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Sorption of uranium(VI) by *Trapa bispinosa* from aqueous solution: effect of pretreatments and modeling studies

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ABSTRACT

In this study, the sorption of uranium(VI) from aqueous solution was investigated using *Trapa bispinosa* (Singhara) in batch system. Different physical and chemical treatments were given to native biomass for enhancing its sorption capacity for uranium(VI). The optimization of different experimental factors such as solution pH, dose of biosorbent, particle size, contact time, temperature, and initial uranium(VI) ion concentration was done. Maximum sorption (171 mg g^{-1}) was observed at pH (5.0), particle size (0.25 mm), biosorbent dose (0.05 g), temperature (50˚C), and initial uranium(VI) ion concentration (400 mg L^{-1}) in 90 min. The obtained data were analyzed by applying equilibrium, kinetic, and thermodynamic models. The uranium(VI) sorption equilibrium data were best fitted in Freundlich adsorption isotherm. The rate of biosorption process was effectively described by applying different kinetic models and the well-fitted model found to be pseudo-second-order. The evaluation of thermodynamic parameters represented that the uranium(VI) sorption process was exothermic, spontaneous, and favorable. The process was made more economical through recovery of uranium(VI) ions using HNO_3. FT-IR analysis of biosorbent confirmed the involvement of functional groups like hydroxyl, carbonyl, and carboxylic groups in the sorption process.

Keywords: Uranium(VI); *Trapa bispinosa*; Sorption; Eluents; Optimization

1. Introduction

Water is among the necessities of living beings that chains all forms of flora and fauna [1] and there are two natural key sources of water such as surface water and groundwater. The rivers, streams, and lakes are dominant sources of fresh water, while well and borehole water are included in groundwater category [2,3]. In present era, the ecological contamination and the decline of some ecosystems are intensified by the augment in industrial activities. The natural sources are mainly polluted by synthetic compounds, heavy metals, waste nuclear liquid, etc. Heavy metals with high atomic weight having specific gravity greater than 5.0 which are five times of water [4]. The metal of our curiosity in the present study was uranium. Uranium, is carcinogenic as well as mutagenic, may cause neurotoxic disorder and genotoxicity in human beings. The radionuclide of the ^{238}U series is

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long-lived and shows hazardous signs due to their high toxicity and radioactivity. Those industries which use radioactive material produced a large quantity of wastewater polluted with uranium contents annually. According to the report of World Health Organization, uranium metal is carcinogenic for human beings and its level of concentration in water should not exceed beyond 50 $mg\,L^{-1}$. The recommended standard of drinkable water by the US Environmental Protection Agency (1996) is 20 $mg\,L^{-1}$ for ^{238}U. Therefore, to avoid any radioactive contamination with the environment, it is mandatory to remove uranium contents from wastewater before their discharge in the surroundings. There are some conventional methods which have been used for the treatment of wastewater like ion exchange, electrochemical treatment, chemical precipitation, and adsorption by activated carbon. However, these methods are effective up to some extent, but when the concentration of metal ions in the aqueous solution is less than 100 $mg\,L^{-1}$, the electrochemical and chemical precipitation becomes ineffective [5]. Biosorption is relatively inexpensive process among all which requires no energy and its self-governing is based on biological metabolism. It is an observable fact that describes the removal of heavy metals ions through the passive binding to dead biomass from an aqueous solution. This phenomenon has been reported for an array of biomass types or viable or killed cells [6].

Physicochemical adsorption, ion exchange, coordination, complexation, chelation, and microprecipitation are significant phenomena which occurred during biosorption. The proteins, lipids, and polysaccharides make the cell wall of biomass and offer various functional groups, e.g. sulfate, phosphate carboxylate, and hydroxyl for the binding of metal ions [5].

In the present research, peels of *Trapa bispinosa* (Singhara) biomass were used for the removal of uranium from infected wastewater. *T. bispinosa* is an aquatic fruit; its superficial covering is very hard and removed after boiling. This removed shell was used in sorption of uranium. The fruit of singhara (common name) is the rich source of starch, thus its starch contents being used by many of the industries for thickening and adhesive purposes, for sizing paper and textiles, for stiffening laundered fabrics, and also in the manufacture of food products. The dried powder of the Singhara has been used in flour to make loaves. Milk suppliers often use its powder in milk to make it creamier. Further, the fruits have been used to cure sore throat, anti-inflammatory, fractures, and anemia. In addition to this, the juice of fruit has been used for the treatment of diarrhea and dysentery [7]. After the usage of inner white fruit, peels are left as a waste product, which has no economical importance. The purpose of this research was to access the potential of peels of *T. bispinosa* biomass for biosorption of U(VI) ions from aqueous solutions. The major chemical constituents of peel are cellulose, hemicelluloses, pectin, lignin, and fibers, having the functional groups –OH, –COOH, and –CHO. The uranyl ions binding on that sorbent surface have been carried out at batch scale where the influence of physicochemical key parameters such as the biosorbent particle size, pH of medium, biosorbent dosage, concentration of metal ions, contact time, and temperature has been considered.

2. Material and methods

2.1. Reagents

All the chemical reagents were of investigative rating and distilled water was used in whole experimental work. A solution of 1,000 $mg\,L^{-1}$ of U(VI) was prepared from $UO_2\,(NO_3)_2{\cdot}6H_2O$ by adding the concentrated H_2SO_4 to remove nitrates and then dissolved it in distilled water. Further working solution was prepared from this stock solution. Arsenazo-III (2.5%) was used for color formation and diethylenetriaminepentaacetic acid (DTPA) (2.5%) as complexion agent. To adjust the pH the solutions of 0.1 N HCl and NaOH was used. The pH meter was calibrated using the buffer solutions of pH 4 and 7.

