Advances in Environmental Research, *Vol. 9, No. 1 (2020) 65-84*
DOI: https://doi.org/10.12989/aer.2020.9.1.065

Optimization of uranium biosorption in solutions by *Sargassum boveanum* using RSM method

Nooshin Hashemi[1], Reza Dabbagh[*2], Mostafa Noroozi[1] and Sama Baradaran[3]

[1]Faculty of Biological Science, Alzahra University, Tehran, Iran
[2]Materials & Nuclear Fuel Research School,
Nuclear Sciences & Technology Research Institute, (NSTRI), Tehran, Iran
[3]Nuclear Sciences & Technology Research Institute, (NSTRI), Tehran, Iran

(Received October 5, 2019, Revised April 4, 2020, Accepted April 7, 2020)

Abstract. The potential use of *Sargassum boveanum* algae for the removal of uranium from aqueous solution has been studied by varying three independent parameters (pH, initial uranium ion concentration, *S. boveanum* dosage) using a central composite design (CCD) under response surface methodology (RSM). Batch mode experiments were performed in 20 experimental runs to determine the maximum metal adsorption capacity. In CCD design, the quantitative relationship between different levels of these parameters and heavy metal uptake (q) were used to work out the optimized levels of these parameters. The analysis of variance (ANOVA) of the proposed quadratic model revealed that this model was highly significant (R^2 = 0.9940). The best set required 2.81 as initial pH(on the base of design of experiments method), 1.01 g/L *S. boveanum* and 418.92 mg/L uranium ion concentration within 180 min of contact time to show an optimum uranium uptake of 255 mg/g biomass. The biosorption process was also evaluated by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models represented that the experimental data fitted to the Langmuir isotherm model of a suitable degree and showed the maximum uptake capacity of 500 mg/g. FTIR and scanning electron microscopy were used to characterize the biosorbent and implied that the functional groups (carboxyl, sulfate, carbonyl and amine) were responsible for the biosorption of uranium from aqueous solution. In conclusion, the present study showed that *S. boveanum* could be a promising biosorbent for the removal of uranium pollutants from aqueous solutions.

Keywords: biosorption; uranium; *Sargassum boveanum*; environmental remediation; wastewater treatment

1. Introduction

One of the most important concerns of the global community is to preserve the environment. The production of waste and disposal in the water has become one of the most important concerns (Varjani *et al.* 2018). Human activities have influenced the environment by producing a huge amount of toxic liquids containing heavy metals, metalloids, radionuclides, and various organic pollutants. Preventing or limiting toxic emissions to the environment is one of the main purposes

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[*] Corresponding author, Ph.D., E-mail: rdabbagh@aeoi.org.ir

http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

of industrial treatment methods. Before discharging pollutants from industrial wastewater into the environment, various physicochemical and biological processes are used to remove these materials. Biosorption is of these processes. It is a physicochemical and non-metabolic process based on several mechanisms including sorption, adsorption, ion exchange, complexation, and sedimentation. By the biosorption process, as a branch of biotechnology, it is tried to remove or recycle organic and inorganic materials from the solution using biological materials such as living or non-living microorganisms and their components, marine algae, plant materials, industrial and agricultural wastes, and natural residues (Fomina & Gadd, 2014). Biosorption is a process that includes solid and liquid phases, in which the soluble species are sorbed. This process is of the benefits such as low cost, high efficiency, and reusable potential (Varjani *et al.* 2018). Some materials can be used as sorbents, of which we can refer to algae, bacteria, fungi, yeast, waste materials derived from agricultural and food industries (Varjani *et al.* 2018). Always excess amounts of heavy metals such as copper, lead, cadmium, nickel, and chromium are drained directly into different soils and waters. The accretion of heavy metals is dangerous for human life and aquatic organisms (Varjani *et al.* 2018). Owing to the accumulation of toxic compounds on the surface, the prediction of water and soil pollution is difficult or impossible (Thiele, 1995). Proper technologies used to remove heavy metals from contaminated environments, including water and soil, are based on physicochemical principles, but the problem with these techniques is their high cost and inadequacy. Thus, biosorption technology, due to its low costs, comfortability and high efficiency, is a proper technique to remove heavy metals from polluted environments (Volesky 1990). Several studies have shown that biosorption is a promising technology for the removal of heavy metals from aqueous solutions. Among microorganisms as good sorbents, algae operate properly thanks to their abundance in fresh and marine waters, their cost-effectiveness, reusability and the high biosorption capacity of metals (He & Chen 2014). Radioactive uranium emissions are generated during the operation of nuclear power plants or related equipment, such as nuclear research laboratories and fuel production plants. Because of radioactivity and high toxicity, uranium is one of the most perilous elements for the environment, and it also causes cancer in humans (Yang & Volesky 1999). Uranium is naturally found in a variety of capacities, but it is fundamentally in the form of hexavalent uranium, uranyl ion (UO_2^{2+}), in solutions with acidic conditions (Kim *et al.* 2011). Uranium can be present in various isotopes such as U-238 (99.27%), U-235 (0.72%) and U-234 (0.01%) (Waseem *et al.* 2015). Pollution with uranium is a threat for water and groundwater at various levels. Consequently, the removal of uranium from nuclear wastes is vital both for the nuclear industry and the environmental cleanup (Gok and Aytas 2009). Various sorbents have been investigated for biosorption of metals, among which algae have many advantages, such as abundance and availability, high strength in metal recovery, producing less toxic sludge and high performance in low concentrations of metals (Dabbagh *et al.* 2018, Kousha *et al.* 2012, Pahlavanzadeh *et al.* 2010, Yu *et al.* 1999). The algae used in this project that were collected from the Persian Gulf is a new brown alga named *S. boveanum*. The cell wall of the brown algae, in which the adsorption occurs, is generally composed of three components: cellulose, which plays a role in its structural strength; alginic acid, which is a polymer of mannuronic acid, guluronic acid and related salts such as sodium, potassium, magnesium, and calcium; and sulfated polysaccharides. Meanwhile, carboxylate and sulfate groups are the dominant active groups in the cell wall of these algae (Romera *et al.* 2007). Along the Persian Gulf and the Oman Sea, the coastal area of Iran is about 1260 kilometers. More than 250 species of algae have been identified in this area (Mehdinezhad *et al.* 2016). On the base of previous screening studies *S. boveanum* alga selected as suitable adsorbent due to more sorption capacity.In addition, the biosorption capacity of brown algae for the removal of various contaminants, such as cadmium, chromium, uranium, and dyes, is well known and very high (Cobas *et al.* 2014). In the present research, the response surface methodology based on central composite design (Sohbatzadeh *et al.* 2016) was used to experimental design and optimization of biosorption of uranium by *S. boveanum*. This method carried out to acquire the most information in the shortest possible time and tools.

