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Sequestering of uranium (VI) onto eucalyptus bark: kinetic, equilibrium and thermodynamic studies

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ABSTRACT

The current study indicates the sequestering of uranium (VI) onto eucalyptus bark. The batch-scale removal of uranium (VI) onto eucalyptus bark has been investigated with various parameters, such as contact times, pH, biosorbent dose, temperatures and initial uranium (VI) concentrations. Value of R^2 and six non-linear regression error functions, namely hybrid fractional error function, Marquardt's percent standard deviation, average relative error, sum of the errors squared, sum of the absolute errors and Chi-square test (χ^2), are considered as tools to predict the most optimum kinetic and isothermal models. The experimental results fitted well to the pseudo-second-order kinetic and Langmuir isothermal models. Maximum sorption capacity (48.99 mg/g) of eucalyptus bark was observed at optimum conditions (pH 6, contact time of 80 min, 0.05-g/L biosorbent dose, 35˚C temperatures and initial uranium (VI) concentration of 90 mg/L). The thermodynamics of uranium (VI) ions sorption onto eucalyptus bark indicates the spontaneous and exothermic nature of the process. The competitive biosorption of Zn(II), Cd(II), Cr(III) and Pb(II) with uranium was studied and results depicted that Cr^{3+} had the most inhibitory effect, while Pb^{2+} had the least inhibitory effect on uranium biosorption. Decrease in peak sharpness in the loaded sample compared to native supports the involvement of functional groups in the sorption process. The results of the study prove that eucalyptus bark is a very useful and economical biosorbent for the removal of uranium (VI) from aqueous solutions.

Keywords: Biosorption; Uranium; Eucalyptus bark; Non-linear regression; Error functions

1. Introduction

The most compelling environmental issue facing the world on the brink of the twenty-first century is the disposal of nuclear waste. With tremendous progress in modern economy, nuclear wastes pollute the environment and endanger human health. Environmental contamination caused by radionuclides, in particular uranium U(VI) and its decay products, is a serious problem worldwide. Uranium is naturally present in both aquatic and terrestrial environments and UO_2^{2+} poses great risks to human health [1,2]. Treatment of such highly toxic waste is essential to meet the maximum acceptable level in water [3]. The general methods employed for the removal of

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uranium ions from aqueous solutions are extraction [4], precipitation [5], ion exchange [6] and sorption [7].

Biological remediation processes offer an environmentally friendly and cost-effective alternative for removing metals/radionuclides pollutants from dilute solutions where physicochemical methods may not be feasible. Biological methods are also considered to be flexible as they may be implemented either *in situ* or ex situ during the cleanup of contaminated water. Such biological methods commonly use microbial consortia, consisting of several species of micro-organisms in the form of bioflocs for removing/degrading the pollutants [8]. Among those approaches, sorption is effectively used for the recovery of uranium ions because of its high efficiency, ease of handling and the availability of different synthetic and natural adsorbents [9]. A number of adsorbents have been exploited for the removal and recovery of uranium ions from contaminated water by different researchers [10].

Biological materials have affinity for inorganic and organic pollutants having enormous biosorption capacity and provide cheap and highly efficient sorbents. The biosorption capacities of various biomasses have been investigated for decontamination of wastewater loaded with heavy metals [11]. The potential of various synthetic adsorbents for uranium removal have also been explored [10,12], but researchers are still focusing on the search for some cheap biomaterials.

In Pakistan, the agricultural waste products represent unused resources being widely available and so they have a great potential and can be used as environmentally friendly biosorbents to remove the heavy metal ions. In this context, this study has been undertaken to develop a new cost-effective sorbent to remove the uranium ions from aqueous solutions. In the present work, eucalyptus bark has been used to remove uranium ions from simulated wastewater. The effect of initial solution pH, sorbent amount, initial uranium ion concentration and temperature on uranium sorption has been investigated.

2. Material and methods

All research work was conducted in Environmental and Material Chemistry Lab, Department of Chemistry, University of Agriculture, Faisalabad. All chemicals used throughout this study were of analytical grade and mainly purchased from Fluka chemicals and included $(UO)_2(NO_3)_2 \cdot 6H_2O$, Arsenazo III Dye, DTPA, H_2SO_4, HNO_3, HCl, EDTA, NaOH, $MgSO_4 \cdot 7H_2O$, etc. All glassware used in the experiments were soaked in 1-N HNO_3 solution and subsequently rinsed with deionized distilled water (DDW) to remove any possible interference by other metals.

2.1. Sorbent uranium (VI) ion determination

Eucalyptus bark used in this work was collected from the D-Ground of the University of Agriculture Faisalabad, Pakistan. Biomass was extensively washed with DDW to remove particulate material from their surface and sundried. Dried biomass was ground using a food processor (Moulinex, France). The biosorbent was sieved through Octagon siever (OCT-DIGITAL 4527-01) to obtain biosorbent with homogeneous known particle size (300 μm). The sieved sorbent was stored in airtight plastic containers for further experiments.

Stock uranium (VI) solution (1000 mg/L) was prepared using $UO_2(NO_3)_2 \cdot 6H_2O$ and the concentration of U(VI) was determined by spectrophotometric method using Arsenazo-III at 655 nm [13].

