

Biosorption of thorium from aqueous solution by Ca-pretreated brown algae *Cystoseira indica*

Ali Reza Keshkar^{*†} and Mohammad Amin Hassani^{**}

^{*}Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, Tehran, Iran

^{**}Department of Chemical Engineering, Faculty of Engineering, University of Tehran, Tehran, Iran

(Received 30 June 2013 • accepted 18 October 2013)

Abstract—The potential use of a biosorbent, *Cystoseira indica*, obtained from the Persian Gulf was investigated for the removal of Th (IV) ions from aqueous solutions by considering equilibrium, kinetic and thermodynamic aspects. The FT-IR spectra of unloaded and Th-loaded biomass indicated various functionalities on the biomass surface including hydroxyl, amide and carboxyl groups, which are responsible for the binding of thorium ions. Th (IV) uptake by *C. indica* was pH dependent. An increase in biosorbent dosage up to 1 g/L caused an increase in the Th (IV) percentage removal. Biosorption process at all studied initial Th (IV) ion concentrations follows the pseudo-second order kinetic model. The biosorption data could be well described by Redlich-Peterson isotherm in comparison to Langmuir and Freundlich isotherms. The maximum sorption capacity of Th (IV) by Langmuir isotherm was estimated to be 169.49 mg/g at 45 °C with pH of 3. The thermodynamic parameters indicated the biosorption of Th on the biomass was a feasible, spontaneous and endothermic process. Th sorption capacity remained unaffected or slightly affected (<10% inhibition) in the presence of several interfering ions such as uranium (VI), nickel (II) and copper (II). The reusability of the biomass was also determined after five sorption-desorption cycles.

Keywords: *Cystoseira indica*, Biosorption, Thorium, Kinetic, Isotherm, Interfering Ions

INTRODUCTION

Industrial development creates unwanted materials along with valuable products. For example, water, air and soil pollution is proved to be seriously damaging to the environment [1,2]. One of these damaging pollutants is heavy metals such as uranium, thorium, cadmium, copper and nickel that are present in wastewaters and industrial effluents [3,4]. The earth's crust contains considerable amount of thorium [5,6]. Thorium also exists in the wastewater of nuclear industry, ore processing and lignite burning. All 12 known isotopes of thorium are radioactive and their presence in the environment is hazardous to people's health [7,8]. Thus, it is vital to investigate potential sorbent and recovery of thorium from aqueous solutions with low cost and available sorbent.

Biosorption is an efficient and cost effective method in comparison with other conventional methods for heavy metal elimination such as precipitation, ion exchange resins and membrane-solvent extraction [9-11]. Anirudhan et al. used a novel composite matrix (poly (methacrylic acid)-grafted chitosan/bentonite composite matrix) to adsorb thorium (IV) from water and sea water and concluded that optimum pH was 5.0. They reported the maximum sorption capacity of the adsorbent 110.5 mg·g⁻¹. They also concluded the feasibility of repeated uses of this composite after four cycles of adsorption-desorption experiments [5]. Kuber and Souza studied the effect of different parameters on batch biosorption of thorium by *Aspergillus fumigatus*, a fungal biomass and observed that the opti-

mum pH was 4 and the maximum uptake was 455 mg·g⁻¹ using Langmuir isotherm [7]. Picardo et al. investigated the continuous thorium biosorption by the seaweed *Sargassum filipendula* in a fixed-bed reactor and reported the critical bed depth 40.0 cm corresponding to 96.5 g biosorbent for complete removal of thorium [4].

Brown algae as a low cost biosorbent has been known to be an effective biomass for heavy metals removal in comparison with other types of biomass as reviewed by Davis et al. [12]. Previous investigations show that adsorption of thorium by brown algae as a low-cost and abundant biosorbent has been rarely ever performed. Our previous study showed that the uptake capacity of uranium by calcium pretreated *Cystoseira indica* was greater than raw *C. indica* algae. This finding could be due to the exposing of active metal-binding sites. The other reason may be due to the removal of surface impurities [13]. Therefore, in this work we studied the potential of sorbent and recovery of Th (IV) ions from aqueous solutions by Ca-pretreated brown algae, *C. indica*. We evaluated the effective parameters, e.g., pH, thorium concentration, contact time, biomass dosage, temperature, sorbent recovery and interfering ions such as uranium (VI), nickel (II) and copper (II) on thorium biosorption process. Equilibrium isotherm, kinetic and thermodynamic parameters were also determined and the effective functional groups that participate in thorium biosorption were characterized using FT-IR analysis.

MATERIALS AND METHODS

1. Biomass Preparation

The brown algae (*C. indica*) samples were collected from the Persian Gulf on the coast of Qeshm, Iran. The collected samples

[†]To whom correspondence should be addressed.

