

# Uranium adsorption by non-treated and chemically modified cactus fibres in aqueous solutions

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**Abstract** The adsorption efficiency of *Opuntia ficus indica* fibres regarding the removal of hexavalent uranium [U(VI)] from aqueous solutions has been investigated prior and after the chemical treatment (e.g. phosphorylation and MnO<sub>2</sub>-coating) of the biomass. The separation/removal efficiency has been studied as a function of pH, uranium concentration, adsorbent mass, ionic strength, temperature and contact time. Evaluation of the experimental data shows that biosorption is strongly pH-dependent and that the MnO<sub>2</sub>-coated product presents the highest adsorption capacity followed by the phosphorylated and non-treated material. Experiments with varying ionic strength/salinity don't show any significant effect on the adsorption efficiency, indicating the formation of inner-sphere surface complexes. The adsorption reactions are in all cases exothermic and relatively fast, particularly regarding the adsorption on the MnO<sub>2</sub>-coated product. The results of the present study indicate that adsorption of uranium from waters is very effective by cactus fibres and particularly the modified treated fibres. The increased adsorption efficiency of the cactus fibres is attributed to their primary and secondary fibrillar structure, which result in a relative relative high specific surface available for sorption.

**Keywords** Uranium · Cactus fibres · Chemical treatment · Adsorption · Waters

## Introduction

Uranium is a ubiquitous natural element with an average concentration in earth's crust of about 3 ppm and constant uranium concentration of about 3 ppm in oceans [1]. Nevertheless, pollution of the environment with uranium and associated health effects to human have recently become of major concern, particularly due to the use of depleted uranium in armour-breaking bullets [2]. Indeed, uranium in environmentally significant concentrations is found near to uranium mining and processing facilities and usually involves large volumes of wastewater. Removal of uranium from such large volumes of wastewaters will require a cost effective remediation technology. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Recently, biosorption is presented as an alternative method for removing toxic metals from wastewater [3]. On the other hand, there is great interest in the development of technologies for uranium recovery from seawater, which would improve the uranium resource availability and sustain long-term fuel supply for nuclear power reactors [4, 5].

Biosorption technologies in which living or dead biomass is used to accumulate heavy metals are methods that often replace conventional processes for remediating metal pollution in wastewaters. However, the major drawback of these microbial systems is cost of growing a sufficient quantity of bacterial or algae biomass. Alternatively, the removal of dissolved metals by plant tissues has been studied using a variety of biomasses that represent by-products from other commercial processes with little commercial value and thus representing good candidates for the development of inexpensive biosorption processes. Natural adsorbents, such as agricultural wastes are inexhaustible, low cost and non-hazardous adsorbent materials and easily disposed by incineration [3, 6, 7]. *Opuntia ficus* is a long domesticated and the most widespread

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cactus species, and economically important crop throughout arid and semiarid parts of the world (e.g. Central America, North Africa and Mediterranean countries) [8]. Besides fruit production, *Opuntia ficus* plants can be used to prevent soil erosion, as fences and windbreaks in horticulture, and animal feed [8, 9]. On the other hand, dead plants could be used as source for biomass, which could act as efficient adsorbents for metal ions [10]. Uranium adsorption on minerals [11] and biomasses is extensively investigated [12] and there are several studies dealing with uranium adsorption on non-treated [6, 13] and chemically modified biomass by-products, particularly with respect to the selective separation of uranium from seawater [5].

The present study deals with the adsorption of uranium by non-treated and chemically modified *Opuntia ficus indica* fibres. Chemical modification, such as phosphorylation and metal (manganese) oxide coating of the biomass by-product is expected to result in novel derivatives with increased separation efficiency and selectivity for metal ions [7]. The main goal of the study is the investigation of various parameters (e.g. pH, uranium concentration, mass of the adsorbent, ionic strength, temperature and contact time) affecting the biosorption performance and the determination of thermodynamic parameters (e.g.  $K_d$ ,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ), which are of fundamental importance for both the assessment of the chemical behaviour of uranium in heterogeneous aquatic systems and the development of water treatment technologies related to (radio)toxic metal ion removal.

## Experimental

All experiments were performed at room temperature ( $23 \pm 2$  °C) under normal atmospheric conditions in aqueous solutions, without background electrolyte added, except those related to the ionic strength effects. Generally, the experiments were performed in duplicate and the mean values have been used for data evaluation. The relative deviation of the corresponding data was always below 5 %, which within the relative uncertainty given for the concentration values determined by photometry. The preparation of the test solutions was carried out by dissolution in the desired aqueous solution the appropriate amount of a U(VI) stock solution (0.1 M) prepared by dissolution of  $\text{UO}_2(\text{NO}_3)_2 \times 6\text{H}_2\text{O}$  in distilled water. pH measurements were performed by a commercial glass electrode (Sentek), which was calibrated prior and after each experiment using a series of buffer solutions (pH 2, 4, 7 and 10, Scharlau).

### *Opuntia ficus* fibres

*Opuntia ficus* cladodes were collected from plants used as effective living fence in a suburb of Nicosia, Cyprus. The

cladodes, which had been broken off the plants, were extensively sun-dried and partially disintegrated. The cladodes were carefully hand-peeled and thoroughly washed by distilled water and the wooden residuals (e.g. primary and secondary fibres) were dehydrated at 70 °C for 15 h and ground for a few minutes in a coffee grinder. The grinded product was sieved and the particle fraction between 200 and 500 microns was selected for the adsorption experiments. Specific surface area measurements based on the Brunauer–Emmett–Teller-theory (BET measurements) by means of  $\text{N}_2$ -adsorption (ASAP 2000, micromeritics) have shown that the material has not internal surface.

