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Biosorption characteristics of uranium(VI) from aqueous medium onto *Catenella repens*, a red alga

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Abstract

The biosorption characteristics of uranium(VI) onto *Catenella repens* (a red alga), were evaluated as a function of pH, biosorbent size, time, biomass dosage, initial uranium concentration and temperature. Within the pH range studied (1.5–7.5), 4.5 was the optimum pH for the uptake of uranium(VI) by *C. repens*. Reduction in particle size did not increase the biosorption capacity. The metal removal was rapid, with more than 90% of total biosorption taking place in 30 min, and equilibrium was attained in 45 min. The maximum metal loading capacity of the alga was 303 mg/g. Within the temperature range studied (15–55 °C), there was no significant change in biosorption, under optimal conditions. Adsorption process could be well defined by both the Langmuir and Freundlich isotherms with r^2 of 0.94 and 0.96, respectively. The kinetic data fitted the pseudo-second-order kinetic model with the r^2 value of 0.99. At a low pH of 2.5, where most of the biomasses show either no or less metal uptake, a good (>15%) metal loading capacity of 25% was achieved. Therefore biosorption characteristics were also evaluated at pH 2.5.

Keywords: Biosorption; Uranium; *Catenella repens*; pH; Isotherm

1. Introduction

The use of conventional treatment methods such as chemical precipitation, reverse osmosis, ion-exchange, filtration, and evaporative recovery are most effective for treatment of liquid effluents containing high concentration of metal ions. However these technologies become expensive or inefficient for treatment of effluents containing metal ions in the range of 100 mg/l [1]. It is therefore important to develop new methods for metal removal and recovery from such effluents, and thus reduce the concentration of these metal ions to low levels. Treatment of such high volume dilute waste is important since concentrations of metal ions at this level are potentially toxic and hazardous to the human beings. The concentration of these metal ions has to be reduced to meet the legislative standards. Furthermore, removal and recovery of economically important metal ions from these waste streams may reduce the loss of metal ions due to the limitation in processing methods. Biosorption is one of the promising technologies that can be utilized for such purposes. It involves the use of dead and live biomass to bind and concentrate heavy metals from very dilute aqueous solutions [2]. Biosorption involves a number of passive, metabolism independent, accumulation processes, and may include physical and chemical adsorption, ion-exchange, coordination, complexation, chelation and micro-precipitation. Cell walls of biomass consist of polysaccharides, proteins and lipids, which offer various functional groups like carboxylate, hydroxyl, sulphate, phosphate, etc. for the binding with metal ions [3–7]. Biosorbents viz., wastes from agricultural and industrial activities, naturally available seaweeds and specially propagated biomass of bacteria, yeast and fungi have been suggested as some of the useful materials for biosorption process [8]. For uranium uptake, biosorbents showing efficient metal uptake (>15% loading capacity) across the pH range 4–5.5 are common [4–7]. Previously, we have reported uranyl ion removal using biosorbents of different origins viz., bacteria, fungi and plant biomass [9–12]. All these biosorbents exhibited good uranium loading capacity, that is, more than 15% in the acidic range at pH 5–5.5. Similar studies have been reported by Yang and Volesky [7] using marine brown alga, *Sargassum fluitans*

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Nomenclature

b	Langmuir constant (l/mg)
C	metal ion concentration after biosorption at any time t (mg/l)
C_0	initial metal ion concentration (mg/l)
C_e	equilibrium metal ion concentration (mg/l)
h	initial rate of uptake (mg/g)min
k_1	pseudo-first-order rate constant (min^{-1})
k_2	pseudo-second-order rate constant (g/(mg min))
K_f	Freundlich biosorption capacity
n	biosorption intensity
q	biosorption capacity (mg/g)
q_e	amount of biosorption at equilibrium (mg/g)
q_{max}	maximum loading capacity (mg/g)
q_t	amount of biosorption at time t (mg/g)
t	time (min)
V	volume of the metal ion solution (l)
W	dry weight of biosorbent (g)

wherein the optimum pH of uranium uptake was 4. Effluents from nuclear industry, containing uranium have a variable pH (acidic to alkaline). To the best of our knowledge there are no reports in the literature on biomass exhibiting good performance (>15% loading capacity) at low pH. Hence use of these biosorbents for biosorption technology in treating such wastewaters becomes technically non-feasible. The fact that algae are naturally abundant, autotrophic, found in all kinds of aquatic bodies with different environmental condition including pH and have shown uranium removal capacity led us to focus our study on biosorbent of algal origin. To the best of our knowledge this is the first comprehensive report on the biosorption of uranium by *Catenella repens* a red alga. Being photosynthetic, this alga does not require expensive carbon sources for its cultivation and culturing. Natural occurrence of this biomass on sea coasts and estuarine waters makes this biomass a cheap source of biosorbent material. It can be collected in bulk from sea coasts, processed and used directly to serve the purpose of uranium biosorption.

