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THERMODYNAMICS, KINETICS AND EQUILIBRIUM STUDIES OF URANIUM SORPTION BY *Gracilaria corticata* RED ALGA

Reza Dabbagh¹, Abolfazl Rojaee^{2*}, Zoheir Heshmatipour²¹Nuclear Science Technology and Research Institute (NSTRI), MNFRS, North Karegar St., Tehran, Iran²Department of Microbiology, Tonekabon Branch, Islamic Azad University, Tonekabon, Iran

Abstract

In this research, the capability of uranium biosorption by dried biomass of the red algae was investigated in a batch system. For the screening of the most appropriate biosorbent, they were placed in 0.5 mmol/L uranium solution with different pH for 3hrs of contact times. The obtained results showed that the species of the *Gracilaria corticata* (*J. Agardh*) are having the maximum rate of the biosorption. Sorption equilibrium was reached within 3hrs of contact time (at pH 4.5), and the results of the kinetic studies showed that the sorption of uranium followed pseudo-second order kinetic model ($R^2=0.999$). The maximum uranium biosorption capacity (q_{max}) by *Gracilaria corticata* alga was 200 mg/g. The biosorption of uranium was found to be an endothermic process with ΔH° of +0.260 kJ/mol. The values of ΔG° (293K) and ΔS° obtained were -0.504 kJ/mol and +1.083 J/mol.K, respectively. The feasibility and spontaneous nature of the sorption process was elucidated by these values. Freundlich isotherm constants, K_F and n , were 0.72 and 0.94, respectively ($R^2=0.988$).

Key words: biosorption, *Gracilaria corticata*, kinetics, thermodynamics, uranium

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1. Introduction

Of the most important and dangerous environmental pollutants, radionuclides and heavy metals available in the industrial wastes are among the most studied (Marandi et al., 2010; Vijayaraghvan et al., 2006). The industrial processes are like mining, battery makings, electroplating, metallurgy, military plants etc. (Cruz et al., 2004; Dabbagh et al., 2007; Kaewsarn and Yu, 2001). Uranium is a silvery-white metallic chemical element in the actinide series of the periodic Table, with atomic number 92. This element occurs in nature in many rocks, minerals and sediments. The principal uranium minerals are uraninite, torbernite, pitchblende, carnotite, uranophane. Uranium is one of the radionuclides which affect the environment and human health, during its extraction from mines, processing and use

and this is because its long-term stability, since it can remain up to million years in the environment (Khani et al., 2006; Volesky, 1990). Therefore, uranium can lead to acute and chronic pollution effects in plants, humans and animals (Ahalya et al., 2008; Volesky, 2003; Williams, 1998).

On the other hand, numerous compounds which include heavy metals can be dissolved easily in water at different concentrations, while metal removal from the aquatic environment is a hard and difficult task (Davis et al., 2000; Davis and Volesky, 2005). Various physico-chemical methods, including ion exchange, reverse osmosis, precipitation, oxidation-reduction and others were developed for heavy metal removal from aqueous solutions (Ghasemi et al., 2011; Gonzalez et al., 1997; Sadeghi et al., 2017; Volesky, 2001). However, these methods are sometimes inefficient in the high volumes and are accompanied

* Author to whom all correspondence should be addressed: e-mail: a.rojaee@yahoo.com; rdabbagh@aeoi.org.ir; P.O. Box: 11365-8486; Fax: 0098-21-88221116

by high costs. Therefore, biological methods are used today, regarded as a part of the acceptable methods in the whole world, and they are used to recycle the industrial wastes (Balan et al., 2017; Barros et al., 2018; Chen and Yang; 2005; Gavrilescu, 2005). Biosorptive accumulation of uranium and other radionuclides is of recent interest for the development of algal based bioremediation strategies to clean up contaminated sites.

Biosorption has some advantages, including low operational costs, lack of production of the chemical sludge, reusability of the sorbent, its effectiveness in reduction of heavy metals concentration at very low quantities, selectivity and usage of the cheap and available sorbents. Biosorption of metal with the aid of the microorganisms can be carried out by the biosorption and bioaccumulation methods. However, in the conducted studies and surveys, it was specified that the biosorption is of the higher efficiency and output (Hlihor et al., 2005; Kapoor and Viraraghvan, 1995; Leusch et al., 1995; Raize et al., 2004).

