ORIGINAL PAPER

Removal of uranium(VI) from aqueous solutions using *Eucalyptus citriodora* distillation sludge

H. N. Bhatti · S. Hamid

Abstract Adsorption and desorption of uranium(VI) from dilute aqueous solutions by *Eucalyptus citriodora* distillation sludge was studied in a batch mode. The potential of *Eucalyptus citriodora* distillation sludge to remove uranium(VI) from aqueous solutions has been investigated at different conditions of solution pH, metal ion concentrations, biosorbent dosage, biosorbent particle size, contact time and temperature. The results indicated that biosorption capacity of *Eucalyptus citriodora* distillation sludge was strongly affected by the medium pH, the biosorbent dose, metal ion concentrations and medium temperature. Reduction in particle size increased the biosorption capacity. Langmuir and Freundlich isotherm models were applied to biosorption data to determine the biosorption characteristics. An optimum biosorption capacity (57.75 mg/g) was achieved with pH 4.0, particle size 0.255 mm, biosorbent dose 0.5 g/100 mL and initial uranium(VI) concentration of 100 mg/L. Uranium(VI) removal by *Eucalyptus citriodora* distillation sludge was rapid, the equilibrium was established within 60 min and pseudo-second-order model was found to fit with the experimental data. The biosorption process decreased with an increase in the temperature indicating its exothermic nature. Pretreatments of biomass with different reagents affected its biosorption capacity. A significant increase (34 %) in biosorption capacity (83.25 mg/g) was observed with benzene treatment. Fourier-transform infra-red studies showed the involvement of carbonyl, carboxyl and amide groups in the biosorption process. The results indicated that sulfuric acid had the best effects as an eluent showing 93.24 % desorption capacity.

Keywords Uranium · Eucalyptus biomass · Biosorption · Recovery · Pretreatments

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Introduction

Uranium is one of the important heavy metals possessing radioactivity and chemical toxicity. Among the naturally occurring actinides, uranium is most abundant radiotoxic heavy metal having average concentration of 1.7 mg/kg and exists in the form of three different radioisotopes ^{238}U (99.27 %, $t_{1/2} = 4.51 \times 10^9$), ^{235}U (0.720 %, $t_{1/2} = 7.13 \times 10^8$) and ^{234}U (0.0055 %, $t_{1/2} = 2.48 \times 10^5$) (Jovanovic et al. 2012; Li et al. 2012). Uranium naturally shows various oxidation states (2+, 3+, 4+, 5+ and 6+), but mostly found in its hexavalent form, U(VI). Usually in nature, uranium is associated with oxygen, forming the uranyl ion (UO_2^{2+}). In strongly reducing conditions like water saturated with organic matter, uranium is often found in tetravalent state (Zou and Zhao 2012). It forms more than 160 mineral species and accounts for 5 % of all known mineral (Kalin et al. 2005).

Uranium is used extensively in different industrial processes and in nuclear industry especially due to its wide applications. Excessive amounts of wastewater containing uranium are produced by the nuclear industry, ore mining and industries that utilize radioisotopes. Uranium released into the environment through various activities can reach the food chain and be ingested by human. Major uranium toxic effects are caused by its chemical toxicity and can accumulate in different body parts, resulting in blood and kidney problem and increase risk of bone and liver cancer

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(Xie et al. 2008). The United States Environment Protection Agency (US-EPA) has set the maximum acceptable level of 30 µg/L and World Health Organization (WHO) strictly recommended a 2 µg/L as the maximum contaminant level (MCL) for uranium (Saifuddin and Dinara 2012). Therefore, the need for economic and effective methods for the removal of uranium and other toxic pollutants from the environment resulted in the development of new separation techniques (Gok and Aytas 2009).

Conventional treatment techniques such as ion-exchange, reverse osmosis, precipitation, flocculation, electrochemical treatment, solvent extraction, adsorption on activated carbon and membrane-related processes are usually applied for the remediation of heavy metals. These techniques are often expensive and inefficient, complicated and have production of toxic chemical sludge and its disposal problems (Dursun 2006; Boota et al. 2009; Bhatti et al. 2010). Hence, it is necessary to find suitable alternative technologies which are affordable, efficient and can compliment or replace the existing methods. Biosorption of metals is one of the possible innovative techniques involved in the remediation of heavy metals and radionuclides from wastewaters and subsurface environment (Tuzen et al. 2008; Bhatti et al. 2009). Biosorption involves the accumulation of heavy metals ions by biological materials either by metabolically mediated methods or by purely physico-chemical means. Like the conventional treatment methods biosorption also suffers with the disposal problem of sludge biomass. However, this technique has high efficiency and selectivity for absorbing heavy metals in low concentrations, cheap in nature, energy-saving, broad operational range of pH and temperature, easy reclamation of heavy metal, easy recycling of the biosorbent, economical nature and eco-friendly behavior (Kratochvil and Volesky 1998; Boddu et al. 2003).