### Phosphorylation of the cactus fibres

The preparation of the phosphorylated material was performed by addition of the fibres (5 g) in 500 ml 1.5 M  $\text{H}_3\text{PO}_4$  solution (Aldrich Chemical Company) and continuous stirring of the suspension for 24 h at room temperature [14]. Following, the solid phase was separated by filtration and washed thoroughly with distilled water until the pH of the filtrates was neutral. The phosphorylated biomass was dried for several days in a desiccator and then stored for later use.

### $\text{MnO}_2$ -coating of the cactus fibres

The preparation of the  $\text{MnO}_2$ -coated material was performed using the reductive precipitation of  $\text{MnO}_2$  oxide onto the biomass substrate, by addition of the fibres (10 g) in 100 ml 2 % (w/v)  $\text{KMnO}_4$  solution (Fisons Scientific Equipment) and continuous stirring of the suspension for 1 h at 50 °C [15]. Following, the solid phase was separated by filtration, washed thoroughly with distilled water and dried for several days in a desiccator.

### Characterization of the non treated and chemically modified biomass by-products

The characterization of the cactus fibres (CF) and the products obtained after chemical treatment was performed by Fourier Transform Infra Red Spectroscopy (FTIR spectrometer 8900, Shimadzu), and acid/base titrations. For the titrations, alkaline biosorbent suspensions (pH 12) of each of the three products (0.25 g in 15 ml of deionized water) were titrated by 0.1 M  $\text{HClO}_4$  standard solutions (BDH Laboratory Supplies) under continuous magnetic stirring. Acid/base titrations were also performed by stepwise adding of 0.1 M  $\text{HClO}_4$  or 0.1 M NaOH to biosorbent suspensions. After each addition of the titrant, the pH was allowed to reach equilibrium and finally measured by means of a pH-meter (Hanna Instruments). FTIR measurements

were performed by means of prepare translucent KBr disks including finely ground biomass was encapsulated at a 10:1 mass ratio.

Adsorption measurements

In order to investigate the effect of various parameters (pH, uranium concentration, mass of the adsorbent, ionic strength, temperature and contact time) on the U(VI) adsorption on non-treated and chemically modified CF, different classes of experiments (e.g. the effect of pH, ionic strength etc.) were conducted. In these experiments the parameter under investigation was varied, while other experimental parameters were kept constant. The effect of pH was studied in an adsorption system: (0.01 g adsorbent and 15 ml of the test solution:  $[U(VI)] = 1 \times 10^{-5} \text{ M}$ ) in which pH was varied between 2 and 8.5 by addition of  $\text{HClO}_4$  or  $\text{NaOH}$ . All test solutions were prepared using 0.1 M  $\text{NaClO}_4$  (Aldrich Co) as the background electrolyte. The effect of the ionic strength (salinity) was performed by addition of  $\text{NaClO}_4$  solution of various concentrations (0.001, 0.01, 0.1, 0.5, 0.7 and 1 M) at constant adsorbent amount (0.01 g), total uranium concentration ( $1 \times 10^{-5} \text{ M}$ ) and the optimum pH value for each adsorbent. For studying the effect of initial uranium concentration, the latter was varied between  $9 \times 10^{-6}$  and  $9 \times 10^{-4} \text{ M}$ , at a prefixed amount of adsorbent (adsorbent dosage = 0.01 g and the optimum pH value for each adsorbent). The effect of the amount of the CF by-products was investigated by adding different amounts of the adsorbents (between 0.005 and 0.2 g) in 15 ml test solutions of constant uranium concentration ( $1 \times 10^{-5} \text{ M}$ ). The effect of temperature was studied between 10 and 70 °C at the same conditions that are described above. For kinetic studies certain amount of the biomasses (0.04 g) were mixed with uranium solution ( $1 \times 10^{-5} \text{ M}$ ). Samples withdrawn at time intervals (usually after an equilibration time of 24 h) were centrifuged and filtered with membrane filters (pore size: 450 nm). Finally, the uranium concentration was determined spectrophotometrically (UV 2401 PC Shimadzu) by means of arsenazo-III, according to a previously described method [16]. For each test solution, a corresponding reference solution was prepared and was similar to the test solution expect that it didn't contain the adsorbent material. The relative amount of U(VI) adsorbed was determined using the following equations:

$$\text{Rel. adsorption}\% = 100 \times \frac{([U(VI)]_0 - [U(VI)]_{\text{aq}})}{[U(VI)]_0} \quad (1)$$

$$K_d = \frac{([U(VI)]_0 - [U(VI)]_{\text{aq}})}{[U(VI)]_{\text{aq}}} \cdot \frac{V}{m} \quad (1\text{kg}^{-1}) \quad (2)$$

where  $[U(VI)]_0 =$  the total uranium concentration ( $\text{mol l}^{-1}$ ) in the system or in the reference solution,  $[U(VI)]_{\text{aq}} =$  uranium concentration ( $\text{mol l}^{-1}$ ) in the test solution,  $V$  (l) is the volume of the test solution and  $m$  (kg) is the mass of the adsorbent.