2.2. Biomass

In this investigational study, the peels of *T. bispinosa* were chosen as sorbent for the removal of U(VI) from aqueous solution. Two varieties of biomass native and dyed were purchased from the Jhang Bazar, Faisalabad, Pakistan. The biomass dried first in sunlight, then kept in oven at temperature of 50°C for 72 h. Using food processor (Molinex, France), dried biomass was cut, ground, and then octagon sieves (OCT-Digital 4527-01) for sieving to obtain homogenous biosorbent with known particle sizes (in the range of 0.25–0.71 mm). The airtight containers were used for the storage purpose of the biomass.

2.3. Batch biosorption studies

For experimental purpose, 1 M HNO_3 was used to rinse the glassware and then with distilled water to remove contaminants. Batch wise sorption studies were carried out in 250 cm^3 conical flasks to elucidate the screening of biomass and influences of different experimental parameters, desorption/recovery. Out of two varieties of biomass of *T. bispinosa*, only peels of native sample were selected on the basis of maximum removal of metal ions. To check the apparent maximum uptake of metal ions from aqueous solution, the effect of different experimental parameters such as pH (1–8), temperature (30, 40, 50, and 60°C), initial metal concentration (10, 20, 30, 40, 50, 100, 200, 300, 400, and 500 ppm), contact time (0, 15, 30, 45, 60,90, 120, 150, and 180 min), biosorbent dose (0.05–0.5 g), and size (with the range of 0.71–0.05 mm) where checked on sorption of metal ions by *T. bispinosa* waste biosorbent. The adjustment of the reaction medium was done with 0.1 M solutions of NaOH and HCl. For maximum sorption, the process was conducted at 1,000 rpm shaking speed.

2.4. Uranium contents determination in the solutions

To analyze contents of uranyl ions in the sample solution, the already reported method was used [8]. The volumes of 1 cm^3 of the sample solution (50 ppm) were pipette out and make the volume up to 25 cm^3 in volumetric flask and then 1 cm^3 of DTPA (2.5%) and 1/2 cm^3 of arsenazoo-III reagent were added. The solution was kept to stand for 2–3 min until the pink violet color was developed that make sure about the formation of uranium–arsenazo-III complex. Then, absorbance of this solution was measured at the wavelength of 655 nm against a corresponding reference, using a cell of 1-cm path length in spectrophotometer.

2.5. Adsorption capacity (q) and % sorption

The quantity of U(VI) ions adsorbed per unit of biosorbent was obtained using the following equation [9]:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

% age sorption is given as [10].

$$\%\ \text{sorption} = (C_i - C_e)/C_i \times 100 \tag{2}$$

The eluted biosorbent metal contents were calculated directly from the quantity of metal desorbed into the solution of eluent using the following equation [11].

$$q_{des} = C_{des} \times V/W \tag{3}$$

The percentage of desorbed metal was calculated as:

$$\%\ \text{desorption} = \left(\frac{q_{des}}{q}\right) \times 100 \tag{4}$$

2.6. FT-IR analysis

The chemical characteristics of *T. bispinosa* (Singhara) biomass were analyzed and interpreted by Bruker Tensor 27 Fourier transform infrared spectrometer with the samples prepared as KBr disks.

2.7. Statistical analysis

The obtained mathematical data represent the mean of three independent experiments. The overall statistical study was done using Microsoft Excel 2007, version Office Xp.

3. Results and discussion

3.1. Screening of biomass

The screening test was performed to select one type of *T. bispinosa* biomass with maximum adsorption potential for the removal of U(VI) ions from aqueous solution. *T. bispinosa* biomass was used in native and dyed forms and after analysis, it was observed that the value of uranium ions uptake by native biomass was higher than the dyed biomass. The data showed that the amounts adsorbed metal by native and dyed were 22.99 and 20.77 mg g^{-1}, respectively, which decided the native biomass as an efficient biosorbent for the uranium sorption and desorption. It was assumed that at the surface of native biomass, the active sites were exposed and show more sorption activity toward the metal ions. On the other hand, the surface of dyed biomass showed less sorption due the reduction of active sites, which were covered by a layer of dye.

3.2. Effect of pretreatments

The biomass can be modified to achieve efficient biosorption of metal ions from aqueous solution. Biomass can be modified by pretreating with alkalis, acids, salts, organic solvents, and surfactants which may or may not increase the sorption capacity of biosorbent. In the present investigational study to evaluate the effect of modification or pretreatment on biomass, 50 mg L^{-1} uranium solution was shaken with 0.05 g of pretreated biosorbent. The results showed that all physical and chemical modifications of biosorbent enhanced the sorption aptitude. The q (mg g^{-1}) values of non-treated, physically, and chemically modified peels of *T. bispinosa* biomass are in the following order: boiled (45.39) > sucrose (43.47) = $CaCl_2 \cdot 2H_2O$ (43.47) > NaCl (40.29) > Triton X100 (39.33) > K_2SO_4 (38.18) > $CaCO_3$ (37.31) > EDTA (37.12) > HNO_3 (36.35) heated (28.47) > tetrachloric acid (27.79) = autoclaved (27.79) > native (22.99) > NaH_2PO_4 (22.90) > $H_2SO_{4.}$ (11.74), and the results are shown in Fig. 1. The maximum removal was found by the boiled biomass because minerals and organic matter were removed from the surface after boiling. The minerals are removed by dissolution process and organic matter due to decomposition. Physical modification enhanced the availability of sorption sites on the biosorbent surface [12–15].

