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BIOSORPTION OF LANTHANUM AND CERIUM FROM AQUEOUS SOLUTIONS USING TANGERINE (*Citrus reticulata*) PEEL: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

Biosorption of lanthanum (III) and cerium (III) from aqueous solution by tangerine (Citrus reticulate) peel has been investigated in a batch system as a function of pH, biosorbent dosage, contact time, and temperature. The equilibrium pH was found to severely affect the biosorption performance; pH 5.0 was found to be an optimum pH for favorable biosorption of La (III) and Ce (III). The biosorption of lanthanum and cerium was investigated by the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models. Maximum biosorption uptakes, according to the Langmuir model, were obtained as 154.86 and 162.79 (mg/g) for La(III) and Ce(III), respectively. The biosorption kinetic was tested with pseudo-first order and pseudo-second order models. The results showed that the kinetics of the biosorption process were described by the pseudo-second order model very well. Thermodynamic parameters including the change of Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) for both sorption systems were determined at four different temperatures. The results showed that the biosorption of La(III) and Ce(III) on tangerine (C. reticulate) peel is a spontaneous and endothermic process. FTIR analysis demonstrated that carboxyl and hydroxyl groups were involved in the biosorption of the metal ions.

Keywords: biosorption; lanthanum; cerium; Isotherm; kinetic, tangerine (Citrus reticulate) peel.

Rare earth elements (REEs) have gained considerable attention due to their unique properties and a guide range of applications [1]. They are widely used in the field of nuclear energy, metallurgy, medicine, chemical engineering, electronics, and computer. From the rare earth elements (REEs), lanthanum has attracted increasing interests due to its unique physical and chemical properties because of increasing demands for advanced new materials [2,3]. Lanthanum is currently used as a pure element or in association with other compounds in catalysts, super

alloys, and special ceramics and in organic synthesis [4]. Cerium, as the most abundant and one of the members of the group, has some well-established uses that are quite different from the others. However, high purity is usually required for the its utilization industry, where it is used, for example, for sulfur control in steels, ceramic, catalyst support, pyrophoric alloys, publishing powders, etc. Cerium is accompanied by other rare earth elements in its minerals, as well as in spent nuclear fuel [5]. The environmental behavior of REEs has attracted great interest in environmental impact assessment of disposed long-lived radioactive waste.

Different methods have been employed to eliminate lanthanides from aqueous solution, such as chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation, electrochemical treatment, and solvent extraction [6]. However, these

processes have some disadvantages, such as high consumption of reagent and energy, low selectivity, high operational cost, and difficult further treatment due to generation of toxic sludge [7]. Biosorption is a relatively new process that has been confirmed as a very promising process in the removal of heavy metal contaminates. The major advantages of biosorption are its high effectiveness in reducing the heavy metals and radionuclide's ions and the use of inexpensive biosorbents. The utilization of agro-wastes as adsorbents is currently receiving wide attention because of their abundant availability and low-cost owing to relatively high fixed carbon content and presence of porous structure [8,9]. One of the important agricultural wastes is peel of different fruits, which can serve as potential adsorbents for the removal of diverse types of pollutants especially metal ions. Different types of fruit peels have been investigated so far for wastewater treatment [10,11]. Adsorption of heavy metal ions on fruit peels has been extensively studied; however, the investigation on the adsorption of lanthanides on fruit peels is still scarce.

The tangerine fruit is cultivated on a large scale in the north of Iran and it has an agronomic importance because the fruits are widely used in nature or in a processed form as concentrated juice. The tangerine peel is one of the pectin-rich fruit wastes whose basic composition is lignin, hemicelluloses, cellulose, and principally pectin, containing hydroxyl and carboxyl functions, which are promptly available to interact with cations [12,13]. The study is further unique as there is no existing report for the removal of any lanthanide elements by tangerine peel.

In this study, the use of tangerine (*C. reticulate*) peel as a biosorbent has been tested for removing lanthanum and cerium ions from aqueous solution. The effects of solution pH, biosorbent dosage, contact time, and temperature have been investigated by batch method. The biosorption isotherms and kinetics have also been analyzed to reveal the adsorption mechanisms.

MATERIALS AND METHODS

Biosorbent preparation

Tangerine fruits were purchased from a local market. The white peel waste was removed from the yellow coating. The peels were then cut into small pieces and extensively washed with double distilled water to remove extraneous materials. The fruit peels were then dried at 75-80 °C in a convection oven until they reached a constant weight, which was accomplished after 24 h. The dried material was then ground and sieved to obtain a particle size lower than 355 μm.

Chemicals

Lanthanum and cerium stock solutions (1000 mg/L) were prepared separately from $La(NO_3)_3 \cdot 6H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (supplied by Merck) in double distilled water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. All reagents used were of analytical reagent grade.

Batch experiments

The adsorption of lanthanum and cerium on tangerine peel was studied using the batch procedure. All experiments were carried out in triplicate and the mean value was used in all cases. For each experimental run, 100 mL aqueous solution of known concentration of La(III) and Ce(III) was taken in polyethylene round-bottom flasks containing determined amount of the tangerine peel. These flasks were agitated at a constant rate of 200 rpm in a temperature controlled shaker (Memmert waterbath WNE 7-45, Germany). In order to evaluate the influence of pH parameter on the biosorption, the experiments were carried out at different pH values between 2.0 and 6.0 by using a Metrohm 691 pH meter. The pH was adjusted using 0.1 M HNO_3 or 0.1 M NaOH. For these experiments the initial La(III) and Ce(III) concentrations was used 20 mg/L and contact time 150 min. The effect of biosorbent dosage on La(III) and Ce(III) removal was investigated by using 20 mg/L initial concentration of lanthanum and cerium concentrations in conjunction with 0.5. 1, 1.5, 2, 2.5 and 3 g/L of tangerine peel. The samples were taken at 5, 10, 20, 30, 45, 60, 75, 90 and 120 min to determine optimal contact time. Equilibrium studies were conducted at optimum conditions with six different initial concentrations of 10, 20, 50, 75, 100 and 200 mg/L. The biosorption experiments were also carried out at 20, 30, 40 and 50 °C to determine the adsorption thermodynamic parameters. The supernatants were filtered through a filter paper and the filtrate was analyzed for La(III) and Ce(III) concentration by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES) (Varian Liberty 150AX Turbo, Australia). A spectrum of the natural biosorbent was recorded with a Bruker Vector 22 (Germany) model Fourier-transform infrared (FTIR) spectrophotometer.

