

ADSORPTIVE REMOVAL AND RECOVERY OF U(VI) BY CITRUS WASTE BIOMASS

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Adsorption and recovery of hexavalent uranium from dilute aqueous solutions by low cost citrus waste biomass was investigated by performing adsorption-desorption studies. Different samples of citrus waste biomasses were screened for removal of U(VI) from aqueous solutions. The results indicated that the biosorption capacity was strongly affected by the solution pH, biosorbent dose, contact time, and initial uranium concentration. Uranium binding by the test biomass was rapid, achieving >79% sorption efficiency within 15 min, and the equilibrium was established in 60 min. Optimum biosorption capacity (q_e) was observed at pH 4.0, biosorbent dose 0.1 % (w/v), initial uranium concentration of 100 mg/L. The kinetic data fitted well to a pseudo-second-order rate equation ($R^2=0.980$). The adsorption process conformed to a Langmuir adsorption isotherm model. Gibbs free energy (ΔG°) and enthalpy change (ΔH°) indicated that reaction was spontaneous and exothermic in nature at the studied temperatures. FT-IR studies showed the involvement of carbonyl, carboxyl, and amide groups in the biosorption process. Treatment of biomass with different reagents affected its biosorption capacity, and maximum removal (70.63%) was recorded with polyethyleneimine (PEI) treated biomass. EDTA had the best effects as an eluent, showing 94.7% desorption capacity.

Keywords: Uranium; Kinetics; Thermodynamics; Recovery; Citrus biomass

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INTRODUCTION

In recent times a surge of industrial activities has intensified environmental problems due to the accumulation of dangerous pollutants such as heavy metals, synthetic compounds, waste nuclear liquids, etc. (Park et al. 2006). Heavy metals are still being used in various industries due to their technological importance. Improper treatment of wastes from these industries raises additional concerns about human health and the environment (Dursun 2006). Aside from the environmental damage, human health is likely to be affected, as the presence of heavy metals beyond a certain limit brings serious hazards to living organisms. Like other heavy metals, uranium (U) is one of the important heavy metals possessing radioactivity and chemical toxicity. Excessive amounts of wastewater containing uranium are produced by the nuclear industry, not only during the ore mining, but also in industrial applications that utilize radioisotopes. Uranium disposed into the environment through various activities can reach the food chain and be ingested by human. Uranium is one of the most seriously threatening heavy

metals. Uranium forms more than 160 mineral species and accounts for 5% of all known minerals (Kalin et al. 2005). The World Health Organization (WHO) has determined that uranium is a human carcinogen, and its permissible limit in water is 50 µg/L. Excessive intakes of U are known to cause severe liver or kidney damage and even death (Xie et al. 2008). Therefore, there is a need for economical and effective methods for the removal of pollutants from the environment, and these have resulted in the development of new separation techniques (Gok and Aytas 2009).

Several conventional treatment methods such as ion-exchange, reverse osmosis, precipitation, flocculation, electrochemical treatment, solvent extraction, adsorption on activated carbon, and membrane related processes are usually applied. These methods are often expensive and inefficient, complicated, or have production of toxic chemical sludge and its disposal problems (Dursun 2006; Satapathy and Natarajan 2006; Hanif et al. 2007; Boota et al. 2009; Bhatti et al. 2010). Hence it is necessary to find suitable alternative technologies that are affordable, efficient, and can compliment or replace the existing methods. Biosorption is becoming one of the more attractive and efficient alternative techniques for the removal of heavy metals and radionuclides from industrial wastewater (Tuzen et al. 2008). Biosorption relies on the capability of biomaterials to bind and concentrate heavy metals/radio-nuclides from very dilute aqueous solution. Compared with conventional treatment methods biosorption has high efficiency and selectivity for absorbing heavy metals in low concentrations, the material is relatively inexpensive, and the process is energy-saving, with a 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).

Removal of uranium and other radionuclides using agricultural/plant biomasses has not been yet studied extensively. Only few reports regarding biosorption of uranium by plant /agricultural waste biomasses are cited in the literature (Yang and Volesky 1999; Bhainsa and D'Souza 2001; Xia et al. 2006; Al-Masri et al. 2010). Since agricultural waste biomasses are available in abundance at low cost, it is necessary to continue searching for the most promising biosorbent from an extremely large pool of readily available and inexpensive biomaterials.

Different varieties of citrus fruit are grown in Pakistan for edible purposes. The citrus fruit is very juicy, sweet-acidic, and rich in flavor pulp. Citrus juice is one of the most favorite drinks worldwide. Biomass left after extraction of juice from citrus fruit, is a waste material having no commercial significance. The aim of present study was to determine the biosorption potential of citrus waste biomass to remove and recover uranium from aqueous solution. The effects of different process parameters such as solution pH, biosorbent dose, contact time, and initial uranium ion concentration on the sorption were investigated.

EXPERIMENTAL

Reagents and Chemicals

All the reagents and chemicals used in the present study were of analytical reagent (RA) grade including uranyl nitrate hexahydrate and arsenazo III, which were

mainly obtained from Sigma-Aldrich Chemical Co, USA. A solution of 1000 mg/L of uranium was prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by dissolving the salt in deionized distilled water. The stock solution was diluted to prepare working solutions as desired.

Preparation of Biosorbent

Waste biomasses of *Citrus grandis* (chokotra), *Citrus aurantifolia* (mitha), and *Citrus sinensis* (mosambi) were collected from local fruit market and dried, first in sunlight then in oven at 60 °C for 72 h. Dried biomasses were cut, ground and sieved to obtain adsorbents with homogenous known particle sizes (0.71 mm, 0.5 mm, 0.35 mm, and 0.25 mm).

Batch Biosorption Experiments

All glassware were washed with 1 M HNO_3 and subsequently rinsed with deionized distilled water to remove any possible interference. Batch biosorption studies were carried out in 250 mL Erlenmeyer flasks to check the influence of pH (1, 2, 3, 4, 5, 6, and 7), biomass concentration (0.025, 0.05, 0.1, 0.15, and 0.2 g), initial uranium concentration (25 to 800 mg/L), contact time (15, 30, 45, 60, 90, 120, 150, 180, and 240 min), and temperature (30, 35, 40, 45, and 50 °C) in order to check the possible maximum removal of the uranium ions. A particle size of 0.255 mm was used in all experiments. A control assay was carried out in accompaniment with each experiment. The experimental flasks were agitated at 100 rpm speed in a rotating shaker for a specified time period. At the end of the experiments, the flasks were removed from the shaker and the solutions were separated from the biomass by filtration through filter paper (Whatman no. 40, ashless). The pH of the medium was adjusted with 0.1 M solutions of Na_2CO_3 and HNO_3 .