1.1. Materials

1.1.1. Collection of biomass

Biomass of red alga *C. repens* was collected from the estuarine waters near the sea coast of Ratnagiri (Maharashtra, India). The biomass after collection was washed thoroughly with tap water. This was followed by washing three times with deionised water and finally by glass distilled water in order to get a clean biomass that is free from silt, sand, diatoms and other epiphytic organisms. After cleaning the biomass was dried at an ambient temperature of $25 \pm 3\,^{\circ}C$ and stored as whole biomass at room temperature.

1.1.2. Chemicals

$UO_2\,(NO_3)_2{\cdot}6H_2O$ (Merck, Germany) was used to prepare the uranium(VI) solution. The pH of the uranium solution was adjusted to required values by using 1 M Na_2CO_3 or 1 M HNO_3.

1.2. Methods

Unless otherwise indicated, for all the biosorption experiments 50 mg of dry biomass was introduced into 50 ml of uranium solution having an initial uranium concentration of 100 mg/l, in 150 ml conical flasks. After 2 h of shaking at 150 rpm and 30 °C, the supernatant was separated by centrifugation (10,000 rpm for 10 min) and used for estimating the dissolved uranium concentration. Estimation of uranium(VI) was done by arsenazo(III) method [13]. Briefly 0.5 ml sample was mixed with 0.1 ml of oxalic acid (4%) and 0.1 ml of arsenazo(III) (0.05%) and diluted with hydrochloric acid (4 M) to a total volume of 2.5 ml before analyzing at a wavelength of 650 nm. The data presented in the result represents the average of triplicate readings ± standard error. Statistical tests for Analysis of variance (One-way ANOVA and Tukey's significance test) were carried out on the experimental results using OriginPro 7.5 software. All experiments were performed using powdered biomass having particle size between 250 μm and 500 μm, at pH 2.5 and 4.5. For each of the experiments, solutions without biomass were used as controls.

The biosorption equilibrium of uranium per unit algal biomass (mg of U/g dry weight of algal biomass) was calculated using following expression:

$$q_e = \frac{(C_0 - C)V}{W} \quad (1)$$

where 'C_0' and 'C' are the concentrations of uranium (mg/l) in the solution before and after the biosorption, respectively, 'V' the volume of uranium solution used in liters and 'W' is the amount of biomass used in grams.

1.2.1. Effect of pH on the uranium biosorption

The range of pH studied was from 1.5 to 7.5. Uranium solution was continuously stirred while adjusting the pH until a constant required reading was observed.

1.2.2. Effect of particle size on uranium biosorption

Dried whole biomass was powdered with help of mortar and pestle and was passed through sieves of different mesh sizes to get the particle sizes <250 μm, and 250–500 μm.

The particles which could pass through the mesh size of 250 μm were regarded as the particles having the size less than 250 μm. Whereas the particles less than 500 μm and higher than 250 μm were those that could pass through the mesh size of 500 μm but were retained by the mesh size of 250 μm. Biomass without powdering was also used for the experiment as whole biomass.

1.2.3. Effect of contact time on uranium biosorption

For sorption kinetic studies, 0.5 ml of sample was withdrawn periodically, centrifuged at 10,000 rpm for 10 min, and the dissolved uranium concentration was estimated.

1.2.4. Effect of biomass concentration on uranium biosorption

Biosorption of uranium was investigated for the following biomass concentrations, 0.1 g/l, 0.5 g/l, 1 g/l, 1.5 g/l and 2 g/l.

1.2.5. Effect of initial uranium concentration

The effect of initial uranium concentrations of 100 mg/l, 200 mg/l, 400 mg/l, 600 mg/l and 800 mg/l on uptake of uranium by the biomass was studied.

1.2.6. Effect of temperature on uranium biosorption

Temperature effects were investigated at five different temperatures $15 \pm 2\,^{\circ}C$, $25 \pm 2\,^{\circ}C$, $35 \pm 2\,^{\circ}C$, $45 \pm 2\,^{\circ}C$ and $55 \pm 2\,^{\circ}C$.

2. Results and discussions

2.1. Effect of pH on uranium biosorption

Initial pH plays an important role in the biosorption of uranium from the aqueous solutions. It influences both, the speciation of uranium in the aqueous solution, and the binding sites present on the surface of biomass [14]. The effect of pH on biosorption of uranium onto *C. repens* was studied in order to find out the optimum pH for the biosorption process, and to find out whether the biomass was able to show a good uranium uptake at extreme pH values. The percent removal of uranium was 22 ± 1.8 at pH 1.5, 64 ± 2.5 at pH 2.5, 79 ± 2.8 at pH 3.5, 76 ± 2 at pH 5.5, 24 ± 2 at pH 6.5, 14 ± 1 at 7.5 and a maximum of 90 ± 1.4 was observed at pH 4.5. Uranium biosorption at different pH values was significantly different ($P < 0.05$, ANOVA). Percent removal of uranium versus pH was plotted (Fig. 1), which resulted in a bell shaped curve.