The calculation of the biosorption uptake (q_e) is given by the mass balance equation:

$$q_e = \frac{V(c_0 - c_e)}{M} \tag{1}$$

where V (L) is the volume of metal solution in contact with the biosorbent; c_0 and c_e (both in mg/L) are the initial and equilibrium concentrations of the metal in

the solution, respectively; and M (g) is the mass of the biosorbent.

The percent biosorption of the metal ions was calculated as follows:

$$\text{Biosorption (\%)} = 100\left(\frac{c_0 - c_f}{c_0}\right) \qquad (2)$$

where c_f is the final metal ion concentration.

The distribution coefficient (K_D) of metal ions between the aqueous phase and the solid phase can be obtained using:

$$K_D = \frac{c_0 - c_e}{c_e} \times \frac{V}{m} \left(\frac{\text{mL}}{\text{g}}\right) \qquad (3)$$

where V/m is the ratio of the volume of metal solution (mL) to the amount of adsorbent (g) in a batch.

The average absolute value of relative error, $AARE$, is used to compare the predicted results with the experimental data. This is defined as follows:

$$AARE =$$

$$= \frac{1}{NDP} \sum_{i=1}^{NDP} \frac{\left|\text{Predicted value - Experimental value}\right|}{\text{Experimental value}}$$

in which NDP is the number of data points.

Theory

Equilibrium isotherm models

Equilibrium data, which are generally known as the adsorption isotherms, are the main requirements to understand the adsorption mechanism. Three common adsorption isotherm models, Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models, are used to evaluate the adsorption data obtained in this study. The Langmuir isotherm considers the adsorbent surface as homogenous with identical sites in terms of energy [14]. The Langmuir equation is given by:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \qquad (4)$$

where q_m (mg/g) and K_L (L/mg) are the Langmuir constants related to monolayer capacity and energy of adsorption, respectively.

The shape of the isotherm can be considered when predicting whether an adsorption system is favorable or unfavorable. The essential characteristic of a Langmuir isotherm can be expressed in terms of dimensionless separation factor or equilibrium parameter R_L, which is defined as:

$$R_L = \frac{1}{1 + K_L c_0} \qquad (5)$$

There are four probabilities for R_L value: for favorable adsorption, $0 < R_L < 1$, for unfavorable adsorption, $R_L > 1$, for linear adsorption, $R_L = 1$, and for irreversible adsorption, $R_L = 0$.

The Freundlich isotherm model is a semi-empirical equation based on the adsorption phenomenon occurred on heterogeneous surface [15]. The Freundlich equation is expressed by:

$$q_e = K_F c_e^{1/n} \qquad (6)$$

where K_F (mg^{1-n}L^n/g) represents the adsorption capacity when adsorbate equilibrium concentration equals to 1, and n represents the degree of adsorption dependence at equilibrium concentration.

Another equation that is used to determine the possible biosorption mechanism is the Dubinin-Radushkevich (D-R) equation, which assumes a constant sorption potential. The non-linear form of D-R isotherm equation [16] is:

$$q_e = q_{max} e^{-\beta \varepsilon^2} \qquad (7)$$

where q_{max} is the D-R monolayer capacity (mmol/g), β a constant related to adsorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as follows:

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

where R is the gas constant (8.314 J/mol K) and T is the temperature (K). The constant β gives the mean free energy, E, of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \qquad (9)$$

Kinetic parameters of adsorption

To study the kinetics of biosorption of La(III) and Ce(III) by tangerine (*C. reticulate*) peel, two of the main models proposed in the literature have been selected to adjust the experimental obtained results and to determine the kinetic parameters.

Pseudo-first order equation

The pseudo-first order equation is generally expressed as follows [17]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (10)$$

where q_e and q_t are the sorption capacity at equilibrium and at any time, t, respectively, in mg/g, and is the pseudo-first order rate constant, in min^{-1}.

After integrating and applying the boundary conditions, for q_t=0 at t=0 and q_t=q_t at t=t, the equation becomes:

$$q_t = q_e \left(1 - e^{-k_1 t}\right) \tag{11}$$

Pseudo-second order equation

Pseudo-first order kinetics model is expressed by the following equation [18]:

$$\frac{dq_t}{dt} = k_2 \left(q_e - q_t\right)^2 \tag{12}$$

where k_2 is the pseudo-second order rate constant, in g/mg·min.

Integrating this equation for the boundary conditions gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right) t \tag{13}$$

Thermodynamic parameters of adsorption

The relationship between the distribution coefficient, K_D, and temperature is given by the van't Hoff equation:

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

where ΔH° is the enthalpy change (kJ/mol), ΔS° is the entropy change (J/mol·K). The values of ΔH° and ΔS° are calculated from the slopes and intercepts of linear regression of $\ln K_D$ *vs*. $1/T$.