Many of biosorbents, such as algae, yeasts, fungi and bacteria are able to adsorb a large spectrum of the metals. This action attributed to the functional groups such as carboxylate, sulfate, sulfonic acids and other electrostatic attraction to negatively charged functional groups existing in their cell walls. In the cell wall of the algae, there are, excepting cellulose, materials such as alginic acid and fucoidan which play a key role in the biosorption of heavy metal ions. Carboxylate groups are the most plentiful groups available in fucoidan, which correlates directly with the capacity of the biosorption (Lodeiro et al., 2005; Raff et al., 2003). Also, due to availability, cheapness, environmental friendliness and renewability of algae, they are considered as a potential candidate for pollution removal by biosorption.

In the current research, out of the seven species of the red algae collected from the coasts of the Oman Sea, the species of *Gracilaria corticata* red alga was found very effective in heavy metals biosorption. The effect of various parameters on the biosorption rate was investigated.

2. Experimental

2.1. Preparation of algae

Gracilaria corticata (J. Agardh), a local red alga obtained from Oman Sea on the coast of Chabahar, Iran was selected out of seven species collected. The biosorbent was extensively washed by water, dried in the sunlight, and supplementary washed by deionized water in laboratory, dried again and then it was ground in a laboratory blender and sorted by sieving (RETSCH AS-200 models) in the sizes of 250 to 500 micrometer.

2.2. Chemicals

All the used solutions in this study were prepared from laboratory pure reagents. A stock

solution for ^{238}U of 120 mg/L or 0.5 mmol/L concentration was prepared using analytical grade salt of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck Co.). For preparation, a specified quantity of the salt was dissolved in deionized water. pH of the solutions was adjusted using the HCl 0.1M and NaOH 0.1M (Merck Co.).

2.3. Experimental conditions

Batchwise adsorption tests were carried out to evaluate the effect of some parameters on adsorption of uranium ions on this adsorbent. After biosorption in different conditions, algal biomass was filtered through Whatman filter paper, and the supernatant was used for metal analysis by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Varian, model liberty 150 AX turbo). In the batch experiments, Erlenmeyer flasks with volume of 100 mL containing 30 mL of solution with different uranium concentrations were used.

All tests were duplicated, and control samples were used. Different pH of solutions were used: 2, 3, 4, 5, 6 and 7, while the initial concentration of uranium was of 7.5, 15, 30, 60, 90, 120, 238 and 476 mg uranium/L respectively. The samples were shaken during 15, 30, 60, 90, 180, 360, 960, and 1440 min to study the effect of contact time on the sorption capacity and to determine optimal contact time. The effect of biomass dose on the adsorption capacity of *G. corticata* was analyzed using 0.5, 1, 2, 4, 8 and 16 g dried alga/L, respectively. All experiments were performed at the room temperature and Erlenmeyer flasks were agitated on a rotatory shaker at 150 rpm.

2.4. A survey of the results and modeling of the biosorption

The amount of uranium ions adsorbed per unit of unloaded sorbent was obtained by using the (Eq. 1) (Volesky, 1990):

$$q = \frac{v(C_i - C_e)}{m} \quad (1)$$

where: q is the amount of uranium adsorbed onto the unit mass of the adsorbent (mg/g), C_i is the concentration of the metal ions before biosorption (mg/L), C_e is the concentration of the metal ions after biosorption (mg/L), v is the volume of the aqueous phase (L), m is the amount of the adsorbent dry weight(g).

2.5. Biosorption isotherms

Data obtained from the test were fitted with Langmuir and Freundlich models, which describe the performance of adsorption species between liquid and solid phases. Langmuir. Both models were developed for a single-layer adsorption, but the Freundlich isotherm provides no information on the monolayer adsorption capacity directly in contrast to the Langmuir model.

2.5.1. Langmuir model

According to Langmuir isotherm, the sorbent surface encompasses a limited number of adsorption sites, while monolayer adsorption is assumed with no movement of adsorbate in the plane surface. No further sorption can take place at that site once it was filled, so that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved (Aslam et al., 2016; Desta, 2013). This model gives information on the maximum rate of biosorption. The Langmuir model is given by Eq. (2) (Qasim et al., 2018; Volesky, 1990):

$$\frac{X}{M} = \frac{abC}{1+bC} \quad (2)$$

where: C is the residual (equilibrium) metal ion concentration left in solution after binding, X/M is the mass of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g), b is the constant related to the affinity between the biosorbent and sorbate or sorption intensity (L/mg), a is the maximum mass of adsorbate adsorbed per unit mass of adsorbent (mg/g).

