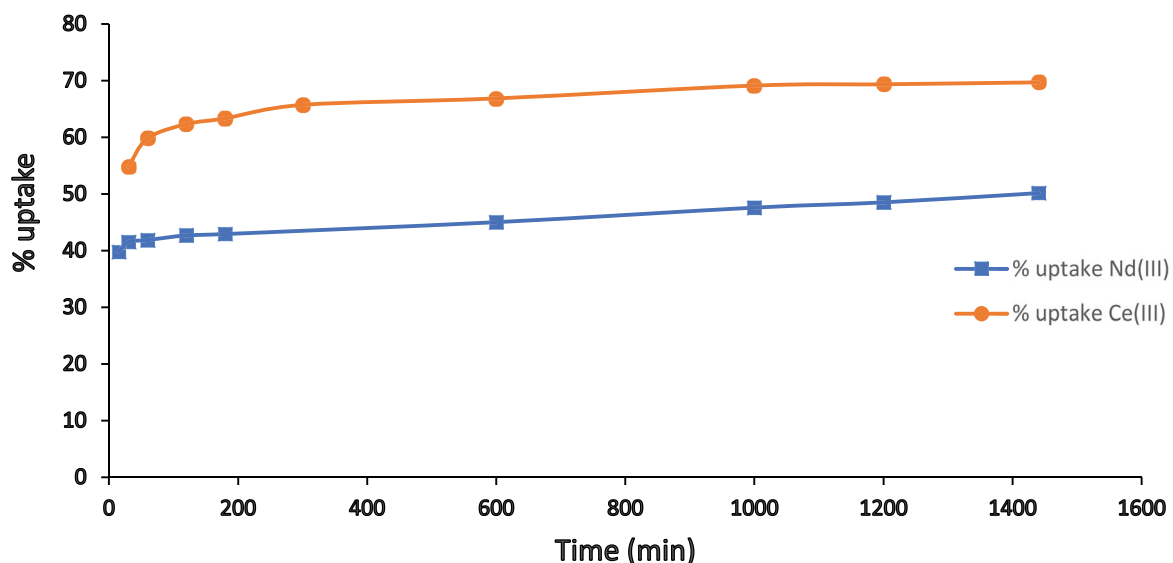


Fig. 7. Percentage uptake of metal ions with time (initial concentration: 30 ppm; 10 mg LL; pH 4; 25°C).

- Dubinin–Radushkevich equations

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \tag{7}$$

- Polanyi potential ε , equals to:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \tag{8}$$

The fundamental feature of this isotherm is the separation factor or equilibrium parameter (R_L), which is defined as follows:

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

where C_0 is the highest initial concentration (mg/L).

The R_L value indicates the nature of the isotherm as follows: the isotherm is irreversible if $R_L = 0$, favorable if $0 < R_L \leq 1$ and unfavorable if $R_L > 1$.

The initial concentration of metal ion can overcome the mass transfer resistance between the metal ion and leaves surface which led to biosorption capacity (q_e) increase with increasing Nd(III) and Ce(III) ions concentration until reaching equilibrium state (Fig. 9).

Table 3
Kinetic parameters

Pseudo-second-order model parameters	Nd(III)	Ce(III)
k_2 (g/mg min)	0.0014	0.0012
q_e (mg/g) calculated	37.17	52.63
q_e (mg/g) experimental	37.60	52.26
R^2	0.9984	0.9998

The biosorption of Nd(III) and Ce(III) ions by LL show high correlation coefficients ($R^2 > 0.99$) for the Langmuir isotherm model (Table 4). This suggests monolayer sorption existed in the sorption process of Nd(III) and Ce(III) ions with homogenous sites of the LL surface [18].

The Langmuir equilibrium constant (K_L) values (Table 4) for Ce(III) ions were higher than Nd(III) ions, indicating that the binding energy of Ce(III) is higher than Nd(III) ions and this agrees with temperature affect results (section 3.2.2).

The R_L values [Eq. (9)] were greater than 0 but less than 1, and the values of n were larger than one (Table 4), indicating that biosorption of Nd(III) and Ce(III) ions by LL was favorable. The Freundlich constant K_f values (Table 4) for the biosorption of Nd(III) and Ce(III) ions increased with increasing temperature, which indicates an endothermic sorption process [50].