The Gibbs free energy change (ΔG°) values (kJ/mol) are calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{15}$$

RESULTS AND DISCUSSION

Effect of pH

The pH value of the aqueous solution has been identified as the most important variable governing the metal ions adsorption on the adsorbent. This is partly because hydrogen ions themselves strongly compete with metal ions for adsorption sites. Figure 1 demonstrates the effect of pH on the removal of La(III) and Ce(III) onto tangerine (*C. reticulate*) peel from aqueous solutions. The biosorption of La (III) and Ce(III) on the biosorbent is determined at different pH values ranging from 2 to 6. Lanthanum and cerium biosorption at pH higher than 6.0 is not considered because a precipitation occurred in the solu-

tion, indicates the hydrolysis of the metal ion with the formation of the corresponding insoluble hydroxide [4]. It can be seen from this figure that the adsorption capacity is low at strong acidic conditions. The previous works had demonstrated that the carboxyl groups present in the biomass have a very important role in the metal biosorption, being responsible for around 90% of metal immobilization in the process [19]. The sorption equilibrium is dependent on the pH because it affects the dissociation of carboxyl groups, since the pK_a of carboxylic groups ranges from 3.8 to 5.0 [20]. The extent of the carboxyl dissociation is higher, as the value of pH increases, producing more free sites for lanthanum and cerium biosorption [21]. The maximum biosorption uptake for La(III) and Ce(III) ions occurred at pH 5.0. Therefore, the pH 5.0 is selected for further experiments.
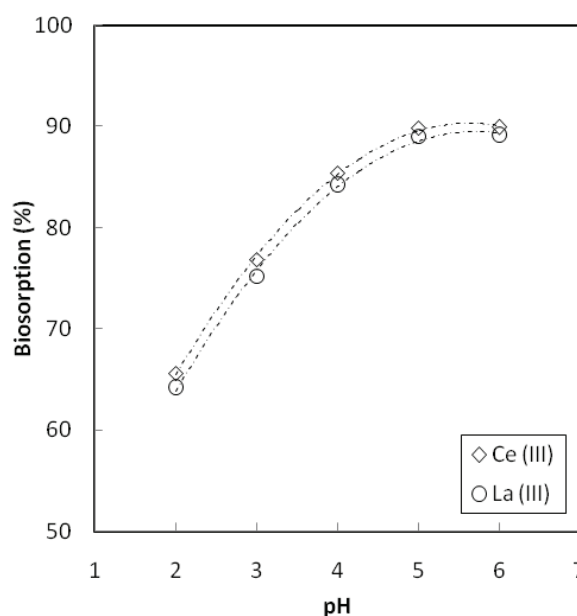

Figure 1. Effect of pH on the biosorption of La(III) and Ce(III) ions on tangerine (C. reticulate) peel (c$_0$: 20mg/L; contact time: 150 min; adsorbent dosage: 1 g/L).

Effect of biosorbent dosage

The effect of biosorbent dosage on the removal of La(III) and Ce(III) is shown in Figure 2. It is observed that the removal efficiency increases with an increase in the biosorbent dosage. The increase in the percentage removal with increase in the biosorbent dosage is due to the increase in the number of adsorption sites. This figure indicates that the biosorption percentage becomes almost constant at 2 g/L for both metal ions. Therefore, the optimum tangerine (*C. reticulate*) peel dosage is selected as 2 g/L and this is used for all further experiments.
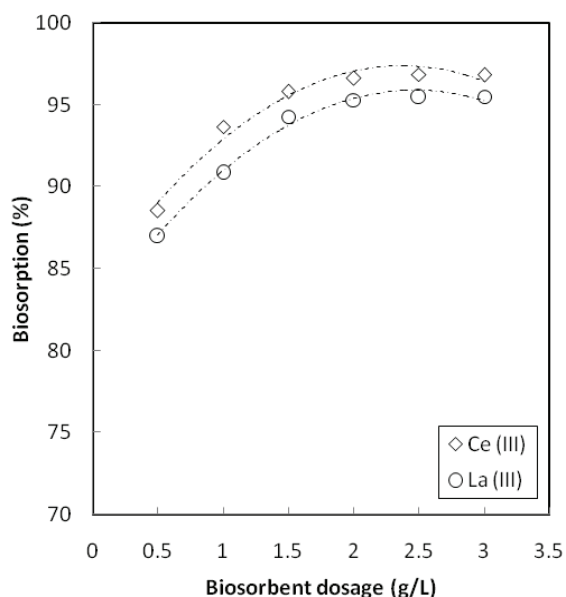
82

Figure 2. Effect of biosorbent dosage on the biosorption of La(III) and Ce(III) ions on tangerine (C. reticulate) peel (c₀: 20 mg/L; contact time: 150 min).