EDTA is a chelating agent and it has a potential to form complexes with other metals ions present in the biomass. EDTA-treated biomass depicted decreased adsorptive removal for the uranium ions present in the aqueous solution. This decreased adsorption capacity of EDTA-treated biomass is due to the fact that it forms complexes with all the metal ions present at the surface of biomass, so structure and chemistry of biomass, which was responsible for adsorption of metal ions completely changed. As a result, biomass pretreated with EDTA showed a decrease in adsorption capacity [16].

The increase or decrease in sorption aptitude after an acidic treatment of biosorbent could be related to polymeric structure of biosorbent and strength/concentration of an acid. The acidic treatment reduced the sorption capacity of sorbent due to the fact that after a certain concentration of an acid, the electro negativity of the biomass decreased due to the remaining H^+ ions on the acidic pretreated biomass. The change in the electro negativity of the biomass resulted in a reduction of biosorption capacity [17]. Acids with certain strength can enhance uptake capacity of biomass by increasing the surface area and porosity of original sample [18].

3.3. Effect of biosorbent size

The effective and utmost surface area of biosorbent material is a striking criterion for maximum sorption. The maximum metal uptake was experiential at the particle size of 0.25 mm by perpetuation the other factors constant. This experiment was conducted to optimize the biosorbent size with the 0.25, 0.35, 0.5, 0.71, and >0.71 mm sizes. The effect of varying the biosorbent particle size on the sorption aptitude q (mg g^{-1}) is shown in Fig. 2. As illustrated in the figure, biosorbent with smaller particle size adsorbed metal ions more competently than that of biosorbent with larger particle size. The maximum biosorption capacity q (20.8 mg g^{-1}) was observed at biosorbent size of 0.25 mm, which was further decline slightly up to 20.6 mg g^{-1} at particle size 0.35 mm, then abruptly decreased up to 19.6 mg g^{-1} at 0.5 mm biosorbent size, 19.3 mg g^{-1} at 0.71 mm, and 18.8 mg g^{-1} at >0.71 mm.

3.4. Effect of pH

The biosorption process significantly depends upon the solution pH, and it influences both the speciation of U(VI) in the aqueous solution and the binding sites present on the surface of biomass [19]. In order to mark out the optimum pH for the sorption process, the effect of pH on uranium biosorption onto *T. bispinosa* (Singhara) was investigated. Uranium sorption by *T. bispinosa* was premeditated at a range of pH 3.0–8.0 by taking the biosorbent dose 0.1 g of particle size 0.25 mm of 50 mg L^{-1} initial metal

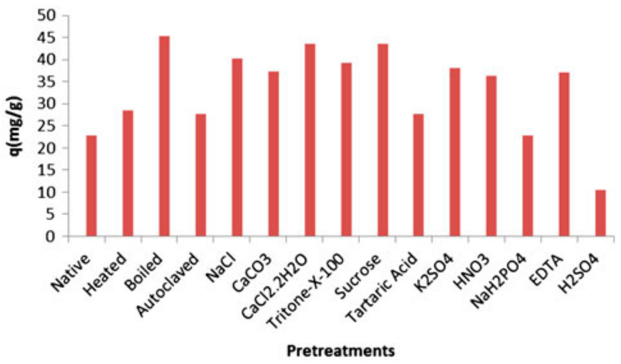

Fig. 1. Effect of pretreatments on *T. bispinosa* (Singhara).

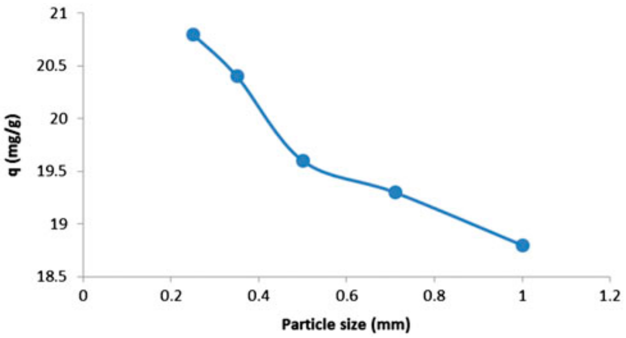

Fig. 2. Effect of biosorbent particle size on the biosorption of U(VI) by *T. bispinosa*.

concentration at the temperature of 30˚C for 3 h at 100 rpm. It is illustrated in Fig. 3 that the maximum biosorption was taken place at acidic pH 5.0 and intense acidic conditions did not favor the sorption aptitude. At pH 3.0, the sorption capacity q was 18.9 mg g^{-1} then at pH 4.0, it was increased up to 21.00 mg g^{-1} and then achieved the maximum value of 21.54 mg g^{-1} at pH 5.0, then it became constant after slight decrement with the value of 21.44 mg g^{-1}, this value remained constant at pH 6.0, 7.0, and 8.0. It is considered that the uranium sorption by *T. bispinosa* was favored at both slight acidic and basic pH.

The uranium(VI) sorption by live and lyophilized *Pseudomonas* biomass within the range of pH 2.0–8.0 was investigated previously. It was analyzed that the initial solution pH considerably affected the equilibrium uranium(VI) uptake capacity [20].