The reason suggested for the decreased biosorption at pH 1.5 could be because at this pH there is a high concentration of H^+ and H_3O^+, which compete with other ions (uranyl) for the binding sites on the surface of the biomass [15]. The reason for increased biosorption at pH 4.5 could be due to the presence of ligands like carboxyl, amino, and phosphate on the surface of biomass, which have pK values in the range of 3–5 [5]. Decrease in the uptake of uranium at higher pH could be due to the formation of uranyl carbonate complexes, as the initial pH of the solution was adjusted with Na_2CO_3, and also, atmospheric CO_2 plays a role in the formation of uranyl carbonate complexes above pH 6 [16]. At higher pH values the aqueous carbonate competes with surface binding sites for uranyl ions and reduces the availability of uranium for biosorption [17]. Also at higher pH formation of solid schoepite ($4UO_3 \cdot 9H_2O$) takes place which decreases the dissolved uranium concentration in solution, and consequently leads to the reduced sorption of uranium onto the biomass [18]. As optimum pH for biosorption process was found to be 4.5, all the subsequent experiments were conducted at this pH. Percent removal of uranium at a low pH of 2.5 was 64 ± 2.5 (from 100 mg/l initial uranium concentration) which was an indication for the possible use of this biomass at pH 2.5. Hence all the experiments were also conducted at pH 2.5.

2.2. Effect of particle size on uranium biosorption

Biosorption of uranium was same for whole biomass and powdered biomass having the particle size of 250–500 μm (Fig. 2). A decrease in biosorption was observed for the particle size <250 μm.

At pH 2.5, q_e for whole biomass was found to be 64 ± 2.8 mg/g, and decreased to 51 ± 2.1 mg/g for powdered biomass of particle size <250 μm.

At pH 4.5, q_e for the whole biomass was 92 ± 1.4 mg/g and decreased to 82 ± 1.7 mg/g for powdered biomass of particle size <250 μm.

For both the pH values biosorption by the investigated particle sizes was significantly different ($P < 0.05$, ANOVA). However, the difference between q_e for whole biomass and biomass having particle size 250–500 μm was not significant ($P > 0.05$, Tukey test). Decreasing the particle size increases the surface area, and is generally expected to increase the biosorption [3]. The reason suggested for the same q_e value for whole biomass and powdered biomass of 250–500 μm particle size could be, because,

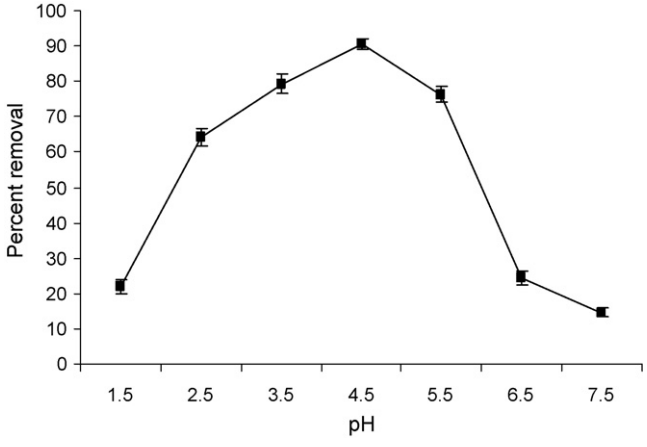

Fig. 1. Effect of pH on uranium(VI) biosorption: $V = 50$ ml, $W = 50$ mg, agitation speed = 150 rpm, contact time = 2 h, temperature = 30 °C, $C_0 = 100$ mg/l.

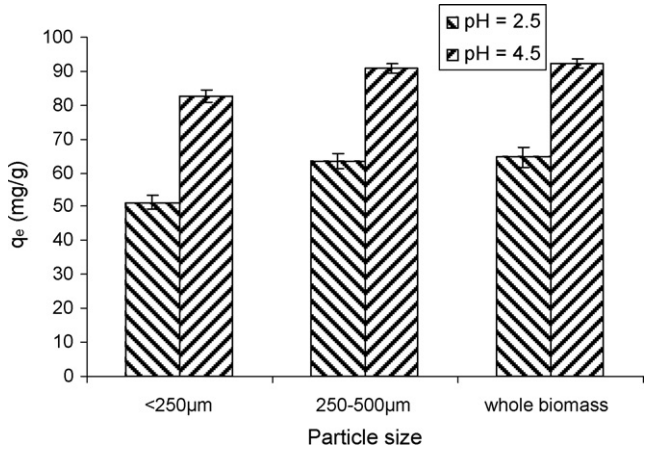

Fig. 2. Effect of particle size on uranium(VI) biosorption: $V = 50$ ml, $W = 50$ mg, temperature = 30 °C, agitation speed = 150 rpm, contact time = 2 h, $C_0 = 100$ mg/l.