The Langmuir model is usually used in linear form as given by (Eq. 3) (Kumar et al., 2010; Qasim et al., 2018; Volesky, 1990):

$$\frac{1}{q} = \frac{1}{q_{max}bCe} + \frac{1}{q_{max}} \quad (3)$$

2.5.2. Freundlich model

The Freundlich model is an empirical one, which assumes a heterogeneous surface available for biosorption. In this model, it is presumed that the most powerful binding sites are filled, firstly, and the rate of the biosorption decreases through increasing the filling degree of sorption sites. The empirical Freundlich equation which describes sorption on a heterogeneous surface is given by Eq. (4), or, in linear form by Eq. (5) (Babalola et al., 2016; Cruz et al., 2004; Kumar et al., 2010; Rybczynska-Tkaczyk and Kornilowicz-Kowalska, 2016; Volesky, 1990):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where: q_e is the mass of the sorbed metal per the biomass weight (mg/g), C_e is the concentration of the metal in solution in the balanced state, K_F is Freundlich constant which shows the sorption capacity, n is the Freundlich constant which shows the sorption intensity of the sorbent.

2.6. Modeling the kinetic of biosorption

There are several models which describe the kinetic of biosorption in discontinuous process, the most applied being the pseudo-first order kinetic model and the pseudo-second order kinetic model.

2.6.1. Pseudo-first order kinetic model

In this model (Eq. 6), it is supposed that the rate of binding sites occupation is proportional with the number of not-occupied sites (Cruz et al., 2004; Saygideger et al., 2005):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where: q_t is the quantity of biosorption in the defined time (mg/g), q_e is the quantity of biosorption in the time of balancing (mg/g), k_1 is the balancing constant of the pseudo-first order reaction.

In its linearized form, $\ln(q_e - q_t)$ is drawn vs. t , and correlation coefficient will be specified.

2.6.2. Pseudo-second order kinetic model

In this model (Eq. 7), it is supposed that the rate of binding sites occupation and the rate of sorption are proportional with the square root of the number of not-filled sites (Cruz et al., 2004; Ho, 2006; Saygideger et al., 2005).

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where: k_2 is the balancing constant of the Pseudo-second order reaction.

In its linearized form, t/q_e is plotted vs. t .

2.7. Thermodynamic parameters

Uranium biosorption studies were carried out at three temperatures: 293, 308 and 323 K to determine some thermodynamic parameters, such as enthalpy change (ΔH°), entropy change (ΔS°) and Gibbs-free energy change (ΔG°) for the system and elucidate sorption mechanism (Aksu, 2002).

The Gibbs-free energy change of the biosorption phenomenon is related to the equilibrium constant by the classic Van't Hoff equation (Eq. 8):

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

where, R is the ideal gas constant having the value as $8.314 \text{ J}\cdot\text{mol}^{-1}$, T is the temperature in K, and K_c° is the standard thermodynamic equilibrium constant.

The thermodynamic equilibrium constant, K_c was determined using Eq. (9):

$$K_c = \frac{C_a}{C_e} \quad (9)$$

where C_a is mg of adsorbent adsorbed per liter, and C_e is equilibrium concentration of solution, mg/L (Sarin et al., 2006).

2.8. Fourier Transform Infrared analysis

To determine the type of algal functional groups and biomass characterization FTIR analysis method was used. Dried *G. corticata* samples used

before and after uranium removal under the optimal conditions was analyzed. This was done by mixing approximately 1 mg dried sample of metal unloaded, and metal loaded *G. corticata* biomass with 5 mg KBr. The mixture was ground to fine powder and pressed under vacuum into pellets. The samples were analyzed in the range 400 cm⁻¹ to 4000 cm⁻¹ wave number using a Bruker spectrophotometer (model Vector 22).