Since the Langmuir equilibrium constant (K_L) and n values in this work (Table 4) are higher than that found in Kucuker et al. [43] ($K_L = 0.029$) for *Chlorella vulgaris*, this means that the binding of neodymium ions by Loquat leaves is stronger than *Chlorella vulgaris*.

As illustrated in Table 4, the free energy of biosorption values (E) calculated from Dubinin–Radushkevich model increased with temperature and reach higher than 8.00 kJ/mol only for Ce(III) ions at 45°C, which insure that physical forces may affect the biosorption mechanism under lower temperature and the mechanism become ion exchange at high temperature [51]. This result agrees with biosorption of cerium by Tangerine (*Citrus reticulata*) peel, where the mean free energy of adsorption was 10.54 kJ/mol and the mechanism is explained by chemical ion-exchange [35].

The maximum uptake capacities (q_m) of LL for neodymium and cerium ions are found to be 41.66 and 53.76 mg/g, respectively (Table 4). The higher adsorption capacity for cerium ion than neodymium ion is due to a smaller hydration shell for cerium ion because of its larger ionic radius [52].

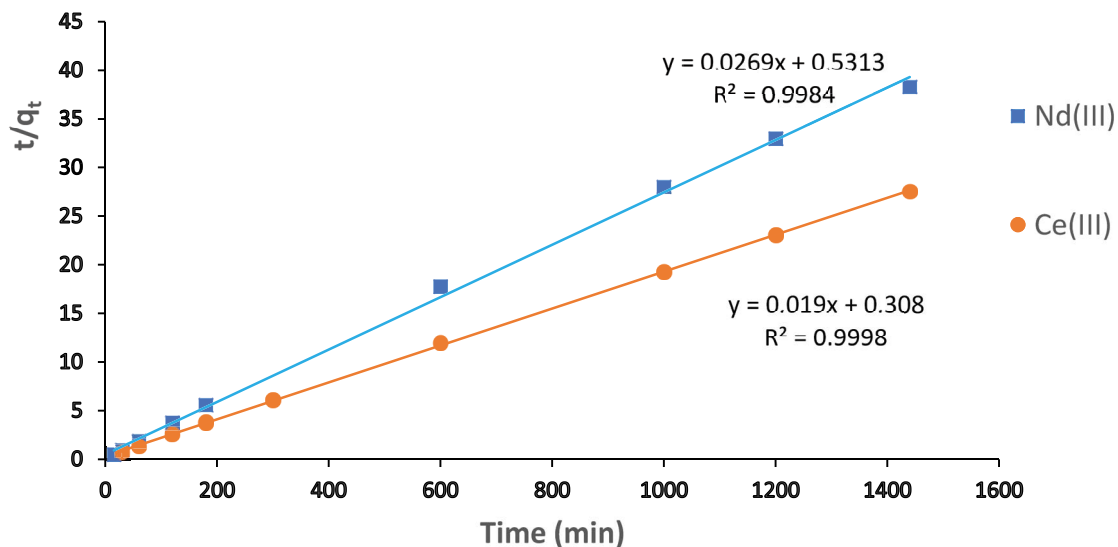


Fig. 8. Pseudo-second-order plots.

3.4. Thermodynamics studies

In order to understand the adsorption process, Gibbs free energy (ΔG°) is calculated according to Eq. (10).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

The K_d (distribution coefficient) was measured from the intercept of $\ln(q_e/C_e)$ vs. q_e (Fig. 10). Change in enthalpy (ΔH°) and entropy (ΔS°), were estimated using Eq. (11).

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

ΔH° and ΔS° were calculated from the slope and intercept, respectively, of a plot of $\ln K_d$ vs. $1/T$, as shown in Fig 11. ΔH° , ΔS° , and ΔG° values are shown in Table 5.

Table 5 shows a negative value of ΔG° , which indicates that biosorption of Nd(III) and Ce(III) ions is energetically favorable and spontaneous. The positive values of ΔH° (Table 5) support the endothermic adsorption onto LL [53].