2.2. Batch biosorption experiments

Batch tests were carried out in 250-cm^3 flasks at 30°C and 125 rpm for specified time period. At the end of experiment, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration (Whatman No. 40, ashless). In order to adjust the pH of the medium, 0.1-N NaOH and HNO_3 were used. Optimization of sorption-affecting parameters was carried out by increasing initial pH, metal ion concentration, biosorbent dose, time and temperature in order to check the maximum possible removal of the metal ions. Control assay was accompanied with each experiment.

The biosorption equilibrium capacity of each metal ion per unit (mg g^{-1}) dry weight of the biomass was calculated using the formula

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

where C_o and C_e are the initial and equilibrium concentrations of metal ions in solution, V is volume of the metal solution of desired concentration in litres and W is the amount of biosorbent in grams.

2.3. Sorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were used to understand the mechanism, controlling the biosorption and interpreting the experimental data, assuming that measured concentrations are equal to cell surface concentrations. Non- linear regression analysis was performed using a statistical software i.e. *R* (Version 2.15.1).

2.3.1. Pseudo-first-order kinetic model

The pseudo-first-order kinetic model [14], based on solid capacity, expresses the mechanism of removal as sorption preceded by diffusion through a boundary. It considers that the sorption is partially first ordered, depending on the concentration of free sites. The pseudo-first-order kinetic model is based on the fact that the change in metal ions concentration with respect to time is proportional to the power one. The non-linear form of model is given below:

$$q_t = q_{\mathrm{e}}(1 - e^{-k_1 t}) \tag{2}$$

where q_{e} and q_t are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the pseudo- first-order rate constant.

2.3.2. Pseudo-second-order kinetic model

The pseudo-second-order kinetic [15] model is based on the assumption that biosorption follows a second rate kinetic mechanism. So, the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites. Non-linear form of the second-order expression used in this study is presented below:

$$q_t = \frac{q_{\mathrm{eK}_2}^2 t}{1 + q_{\mathrm{eK}_2} t} \tag{3}$$

where q_{e} and q_t in the pseudo-second-order equation are the amounts of metal ions adsorbed onto the adsorbent (mg/g) at equilibrium and at time t (min), respectively, and k_2 is the pseudo-second-order rate constant (g/mg min).

2.4. Equilibrium study

Adsorption isotherms are used to characterize the biosorption process and for evaluating biosorption capacity. An isotherm describes the relationship between the amount of sorbate sorbed and the metal ion concentration remaining in the solution. Non-linear regression analysis of equilibrium models was performed using a statistical software i.e. *R* (Version 2.15.1).

2.4.1. Freundlich isotherm

The Freundlich [16] equation is an empirical equation employed to describe heterogeneous systems, in which it is characterised by the heterogeneity factor $1/n$. Hence, the empirical equation can be written as:

$$q_{\mathrm{e}} = K_{\mathrm{F}} C_{\mathrm{e}}^{\frac{1}{n}} \tag{4}$$

K_{F} and n are Freundlich constants related to the sorption capacity and sorption intensity, respectively.

2.4.2. Langmuir isotherm

Langmuir [17] proposed a theory to describe the sorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm is found to be successful for its application to many real sorption processes of monolayer adsorption. The Langmuir equation is based on the assumption of a structurally homogeneous sorbent, where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate. Therefore, a saturation value is reached beyond which no further sorption can take place. The saturated or monolayer (as $C_{\mathrm{e}} \to \infty$) capacity can be represented by the expression:

$$q_{\mathrm{e}} = \frac{q_{\mathrm{m}} K_{\mathrm{a}} C_{\mathrm{e}}}{1 + K_{\mathrm{a}} C_{\mathrm{e}}} \tag{5}$$

where q_{e} is the amount of metal ions sorbed on the biomass (mg/g) at equilibrium, C_{e} is the equilibrium concentration of metal ions (mg/L), q_{m} is the maximum biosorption capacity, describing a complete monolayer adsorption (mg/g) and K_{a} is sorption equilibrium constant (L/mg) that is related to the free energy of biosorption.

2.5. Error functions

The optimization procedure requires the error functions in order to evaluate the best-fit isotherm to explain the experimental kinetic and equilibrium data [18,19]. To optimize the kinetic and equilibrium models, six different non-linear regression functions, given in detail in Table 1, were used.