3. Results and discussion

3.1. Screening of the best biosorbent

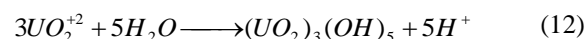
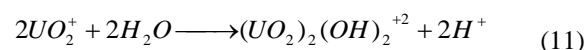
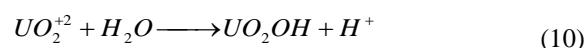
Seven species of the red algae which have been isolated from the coasts of the Oman Sea in collaboration with the Chabahar Fishery Office are as following: *Botriocladia leptopoda*, *Gracilaria arcuata zanardini*, *Gracilaria corticata*, *Hypnea valentiae*, *Melanothamnus somalensis*, *Sarconema filliform*, *Scinaia carnosa*.

In previous researches, it was specified that pH is one effective factor in the rate of biosorption by the algae and the pH of 2; 4 and 6 were found as efficient pH (Abou-El-Souod and El-Sheekh, 2016; Khani et al., 2006). Also, in most of our experimental studies, the maximum biosorption was found for contact time values of 2 to 4 hours and shaking rate of 150 rpm. Similar conditions were reported by other authors, as well (Raff et al., 2003; Saygideger et al., 2005; Volesky, 1990).

To select the best biosorbent we contacted algae biomasses with 0.5 mmol/L uranium solution for 3hr. The suspensions were agitated on a rotatory shaker at 150 rpm, 25°C, and at pH values of 2, 4 and 6, respectively. After the contacting time was over, the maximum rate of biosorption among the species was observed at pH of 4 for *G. corticata* alga (Fig. 1). Therefore, this alga was selected for further biosorption studies study and analysis of the influence of various parameters such as contact time, pH, different biomass values and uranium concentration on the process performance.

3.2. pH effect on uranium biosorption

pH is one of the most effective factors in heavy metals and nuclides biosorption (Chung et al., 2014; Gavrilesco et al., 2009). The metal ion binding in biosorption could be attributed to several mechanisms such as, complexation, ion exchange and micro precipitation. For algae biomass, ion exchange has been considered as the main mechanism responsible for metal sequestering (Bulgariu et al., 2013; Khani et al., 2006). The main mechanism of uranium biosorption is the ionic exchange and the reactions of exchanging the hydrolyzed ions (of UO₂²⁺) are as following:



Active binding sites are affected by pH severely. If they are of the weak acidic or basic type, they are influenced by pH harshly since a competition is to be created between the H⁺ ion and metal ions in the low quantities in order to connect to the sites. However, in this competition, the concentration of the H⁺ ions overcomes the metal ions and occupy earlier the binding sites. On the other hand, at pH<2, uranium appears in form of anionic compounds, which cannot be replaced with the proton of the functional groups available in the surface of algae. At low pH, some binding sites are not available to the divalent UO₂²⁺ ion; therefore, the rate of the metal biosorption decreased.

However, due to the increase of pH, the competitive effect of the positive ions decreases and the action of binding the metal ion to the binding sites takes place better, but declined with a further increase in pH, when uranium appears in the solution as precipitates.

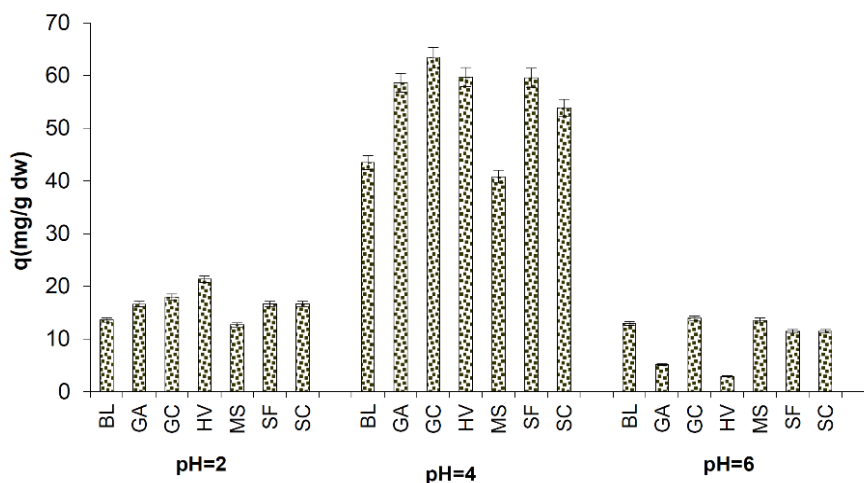


Fig. 1. The capacity of uranium biosorption at the screening stage by the various species of red algae (contact time: 3hrs; biomass:1g/L; U: 0.5 mmol/L)

As seen in Fig. 2, in the higher pH, the rate of the uranium biosorption decreases. At lower pH, the possibility of the biosorption for uranium ions and the process of the biosorption decreased from the reasons mentioned earlier. So, the maximum biosorption was found at pH 4-5, which was selected as optimum pH (Fig. 2).