During the last few years some studies have been carried out for the removal of uranium from aqueous systems using various biomaterials. Some low-cost biosorbents such as sargassum biomass (Yang and Volesky 1999), water hyacinth (Bhainsa and D'Souza 2001), algal biomass (Kalin et al. 2005), banyan leaves, red algae (Bhat et al. 2008), alginate beads (Gok and Aytas 2009), *Aspergillus fumigatus* (Wang et al. 2010), citrus biomass (Saleem and Bhatti 2011), pine saw dust (Zou and Zhao 2012), etc. have been exploited for various workers. However, these low-cost biosorbents have generally low adsorption capacity and require large amounts of adsorbents. Since agricultural waste biomasses are available in abundance and cheap materials, it is necessary to continue searching for the most promising adsorbents.

Eucalyptus citriodora is an evergreen plant and its leaves yield a lemon-scented oil rich in citronellal, used in perfumery. Biomass left after the extraction of essential oils is a waste material having no commercial significance. Natural occurrence of this biomass makes this biomass a cheap source as biosorbent material having high-specific surface area (4.56 m^2/g as determined by nitrogen adsorption BET method). Therefore, the goals of this research work were to explore the feasibility for removal of uranium by *Eucalyptus citriodora* distillation sludge (ECDS), investigate the biosorption capacity of ECDS and analyze the surface interactions between ECDS and U(VI).

Materials and methods

Chemicals and biomass

All the chemicals used in the present study were of analytical reagent (RA) grade including uranyl nitrate hexahydrate [$UO_2(NO_3)_2 \cdot 6H_2O$], Arsenazo III, diethylenetriaminepenta acetic acid (DTPA) which were mainly obtained from Sigma Chemical Co, USA. A solution of 1,000 mg/L of uranium was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ by dissolving the salt in deionized distilled water (DDW). ECDS used in this work was collected from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture Faisalabad, Pakistan. It was extensively washed with distilled water to remove particulate material from their surface then dried first in sun then in oven at 60–70 °C. Dried biomass was ground and sieved to obtain the different sizes of biosorbent.

Biosorption experiments

All glassware were washed with dilute solution nitric acid (HNO$_3$) and subsequently rinsed with DDW to remove any possible interference. Batch biosorption studies were carried out in 250-mL conical flasks to observe the effect of pH (2–8), biosorbent particle size (0.255–0.71 mm), biomass dosage (0.1–0.7 g/100 mL), initial uranium concentration (25–300 mg/L), contact time (5–240 min) and temperature (30–50 °C) to check the optimal removal of the U(VI). The pH of the solution medium was adjusted with 0.1 M solutions of sodium carbonate (Na$_2$CO$_3$) and HNO$_3$. Control assays were also run with each experiment. The conical flasks were agitated at 100 rpm speed in a rotating shaker for a specified time period. At the end of the experiments, the conical flasks were removed from the shaker and the solutions were centrifuged at 5,000 rpm for 15 min to separate the biomass from the solution. The supernatant was used for U(VI) analysis.

Uranium analysis

U(VI) analysis was carried out using colorimetric method (Bhatti et al. 1991) Appropriate amount (0.5 mL) of the

sample solution was pipetted out into a 25-mL volumetric flask, 1 mL of complexing solution (2.5 % DTPA) and 0.5 mL Arsenazo-III reagent solution were added. The volume was made up with DDW (pH 2.0) and the solution was allowed to stand for 2–3 min. The pink–violet coloration that developed due to the formation of uranium–Arsenazo-III complex was measured at 655 nm against a corresponding reagent blank, using a 1-cm path cell in an Optima sp-300 spectrophotometer.

Biomass pretreatments

ECDS biomass was physically modified using heating and boiling (5 g of biosorbent/100 mL of H_2O, heated or boiled for 10 min). In case of chemical pretreatments 5 g of the biomass was soaked with 100 ml of 5 % solutions of sodium hydroxide, acetic acid, ammonium sulfate, acetone, nitric acid, ethylenediamminetetraacetic acid disodium salt (EDTA), hydrochloric acid, sulfuric acid, ethanol, methanol, benzene, glutaraldehyde, poly(ethyleneimine) (PEI) and ammonium chloride. These flasks containing chemically treated ECDS biomass were agitated for 30 min at 100 rpm and 30 °C. All the pretreated samples were allowed to stand for a night at room temperature. The treated biomasses were extensively washed with DDW and filtered thoroughly. After filtration the residues were dried at 60 °C for 24 h and then the dried biomasses were used in adsorption experiments under optimum conditions (Bhatti et al. 2009).