Results and discussion

Preparation and characterization of the chemically treated cactus fibres

The main constituents of the CF obtained are polysaccharides including cellulose and therefore the adsorption of toxic metal ions is basically attributed to  $\text{R-CH}_2\text{-OH}$  alcohol group at the glucose units of the biopolymers [10]. Phosphorylation of the CF leads to the conversion of the hydroxyl groups to phosphate groups upon esterification of the alcoholic groups by phosphoric acid according to the following Eq. (3):



As a result, the almost neutral surface of the CF becomes acidic, as indicated by the corresponding acid/base titration curve in Fig. 1. The average pK value of the surface groups is about 3, which is characteristic for phosphorylated surfaces [17]. In comparison, the inflection point of the titration curve before phosphorylation is close to pH 7, because of the low acidity of the alcoholic hydroxyl groups ( $\text{pK} > 15$ ). According to the corresponding titration curve even in the strong alkaline pH (pH 11) region no deprotonation occurs, whereas proton consumption observed in

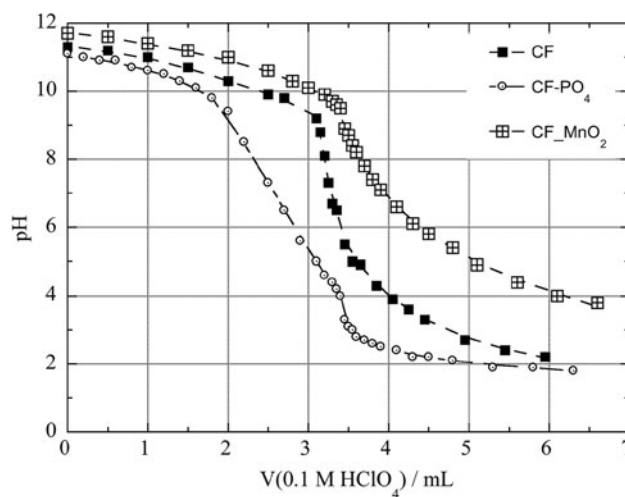


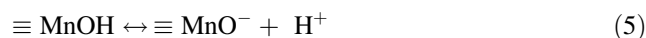
Fig. 1 Acid-base titrations of non-treated (CF) and treated cactus fibres with  $\text{H}_3\text{PO}_4$  (CF- $\text{PO}_4$ ) and  $\text{KMnO}_4$  (CF/ $\text{MnO}_2$ ). The pH of the biosorbent suspensions was prior titration adjusted to pH 12 by 0.1 M  $\text{NaOH}$  addition

the acidic pH region is attributed to the rapid protonation of the glycosidic oxygen atom, which finally results in the acid-catalysed hydrolysis of cellulose [18]. The increased surface acidity upon phosphorylation is of particular importance, because the surface can be deprotonated and become negatively charged even at  $\text{pH} < 4$ . Hence, the phosphorylated biomass becomes more attractive for positively charged metal ions, even in the acidic pH region and the surface can bind metal ions specifically with higher affinity to phosphates.

The FTIR spectra prior and after phosphorylation of the CF are shown in Fig. 2. The broad peak at  $3,430\text{ cm}^{-1}$  is attributed to hydroxyl stretching vibrations, while the peaks at  $2,850\text{--}2,900\text{ cm}^{-1}$  are assigned to aliphatic C–H groups [7, 13]. Although the spectra corresponding to chemically treated and non-treated CF differ from one another (different relative intensities), they don't show any distinct/characteristic peaks, which could be attributed to chemical modification (phosphorylation and manganese oxide coating) most probably because of the broad absorption bands in the spectra and the relative low ratio of inorganic to organic material.

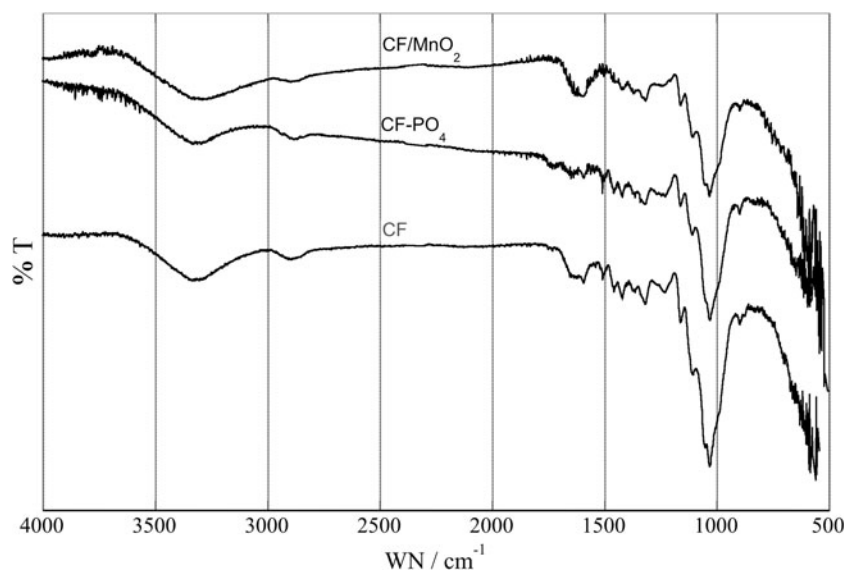
Manganese oxide has been widely used for the separation of radiotoxic metal ions from aqueous solutions [7, 15, 19]. The  $\text{MnO}_2$ -coating of the CF has been performed to enhance the adsorption capacity and selectivity of the by-product, because of the dramatic modification of the surface (organic to inorganic) and the fact that  $\text{MnO}_2$  presents extraordinary affinity for cations [7, 19]. The  $\text{MnO}_2$  coating of the CF particles has been performed by reduction of  $\text{MnO}_4^-$  by reductive groups on the CF surface (e.g. R–OH) and subsequent deposition of the resulting  $\text{MnO}_2$  on the particle surface, which is indicated by textural changes (change of color to black and higher density) of

the material. Upon coating of the CF the surface charge of the  $\text{MnO}_2$ -coated material is determined by the  $\text{MnO}_2$  surface properties.  $\text{MnO}_2$  forms a colloidal coating on the CF. Hydrated  $\text{MnO}_2$  gains surface charge through protonation and deprotonation according to reactions described by Eqs. (4) and (5).