Determination of Uranium Contents

To determine the contents of uranium, 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 of arsenazo-III reagent solution were added. The volume was made up with distilled water (pH 2.0) and the solution was allowed to stand for 2 to 3 min (Bhatti et al. 1991). 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.

Pretreatments of Biomass

Citrus grandis biomass was physically modified by boiling (5 g of biosorbent/100 mL of H_2O , boiled for 10 min). In case of chemical pretreatments 5 g of the biomass of suitable size was soaked with 100 mL of 5% solutions of sodium hydroxide, acetic acid, K-carragen, ammonium sulphate, acetonitrile, acetone, 2-propanol, nitric acid, calcium alginate, perchloric acid, EDTA, hydrochloric acid, sodium alginate, benzene, Tween-80, glutaraldehyde, PEI, calcium chloride, and SDS. These flasks containing chemically treated 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 deionized distilled water (DDW) and filtered thoroughly.

After filtration, the residues were dried at 40 °C for 24 h, and then the dried biomasses were used in adsorption experiments under optimum conditions (Bhatti et al. 2009).

Desorption and Recovery of Uranium

Different eluting solutions such as EDTA, NaNO₃, NH₄NO₃, NaHCO₃, (NH₄)₂SO₄, sodium citrate, HCl, CaCl₂, H₂SO₄, H₂O, NH₄Cl, Na₂CO₃, NaNO₂, KH₂PO₄, sodium acetate, NaCl, KHCO₃, HNO₃, NaOH, and MgSO₄ were tried in an effort to release the accumulated metal ions. Consecutive batch biosorption and desorption experiments were performed in order to test the ability of biosorbent to be reutilized after regeneration. Before the desorption experiments the adsorption experiments were carried out under optimum conditions and the biomass of adsorption experiments was dried at 40 °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 its 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 uranium ions adsorbed per unit of sorbent and percentage sorption were obtained by using the following equations,

$$q = (C_i - C_e)V/W \quad (1)$$

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

where q is the amount of uranium adsorbed (mg/g), V is volume of aqueous phase (L), C_i is initial metal ion concentration (mg/L), C_e is equilibrium metal ion concentration, and M 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,

$$q_{des} = C_{des}V/W \quad (3)$$

where q_{des} is eluted metal content (mg/g) and C_{des} is metal concentration in eluent solution (mg/dm³). The percentage of desorbed metal was evaluated as:

$$\% \text{ desorption} = [q_{des}/q] \times 100 \quad (4)$$

Thermodynamic Studies

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

$$\Delta G^\circ = - RT \ln K_c \quad (5)$$

where $K_c = (q/C_e)$, R is the gas constant (8.314J/molK), and T is the absolute temperature (K). According to the van't Hoff equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\log(q/C_e) = -\Delta G^\circ/2.303RT = -\Delta H^\circ/2.303RT + \Delta S^\circ/2.303RT \quad (7)$$

The values of ΔG° and ΔH° for uranium biosorption were determined from the slope and intercept of the van't Hoff graph.

FTIR and EDX Studies

The functional groups of *Citrus grandis* biomass were analyzed with a Bruker Tensor 27 Fourier transform infrared (FTIR) spectrometer with the samples prepared as KBr discs. 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.

Statistical Analysis

All experiments were carried out in triplicate to ensure reproducibility. All results are reported as mean \pm SD.

RESULTS AND DISCUSSION

Screening of Biomass

Initially the waste biomass of *Citrus grandis* (chokotra), *Citrus aurentifolia* (mitha), and *Citrus sinensis* (mosambi) were screened for maximum uranium biosorption. A definite amount of each biomass (0.1 g) was added to 250 mL conical flask containing 100 mg/L of uranium solution (pH 4; temperature 30 °C) and shaken at 100 ppm for 6 h. After proper shaking, the solution was separated from the biomass by filtration. The results of biosorption capacity of *Citrus grandis* (chokotra), *Citrus aurentifolia* (mitha) and *Citrus sinensis* (mosambi) for uranium from aqueous solution are shown in Fig. 1. The results indicated that the highest biosorption capacity (45.63 mg/g) was observed with *Citrus grandis* (chokotra) biomass and minimum (12.3 mg/g) with *Citrus sinensis* (mosambi) biomass. Hence, *Citrus grandis* (chokotra) biomass was selected for use in the subsequent study.

Effect of pH

It is well known that initial pH of solution plays an important role in the biosorption of heavy metal ions from the aqueous solutions. It influences both the speciation of uranium in the aqueous solution and the ionization of functional groups present on the surface of biomass. The effect of pH on biosorption of uranium onto citrus waste biomass was studied in the pH range from 1.0 to 7.0 in order to determine the optimum pH for the biosorption process and to find out whether the biomass was able to

show good uranium uptake at extreme pH values. The results of biosorption capacity q of biomass versus pH are plotted in Fig. 2. The results indicate that biosorption of uranium increased with an increase in pH from 1.0 to 4.0 and then decreased at pH 5.0. Maximum biosorption capacity (45.63 mg) was observed at pH 4. Uranium biosorption at different pH values was significantly different. The results show that the extremely acidic conditions did not favor sorption of uranium. Under acidic conditions there were high concentrations of H^+ and H_3O^+ ions, which competed with the uranyl ions for binding sites on the surface of biomass, resulting in a decreased biosorption of uranium (Sar and D' Souza 2002). Optimum uptake of uranium at pH 4.0 could be due to the presence of carboxyl, hydroxyl, or amino functionalities, etc., on the surface of biomass.