2. Materials and methods

2.1 Materials

A stock solution of U (VI) was prepared by dissolving 2 g of $UO_2(NO_3)_2.6H_2O$ (Merck) in a 1000 ml of deionized water. The solution was diluted for different uranium (VI) concentration by deionized water as different required working solutions. The initial pH of each working solution measured and adjusted by addition of 0.1N and 1N HCl and 0.1n and 1N NaOH. In order to adjust the pH in the experiments, the buffer was not used due to the unknown effects of buffering compounds on the biosorption process (Klimmek *et al.* 2001). To determine the final concentration of the working solutions, 65% HNO_3 (Merck) was used.

2.2 Instruments

To determine the desired size of adsorbent, the quern (TEFAL Blender model) and 500µ and 1000µ meshes were used. All experiments were conducted in 100 ml Erlenmeyer flasks. The pH of the solution was measured and adjusted with a pH meter (Metrohm 774, Swiss) or (Metrohm 774, Swiss). A shaker incubator (GALENCAMP, USA) was used for agitating the flasks. At the end of the biosorption process, filter paper (Whatman 41, Sigma-Aldrich, USA) was used to separate biosorbent from solutions. Algal biosorbent dried in an oven (Heraeus, Germany). All of the filtrates were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-AES, Optima, Model 7300 DV). In order to determine the functional groups on the surface of biosorbent contributed in biosorption, the Fourier Transform Infrared (FTIR) spectrometer (Bruker, VECTOR-22) was used. Scanning electron microscope (SEM, ZEISS, Germany) was used for the observation of biosorbent surface before and after of uranium biosorption. For the elemental mapping and characterization of the elemental composition of biosorbent, EDX spectrum of the biosorbent was also depicted.

2.3 Preparation of algal biomass

The brown algae (*S. boveanum*) sample collected from the Persian Gulf and Oman sea was extensively washed with distilled water several times in order to remove salts and then sun-dried. The sample dried in an oven at 60°C overnight to reach a constant weight (Cobas *et al.* 2014). The dried biomass was ground and sieved to a particle size of 0.5-1 mm using the standard test sieves. In this work, the intact biomass of *S. boveanum* because of its high potential in uranium removal was used for the biosorption process.

2.4 Batch biosorption experiments

We performed batch sorption experiments to evaluate the impact of various parameters such as pH, initial uranium concentration, biosorbent dosage and determination of the equilibrium value of each parameter. All experiments were conducted at constant temperature of 30°C, shaking rate of 150 rpm and contact time of 180 min. 100 ml Erlenmeyer flasks containing 50 ml of the metal solution, were used for all experiments. The desired concentration of metal solutions was obtained by further dilutions of the stock solution. The initial pH of solutions was measured with a pH meter and adjusted in desired values by use of HCl and NaOH solutions as already mentioned. After 3 h of agitation, the solutions filtered and separated from the biosorbents by Whatman 41 filter paper and the filtrate samples were analyzed for the residual uranium ion concentration by inductively coupled plasma spectroscopy. Finally, SEM-EDX imaging was used to investigate the changes in the surface of biosorbent before and after uranium biosorption and determination the elemental composition of biosorbent. For the determination of possible functional groups and binding sites participated in metal uptake, the FTIR spectra of biosorbent obtained using FTIR spectrometer between 400 and 4000 cm^{-1}. The amount of metal ions sorbed in an equilibrium state was named as adsorption capacity (q_e) and calculated through Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, C_0 and C_e are the initial and equilibrium concentration of metal ions in the solution in mg/L, V is the volume of solution in L and m is weight of dried biosorbent in g.

2.5 Experimental design using RSM method

Overall, the term of optimization refers to identifying the conditions in which the best possible response can be introduced as a result of a process. The design of experiment (DOE) plays a significant role in optimization of a process using the exclusive and interactive effects of independent variables simultaneously. Among several multivariate techniques, RSM has been used as one of the applicable technique for experimental designs (Sohbatzadeh *et al.* 2016). RSM is an approach which combines various statistical and mathematical techniques to improve a process (Kiran *et al.* 2007). The basis of RSM method is the fit of mathematical models (linear, quadratic, polynomial squares and others) to the experimental results from the designed experiment and ultimately validation of the proposed model using statistical techniques. Process behavior is defined by the following quadratic Eq. (2) (Sohbatzadeh *et al.* 2016):

$$Y = A_0 + \sum_{i=1}^{n} A_i X_i + \sum_{i=1}^{n} A_{ii} X_i^2 + \sum_{i \neq 1 j=1}^{n} A_{ij} X_i X_j + \varepsilon \tag{2}$$

where, Y is the predicted response; X_i and X_j are the independent variables; A_0 shows the constant coefficient; A_i, A_{ii} and A_{ij} demonstrate the interaction coefficients of different linear, quadratic and second-order terms respectively; n indicates the number of independent variables and ε shows the random error. The accuracy of this polynomial model was determined by determined coefficient (R^2). F-value (Fisher variation ratio) and probability value (Prob > F) were used to evaluate the significance of the model (Sohbatzadeh *et al.* 2016). In this research, the RSM method was applied to evaluate the uranium removal process from aqueous solution in order to reach the optimal uptake capacity (q_e) as a desirable response. In order to evaluate the concurrent effect of parameters on the biosorption process and its optimization, the Design-Expert 7.0 (Stat-Ease, Inc) software was used. Three independent variables including pH, initial concentration of U(VI) and biosorbent dosage were coded at five levels: −α, -1, 0, +1 and +α and a design of 20 experiments was employed for this model. The optimized values of the selected variables were calculated by solving the regression equation.