It was practiced over the succession tests that sever acidic condition could not favor the sorption of uranium ions and both types of biomass showed similar behavior. The increment in pH from 3.0 to 5.0 has lead to the increment of sorption of metal ions with the maximum loading being attained at pH 5.0 (225.56 ± 14.24 mg U g^{-1} or 458 ± 27.15 mg U g^{-1}, respectively). The lyophilized biomass showed a sharp decline with an additional rise in pH and living complement seemed less affected. According to the obtained results, the role of pH may be explained by (i) higher solubility of metal ions and the competition by acidic proton for metal ions in the acidic environment, (ii) at higher pH (4.0–5.0), the mounting binding by the biomass of monovalent species like UO_2OH^+, and $(UO_2)_3(OH)_5^+$ over the divalent ions UO_2^{2+} at low pH (2.0), and (iii) the decrease in the sorption of uranium ions because the dissolved uranyl concentration decreased in the solution due to the formation of solid schoepite ($4UO_39H_2O$) [21].

3.5. Effect of biosorbent dose

In the present investigation, the biosorbent dosage seems to have immense influence on the process. The sorbent–sorbate equilibrium of the solution medium is determined by dose of biomass which is a considerable factor for metal uptake aptitude. The availability of binding sites for metal uptake depends upon the dose of biosorbent [10].

Maximum biosorption of 23.91 mg g^{-1} was taken place at 0.05 g of biosorbent for uranium solution. The results of experiment are shown in Fig. 4. The q (mg g^{-1}) was continuously decreased as the amount of biosorbent increased. The minimum sorption was observed at 0.5 g of biosorbent dose. The supplementary augment in biomass concentration was incapable to produce the momentous subtraction due to low metal ion concentration in solution [22]. The above results could be depicted as a consequence of partial aggregation of biomass at higher level of dose leads to decrease in effective surface area for the biosorption [23]. The influence of biosorbent dose on uptake of uranium ions was analyzed; the results indicated that uranium uptake at pH 5.0 increased from 0.2 to 10 g L^{-1} [24].

3.6. Effect of contact time

The most considerable criterion for an economical wastewater treatment system is equilibrium time. The effect of contact time on the adsorptive removal of uranium by *T. bispinosa* biomass was investigated by varying the contact time from 15 to 240 min. The results indicated that the biosorption of uranium by *T. bispinosa* increased initially with the increase in contact time and maximum removal (22.0 mg g^{-1}) was achieved in 90 min at constant value of pH, biosorbent

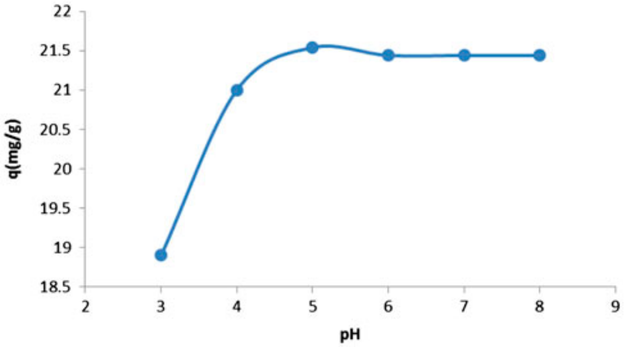

Fig. 3. Effect of pH on the sorption of U(VI) by *T. bispinosa*.

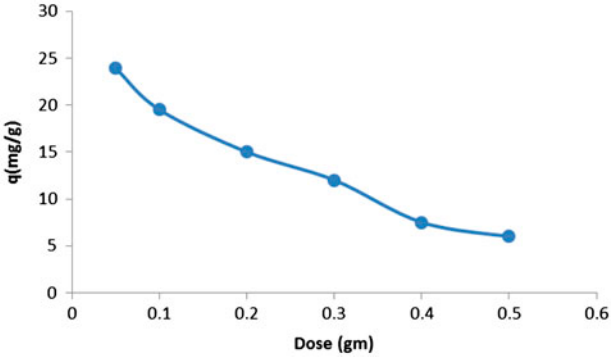

Fig. 4. Effect of biosorbent dose on the sorption of U(VI) by *T. bispinosa*.

dosage, size of biosorbent particles, initial uranium ion concentration, and temperature. The results are shown in Fig. 5. It was estimated that kinetics of sorption of U(VI) could be explained by two phases: an initial phase which was rapid where quick adsorption was done and contributed significantly to metal ions uptake, and the second phase was a slower phase which does not contribute appreciably to the total metal adsorption [23]. The first phase was considered to be the immediate adsorption phase or exterior surface and adsorption occurred steadily where intraparticle diffusion controls the adsorption rate until the metal uptake reached equilibrium.

3.6.1. Kinetic modeling

Arithmetical models that illustrate the trend of batch sorption process operated under diverse experimental situation are very beneficial to scale-up process of optimization. In array to test out the mechanism of biosorption of uranium by *T. bispinosa*, the investigational statistics is subjected under different models of kinetics. To expose the rate of metal biosorption in batch systems, many models with varying degrees of complexity have been recognized. The model which not only represents the obtained information clearly but also suggests reasonable sorption mechanism will be the favored kinetic model. In this work, the experimental data were subjected under two different kinetic models. These kinetic models included pseudo-first-order Lagergren and pseudo-second-order. The pseudo-first-order [25] Lagergren model is expressed as:

$$\log\,(q_{\mathrm{e}} - q_t) = \log q_{\mathrm{e}} - K_1 \cdot \frac{t}{2.303} \tag{5}$$

where q_{e} and q_t represent the amounts of adsorbed metal ions on the biosorbent at the equilibrium and any time t, respectively, $k_1(\mathrm{min}^{-1})$ is the Lagergren rate constant of the first-order biosorption. q_{e} and k_1 can be calculated from the slope and the intercept of the slope of the plot log (q_{e}–q_t) vs. t.