The pH value at which colloidal  $\text{MnO}_2$  dispersed in an electrolytic solution exhibits zero net electrical charge on the surface corresponds to the point of zero charge value and is expected to be similar to other oxides of the  $\text{MO}_2$  type reported in the literature (e.g.  $\text{SiO}_2$ : pH 2,  $\text{ZrO}_2$ : pH 4,  $\text{SnO}_2$ : pH 4.5,  $\text{TiO}_2$ : pH 6) [19]. Hence within the pH range of interest colloidal  $\text{MnO}_2$  is most probably neutral or negatively charged. Acid/base titration curves (Fig. 1) of the  $\text{MnO}_2$ -coated material clearly indicate the successful preparation of the desired product. However, the corresponding FTIR spectra of the chemically treated and non-treated CF (Fig. 2), although different, don't show any distinct/characteristic peaks, most probably because of the broad absorption bands and the relative low ratio of inorganic to organic phase. The non-treated and chemically modified CF samples have been used as adsorbents for U(VI) from aqueous solutions. The advantage of using biomass by-products as adsorbents is of particular interest because of their availability and low-cost. The latter compensates the limitations in recycling the biomass by-products and allows thermal treatment (e.g. burning) of the organic material, which results in significant reduction of waste material and recovery of the metals.

**Fig. 2** IR spectra of non-treated (CF) and cactus fibres treated with  $\text{H}_3\text{PO}_4$  (CF- $\text{PO}_4$ ) and  $\text{KMnO}_4$  (CF/ $\text{MnO}_2$ )

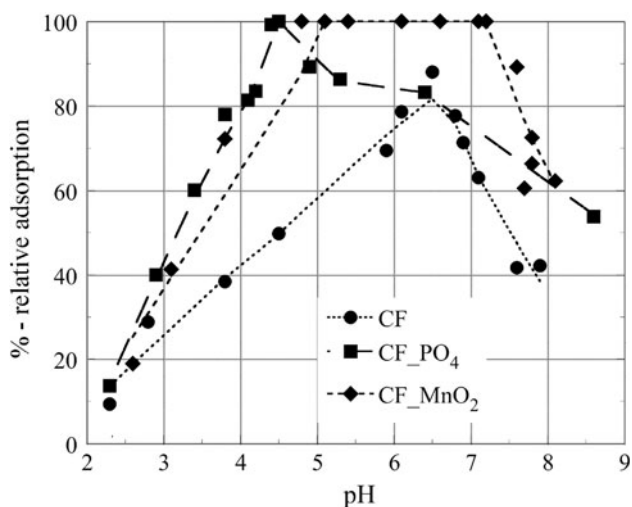
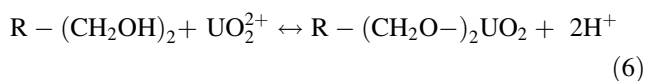


Adsorption experiments

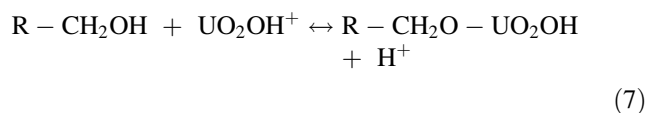
pH effect

The relative adsorption is related to the chemical affinity of the surface for the adsorbate, which depends on both the chemical behaviour of U(VI) in solution and the surface charge of the adsorbent. Hence, the solution pH is one of the most important parameters affecting adsorption on surfaces, because pH may govern both the chemical behavior of a metal ion in solution and the surface charge of an adsorbent. To study the effect of pH on the U(VI) adsorption, samples of the three different biomass by-products were conducted with U(VI) solutions at different pH (2 < pH < 9).

The effect of pH on the relative adsorption of U(VI) on the three different materials is shown in Fig. 3. In the case of the non-treated CF the relative adsorption increases with increasing pH and reaches a maximum value (~85 %) at pH > 6. For pH values below 6 the relative adsorption decreases almost linearly with pH and its value becomes almost zero at pH 2. Because pH < 6 U(VI) is exclusively present in the form of positively charged species [e.g.  $UO_2^{2+}$ ,  $UO_2(OH)^+$ ] [1, 20], the adsorption of the metal ion is solely governed by cation exchange reactions and hence the proton concentration in solution. The corresponding cation-exchange reaction between protons and U(VI) cations on the CF surface, is formulated by Eqs. (6) and (7).

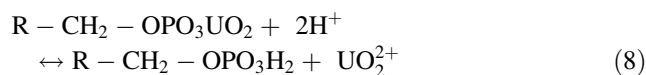


**Fig. 3** Adsorption of U(VI) on non-treated (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres, as a function of pH variations (0.01 g of biomass,  $[U(VI)]_{tot} = 1 \times 10^{-5} \text{ mol l}^{-1}$ ,  $I = 0.1 \text{ mol l}^{-1} \text{ NaClO}_4$ ,  $T = 23 \pm 2 \text{ }^\circ\text{C}$ , 24 h of reaction time)



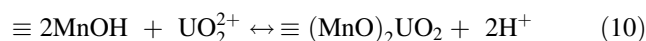
Above pH 6.5 the values of the relative adsorption decreases dramatically because of the formation of U(VI)-carbonato species [e.g.  $UO_2(CO_3)_n^{(2n-2)-}$ ], which predominate in alkaline solutions and compete the formation of U(VI) adsorbed species.