In addition, the values of ΔS° (Table 5) were found to be positive due to the exchange of the Nd(III) and Ce(III) ions with more water molecule present on the surface of leaves and the dehydration of the adsorbed hydrated metal ions, which would cause an increase in the entropy during the biosorption process [54]. Comparable results ($\Delta G^\circ = -19.476$, $\Delta H^\circ = 14.988$ kJ/mol and $\Delta S^\circ = 0.114$ kJ/mol K at 30°C) were found for biosorption of Ce(III) ions by *Platanus orientalis* leaf powder [21]. The highest adsorption capacity (q_e) for removing Nd(III) and Ce(III) ions by LL compared with other adsorbents (Table 1), make it a promising cheap material for removing Nd(III) and Ce(III) ions.

3.5. Desorption studies

Desorption processes are important to recover metal ions and regeneration of sorbent.

Nitric acid (0.1 M) was used to recover Nd(III) and Ce(III) ions from loaded leaves. According to desorption data (Table 6 and Fig. 12), 70.0% of the adsorbed Nd(III) by LL was released whereas 60.9% of the adsorbed Ce(III) was released using HNO_3 solution. This result indicates the

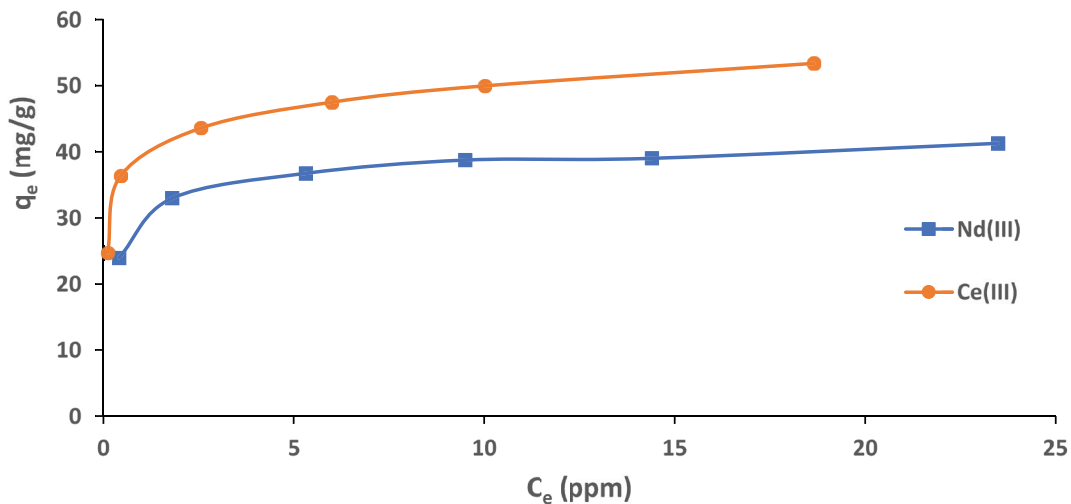


Fig. 9. Adsorption isotherms of metal ions (10 mg LL; pH 4.0; 25°C).

Table 4
Isotherm parameters for biosorption of Nd(III) and Ce(III) ions at different temperatures

T (°C)	Langmuir isotherm			Freundlich isotherm			Dubinin–Radushkevich				
	R^2	q_m (mg/g)	K_L (L/mg)	R_L	R^2	n (L/mg)	K_F (mg/g)	R^2	β (mol ² /kJ ²)	q_m (mg/g)	E (kJ/mol)
Nd(III)											
25	0.9989	41.66	1.72	0.019	0.9381	7.74	28.5	0.9229	0.0517	38.3	3.10
35	0.9983	50.50	2.38	0.014	0.9505	7.92	35.6	0.9113	0.0164	45.9	5.52
45	0.9940	57.80	3.20	0.010	0.9435	8.10	42.2	0.9208	0.0087	51.4	7.58
Ce(III)											
25	0.9981	53.76	2.27	0.014	0.9458	7.05	36.6	0.9264	0.0227	47.90	4.70
35	0.9971	56.18	2.83	0.011	0.9133	8.32	40.5	0.9481	0.011	50.63	6.70
45	0.9974	58.14	3.74	0.009	0.9406	9.26	43.9	0.9504	0.006	52.10	8.90