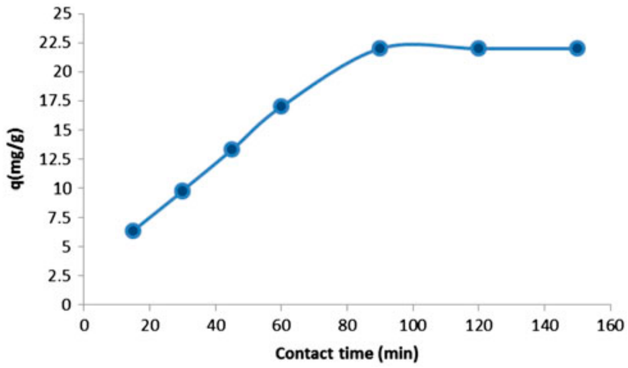

Fig. 5. Effect of contact time on the sorption of U(VI) by *T. bispinosa*.

The biosorption mechanism of *T. bispinosa* over the range of contact time can be best explained by the pseudo-second-order kinetic model [26]. This equation is shown below:

$$\left(\frac{t}{q_{\mathrm{t}}}\right) = \frac{1}{K_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \tag{6}$$

where q_{e} and q_{t} are the amount of U(VI) adsorbed on adsorbent (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). Based on the experimental data of q_{t} and t, the equilibrium adsorption capacity (q_{e}) and the pseudo-second-order rate constant (k_2) can be evaluated from the slope and intercept of a plot of t/q_{t} vs. t (Table 1).

3.7. Effect of temperature

Temperature is a vital parameter because it decides whether the reaction is endothermic or exothermic. The effect of temperature on the metal sorption experiment was examined at four different temperatures, 30, 40, 50, and 60°C as shown in Fig. 6. The metal uptake increased as the temperature increased and reached the maximum value of 34.14 mg g^{-1} at 50°C, then decreased slightly to 29.04 mg g^{-1} at 60°C. During the experiment, biosorbent dose, pH, initial metal concentration, time contact, and particle size kept constant. The trial was also done with different concentrations (50–300 mg L^{-1}) at different temperatures, and then it was established that maximum sorption was occurred at 50°C and the sorption capacity of biomass decreased at 60°C, and the results are depicted in figure. There are many suggested reasons for the temperature-dependent variation in metal ions sorption, such as at higher temperature, the greater affinities of biosorbent sites for the metal ions or an augment in binding sites on the relevant biomass, while at lower temperature, the mobility of potent binding sites on the surface of biosorbent material is decreased [27].

3.8. Thermodynamics of U(VI) sorption

The standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) are vital parameters of thermodynamics.

Table 1
Comparison of the kinetic parameters for the sorption of U(IV) on *T. bispinosa*

Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order		
q_e (mg/g)	K_1	R^2	q_e (mg/g)	q_e (mg/g)	K_1	R^2
18.83	0.025	0.9121	22.00	24.75	0.002	0.9521

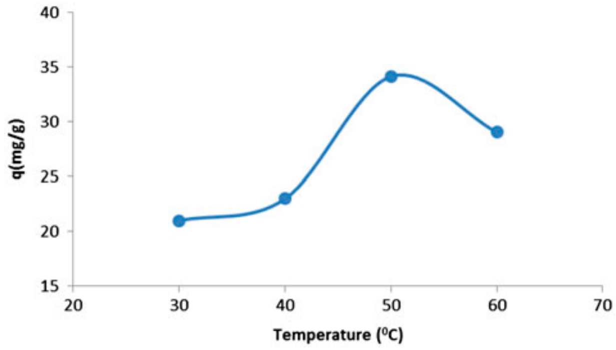

Fig. 6. Effect of temperature on the sorption of uranium (VI) by *T. bispinosa*.

The relation of these parameters can be expressed as:

$$\ln K_c = \left(\frac{\Delta H}{R}\right) \times \frac{1}{T} + \Delta S/R \tag{7}$$

where $K_c = (q/C_e)$ is the distribution coefficient (mL g^{-1}). The values of ΔH° and ΔS° are calculated from the slope and intercept of the linear variation of the plot between log (q/C_e) and $1/T$. The value of ΔG° is calculated as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8}$$

The negative value of ΔH° suggests that the process is exothermic with ΔH° value −23.398 kJ mol^{-1}. The negative values of ΔG° at every temperature give the spontaneity of the reaction [9]. The positive values of entropy change ΔS° suggest that randomness increases as the reaction proceeds and biosorption of uranium ions onto the biosorbent is a favorable process (Table 2).

3.9. Effect of initial metal concentration

The kinetics of adsorption is a function of the initial metal ion concentration, which makes it an imperative factor for the judgment of effective biosorption [28]. The apparent capacity of *T. bispinosa* for uranium sorption was determined at different concentrations (50, 100, 200, 300, 400, and 500 mg L^{-1}). Fig. 7 shows the relation between metal uptake capacitates and the metal ion concentration, as the metal ion concentration increases, the ability of biosorbent also increases. The highest removal of uranium occurred at 300 mg L^{-1}. It was investigated that with an increase in concentration of metal ions, the uptake of biosorbent was also amplified. For the whole range of concentrations, the biosorption capacities were rapid and continue. The highest sorption of uranium ions taken up by *T. bispinosa* was 180 at 300 mg L^{-1} of initial metal ion concentration. This increase was due to higher probability of collision between metal ions and biosorbent. In this important parameter of sorption, the amount of biosorbent with specific binding sites

Table 2
Thermodynamic parameters for the sorption of U(IV) on *T. bispinosa*

Temperature (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})
303	−48.058	−24.398	78.085
313	−48.838		
323	−49.619		
333	−50.400		