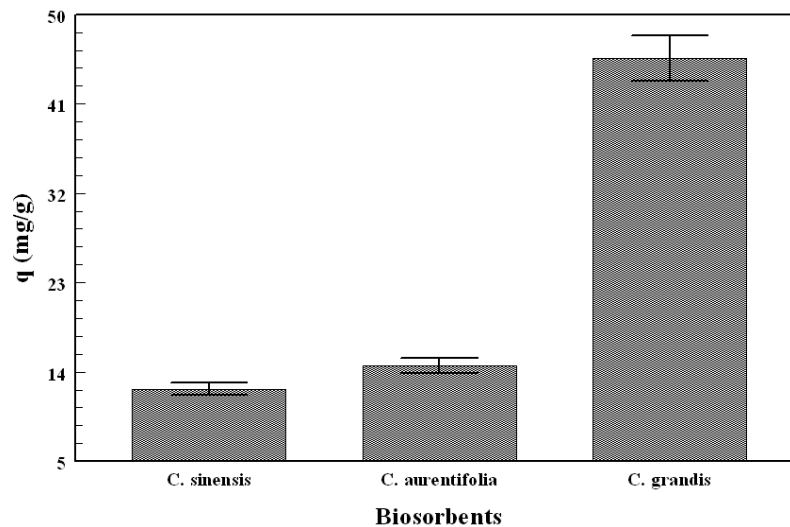


Fig. 1. Screening of citrus waste biomasses

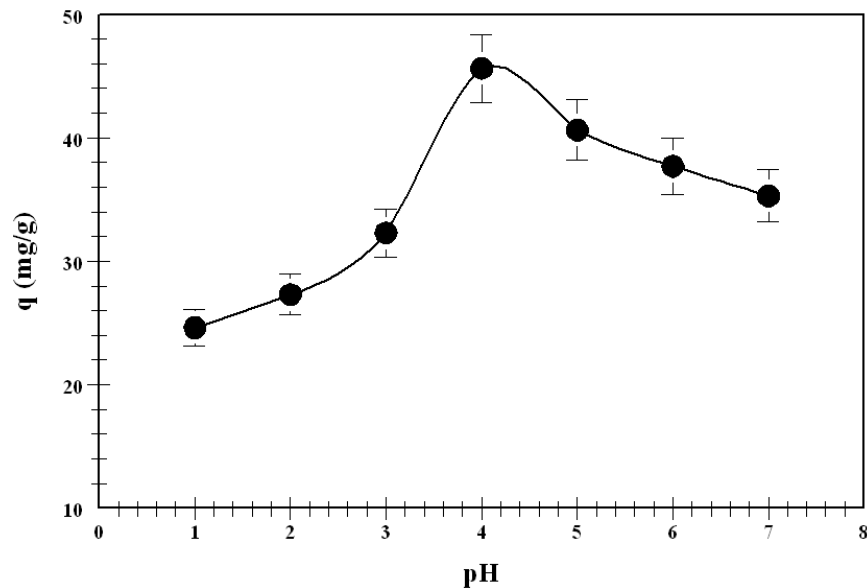


Fig. 2. Effect of pH on the sorption of uranium by citrus waste biomass

Decrease in the uptake of uranium at higher pH could be due to the formation of uranyl complexes such as, UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$. These complexes compete with functional binding sites for uranyl ions and reduce the availability of uranium for biosorption (Wazne et al. 2006). Sometimes formation of solid schoepite ($4\text{UO}_3 \cdot 9\text{H}_2\text{O}$) also takes place at higher pH, which further decreases the dissolved uranium concentration in the solution and consequently reduces biosorption on the biomass (Saxena et al. 2006). Our results are in accord with those of Gok and Aytas (2009), who 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 Biomass Dose

For effective metal ions sorption the biosorbent dose is a significant factor to be considered. It determines the sorbent-sorbate equilibrium of the system. Dose of biosorbent added in to the solution also determines the number of binding sites available for biosorption. The effect of citrus waste biomass dosage on the removal of uranium (VI) was studied using different dosage in the range of 0.025 to 0.2 % (w/v). Figure 3 shows the variation of biosorption capacity and percent removal versus biomass concentration. Results show that biosorption capacity of citrus waste biomass was highly dependent on its concentration in the solution. As shown in the figure, the biosorption capacity increased with the increase of biosorbent dose, this was due to increased surface area of the biosorbent, which in turn increased the number of binding sites. Maximum uranium uptake (38.97 mg/g) was observed with 0.1 % dose. But the uranium uptake decreased from 17.07 to 11.65 mg/g when the biosorbent dose increased from 0.1 to 0.2%.

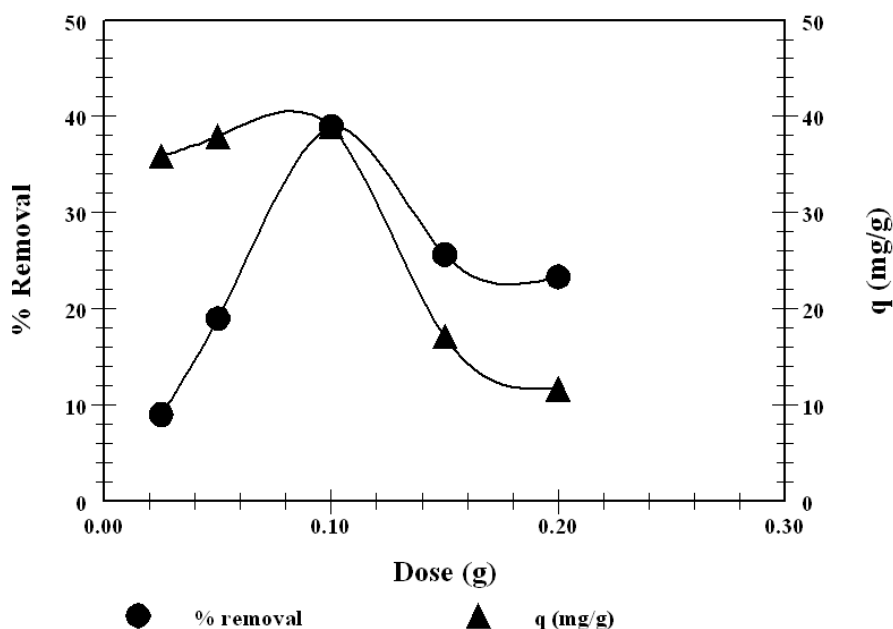


Fig. 3. Effect of biosorbent dose on the sorption of uranium by citrus waste biomass

These results can be explained as a consequence of a partial aggregation and screening effect on the biomass surface, which occurred at high biomass dose, thus giving rise a decrease of active sites and lower uranium uptake per unit mass of biosorbent (Boota et al. 2009; Bhatti et al. 2009). Similarly biosorption of U(VI) by immobilized *Aspergillus fumigatus* beads decreased from 7.2 to 1.7 mg/g when the biosorbent dose increased from 1 to 3.5 % (Wang et al. 2010).