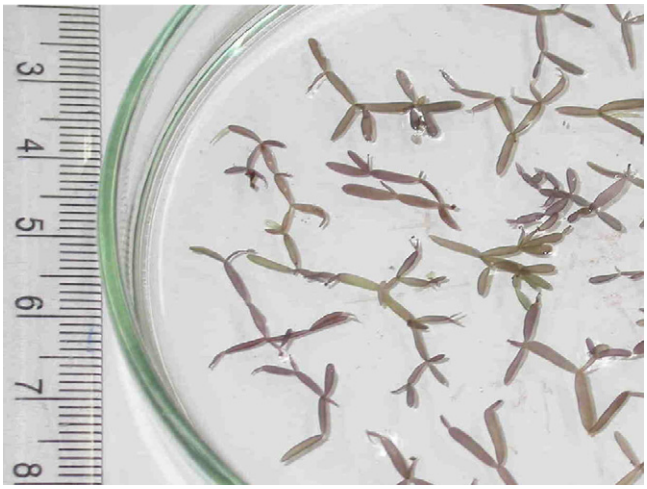

Fig. 3. Habit of *C. repens* (whole biomass). Dichotomous branching—a morphological characteristic of this alga.

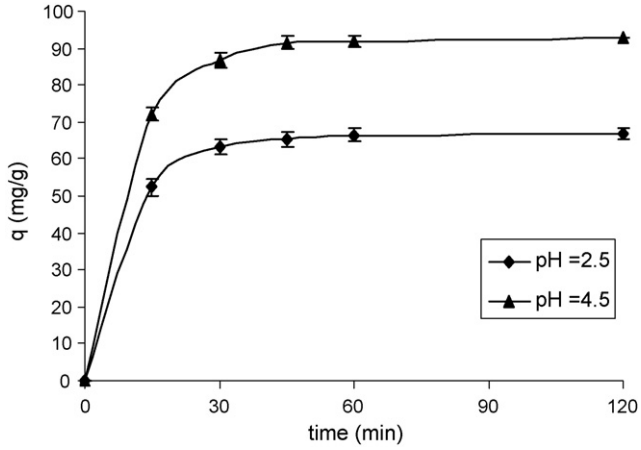

Fig. 4. Time kinetics of uranium(VI) biosorption: $V = 50$ ml, $W = 50$ mg, temperature = 30 °C, agitation speed = 150 rpm, $C_0 = 100$ mg/l.

the different particle sizes investigated had the same thickness (dimension which determines the diffusion distance), since the size grading by standard sieves works on the two dimensions of length and breadth only [19]. However the reduced metal uptake by lower particle size (<250 μm), reported in our studies could be due to the damage to the binding sites by grinding, which consequently would have resulted in reduced availability of binding sites for the uranium.

Fixed-bed reactors are commonly used for the continuous removal of uranium. When the biosorbent in the bed is in powdered form, it causes an excessive compression of the bed [16]. The use of whole biomass for designing a continuous process can eliminate the cost of immobilization, which can be an additional advantage besides the higher biosorption by whole biomass. Thallus of *C. repens* is characterized by dichotomous branching (Fig. 3), which may help in decreasing excessive compression of the bed.

2.3. Effect of contact time on uranium biosorption

The study of effect of contact time on the biosorption of uranium by *C. repens* revealed that the equilibrium state could be achieved in 45 min with the q_e of 65 ± 2.1 mg/g at pH 2.5, and 91 ± 1.7 mg/g at pH 4.5. After the equilibrium was achieved, q_e remained constant (studied for 24 h, data not shown). The initial stage of sorption was rapid, followed by a slow stage. In first 15 min of contact, q_e of 52 ± 2.1 mg/g at pH 2.5, and 72 ± 1.8 mg/g at pH 4.5 could be achieved. The plot of q_e versus time is shown in Fig. 4. This figure also indicates that sorption took place in two stages, first one was rapid surface adsorption and the second one was a slow intracellular diffusion [3,20]. The higher rate of biosorption in initial stage of biosorption could be due to electrostatic interactions, between metal ions and surface ligands on the algal biomass. These binding sites present on surface of the biomass start binding to uranyl ions as soon as they come in contact with each other. As time progresses availability of binding sites reduces, thus reducing the rate of biosorption. Rapid sorption that we have observed is considered as a good characteristic of a biosorbent, as it allows short solution–sorbent contact time, and also allows the use of shallow contact beds of sorbent materials in column applications [1]. For all the subsequent studies it was ensured that enough time for contact of biomass with uranyl solution was provided. Therefore, for all of the subsequent studies instead of presenting the data for 45 min contact time, data for 2 h has been presented.

2.4. Effect of biomass concentration on uranium biosorption

The effect of biomass concentration on the biosorption of uranium studied at pH 2.5 and 4.5 is shown in Fig. 5. Biomass concentration appeared to influence the biosorption process. The q_e was found to decrease concomitantly with the increments in biomass concentration.