Effect of contact time

The contact time is one of the most important parameters for successful usage of the biosorption in practical and rapid sorption application [22,23]. Figure 3 shows the effect of the contact time on the biosorption of La(III) and Ce(III) ions onto tangerine (*C. reticulate*) peel. It can be seen that the percent removal rapidly increases with increase in the contact time up to 60 min. The rapid biosorption rate at the beginning 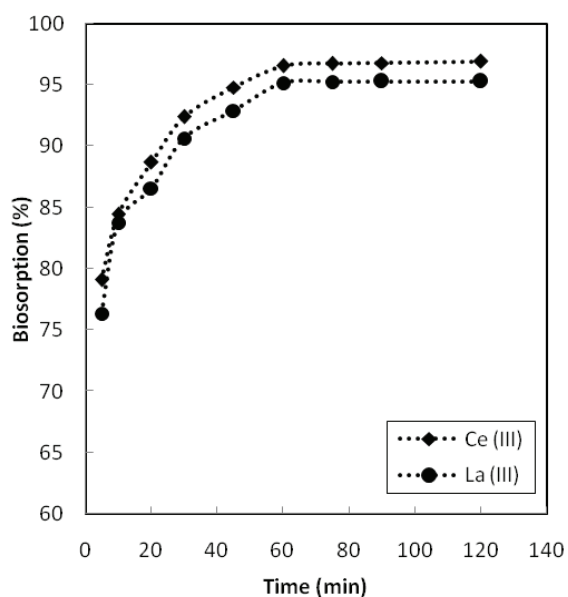of biosorption process may be explained by an increase in the number of active metal-binding sites on the biosorbent surface, which would result in an increased concentration gradient sorbate in the solution and on the biomass surface. After an increase in the contact time, the occupation of the remaining vacant sites would be difficult due to the repulsive forces between La(III) and Ce(III) ions on the solid and the liquid phases. The optimum contact time is selected as 60 min for further experiments.

Biosorption isotherm models

The Langmuir, Freundlich, and D-R isotherm plots for Ce(III) and La(III) are given in Figures 4 and 5, respectively. The calculated results of the Langmuir, Freundlich and D-R isotherm constants are given in Table 1. As seen from Figures 4 and 5 and Table 1, both the Langmuir and Freundlich isotherm models fit the experimental data appropriately. The mean free energy E (kJ/mol) gives information about sorption mechanism, physical or chemical. If the E value is between 8 and 16 kJ/mol, the adsorption process follows by chemical ion exchange and if $E < 8$ kJ/mol, the adsorption process is of a physical nature [24]. The mean adsorption energy (E) was calculated as 9.05 kJ/mol for the adsorption of La(III) and 10.54 kJ/mol Ce(III) onto tangerine (*C. reticulate*) peel. These results suggest that the biosorption process of lanthanum and cerium ions onto tangerine (*C. reticulate*) peel may be carried out by chemical ion-exchange mechanism because the mean free energy lies within 8-16 kJ/mol. The maximum biosorption (q_m) of tangerine (*C. reticulate*) peel for lanthanum and cerium ions is found to be 154.86 and 162.79 mg/g, res-

Figure 3. Effect of contact time on uptake of La(III) and Ce(III) ions by tangerine (C. reticulate) peel (c₀: 50mg/L).
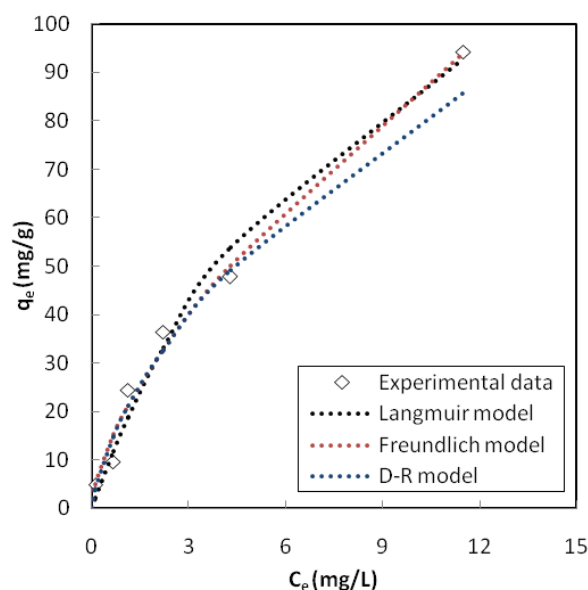

Figure 4. Langmuir, Freundlich and D-R isotherm plots for the biosorption of Ce(III) onto tangerine (C. reticulate) peel.
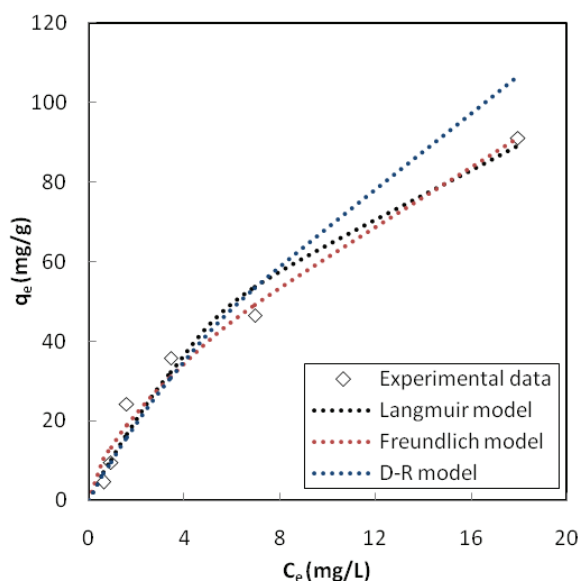
Figure 5. Langmuir, Freundlich and D-R isotherm plots for the biosorption of La(III) onto tangerine (C. reticulate) peel.

pectively. The R_L values ranges from 0.0615 to 0.567 for La(III) and 0.0416 to 0.465 for Ce(III) ions. These values show that the biosorption of La(III) and Ce(III) ions onto tangerine (C. reticulate) peel is favorable

within the experimental conditions studied. The maximum La(III) and Ce(III) ions sorption capacity, q_m, of the present study are compared with the other adsorbents reported in the literature (Table 2). This table shows that the capacity of tangerine (C. reticulate) peel for lanthanum and cerium is higher than most of the adsorbents reported in the literature.