Effect of Initial Uranium Concentration

The rate of biosorption is a function of initial concentration of metal ions, which makes it an important factor to be considered for effective biosorption. Hence a higher initial concentration of uranium will enhance the adsorption process. The percent removal and biosorption capacity (q) at different uranium concentrations are presented in Fig. 4. The plot shows two phases. In the first phase a steep increase in q is observed, and in the second phase the increase is slow. The steep increase in the q was observed for the initial uranium concentration of 25 to 100 mg/L. At low uranium concentration, 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 is expected to result in the increase of q until the saturation of biomass is attained. A maximum value of q (38.97 mg/g) was observed with a concentration of 100 mg/L. This might be due to the saturation of binding sites and increase in the number of ions competing for the available sites in the biomass for binding of uranium at higher concentration (Hanif et al. 2007; Zabair et al. 2008). Moreover, higher concentration of metal ions enhances the mass transfer driving force and increases the metal ions adsorption per unit mass of biosorbent (Aksu 2002)

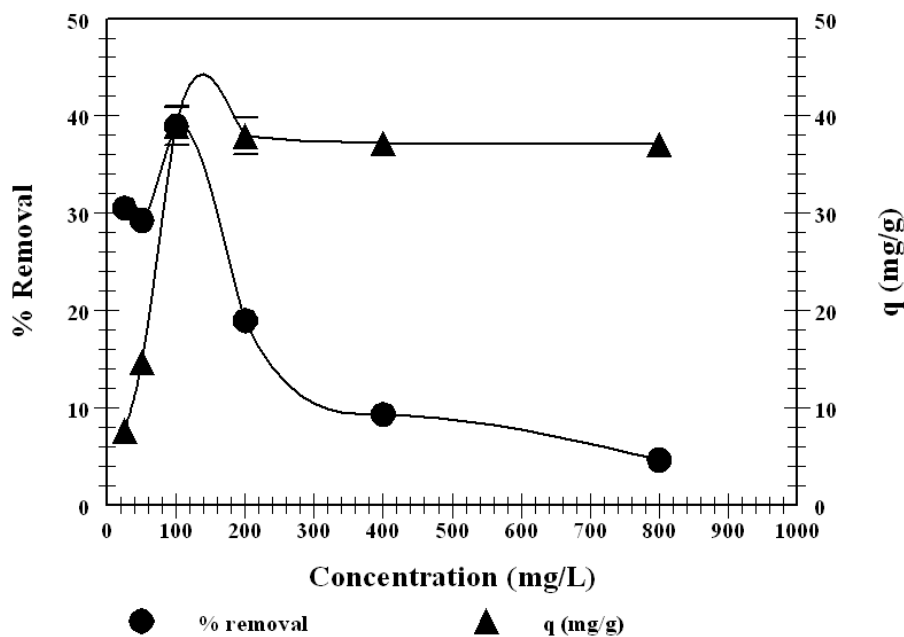


Fig. 4. Effect of initial metal ion concentration on the sorption of uranium by citrus waste biomass

Effect of Contact Time

Equilibrium time is one of the important parameters for an economical wastewater treatment system. The effect of contact time on the biosorption of uranium (VI) on citrus waste biomass was investigated over time intervals from 15 up to 240 min. Figure 5 shows the variation in biosorption capacity as a function of contact time. The results show that adsorption capacity of biomass increased with an increase in contact time and reached a maximum (95.63 mg/g) at about 60 min, thereafter remaining almost constant up to 240 min. In general, about 65% of the total uranium ions biosorption was achieved within 60 min. Therefore, in subsequent experiments 90 min was deemed more than sufficient to establish equilibrium and used in all subsequent study. Gok and Aytas (2009) reported that equilibrium was reached after 90 min during biosorption of U(VI) from aqueous solution using calcium alginate beads.

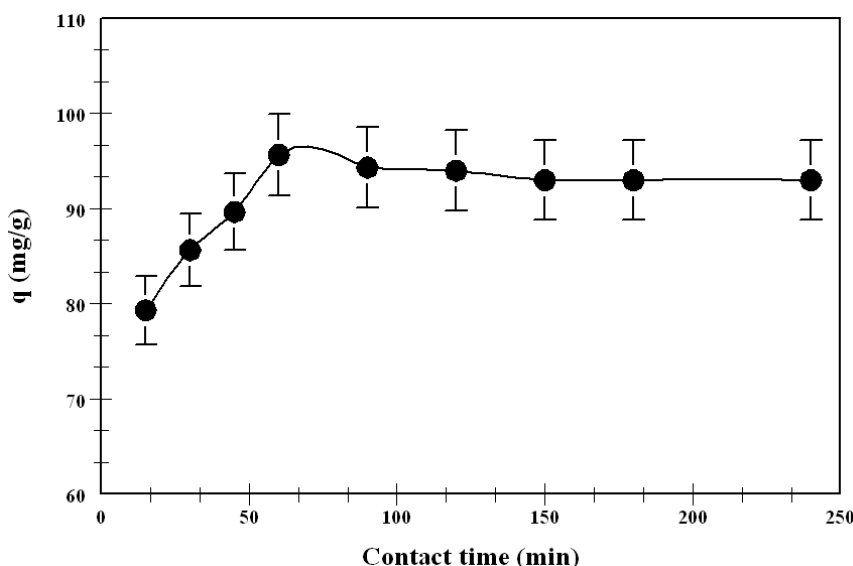


Fig. 5. Effect of contact time on the sorption of uranium by citrus waste biomass

Equilibrium Isotherm and Kinetic Studies

Modeling of equilibrium data was done by using the most widely used Langmuir (Langmuir 1918) and Freundlich isotherm (Freundlich 1906) models. 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,

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (8)$$

where q_e is the metal ion sorbed (mg/g), C_e the equilibrium concentration of metal ions solution and K_L is the Langmuir adsorption constant. The heterogeneous adsorption capacity, q_e (mg/g) of citrus waste biomass for uranium ions was determined by following equation of the Freundlich isotherm:

$$\log q_e = \frac{1}{n} \log C_e + \log k \quad (9)$$

In the present investigation the Langmuir transformation was found to be linear and the value of q_{max} as calculated from Langmuir model was in good agreement with that of the experimental value (Table 1). The good fit to the Langmuir adsorption isotherm model suggests monolayer sorption of uranium on citrus waste biomass.

Table 1. Comparison between Langmuir and Freundlich Isotherm Parameters for Uranium Sorption by *Citrus grandis*

Langmuir isotherm parameters				Experimental value	Freundlich isotherm parameters			
q_{max} (mg/g)	b	R^2	R_L	q (mg/g)	q_{max} (mg/g)	K	$1/n$	R^2
39.37	0.029	0.994	0.26	38.97	277	11.64	0.7713	0.738

Kinetic data were fitted using Lagergren pseudo-first order model (Lagergren 1898), a pseudo-second order model (Blanchard et al. 1984), and an intraparticle diffusion (Weber and Morris 1963) model to investigate the mechanism of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes. The first-order Lagergren equation is given as:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads} t}{2.303} \quad (10)$$

The pseudo-second order equation is,

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{t}{q_t} \quad (11)$$

where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t the mass of metal at time t (min.), $k_{1,ads}$ the first order reaction rate of adsorption (per min.), and $k_{2,ads}$ the pseudo-second order rate constant of adsorption (mg/g. min).

