

# Investigation of uranium biosorption from aqueous solutions by *Dictyopteris polypodioides* brown algae

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**Abstract** The biosorption of uranium from aqueous solutions by *Dictyopteris polypodioides* brown algae was investigated. The effect of pH, uranium concentration, mass of the adsorbent, temperature and contact time on the removal efficiency were studied and the results were simulated by Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. Kinetics data could be satisfactorily reproduced by the pseudo-second order equation and thermodynamic parameters were determined in order to evaluate the uranium uptake behavior. SEM/EDS and FT-IR were additionally used to characterize the algae and comprehend the sorption process which can be described as a combination of several mechanisms, including physical sorption, ion exchange and complexation.

**Keywords** Uranium · Biosorption · Brown algae · Isotherms · Kinetics

## Introduction

Uranium is a naturally occurring radioactive element with an average concentration in earth's crust of about 3 ppm and constant uranium concentration of about 3 ppb in oceans. Natural uranium is a mixture of three isotopes:

$^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ . The most common isotope is  $^{238}\text{U}$ ; it makes up about 99 % of natural uranium by mass. The EPA classified natural uranium or depleted uranium with respect to carcinogenicity because in general, uranyl is considered to be more chemically toxic as a heavy metal than as a radioelement [1–6].

Uranium, as it is known, is associated with mine and mill sites, also occurs naturally at elevated levels in rock, soil, surface water, and groundwater. On the other hand, the nuclear power production, the utilization of phosphate fertilizers, copper metallurgy, military activities and production of conventional energy have resulted in the generation of significant amounts of radioactive wastewater containing uranium with tremendous environmental impact. Removal of uranium from such large volumes of wastewaters will require a cost effective remediation technology [7–9].

The uranium removal from aqueous media can be performed through various processes, such as ion exchange, complexation, chemical precipitation, membrane separation, adsorption using both natural and synthetic sorbents, bio-accumulation and biosorption [10–15]. Biosorption has attracted a significant focus in recent years and can be regarded as an innovative technology replacing conventional processes for remediating metal pollution in wastewaters, because it offers several advantages, such as low operating cost, high sorption capacity, easy regeneration, high efficiency in dilute effluents detoxification, minimal volume of disposable sludge and high environmental viability [16–18]. Biosorption is a term that describes the removal of heavy metals by the passive binding to non-living biomass from an aqueous solution. This implies that the removal mechanism is not metabolically controlled. Biosorption occurs through interaction of the metal ions with functional groups found in the cell wall

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biopolymers (e.g. alginate) of either living or non-living organisms. Although both living and non-living forms of biomass exhibit relatively high affinities to heavy metals, the use of dead biomass for metal sequestration and immobilization is more advantageous because there are no toxicity concerns, no requirements of growth media or nutrients and there are easy techniques to desorb contaminants from the biomass and reuse them [19–21].

Many types of biosorbents (i.e. fungi, bacteria, yeasts, sea vegetables) were recently investigated for their ability to sequester heavy metals from diluted aqueous solutions [22–30]. Sea vegetables are algae that mainly come from marine environment. Marine organism, such as seaweed is well known to concentrate metals and in some cases has been used as monitor of seawater pollution. Marine algae proliferate ubiquitously and abundantly in the littoral zones of world oceans, they are rather stable and fast growing [16–18, 31–34].

*Dictyopteris polypodioides*, which is used as biosorbent in the present work, is a species of brown algae most commonly found at low water and shallow subtidal [35]. It is widely distributed and locally abundant in summer period. The aim of the present work was to investigate the interaction of the brown algal sample *Dictyopteris polypodioides* with uranium aqueous solutions. Batch experiments have been performed to explore uranium biosorption properties of this brown marine macro algae. Aiming in development of low cost—high efficiency water treatment technologies related to (radio) toxic metal ion removal, various parameters (e.g. pH, uranium concentration, mass of the adsorbent, temperature and contact time) have been studied and thermodynamic parameters (e.g.,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) have been evaluated. The effect of the above parameters on the biosorption is of fundamental importance for the assessment of the chemical behavior of uranium in aquatic systems. Furthermore, emphasis is given to understand the mechanism of the U-biosorption on brown algae by application of complementary characterization techniques (SEM/EDS, FT-IR).