Desorption studies

Different eluting reagents like EDTA, ammonium sulfate, hydrochloric acid, sulfuric acid, ammonium chloride, nitric acid, sodium hydroxide and acetic acid were tried to desorb the adsorbed uranium ions. Consecutive batch adsorption and desorption experiments were performed to test the ability of ECDS to be reutilized after regeneration. Before the desorption experiments, the adsorption experiments were carried out under optimum conditions and the ECDS biomass of adsorption experiments was dried at 60 °C for 24 h, then optimum dose of this uranium loaded biomass was added in 250-ml flasks containing 100 ml of 0.1 M of each eluent. The eluent which showed the maximum desorption efficiency was selected for final recovery of uranium ions using various concentration (0.05, 0.1, 0.15, 0.2 and 0.25 M). After optimizing the strength of the selected eluent the consecutive adsorption–desorption cycles were carried out five times.

The amount of U(VI) adsorbed per unit mass of ECDS, percentage adsorption and the distribution constant (K_d) were calculated using the following equations:

$$q_e = (C_i - C_e)V/W \tag{1}$$

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

$$K_d = \frac{\text{Amount of metal ion in adsorbent}}{\text{Amount of metal ions in solution}} \tag{3}$$

q_e is the biosorption capacity(mg/g) under equilibrium conditions, V is volume of aqueous phase (mL), C_i is initial metal ion concentration (mg/L), C_e is equilibrium metal ion concentration and W is the amount of biosorbent (g).

The eluted biomass metal contents were calculated directly from the amount of metal desorbed into the eluent solution by using the following equation.

$$q_{des} = C_{des} V/W \tag{4}$$

q_{des} is desorption capacity (mg/g) and C_{des} is metal concentration in eluent solution or desorbed concentration of metal ion (mg/L)

The percentage of desorbed/eluted metal is evaluated as % elution

$$\% \text{ elution } = [q_{des}/q_e] \times 100 \tag{5}$$

Thermodynamics of uranium adsorption

The thermodynamic parameters such as standard Gibbs free energy (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy of adsorption (ΔS^0) were calculated from the following equation:

$$\Delta G^0 = -RT \ln K_c \tag{6}$$

where $K_c = (q_e/C_e)$

R is the gas constant (8.314 J/mol K), T is the absolute temperature (K) and K_c is the equilibrium constant.

According to van't Hoff equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{7}$$

$$\log(q_e/C_e) = -\Delta G^0/2.303RT$$
$$= -\Delta H^0/2.303RT + \Delta S^0/2.303R \tag{8}$$

The values of ΔG^0 and ΔH^0 for U(VI) biosorption were determined from the slope and intercept of van't Hoff graph.

FTIR and EDX studies

The functional groups of ECDS biomass were analyzed by Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer with the samples prepared as potassium bromide (KBr) disks. The existence of uranium ions on the surface of biomass was confirmed by energy dispersive X-ray spectroscopy (EDX, Perkin-Elmer, USA). The biomass sample was covered with a thin layer of gold and an electron-accelerated voltage of 20 kV was applied.

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Statistical analysis

All the experiments were run in triplicate and results are reported as mean ± SD. The error bars have been shown on the graphs.

Results and discussion

Effect of medium pH

Aqueous solution pH is a critical parameter as it affects surface charge of the biosorbent, the degree of ionization and the speciation of adsorbate species, and concentration of the counter ions on the functional groups of the biosorbent. The solution chemistry of the heavy metals such as hydrolysis, complexation by organic or inorganic ligands, redox reactions and precipitation are also strongly influenced by pH (Ozer and Ozer 2003). Uranium sorption by ECDS was studied in the pH region between 2.0 and 8.0 and the results regarding biosorption capacity (mg/g) and K_d are shown in Fig. 1. As seen from the figure, the biosorption capacity q_e of biomass and K_d increase with an increase in pH of the medium from 2.0 to 4.0, and then show a decrease at 5.0. Extremely acidic conditions (pH 2.0) did not favor uranium biosorption. Maximum uptake (47.75 mg/g) was attained at pH 4.0, with a further rise in pH, uranium biosorption by ECDS showed a sharp decline. Under acidic conditions there is high concentration of H^+ and H_3O^+ ions which compete with the uranyl ions for binding sites on the surface of biomass, resulting in a decreased biosorption of uranium (Sar and D' Souza 2002). Decrease in the biosorption capacity of ECDS and K_d for uranium ion at higher pH could be due to the formation of uranyl complexes such as, UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$. These complexes may compete with functional binding sites for uranyl ions and reduce the availability of uranium for biosorption and hence K_d (Wazne et al. 2006). Gok and Aytas (2009) also observed maximum biosorption of uranium (76 %) by calcium alginate
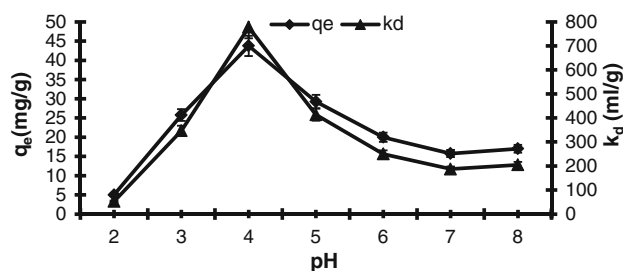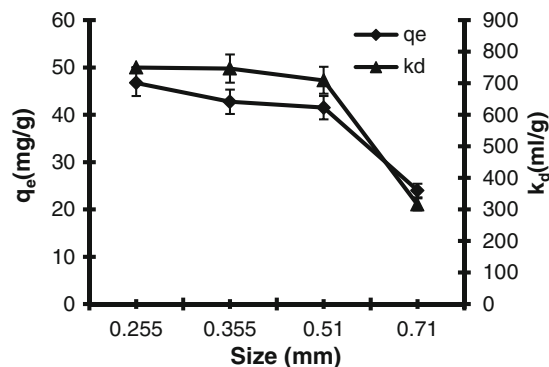
beads from aqueous solution at pH 4.0. Therefore, an optimum pH 4.0 was selected in all subsequent experiments.