Biosorption kinetics

Figures 6 and 7 show the agreement between experimental data with calculated values using Eqs. (7) and (9) for Ce(III) and La(III) ions, respectively. The values of rate constant are presented in Table 3 along with correlation coefficient and AARE values. The comparison of the pseudo-first and second order kinetic models indicates that the sorption can be well defined by pseudo-second-order kinetics than pseudo-first-order kinetics for the biosorption of both metal ions onto tangerine (C. reticulate) peel.

Biosorption thermodynamics

Based on Eq. (9), the $\Delta H°$ and $\Delta S°$ parameters were calculated from the slope and intercept of a van't Hoff plot of ln K_D vs. $1/T$ yields, respectively (Figure 8). The values of Gibbs free energy change were cal-

Table 1. Langmuir, Freundlich and D-R constants for the biosorption of lanthanum and cerium on tangerine (C. reticulate) peel

Isotherm model	Parameter	La(III)	Ce(III)
Langmiur model	q_m / mg g^{-1}	154.86	162.79
	K_L / L mg^{-1}	0.0762	0.115
	R^2	0.982	0.974
	AARE / %	20.60%	19.88%
Freundlich model	$1/n$	0.650	0.642
	K_F	13.93	19.63
	R^2	0.979	0.988
	AARE / %	33.89%	14.80%
D-R model	q_{max} / mg g^{-1}	0.01712	0.00767
	β / mol^2 kJ^{-2}	0.0061	0.0045
	E / kJ mol^{-1}	9.05	10.54
	R^2	0.934	0.954
	AARE / %	21.12%	18.08%

Table 2. Comparison of adsorption potential (q_m / mg g^{-1}) of various adsorbents for lanthanum and cerium removal from aqueous solution

Adsorbent	Lanthanum	Cerium	Reference
Pinus brutia leaf powder	22.94	17.24	[23]
Turbinaria conoides	154.7	152.8	[24]
Bamboo charcoal	120.0	-	[25]
Platanus orientalis leaf powder	28.65	32.05	[26]
Sargassum sp. Biomass	91.68	-	[27]
Sargassum polycystum	139.0	-	[28]
Iron oxide loaded calcium alginate beads	123.5	-	[29]
Magnetic alginate-chitosan gel beads	97.1	-	[30]
Cladophora hutchinisia	-	74.9	[31]
Modified Pinus brutia leaf powder	-	62.1	[32]
Tangerine (C. reticulate) peel	154.86	162.79	Present study

culated from Eq. (10). The values of ΔH°, ΔS° and ΔG° are given in Table 4. The negative ΔG° values indicate thermodynamically feasible and spontaneous nature of the biosorption. The positive ΔH° values indicate the endothermic nature of the biosorption process of La(III) and Ce(III) at 20-50 °C. 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 biosorption process.
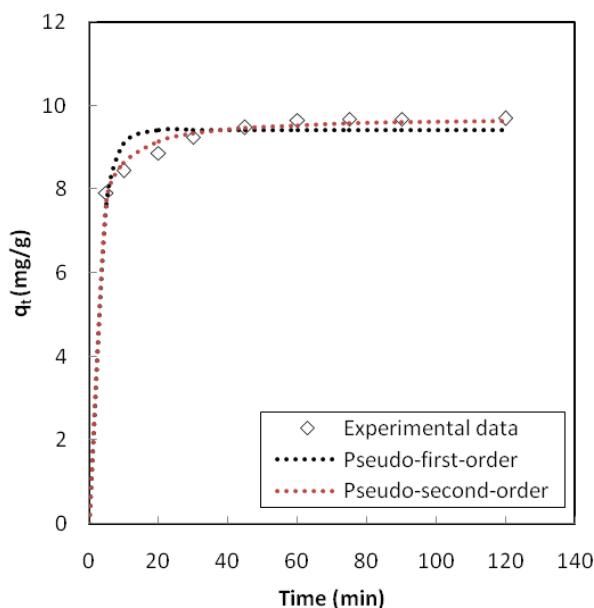

Figure 6. Plot of pseudo-first order and pseudo-second order kinetic models for biosorption of Ce(III) onto tangerine (C. reticulate) peel.
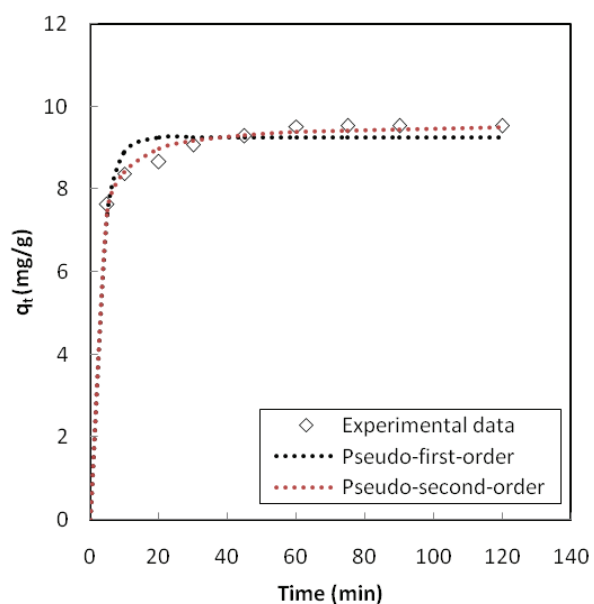

Figure 7. Plot of pseudo-first order and pseudo-second order kinetic models for biosorption of La(III) onto tangerine (C. reticulate) peel.