## Materials and methods

### Materials

All reagents used in the experiments were of analytical grade (AR). Ultra pure water prepared with a water purification system (Millipore Model) including Elix and Mili-Q was used in the experiments. A stock solution of 1000 mg/L of uranium was prepared from  $[\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$  (Merck) by dissolving the salt in pure distilled water. Diluted solutions were prepared from the stock solution at room temperature in pure distilled water. The

pH of each test solution was adjusted to the required value with 0.1 M  $\text{HNO}_3$  solution and  $\text{Na}_2\text{CO}_3$  powder in the beginning of all experiments.

*Dictyopteris polypodioides* samples, e.g. brown marine macro algae, were collected by hand at the depth of 1.0–1.5 m of Izmir Bay Aegean Sea (Turkey). For the sorption studies, harvested fresh macro algae samples were rinsed with tap water, washed intensively with distilled water to remove the salts (sodium, potassium, magnesium and calcium) and then dried at 40 °C for 24 h. The dry biomass was grounded and sieved by a British standard mesh (<125  $\mu\text{m}$ ) sieve. The sieved biomass sample was then stored in polypropylene container in a desiccator.

### Instrumentation

The surface of the biosorbent was examined, before and after the sorption procedure, by scanning electron microscopy (SEM) using the JEOL JSM 840A electron microscope equipped with an energy-dispersive X-ray (EDS) INCA micro-analytical system (operating conditions: accelerating voltage 20 kV, probe current 45 nA and counting time 60 s, with ZAF correction being provided on-line). A JEOL JEE-4X vacuum evaporator was used for coating of the samples with carbon before the examination. A Thermo Scientific Nicolet 6700 FT-IR spectrometer was applied to record the FT-IR spectra. The point of zero charge was also determined using a solution of  $\text{KNO}_3$  (pH region 2–11).

Uranium (VI) concentration was determined by UV–Vis spectrophotometer (Shimadzu UV–Vis 1601 Model). The biosorption experiments were carried out by batch technique using a thermostatic shaker bath GFL–1083 Model. WTW InoLab series pH–720 Model pH meter was used to adjust and measure the pH of samples. A Binder Model oven was used to dry the samples.

### Biosorption experiments

The biosorption of uranium on the brown macro algae was investigated in batch experiments. The effects of the initial pH of the solution ( $\text{pH}_{\text{init}}$ ), initial uranium concentration, biomass dosage, contact time and temperature were studied in order to investigate the removal process of uranium from aqueous solutions. 0.01 g of the biosorbent was contacted in polyethylene flasks in a shaking bath with 10 mL of uranium solution ( $C_{\text{init}}$  10–250 mg/L). After separation of the solid and liquid phase by filtration (125 mm  $\varnothing$ ), the equilibrium pH was measured and the uranium concentration in the supernatant was photometrically determined using the TOPO-DBM (trioctyl phosphine oxide and dibenzoyl methane)-pyridine method at 405 nm [36]. The amount of sorbed uranium (VI) was calculated from the

difference between the initial and the equilibrium concentration of uranium in aqueous solutions. The obtained data were used to calculate the quantity of uranium removed per unit mass of the sorbent in mg/g, as well as the biosorption percentage (%) and distribution coefficient ( $K_d$ ) (mL/g). The uranium uptake data were modeled using the Langmuir, Freundlich and Dubinin–Radushkevich isotherm equations whereas the kinetics data using the pseudo-first and pseudo-second order equations [13, 37–41].

The results were expressed as biosorption percentage (%) and distribution coefficient ( $K_d$ ) (mL/g), which were calculated by using the following equations:

$$\text{Biosorption (\%)} = \frac{C_i - C_e}{C_i} \times 100. \tag{1}$$

$$K_d = \frac{C_i - C_e}{C_e} \times \frac{V}{m} \text{ (mL/g)}. \tag{2}$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of uranium (mg/L) in solutions, respectively.  $V$  is the volume of the aqueous phase (mL), and  $m$  is the weight of the biosorbent (g). All experiments were conducted in triplicates and the relative errors of the data were less than 5 %. Precipitation or sorption of uranium on the walls of polyethylene flask was found to be negligible as determined by running the blank experiments.