Effect of biosorbent size

The biomass particle size determines the surface area of the biosorbent. The effect of altering the biosorbent particle size on the biosorption capacity q_e of ECDS and K_d was investigated and the trends are illustrated in Fig. 2. The results indicated that biosorption capacity and K_d decreased with an increase in particle size of ECDS. Maximum biosorption capacity (47.82 mg/g) and K_d value were observed with 0.255 mm particle size while largest particle size (0.71 mm) exhibited less adsorption for uranium ions as well as K_d. This was most probably due to increase in total surface area, which provided more adsorption sites for the metal ions. The finely grounded biomass up took the metal ions more rapidly and the equilibrium was established faster than those achieved with large particle-sized biomass. These observations are in accord with our previous results in which adsorption capacity of biomass decreased with an increase in the size of adsorbents (Bhatti et al. 2009, 2010).
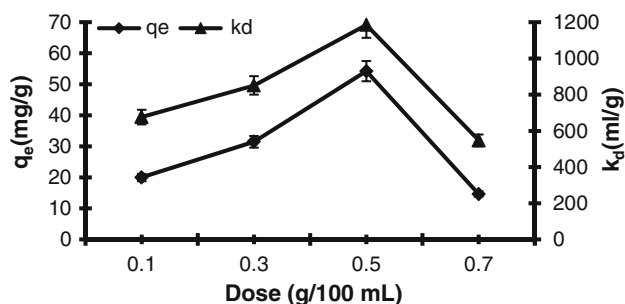
Effect of biosorbent dose

The dependence of U(VI) biosorption on biosorbent dose was studied by varying the amount of biosorbent while keeping pH (4), biosorbent particle size (0.255 mm), initial uranium ion concentration (100 mg/L), shaking speed (100 rpm) and temperature (30 °C) constant. Biosorbent dose seems to have a great influence on the biosorption process. Results revealed that maximum biosorption capacity (57.75 mg/g) and K_d were observed with 0.5 g/ 100 mL of U(VI) solution (Fig. 3). The results showed that biosorption capacity of ECDS and K_d increased with

Fig. 1 Effect of pH on the adsorption of U(VI) by ECDS (dose 0.5 mg/100 mL; concentration 100 mg/L, time 45 min; size 0.255 mm; temperature 30 °C)

Fig. 2 Effect of adsorbent size on the adsorption of U(VI) by ECDS (dose 0.5 mg/100 mL; concentration 100 mg/L, time 45 min; pH 4; temperature 30 °C)

Fig. 3 Effect of adsorbent dose on the removal of U(VI) ECDS (time 45 min; concentration 100 mg/L, size 0.255 mm; pH 4; temperature 30 °C)

increase in biosorbent dose. The increase is due to increased surface area of the biosorbent, which in turn increases the number of binding sites. But the biosorption capacity q_e and K_d decreased when the biosorbent dose is increased above the optimum value. The decrease is due to partial aggregation and screening effect on the biomass surface which occurred at high biomass dose (Boota et al. 2009). Such aggregation would lead to a decrease in total surface area of the sorbent and increase in diffusional path length. The aggregation of the biosorbent depends on the size of the particle. The smaller the size, greater would be the chances of aggregation. Similarly biosorption of U(VI) by immobilized *Aspergillus fumigatus* beads decreased from 7.2 to 1.7 mg/g when the adsorbent dose is increased from 1 to 3.5 % (Wang et al. 2010).