On the other hand, the phosphorylated CF present even at low pH values (pH ~ 4.5) the highest adsorption capacity (100 %) for U(VI). The shift of more than 2.5 pH units to the acidic area of the maximum values of the relative adsorption is related to lower pK (pH ~ 3) values of the organophosphate moieties present on the CF surface upon phosphorylation. The protonation of the organophosphate moieties results in the gradual decreasing of relative adsorption of U(VI) for pH < 4. The corresponding reactions are described by Eqs. (6) and (7).



Between pH 4 and 6.5 the relative adsorption decreases (~20 %) most probably because of the hydrolysis of  $UO_2^{2+}$  to  $UO_2OH^+$ , which results in lower affinity of the hydrolysed species for the phosphorylated biomass surface. This is expected since electrostatic interactions play a significant role in the formation of surface complexes between cations and the phosphorylated biomass surface [7].

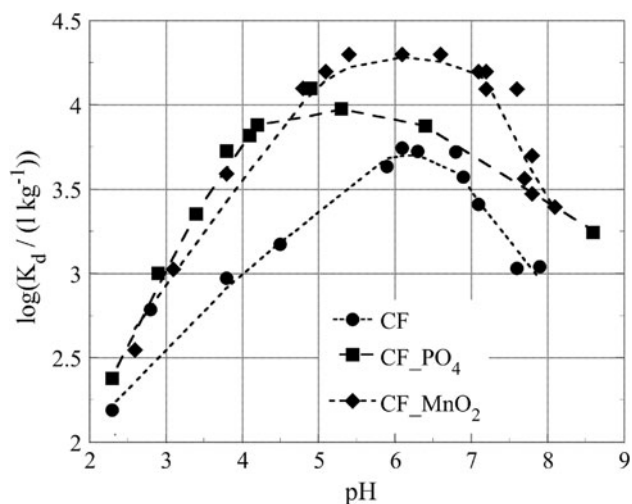
In the case of MnO<sub>2</sub>-coated CF, the highest value of the relative adsorption (100 %) is observed in the pH range between 4.5 and 7.5. Above pH 7.5 the relative adsorption of U(VI) on the MnO<sub>2</sub>-coated biomass decreases because of the formation of U(VI)-carbonato species [e.g.  $UO_2(CO_3)_n^{(2n-2)-}$ ], which compete with the formation of U(VI) adsorbed species. In the acidic pH region the cation exchange capacity of the hydrous MnO<sub>2</sub> decreases significantly with decreasing pH (pH < 4.5) and results in lower relative adsorption of U(VI) (Fig. 3). On the other hand, the adsorbate in the studied pH range is expected to be present predominantly in the form of  $UO_2^{2+}$  aquocations [1, 20]. Assuming that only the adsorption of  $UO_2^{2+}$  on the neutral MnO<sub>2</sub> surface takes place, the chemical reactions at the solid-liquid interface can be described by Eqs. (9) and (10)



Distribution coefficient ( $K_d$ ) values

The distribution coefficient ( $K_d$ ) is an important parameter in estimating the adsorption potential of dissolved

contaminants by adsorbent materials. To investigate the affinity of the non-treated and chemically modified biomass by-product for U(VI) adsorption, experiments have been performed at room temperature ( $23 \pm 2$  °C) and  $I = 0.1$  M in which pH was varied between 2 and 8.5. According to Fig. 4 the  $K_d$  values ( $[U(VI)]_{ads}/[U(VI)]_{aq}$ ) as a function of pH behave similarly to the relative adsorption values. Moreover, the  $K_d$  data clearly indicate that the chemically treated products present by far the highest affinity for U(VI) for a wide pH range, especially in the case of the  $MnO_2$ -coated CF. Specifically, the  $K_d$  values evaluated at the optimum pH for each CF type are  $6,000$   $l\ kg^{-1}$  (pH 6.0),  $13,000$   $l\ kg^{-1}$  (pH 4.5–5.0) and  $15,000$   $l\ kg^{-1}$  (pH 4.5–7.5) for the non-treated, phosphorylated and  $MnO_2$ -coated CF, respectively. These values, which are significantly higher than  $K_d$  values reported in literature for metal ion adsorption on non-treated and chemically modified biomass by-products [5–7, 13], could be attributed to the fine primary and secondary fibres constituting the present biomass and resulting in a relative enormous specific surface available for adsorption. The relatively high specific surface available for adsorption is basically attributed to fibrous character of the adsorbent, because no internal surface (porosity) could be determined. It has to be noted that to our knowledge this is the first time that  $K_d$  values have been reported for the adsorption of U(VI) on non-treated and chemically modified biomasses, particularly CF.  $K_d$  values corresponding to U(VI) adsorption on biomass by-product of plant origin are of particular interest for the development of water treatment technologies based on adsorption.



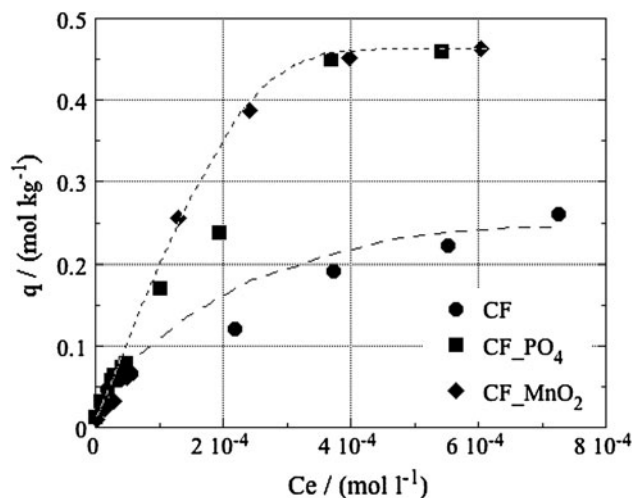
**Fig. 4** Effect of pH on the distribution coefficient ( $K_d$  values) of the U(VI) adsorption onto non-treated (CF), phosphorylated (CF- $PO_4$ ) and  $MnO_2$ -coated (CF/ $MnO_2$ ) cactus fibres (0.01 g of biomass,  $[U(VI)]_{tot} = 1 \times 10^{-5}$  mol  $l^{-1}$ ,  $I = 0.1$  mol  $l^{-1}$   $NaClO_4$ ,  $T = 23 \pm 2$  °C, 24 h of reaction time)