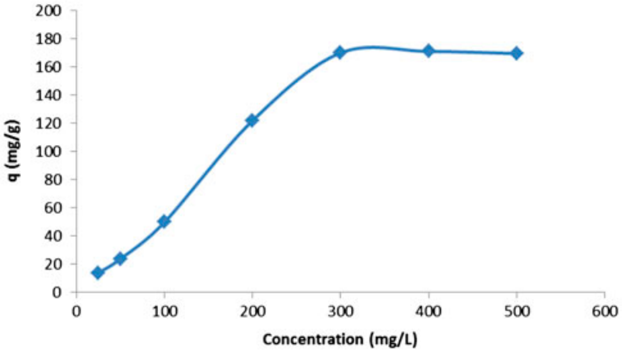

Fig. 7. Effect of concentration in the biosorption of uranium(VI) by *T. bispinosa*.

was constant; however, the number of uranyl ions increased. The saturation of biosorbent by uranyl ions could not be achieved with the low concentration of uranium solution because the number of uranyl ions was smaller as compared to binding sites present on the biosorbent surface. The binding sites of biosorbent got saturated with the metal ions by increasing the metal concentration, so the availability of binding sites for the metal ions decreased. That is why the initial stage of biosorption was fast, and slowed down as the saturation reached [19]. In addition, increasing the initial uranium concentration increased the number of collisions between uranium ions and the adsorbent, which enhanced the adsorption process [29,30].

3.10. Equilibrium modeling

The equilibrium modeling of the experimental data is imperative for the industrial application of biosorption process. It is important for the evaluation of biosorbent materials under different experimental circumstances. The expression of this relationship is termed as an adsorption isotherm [9]. Three different equilibrium isotherms (Freundlich, Langmuir, and Doubinin–Radushkevich) have been applied on the experimental results.

The Freundlich equation is the empirical relationship and it is based on the assumption that the energy of adsorption of metal binding sites depends upon whether or not the adjacent sites are already occupied.

Freundlich isotherm is represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{9}$$

where q_e—metal ion adsorbed (mg g^{-1}), C_e—equilibrium concentration of metal ion solution (mg L^{-1}), k and n—Freundlich constants.

Using linear regression from the plot of log q_e against constant log C_e (Fig. 8). The magnitudes of k and $1/n$ were determined, k expresses the degree of potency of adsorption and $1/n$ describes whether adsorption remains constant or decreases with increasing adsorption concentrations. The q_{max}, which is significant to identify which biosorbent, has the highest metal uptake capacity. The R^2 and q_{max} values for ^{238}U suggested that the sorption phenomenon is well described by Freundlich isotherm which symbolizes that multilayer of sorbate was formed on biosorbent [31]. To get the equilibrium data, initial U(VI) concentrations were varied; however, the concentration of biomass was kept constant (Table 3).

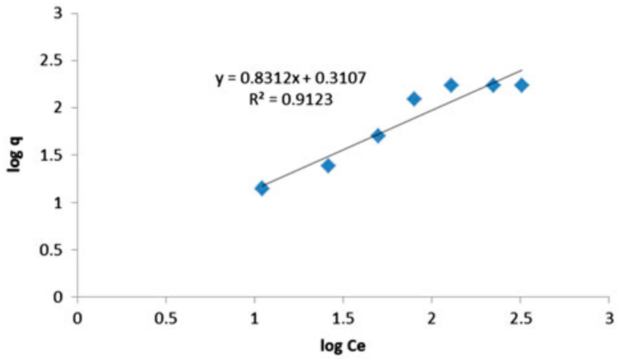

Fig. 8. Application of Freundlich adsorption isotherm on the experimental results of effect of concentration of uranium(VI) by *T. bispinosa*.

The Langmuir model [32,33] is based on the assumption that uptake of metal ions depends upon the monolayer of solute on the sorbent surface and there is no interaction between the adsorbate on adjacent sites.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{10}$$

where q_e—amount of metal ions adsorbed on the biosorbent(mg g^{-1}), C_e—equilibrium concentration of metal ions, q_m—maximum biosorption capacity describing monolayer adsorption (mg g^{-1}), k_a—adsorption equilibrium constant (L mg^{-1}) that is related to the free energy of biosorption.

Table 3
Comparison of the isotherm parameters for the sorption of U(IV) on *T. bispinosa*

Freundlich isotherm parameters	
q_e (mg g^{-1})	187
q_m (mg g^{-1})	171
k	2.04
n	1.20
R^2	0.912
Langmuir isotherm parameters	
q_e (mg g^{-1})	384.6
q_m (mg g^{-1})	171
b	272.3
R^2	0.589
Doubinin–Radushkevich isotherm parameters	
q_e (mg g^{-1})	119.9
q_m (mg g^{-1})	171
$K \times 10^4$ (mol^2 KJ^{-2})	0.0003
E (KJ mol^{-1})	41.6
R^2	0.729

Doubinin–Radushkevich (D–R) isotherm model is based on the fact that there is no homogeneous surface or constant biosorption potential [34]. It is used for the estimation of the porosity apparent free energy.

The linear form of (D–R) isotherm model can be seen below:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{11}$$

where β is the constant corresponding to the adsorption energy, q_m is the theoretical saturation capacity, and ε is the Polanyi potential which is calculated from the equation below:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{12}$$

where R (8.314 J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature.