Effect of contact time

The equilibrium time is one of the important parameters for an economical wastewater treatment system. The effect of contact time on the biosorption of uranium by ESDS was studied over time intervals from 5 up to 240 min. Figure 4 shows the amount of uranium biosorbed as a function of contact time. As seen from the
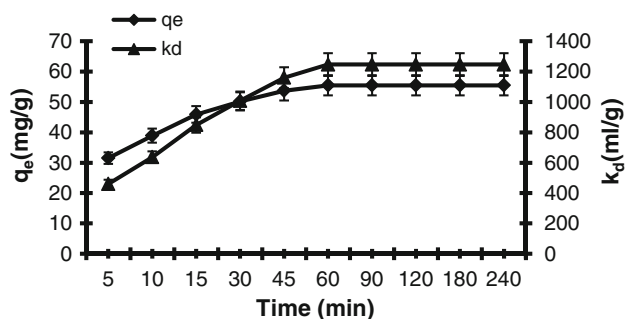
plot, the biosorption rate was rapid in the first 30 min, reaching about 90 % of the total biosorption capacity. Same trend was also recorded for the K_d. Equilibrium was established within 60 min. A biosorption capacity of 57.75 mg/g was observed under optimal conditions of pH (4.0), biosorbent dosage (0.5 g/100 mL), biosorbent particle size (0.255 mm), initial metal ion concentration (100 mg/L), shaking speed (100 rpm) and temperature 30 °C. Therefore, in subsequent experiments, 90 min was deemed more than sufficient to establish equilibrium and used in all subsequent measurements. Gok and Aytas (2009) reported that equilibrium was reached after 90 min during biosorption of U(VI) from aqueous solution using calcium alginate beads.

Effect of initial uranium concentration

The rate of biosorption is a function of the initial metal ion concentration, which makes it an important factor to consider for effective biosorption. The initial concentration of uranium provides an important driving force to overcome all mass transfer resistance of uranium between the aqueous and solid phases. The biosorption capacity of ECDS for uranium was determined at different concentrations (25–300 mg/L). It was observed that the biosorption capacity of ECDS and K_d both increased with an increase in the uranium ion concentration. The maximum K_d and uptake capacity of ECDS (57.86 mg/g) were observed with the initial uranium concentration of 100 mg/L (Fig. 5), but K_d later decreased. This might be due to the saturation of the adsorption sites and increase in the number of ions competing for the available binding sites in the adsorbent for complexation of uranium at higher concentration (Bai and Abraham 2003). Moreover, the increase in uranium concentration enhanced the mass transfer driving force which enhanced the biosorption process at equilibrium (Aksu 2002; Zubair et al. 2008). In addition, increasing metal ion concentrations increased the number of collision
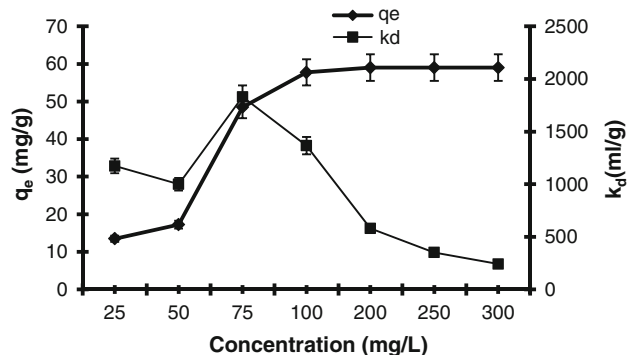

Fig. 4 Effect of time on the removal of U(VI) by ECDS (dose 0.5 g/100 mL; concentration 100 mg/L, size 0.255 mm; pH 4; temperature 30 °C; contact time 5–240 min)

Fig. 5 Effect of concentration on the removal of U(VI) by ECDS (dose 0.5 g/100 mL; temperature 30 °C, size 0.255 mm; time 60 min; pH 4)

between metal ions and the adsorbent, which enhanced the biosorption process (Aksu 2002).

Equilibrium isotherm and kinetic studies

Modeling of equilibrium data was done using most widely used Langmuir (1918) and Freundlich isotherm (1906) models. The monolayer coverage of the sorbate on a sorbent surface at constant temperature is represented by Langmuir isotherm, the biosorption of solute from aqueous solution onto the biosorbent surface is occurred as monolayer biosorption on the homogeneous number of exchanging sites. The Langmuir isotherm considers sorption as a chemical phenomenon. In the Langmuir model, maximum monolayer adsorption capacity, q_{max} (mg/g), and other parameters were determined from following equation:

$$\frac{Ce}{qe} = \frac{1}{qMaxK_L} + \frac{Ce}{qMax} \tag{9}$$

where q_e is the biosorption capacity at equilibrium (mg/g), C_e the equilibrium concentration of metal ion solutions, q_{max} represents the maximum biosorption capacity and K_L is the Langmuir biosorption constant representing the ratio of biosorption/desorption rates.

The biosorption capacity q_e (mg/g) of ECDS for uranium ions was determined by following equation of Freundlich isotherm:

$$\log qe = \frac{1}{n}\log Ce + \log k \tag{10}$$

k and n are constants for Freundlich equation; where k is a measure of adsorption capacity and $1/n$ the intensity of adsorption. In the present investigation, Freundlich transformation was found to be linear and value of q_{max} as calculated from Freundlich model was in good agreement with that of the experimental value (Table 1). The good fit to the Freundlich adsorption isotherm model suggests multilayer sorption of U(VI) on ECDS and biosorption mechanism is through physical forces.