3.3. Effect of biomass dose on uranium biosorption

Among the factors affecting the rate of biosorption by *G. corticata* alga, the dose of biomass was found as relevant in our experiments. Tests were carried out with various doses of dry algae biomass (0.5, 2, 4, 8 and 16g/L).

As shown in Fig. 3, by increasing biomass value up to 2g/L, the rate of the biosorption increased due to the increasing of the binding sites, but by the excessive increase of the quantity of biomass, the action of the biosorption doesn't perform well and became almost constant due to the disturbance in filling of the binding sites (Kapoor and Viraraghvan, 1995; Marandi et al., 2007, 2010; Raize et al., 2004).

Therefore, sorption capacity does not increased noticeably at biomass doses over 2 g/L.

3.4. Effect of initial uranium concentration on biosorption

The influence of initial concentration of the metal ions in the tested solution was found also relevant for uranium biosorption, in particular by *G. corticata* alga (Dabbagh et al., 2008; Khani et al., 2006; Saygideger et al., 2005; Volesky, 1990; Williams, 1998). The difference of the concentration; between the substance bound to the sorbent, and the substance remained in the solution represent the driving force (potential) of biosorption. Therefore, generating and maintaining this potential for mass transfer, the rate of process could be improved. This action is performed up to a certain limit as a result of increasing metal concentration on the biosorbent surface. Therefore, even though the metal concentration in solution is increased, a noticeable enhancing in the biosorption rate is not observed any more due to the saturation of the biomass surface.

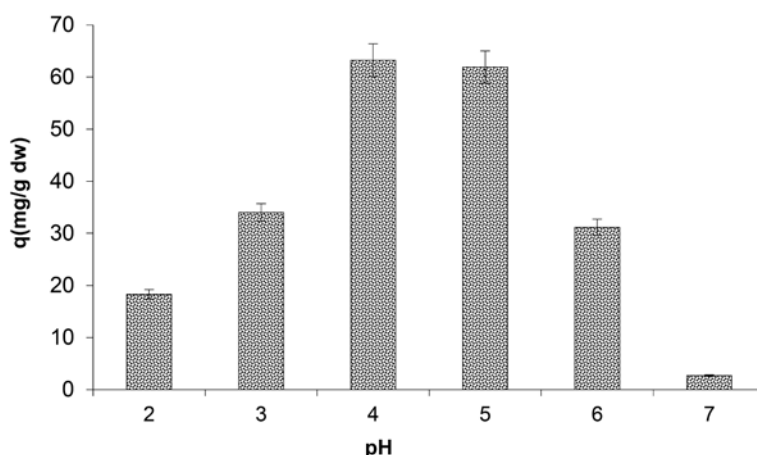


Fig. 2. Effect of pH on the uranium biosorption by *G. corticata* alga (contact time: 3hrs; biomass: 1g/L; U: 0.5 mmol/L; 150rpm)

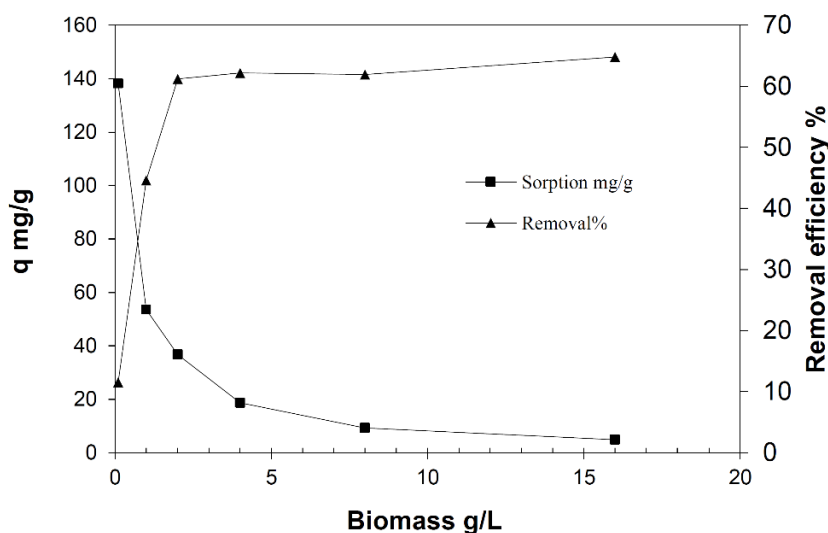


Fig. 3. Effect of the biomass concentration on the uranium biosorption by *G. corticata* alga (pH: 4.5; contact time: 3hrs; U: 0.5 mmol/L)