The intraparticle diffusion equation can be written as follows,

$$q_t = K_{pi} t^{1/2} + C_i \quad (12)$$

where C_i is the intercept which describes the foundry layer thickness and K_{pi} (mg/g min^{1/2}) is the rate constant of intraparticle diffusion.

Application of different kinetic models to uranium biosorption by citrus waste biomass suggest that uranium biosorption by citrus waste biomass follows the pseudo-second-order model which indicates that the adsorption of uranium is proportional to the square of vacant sites of biomass. The value of q_e obtained from pseudo-second-order model is in close agreement with that of the experimental value, while the value obtained

from pseudo-first-order model was quite small (Table 2). Application of Weber-Morris equation to kinetic data reveals that uranium biosorption did not follow these equations, as shown by the low values of correlation coefficients.

Table 2. Comparison between Kinetic Models for Uranium Sorption by *Citrus grandis*

q (mg/g)	First order			Second order			Intraparticle diffusion			
	q_e (mg/g)	K_1	R^2	q_e (mg/g)	k_2	R^2	q_e (mg/g)	K	C	R^2
95.63	8.35	0.007	0.658	95.82	0.003	0.980	89.08	0.939	81.908	0.479

Effect of Temperature and Thermodynamic Analysis

The effect of temperature on the biosorption capacity of citrus waste biomass was studied within the temperature range 30 to 50 °C, and the results are shown in Fig. 6. As can be seen from the figure, the biosorption capacity decreased with increase in the temperature, indicating that the biosorption of uranium (VI) on citrus waste biomass was exothermic. Maximum biosorption capacity (45.63 mg/g) was observed at 30 °C, which decreased to 14.30 mg/g at 50 °C. The decreased in biosorption capacity with increasing temperature might be due to the decreased surface activity. Moreover, at higher temperature the thickness of the boundary layer decreases due the increased tendency of the metal ion to escape from the metal surface to the solution phases, which results in a decrease in the biosorption capacity (Jnr and Spiff 2005; Bhatti et al. 2009). Bhat et al. (2008) investigated the biosorption of uranium (VI) from aqueous medium onto red alga. Within the temperature range studied (15 to 55 °C) there was no significant change in the biosorption capacity.

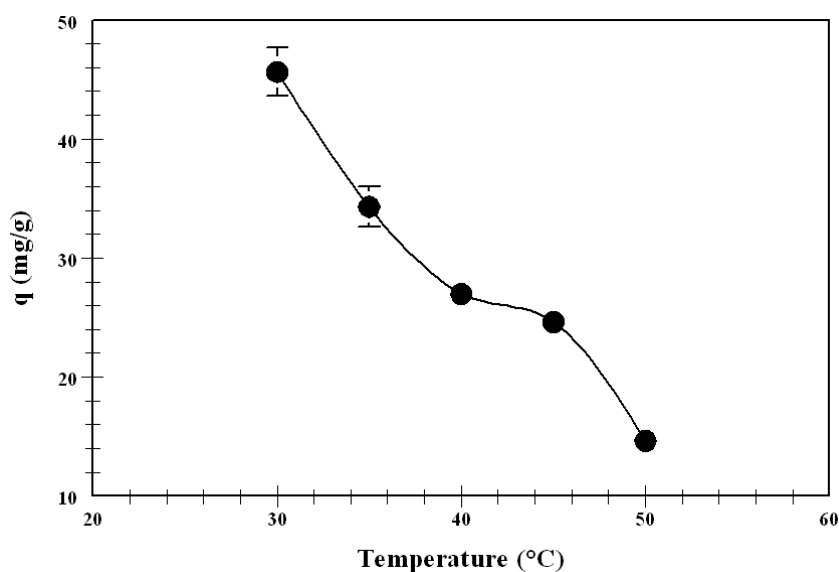


Fig. 6. Effect of temperature on the sorption of uranium by citrus waste biomass

The values of thermodynamic parameters for biosorption of uranium (VI) ions on citrus waste biomass are given in Table 3. The negative value of enthalpy change, ΔH° shows that the adsorption of uranium (VI) is an exothermic process. The numerical value of Gibbs free energy, ΔG° increased with increase in temperature, indicating that the reaction is spontaneous at 30 °C and less favorable at higher temperature. The negative value of ΔS° suggests the decreased randomness at the solid-solution interface during adsorption of uranium (VI) on citrus waste biomass.

Table 3. Thermodynamic Parameters for the Sorption of Uranium on *Citrus grandis* at Different Temperatures

T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	R ²
303	0.44	-60.32	-0.200	0.959
308	1.66			
313	2.59			
318	2.96			
323	4.81			

Effect of Pretreatments

The results regarding the effects of different pretreatments on the biosorption capacity of citrus waste biomass are shown in Fig. 7. As seen from the figure, boiling, acids, alkali, ammonium sulphate, surfactants, and glutaraldehyde treatments decreased the metal uptake capacity of biomass as compared to native. The decrease might be due to the damaging of binding sites of biomass on boiling, protonation of biomass with acids, destruction of autolytic enzymes responsible for putrefaction of biomass by alkali, and masking of active sites by glutaraldehyde (Zubair et al. 2008; Boota et al. 2009; Bhatti et al. 2010).