Table 3. Kinetic parameters of pseudo-first and pseudo-second order models for the biosorption of La(III) and Ce(III) onto tangerine (C. reticulate) peel

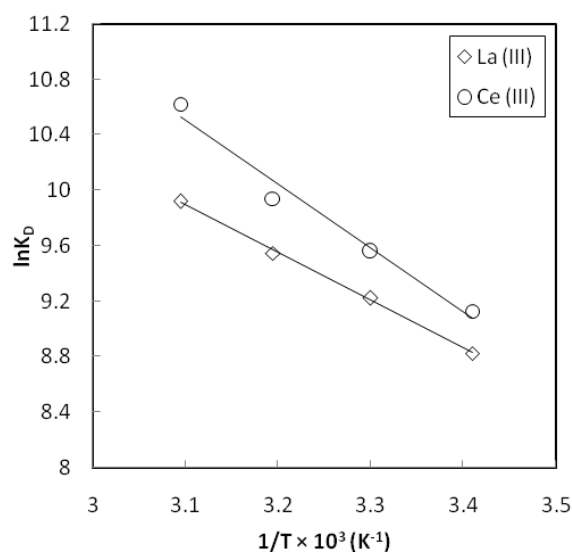| Ion sorbed	Pseudo-first-order kinetic model parameters			
	k_1 / min^{-1}	q_e / mg g^{-1}	R^2	AARE /%
La(III)	0.322	9.25	0.722	3.23
Ce(III)	0.335	9.41	0.680	3.34
Ion sorbed	Pseudo-second-order kinetic model parameters			
	k_2 / g mg^{-1} min^{-1}	q_e / mg g^{-1}	R^2	AARE /%
La(III)	0.763	7.44	0.945	1.22
Ce(III)	0.715	6.86	0.952	1.23

Figure 8. Plots of ln K_D vs. 1/T for the lanthanum and cerium biosorption on tangerine (C. reticulate) peel.

Table 4. Thermodynamic parameters for the biosorption of lanthanum and cerium on tangerine (C. reticulate) peel

Metal ion	ΔG° / kJ mol^{-1}				ΔH°	ΔS°
	t / °C				kJ mol^{-1}	kJ mol^{-1} K^{-1}
	20	30	40	50		
La(III)	-21.58	-23.29	-25.0	-26.71	28.57	170.85
Ce(III)	-22.07	-24.13	-26.19	-28.25	38.34	206.18

Scanning electron microscope (SEM) analysis of biosorbent

The scanning electron micrographs enable the direct observation of the surface microstructures of different adsorbents. The SEM image of unloaded and loaded biosorbent (Figure 9) reveals that the biosorbent has some cavities in its structure. Based on this fact, it could be concluded that the biosorbent presented an adequate morphology for metal adsorption. The micrograph clearly shows the presence of particles over the surface of loaded biosorbent absent in fresh biosorbent.
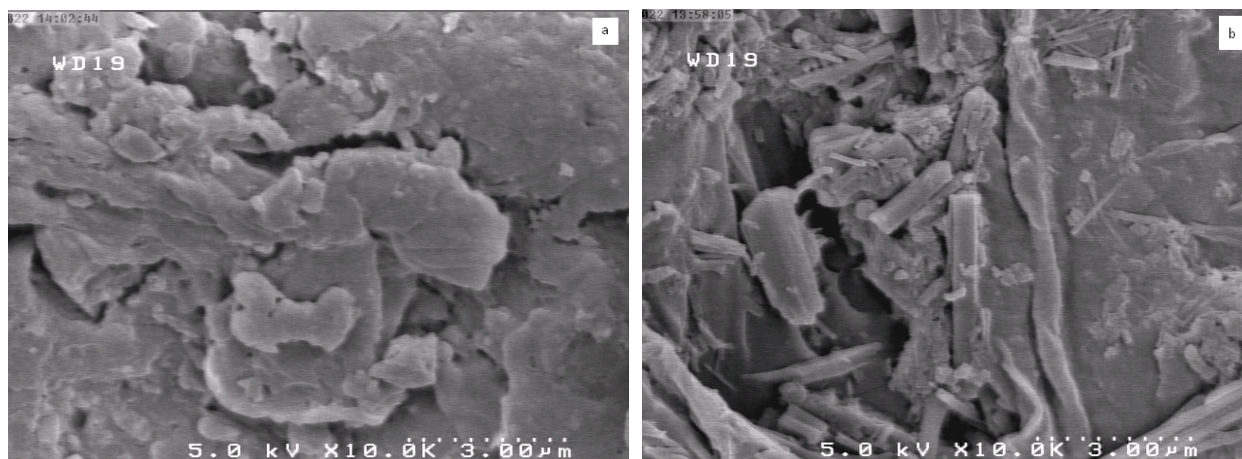
Figure 9. SEM image of a) fresh tangerine (C. reticulate) peel, b) lanthanum loaded tangerine (C. reticulate) peel.