The mean free energy of biosorption E can be defined as the free energy change when one mole of ion is transferred from infinity in solution to the biosorbent. E can be calculated from the β value by the following relation:

$$E = 1/(2\beta)^{1/2} \tag{13}$$

The value of this parameter can give information about biosorption mechanism. Values of correlation coefficient and other D–R model parameters have been presented in Table 3 which indicates low fitness of D–R model to the experimental data.

3.11. Recovery of U(VI) from biosorbent

Although the biosorption is a very beneficial process for the decontamination of wastewater tainted with heavy metals, however, the loaded biomass that contains uranium is not safe for dumping due to its radioactive nature. Therefore, it is indispensable to regenerate and recycle of biosorbent so as to defend the environment from its detrimental effects. The loaded biomass can be regenerated by shaking with some appropriate solutions which must be inexpensive, effective, non-polluting, and non-damaging to the adsorbent. For this purpose, 0.1 M HNO_3, K_2SO_4, EDTA, NH_4Cl, KH_2PO_4, CH_3COOH, HCl, H_2SO_4, $NaNO_3$, and CH_3COONa solutions were used. For recovery of uranium, 0.05 g of metal-loaded biosorbent was added to each of the above eluting agents. After elution of metal, concentration of metal ions in each of the above solution was determined as shown in Fig. 9. 0.1 M HNO_3 was found to be the best eluting agent for the elution of uranium. The second best eluting agent for desorption of uranyl ions was HCl. The reason was that under acidic condition, the biosorbent surface was protonated by H^+ ions to make possible desorption of positively charged metal ions from the adsorbent surface.

After the selection of appropriate eluent, desorption was carried out by varying the strength of HNO_3, i.e. 0.1, 0.2, 0.3, 0.4, and 0.5 M. It was found that the maximum desorption was occurred by 0.2 M HNO_3. The results are shown in Fig. 10.

It was eluted the uranium-loaded biomass by various eluents, such as $NaHCO_3$, $(NH_4)_2SO_4$, and by mineral acids [11]. The mineral acids, such as diluted H_2SO_4, HNO_3, and HCl, were effective in uranium desorption and the biomass damage caused by the acid elution was negligible. For example, the uranium-loaded biomass with various initial uranium loadings could be eluted by 0.1 N HCl solutions almost completely. The biomass weight loss during the acidic

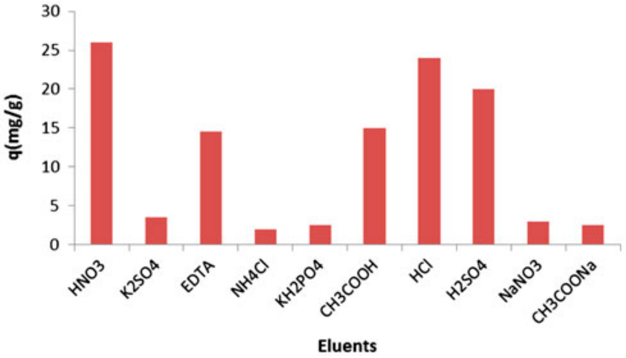

Fig. 9. Effect of eluting agents on the desorption of U(VI) by *T. bispinosai*.

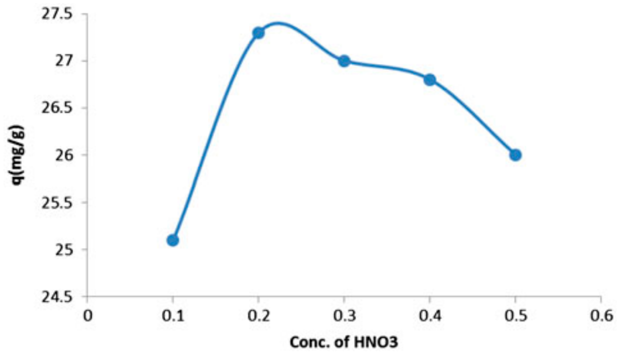

Fig. 10. Effect of different concentrations of HNO_3 on the desorption of U(VI) by *T. bispinosa*.

desorption process was less than 5%. The biomass was also protonated at the same time and was ready for the next run of uranium biosorption. The high elution efficiency, low biomass damage, and low cost made the dilute mineral acid elution quite appropriate for further consideration. The results are shown in Fig. 11.

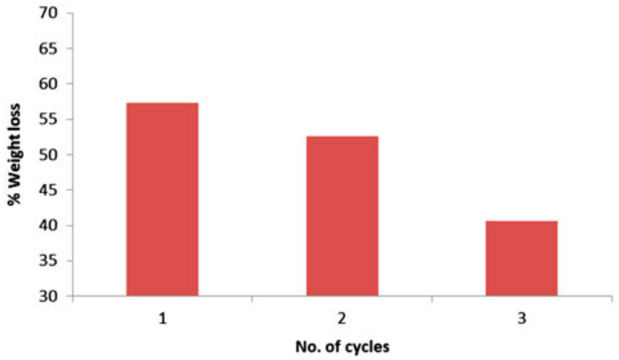

Fig. 11. Cyclic study and percentage weight loss of biomass.