In order to understand the rate limiting step of U(VI) biosorption on ECDS, Lagergren pseudo-first-order (Lagergren 1898) and pseudo-second-order models were applied to describe the kinetic characteristics of the biosorption process. Pseudo-first-order kinetic model is based on the fact that the change in adsorbate concentration with

respect to time is proportional to the number of binding sites on the adsorbent. The linearized first-order Lagergren equation is given as:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}t}{2.303} \tag{11}$$

According to pseudo-second-order model the change in the adsorbate concentration with respect to time is proportional to square of binding sites. The pseudo-second- order equation is

$$t/q = 1/k_{2,ads}q_e^2 + t/q_e \tag{12}$$

where q_e is the biosorption capacity at equilibrium (mg/g), q the biosorption capacity at time t (min), $k_{1,ads}$ the first-order reaction rate of adsorption (per min), $k_{2,ads}$ the pseudo-second-order rate constant of adsorption (mg/g min). Application of different kinetic models to uranium biosorption suggested that uranium biosorption by ECDS followed the pseudo-second-order model rather than pseudo-first-order kinetic model (Table 2). The value of q_e obtained from pseudo-second-order model was in close agreement with that of the experimental value while the value obtained from pseudo-first-order model was quite small (Table 2). The results suggested that the kinetic data followed the pseudo-second-order kinetics in case of U(VI) biosorption on ECDS biomass.

Effect of temperature

Temperature is found to be a critical parameter in the removal of metal ions, but this is only for energy-dependent mechanisms. Many biosorption processes are affected to a limited extent under a certain range of temperature. The effect of temperature variation on the biosorption of U(VI) ions on ECDS from aqueous solution was investigated in the temperature range of 30–50 °C. As seen in Fig. 6, the biosorption capacity of ECDS and K_d decreased with an increase in the temperature indicating that biosorption of U(VI) on ECDS was exothermic in nature. Maximum biosorption capacity (57.80 mg/g) and K_d were observed at 30 °C which decreased to 46.0 mg/g at 50 °C. The decrease in biosorption capacity and K_d with increasing temperature might be due to the decreased surface activity. According to adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorb from the

Table 1 Comparison between Langmuir and Freundlich isotherm parameters for U(VI) adsorption on ECDS

Metal	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters		
	q_{max} (mg/g)	K_L (l/mg)	R^2	q_{max} (mg/g)	q_{max} (mg/g)	k (mg/g)	R^2
U(VI)	10.13	0.002	0.581	57.75	54.49	0.508	0.946

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Table 2 Comparison between kinetic models for U(VI) adsorption on ECDS

Metal	Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
	q_e (mg/g)	$k_{1,ads}$ (mg/g)	R^2	q_e (mg/g)	q_e (mg/g)	$k_{2,ads}$ (mg/g)	R^2
U(VI)	0.435	−0.06	0.983	57.75	58.8	2,769.92	0.999
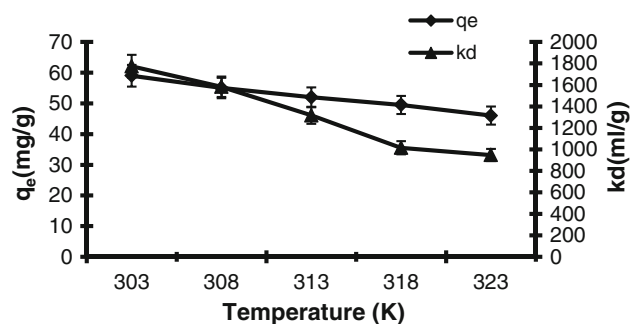
Fig. 6 Effect of temperature on the removal of U(VI) by ECDS (dose 0.5 g/100 mL; size 0.255 mm; time 60 min; pH 4; concentration 100 mg/L)

surface at elevated temperatures (Jnr and Spiff 2005; Bhatti et al. 2010). As the process of biosorption is exothermic in nature, so by increasing the temperature rate of biosorption should decrease. The results are in accordance with biosorption theory. Bhat et al. (2008) investigated the biosorption of U(VI) from aqueous medium onto red alga and found no significant change in the biosorption capacity within the temperature range studied (15–55 °C).