E-mail: akeshkar@aeoi.org.ir

Copyright by The Korean Institute of Chemical Engineers.

were washed with distilled water and were dried in an oven at 50 °C to reach a constant weight. The dried algae was ground and sieved to a particle size of 1-2 mm. 10 g of powdered biomass was treated with 0.1 M CaCl₂ solution in 1,000 ml distilled water for 12 h at agitation rate of 150 rpm. Finally, the treated biomass was dried in an oven at 50 °C.

2. Analysis of Thorium Concentration

Thorium concentration after batch processes was determined by inductively coupled plasma spectroscopy (ICP, Varian, Model Liberty 150 AX Turbo). The ICP analysis was performed at wavelength of 283.730 nm.

3. Biosorption Experiments

All thorium solutions were prepared by diluting stock of 1,000 mg/L thorium obtained from dissolving thorium nitrate pentahydrate (Th(NO₃)₅·5H₂O, Merck supplied) in distilled water. Uranium (VI), nickel (II) and copper (II) solutions were also prepared by dissolving their nitrate salts (Merck) in distilled water. The pH of solutions was measured with a pH meter (Metrohm, Model 780) and adjusted by use of 0.1 N HCl and 0.1 N NaOH solutions during batch experiments. Experiments were carried out in 250 ml Erlenmeyer flasks containing 100 ml of solution at the desired pH, temperature, thorium concentration and biomass dosage. An incubator shaker (INFORS multitron, Switzerland) was used for agitating the flasks. The amount of thorium uptake *q* (mg/g) and the percentage removal were calculated according to the following equations:

$$q = \frac{(C_i - C_f)V}{M} \quad (1)$$

$$\text{Percentage removal (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (2)$$

where *C_i* and *C_f* (mg/L) are the initial and final concentrations, respectively. *V* (L) is the volume of thorium solution, and *M* (g) is the mass of biomass. Each analysis was repeated three times and the results given were the average values. The deviation was less than 5%.

RESULT AND DISCUSSION

1. FT-IR Analysis

The FT-IR (Fourier transform infrared) spectroscopy method is

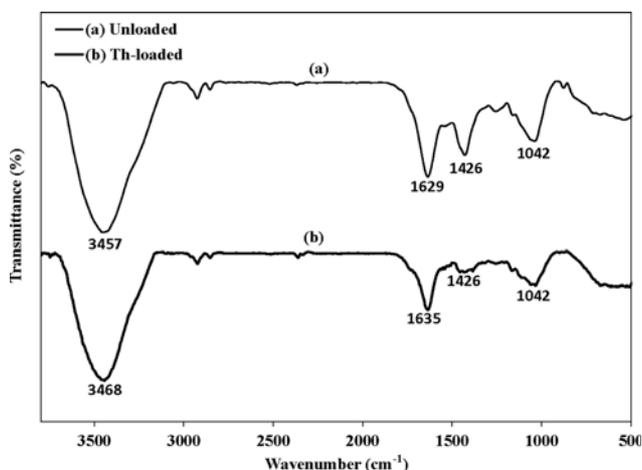


Fig. 1. FT-IR spectrum of unloaded and Th-loaded biomass.

a useful tool to characterize the functional groups that participate in biosorption [14]. Fig. 1 shows the FT-IR spectra of unloaded and Th-loaded biomass. The strong band at 3,457 cm⁻¹ is assigned to the bound hydroxyl (-OH) or amide (-NH₂) groups of the unloaded *C. indica*. The peaks at around 1,629 and 1,426 cm⁻¹ are due to asymmetric and symmetric carboxyl (-C=O) stretching groups, and the peak at 1,042 cm⁻¹ can be attributed to C-O stretching groups. The comparison of unloaded and Th-loaded FT-IR spectra illustrates that the peaks at 3,457 and 1,629 cm⁻¹ are shifted to 3,468 and 1,635 cm⁻¹, respectively. These shifts indicate that hydroxyl, amide and carboxyl functional groups participate in biosorption process and ion exchange happens between thorium and hydrogen atom of these functional groups [15]. Similar results were reported for the biosorption of different heavy metals on various species of algae, namely, biosorption of cadmium and aluminum using red and brown algae, respectively [15,16], and biosorption of copper by dried biomass of red, green and brown algae [17].

2. Effect of pH

The carboxylic group is the most abundant acidic functional group in the cell walls of the brown algae [18]. pH of aqueous solution has a significant effect on biosorption process of heavy metals and can affect the metal ion solubility and ionization of functional groups of the biomass [19]. Fig. 2 shows the effect of pH on the percentage removal after 24 h agitation in the initial pH range of 2.0-6.0 and initial thorium concentration of 100 mg/L at temperature of 25 °C and biomass dosage 1 g/L. As can be seen, the percentage removal of thorium increases initially by an increase in pH, and it reaches a maximum and then decreases as the pH increases. Maximum removal was found to be 98% at pH 3. Minimum percentage removal (16%) was observed at pH 6. Poor uptake in lower pH may be due to the competition with the H₃O⁺ ions for binding sites. At lower pH, H₃O⁺ concentration is greater than its value in upper pH and occupies more binding sites [20]. Also, the effect of pH can be attributed to the ionic species that are present at different pH. The major ionic type at pH 2 is Th⁴⁺, which is not appropriate to be adsorbed by biomass binding sites. As the pH increases from 2, the formation of hydrolyzed species such as Th(OH)₄ and Th(OH)₂²⁺ initiates, which is suitable for biosorption process. Decrease of biosorption