3.12. FT-IR study

FT-IR spectrum of *T. bispinosa* (Singhara) was studied in the range of 400–4,000 cm^{-1} and is presented in Fig. 12(a). The presence of peak at 3,608.1 cm^{-1} depicts the presence of N–H group on the surface of *T. bispinosa*

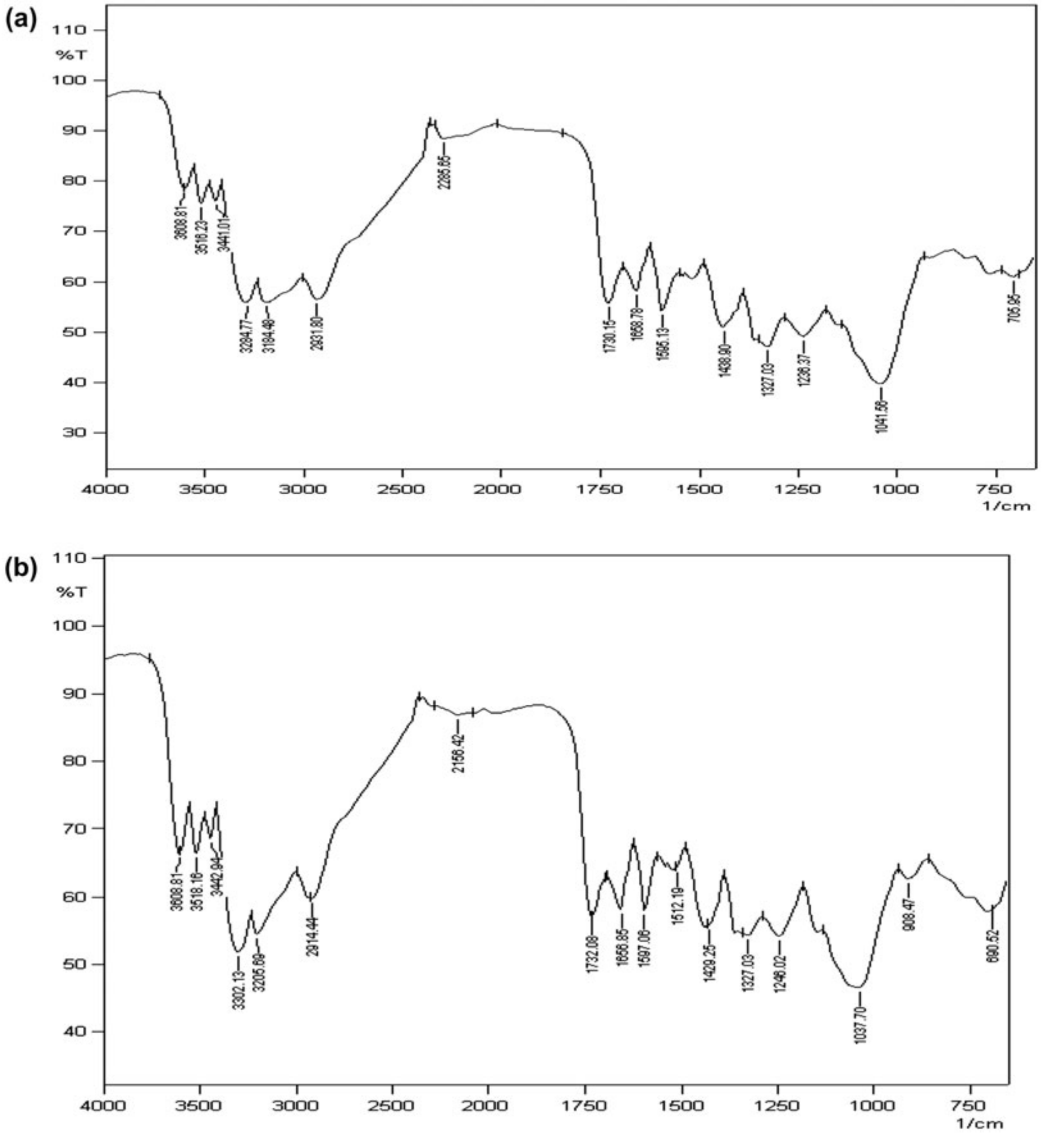

Fig. 12. FT-IR spectra of (a) native and (b) loaded U(IV) *T. bispinosa.*

biomass. Peak at 3,284 cm^{-1} indicates the presence of O–H group (carboxylicacids, phenols, and alcohols) on the surface of biosorbent as in cellulose, pectin, and lignin. The presence of peak at 2,931 cm^{-1} indicates the stretching vibrations of C–H and revealed the presence of –CH and CH groups. The presence of peak at 2,285 cm^{-1} is due to the $C\equiv C$ stretching vibrations. The C=O stretching vibrations are allocated due to presence of peak at 1,730 cm^{-1}. The band appeared at 1,500 cm^{-1} showed that the biomass surface contained the amino groups. These peaks were found to be involved in the adsorption of uranium(VI) onto the surface of *T. bispinosa* biomass. The involvement of these functional groups in the adsorption of uranium(VI) was confirmed due to the vanishing or disappearance of these groups at lower frequencies after the adsorption process and it is presented in the FT-IR spectra of loaded biomass in Fig. 12(b).

4. Conclusion

The biosorption of uranium(VI) ions from aqueous solution by *T. bispinosa* biomass was investigated in batch system with respect to medium pH, contact time, biosorbent dose, initial metal ion concentration, temperature, and particle size of biosorbent. The results indicated that maximum sorption (171 $mg\,g^{-1}$) was observed at pH (5.0), particle size (0.25 mm), biosorbent dose (0.05 g), temperature (50°C), and initial uranium(VI) ion concentration (400 $mg\,L^{-1}$) in 90 min. Different kinetic and equilibrium models were also applied on the experimental results and desorption study was also conducted. Other researchers have also worked on the adsorption of uranium(VI) ions using agricultural wastes, but their results indicate less removal as compared to the present work [35,36], which was less than the present work (171 $mg\,g^{-1}$). The results indicated that *T. bispinosa* biomass could be used as an efficient adsorbent for the removal of uranium ions from aqueous solutions.

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