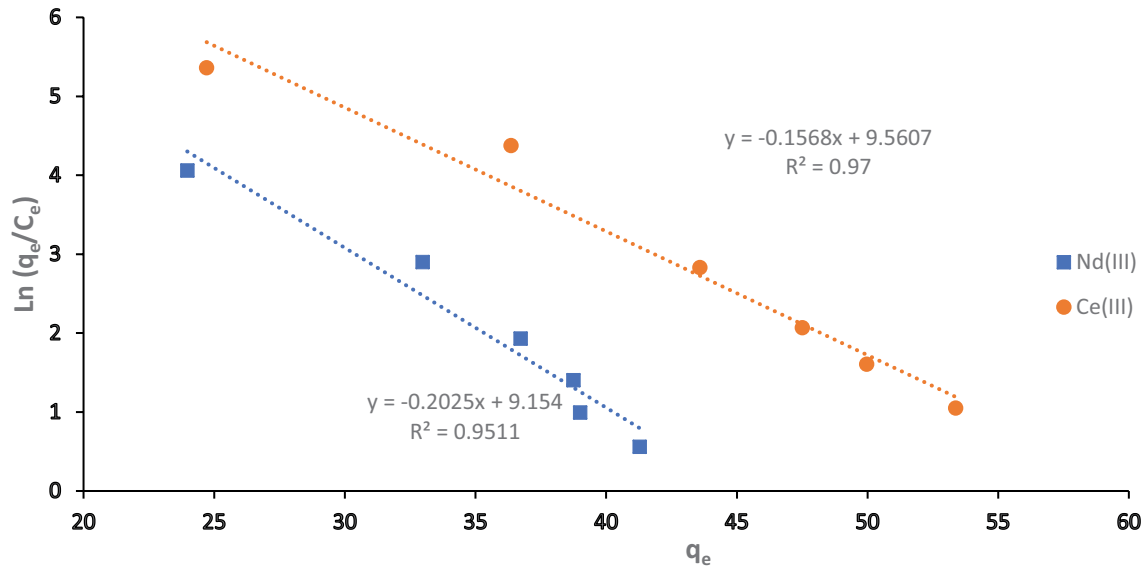


Fig. 10. $\ln(q_e/C_e)$ vs. q_e at 25°C.

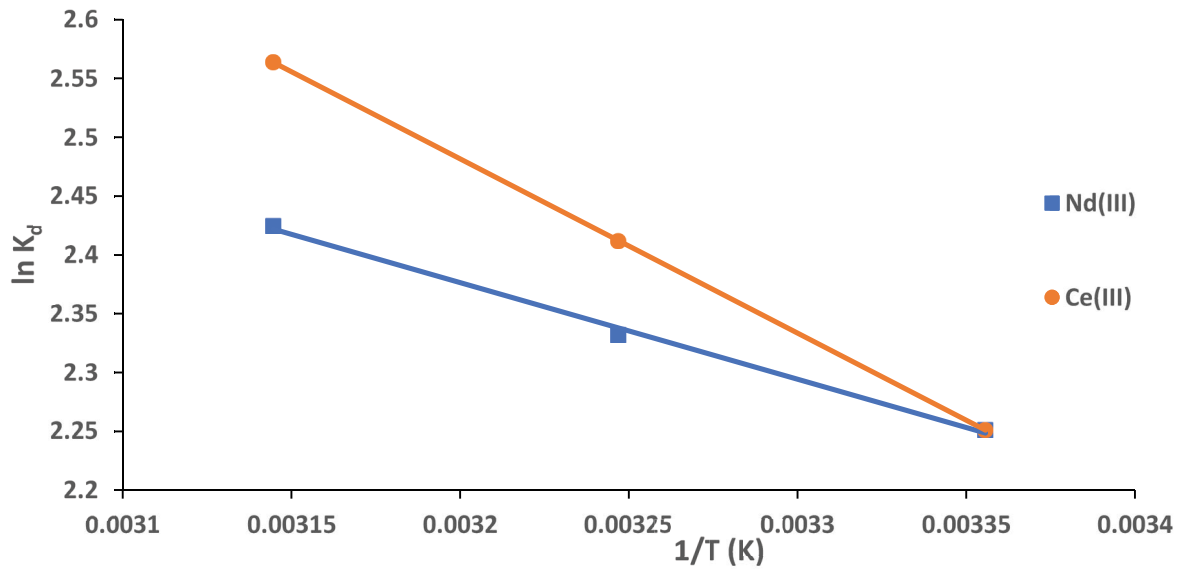


Fig. 11. $\ln K_d$ vs. $1/T$.