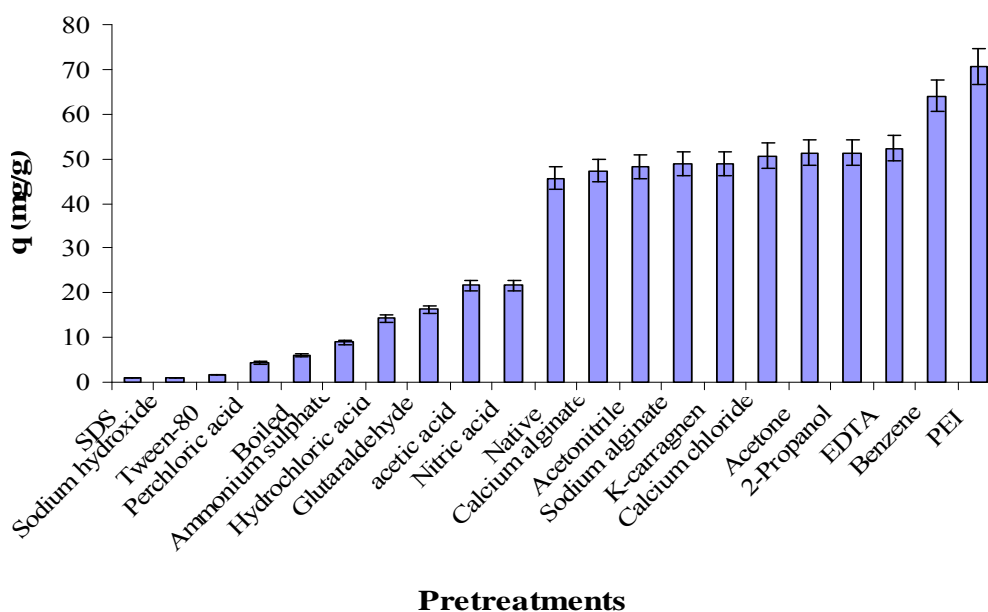


Fig. 7. Effect of pretreatments on biosorption capacity of citrus waste biomass

Ammonium sulphate is a salting agent, capable of bringing about precipitation, which decreases the sorption capacity of biomass. On the other hand, the reduction in uranium adsorption capacity by SDS and Tween-80 treated biomass might be due to the masking of binding sites by interaction with these surfactants.

Chemical treatments with PEI and benzene enhanced the biosorption capacity significantly, in contrast to the other reagents used. A biosorption capacity of 70.63 and 64 mg/g was observed with PEI and benzene, respectively. Removal of surface impurities, rupture of cell membrane and exposure of available binding sites for metal biosorption after pretreatment might be responsible for the increase in metal biosorption. PEI is a well known chelating agent. Treatment of biomass with organic solvents generally enhanced the removal efficiency of biomass. Extraction with organic solvents removed the protein and lipid fractions from the biomass surface (Ashkenazy et al. 1997). Thus, this treatment might expose more metal binding sites and improved the adsorptive property of the biomass.

Desorption and Recovery

Desorption of metal ions from metal-loaded biomass may provide some insight into the extent of metal ion penetration into the cell wall structure of biosorbent. Recovery of metal ions adsorbed onto the biomass is one of the important aspects of any successful biosorption process development. For repeated use of biosorbent, adsorbed metal ions should be easily removed under suitable conditions.

Desorption of the adsorbed uranium (VI) ions from citrus waste biomass was studied in a batch mode using different eluents, and the results are shown in Fig. 8. As seen from the figure, EDTA proved to be a good desorbent (94.7% desorption), followed by HCl (89.71% desorption). EDTA showed strong regeneration efficiency, which is attributed to its strong complexing ability with uranium (VI) ions.

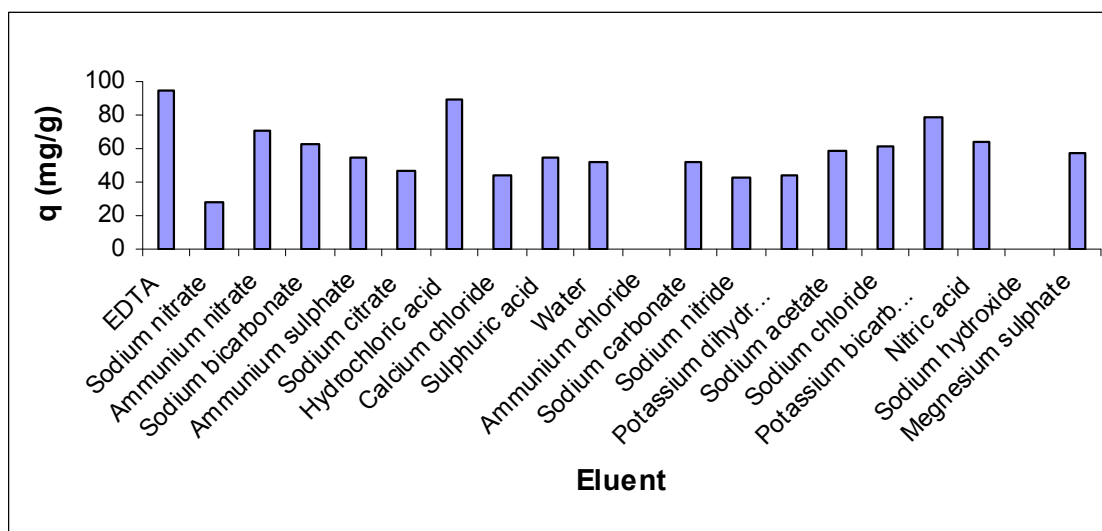


Fig. 8. Recovery of the uranium by different eluents

After optimizing the strength of EDTA solution (0.1 M) the same procedure was repeated for the consecutive adsorption-desorption cycles five times. The results of cyclic study are presented in Fig. 9. The figure indicates that the desorption of uranium (VI) ions from metal-loaded biosorbent resulted in more than 70% metal ions recovery. The biosorption efficiency did not change significantly, and only a 10% decrease was observed up to three biosorption-desorption cycles (Fig. 9). These results show that the citrus waste biomass has a good potential for the removal of uranium ions repeatedly from aqueous solution without any detectable loss in the total biosorption capacity.