At low concentrations, sorption sites took up the available metal rapidly. However, at higher concentrations, the metal should diffuse to the biomass surface by intra particle diffusion mechanism. Experiments using aqueous solutions with various concentrations of the uranium (7.5, 15, 30, 60, 90, 120, 238 and 470 mg/L) showed that the maximum rate of biosorption has been observed at the concentration of 238mg/L.

3.5. Effect of contact time on metal removal

Results showed that the optimum agitation time was approximately 180 minutes. In many cases adsorption occurs during the initial 30 to 60 minutes. Increasing the contact time after 180 minutes doesn't have a significant effect on the biosorption capacity, and it is not economically (Fig. 4).

3.6. Biosorption isotherms

The Langmuir and Freundlich model parameters with the correlation coefficients (R^2) for the biosorption of uranium on the selected biosorbent are shown in Table 1. The regression correlation coefficients ($R^2=0.978$) for the Langmuir model show

that the adsorption process of uranium by *G. corticata* alga is well defined by this model. As it has been shown in Table 1, the maximum adsorption capacity (q_{max}) for uranium by the *G. corticata* alga is estimated at 200 mg/g. However, the results from modeling by Freundlich isotherm showed that the equilibrium data fitted very well to this model ($R^2=0.998$).

3.7. Biosorption mechanism

Infrared spectra of *G. corticata* biomass samples before, and after uranium bindings at pH 4.5 are shown in Fig. 5. The difference between the two spectra was seen in the absorbance wave number and intensities. The saturated biomass displayed new absorbance bands in 1635 and 1437 cm^{-1} . These bands showed weak and strong stretching of the carbon-oxygen bonds in the carboxyl groups (Lodeiro 2006; Yang, 2008). Therefore, it results that UO_2^{2+} ions could be bound to the (-C-O) groups and create the structure similar to that from Fig. 6 (Ghasemi et al., 2010; Volesky, 2001, 2003; Williams, 1998). The bands at 1119 cm^{-1} were due to the -C-O stretching of ether. Also, a broad region around 3451 and 2930 cm^{-1} could be related to the stretching bond of -OH and -CH groups (Yang, 2008).

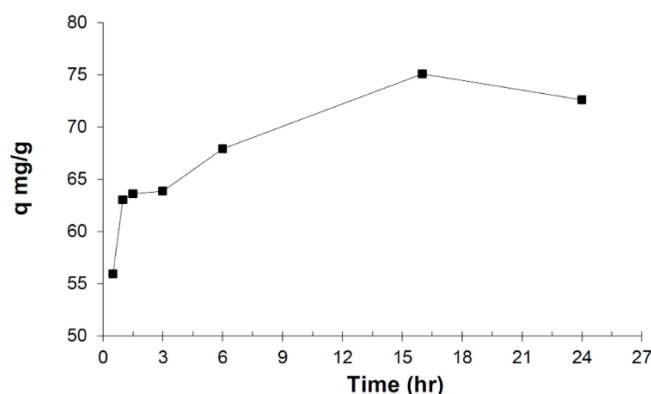


Fig. 4. Effect of the contact time on the uranium biosorption by *G. corticata* alga (pH: 4.5; biomass:1g/L; U: 0.5 mmol/L)

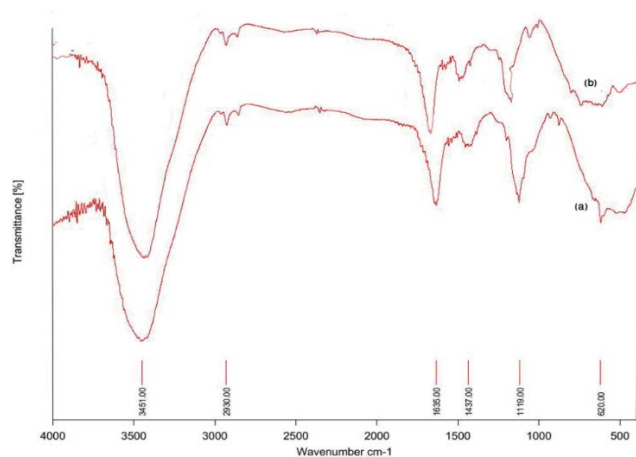


Fig. 5. FTIR spectrum of the natural biomass (a) and the biomass after uranium biosorption (b)