2.6 Isotherm models

Biosorption isotherms were used to describe the biosorption experimental data, biosorption mechanisms, surface characteristics and the biosorbent tendency to radionuclides or heavy metal ions. Creating a proper correlation for equilibrium curves is necessary to optimize the design of a biosorption system for the removal of metals from effluents (Vijayaraghavan *et al.* 2006). Parameters of biosorption isotherms were estimated by linear and nonlinear correlation analysis. In this study, the results obtained from the models were used to determine the best-fitted isotherm to experimental data. Different isotherm models such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and, Flory-Huggins were used to analyze the equilibrium data but among these various methods Langmuir and Freundlich's models were widely used in biosorption processes. U (VI) biosorption of *S. boveanum* isotherms was studied in different initial concentrations of uranium under optimum conditions obtained from the design of the experiment. Four famous isotherm models in biosorption process, including Langmuir, Freundlich, Temkin, and D-R were used to describe and analyze the experimental data. The fitting of isotherm models with biosorption behaviors is characterized by the determined coefficient (R^2) showed in Eq. (3).

$$R^2 = \frac{\sum(q_{e,exp} - \overline{q_{e,cal}})^2}{\sum(q_{e,exp} - \overline{q_{e,cal}})^2 + \sum(q_{e,exp} - q_{e,cal})^2} \tag{3}$$

In the above equation, $q_{e,exp}$ represents the number of uranium ions sorbed on biomass obtained from experimental results, $q_{e,cal}$ shows the number of uranium ions from models, and $\overline{q_{e,cal}}$ indicates the average of $q_{e,exp}$ and $q_{e,cal}$. The value of R^2 can vary from 0 to 1 and if the model predictions are fitted to experimental results the value of R^2 approaches to 1 (Gök *et al.* 2017). The Langmuir model is the most used biosorption isotherm based on the following principles: existence of the fixed and defined binding sites in which biosorptions occur; having the same energy of binding sites for a particular biosorbent (Ngah & Fatinathan 2010), and generally based on the homogeneity assumptions such as availability of binding sites equally, monolayer sorption of metals on the surface of biosorbent and the lack of interaction between sorbed species. The linear and nonlinear forms of this isotherm are as follows in Eqs. (4) and (5), respectively (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \tag{4}$$

$$q_e = \frac{Q_0 b_L C_e}{1 + b_L C_e} \tag{5}$$

In these equations, q_e indicates the amount of sorbed metal ions on the surface of biomass in mg/g, C_e is the equilibrium concentration of uranium in aqueous solution in mg/L, Q_0 in mg/g and b_L in L/mg are the Langmuir constants that indicate uptake capacity and the energy of biosorption, respectively. Q_0 and b_L can be calculated from slope and intercept of linear diagrams of C_e/q_e against C_e. A dimensionless constant, described as a separating factor, in the form of Eq. (6), is the necessary character for Langmuir isotherm and can be calculated to evaluate the desirability of the biosorption process. We define the separating factor as bellow (Langmuir 1918):

$$R_L = \frac{1}{(1 + b_L C_i)} \tag{6}$$

where, b_L and C_i in mg/L are the Langmuir constants of nonlinear regression, respectively. There are four probable values for R_L: $R_L > 1$ for unfavorable adsorption isotherms, $R_L = 1$ for linear biosorption, $0 < R_L < 1$ for the favorable adsorption isotherms and $R_L = 0$ calculate for irreversible biosorption process (Langmuir 1918).

The Freundlich isotherm indicates the heterogeneous adsorption process and the active sites with different energy of biosorption. It is assumed that the strong binding sites are occupied at first and then the power of uptake decrease with the increase of these occupied sites (Gök *et al.* 2017). In general Freundlich isotherm describes multilayer adsorption on a heterogeneous surface with an unequal distribution of adsorption energies (Hui *et al.* 2013). Freundlich isotherm is defined as Eq. (7):

$$q_e = K_F X C_e^{1/n} \tag{7}$$

Freundlich isotherm can be converted to the following linear form of Eq. (8) (Gök *et al.* 2017):

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \tag{8}$$

where, K_F represents the Freundlich constant that shows sorption capacity and the power of biosorption and n_F is the heterogeneity factor related to the intensity and distribution of bonds. The constants of linear Freundlich model can be calculated by plotting the log q_e against log C_e (Gök *et al.* 2017).

The Temkin model is about the linear decrease of the biosorption process heat along with surface coverage and the linear form of this isotherm is represented as follows in Eq. (9) (Yi *et al.* 2016):

$$q_e = BLnA + BLnC_e \tag{9}$$

where, A is an equilibrium parameter that describes the maximum binding energy (L/g) and B is a dimensionless constant corresponding to the temperature and adsorption system (Yi *et al.* 2016).

The D-R model is applied to express information on the nature of biosorption and distinguishes between physical and chemical adsorption (Boparai *et al.* 2011). Generally, this isotherm model shows that the biosorption process occurs onto both homogeneous and heterogeneous surfaces. This isotherm is expressed in an Eq. (10) in a linear form as bellow (Cobas *et al.* 2014):

$$ln\, q_e = \ln q_m - \beta \varepsilon^2 \tag{10}$$

where, q_m denotes the monolayer adsorption capacity (mg/g), β represent the constant related to biosorption energy (mol^2/kJ^2) and ε (J/mg) indicates the Polanyi potential of equilibrium concentration, which can be defined as follows in Eq. (11) (Cobas *et al.* 2014, Yi *et al.* 2016):

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{11}$$

E (kJ/mol) is the mean free energy of biosorption, which is calculated as following Eq. (12) (Huang *et al.* 2010):

$$E = \frac{1}{\sqrt{2\beta}} \tag{12}$$

The range of mean biosorption energy varies from 0 to 8 and from 8 to 16 kJ/mol for physical and chemical biosorption, respectively (Yi *et al.* 2016).

3. Results

Sargassum boveanum is an indigenous macroalga collected from the Persian Gulf on the coast of Bandarabbas, therefore, there is still no research on its sorption capacity for heavy metals. This brown alga due to its similarity with other brown algae in special cell wall structure as well as its high performance in biosorption of uranium in aqueous solutions could be used as one of the best algal sorbents in water, wastewater and liquid nuclear wastes.

3.1 RSM approach for biosorption optimization

The interactive and main effects of process parameters were investigated using central composite design under response surface methodology. The range and level of variables evaluated in this study were selected in order to find the optimum condition for the sorption process that are shown in Table 1.