### Results and discussion

The determination of the point of zero charge (PZC) presented in Fig. 1, showed that the surface of the brown algae was negatively charged in the pH region 5.5–11 (–33 up to –12 mV), indicating its ability to adsorb cations. This is also in agreement with measurements appeared in the literature [35]. Figure 2 presents SEM microphotographs of the brown algae, where the characteristic flattened ultrastructure of cellulose microfibrils can be observed, exhibited random orientation [16]. According to EDS analysis the algae contains mainly oxygen (55–60 %), sulfur (~10 %), calcium (~10 %) as well as small quantities of

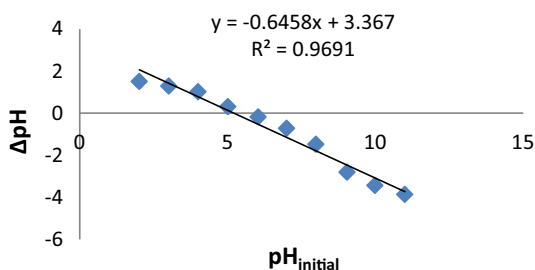


Fig. 1 Diagram  $\Delta\text{pH}$ – $\text{pH}_{\text{initial}}$  (Point of zero charge evaluation)

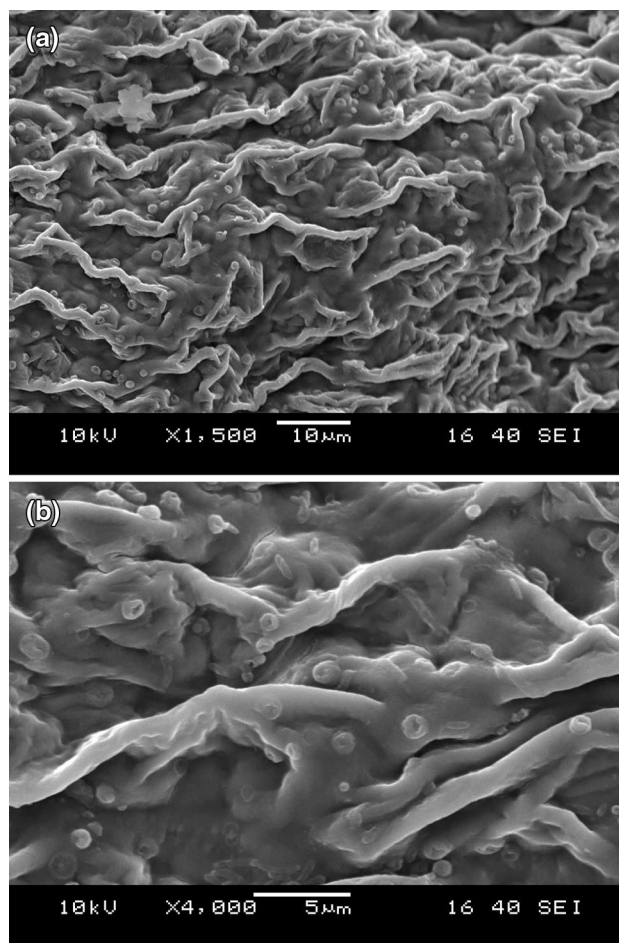
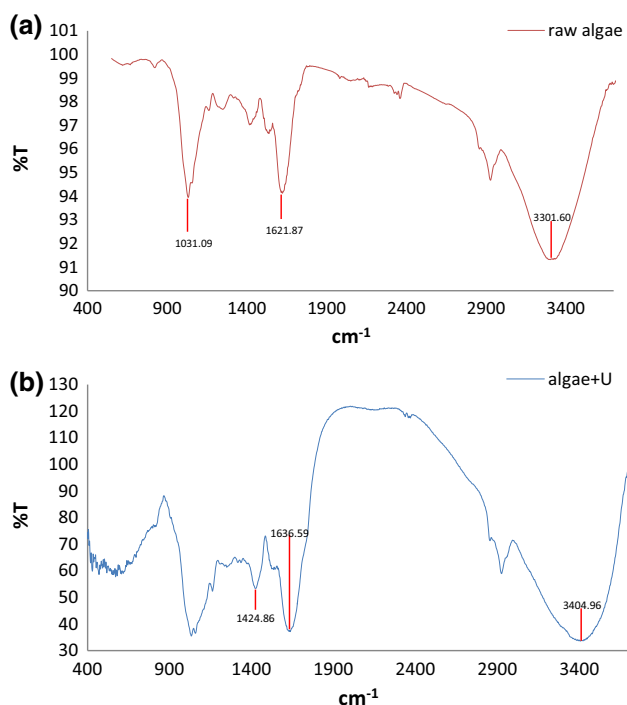