Table 1
Error Functions

Error functions	Abbreviation	Definition/expression	Ref
Sum squares errors	ERRSQ/SSE	$\sum_{i=1}^{n}(q_{\text{e,exp}} - q_{\text{e,calc}})_i^2$	[20]
Hybrid fractional error function	HYBRID	$\frac{100}{n-P}\sum_{i=1}^{n}\left[\frac{q_{\text{e,exp}}-q_{\text{e,calc}}}{q_{\text{e,exp}}}\right]_i$	[21]
Average relative error	ARE	$\frac{100}{n}\sum_{i=1}^{n}\left[\frac{q_{\text{e,exp}}-q_{\text{e,calc}}}{q_{\text{e,exp}}}\right]_i$	[22]
Sum of absolute error	EABS	$\sum_{i=1}^{n}\left[q_{\text{e,exp}}-q_{\text{e,calc}}\right]_i$	[23]
Marquardt's percent standard deviation	MPSD	$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{q_{\text{e,exp}}-q_{\text{e,calc}}}{q_{\text{e,exp}}}\right)_i^2}$	[24]
Nonlinear chi-square test	χ^2	$\sum_{i=0}^{n}\frac{(q_{\text{e,exp}}-q_{\text{e,cal}})^2}{q_{\text{e,calc}}}$	[20]

2.6. Effect of interfering ions

In order to study the effect of co-metal ions, the biosorption studies were performed by adding different concentrations of Cd^{2+}, Pb^{2+}, Zn^{2+} and Cr^{3+} ions (25–100 mg/L) in uranium and the concentration of uranium was kept constant at 50 mg/L.

2.7. Desorption of sorbed U(VI) ions

Metal sorbed by the biomass was regenerated using an appropriate eluting agent such as 0.1-N H_2SO_4, 0.1-N HNO_3, 0.1-N NaOH, 0.1-N EDTA or 0.1-N $MgSO_4{\cdot}7H_2O$.

2.8. Biosorbent characterization

The biosorbent was characterized for its functional groups using Fourier transform infrared spectrometer (FTIR) analysis. The chemical characteristics of eucalyptus bark biomass were analysed and interpreted by Bruker Tensor 27 FTIR using the KBr disc method.

2.9. Statistical analysis

All the experiments were performed in duplicates and the results were presented as ±SD. The value of coefficient of determination (R^2) for non-linear regression was evaluated by following the formula [20]:

$$R^2 = \frac{(q_{\text{e,exp}} - \overline{q_{\text{e,calc}}})^2}{\Sigma(q_{\text{e,exp}} - \overline{q_{\text{e,calc}}})^2 + (q_{\text{e,exp}} - q_{\text{e,calc}})^2} \quad (6)$$

The subscripts "exp" and "calc" are used for experimental and theoretical values calculated from the model.

3. Results and discussions

3.1. Effect of initial solution pH

The pH of the solution has been identified as one of the most important parameters affecting metal ion sorption. This is partly because hydrogen ions themselves are strongly competing with the sorbate. Uranium sorption by eucalyptus bark was studied in the pH range of 2.0–9.0. The results regarding the effect of pH on the removal of U(VI) by eucalyptus bark at biomass dosage 0.1 g, initial metal ion concentration 50 mg/L, shaking speed 125 rpm and temperature 30°C are shown in Fig. 1(a). As reflected from results, the extremely acidic conditions pH 2.0 did not favour uranium sorption and by increasing pH, sorption of U(VI) also increased. Maximum uptake (22.64 mg/g) of U(VI ions was attained at pH 6.0. However, with further increase in pH, uranium sorption by eucalyptus bark showed a sharp decline because OH^- ions increased the hindrance of diffusion as well as some of the trivalent cations may react with OH^- ions, and thereby decrease the free metal ions available in the solution. Psareva [25] studied the effect of pH on the adsorption of U(VI) onto PGCPCOOH over the pH range 2.0–9.0. The adsorption of U(VI) sharply increased with increase in pH from 2.0 to 4.0, and then remained stable up to 6.0 and then started decreasing. Maximum adsorption occurred at pH 6.0, and hence pH 6.0 was used in all further studies. Maximum removal (98.3%) was observed at an initial concentration of 50 mg/L at pH 6.0.

At low pH value, the competition between H_3O^+ and UO_2^{2+} limits the uptake efficiency. At lower pH, the predominant species of U(VI) is UO_2^{2+}, but at higher pH values, the hydrolysis products such as $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)^{5+}$ are formed. Since the uptake of U(VI) increases with pH