The central composite design matrix of the coded values with the results of experimental runs is shown in Table 2. A polynomial regression on the basis of the central composite design was performed to show the association between the responses and coded values obtained from the software. The maximum adsorption capacity of metal obtained after 180 minutes has been reported in Table 3 in the form of 20 runs. We introduced the best-fitted data quadratic model in the form of a regression equation:

$$q = -90.36278 + 65.25266pH + 1.23027InitialConc. - 59.00931Biosorbentdosage - 0.030653pH \times InitialConc. + 13.67262pH \times Biosorbentdosage - 0.23380InitialConc. \times Biosorbentdosage - 13.17264pH^2 - 5.92264E\text{-}004InitialConc.^2 + 7.90364Biosorbentdosage^2$$

Statistical significance of the main and interactive effects of variables and quadratic model equation evaluated by analysis of variance (ANOVA) is given in table 4. To evaluate the statistical significance of the model equation, we conducted F-test ANOVA. The amounts of F-values and P-values determine the significance of each coefficient. The large value of F-value and the P-value less than 0.05 revealed the significance of variables in a high level of confidence (Sohbatzadeh *et al.* 2016). As seen in Table 4, the coefficients for the first order effects (A: pH, B: concentration, and C: biosorbent dosage) were highly significant in comparison with interaction terms ($P < 0.0001$). In addition, according to Table 4, the two-second order term A^2 and B^2 and the two interaction terms AC and BC had a significant effect on the biosorption process ($P < 0.05$). Also, the F-value (182.94) with a low probability value ($P < 0.0001$) shows the high capability and significance for this regression model. The goodness of model fitting was also checked by the multiple determined coefficient (R^2) (Marques *et al.* 2013). In this study, the multiple determined coefficient was 0.9940, which revealed that this regression was statistically significant and this model could express a good correlation between the responses and independent variables and only 0.6% of total variations was not explained by this model. The predicted multiple determined coefficient value (pred. $R^2 = 0.9644$) is in reasonable agreement with adjusted multiple determined coefficient value (adj. $R^2 = 0.9885$). The value of adj. R^2 shows that only less than 1.15% of the variations could not explain by this model (Ding & Sartaj 2015). In addition, a relatively smaller

Table 1 Levels and ranges of independent variables

Independent variables	Range and level				
	-α	-1	0	+1	+-α
pH (A)	2.00	2.8100	4.00	5.1900	6.00
Initial uranium ion concentration, mg/L (B)	100	181.08	300	418.92	500
S. boveanum dosage, g/L (C)	0.50	1.0100	1.75	2.4900	3.00

Table 2 Experimental design matrix for three variables based on central composite design (CCD)

Experimental Run	Variables						Response *q*(mg/g)
	Coded values			Real value			
	A	B	C	A	B	C	
1	+α	0	0	5.19	418.92	2.49	75.000
2	-1	-1	+1	6.00	300.00	1.75	25.710
3	0	0	0	4.00	300.00	1.75	132.28
4	-1	-1	-1	5.19	418.92	1.01	167.24
5	+1	-1	+1	4.00	100.00	1.75	47.420
6	-1	+1	_1	4.00	300.00	1.75	136.28
7	0	0	0	4.00	300.00	1.75	123.71
8	0	0	0	2.81	418.92	1.01	255.00
9	0	0	+α	5.19	181.08	2.49	40.000
10	+1	+1	+1	4.00	300.00	1.75	134.00
11	+1	+1	-1	4.00	300.00	3.00	89.500
12	0	0	0	4.00	500.00	1.75	170.00
13	+1	-1	-1	4.00	300.00	0.50	200.00
14	0	+α	0	2.81	181.08	1.01	120.00
15	-α	0	0	4.00	300.00	1.75	135.71
16	0	0	0	2.81	418.92	2.49	120.00
17	0	-α	0	4.00	300.00	1.75	134.85
18	0	0	- α	5.19	181.01	1.01	44.000
19	-1	+1	-1	2.00	300.00	1.75	133.71
20	0	0	0	2.81	181.08	2.49	62.800

Table 3 Observed and predicted values

Run no.	Actual values	Predicted values	Residual
1	75.000	73.05	1.95
2	25.710	29.300	-3.59
3	132.28	132.78	-0.50
4	167.24	159.78	7.64

Table 3 Continued

Run no.	Actual values	Predicted values	Residual
5	47.420	40.460	6.96
6	136.28	132.78	3.50
7	123.71	132.78	-9.07
8	255.00	253.02	1.98
9	40.000	41.440	-1.44
10	134.00	132.78	1.22
11	89.50	86.640	2.86
12	170.00	177.72	-7372
13	200.00	203.63	-3.63
14	120.00	121.40	-1.40
15	135.71	132.78	2.93
16	120.00	117.96	2.04
17	134.85	132.78	2.07
18	44.000	45.500	-1.50
19	133.71	130.89	2.82
20	62.080	69.000	-6.92

Table 4 Regression analysis using response surface quadratic model

Source	Degrees of freedom	Sum of squares	Mean square	F-value	Prob>F
Model	9	62757.61	6973.070	182.94	<0.0001
A	1	12457.81	12457.81	326.83	<0.0001
B	1	22743.09	22743.09	596.66	<0.0001
C	1	16520.88	16520.88	433.42	<0.0001
AB	1	150.3400	150.3400	3.9400	0.0751
AC	1	1168.380	1168.380	30.650	0.0002
BC	1	3416.340	3416.340	89.630	<0.0001
A^2	1	5001.250	5001.250	131.21	<0.0001
B^2	1	1011.030	1011.030	26.520	0.0004
C^2	1	274.7300	274.7300	7.2100	0.0229
Residual	10	381.1700	38.12000	-	-
Lack of Fit	5	272.0600	54.41000	2.4900	0.1694
Pure Error	5	109.1200	21.82000	-	-
Total	19	63138.78	-	-	-

value of the coefficient of variance ($CV = 5.26$) shows the reliability and good precision of the experiments done (Ghorbani *et al.* 2008).

3.2 Interactional effect of pH and initial concentration of metal ion on the metal uptake

The effect of pH and initial uranium ion concentrations with the interaction of these factors is shown in Fig. 1. The adsorption capacity of uranium is strongly affected by the pH of the solution. This behavior is due to the effect of pH on the distribution of hexavalent uranium species in solution and protonated state of functional groups on the surface of biosorbent (Marques Neto *et al.* 2013). By adjusting the pH on 2, a small amount of metal uptake was reported. This behavior was due to the uranium ions competition which is in the forms of UO_2^{2+} in solution and hydrogen ions for the binding sites located on the surface of biosorbent, and also due to the electrostatic repulsion between protonated structural groups and metal cations (Liu *et al.* 2013). A notable increase in uptake capacity was observed with the increase of solution pH ranging from 2.5 to 3.5 as well as metal ion concentrations ranging from 100 to 420 mg/L simultaneously. In other words, metal uptake increased by increasing initial metal ion concentration. Maximum uptake capacity of uranium was seen in the initial solution pH of 2.81 and initial uranium concentration of 418.92 mg/L. By increasing the pH, the surface charge of biosorbent became less positive due to deprotonation of binding sites which finally led to electrostatic interaction of uranium ions and biosorbent surface (Han *et al.* 2006). In fact, in the higher concentration of metal ions in the solution, the active sites of *S. boveanum* are surrounded by more metal ions and the biosorption process occurs more. Hence, the uptake capacity of metal ions (q) will increase by increasing the initial metal ions concentration. In the biosorption process of uranium by *S. boveanum*, low variation of uptake capacity was observed in pH ranging from 2.81 to 4. However, by increasing the pH to 5, the amount of uptake capacity decreases and the uptake capacity will be lower in pH 6 because of partial possible precipitation of $UO_2(OH)_2$ (Naeem *et al.* 2017).