Fig. 2 SEM microphotographs of raw *Dictyopteris polypodioides*

metals (aluminum, silicon, iron, magnesium, potassium). The FT-IR spectrum of the brown algae is presented in Fig. 3a. According to the literature, the cell walls of *Dictyopteris polypodioides*, which are responsible for the sorption process, mainly contain cellulose, alginic acid and sulphated polysaccharides. The spectrum of *Dictyopteris polypodioides* was measured by a FT-IR spectrometer within the range of 550–4000  $\text{cm}^{-1}$  wave number. In the recorded spectrum the band at 3301.6  $\text{cm}^{-1}$  corresponds to O–H, the peaks at 1422.92  $\text{cm}^{-1}$  and 1621.87  $\text{cm}^{-1}$  correspond to asymmetric and symmetric carboxyl ( $-\text{C}=\text{O}$ ) stretching groups respectively, whereas the peak at 1031.09  $\text{cm}^{-1}$  indicates the presence of C–O group [16, 25]. In order to characterize the functional groups participating in biosorption, the FT-IR pattern of the U-loaded biomass was recorded and presented in the same figure (Fig. 3b). The comparison of unloaded and U-loaded FT-IR spectra illustrates that the peaks at 3301.60, 1621.87 and 1422.92  $\text{cm}^{-1}$  are shifted to 3404.96, 1636.59 and 1424.86  $\text{cm}^{-1}$ , respectively. These shifts indicate that hydroxyl and carboxyl functional groups participate in



**Fig. 3** a FT-IR spectrum of raw *Dictyopterus polypodioides* and b FT-IR spectrum of *Dictyopterus polypodioides* after treatment with a 50 mg/L uranium solution of initial pH 6

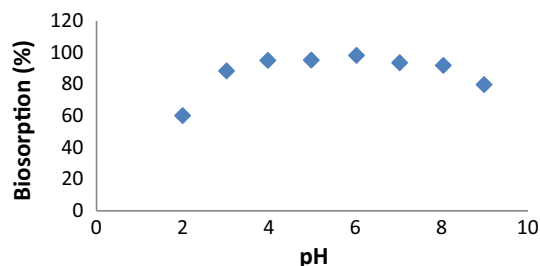
biosorption process and ion exchange between uranium and hydrogen atom as well as complexation with carboxyl groups, is most probably the dominated mechanism of biosorption of uranium on brown algae. The carboxylic groups are generally the most abundant acidic functional groups in the brown algae and the removal capacity of the algae is directly related to the presence of these sites on the alginic polymer [19, 29].

### Effect of pH and adsorbent dose

The uranium sorption is a complex phenomenon which is dependent on aqueous chemistry of the element as well as the properties of the sorbent (e.g. chemical composition, particle size). Among the important factors controlling the uranium uptake is the pH, determining its species available in solution and influencing the surface charge of the sorbent material, as well as its concentration. Generally, in acidic solutions the cationic species of uranium are dominant [12, 13]. It was observed that the biosorption process is dependent on the initial pH of the solution. The amount of metal ion adsorbed increased with increase of the pH value and the highest removal efficiency (98 %) was observed at the pH 6. In the acidic region, the metal ion uptake was inhibited and this can be attributed to the presence of  $\text{H}_3\text{O}^+$  ions, competing with the uranium

species for the same adsorption sites [12]. At low pH values, the uranium is present in the solution mainly in the form of free  $\text{UO}_2^{+2}$  ions, and it was competing with protons for the binding sites on the biomass whereas at higher pH values (around 6) formation of hydroxy-uranyl species is observed as it was revealed by the code MEDUSA for the investigated concentrations region [42]. The equilibrium pH ( $\text{pH}_{\text{eq}}$ ) also plays an important role because after the addition of the sorbent the pH is gradually altered. In our case the  $\text{pH}_{\text{eq}}$  values found to be quite similar with the  $\text{pH}_{\text{init}}$  values. As can be seen in Fig. 4, the biosorption of uranium reaches the maximum value at pH 6 and then decreases to 79.6 % at pH 9. At higher pH values, the speciation of U(VI) is dominated by a series of strong aqueous carbonate complexes which increase the solubility of uranium at these environmental conditions. According to the result, pH 6 was found to be appropriate for maximum biosorption and used in all subsequent experiments. Similar results have been reported in literature for biosorption of uranium [24, 28, 29]. For example, uranium uptake of *Bacillus mucilaginosus* was studied at pH ranging from 2 to 7 and pH 5 was selected as the best value [24]. Furthermore Bozkurt et al. investigated the biosorption of uranium onto *Ulva gigantea* (Kützinger) bliding and observed that the adsorption increased with increasing pH from 2 to 3, remained stable until pH 6 and then decreased with increasing pH from 6 to 9 [28].