Table 5
Thermodynamic functions at 25°C

Metal ion	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)
Nd(III)	-5.57	6.83	0.041
Ce(III)	-5.56	12.32	0.060

stronger interaction between Ce(III) ions and Loquat leaves surface which agrees with the high adsorption capacity and K_L values found for Ce(III) than Nd(III) ions and cation exchange mechanism [21].

Table 6
% Cumulative recovery of Nd(III) than Ce(III) ions from loaded LL

	Nd(III)	Ce(III)
Recovery stage	% Desorption	
1st 10.0 mL	56.0%	50.3%
2nd 10.0 mL	12.5%	10.0%
3rd 10.0 mL	1.5%	0.6%
4th 10.0 mL	–	–
% Cumulative recovery	70.0%	60.9%

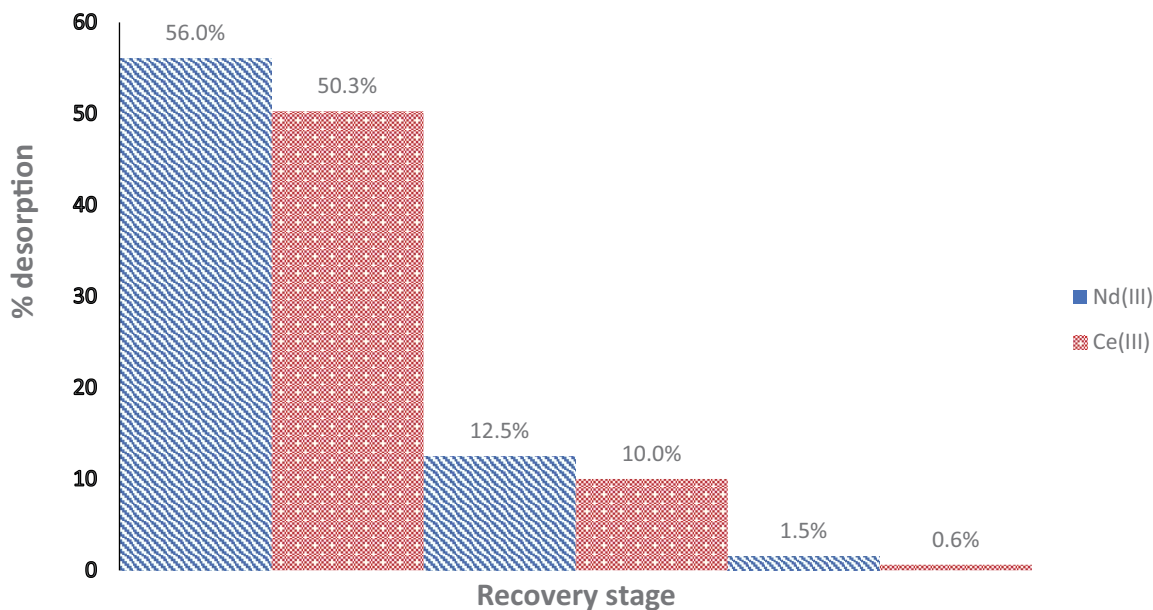


Fig. 12. % Desorption of Nd(III) and Ce(III) form Loquat leaves.

4. Conclusions

Loquat leaves are considered as effective adsorbents for removal of Nd(III) and Ce(III) ions from aqueous solution. Pseudo-second-order represent the kinetic adsorption for Nd(III) and Ce(III) ions after 60 min of reaching equilibrium at pH 4.0. The isotherm data fitted Langmuir model with monolayer adsorption capacity (q_m) for Nd(III) and Ce(III) to be 42 and 54 mg/g, respectively at 25°C. Thermodynamic results ensure spontaneous adsorption of Nd(III) and Ce(III) ions with positive enthalpy and entropy. The highest percent recovery from (LL) (70.0%) obtained using 0.1 M HNO₃ for Nd(III) than Ce(III) ions. Loquat leaves can be used as alternative biosorbent for removing Nd(III) and Ce(III) ions because of the advantages of being natural, highly available, low-cost, rapid biosorption rate, biodegradable and relatively high uptake capacity.

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