At pH 2.5, highest value of q_e (259 ± 6.6 mg/g) was observed at the biomass concentration of 0.25 g/l. The observed q_e for the biomass concentration of 1 g/l was 67 ± 3.9 mg/g. On further

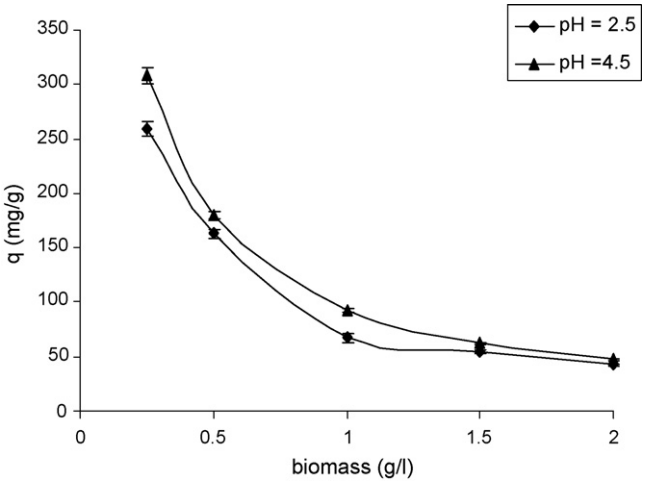

Fig. 5. Effect of biomass concentration on uranium sorption: $V = 50$ ml, temperature = 30 °C, agitation speed = 150 rpm, $C_0 = 100$ mg/l.

increasing the biomass concentration to 2 g/l, the decrease in q_e was not too steep, as can be seen in Fig. 5.

Same trend was followed at pH 4.5. The highest value of q_e observed was 308 ± 7.4 mg/g at 0.25 g/l of biomass concentration.

At high biomass concentration, there would have been a fast superficial adsorption onto the surface of biomass, which would have resulted in a low metal ion concentration in the solution. At a low metal ion concentration, the metal ion sorbed is low, because of the lower driving force (by a lower concentration gradient pressure). Thus an efficient use of sorptive capacity of the biosorbent is not reflected [18].

2.5. Effect of initial uranium concentration on uranium biosorption

The effect of initial uranium concentration on the biosorption is shown in Fig. 6. The plot shows two phases. In the first phase a steep increase in q_e is seen at both the pH values studied, and in the second phase increase was slow. The steep increase in the q_e was observed for the initial uranium concentration of 100–400 mg/l.

The highest value of q_e was 221 ± 7 mg/g at pH 2.5, with C_e of 378 mg/l, and 278 ± 2 mg/g at pH 4.5 with a C_e of 522 mg/l present in the solution.

The biomass concentration being constant (1 g/l) the number of binding sites was same. However, the number of uranyl ions increased with the concomitant increase in uranium concentration. At low uranium concentrations solution, saturation of biomass by uranyl ions could not be achieved as the number of uranyl ions was smaller than the number of binding sites present on the biomass. Increasing the concentration of uranium in the solution was expected to result in the increase of q_e, till the saturation of biomass was attained. Once the binding sites present on the biomass got saturated with the uranium, the availability of binding sites for the uranium decreased. This could explain why the initial stage was fast, and slowed down as the saturation was achieved.

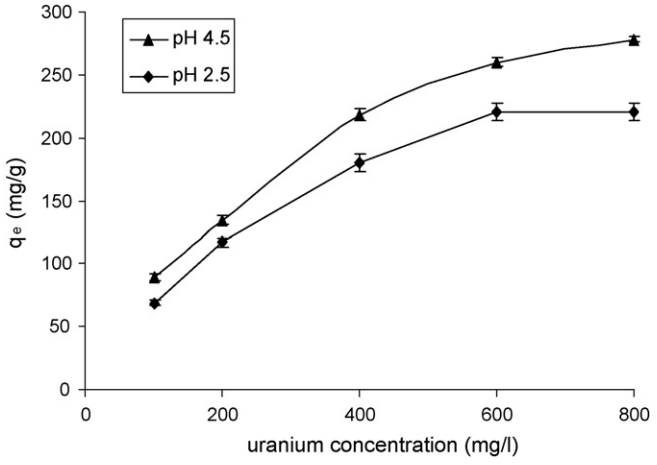

Fig. 6. Effect of initial uranium(VI) concentration on sorption: $V = 50$ ml, $W = 25$ mg, $C_0 = 100$–800 mg/l, temperature = 30 °C agitation speed = 150 rpm, contact time = 2 h.