The values of thermodynamic parameters for biosorption of U(VI) on ECDS are given in Table 3. The value of enthalpy of biosorption (ΔH^0) is −35.75 kJ/mol indicating exothermic nature. The negative value of ΔG^0 indicated that the adsorption of U(VI) ion on ECDS is spontaneous at 30 °C. However, with increase in temperature, the adsorption decreases due to increase in free energy. Therefore, high temperature is not favorable for U(VI) ion removal by ECDS. The value of ΔS^0 suggests the decreased randomness at the solid–solution interface during biosorption of U(VI) on ECDS. Contrary to our findings, Donat and Ayata (2005) found that biosorption of U(VI) on to *Ulva* sp.–Na bentonite composite adsorbent

Table 3 Thermodynamic parameters for the removal of U(VI) on ECDS at different temperatures

T(K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)	R^2
303	−1.76	−35.75	0.112	0.93
308	−1.61			
313	−0.92			
318	−0.13			
323	7.2			

was endothermic in nature and value of ΔG^0 decreased with an increase in the temperature.

Effect of pretreatments

Metal ion affinities to the biomass can be modified by physical and/or chemical pretreatment of the biomass with alkali, acids, salts and organic solvents, which may increase or decrease the amount of the metal ions biosorbed. The physical treatments include simple heating, boiling or autoclaving. These treatments are easy and low costs, but sometimes no chemical modification in the structure of biomass is possible. The chemical treatments usually result in the modification in the functional moieties of the biomass thus altering its biosorption capacity. However, the major limitations include high cost and environmental problems. The results indicated that physical modification of biomass did not affect the biosorption capacity significantly. Chemical treatment with acids, alkali, EDTA, ammonium sulfate and glutaradehyde decreased the biosorption capacity of ECDS as compared to native biomass. The decrease in biosorption capacity of ECDS might be due to the damaging of binding sites of biomass on protonation of biomass with acids, destruction of autolytic enzymes responsible for putrefaction of biomass by alkali and masking of active sites by glutaradehyde (Zubair et al. 2008; Boota et al. 2009; Bhatti et al. 2010). Ammonium sulfate is a salting agent it can cause precipitation, which decreased the sorption capacity of biomass.

Chemical treatments with benzene, acetone, ethanol, methanol, ammonium chloride and PEI enhanced the biosorption capacity significantly as compared to native ECDS. A biosorption capacity of 83.25 and 59.5 mg/g was observed benzene and PEI treatment respectively. Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for metal ions' adsorption after pretreatment might be responsible for the increase in adsorption capacity (Bhatti et al. 2009). PEI is a well-known chelating agent. Treatment of biomass with organic solvents generally enhanced the removal efficiency of biomass. Extraction with organic solvents removes the proteins and lipid fractions from the biomass surface (Ashkenazy et al. 1997). Thus, this treatment might expose more metal binding sites and improved the biosorptive property of the biomass.

Desorption and recovery studies

The use of biosorbent in the wastewaters treatment depends not only on the biosorption capacity, but also 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 metal ions, the saturated adsorbent which contains U(VI) is not safe for disposal due to its radioactive nature. Therefore, it is important to devise a method for the regeneration and reuse of biosorbent so as to protect the environment from its harmful effects. Desorption of the biosorbed U(VI) ions from ECDS was studied in a batch mode using different eluents like HNO_3, H_2SO_4, CH_3COOH, HCl, NaOH, $(NH_4)_2SO_4$, NH_4Cl and EDTA (0.1 N) solution. The results showed that H_2SO_4 solution was found to be the best eluting agent for the elution of uranium. It is clear from the results that acids are the good desorbing reagents. This may be due to the protonation of biomass under acidic conditions that make possible desorption of positively charged metal ions from the adsorbent surface.

The reusability of biosorbent was tested in five consecutive sorption–desorption cycles. For this cyclic study, biomass at concentration of 0.5 g/0.1 L of uranium solution was used and 0.1 M H_2SO_4 was used as an eluent for desorption experiments. Both biosorption capacity and elution efficiency were measured after equilibrium time. In order to interpret the total efficiency of biosorbent, the data were proceeded to calculate the % desorption/elution and % decrease in dry weight of biosorbent/% weight loss for each cycle. For first cycle, the values of % elution and % wt loss were 96 and 8, and decreased to 94 and 6.4, respectively. The results indicated that on increasing number of cycles %wt loss increases with decrease in % elution and for five consecutive sorption–desorption cycles maximum loss is less than 10 % for both parameters of efficiency. It can be concluded that on increasing the number of cycles, total efficiency of biosorbent in terms of % wt loss and % elution decreases. This decrease suggested that five consecutive biosorption–desorption cycles are enough for reusability.