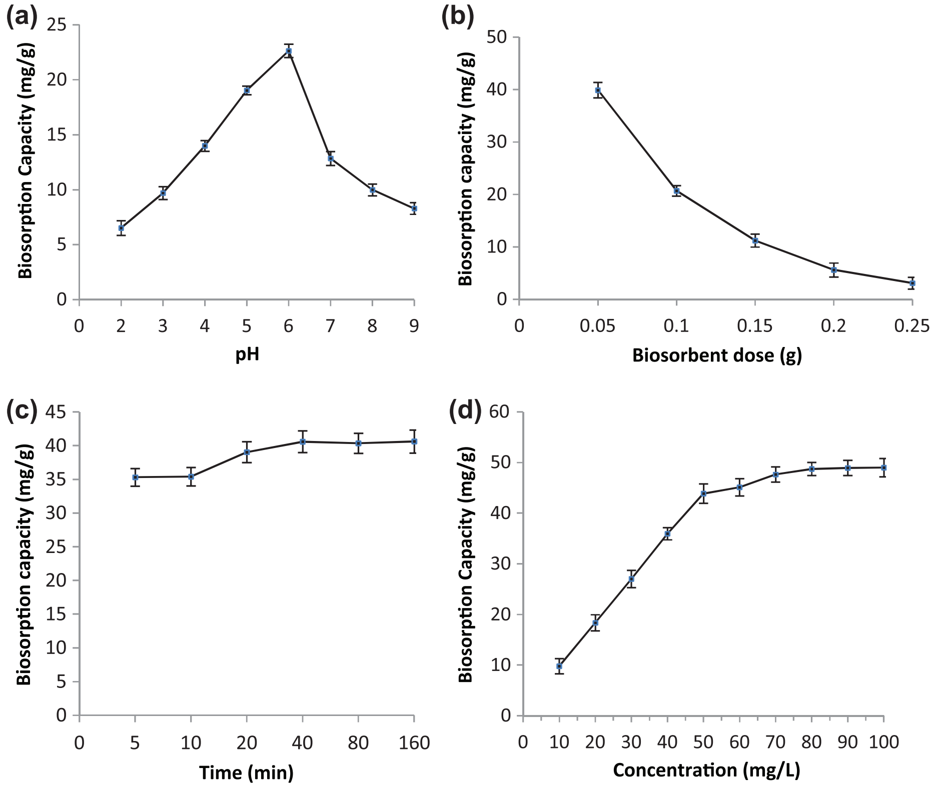

Fig. 1. (a) Effect of initial solution pH on uranium sorption onto eucalyptus bark, (b) effect of sorbent amount on uranium sorption onto eucalyptus bark, (c) effect of time on uranium sorption onto eucalyptus bark and (d) effect of initial metal ion concentration on uranium sorption onto eucalyptus bark.

and then remains constant in the pH range 4.0 to 6.0, biosorbent binds these hydroxo complexes very well. At the pH range 4–6, it is believed that ion exchange and complexation processes are major mechanisms for the removal of U(VI) ions [26].

3.2. Effect of biosorbent dosage

The dependence of U(VI) sorption on biosorbent dosage was studied by varying the amount of biosorbent while keeping pH (6), initial metal ion concentration (50 mg/L), shaking speed 125 rpm and temperature (30˚C) constant. The effect of biosorbent dose on the sorption of U(VI) at pH 6.0 is shown in Fig. 1(b). Results revealed that maximum biosorption was attained at 0.05 g/L for U(VI) solution. The percentage of uranium removal from aqueous solution was found to decrease with the increase in biomass concentration. Maximum biosorption was attained at 0.05-g/50-mL uranium solution.

The dosage of a biosorbent strongly influences the extent of biosorption. In many instances, lower biosorbent dosages yield higher uptakes and lower percentage removal. An increase in the biomass concentration generally increases the amount of solute biosorbed due to the increase in surface area of the biosorbent, which in turn increases the number of binding sites. Quantity of biosorbed solute per unit weight of biosorbent decreases with increase in the biosorbent dosage, which might be due to the complex interaction of several factors. At high sorbent dosages, the available solute might be unable to completely cover the available exchangeable sites on the biosorbent, usually resulting in low solute uptake. Also, the interference between binding sites due to increased biosorbent dosages cannot be overruled, as this will result in a low specific uptake [27].

3.3. Effect of contact time

The equilibrium time is one of the important parameters for development of an economical wastewater treatment system. The study of effect of contact time on the biosorption of uranium by eucalyptus bark revealed that the equilibrium could be achieved in 80 min at constant values of pH (6.0), biosorbent dosage (0.05 g/L), initial metal ion concentration (50 mg/L) and temperature 30˚C with the q_e of

40.64 mg/g. The results are shown in Fig. 1(c). After the equilibrium was achieved, biosorption capacity (q_e) remained constant. Sorption took place in two stages; first one was rapid surface sorption and the second one was a slow intracellular diffusion. The higher rate of biosorption at initial stage of biosorption could be due to electrostatic interaction between metal ions and ligands present on the surface of the biomass. The binding sites present on the surface of the biosorbent started binding to form uranyl ions as soon as they came in contact with each other. With the passage of time, the availability of binding sites reduced and the rate of biosorption also reduced. Further increase in contact time did not show any increase in biosorption. Lower bioorption rate in the latter stage was due to the difficulty faced by uranyl ions to occupy the remaining vacant surface sites because of forces between the solute molecules of the solid and bulk phase [28].

3.4. Sorption kinetics

To understand the controlling mechanism of biosorption, most commonly used pseudo-first- and pseudo-second-order kinetic models were employed to interpret the experimental data. The value of R^2 and comparison of experimental and theoretical q_e calculated from kinetic models (see Table 2) showed that the pseudo-second order is best fitted to the experimental kinetic data. Kinetic models' curve (shown in Fig. 2(a)) shows that there is a good agreement between the experimental data and values by the pseudo-second-order kinetic model. The error function values also support fitting of data to the pseudo-second-order kinetic model as shown in Fig. 2(b). The fitness of the pseudo-second-order kinetic model has been already reported in previous reports on U(VI) removal by different adsorbents [28,29].