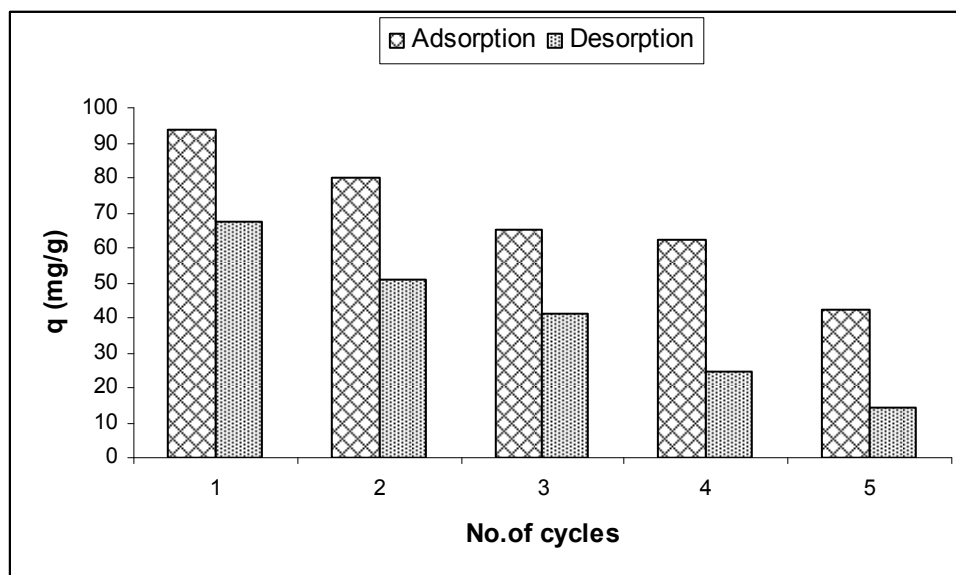


Fig. 9. Cyclic study of uranium adsorption-desorption on citrus waste biomass

Infrared Analyses

The infrared spectra of citrus waste biomass were recorded before and after uranium adsorption in order to get information about the interaction between metal ions and binding sites. This FT-IR analysis permits spectroscopic observation of biosorbent surface in the range 4000 to 400 cm^{-1} . Figure 10 (a) and (b) shows the characteristics peaks in agreement with the possible presence of amino, amido, carboxylic, hydroxyl, and carbonyl groups. In the case of the control (uranium untreated) a sharp peak at a frequency level of 3600 cm^{-1} and two absorption bands one near 3500 cm^{-1} and one 3400 cm^{-1} representing O-H and N-H stretching vibrations are observed. In case of metal-loaded biosorbent a broad band near 3600 cm^{-1} may be assigned to the H-bonded OH and NH groups (Asgher and Bhatti, 2010). The appearance of a strong band just below 3000 cm^{-1} may be due to antisymmetric stretching of the C-H bond. The presence of sharp peak near 1700 cm^{-1} denotes the presence of C=O stretching, while a peak near 1600 cm^{-1} may be attributed to C=O or C=N stretching of carboxylic or imines. The band near 1000 cm^{-1} may be assigned to stretching vibration of C-O group. In case of metal loaded spectra the overall reduction in intensity of peaks suggested that these functional moieties might be involved in the biosorption of uranium (VI) on citrus biomass.

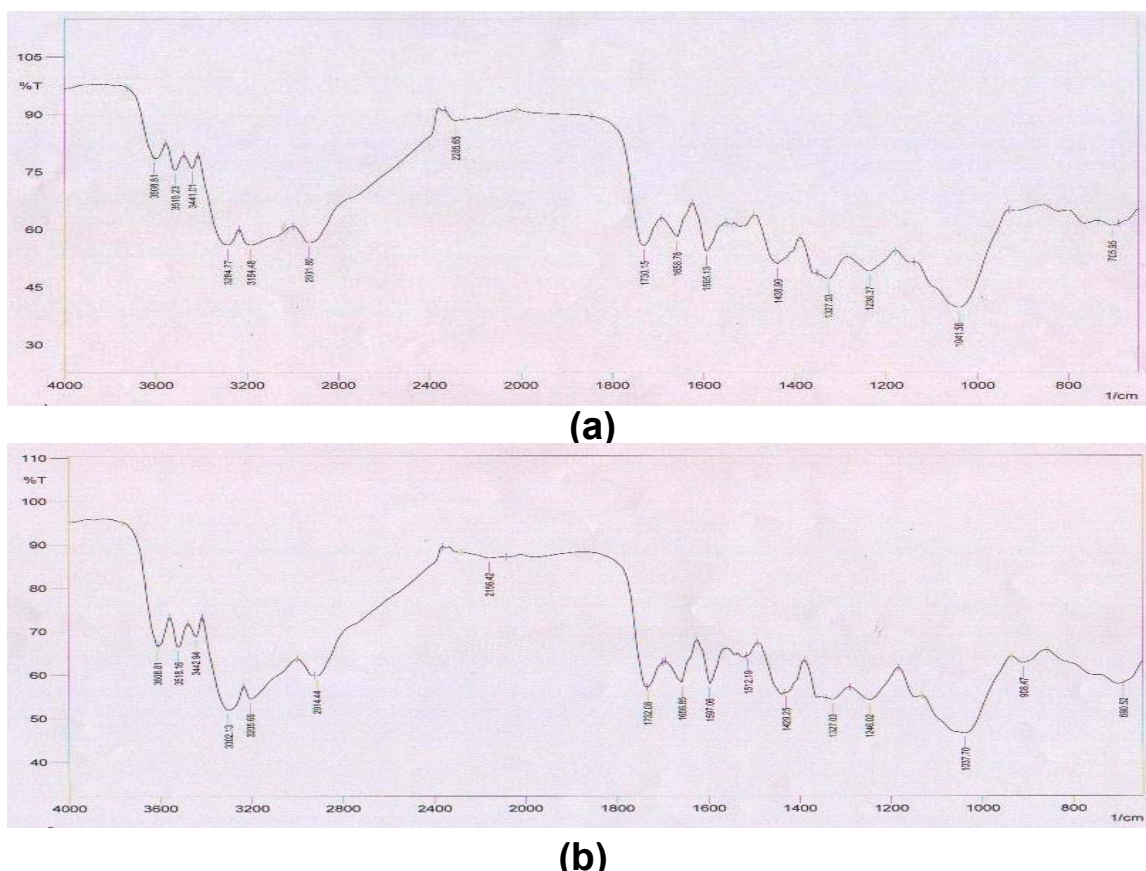


Fig. 10. FT-IR spectrum of (a) native and (b) uranium loaded citrus waste biomass

CONCLUSIONS

In this study citrus waste biomass was used to recover uranium (VI) ions from aqueous solutions. The results indicate that removal of uranium (VI) is strongly dependent on pH of the medium and maximum removal is observed at pH 4. Increasing temperature had an unfavorable effect on the biosorption capacity of citrus biomass. The highest biosorption capacity was recorded with benzene-treated biomass, which changes the biosorptive characteristics of cell wall constituents resulting in the availability of more binding sites. The equilibrium data were described well by a Langmuir isotherm, indicating that the adsorption of uranium on biomass was as a monolayer. The biosorption of uranium (VI) ions on citrus biomass followed pseudo-second-order kinetics. Furthermore, as citrus waste biomass is readily available, it can be employed for treatment of wastewaters containing radionuclides.

REFERENCES CITED

Aksu, Z. (2002). "Equilibrium and kinetic modeling of cadmium (II) biosorption by *C. vulgaris* in batch system: Effect of temperature," *Sep. Purif. Technol.* 21, 285-294.