Infrared and EDAX analyses

The changes in the functional groups and surface properties before and after adsorption of U(VI) on ECDS biomass were recorded as FT-IR spectrum. In general, the FT-IR spectra of plant biomasses have intense peaks in the range of 3,600–3,200/cm (Asgher and Bhatti 2010). In case of native biomass, a sharp peak at a frequency level of 3,600/cm and two absorption bands one near 3,500/cm and one 3,400/cm may be arising due to non-associated O–H stretching vibration and the antisymmetric and symmetric stretching vibrations of the two N–H bonds, respectively. However, in case of uranium-loaded biomass a broad band near 3,600/cm may be assigned to the hydrogen bonded O–H and N–H groups (Singh et al. 2009). In case of uranium-loaded ECDS, a broad band near 3,600/cm may be assigned to the H-bonded –OH and –NH groups. The appearance of a strong band just below 3,000/cm may be due to antisymmetric stretching of C–H bond. The presence of sharp peak near 1,700/cm denotes the presence of C=O stretching

Fig. 7 EDX-spectrum of **a** native and **b** uranium-loaded ECDS

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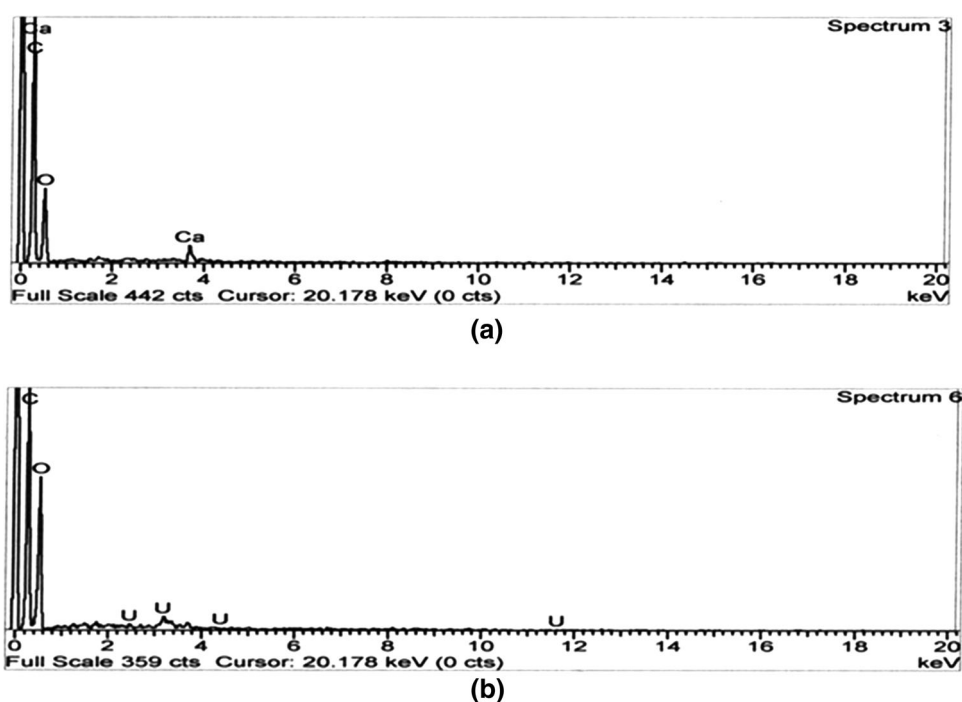
while peak near 1,600/cm may be attributed to C=O or C=N stretching of carboxylic or imines. The band near 1,000/cm may be assigned to stretching vibration of C=O group in the bonding. The IR spectral analysis before and after uranium loading indicated that the key components and structure remained integral; however, there is a substantial decrease in the intensity at 1,700–1,500/cm which is due to –NH bending and 3,600–3,400/cm due to –OH and –NH groups (Wang et al. 2010). The decrease in absorption intensity in these regions after adsorption of uranium indicated that hydroxyl, carboxyl and –NH group are involved in uranium binding. However, the –NH group plays a critical role in uranium $(UO_2)^{2+}$ binding to ECDS biomass.

In order to know the chemical and elemental information about uranium adsorption and desorption different samples (native and uranium treated) of ECDS were subjected to X-ray energy dispersion (EDAX) analysis and results are shown in Fig. 7a, b. The EDAX spectrum of the ECDS before adsorption exhibits distinct calcium, oxygen and carbon peaks, indicating the presence of substantial amounts of these elements in the adsorbent. After uranium adsorption, all peaks of other metal ions diminished and spectra showed distinctive signal for uranium ions only.

Conclusion

In this study, Eucalyptus distillation sludge biomass was exploited for the removal of U(VI) from aqueous solutions. Maximum biosorption capacity (57.75 mg/g) of ECDS was observed with pH 4.0, particle size 0.255 mm, biosorbent dose 0.5 g/100 mL and initial U(VI) concentration of 100 mg/L. The biosorption of U(VI) on ECDS biomass was exothermic in nature. Pretreatments of ECDS with different reagents affected its biosorption capacity. A significant increase (34 %) in biosorption capacity of ECDS (83.25 mg/g) was observed with benzene treatment. The Freundlich biosorption model could be used to describe this biosorption process, suggesting that this process is complicated multistep form. FT-IR studies showed the involvement of carbonyl, carboxyl and amide groups in the biosorption process. The results of this study showed that ECDS could be successfully used to remove U(VI) from aqueous effluents.

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