3.3 Interactional effect of pH and biosorbent dosage on the metal uptake

Fig. 2 shows the effect of biosorbent dosage and the pH of the aqueous solution and the interaction of these two factors on uptake capacities value. It is obvious that the lower amount of biosorbent dosage leads to more uptake of metal ions due to more interaction of adsorbate to the binding sites until these binding sites are unsaturated. The results show that the adsorption capacity at higher biosorbent dosage decreases because of the presence of more binding sites on the surface of biosorbent. Consequently, the number of available binding sites for metal ions will increase and distribute in more surface sites of biosorbent (Ahmad *et al.* 2012). In this study, by increasing the biosorbent dosage ranging from 1 to 3 g/L the amount of metal uptake decreased and the optimum value of this factor was reported to be 1.01 g/L. This may be explained by increasing the availability of binding sites at lower biosorbent dosage. By the increase in biosorbent dosage, the binding sites located at the cell surface remain unsaturated during the biosorption reaction (Zou, Han, Chen, Shi, & Hongmin, 2006). It means that the higher values of uranium ions uptake are obtained by the increase in initial solution pH to 2.81 and decrease in biosorbent dosage to 1.01 g/L, simultaneously.

3.4 Interactional effect of biosorbent dosage and initial metal ion on the metal uptake

We have shown the association between initial metal ion concentration and biosorbent dosage in Fig. 3. In this figure, pH is an actual factor that was set on 2.81. By the increase in initial uranium concentration, the values of metal uptake increase that is due to an increase in driving force of

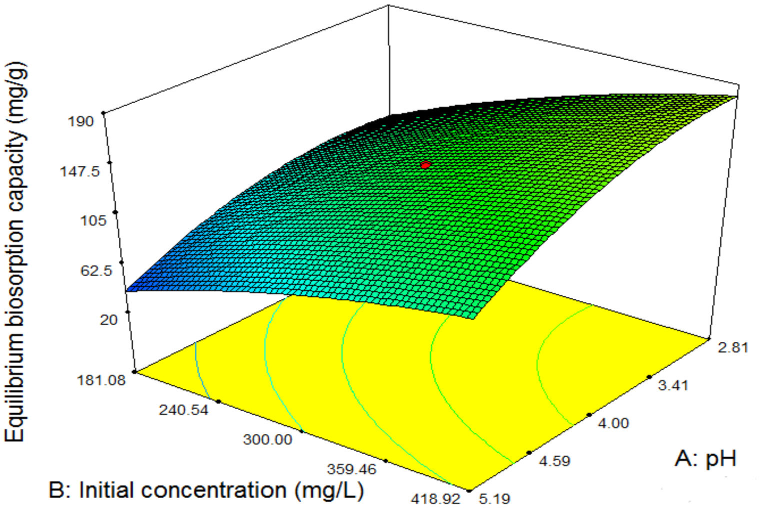


Fig. 1 Response surface plot indicating the effect of pH and initial uranium ion concentration on the metal uptake (*q*)

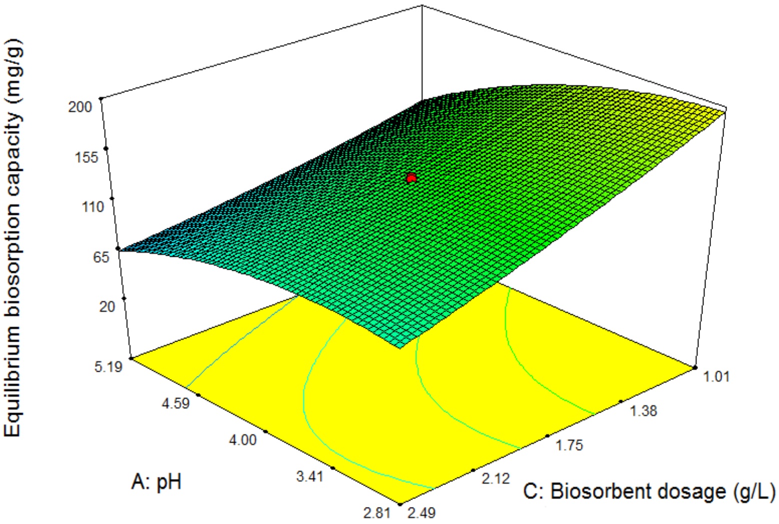


Fig. 2 Response surface plot indicating the effect of pH and biosorbent dosage on the metal uptake (*q*)

concentration gradient ratio to the initial metal ion concentration which ultimately overcomes the mass transfer resistance and occupies the binding sites located on the surface of biosorbent (Mirzabe & Keshtkar 2015). Higher values of binding sites ratio to the initial metal ion concentrations are obtained in lower values of biosorbent dosage and higher values of initial concentration of uranium ions (Sağ & Kutsal 1996). According to Fig. 3, by an increase in biosorbent dosage, the uptake capacity of U (VI) ion per unit mass of biosorbent (q_e, mg/g) decreased. An increase in biosorbent dosage can lead to increase in biosorbent surface area and available binding sites. However, with increasing the biosorbent dosage, the values of uptake

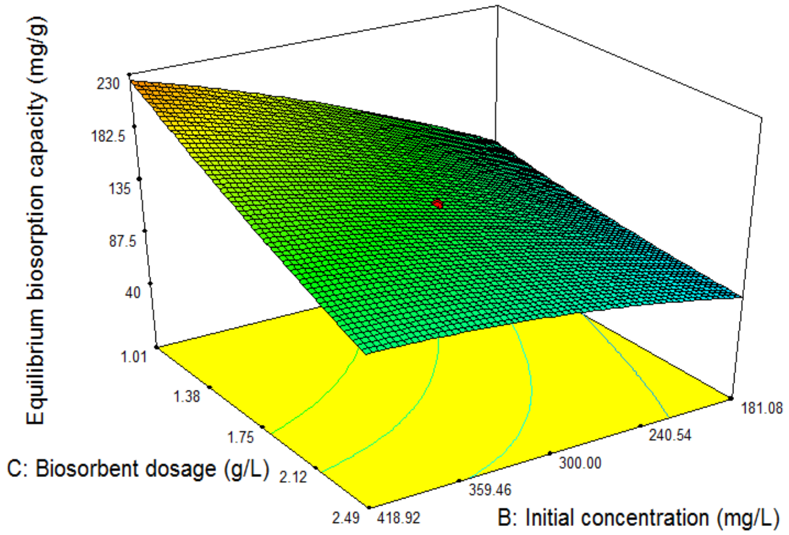


Fig. 3 Response surface plot indicating the effect of biosorbent dosage and initial uranium ion concentration on the metal uptake (q)

capacity (q_e) decreased. The reason for this feature lies in the adsorption sites, which remain unsaturated during the biosorption reaction whereas the number of available sites for adsorption reaction increases by increasing the biosorbent dosage (Vasudevan *et al.* 2002).