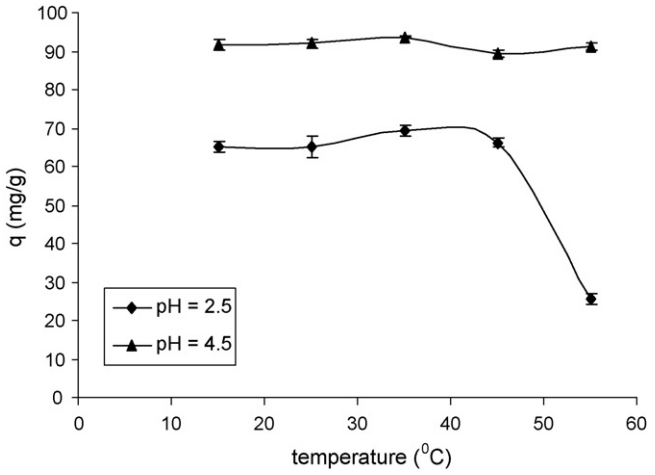

Fig. 7. Effect of temperature on uranium biosorption: $V = 50$ ml, $W = 25$ mg, $C_0 = 100$ mg/l, agitation speed = 150 rpm, contact time = 2 h.

The difference in metal loading capacity of *C. repens* at pH 2.5 and 4.5 could be because, the different functional groups (carboxylates, hydroxyl, sulphate, phosphate, etc.) present on surface of the biomass, ionize at pH around their pK values [21,4]. Thus, the functional groups which are in ionized form at pH 4.5 may not be ionized at pH 2.5. Therefore at pH 2.5 and 4.5, number of binding sites available for the sorption of uranium would not be same.

2.6. Effect of temperature on biosorption of uranium

The plot of effect of temperature on the biosorption of uranium by *C. repens* is shown in Fig. 7. The q_e at pH 2.5 was 67 ± 2 mg/l in the temperature range of 15–45 °C. When the temperature was increased from 45 °C to 55 °C, q_e decreased to 25.6 ± 1.4 mg/g, suggesting the sorption process was an energy dependent mechanism [21]. These results suggested a weak interaction between uranyl ions and binding sites of biomass at pH 2.5. These weak interactions could be due to Vander-waal's interactions, hydrogen bonding, etc., which are broken at high temperatures. This could be the reason, that at a high temperature of 55 °C, a steep decrease in uranium uptake was observed.

The uranium uptake at pH 4.5 seemed to be an energy independent mechanism, as it was not affected by temperature across the range of 15–55 °C at pH 4.5. Statistical analysis (ANOVA) showed that the biosorption across the studied temperature range at pH 2.5 was significantly different ($P < 0.05$). Further, statistical analysis by Tukey test revealed, that, it was only the biosorption at 55 °C, which was significantly different from the biosorption at other temperatures. At pH 4.5, biosorption studied across the temperature range was not significantly different ($P > 0.05$).

2.7. Kinetic modeling

Kinetics of uranium uptake was modeled using the pseudo-first-order and pseudo-second-order Lagergren equation. The pseudo-first-order reaction of Lagergren for sorption can be

expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the amount of metal sorbed per unit weight (mg/g dry weight) of biosorbent at equilibrium and at any time t (min), respectively and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The integrated form of the above equation after applying the boundary conditions, for $t = 0$, $q_t = 0$, becomes

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t \quad (3)$$

The value of the rate constant (k_1) and q_e for the pseudo-first-order sorption reaction can be obtained by plotting $\log(q_e - q_t)$ versus t.

The pseudo-second-order rate of Lagergren [22] can be expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 (g/(mg min)) is the rate constant for the pseudo-second-order sorption. The integrated linear form of Eq. (4) can be represented as follows:

$$\frac{t}{q} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) t \quad (5)$$

The pseudo-second-order rate constant (k_2) and q_e can be calculated from the intercept and slope of the linear plot of t/q_t versus t.

The plots for pseudo-first-order kinetics, $\log(q_e - q_t)$ versus t, and pseudo-second-order kinetics, t/q_t versus t are shown in Fig. 8a and b, respectively. The kinetics data could be well described by pseudo-second-order plot.

The observed experimental values for q_e, and the values obtained from the plots of pseudo-first-order, and pseudo-second-order kinetics are shown in Table 1. The r^2 value of pseudo-first-order rate kinetics was 0.97 at pH 2.5 and 4.5, and for pseudo-second-order rate kinetics was 0.99 at pH 2.5 and 4.5. The observed experimental q_e values were close to the values of q_e obtained from the slope of the linear plot for the pseudo-second-order rate kinetics (t/q_t vs. t), as shown in Table 1. Therefore, the pseudo-second-order rate kinetic model best described the experimental data.

The initial rate of uptake (h) was calculated using the expression $h = k_2 {q_e}^2$. It was found to be 26.7 (mg/g)min and 43.4 (mg/g)min, at pH 2.5 and 4.5, respectively.