- Al-Masri, M. S., Amin, Y., Al-Akel, B., and Al-Naama, T. (2010). "Biosorption of cadmium, lead and uranium by powder of popular leaves and branches," *Appl. Biochem. Biotechnol.* 160, 976-987.
- Asgher, M., and Bhatti, H. N. (2010). "Mechanistic and kinetic evaluation of biosorption of reactive azo dyes by free, immobilized and chemically treated *Citrus sinensis* waste biomass," *Ecol. Eng.* 36, 1660-1665.
- Ashkenazy, R., Gottlieb, L., and Yannai, S. (1997). "Characterization of acetone washed yeast biomass functional groups involved in Pb^{2+} biosorption," *Biotechnol. Bioeng.* 5, 1-10.
- Bhainsa, K. C., and D'Souza, S. F. (2001). "Uranium (VI) biosorption by dried roots of *Eichhornia crassipes* (water hyacinth)," *J. Environ. Sci. Health A* 36, 1621-1631.
- Bhat, S. V., Melo, J. S., Chaugule, B. B., and D'Souza, S. F. (2008). "Biosorption characteristics of uranium (VI) from aqueous medium onto *Catenella repens*, a red alga," *J. Hazard. Mater.* 158, 628-635.
- Bhatti, H. N., Bajwa, I. I., Hanif, M.A., and Bukhari, I. H. (2010). "Removal of lead and cobalt using lignocellulosic fiber derived from *Citrus reticulata* waste biomass," *Korean J. Chem. Eng.* 27, 218-227.
- Bhatti, H. N., Khalid, R., and Hanif, M. A. (2009). "Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge," *Chem. Eng. J.* 148, 434-443.
- Bhatti, T. M., Mateen, A., Amin, M., Kauser, A. M., and Khalid, A. M. (1991). "Spectrophotometric determination of uranium (VI) in bacterial leach liquors using Arsenazo-III," *J. Chem. Technol. Biotechnol.* 52, 331-341.
- Blanchard, G., Maunaye, M., and Martin, G. (1984). "Removal of heavy metals from waters by means of natural zeolites," *Water Res.* 18, 1501-1507.
- Boddu, V. M., Abburi, K., Talbott, J. L., Smith, E. D. (2003). "Removal of Cr (VI) from wastewater using a new composite chitosan biosorbent," *Environ. Sci. Technol.* 37, 4449-4456.
- Boota, R., Bhatti, H. N., Hanif, M. A. (2009). "Removal of Cu(II) and Zn(II) using lignocellulosic fiber derived from *Citrus reticulata* (Kinnow) waste biomass," *Sep. Sci. Technol.* 44, 4000-4022.
- Dursun, A. Y. (2006). "A comparative study on determination of the equilibrium, kinetic and thermodynamic parameters of biosorption of copper(II) and lead(II) ions onto pretreated *Aspergillus niger*," *Biochem. Eng. J.* 28, 187-195.
- Freundlich, H. (1906) "Adsorption in solution," *Phys. Chem. Soc.* 40, 1361-1368.
- Gok, C., and Aytas, S. (2009). "Biosorption of uranium (VI) from aqueous using calcium alginate beads," *J. Hazard. Mater.* 168, 504-508.
- Hanif, M. A., Nadeem, R., Bhatti, H. N., Ahmad, N.R., and Ansari, T.M. (2007). "Ni(II) biosorption by *Cassia fistula* (Golden Shower) biomass," *J. Hazard. Mater.* 139, 345-355.
- Jnr, M. H., and Spiff, A. I. (2005). "Effect of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by *Caladium bicolor* (wild cocoyam) biomass," *Elec. J. Biotechnol.* 8, 162-169.
- Kalin, M., Wheeler, W. N., and Meinrath, G. (2005). "The removal of uranium from mining waste water using algal/microbial biomasses," *J. Environ. Radio.* 78, 151-177.

- Kratochvil, D., and Volesky, B. (1998). "Advances in the biosorption of heavy metals," *Trends Biotechnol.* 16, 291-300.
- Lagergren. (1898). "Zur theorie der sogenannten Adsorption geloster Stoffe," *Kunliga Svenska Vetenskapsakademiens, Handlingar Band 24*, 1-39.
- Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica, and platinum," *J. Am. Chem. Soc.* 40, 1361-1368.
- Park, D., Yun, Y., Jo, J. H., and Park, J. M. (2006). "Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-scale feasibility test," *Ind. Eng. Chem. Res.* 45, 5059-5065.
- Sar, P., and D Souza, S. F. (2002). "Biosorption of thorium (IV) by a *Pseudomonas* biomass," *Biotechnol. Lett.* 24, 239-243.
- Satapathy, D., and Natarajan, G. S. (2006). "Potassium bromate modification of the granular activated carbon and its effect on nickel adsorption," *Adsorption* 12, 147-154.
- Saxena, S., Prasad, M., and D'Souza, S. F. (2006). "Radionuclide sorption onto low cost mineral adsorbent," *Ind. Eng. Chem. Res.* 45, 9122-9128.
- Tuzen, M., Saygi, K. O., Usta, C., and Soylak, M. (2008). "*Pseudomonas aeruginosa* immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions," *Bioresour. Technol.* 99, 1563-1570.
- Wang, J., Hu, X., Liu, Y., Xie, S., and Bao, Z. (2010). "Biosorption of U(VI) by immobilized *Aspergillus fumigatus* beads," *J. Environ. Radioact.* 101, 504-508.
- Wazne, M., Meng, X., Korfiatis, G. P., and Christodoulatos, C. (2006). "Christodoulatos carbonate effects on hexavalent uranium removal from water by nanocrystalline titanium dioxide," *J. Hazard. Mater.* 136, 47-52.
- Weber, W. J., and Morris, J.C. (1963). "Kinetics of adsorption on carbon solution," *J. Sanit. Eng. Div. A. Soc. Civil Eng.* 89, 31-59.
- Xia, L. S., Wang, M., Deng, C. A., and Fu, S. F. (2006). "Synergistic aeration biosorption of uranium-containing wastewater by banyan leaves-activated sludge," *J. Nucl. Radioac.* 28, 231-235.
- Xie, S., Yang, J., Chen, C., Zhang, X., Wang, Q., and Zhang, C. (2008). "Study on biosorption kinetics and thermodynamics of uranium by *Citrobacter freundii*," *J. Environ. Radioac.* 99, 126-133.
- Yang, J., and Volesky, B. (1999). "Biosorption of uranium on *Sargassum* biomass," *Water Res.* 33, 3357-3363.
- Zubair, A., Bhatti, H. N., Hanif, M. A., and Shafqat, F. (2008). "Kinetic and equilibrium modeling for Cr(III) and Cr(VI) removal from aqueous solutions by *Citrus reticulata* waste biomass," *Water Air Soil Pollution*, 191, 305-318.

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