3.5 Biosorption isotherms

The results of uranium removal by *S. boveanum* in different equilibrium concentrations have been shown in Figs. 4-7. Biosorption of metals may be affected by various physical or chemical factors. In order to understand the biosorption mechanism and the surface characteristics of biosorbent, the mathematical models expanded by Langmuir, Freundlich, Temkin as well as D-R were applied to experimental data showed in Table 5. In addition, the determined coefficients (R^2) and isotherm constants for linear equations of mentioned isotherms are represented in Table 5. Based on R^2 values, maximum biosorption capacity for Langmuir model was found to be 500 mg/g at 30℃. Thus, in comparison with other isotherm models, the Langmuir isotherm model shows the best-fitted values (R^2 = 0.9077). This model was able to describe the relationship between the amount of sorbed metal ions and the equilibrium concentration of them in the solution. In other words, on the surface of *S. boveanum* distribution of uranium ions in monolayer form were taken place on the homogenous binding sites. The equilibrium state is achieved, when this monolayer is entirely saturated (Sohbatzadeh *et al.* 2016). The affinity for binding sites on the surface of *S. boveanum* with a value of 0.046 shows the strong association between surface binding sites of *S. boveanum* and uranium ions. The regression coefficient for Freundlich model is 0.8763. The values of Freundlich model parameters K_F and n were calculated to be 36.14 and 1.7, respectively. The "*n*" values greater than 1 show the good intensity and favorability of U (VI) biosorption onto *S. boveanum* under studied conditions. The "*n*" parameter can be introduced as 1/*n* indicating the degree of surface heterogeneity. A smaller 1/*n* value represents more heterogeneity of the biosorbent surface while a value closer to or even one indicates a biosorbent with more

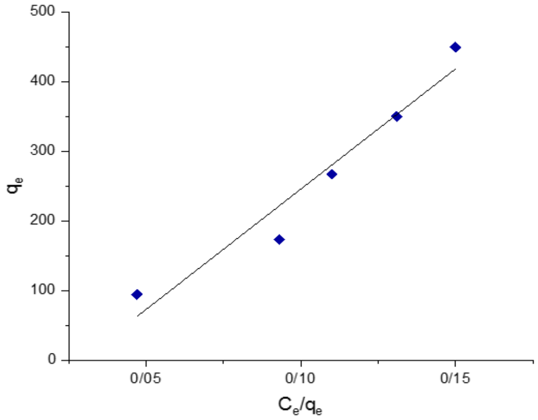


Fig. 4 Langmuir isotherm of uranium biosorption by *S. boveanum*

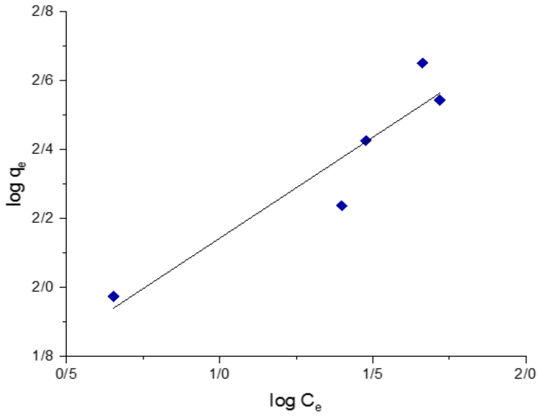


Fig. 5 Freundlich isotherm of uranium biosorption by *S. boveanum*

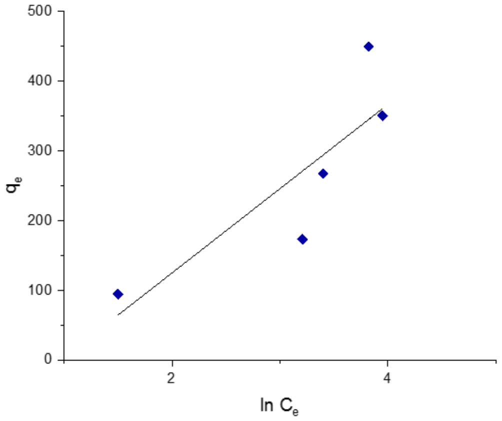


Fig. 6 Temkin isotherm of uranium biosorption by *S. boveanum*

homogenous binding sites (Sohbatzadeh *et al.* 2016). The obtained 1/*n* value for *S. boveanum* was equal to 0.58, indicating the homogeneity of *S. boveanum* binding sites for the biosorption of U