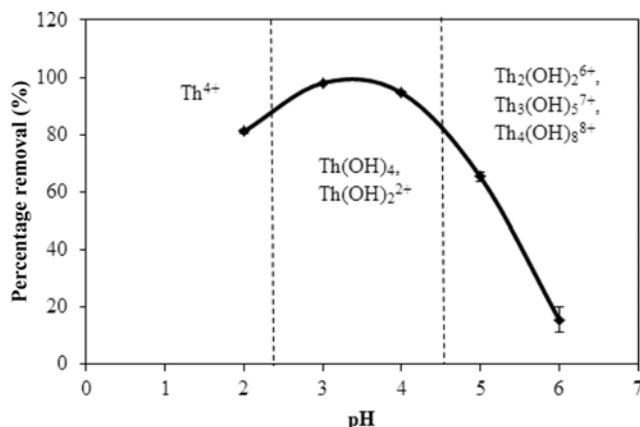


Fig. 2. Effect of pH on the percentage removal of thorium by *C. indica* brown algae (initial thorium concentration=100 mg/L, temperature=25 °C, biomass dosage=1 g/L, agitation rate=150 rpm, contact time=24 h).

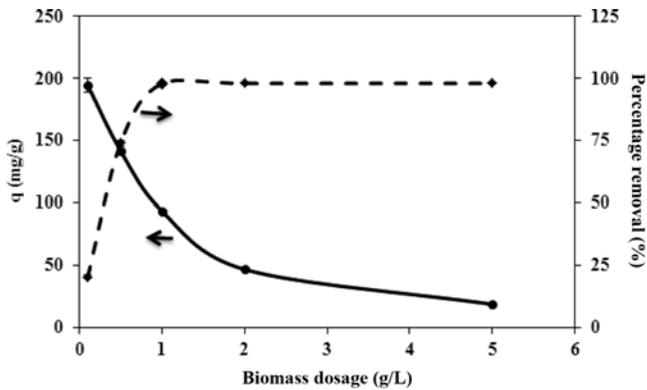


Fig. 3. Effect of biomass dosage on thorium uptake and the percentage removal (pH=3, initial thorium concentration=100 mg/L, temperature=25 °C, agitation rate=150 rpm, contact time=6 h).

uptake at higher pH, shown in Fig. 2, may be due to the formation of $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_3(\text{OH})_3^{7+}$ and $\text{Th}_4(\text{OH})_4^{8+}$ complexes, which decreases the free metal ions [5,7,21-23]. Consequently, the optimum pH for further biosorption studies was selected 3.

3. Effect of Biomass Dosage

The effect of biomass dosage in the range of 0.1-5 g/L on the thorium uptake and percentage removal by *C. indica* at the initial thorium concentration of 100 mg/L and temperature of 25 °C is shown in Fig. 3. The percentage removal largely increased from 20% to 98% as the biomass dosage of *C. indica* increased from 0.1 g/L to 5 g/L. This could be expected because the higher the biomass dosage in the solution, the greater the availability of exchangeable sites for the ions. However, there was only a slight change in the thorium removal when the biomass dosage was over 1 g/L. Furthermore, thorium uptake decreased with the increase of biomass dosage. This decrease in thorium uptake obviously occurred due to the decrease in availability of the thorium ions per unit biomass dosage.

4. Biosorption Kinetics

Equilibrium contact time and kinetics data are very important for designing and controlling of biosorption processes. The kinetic process of Th (IV) biosorption at different initial Th (IV) concentrations was analyzed using the pseudo-first order and pseudo-second order kinetic models. These two models and their linear forms are expressed as:

The pseudo-first order model [24]:

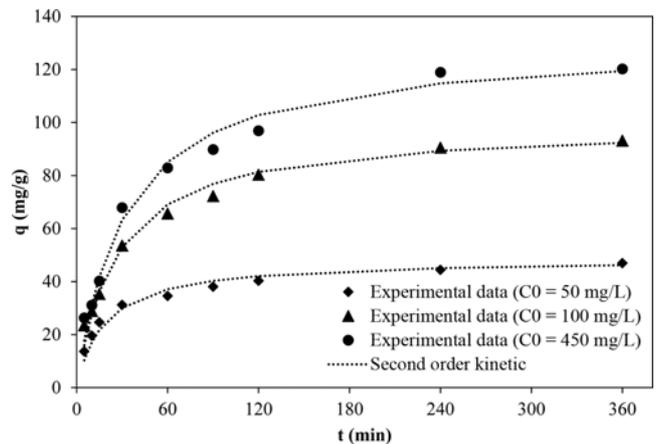


Fig. 4. Effect of contact time on thorium uptake at different initial thorium concentrations (pH=3, temperature=25 °C, biomass dosage=1 g/L, agitation rate=150 rpm).