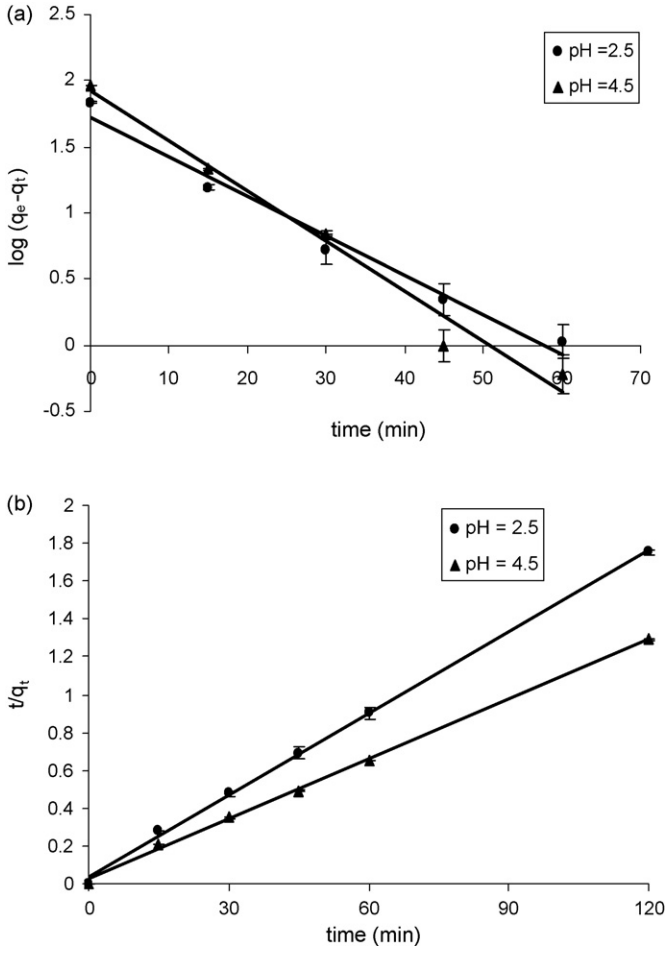

Fig. 8. (a) Pseudo-first-order plot ($\log(q_e - q_t)$ vs. t): $V = 50$ ml, $W = 50$ mg, temperature = 30 °C, agitation speed = 150 rpm, contact time = 2 h, $C_0 = 100$ mg/l. (b) Pseudo-second-order plot (t/q_t vs. t), $V = 50$ ml, $W = 50$ mg, temperature = 30 °C, agitation speed = 150 rpm, contact time = 2 h, $C_0 = 100$ mg/l.

2.8. Equilibrium modeling

Adsorption curve data were fitted to linearised Langmuir and Freundlich adsorption isotherms [23,24]. The Langmuir isotherm is a means to interpret hyperbolic adsorption data. It is basically the same equation used in Michaelis–Menten enzyme kinetics, and describes the adsorption of metal ions to a finite number of ligand sites in a single layer on the cell surface.

Linearised form of Langmuir isotherm can be represented as follows:

$$\frac{C_e}{q_e} = \left[\left(\frac{1}{q_{max}}\right)\left(\frac{1}{b}\right)\right] + \frac{C_e}{q_{max}} \quad (6)$$

Table 1
Pseudo-first-order, pseudo-second-order, and experimental values for *C. repens* at pH 2.5 and 4.5

pH	Experimental, q_e (mg/g)	Pseudo-first-order			Pseudo-second-order			Initial rate, h (mg/g)min
		k_1 (min^{-1})	q_e (mg/g)	r^2	k_2 ($\times 10^{-3}$ min^{-1})	q_e (mg/g)	r^2	
2.5	67.2	0.068	52.1	0.97	5.5	69.4	0.99	26.7
4.5	93.7	0.087	84.0	0.97	4.89	94.3	0.99	43.4