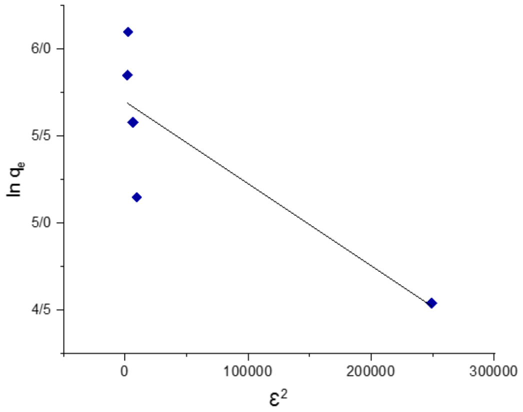


Fig. 7 D-R isotherm of uranium biosorption by *S. boveanum*

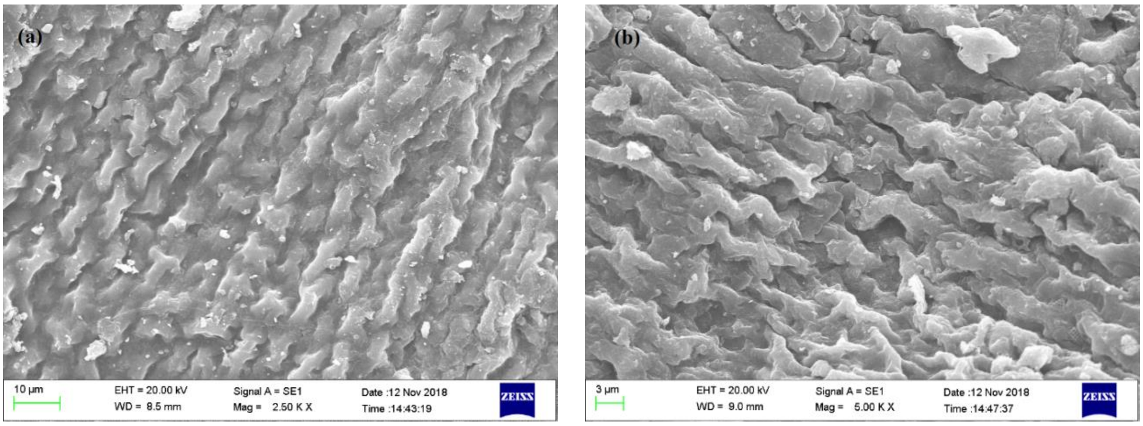
Table 5 Isotherm constants of Langmuir and Freundlich for the uranium biosorption by *S. boveanum*

Model	Parameter	Value
Langmuir	Q_0 (mg/g)	500.00
	b (L/mg)	0.0460
	R^2	0.9077
Freundlich	K_F (mg/g)	36.140
	n	1.7000
	R^2	0.8763
Temkin	A (L/mg)	0.3800
	B	120.78
	R^2	0.7174
D-R	q_m (mg/g)	298.44
	B (mol^2/kJ^2)	5 x 10^{-6}
	E (kJ/mol)	0.3000
	R^2	0.6982

Table 6 Comparison of the uranium maximum adsorption capacity with different sorbents

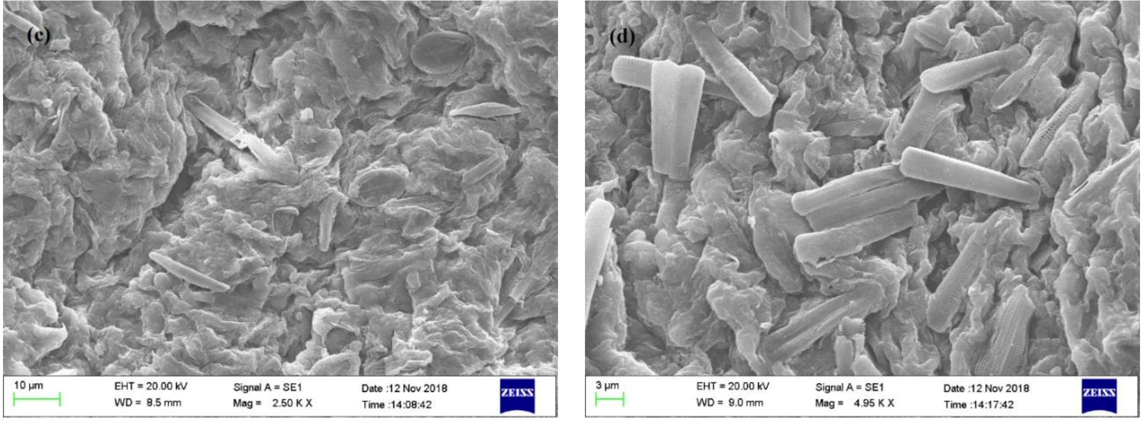
Bisorbent type	Maximum absorption capacity, q_{max} (mg/g)	References
Algae		
Sargassum boveanum	500.0	Current research
Clorella vulgaris	14.30	(Vogel *et al.* 2010)
Sargassum fluitans	560.0	(Yang *et al.* 1999)
Scenedesmus obliquus	75.00	(Zhang *et al.* 1997)
Padina sp.	434.8	(Hanssan Khani *et al.* 20111)
Cystoseira indica	256.0	(Anayurt *et al.* 2009)

(VI) (Ngah & Fatinathan 2010). The figure for R^2 for Temkin and D-R models increased to 0.7174



(a) The surface of *S. boveanum* before adsorption of uranium with 2500 magnification

(b) The surface of *S. boveanum* before adsorption of uranium with 5000 magnification



(c) The surface of *S. boveanum* after uranium adsorption with 2500 magnification

(d) The surface of *S. boveanum* after uranium adsorption with 5000 magnification

Fig. 8 Micrographs of a scanning electron microscope

and 0.6982, respectively. Moreover, we estimated the values of A, B of Temkin isotherm and q_m and β of D-R isotherm by the plots shown in Fig. 6 and 7. We also estimated the E value for D-R isotherm to be 0.3 kJ/mol, indicating a physiosorption process. The maximum adsorption capacity of different sorbents shown in Table 6.

3.6 Biosorbent characterization

Figs. 8(a) and 8(b) show the scanning electron microscopy image of the surface of *S. boveanum* before biosorption of uranium at 2500× magnification and at 5000× magnification, respectively. Figs. 8(c) and 8(d) show SEM image of *S. boveanum* after uranium sorption at 2500× magnification and at 5000× magnification, respectively. As we can see from figures, the surface of *S. boveanum* has different morphologies. The surface of *S. boveanum* shows branched and porous fibrillar matrix before the biosorption of uranium. After biosorption, the regular fibrillar matrix deformed and new small filaments were observed. This porous matrix related to the alginic acid