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

The pseudo-second order model [25]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where q_e and q_t (mg/g) are the amount of thorium uptake at equilibrium and time t (mg/g), respectively, k_1 is the pseudo-first order rate constant (min^{-1}) and k_2 is the pseudo-second order rate constant ($\text{g}/(\text{mg} \cdot \text{min})$). Fig. 4 depicts the experimental data and the results of the second order kinetic model of thorium uptake at different initial thorium concentrations at pH 3 and temperature of 25 °C. Thorium uptake increases with an increase in contact time initially, and then approaches a maximum thorium uptake and reaches equilibrium after 6 h. On the other hand, almost 60% and 97% of thorium are adsorbed in the first 0.5 h and 4 h, respectively, which can be due to more unoccupied binding sites initially. Equilibrium sorption capacity according to the experiments and the constants of kinetic models are presented in Table 1. As can be seen in Table 1, the regression coefficients of the pseudo-second order model are greater

Table 1. The constants of kinetic models for thorium biosorption by *C. indica*

Initial concentration (C_i)	$q_{e, \text{experiment}}$ (mg/g)	Pseudo-first order model			Pseudo-second order model		
		k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 ($\text{g}/(\text{mg} \cdot \text{min})$)	q_e (mg/g)	R^2
50 $\text{mg} \cdot \text{L}^{-1}$	47.09	0.058	41.16	0.976	0.00112	48.54	0.998
100 $\text{mg} \cdot \text{L}^{-1}$	93.58	0.032	85.25	0.983	0.00039	99.01	0.998
150 $\text{mg} \cdot \text{L}^{-1}$	120.31	0.027	110.90	0.968	0.00024	129.87	0.997

The pseudo-first order model parameters applicable to initial concentrations between 50 and 150 mg/L

$$K_1 = 0.105 + (1.15 \times 10^{-3}) C_i - 4.2 \times 10^{-6} C_i^2 \quad q_{e, \text{first order}} = -21.37 + 1.435 C_i - 3.688 \times 10^{-3} C_i^2$$

The pseudo-second order model parameters applicable to initial concentrations between 50 and 150 mg/L

$$k_2 = 8.1 \times 10^{-3} + (2.488 \times 10^{-4}) C_i - (1.288 \times 10^{-6}) C_i^2 \quad q_{e, \text{second order}} = 21.54 + 1.5977 C_i - 3.922 \times 10^{-3} C_i^2$$

than the pseudo-first order model. Moreover, the theoretical equilibrium sorption capacities calculated by the pseudo-second order model have more conformity with the experimental values. Thus, the pseudo-second order model achieves a better conformity with the experimental data. In addition, with an increase in the initial thorium concentration, both the first and second order rate constants decrease; however, the second order equilibrium constant decreases with a higher rate because of the power of the second order kinetic model. The constants of kinetic models obtained at different initial thorium concentrations were fitted quadratic equations and are presented in Table 1. Note that it is better to employ the model for the initial concentrations between 50 and 150 mg/L.

5. Biosorption Isotherms

Two-parameter isotherms of Langmuir and Freundlich and three-parameter isotherm of Redlich-Peterson were used to fit thorium biosorption by *C. indica*. These models were selected for their simplicity and easily interpretable constants.

The Langmuir model assumes that all adsorption points have the same heat of adsorption and sorption takes place at a specific homogeneous surface. This model is described by the following equation [26]:

$$q_e = \frac{q_{max} b_L C_e}{1 + b_L C_e} \quad (7)$$

where q_e and C_e are equilibrium uptake (mg/g) and equilibrium concentration (mg/L), q_{max} is the maximum biosorption capacity (mg/g), b_L is related to the affinity of biosorbent for the sorbate (L/mg). Thus, for a good biosorbent, higher q_{max} and more affinity (b_L) are desirable.

The Freundlich model is based on a heterogeneous adsorption surface and on the idea that there exist fewer adsorption points for the higher heat of adsorption. This isotherm is represented as [27]:

$$q_e = K_F C_e^{1/n_F} \quad (8)$$

where K_F and n_F are related to biosorption capacity and intensity, respectively.