#### Effect of uranium concentration

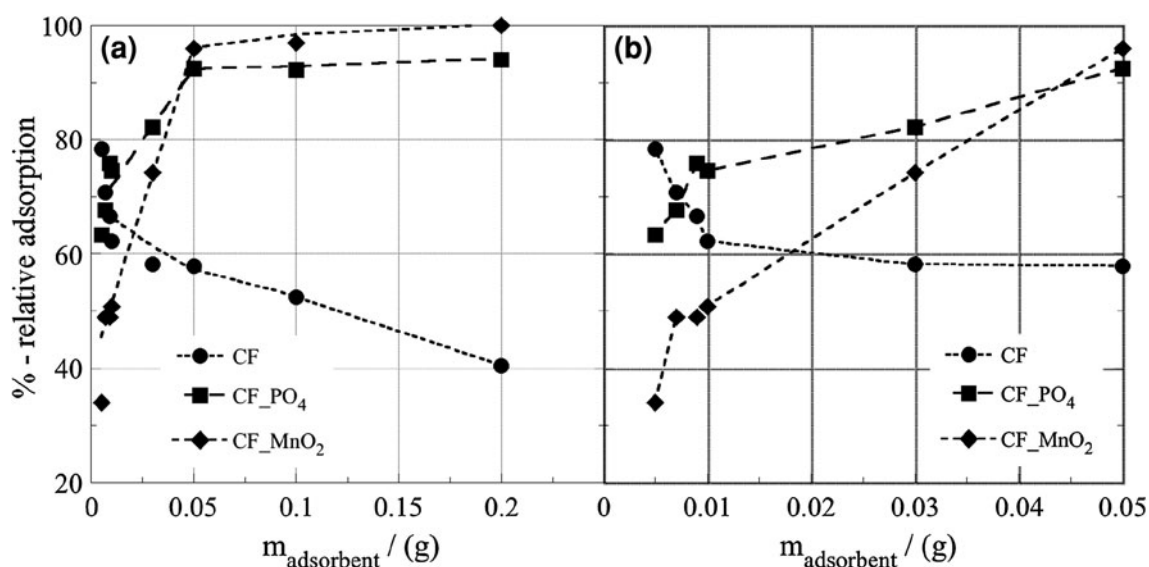
In order to evaluate the maximum adsorption capacity ( $q_{max}$ ) adsorption experiments with varying uranium concentrations have been performed at the optimum pH for each cactus biomass adsorbent. The corresponding isotherms are graphically shown in Fig. 5. The experimental data are well fitted by the Langmuir isotherm ( $R = 0.95$  for CF,  $R = 0.97$  for phosphorylated CF and  $R = 0.97$  for CF coated with  $MnO_2$ ). According to the results, the experimental  $q_{max}$  values are  $\sim 0.26$  mol  $kg^{-1}$  ( $62$  mg  $g^{-1}$ ),  $0.45$  mol  $kg^{-1}$  ( $107$  mg  $g^{-1}$ ) and  $0.46$  mol  $kg^{-1}$  ( $110$  mg  $g^{-1}$ ), for non treated CF, phosphorylated CF and CF coated with  $MnO_2$ , respectively, indicating high adsorption capacities for uranium metal ion. Further, the  $q_{max}$  values of the chemically treated adsorbents clearly show that chemical modification of the adsorption material improves its adsorption attributes and  $MnO_2$  CF can be used as an alternative for  $MnO_2$  resins [15].

#### Effect of mass adsorbent

The dependence of U(VI) adsorption on dose was studied by varying the amount of adsorbents while keeping the other parameters constant. The relative adsorption of U(VI) on the investigated biomass by-products as a function of mass adsorbent is shown in Fig. 6a, b (expanded scale). The results indicate that the three products behave very different from one another. In the case of the non treated CF, the relative amount of adsorbed U(VI) decreases with increasing biomass dose most probably due to partial aggregation and a screening effect on the biomass surface,



**Fig. 5** Adsorption isotherms of the U(VI) adsorption onto non-treated (CF), phosphorylated (CF- $PO_4$ ) and  $MnO_2$ -coated (CF/ $MnO_2$ ) cactus fibres (0.01 g of biomass,  $[U(VI)]_{tot} = 9 \times 10^{-6}$ – $9 \times 10^{-4}$  mol  $l^{-1}$ , pH = optimum pH value,  $I = 0.1$  mol  $l^{-1}$   $NaClO_4$ ,  $T = 23 \pm 2$  °C, 24 h of reaction time)



**Fig. 6** Effect of the adsorbent dose on the U(VI) adsorption onto non-treated (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres (0.005–0.2 g of biomass, [U(VI)]<sub>tot</sub> = 1 × 10<sup>-5</sup>

mol l<sup>-1</sup>, pH = optimum pH value, I = 0.1 mol l<sup>-1</sup> NaClO<sub>4</sub>, T = 23 ± 2 °C, 24 h of reaction time). **a** Full-scale (0–0.25 g) and **b** expanded scale (0–0.05 g)

