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Europium adsorption by non-treated and chemically modified *opuntia ficus indica* cactus fibres in aqueous solutions

Melpomeni Prodromou, Ioannis Pashalidis*

Department of Chemistry, University of Cyprus, P.O. Box 20537, Cy-1678 Nicosia, Cyprus, Tel. +357 22892785; email: prodromou.melpomeni@ucy.ac.cy (M. Prodromou), Tel. +357 22892761; email: pspasch@ucy.ac.cy (I. Pashalidis)

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ABSTRACT

The sorption efficiency of *Opuntia ficus indica* cactus fibres regarding the removal of trivalent europium (Eu(III)) from aqueous solutions has been investigated prior and after the chemical treatment (phosphorylation and MnO_2-coating) of the biomass. The removal efficiency has been studied as a function of pH, europium concentration, mass of the adsorbent, ionic strength, temperature and contact time. Evaluation of the experimental data shows that biosorption is strongly pH-depended and that the MnO_2-coated product presents the highest sorption capacity followed by the non-treated and phosphorylated material. Results have been analysed by Langmuir, Freundlich and Dubinin–Radushkevich isotherms, and the Langmuir model is more suitable to describe the process. The sorption reactions are entropy-driven, and the kinetics follows a pseudo-first order rate expression, described by Lagergren. In addition, the results show that the fibres of the *Opuntia ficus indica* cactus possess significantly higher sorption capacity than other biomass by-products reported in literature and that the removal of europium from contaminated waters is expected to be more effective in the case of the chemically treated biomasses.

Keywords: Europium; Cactus fibres; Chemical treatment; Waters; Increased sorption capacity

1. Introduction

Sorption processes are considered as a powerful instrument for the removal of heavy, radiotoxic or precious metals from waste solutions. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive and further generate huge quantity of toxic chemical sludge [1]. Recently, biosorption is emerging as a potential alternative method for removing toxic radioactive metals from wastewater [2–5].

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 industrial 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

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*Corresponding author.

disposed by incineration [3,6,7]. *Opuntia ficus* is an old domesticated and the most widespread cactus species, and economically important crop throughout arid and semi-arid 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].

This study deals with the adsorption of europium by non-treated and chemically modified *Opuntia ficus indica* fibres. Europium is used as a non-radioactive analogue for trivalent actinides, such as americium and curium, because trivalent actinides and lanthanides present similar chemical behaviour in solid and aqueous phase, which is attributed to the fact that the f-elements have almost identical ionic radii [11].

The main goal of the study was to investigate the role of chemical modification of the biomass on the adsorption process, the effect of the various parameters (e.g. pH, europium concentration, mass of the adsorbent, ionic strength, temperature and contact time) on the biosorption performance and the determination of thermodynamic parameters (e.g. K_d, ΔG, ΔH and ΔS), which are of fundamental importance for both the assessment of the chemical behaviour of trivalent actinides in heterogeneous aquatic systems and the development of water treatment technologies related to (radio)toxic metal ion removal.

2. Experimental

All experiments were performed at room temperature (23 ± 2°C) under normal atmospheric conditions in 0.1 M $NaCO_4$ solutions, 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 preparation of the test solutions was carried out by dissolution in the desired aqueous solution the appropriate amount of a europium(III) stock solution (0.1 M) prepared by dissolution of $Eu(NO_3)_3 \cdot 5H_2O$ 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).

2.1. Opuntia ficus *fibres*

Opuntia ficus cladodes were collected from plants used as effective living fence in a suburb of Nicosia, Cyprus. The cladodes collected were broken off ones, which were extensively 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 μm was selected for the adsorption experiments.

2.2. *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 H_3PO_4 solution (Aldrich Chemical Company) and continuous stirring of the suspension for 24 h at room temperature [12]. 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.

2.3. *MnO_2-coating of the cactus fibres*

The preparation of the MnO_2-coated material was performed using the reductive precipitation of MnO_2 oxide onto the biomass substrate, by addition of the fibres (10 g) in 100 ml 2% (w/v) $KMnO_4$ solution (Fisons Scientific Equipment) and continuous stirring of the suspension for 1 h at 50°C [13]. Following, the solid phase was separated by filtration, washed thoroughly with distilled water and dried for several days in a desiccator.