The influence of ratio solid/liquid phase on the uranium sorption on brown algae was studied, varying the amount of adsorbent from 0.5 to 20 g/L and keeping the other parameters (pH, concentration, and contact time) constant as it is presented in Fig. 5. It was observed that the percent removal of uranium increases from 87.3 to 94.5 % for adsorbent dose 0.5 and 5.0 g/L respectively, due to greater availability of the surface area at higher concentration of the adsorbent. Further increase of the adsorbent dose resulted in slight increase of the % uranium removal. This could be attributed to overlapping of the adsorption sites as a result of the excess number of adsorbent particles.



**Fig. 4** Effect of pH on the removal efficiency

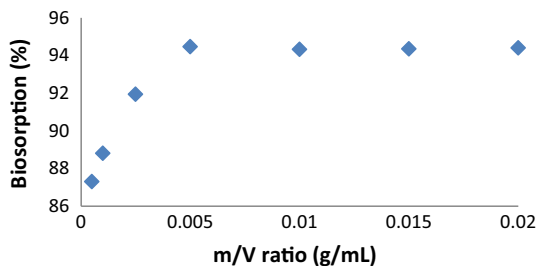


Fig. 5 Effect of adsorbent dose on the removal efficiency

**Effect of initial concentration**

The effect of initial uranium solution concentration (in the range 10–250 mg/L) on biosorption was investigated and the results were showed in Fig. 6. From this figure it can be seen that the % removal decreased with the increase of the initial solution concentration. This is probably connected to the fact that at a fixed adsorbent dose, the number of active adsorption sites remained unchanged, while at higher solution concentrations, more adsorbate ions are existing and the removal efficiency is reduced from 100 % for the concentration of 25 mg/L to 89 % for the concentration of 250 mg/L.

The SEM images of the algae after interaction for 24 h with 50 mg/L uranium solution of initial pH 6 are shown in Fig. 7, whereas the presence of different elements as revealed by EDS analysis is given in Fig. 8. According to SEM/EDS examination, there was satisfying uranium distribution on the surface of the material as can be seen in Fig. 7b, c and its concentration was estimated to be between 6 and 20 % in different points. The uranium was uniformly distributed on the surface following the distribution of sulphur and calcium, whereas the distribution of

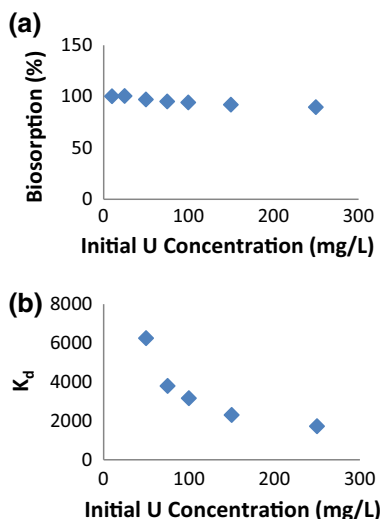


Fig. 6 Effect of initial concentration on the removal efficiency

oxygen and silicon is rather oriented as it is illustrated in Fig. 7d–f. The sulfonic acid groups play also a role in metal binding and the presence of other cations existing in the sorbent like Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup> contributes to the ion exchange [7, 19, 29]. The SEM/EDS data in combination with the FT-IR data indicate that the uranium uptake is being mainly extracellular or occurring discretely at the cell wall, as result of different processes (e.g. adsorption, ion exchange, complexation).

The uranium uptake data were modeled using the Langmuir, Freundlich and Dubinin–Radushkevich isotherm equations and the results are presented in Tables 1 and 2, respectively. The determined maximum capacity (in mg/g) describes the total capacity of the biosorbent for uranium and the R<sub>L</sub> values were calculated within the range of 0–1 confirming the favorable character of the uptake of the uranium by brown algae. As seen from the Table 2, Freundlich model is very suitable for describing the biosorption equilibrium of uranium by the algae and indicates that sorption process occurs on heterogeneous surface.