3.5. Effect of initial metal ion concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of uranium between the aqueous and solid phases. The rate of biosorption is a function of the initial metal ion concentration, which makes it an important factor to consider the effectiveness of biosorption. The apparent capacity of eucalyptus bark for uranium was determined at different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L). Fig. 1(d) is showing the relation between capacities and the metal ion concentrations, which shows that as the metal ion concentration increases, the capacity of biosorbent also increases. The maximum removal of uranium occurred at 90 mg/L. It was found that the amount of the uranium taken up by eucalyptus bark increased with the increase in the concentration of uranium and then reached a saturated value. This increase was due to higher probability of collision between metal ions and biosorbent and also due to the penetration of metal ions inside the cells rather than surface adsorption [12].

3.6. Equilibrium modelling

Equilibrium data were fitted to both widely used Freundlich and Langmuir isothermal equations. The value of R^2 (Table 3) shows that data can be well described by Langmuir isotherm. The value of R_L helps in estimating the nature of the sorption process ($R_L > 1$: Unfavourable biosorption mechanism; $R_L = 1$: Linear; $0 < RL < 1$: Favourable; and $R_L = 0$: Irreversible).

The values of R_L obtained in the present study are in the range of 0–1 (Table 3), describing that the biosorption process is favourable for uranium removal from wastewater using eucalyptus bark. Isothermal curves in Fig. 2(c) show that the experimental data is in good agreement with the Langmuir isotherm when compared to the Freundlich isotherm. Comparison of error function values for Langmuir and Freundlich (See Fig. 2(d)) models shows that Langmuir is better fit isotherm for the equilibrium data, as the error function values obtained for Langmuir are small when compared to Freundlich. Similar results are already reported in the literature [30,31].

Table 2
Comparison of q_e obtained from the pseudo-first-order and Pseudo-second-order models for uranium biosorption by eucalyptus bark

	Pseudo-first-order			Pseudo-second-order		
Experimental q_e (mg/g)	q_e (mg/g)	$k_{1.ads}$ (min^{-1})	R^2	q_e (mg/g)	$k_{2.ads}$ (g/mg min)	R^2
40.64	39.514	0.410	0.5041	40.795	0.02618	0.844

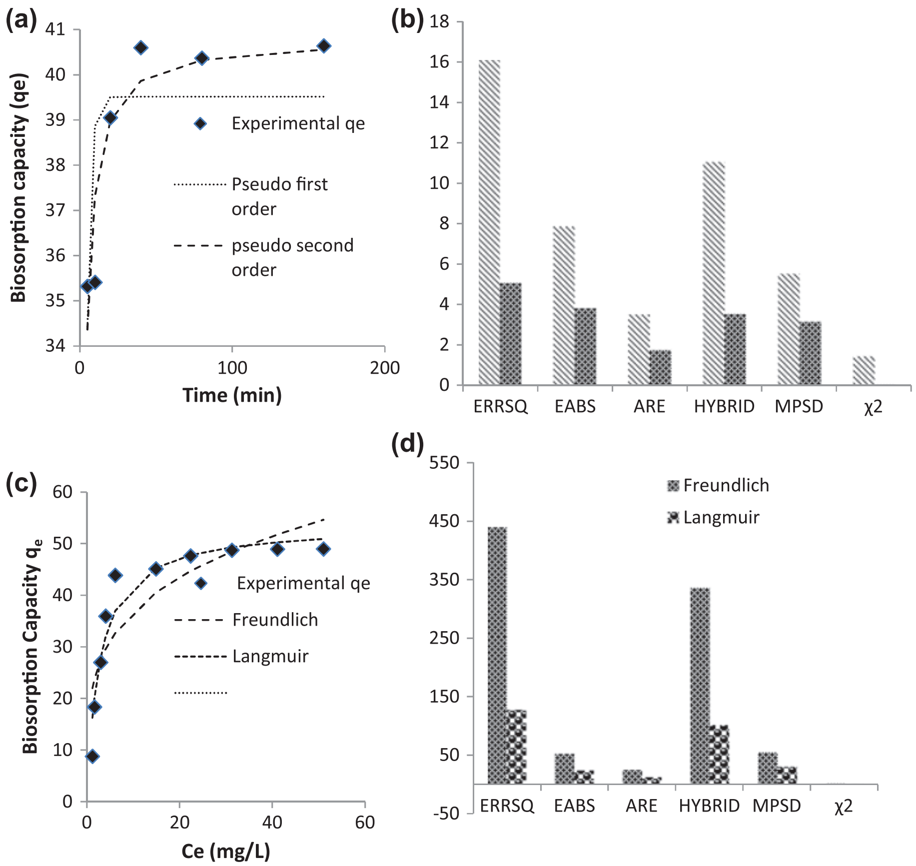

Fig. 2. (a) Experimental data and predicted pseudo-first-order and pseudo-second-order kinetic models for uranium sorption onto eucalyptus bark, (b) non-linear regression error functions for pseudo-first- and pseudo-second-order kinetic models for uranium sorption onto eucalyptus bark, (c) experimental data and predicted Freundlich and Langmuir isotherms for uranium sorption onto eucalyptus bark and (d) non-linear regression error functions for Freundlich and Langmuir isotherms for uranium sorption onto eucalyptus bark.