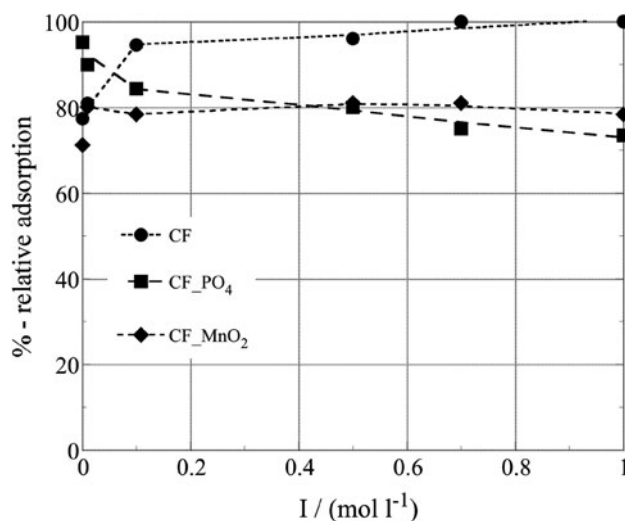
which results in decreasing the number of active sites available for U(VI) adsorption and hence in lower uranium uptake per unit mass of biosorbent. On the other hand, the relative adsorption of U(VI) on the modified treated CF increases with increasing the amount of the chemically modified biomasses until U(VI) is quantitatively removed from solution. Evaluation of the maximum biosorption capacity from the experimental data results in values far higher than corresponding values obtained from the previous experiments regarding U(VI)-adsorption on biomass by-products [5–7, 13].

*The effect of ionic strength/salinity on the adsorption efficiency*

Furthermore, the effect of ionic strength ([NaClO<sub>4</sub>] = 0.001, 0.01, 0.1, 0.5, 0.7 and 1 M) on the relative adsorption of U(VI) was investigated, in order to understand the interaction mechanisms on which U(VI) binding on the three different types of biomass by-products is based. The experimental data obtained from the corresponding experiments are graphically summarized in Fig. 7, showing clearly that the relative adsorption of CF-PO<sub>4</sub> (phosphorylated CF) is stronger affected by increasing salinity, as the relative adsorption decreases from 100 to 80 %. This effect indicates that binding between the phosphate moieties on the CF surface and U(VI) is affected by electrostatic interactions.

On the other hand, the relative adsorption of the MnO<sub>2</sub>-coated cactus fibres (CF-MnO<sub>2</sub>) is almost not affected by increasing salinity and indicates specific interactions

between U(VI) and the hydroxy-groups of the MnO<sub>2</sub> surface. The specific interactions could be attributed to the formation of inner-sphere complexes, which are only little affected by salinity changes [7]. Regarding the U(VI) adsorption on the non-treated CF, the relative adsorption increases slightly with increasing ionic strength. This could be attributed to the decrease of the activity coefficient values of the cationic species [e.g. H<sup>+</sup> and UO<sub>2</sub>(OH)<sup>+</sup>].



**Fig. 7** Effect of the ionic strength/salinity ([NaCl]) on the U(VI) adsorption onto non-treated (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres (0.01 g of biomass, [U(VI)]<sub>tot</sub> = 1 × 10<sup>-5</sup> mol l<sup>-1</sup>, pH = optimum pH value, I = 0.001–1 mol l<sup>-1</sup> NaClO<sub>4</sub>, T = 23 ± 2 °C, 24 h of reaction time)

**Table 1** Thermodynamic parameters ( $\log K_d$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ) for the formation of surface complexes of uranium with non-treated cactus fibres (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres, obtained from varying temperature experiments

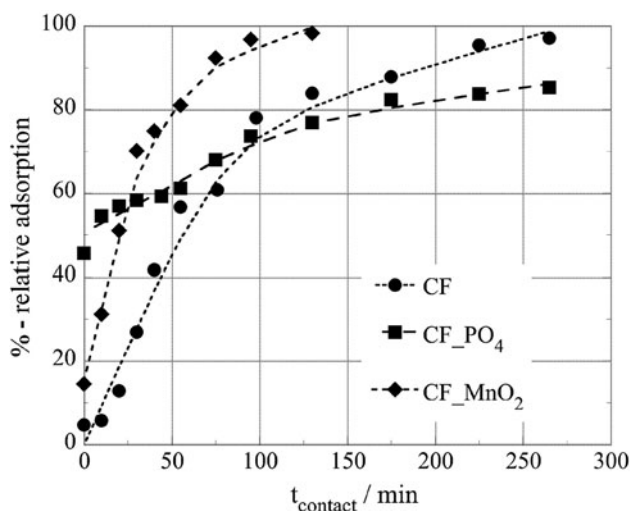
| Surface complex           | $\log K_d$ (25 °C) | $\Delta H^\circ$ (kJ mol <sup>-1</sup> ) | $\Delta S^\circ$ (J Kmol <sup>-1</sup> ) | $\Delta G^\circ$ (kJ mol <sup>-1</sup> ) |       |       |       |       |       |
|---------------------------|--------------------|--|--|--|-------|-------|-------|-------|-------|
|                           |                    |  |  | 283 K                                    | 298 K | 313 K | 323 K | 333 K | 343 K |
| U(VI)-CF                  | 4.3                | 31.9                                     | 190                                      | -21.7                                    | -24.5 | -27.4 | -30.0 | -31.2 | -33.1 |
| U(VI)-CF-PO <sub>4</sub>  | 3.9                | 23.1                                     | 155                                      | -20.7                                    | -23.0 | -25.3 | -26.9 | -28.4 | -30.0 |
| U(VI)-CF/MnO <sub>2</sub> | 3.7                | 67.1                                     | 295                                      | -16.4                                    | -20.9 | -25.3 | -28.2 | -31.2 | -34.2 |