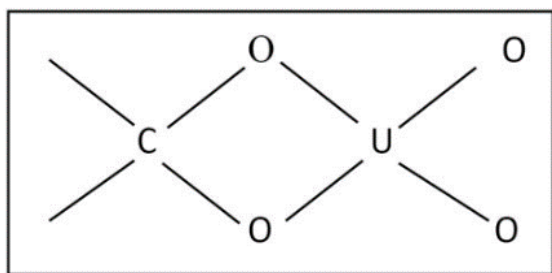


Fig. 6. UO_2^{2+} ions binding to the (-C-O) groups

3.8. Modeling biosorption kinetics

The study of biosorption kinetics was performed based on the results addressing the variation of metal concentration in time. Biosorption kinetics give valuable information on biosorption mechanism. We have applied the two kinetic models: pseudo first order kinetic model and pseudo second order kinetic model. The resulted kinetic parameters are shown in Table 2 and Figs. 7 and 8.

Sorption equilibrium was fulfilled up to 3hrs in this experiment. The kinetic studies demonstrated that

a pseudo-second-order kinetic model fitted the experimental data very well ($R^2=0.999$).

3.9. Thermodynamic studies

To assess the effect of temperature on biosorption performance, experiments were conducted at temperatures of 293, 308 and 323 K (20, 35 and 50°C). The values of enthalpy and entropy changes were calculated from the slope and intercept of the plot $\ln Kc$ versus $1/T$ (Fig. 9). In this experiment the values of ΔG^0 were -0.504, -0.410 and -0.277 kJ/mol at temperatures of 293, 308 and 323K, respectively (Table 3). The values of enthalpy (ΔH^0) and entropy changes (ΔS^0) were found out to be +0.260 KJ/mol and +1.083 J/mol.K respectively. The negative value of ΔG^0 confirms the feasibility of the process and the spontaneous nature of uranium biosorption. The positive values of ΔH^0 for uranium removal showed the endothermic nature and irreversible character of the process. The positive value of ΔS^0 suggests a high degree of disorder at the solid-solution interface during the adsorption process. The decrease in entropy, S^0 , shows that the sorbed ions are stable on the solid surface.

Table 1. Freundlich and Langmuir isotherm parameters obtained for biosorption of uranium by *G. corticata*

Adsorbent	Freundlich isotherm			Langmuir isotherm		
	K_F	n	R^2	q_{max} (mg/g)	b	R^2
<i>Gracillaria corticata</i>	0.72	0.94	0.988	200	0.0051	0.978

Table 2. Comparison between adsorption parameters of Lagergren pseudo-first-order model and pseudo-second-order kinetic model applied for biosorption of uranium by *G. corticata*

Pseudo first order kinetic model				Pseudo second order kinetic model			
T: K; (°C)	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg·min)	q_e (mg/g)	R^2	q_{exp} (mg/g)
293; (20)	0.008	22.39	0.861	0.062	66.67	0.999	66.19
308; (35)	0.15	26.36	0.914	0.080	71.43	0.999	64.77
323; (50)	0.007	27.16	0.941	0.107	62.5	0.998	63.07