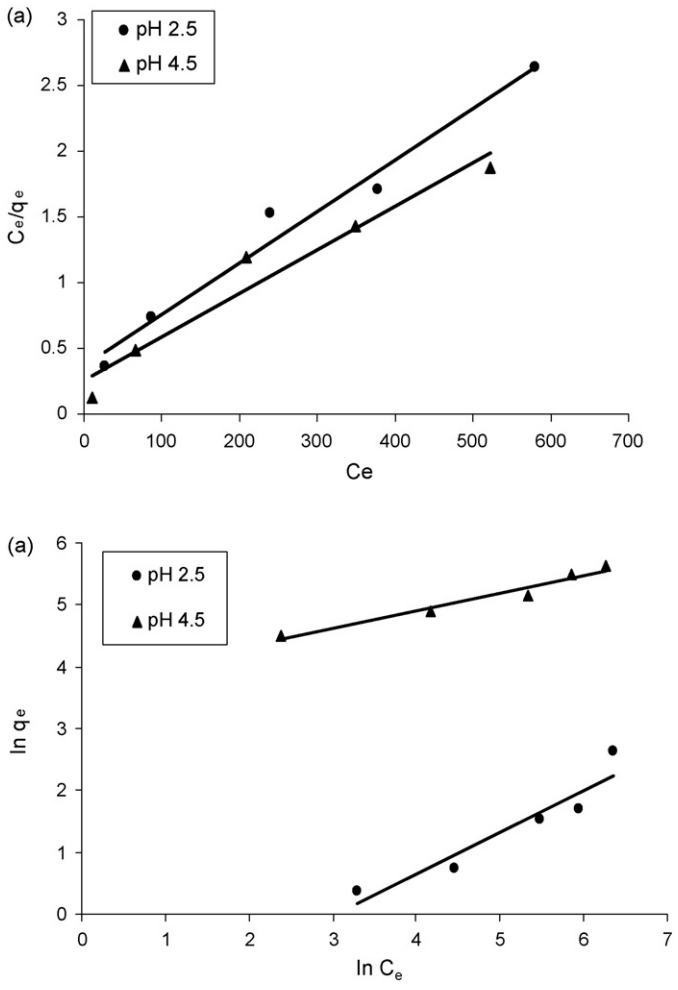

Fig. 9. (a) Langmuir isotherm: $W = 50$ mg, $C_0 = 100$ mg/l, temperature = 30 °C, agitation speed = 150 rpm, contact time = 2 h. (b) Freundlich isotherm. $W = 50$ mg, $C_0 = 100$ mg/l, temperature = 30 °C, agitation speed = 150 rpm, contact time = 2 h.

Where 'q_{max}' is the maximum metal uptake (mg/g) and 'b' the ratio of adsorption/desorption rates related to energy of adsorption. The linearised form of Freundlich equations is as follows:

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \quad (7)$$

where 'q_e' is the equilibrium metal uptake capacity (mg/g), and 'C_e' is the residual uranium concentration in the solution (mg/l). The constant 'K_f' represents Freundlich constant and it is a measure of adsorption capacity and '1/n' the intensity of adsorption. The Langmuir and Freundlich isotherms for the biosorption of uranium onto *C. repens* at pH 2.5 and 4.5 are given in Fig. 9a and b, respectively. The r^2, b and q_{max} values at both the pH values are shown in Table 2. The metal loading capacity (q_{max}) was calculated from the slope of the plot C_e/q_e versus C_e and was found to be 256 mg/g and 303 mg/g at pH 2.5 and 4.5, respectively. The data fitted both the Langmuir ($r^2 = 0.94$) and Freundlich ($r^2 = 0.96$) isotherm at pH 4.5. However at pH 2.5, data fitted Langmuir ($r^2 = 0.97$) better than Freundlich ($r^2 = 0.89$) isotherm.

Table 2
Values obtained from Freundlich and Langmuir isotherms

pH	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b	r^2	K_f	n	r^2
2.5	256.4	0.01	0.97	0.12	1.47	0.89
4.5	303.0	0.12	0.94	43.18	3.50	0.96

'K_f' and 'n' were calculated from the intercept and slope of the plot $\ln q_e$ versus $\ln C_e$. 'n' was 1.4 and 3.5, at pH 2.5 and 4.5, respectively. The value obtained for 'n' in the range $1 < n < 10$, being the suggestive of a beneficial adsorption [5] indicated a beneficial biosorption by *C. repens* at both the pH values. There are reports on biosorbents for uranium having higher q_{max} values as compared to the q_{max} achieved in this study [5]. But to the best of our knowledge, there are no reports on uranium sorbents from biological origin having a good metal loading capacity (>15%) at pH 2.5. Yang and Volesky [7] reported *Sargassum*, a brown alga having a uranium loading capacity of 15% at pH 2.6. Kalin et al. [5] while reviewing the use of algae and microbes, for the removal of uranium from mining waste waters, reported the uranium loading capacity of 0.28% for *Chlorella* at pH 3.5, 0.42% for *Rhizopus arrhizus* at pH 3.5, and 0.2% for *Penicillium* spp. at pH 3.5. A biosorbent having a metal loading capacity of more than 15% is considered as a good biosorbent. The metal loading capacity reported in our study at pH 2.5 is >25%. As compared with the existing biosorbents, the use of *C. repens* at low pH may lead to an efficient and cost effective treatment method for uranium removal from aqueous wastes having a low pH.

3. Conclusions

This work describes the potential of a red sea weed *C. repens* with regard to the following points:

- The common occurrence of *C. repens* in estuarine waters, and its photosynthetic property makes it a cost effective biosorbent.
- Biosorption of uranium(VI) onto *C. repens* was very fast. The equilibrium could be achieved in 45 min of contact time.
- There are many reports on biosorbent materials for uranium(VI), which have performed efficiently with a metal loading capacity of more than 15% at pH 4–5. But among the reported biosorbent materials for uranium(VI) uptake, to the best of our knowledge, none have performed with an efficient metal loading capacity (>15%) at pH 2.5. This study is reporting a low cost biosorbent material for uranium(VI) uptake from aqueous medium having a metal loading capacity of 25% at pH 2.5 and the ability of uranium removal from aqueous medium across the pH range of 2.5–5.5.
- The biomass works more efficiently as whole biomass, and there is no need of powdering the biomass. This is an added advantage for this biosorbent material. While using the fixed-bed reactors for continuous removal of uranium(VI), the use

of whole biomass is preferred, because it decreases the compression of the bed.

C. repens thus seems to be a promising biosorbent for the removal of uranium(VI) from dilute aqueous solutions having low pH.

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