### The effect of temperature on the adsorption efficiency

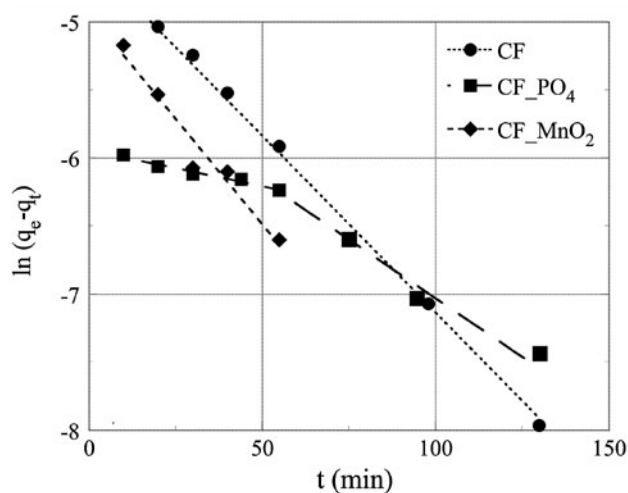
The effect of temperature on uranium adsorption on CF was investigated to estimate the corresponding thermodynamic data based on the van't Hoff equation. Evaluation of the data shows that adsorption of U(VI) on CF is an exothermic, both enthalpy- and entropy-driven spontaneous process. The corresponding values of the thermodynamic parameters, which are summarized in Table 1, indicate clearly that the MnO<sub>2</sub> coated product presents the highest chemical affinity ( $\Delta H^\circ = 67.1$  kJ mol<sup>-1</sup>) for U(VI), followed by the non-treated ( $\Delta H^\circ = 31.9$  kJ mol<sup>-1</sup>) and phosphorylated product ( $\Delta H^\circ = 23.1$  kJ mol<sup>-1</sup>). Generally, the values of the thermodynamic parameters evaluated are close to corresponding values reported in literature for similar systems [5–7, 13]

### Kinetic measurements

According to Fig. 8, which shows the relative amount of adsorbed U(VI) as a function of time, the adsorption of U(VI) on the three different biomass products is relatively

**Fig. 8** Relative adsorption as a function of time corresponding to U(VI) adsorption onto non-treated (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres (0.04 g of biomass in 60 ml U(VI) solution,  $[U(VI)]_{tot} = 1 \times 10^{-5}$  mol l<sup>-1</sup>,  $I = 0.1$  mol l<sup>-1</sup> NaClO<sub>4</sub>, pH = optimum pH value,  $T = 23 \pm 2$  °C)

fast but differs from one another. The adsorption on the MnO<sub>2</sub>-coated biomass seems to be the fastest, whereas the adsorption on the phosphorylated biomass occurs in two steps indicating two different adsorption mechanisms for the U(VI) binding on the phosphorylated biomass (Fig. 9). Evaluation of corresponding data by the first order rate expression described by Lagergren [21] results in values for the reaction rate constant ( $k_{ads}$ ), which are summarized in Table 2. The  $k_{ads}$  for the adsorption of U(VI) on CF are similar to corresponding values reported in literature for similar systems [5–7, 13].

**Fig. 9** Lagergren-plots corresponding to U(VI) adsorption onto non-treated (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres**Table 2** Reaction rate constant (min<sup>-1</sup>) for the uranium adsorption onto non-treated cactus fibres (CF), phosphorylated (CF-PO<sub>4</sub>) and MnO<sub>2</sub>-coated (CF/MnO<sub>2</sub>) cactus fibres (0.04 g of biomass in 60 ml U(VI) solution,  $[U(VI)]_{tot} = 1 \times 10^{-5}$  mol l<sup>-1</sup>,  $I = 0.1$  mol l<sup>-1</sup> NaClO<sub>4</sub>, pH = optimum pH value,  $T = 23 \pm 2$  °C)

| Adsorbent           | Reaction rate constant, $k_{ads}$ (min <sup>-1</sup> ) |                   |
|---------------------|--|-------------------|
|                     | 1st Step   | 2nd Step          |
| CF                  | $0.026 \pm 0.001$                                      | –                 |
| CF-PO <sub>4</sub>  | $0.005 \pm 0.001$                                      | $0.016 \pm 0.001$ |
| CF/MnO <sub>2</sub> | $0.031 \pm 0.004$                                      | –                 |



## Conclusions

In this study non-treated and chemically modified *Opuntia ficus indica* CF were used to adsorb U(VI) ions from aqueous solutions. The results indicate that the non-treated opuntia CF show increased affinity for U(VI), which is further improved by chemical modification of the biomasses. U(VI) adsorption is strongly dependent on pH and differs significantly from one product to another, indicating that the MnO<sub>2</sub> coated product presents the highest relative adsorption in a wide pH range (4.5 < pH < 7.5), followed by the phosphorylated (pH = 4) and non-treated product (pH = 6.5). Increasing temperature affects positively the adsorption capacity and the corresponding data evaluation indicates that both  $\Delta H$  and  $\Delta S$  favor biosorption. The equilibrium data were described well by a Langmuir isotherm, indicating that the adsorption of uranium on biomass is based on specific chemical interactions. The biosorption of U(VI) ions on the non-treated and chemically modified CF follows a pseudo-first-order kinetics. CF are very effective biosorbents basically because of the relative high surface available for sorption because of the primary and secondary fibres constituting this biomaterial.

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