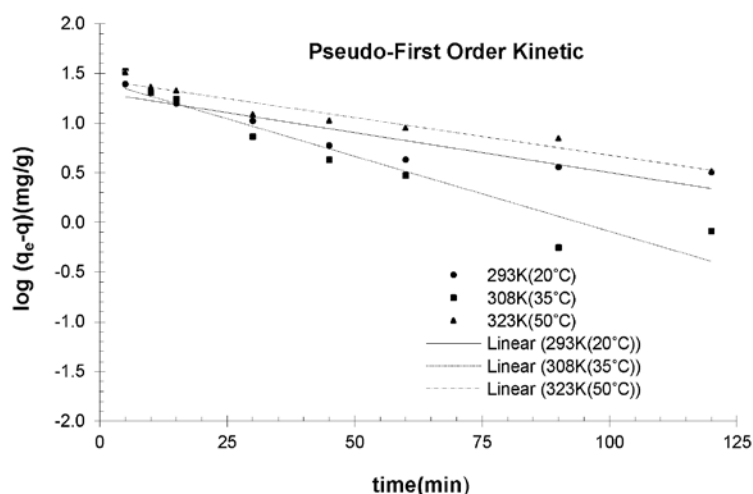


Fig. 7. Pseudo-first order kinetic modeling of uranium biosorption by *G. corticata* alga

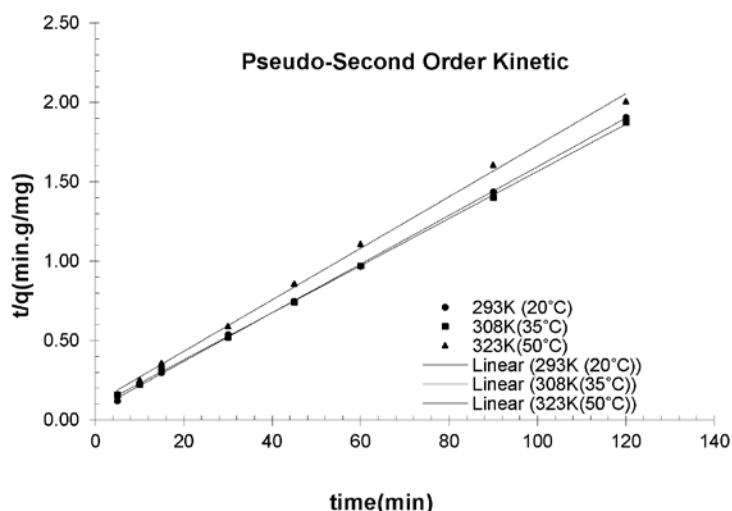


Fig. 8. Pseudo-second order kinetic modeling of uranium biosorption by *G. corticata*

Table 3. Thermodynamic parameters for adsorption of uranium by *G. corticata*

T/ K	$\Delta G^0/ \text{KJ/mol}$	$\Delta H^0/ \text{KJ/mol}$	$\Delta S^0/ \text{J/mol.K}$
293	-0.504	+0.260	+1.083
308	-0.410		
323	-0.277		

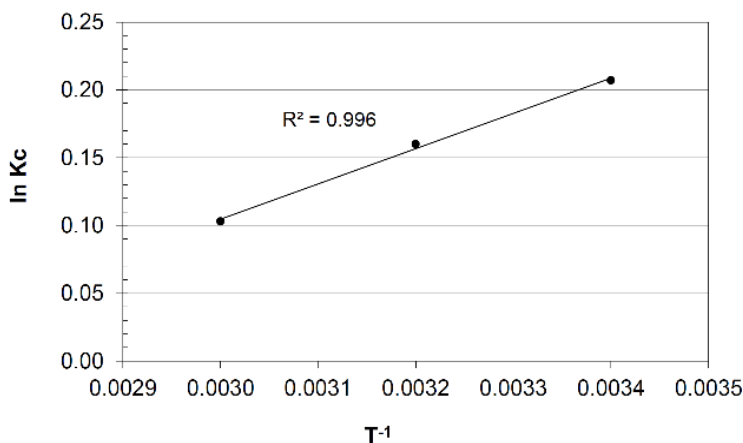


Fig. 9. Plot of $\ln K_c$ versus $1/T$ for the sorption of uranium by *G. corticata*

4. Conclusions

The obtained results demonstrate the effectiveness of the *G. corticata* red alga in the biosorption of uranium. Experimental and maximum adsorption capacities (Langmuir isotherm) were 66.19 mg/g (approx. 53% removal; 1g/L biomass) and 200mg/g respectively. The appropriate pH for uranium biosorption was 4.5, and the maximum capacity of biosorption in this study occurred at 238 mg/L uranium concentration.

Results showed that the uranium biosorption by the *G. corticata* biomass was found to follow pseudo-second order kinetics ($R^2=0.999$) and the adsorption equilibrium data fitted very well to the Freundlich model. This plentiful biosorbent is introduced as a cost-effective candidate to sorption and separation of uranium.

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