Table 3
Comparison of q_{max} obtained from the Langmuir and Freundlich adsorption isotherms for uranium biosorption by eucalyptus bark

	Langmuir			Freundlich		
Experimental q_{max} (mg/g)	q_{max} (mg/g)	R_L (L/mg)	R^2	K_F (mg/g) (L/mg)^n	n	R^2
48.93	53.629	0.033	0.932	21.067	0.2421	0.768

3.7. Effect of temperature

Temperature is found to be a critical parameter in the sorption of uranium. The maximum sorption occurred at 30°C and decreased continuously by increasing the temperature at constant values of pH (6.0), biosorbent dosage (0.05 g), initial metal concentration (50 mg/L.) and shaking speed (125 rpm). The effect of temperature on the metal biosorption experiments was examined at seven different temperatures, 30, 35, 40, 45, 50, 55 and 60°C as shown in Fig. 3. The maximum equilibrium uptake for uranium was found to be at 30°C. Further increase in temperature resulted in decreased uptake of uranium. According to the adsorption theory, adsorption decreases with the increase in temperature and molecules sorbed earlier on a surface tend to desorb from the surface at elevated temperatures. As the process of biosorption is exothermic in nature, increase in the temperature rate of biosorption should decrease. But here, by increasing the temperature from 30–35°C, the rate of biosorption

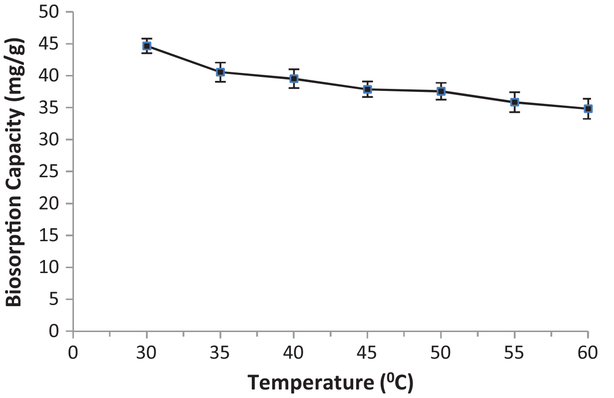

Fig. 3. Effect of initial temperature on uranium sorption onto eucalyptus bark.

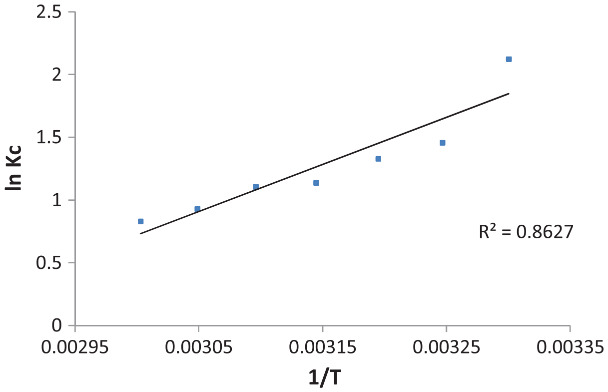

Fig. 4. Graph between lnKc and $1/T$ to determine the thermodynamic parameters.

increased, meaning that the process of chemisorption is involved. So, by increasing the temperature, the process of biosorption increased. However, further rise in temperature results in the destruction of the biosorbent. As a result, the process of biosorption decreased.

Temperature seems to affect biosorption only to a lesser extent within the range from 20 to 35°C. Higher temperatures usually enhance sorption due to the increased surface activity and kinetic energy of the solute; however, physical damage to the biosorbent can be expected at higher temperatures. Due to the exothermic nature of some biosorption processes, an increase in temperature has been found to reduce the biosorption capacity of the biomass. It is always desirable to conduct/evaluate biosorption at room temperature, as this condition is easy to replicate.

3.8. Thermodynamic parameters of biosorption

The thermodynamic parameters of ΔH° and ΔS° were obtained from the plot between ln Kc vs. $1/T$ plot (Fig. 4). The Gibbs free energies (ΔG°) were calculated at different temperatures from Eq. (6):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

ΔH° and ΔS° were determined from the Eq. (7).

$$\ln \mathrm{Kc} = -(\Delta H^\circ/R)1/T + \Delta S^\circ/R \tag{8}$$

where $\mathrm{Kc} = (q_e/C_e)$ is the distribution coefficient ($\mathrm{mL\ g^{-1}}$).

Gibbs free energies' (ΔG°) values (Table 4) are negative at all temperatures. The negative values of Gibbs free energy suggest that the biosorption process is spontaneous or feasible. The negative value of ΔH° indicates that the nature of biosorption is exothermic. The negative value of ΔS° suggests decreased randomness at the solid/solution interface during the biosorption of of uranium by eucalyptus bark. Hanif et al. [30] reported that Zr (IV) removal by fungus is an exothermic process.