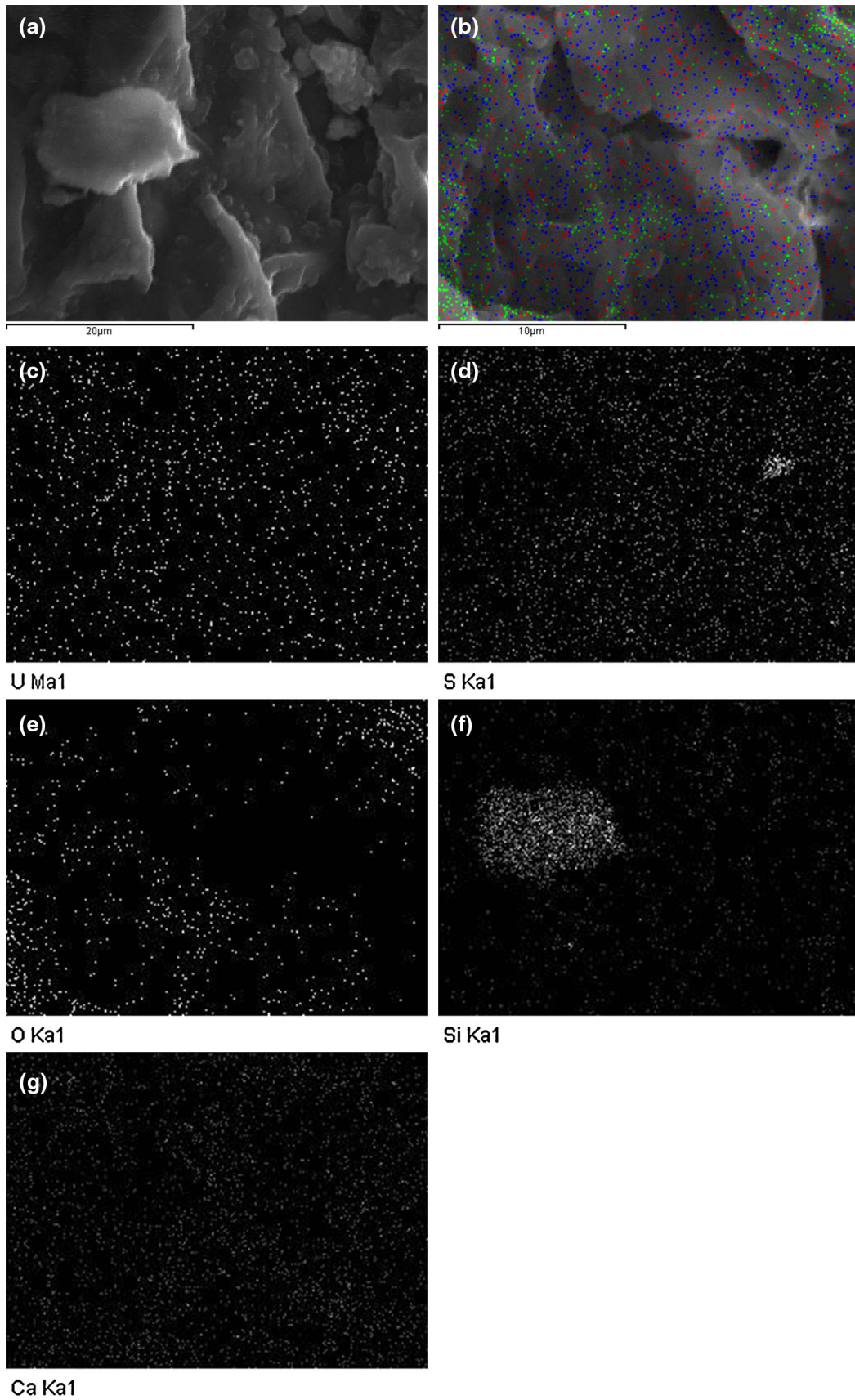
The data of the maximum uptake capacity are reported in Table 2 and are comparable with uptake values available in the literature under experimental conditions similar to those adopted in this work. For example Aytas et al. have found uptake values up to 50 mg/g using a biocomposite absorbent of marine algae and yeast. Srivastava et al. have reported uptake values up to 75 mg/g using a biomass of plants and Zou et al. values up to 60 mg/g using a biosorbent of pine sawdust [21, 26, 29]. On the other hand, higher uptake values (300–500 mg/g) were reported by Ghasemi et al., Khani and Moghaddam et al., using treated algae biomass as biosorbents [16–18, 31].