2.4. *Characterization of the non-treated and chemically modified biomass by-products*

The characterization of the cactus fibres and the products obtained after chemical treatment was performed by Fourier transform infra red spectroscopy (FTIR) (FTIR spectrometer 8900, Shimadzu), acid–base titrations, scanning electron microscopy (SEM) (SEM, Vega TS5136LS-Tescan) and specific surface area BET measurements (based on the Brunauer–Emmett–Teller theory) by means of N_2-adsorption (ASAP 2000, micromeritics), as described elsewhere [14,15].

2.5. *Adsorption measurements and data evaluation*

In order to investigate the effect of various parameters (pH, Eu(III) concentration, mass of the adsorbent, ionic strength, temperature and contact time) on the

Eu(III) adsorption on non-treated and chemically modified cactus fibres, 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: $[\mathrm{Eu(III)}] = 1 \times 10^{-5}$ M) in which pH was varied between 1 and 8 by addition of $HClO_4$ or NaOH. All test solutions were prepared using 0.1 M sodium perchlorate ($NaClO_4$, Aldrich Co) as the background electrolyte. The effect of the ionic strength (salinity) was performed by addition of $NaClO_4$ 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 europium concentration (1×10^{-5} M) and the optimum pH value for each adsorbent. For studying the effect of initial europium concentration, the latter was varied between 9×10^{-6} and 9×10^{-4} M, at a prefixed amount of adsorbent (adsorbent dosage = 0.01 g and the optimum pH value for each biomass). The effect of the amount of the cactus fibres 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 europium concentration (1×10^{-5} M). The effect of temperature was studied between 10 and 60°C at the same conditions that are described above. For kinetic studies, certain amount of the biomasses (0.04 g) was mixed with europium solution (1×10^{-5} 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 metal 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, which was similar to the test solution except that it did not contain the adsorbent material. The relative amount of Eu(III) adsorbed was determined using the following equations:

$$\text{rel.adsorption\%} = 100 \times \frac{([\mathrm{Eu(III)}]_0 - [\mathrm{Eu(III)}]_{\mathrm{aq}}}{[\mathrm{Eu(III)}]_0} \quad (1)$$

$$K_{\mathrm{d}} = \frac{([\mathrm{Eu})(\mathrm{III})]_0 - [\mathrm{Eu(III)}]_{\mathrm{aq}})}{[\mathrm{Eu(III)}]_{\mathrm{aq}}} \cdot \frac{V}{m} (1 \text{ kg}^{-1}) \quad (2)$$

where $[\mathrm{Eu(III)}]_o$, the total europium concentration ($\mathrm{mol\,l^{-1}}$) in the system or in the reference solution; $[\mathrm{Eu(III)}]_{aq}$, europium concentration ($\mathrm{mol\,l^{-1}}$) in the test solution; V (l) is the volume of the test solution and m (kg) is the mass of the adsorbent.

Furthermore, the K_d values have been used together with the linear form of the van't Hoff Eq. (3) and the Gibbs free energy isotherm Eq. (4) to estimate the corresponding thermodynamic data

$$\ln K_{\mathrm{d}} = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R} \quad \text{or} \quad 2.3 \cdot \log_{10} K_{\mathrm{d}} = -\frac{\Delta H^0}{R \cdot T} + \frac{\Delta S^0}{R} \quad (3)$$

$$\Delta G^0 = -R \cdot T \cdot \ln K_{\mathrm{d}} \quad (4)$$

Moreover, the adsorption data obtained from experiments of varying Eu(III) concentration at the optimum pH for each adsorbent have been fitted by three different model isotherms:

$$\text{Langmuir: } \frac{1}{q} = \frac{1}{q_{\max} \cdot K_{\mathrm{L}} \cdot C_{\mathrm{e}}} + \frac{1}{q_{\max}} \quad (5)$$

$$\text{Freundlich: } \log_{10} q = \log_{10} K_{\mathrm{F}} + \frac{1}{n} \cdot \log_{10} C_{\mathrm{e}} \quad (6)$$

and

$$\text{Dubinin–Radushkevich: } \ln q = \ln q_{\max} - \kappa \cdot \varepsilon^2, \quad (7)$$

where q, adsorbed concentration of metal ($\mathrm{mol\,kg^{-1}}$); C_e, concentration of metal in solution ($\mathrm{mol\,L^{-1}}$); q_{max}, Maximum adsorbed concentration of metal ($\mathrm{mol\,kg^{-1}}$); K_L, Langmuir constant; K_F, Freundlich constant; $1/n$, Adsorption strength; κ, Dubinin–Radushkevich isotherm constant ($\mathrm{mol^2\,kJ^{-2}}$); ε, Dubinin–Radushkevich isotherm constant.