To improve the data prediction, a three-parameter isotherm model was used. Redlich-Peterson is another empirical equation, designated as the "three parameter equation," which is capable to represent adsorption equilibria over a wide concentration range. This equa-

tion is described by the following equation [28]:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^{\beta_{RP}}} \quad (9)$$

where K_{RP} (L/g) and α_{RP} (L/mg) are the Redlich-Peterson constants and β_{RP} ($0 < \beta_{RP} < 1$) is the Redlich-Peterson model exponent. Redlich and Peterson incorporated the characteristics of Langmuir and Freundlich isotherms into a single equation. When $\beta_{RP}=1$, the Redlich-Peterson model converts into the Langmuir isotherm, and for $\beta_{RP}=0$ this model converts into Henri's law. Moreover, for a high metal concentration, this equation can be reduced to the Freundlich isotherm. This model fits the experimental data accurately in several systems, namely, biosorption of Cd (II), Cu (II), Ni (II) and Zn (II) ions on brown algae [3], biosorption of Mn (II) by locally isolated *Bacillus* species and sewage activated sludge [29] and adsorption of Th (IV) using poly(methacrylic)-grafted chitosan/bentonite composite matrix [5].

The constants of these models at different temperatures are presented in Table 2. As it can be seen, maximum biosorption capaci-

Table 2. The isotherm models constants for thorium biosorption by *C. indica*

Isotherm models	Temperature (°C)		
	25	35	45
Langmuir constants			
q_{max} (mg/g)	158.73	166.67	169.49
b_L (L/mg)	0.274	0.331	0.663
R^2	0.975	0.978	0.932
Freundlich constants			
K_F (L/g)	57.93	63.41	68.94
n_F	5.06	5.20	5.61
R^2	0.849	0.835	0.861
Redlich-Peterson constants			
K_{RP} (L/g)	58.16	72.54	136.90
α_{RP} (L/mg)	0.47	0.53	1.12
β_{RP}	0.953	0.963	0.941
R^2	0.989	0.987	0.996

Table 3. The thorium sorption capacity by different sorbents

Sorbent	q_{max} (mg/g)	ΔG° (kJ/mol)			ΔH° (kJ/mol)	ΔS° (kJ/(mol·K))	References
		25 °C	35 °C	45 °C			
<i>Aspergillus fumigatus</i>	455	-	-	-	-	-	Bhainsa and Souza [7]
Polyvinyl alcohol/titanium oxide nanofiber	238.1	-5.654	-6.306	-7.622	15.331	0.071	Abbaszadeh et al. [30]
<i>R. arrhizus</i>	97	-	-	-	-	-	Gadd et al. [31]
Crystalline tin oxide nanoparticles	62.50	-18.24	-19.54	-	20.80	0.13	Nilchi et al. [32]
<i>Penicillium chrysogenum</i>	142	-	-	-	-	-	Tsezos and Volesky [33]
<i>Aspergillus niger</i>	22	-	-	-	-	-	
Peat moss treated with HNO ₃	-	-15.196	-15.708	-16.219	0.040	0.051	Humelnicu et al. [34]
Peat moss treated with NaOH	-	-15.572	-16.096	-16.620	0.034	0.052	
<i>Bacillus megaterium</i> IAM 1166	74	-	-	-	-	-	Nakajima and Tsuruta [35]
<i>Micrococcus luteus</i> IAM 1056	77	-	-	-	-	-	
<i>Cystoseira indica</i>	169.49	-27.40	-28.81	-31.58	34.58	0.207	This work

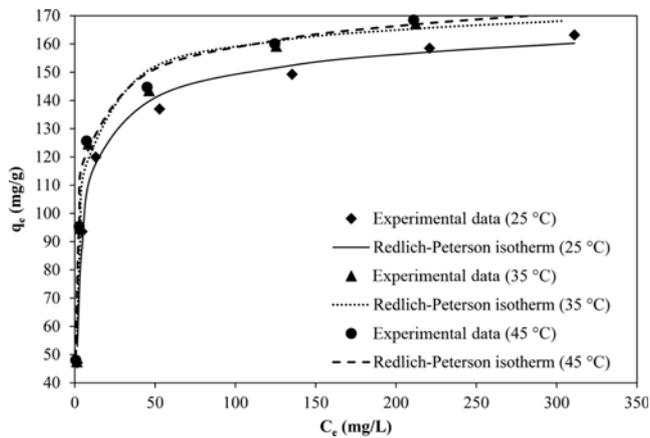


Fig. 5. Fit of Langmuir, Freundlich and Redlich-Peterson isotherms for thorium uptake at 25 °C (pH=3, biomass dosage=1 g/L, agitation rate=150 rpm, contact time=6 h).

ties from the Langmuir isotherm are 158.73, 166.67 and 169.49 mg/g at 25, 35 and 45 °C, respectively. Also, the three-parameter isotherm of Redlich-Peterson has the best coincidence with experimental data ($R^2 > 0.987$). Moreover, the Langmuir isotherm describes biosorption data better than the Freundlich isotherm, which can be concluded from the values of β_{RP} (that are close to unity). Table 3 compares thorium sorption capacity using different sorbents with this study. *C. indica* has a good biosorption capacity in comparison with other types of sorbents. As shown in Fig. 5, plots of Redlich-Peterson isotherms at different temperatures are compared with experimental data to show good capability of this model to fit isotherm data.