**Effect of contact time and temperature**

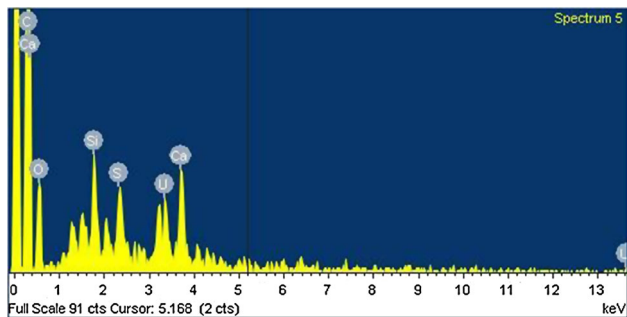
The effect of contact time on uranium biosorption on algae was studied using solutions of initial concentration 50 mg/L at pH<sub>init</sub> 6. Figure 9 shows the effect of contact time on the uptake for a time period up to 180 min at the temperatures 20, 30, 40 and 50 °C. It is obvious that the adsorption percentage increases slightly (from 95 at 20 °C to 97 at 50 °C) with the time and the state of equilibrium is reached faster when the temperature is increased (from 90 min at 20 °C to 15 min at 50 °C). This behavior usually occurs in the case of physical adsorption.

*Kinetic modelling and thermodynamic parameters*

To define the sorption kinetics of U(VI) onto the brown algae, the kinetic parameters of the sorption process by the pseudo-first order and pseudo-second order equations were investigated.



**Fig. 7** SEM microphotographs of *Dictyopterus polypodioides* after interaction for 24 h with 50 mg/L uranium solution of initial pH 6: **a** image, **b** mapping of U (red), S (blue) and O (green), **c–g** mapping of different elements. (Color figure online)



**Fig. 8** EDS analysis of *Dictyopterus polypodioides* loaded with uranium

**Table 1** Utilized isotherms in biosorption studies

Name	Isotherm equation
Langmuir	$q_{eq} = \frac{q_{max} K C_{eq}}{1 + K C_{eq}}$
Freundlich	$q_{eq} = K_F C_{eq}^{1/n}$
Dubinin–Radushkevich	$q_{eq} = -n(\log^2(K \times C_{eq})) + \log q_{max}$

$q_{eq}$ ,  $C_{eq}$  equilibrium concentration of uranium in solid and liquid phase, respectively;  $q_{max}$  the maximum sorption capacity (mg/g);  $K$  the equilibrium constant;  $n$  parameter characterizing the system heterogeneity

The pseudo-first order equation:

$$\frac{dq_t}{dt} = k_1 \times (q_e - q_t) \tag{3}$$

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} \times t \tag{4}$$

and the pseudo-second order equation:

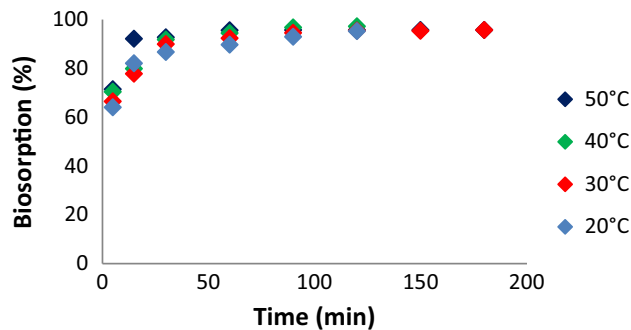
$$\frac{dq_t}{dt} = k_2 \times (q_e - q_t)^2 \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} \tag{6}$$

where  $k_1$  and  $k_2$  are the rate constants for the pseudo-first and the pseudo-second order kinetic equations and  $q_e$  and  $q_t$  the uranium mass retained per weight unit of the sorbent

**Table 2** The constants of isotherm models for U(VI) biosorption by *Dictyopterus polypodioides*

Experimental conditions	Langmuir				Freundlich			Dubinin–Radushkevich		
	$K_L$ (L/mg)	$q_{max}$ (mg/g)	$R^2$	$(q_{max})_{exp}$ (mg/g)	$K_F$ (mg/g)	$n$	$R^2$	$q_{max}$ (mg/g)	$K_{ad}$ (mol <sup>2</sup> /KJ <sup>2</sup> )	$R^2$
pH6	0.082	62.5	0.93	44.5	7.24	1.84	0.99	27.2	$7 \times 10^{-7}$	0.65



**Fig. 9** The effect of time on the uptake of uranium by *Dictyopterus polypodioides* ( $C_{init}$  50 mg/L,  $pH_{init}$  6)

at equilibrium and at time  $t$ , respectively. The parameters obtained by the fitting of all experimental data using the above mentioned kinetic equations are given in Table 3.