3.9. Recovery of U(VI) from the biosorbent

The use of biosorbent in the wastewater treatment depends not only on the biosorptive capacity, but also

Table 4
Thermodynamic parameters for the biosorption of uranium by eucalyptus bark

Temperature (K)	ΔG° ($\mathrm{kJ\ mol^{-1}}$)	ΔH° ($\mathrm{kJ\ mol^{-1}}$)	ΔS° ($\mathrm{J\ K^{-1}\ mol^{-1}}$)
303	−4.651	−31.17	−87.51
308	−4.213		
313	−3.776		
318	−3.338		
323	−2.901		
328	−2.463		
333	−2.026		

on how well the biomass can be regenerated and used again. Although biosorption is a very useful process for the purification of wastewater polluted with heavy metals, however, the saturated biosorbent which contains U(VI) is not safe for disposal due to its radioactive nature. Therefore, it is important to devise a method for regeneration and reuse of biosorbent so as to protect the environment from its harmful effects. For this purpose, it is essential to desorb the sorbed metals and thus regenerate the biosorbent for another cycle of application. The regeneration of the adsorbent can be achieved by shaking the loaded biosorbent with an appropriate desorbing solution that must be cheap, effective, non-polluting and non-damaging to the adsorbent. For this purpose, 0.1-N HNO_3, H_2SO_4, NaOH, EDTA and $MgSO_4·7H_2O$ solutions were used.

For the recovery of uranium metal, 1.0-g 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. 0.1-N H_2SO_4 was found to be the best eluting agent for the elution of uranium as shown in Fig. 5. It is clear from the results that acids are good desorbing reagents [12,32]. The reason was that under acidic conditions, the biosorbent surface was protonated by H_3O^+ ions to allow the desorption of positively charged metal ions from the adsorbent surface.

3.10. Effect of interfering ions

Wastewaters such as industrial effluents may also contain large amounts of various heavy metal ions in addition to uranium metal ions. Hence, the effect of these ions on the biosorption of uranium onto eucalyptus bark was studied. Fixing the concentration of the metal under study at 50 mg/L, the competitive biosorption of Zn(II), Cd(II), Cr(III) and Pb(II) with uranium was studied by varying the concentration of these ions from 25 to 100 mg/L. The results depicted that the equilibrium uptake of uranium metal ion was reduced by the presence of other metals in the mixture. It is clear from the Fig. 6 that individual sorption yield of the metal under study decreases with increase in concentrations of other metal ions. It was found that Cr^{3+} had the most inhibitory effect on uranium biosorption and Pb^{2+} had the least inhibitory effect on uranium biosorption. The order of inhibitory effect of these metal ions on uranium biosorption is given as:

$$Cr^{3+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$$

3.11. FTIR studies

The FTIR technique was used to examine the surface groups present on the eucalyptus bark involved in sorption and compare the changes in these groups after U ion sorption. The transmission FTIR spectra in the range of 4,000–400 cm^{-1} for native and U loaded eucalyptus bark are shown in Fig. 7, demonstrating the complex nature of the biomass, containing large number of bands.

The broad main peak found in native unloaded eucalyptus bark was found at 3,363.28 cm^{-1}, which corresponds to the –O–H carboxylic group on the surface of the biosorbent as in cellulose, pectin and lignin. The presence of a peak in the region of 2,927.57 cm^{-1} in the native biosorbent may be due to the aliphatic –C–H group. The peak at 1,726.74 cm^{-1} is representing the C=O (carboxylic acid) group. The peak in the range of 1,513–1,611 cm^{-1} can be assigned to the C–C group in alkanes. The peak in the range of 1,231.48 cm^{-1} may

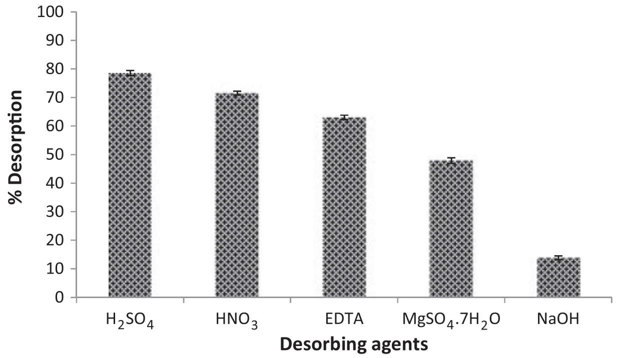

Fig. 5. Effect of desorbing agents onto uranium desorption.

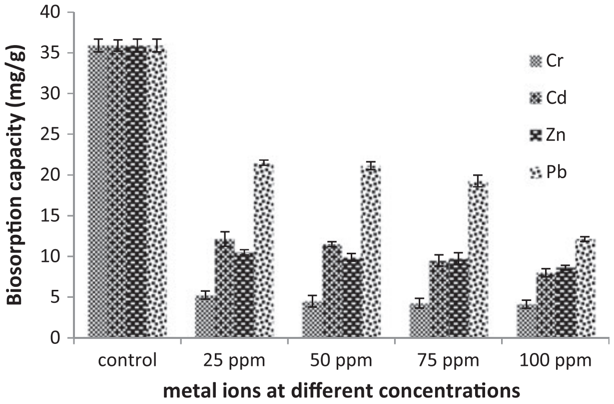

Fig. 6. Effect of co-metal ions on uranium removal by eucalyptus bark.