6. Thermodynamic Parameters

Thermodynamic parameters in terms of the Gibbs free energy change (ΔG°), the enthalpy change (ΔH°) and the entropy change (ΔS°) were calculated to describe thermodynamic behavior of the biosorption of thorium by *C. indica*. The Gibbs free energy change can be calculated from the following equation:

$$\Delta G^\circ = -RT \ln(K_c) \quad (10)$$

where R is the universal gas constant (8.314 J/(mol.K)), T is the

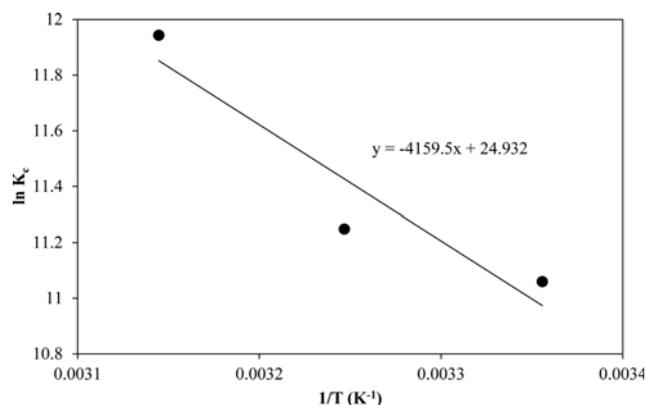


Fig. 6. Plot of $\ln K_c$ vs. $1/T$ (pH=3, initial thorium concentration =100 mg/L, biomass dosage=1 g/L, agitation rate=150 rpm, contact time=6 h).

absolute temperature (K) and K_c is the equilibrium constant (L/mol). The enthalpy and entropy changes were estimated from the slope and intercept of the plot of $\ln(K_c)$ versus $1/T$ according to the van't Hoff equation (Fig. 6):

$$\ln(K_c) = \Delta S^\circ/R - \Delta H^\circ/RT \quad (11)$$

In this study, the thermodynamic parameters have been calculated using the Langmuir isotherm, i.e., by replacing the equilibrium constant, K_c from Eqs. (10), (11) by the Langmuir isotherm constant, b_L in the unit of L/mol [1,36]. The values of ΔG° were found to be -27.40, -28.81 and -31.58 kJ/mol at 25, 35 and 45 °C, respectively. The negative values of the Gibbs free energy change show the thermodynamically feasible and spontaneous nature of the biosorption of thorium on *C. indica*. The increase in ΔG° along with the rise of temperature indicates more feasibility of biosorption process at higher temperature. The value of ΔH° was calculated to be 34.58 kJ/mol, which emphasizes that the biosorption of thorium by *C. indica* is endothermic and the sorption capacity increases with increasing of temperature. Calculated value for ΔH° also indicated basically chemical adsorption for Th (IV) on *C. indica*, since the critical value set for differentiating between physical and chemical mechanisms is 20 kJ/mol [37]. Moreover, the positive value of the entropy change (0.207 J/(mol.K)) indicates an increase in the randomness at the solid-solution interface during the biosorption process. The values of ΔG° , ΔH° and ΔS° for biosorption of thorium by *C. indica* are compared with other adsorbents in Table 3. Biosorption of thorium by different adsorbents is feasible, spontaneous and endothermic with increase in the randomness at the solid-solution interface as it was seen for *C. indica*.

7. Effect of Interfering Ions

Several heavy metal ions may be present in wastewater or industrial waste liquids. Thus, thorium biosorption in the presence of interfering ions such as U (VI), Ni (II) and Cu (II) was investigated. For this purpose, binary solutions containing constant thorium concentration 100 mg/L and different interfering ion concentrations in the range of 10-100 mg/L were made. Fig. 7 shows that thorium biosorption has not changed considerably in the presence of nickel

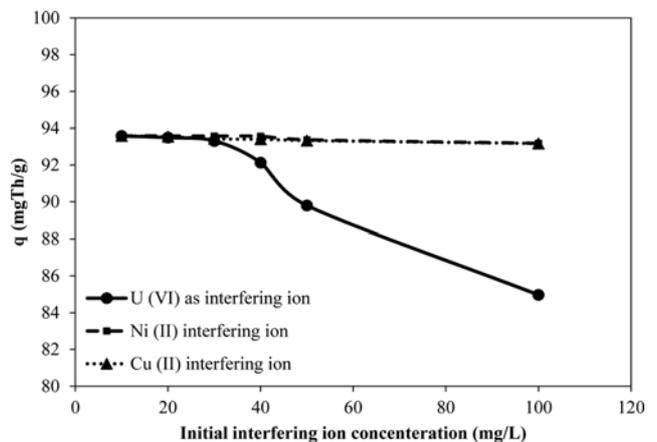


Fig. 7. Effect of interfering ions on thorium uptake (pH=3, initial thorium concentration=100 mg/L, temperature=25 °C, biomass dosage=1 g/L, agitation rate=150 rpm, contact time=6 h).