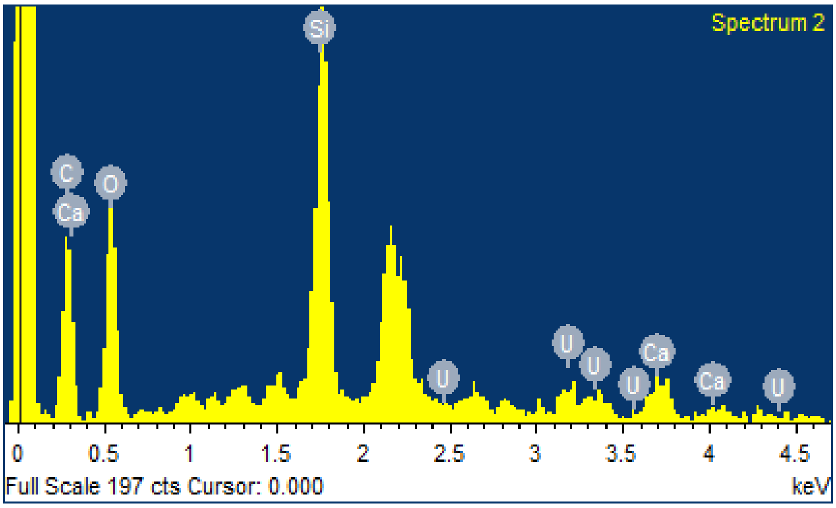


Fig. 9 EDX analysis of uranium bounded to the *S. boveanum* surface

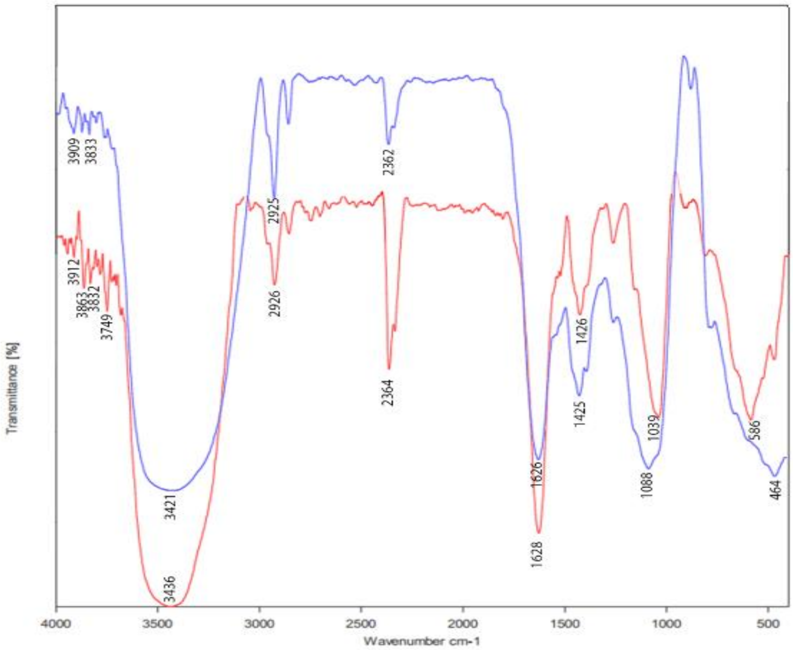


Fig. 10 FTIR spectra of *S. boveanum* before and after of biosorption

might enable the uranyl ions to easily infiltrate and be adsorbed. So, this porous matrix is a very suitable place for the sorption of uranium ions and may proceed faster action of biosorption. Fig. 9 presents an EDX analysis, indicating the presence of uranium bounded to the surface of *S. boveanum*. To realize the nature of functional biomolecules located in the biomass and involved in the biosorption of metals, FTIR analysis of the sorbent before and after the biosorption process was used. The FTIR spectra in the range of 4000-400 cm^{-1} for both raw and saturated biosorbents are shown in Fig. 10. The intense broad absorbance from 3600 to 3200 cm^{-1} is attributed to the hydrogen groups of O-H stretching modes of vibration in hydroxyl, alcohols functional groups and N-H stretching vibrations of amines and amides. Moreover, the 2925 and 2854 cm^{-1} bands can be assigned to C-H, -CH, $-CH_2$ and $-CH_3$ methyl groups stretching vibrations (Sohbatzadeh *et al.* 2016). The biosorption peaks at 1626 and 1425 cm^{-1} can be assigned to the carboxylate ions (-COOM) (He & Chen 2014). The 1088 cm^{-1} band could correspond to C-O stretching vibration modes in sulfur, phosphorous and alcoholic groups. After biosorption of uranium, the FTIR spectrum of *S. boveanum* shows the changes in some of the peaks wavenumber and intensity. The adsorption intensity at 2925, 1626, 1425, 1088 cm^{-1} enhanced and shifted to 2926, 1628, 1426, 1039 cm^{-1} respectively. Ultimately, there are different functional groups participated in biosorption of uranium by *S. boveanum* such as hydroxyl, carboxyl, methyl and amine groups. The band appeared at 1425 cm^{-1} is due to alginates in brown algae. Alginate is a polysaccharide containing α-L-guluronic and 1,4-β-D-mannuronic acids (Castro *et al.* 2017). After interaction with uranium, this band shifted from 1425 cm^{-1} to 1426 cm^{-1}, suggesting that carboxylate groups have clearly participated in the binding of uranium ions to the biomass. It is noteworthy that after the biosorption process, the peak at 1088 cm^{-1} shifted to 1039 cm^{-1}. This bound assigned to the stretching vibration of C=S bound of sulfonic acid. Sulfonic acid participated in the formation of fucoidan. This compound also plays an important role in metal biosorption.

4. Conclusions

The purpose of the present study was to find out and optimize the uranium adsorption capacity of a new biosorbent *S. boveanum*. This study demonstrated that the use of central composite design through determining the conditions led to high metal uptake from aqueous solution. The obtained results of the uranium removal in an aqueous solution using *S. boveanum* showed a decrease of uptake capacity at low and high values of initial pH. An optimum condition for uranium uptake of 255 mg/g biomass was achieved with RSM approach under Design-Expert software at initial uranium ion concentration of 418.92 mg/L, pH 2.81(on the base of design of experiments method) and *S. boveanum* dosage of 1.01 g/L. The findings also showed that the metal removal decreased with increasing biosorbent dosage. The fit of the model proposed by RSM was checked by the multiple determined coefficient (R^2). In this case, the value of the multiple determined coefficient ($R^2 = 0.9940$) indicated that this model was able to predict uranium biosorption experimental data to determine the optimal condition and only 0.6% of the variation was not explained by this model. Statistical analysis showed that all applied independent variables (pH, the initial concentration of U (VI) and biosorbent dosage) in this process were significant. The FTIR spectroscopy confirmed that different functional groups and binding sites such as; carboxyl, sulfate, hydroxyl, amine and methyl groups participated in uranium biosorption. Among these groups, carboxyl and sulfur groups were the most groups participated in this process. Equilibrium data were well fitted to Langmuir isotherm due to higher values of R^2 from Langmuir isotherm over R^2 values for other applied isotherms. The higher value of R^2 and maximum uptake capacity of 500 mg/g obtained from Langmuir isotherm supports the use of this brown alga for uranium and other heavy metals removal in the wastewater treatment system. In addition, due to naturality of *S. boveanum* and its abundance, this sorbent may be used as a low-cost source for heavy metals removal from waters, wastewaters and liquid nuclear wastes and it could be an alternative sorbent to more costly sorbents such as activated carbon and methods like solvent extraction and membrane technologies. Further research is necessary to clarify competitive ion’s effect on the sorption capacity. Also, more investigations such as real uranium-bearing liquid waste and so column test needed to use this kind of adsorbent in practical situations.

Acknowledgments

The research described in this paper was financially supported by the Biological Science department of Alzahra University and the Nuclear Sciences & Technology Research Institute of Tehran and INFPPC.

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