FTIR analysis of biosorbent

The pattern of biosorption onto plant materials is attributable to active groups and bonds present on them [33]. The FTIR spectrum of tangerine peel are plotted to determine the vibration frequency changes in the functional groups in the biosorbent. The FTIR spectrum of tangerine (*C. reticulate*) peel is shown in Figure 10. The spectra display a number of absorption peaks, indicating the complex nature of the examined biosorbent. The broad and intense absorption peak around 3424 cm^{-1} indicates the existence of free and intermolecular bonded hydroxyl groups. The O−H stretching vibrations occur within a broad range of frequencies indicating the [presence of "free" hydroxyl groups and bonded O−H bands of carboxylic acids. The peaks observed at 2930 cm^{-1} can be assigned to stretching vibration of C−H group. The carbonyl band (C=O) of un-ionized carboxylate stretching carboxylic acid or pectin ester is located at 1750 cm^{-1}, while the bands peak at 1651 and 1443 cm^{-1} may be attributed to asymmetric and symmetric stretching vibration of C=O groups. The strong C−O band at 1064 cm^{-1} due to −OCH$_3$ group, also confirms the presence of lignin structure in tangerine peel [34]. The additional peak at 625 cm^{-1} can be assigned to bending modes of aromatic compounds. It is well indicated from the FTIR spectrum of tangerine peel that carboxyl and hydroxyl groups are present in abundance. The sorption of lanthanum and cerium on the tangerine peel biomass may likely due to the electrostatic attraction between these groups and cationic metal molecule. At pH above 4, the carboxylic are deprotonated and negatively charged carboxylate ligands bind the positively charged
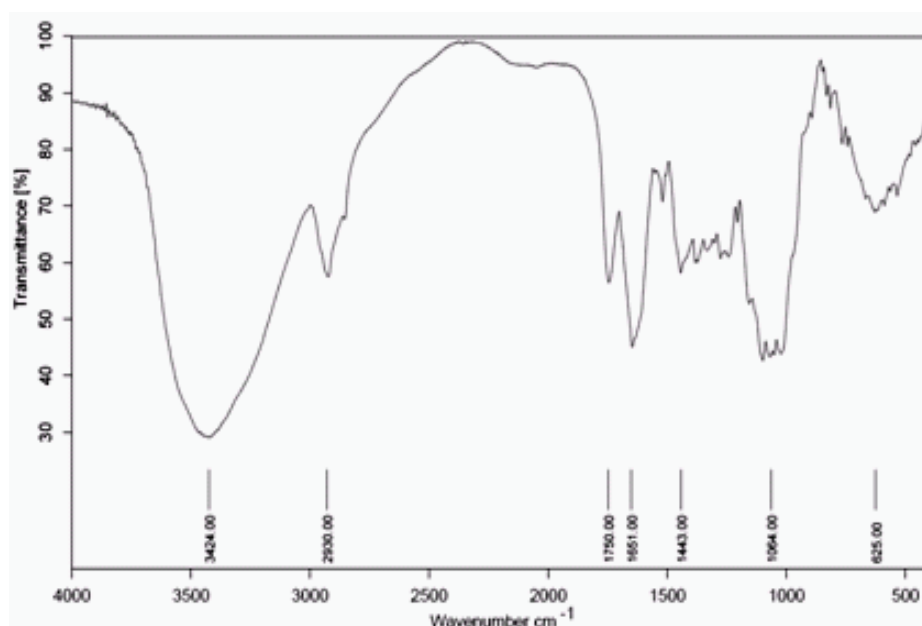

Figure 10. FTIR spectra of natural tangerine (C. reticulate) peel.

metal molecules. This confirms that the sorption of La(III) and Ce(III) is an ion exchange mechanism between the negatively charged groups present in the cell wall of tangerine (*C. reticulate*) peel and the cationic metal molecules.

CONCLUSIONS

In this study, the use of tangerine (*C. reticulate*) peel as a natural biosorbent was tested for La(III) and Ce(III) ions from aqueous solution. The batch study parameters, pH of solution, biosorbent dosage, contact time, and temperature were found to be effective on biosorption efficiency of La(III) and Ce(III). From the Langmuir model the maximum biosorption capacity were found to be 154.86 and 162.79 mg/g for La(III) and Ce(III), respectively. The mean free energy evaluated from the D-R model indicated the biosorption of La(III) and Ce(III) onto tangerine (*C. reticulate*) peel was taken place by chemical ion-exchange. The kinetic studies showed that the biosorption process followed well the pseudo-second order kinetic model. The calculated thermodynamic parameters showed the feasibility, endothermic and spontaneous nature of the biosorption of La(III) and Ce(III) onto tangerine (*C. reticulate*) peel. FTIR analysis showed that the main functional sites taking part in the sorption of La(III) and Ce(III) included carboxyl and hydroxyl groups. The results of this study showed that tangerine (*C. reticulate*) peel can be used as an alternative biosorbent for the treatment wastewater containing La(III) and Ce(III) ions because of advantages of being natural, low-cost biomass and having high biosorption capacity, and reasonably rapid biosorption rate.

Nomenclature

c_e metal concentration at equilibrium (mg/L)
c_f final metal ion concentration (mg/L)
c_0 initial metal concentration (mg/L)
E free energy change (J/mol)
$\Delta G°$ Gibbs free energy change (J/mol)
$\Delta H°$ enthalpy change (J/mol)
k_1 pseudo-first-order rate constant of the sorption (1/min)
k_2 pseudo-second-order rate constant of the sorption (g/(mg·min))
K_D distribution coefficient (mL/g)
K_L Langmuir model constant (L/mg)
K_F Freundlich model constant
M mass of the biosorbent (g)
n Freundlich sorption intensity
q_e amount of adsorbed metal per weight of biosorbent at equilibrium (mg/g)

q_m maximum metal sorption capacity from Langmuir model (mg/g)
q_t amount of adsorbed metal per weight of biosorbent at time t (mg/g)
R universal gas constant (8.314 J/mo·K)
R_L separation factor (-)
$\Delta S°$ entropy change (J/mol·K)
t time (min)
T absolute temperature (K)
V volume of metal solution (L)
ε Polanyi potential (J/mol)
β Constant connected with the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2).

REFERENCES

[1]   M.J. Greaves, H. Elderfield, E.R. Sholkovitz, Marine Chem. **68** (1999) 31-38

[2]   K. Kondo, E. Kamio, Desalination **144** (2002) 249-254

[3]   T.R. Tao, V.M.N. Biju, Critical Rev. Anal.Chem. **30** (2000) 179-220.