and copper and has reduced slightly at higher concentration of uranium. The order of inhibition by these interfering ions was Ni (II) < Cu (II) < U (VI). However, the highest concentration of uranium (100 mg/L) decreases only 10% of thorium biosorption capacity. In the absence of U (VI) ions, the thorium sorption capacity was 93.58 mg/g. When the concentration of uranium increased from 0 to 100 mg/L, the thorium sorption capacity decreased to 84.97 mg/g. This low inhibitory effect of competitive U (VI) ions on the thorium sorption capacity is in agreement with Sar and D'souza's work. They investigated the effect of several interfering ions on biosorption of thorium (IV) by a *Pseudomonas* biomass, and observed that thorium binding remained unaffected or slightly affected (<20% inhibition) in the presence of other interfering ions such as U (IV), Cd (II), Ni (II), Co (II), Pb (II) and Cu (II) [38]. These observations can be due to the conditions of the experiments, which is optimum for thorium biosorption. The pH of experiments is 3, while the optimum pH of uranium, nickel and copper biosorption by different brown algae is between 4 to 6 [1,3,12].

8. Regeneration of Biomass

Regeneration of the biomass for repeated use is an important issue for improvement of economic aspect of biosorption processes. For this purpose, 0.1 g of loaded thorium biomass was treated with 100 mL of 1 M CaCl₂ solution for 3 h at temperature 25 °C and with agitation rate of 150 rpm, and the treated biomass was used for biosorption process again. Fig. 8 shows equilibrium sorption capacity of thorium after five steps of sorption-desorption process. The sorption capacity of thorium by *C. indica* decreased from 93.58 mg/g in the first step to 82.37 (88%), and 74.87 (80%) mg/g after two and five steps of the sorption-desorption process, respectively. Therefore, *C. indica* could be reused several times without a significant decrease in biosorption capacity.

CONCLUSION

This paper focused on the characteristics of batch biosorption of thorium by Ca-pretreated brown algae (*Cystoseira indica*). The impact of effective design parameters including pH, biomass dosage, contact time, temperature and interfering ions was investigated. It

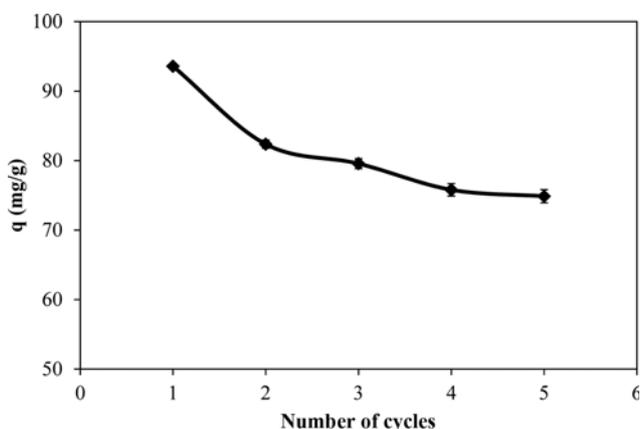


Fig. 8. Thorium equilibrium sorption capacity at five stages of sorption-desorption process (pH=3, initial thorium concentration=100 mg/L, temperature=25 °C, biomass dosage=1 g/L, agitation rate=150 rpm, contact time=6 h).

could be found from FT-IR analysis that hydroxyl, amide and carboxyl functional groups involved in thorium biosorption and ion exchange mechanism had a vital role in biosorption process. Maximum thorium uptake was observed at pH 3. The biosorption process was reached equilibrium at 6 h, and the pseudo-second order kinetic model fitted the experimental data ($R^2 > 0.995$) better than the pseudo-first order model ($R^2 > 0.985$). The parameters of kinetic models were also presented as quadratic equations for estimation of sorption capacity in the initial concentrations between 50 and 150 mg/L. The three-parameter isotherm of Redlich-Peterson could describe accurately the equilibrium sorption data ($R^2 > 0.987$). The maximum sorption capacity was calculated to be 169.49 mg/g from Langmuir isotherm at 45 °C. Estimation of thermodynamic parameters in terms of ΔG° , ΔH° and ΔS° showed feasible, spontaneous and endothermic nature of thorium biosorption and increase in the randomness at the solid-solution interface. Biosorption process in the presence of nickel (II), copper (II) and uranium (VI) ions illustrated that thorium uptake is not changed by nickel and copper and is decreased to 90% of initial sorption capacity at higher amount of uranium. It could be seen from regeneration processes that *C. indica* could be reused several times. The uptake capacity decreased to 80% of initial sorption capacity after five steps of sorption-desorption.