As it is shown in Fig. 10 and Table 3, the kinetics of the removal of uranium by brown algae seems to be described by the pseudo second order model, giving a straight line in the plot  $t/Q_t$  for all investigated temperatures (20, 30, 40 and 50 °C). Constructing the plot of  $\log k_2$  as a function of  $1/T$  it was possible to calculate the activation energy ( $E_a$ ) of the uptake process using the Arrhenius equation

$$k = A \times e^{-(E_a/R \times T)} \tag{7}$$

where,  $k$  is the rate coefficient,  $A$  is a constant,  $E_a$  is the activation energy,  $R$  is the universal gas constant and  $T$  is the temperature (in Kelvin). The obtained activation energy ( $E_a$ ) was 18.43 kJ/mol ( $R^2 = 0.953$ ). According to the literature, the reactions controlled by diffusion exhibit activation energy values in the range of 5–20 kJ/mol [41].

Using the equations below, Gibbs free energy ( $\Delta G^\circ$ ), entropy ( $\Delta S^\circ$ ) and enthalpy ( $\Delta H^\circ$ ) were also calculated:

$$\Delta G^\circ = -\ln K_d \tag{8}$$

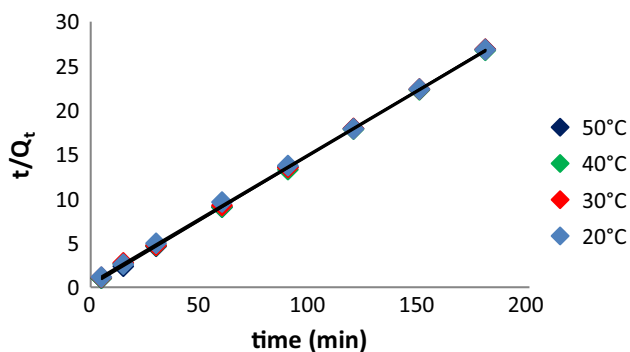
$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{10}$$

The thermodynamic parameters given in Table 4 show that the process of biosorption is endothermic, as indicated by the positive  $\Delta H^\circ$  value and spontaneous in nature due to the negative  $\Delta G^\circ$  values. The positive value of  $\Delta S^\circ$  indicates increased randomness at the solid/solution interface during the biosorption of uranium onto brown algae. The

**Table 3** Kinetic parameters for the uranium uptake by *Dictyopteris polypodioides* at 20, 30, 40 and 50 °C

Temperature (°C)	Pseudo-first order equation			Pseudo-second order equation		
	$k_1$ (min <sup>-1</sup> )	$q_{\text{calc}}$ (mg/g)	$R^2$	$k_2$ (g/(mg min))	$q_{\text{calc}}$ (mg/g)	$R^2$
20	0.0040	4.47	0.754	0.04276	6.84	0.9992
30	0.0053	4.55	0.757	0.05051	6.87	0.9997
40	0.0037	4.16	0.964	0.06127	6.90	0.9998
50	0.0147	4.63	0.714	0.08794	6.94	0.9990

**Fig. 10** Pseudo second order kinetics of uranium sorption onto brown algae as function of time**Table 4** Thermodynamic parameters for the adsorption of uranium onto brown algae

$T$ (K)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)	$E_a$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)
293	14.6	0.118	18.4	-20.2
303				-21.2
313				-22.3
323				-23.7

magnitude of the sorption energy characterizes an ion exchange type reaction [11].

## Conclusions

In this study, the biosorption of U(VI) ions was studied on *Dictyopteris polypodioides* (brown algae) using batch technique under different experimental conditions. Biosorption efficiency was found to reach the value of 94 %, under the optimized experimental conditions (pH 6,  $C_i$ : 50 mg U/L, contact time: 120 min, biomass dosage: 5 g/L, temperature: 303 K). The kinetic experiments were carried out at different temperatures and the results have shown that the sorption process fits well into a pseudo-second order mechanism. The present results demonstrate that the Freundlich and Langmuir model fit better than the Dubinin–Radushkevich model for the biosorption equilibrium data. Calculation of the thermodynamic parameters

characterizing the biosorption process assumed variation of temperature. The positive value of  $\Delta H^\circ$  shows that the biosorption of uranium on *Dictyopteris polypodioides* is an endothermic process whereas the negative values for  $\Delta G^\circ$  suggest feasibility and spontaneous sorption. A rapid sorption in the initial stages of equilibration was observed and the calculated activation energy (18.4 kJ/mol) is characteristic of an ion exchange type adsorption but the overall observations suggest that the biosorption process was administrated by combination of several mechanisms, such as physical sorption, ion exchange and complexation. Based on this work, brown algae *Dictyopteris polypodioides* can effectively remove the uranium ions from dilute aqueous solutions and it is a suitable biosorbent with low cost, non-toxic, biocompatible, environmental friendly and biodegradable nature.

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