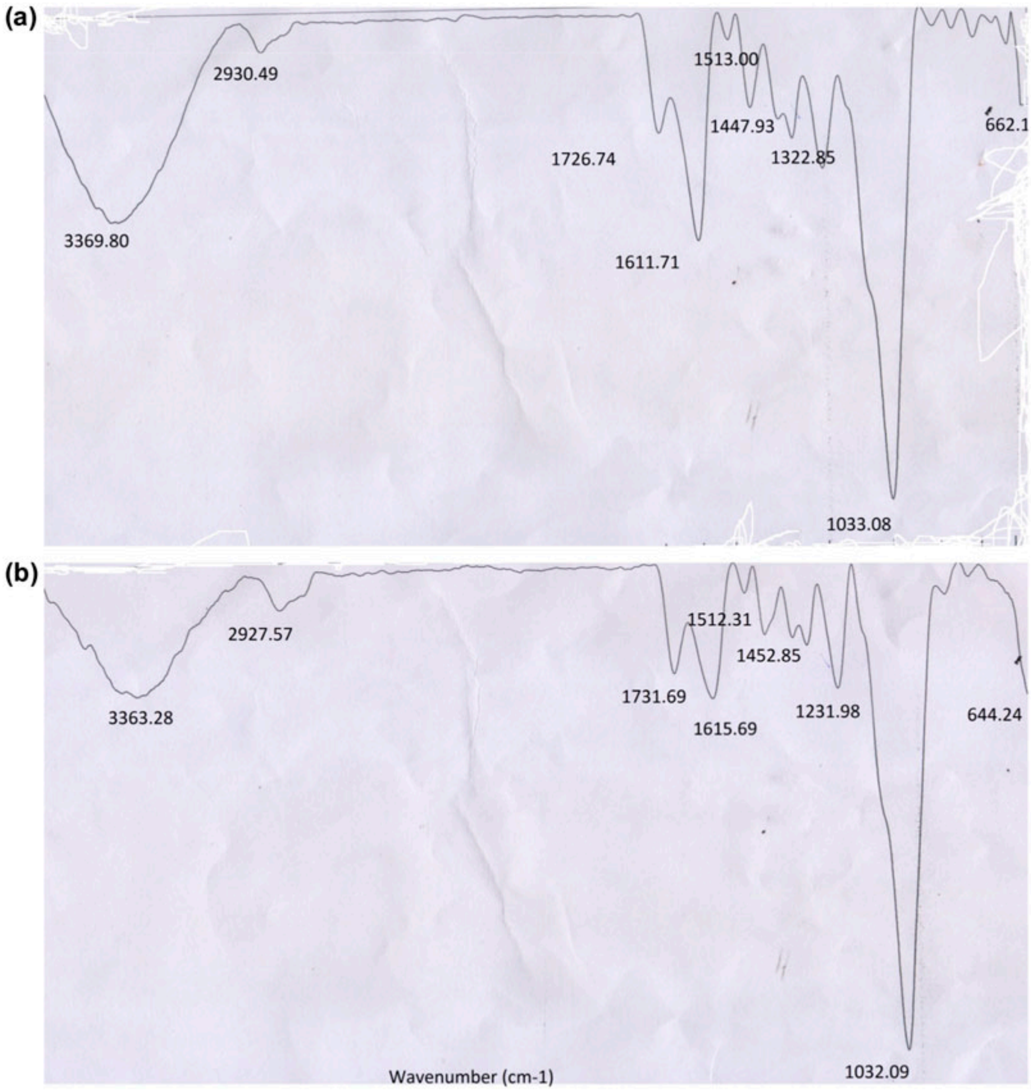

Fig. 7. FTIR spectra (a) Native eucalyptus bark and (b) Uranium-loaded Eucalyptus bark.

be due to the –C–O (Alcohol, ether or/and ester carboxylic acid) group. The sharp peak at 1,033.08 cm^{-1} may indicate the stretching vibrations of the C–O group of ether [33,34]. The close comparison of the native and loaded eucalyptus bark shows that the peak sharpness decreased in the loaded FTIR spectrum, which supports the involvement of these functional groups in the sorption process.

4. Conclusions

In this study, the sorption properties of eucalyptus bark for uranium (VI) were investigated. The binding capacity of uranium (VI) with eucalyptus bark was strongly dependent on the initial pH, initial uranium (VI) concentration and temperature.

(1) The experimental results fitted well to the pseudo-second-order kinetic and Langmuir isothermal models. Maximum sorption capacity (48.99 mg/g) of eucalyptus bark was observed at optimum conditions (pH 6, contact time of 80 min, 0.05 g/L biosorbent dose, 35°C temperatures and initial uranium (VI) concentration of 90 mg/L). It was noted that an increase in the temperature resulted in a lower metal loading per unit weight of eucalyptus bark.

(2) Various thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated from the data. The thermodynamics of uranium (VI) ion/eucalyptus bark system indicates the spontaneous and exothermic nature of the process.
(3) Desorbing agent H_2SO_4 was proved best to desorb the sorbed uranium ions from eucalyptus bark.
(4) The interfering metal ions show the inhibitory effect on the sorption process. It was found that Cr^{3+} had the most inhibitory effect on uranium biosorption and Pb^{2+} had the least inhibitory effect on uranium biosorption. The order of inhibitory effect of these metal ions on uranium biosorption is given as: $Cr^{3+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$.

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