[4]   M.C. Palmieri, B. Volesky, O. Garcia, Hydrometallurgy **67** (2002) 31-36

[5]   L. Jelinek, W. Yuezhou, M. Kumagai, J. Rare Earths **24** (2006) 385-391

[6]   F. Fu, Q. Wang, J. Environ. Manage. **92** (2011) 407-418

[7]   D.A. Wase (Ed.), Biosorbent for Metal Ions, CRC Press, London, 1997, pp. 11-88

[8]   S. Babel, T. A. Kurniawan, J. Hazard. Mater. **B97** (2003) 219-243

[9]   J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, J. Environ. Manage. **85** (2007) 262-274

[10]   A. Bhatnagar, A. K. Minocha, M. Sillanpää, Biochem. Eng. J. **48** (2010) 181-186

[11]   A.B. Pérez-Marín, V. Meseguer Zapata, J.F. Ortuno, M. Aguilar, J. Sáez, M. Lloréns, J. Hazard. Mater. **B139** (2007) 122-131

[12]   F.A. Pavan, A.C. Mazzocato, R.A. Jacques, S.L.P. Dias, Biochem. Eng. J. **40** (2008) 357-362.

[13]   [13]. Y.-C. Wang, Y.-C., Chuang, Y.-H., Ku, Food Chem. **102** (2007) 1163-1171.

[14]   [14]. I. Langmuir, J. Am. Chem. Soc. **40** (1918) 1361-1403.

[15]   [15]. H.M.F. Freundlich, Über die adsorption in lösungen, Z. für Phys. Chem. **57A** (1906) 385-470

[16]   M.M. Dubinin, E.D. Zaverina, L.V. Radushkevich, Zh. Fiz. Khim. **21** (1947) 1351-1362

[17]   S. Lagergren, K. Sven. Vetenskapsakademiens. Handl. **24** (1989) 1-39

[18]   Y.S. Ho, G. McKay, Process Biochem. **34** (1999) 451-465

[19]   D. Kratochvil, B. Volesky, Trends Biotechnol. **16** (1998) 291-300

[20]   J.D. Roberts, M.C. Caserio, Basic Principles of Organic Chemistry, 2nd ed., W. A. Benjamin Inc., 1977, p. 792

[21]   M. Ledin, Earth-Sci. Rev. **51** (2000) 1-31

[22] C. Kütahyali, Ş. Sert, B. Çetinkaya, S. Inan, M. Eral, Sep. Sci. Technol. **45** (2010) 1456-1462

[23] K. Vijayaraghavan, M. Sathishkumar, R. Balasubramanian, Ind. Eng. Chem. Res. **49** (2010) 4405-4411

[24] A. Sarı, M. Tuzen, J. Hazard. Mater. **158** (2009) 500-507

[25] Ch. Qing, J. Rare Earths **28** (2010) 125-131

[26] Ş. Sert, C. Kütahyali, S. İnan, Z. Talip, B. Çetinkaya, M. Eral, Hydrometallurgy **90** (2008) 13-18

[27] R.C. Oliveira, O. Garcia Jr., Adv. Mater. Res. **71-73** (2009) 605-608

[28] V. Diniz, B. Volesky, Water Res. **39** (2005) 239-247

[29] D. Wu, J. Zhao, L. Zhang, Q. Wu, Y. Yang, Hydrometallurgy **101** (2010) 76-83

[30] D. Wu, L. Zhang, L. Wang, B. Zhu, L. Fan, J. Chem. Technol. Biotechnol. **86** (2010) 345-352

[31] C. Kütahyali, Ş. Sert, B. Çetinkaya, E. Yalçıntaş, M.B. Acar, Wood Sci. Technol., DOI: 10.1007/s00226-011-0437-8.

[32] A. Sarı, M. Tuzen, Chem. Eng. J. **158** (2010) 200-206

[33] M. Minamisawa, H. Minamisawa, S. Yoshida, N. Taki, J. Agr. Food Chem. **52** (2004) 5606-5611

[34] N.V. Farinella, G.D. Matos, M.A.Z. Arruda, Bioresour. Technol. **98** (2007) 1940-1946.

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NAUČNI RAD

BIOSORPCIJA LANTANA I CERIJUMA IZ VODENIH RASTVORA POMOĆU KORE MANDARINE (*Citrus reticulata*): RAVNOTEŽNA, KINETIČKA I TERMODINAMIČKA ISPITIVANJA

Biosorpcija lantana (III) i cerijuma (III) iz vodenog rastvora pom0ću kore mandarine (Citrus reticulate) je ispitivana u šaržnom sistemu kao funkcija pH, doze biosorbenta, kontaktnog vremena i temperature. Nađeno je da ravnotežni pH ozbiljno utiče na učinak biosorpcije; pH 5.0 je optimalan za biosorpciju La (III) i Ce (III). Za ovu biosorpciju primenjeni su Langmuirov, Freundlichov i Dubinin-Radushkevichev isotermni model. Maksimalna biosorpcija La(III) i Ce(III) prema Langmuirov modelu bila je 154,86, odnosno 162,79 mg/g. Kinetika biosorpcije je proverena modelima pseudo-prvog i pseudo-drugog reda. Rezultati su pokazali se kinetika biosorpcije dobro opisuje modelom pseudo-drugog reda. Termodinamičke veličine, Gibbsova slobodna energija, promena entalpije i promena entropije za oba sorpciona sistema, određene su na četiri različite temperature. Ovi rezultati su pokazali da je biosorpcija La (III) i Ce (III) na kori mandarine spontan i endoterman process. FTIR analiza je pokazala da su karboksilne i hidroksilne grupe uključene u biosorpciju navedenih metala.

Ključne reči: biosorpcija; lantan, cerijum, izoterma, kinetika, kora mandarine, Citrus reticulate.