REFERENCES

1. H. Pahlavanzadeh, A. R. Keshtkar, J. Safdari and Z. Abadi, *J. Hazard. Mater.*, **175**, 304 (2010).
2. D. Humelnicu, G. Drochioiu and K. Popa, *J. Radioanal and Nucl. Chem.*, **260**(2), 291 (2004).
3. Y. Liu, Q. Cao, F. Luo and J. Chen, *J. Hazard. Mater.*, **163**, 931 (2009).
4. M. C. Picardo, A. C. d. M. Ferreira and A. C. A. d. Costa, *Biore-sour. Technol.*, **100**, 208 (2009).
5. T. S. Anirudhan, S. Rijith and A. R. Tharun, *Colloids Surf. A.*, **368**, 13 (2010).
6. N. Manikandan, C. S. S. Prasath and S. Prakash, *Indian J. Geo-Mar Sci.*, **40**(1), 121 (2009).
7. K. C. Bhainsa and S. F. D'Souza, *J. Hazard. Mater.*, **165**, 670 (2009).
8. L. E. Macaskie, *Crit. Rev. Biotechnol.*, **11**, 41 (1991).
9. F. J. Alguacil, M. Alonso, F. Lopez and A. Lopez-Delgado, *Chemosphere*, **72**, 684 (2008).
10. Y. Mao, H. Hu and Y. Yan, *J. Environ. Sci.*, **23**(7), 1104 (2011).
11. M. M. Matlock, B. S. Howerton and D. A. Atwood, *Water Res.*, **36**, 4757 (2002).
12. T. A. Davis, B. Volesky and A. Mucci, *Water Res.*, **37**, 4311 (2003).
13. M. Ghasemi, A. R. Keshtkar, R. Dabbagh and S. J. Safdari, *J. Hazard. Mater.*, **189**, 141 (2011).
14. B. Volesky, *BV Sorbex, Inc., Canada* (2003).
15. A. Sari and M. Tuzen, *J. Hazard. Mater.*, **171**, 973 (2009).
16. A. Sari and M. Tuzen, *J. Hazard. Mater.*, **157**, 448 (2008).
17. V. Murphy, H. Hughes and P. McLoughlin, *Water Res.*, **41**, 731 (2007).
18. E. Percival and R. McDowell, London, UK: Academic Press (1967).
19. C. Gok and S. Aytas, *J. Hazard. Mater.*, **168**, 369 (2009).
20. J. T. Matheickal, Q. M. Yu and G. M. Woodburn, *Water Res.*, **33**, 335 (1999).
21. C. F. Baes and R.E. Mesmer, *The hydrolysis of cations*, Wiley New

- York, **68** (1976).
22. M. Tsezos and B. Volesky, *Biotechnol. Bioeng.*, **24**, 955 (1982).
23. L. Cromieres, V. Moulin, B. Fourest, R. Guillaumont and E. Giffaut, *Radiochim. Acta*, **82**, 249 (1998).
24. M. V. Subbaiah, Y. Vijaya, A. S. Reddy, G. Yuvaraja and A. Krishnaiah, *Desalination*, **276**(1), 310 (2011).
25. Y. S. Ho and G. McKay, *Process. Biochem.*, **34**, 451 (1999).
26. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
27. H. J. Freundlich, *Phys. Chem.*, **57**, 358 (1906).
28. J. Febrianto, A. N. Kosasih, J. Sunarso, Y.-H. Ju, N. Indraswati and S. Ismadji, *J. Hazard. Mater.*, **162**, 616 (2009).
29. H. A. Hasan, S. R. S. Abdullah, N. T. Kofli and S. K. Kamarudin, *J. Environ. Sci.*, **111**, 34 (2012).
30. S. Abbasi-Zadeh, A. R. Keshkar and M. A. Mousavian, *Chem. Eng. J.*, **220**, 161 (2013).
31. G. M. Gadd, C. White and L. de Rome, *In: Biohydrometallurgy: proceedings of the international symposium, Warwick 1987 (Norris PR, Kelly DP) Science and Technology Letters, Kew, Surrey*, 421 (1988).
32. A. Nilchi, T. S. Dehaghan and S. R. Garmarodi, *Desalination*, 11374 (2012).
33. M. Tsezos and B. Volesky, *Biotechnol. Bioeng.*, **23**, 583 (1981).
34. D. Humelnicu, L. Bulgariu and M. Macoveanu, *J. Hazard. Mater.*, **174**(1), 782 (2010).
35. A. Nakajima and T. J. Tsuruta, *Radioanal Nucl. Chem.*, **260**, 13 (2004).
36. Y. Liu, *Colloids Surf. A.*, **274**, 34 (2006).
37. S. Yalcin, S. Sezer and R. Apak, *Environ. Sci. Pollut. Res.*, **19**, 3118 (2012).
38. P. Sar and S. F. D'souza, *Biotechnol. Lett.*, **24**, 239 (2002).