3. Results and discussion

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

SEM images of the non-treated and chemically modified cactus fibres show that chemical modification does not affect the surface texture of the fibres and even after chemical modification the fibres keep their laminated texture [14,15]. The material consists of microchannels, which are responsible for an effective transport of fluids and increased external surface available for sorption. In addition, SEM–EDX analysis performed on cactus fibres obtained after Eu(III) sorption has confirmed the sorption of the metal ion on the biomass surface. Despite the increased external surface, BET measurements indicate that there is no internal mesoporous surface (BET surface <5 $m^3 g^{-1}$) available for sorption [14,15].

Characterisation of the materials by acid–base titrations (Fig. 1) reveals significant differences after chemical treatment indicating successful addition of phosphate groups and oxide coating of the cactus biomass. Specifically, upon coating by MnO_2-oxide, the almost neutral reacting suspension of the non-treated fibres buffers the pH of the suspension at pH 4, a value corresponding to the point of zero charge (pzc ~4) of MnO_2 particles [17]. On the other hand, after phosphorylation (e.g. conversion of the alcohol groups of cellulose to phosphoric acid esters), analysis of the titration curve indicates the presence of acidic groups, which exhibit considerable buffer capacity in the pH range between 2 and 4.5 and indicate the mean value of the primary deprotonation constant of the phosphate groups, which is $pK_a \sim 3$. The shape of the titration curve in the buffer zone is characteristic for polyelectrolytes and proves the predominance of the phosphoric acid moieties on the biosorbent surface [18]. The mean acid dissociation constant of the alkyl monoester of phosphoric acid in phosphate-containing polymers is about one order of magnitude lower ($pK_{a1} \sim 3$) compared to the primary acid dissociation constant of the phosphoric acid itself and the corresponding monomeric alkyl esters ($pK_{a1} \sim 2$) [19].

The FTIR spectra (Fig. 2) of the non-treated and chemically modified (phosphorylated and MnO_2-coated) fibres are generally similar to a typical cellulose spectrum, and all spectra include the characteristic peaks of the glucose units of the biopolymer. The characteristic peaks assigned to the stretching bands of the phosphate moieties (v(P-OH) = 976 cm^{-1} and v(P-OC) = 1,057 cm^{-1}) [20] and the MnO_2 particles (v(O–Mn–O) = 539 cm^{-1})) [21] are overlapped by the cellulose peaks. Nevertheless, small changes in the relative adsorption intensity at the respective peak positions indicate that the successful modification of the cactus fibres [14,15]. The spectra of the samples after Eu(III) sorption (bold lines) differ significantly from the corresponding spectra prior metal sorption, particularly in the case of the phosphorylated and the non-treated fibres. The most affected peaks are those corresponding to the primary alcohol group of the glucose units indicating that this is the active site of the biosorbent. In addition, there is no remarkable change in the spectra corresponding to the MnO_2-coated fibres proving that in this case, the metal adsorption occurs basically on the metal oxide surface.

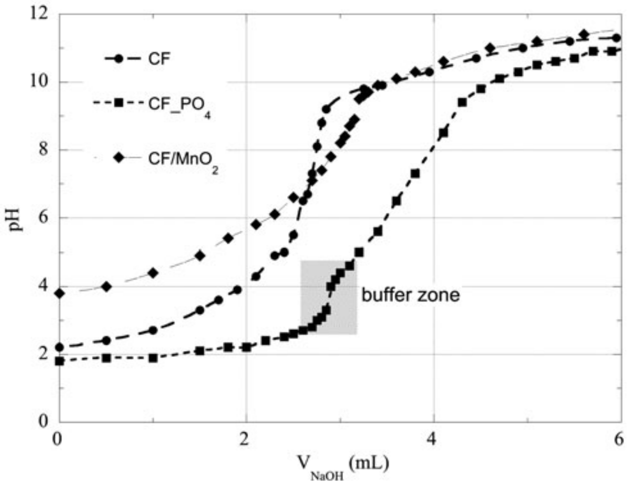

Fig. 1. Acid–base titrations curves of non-treated (CF) and chemically modified cactus fibres (CF-PO_4 and CF/MnO_2).

3.2. Adsorption experiments

3.2.1. 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 Eu(III) 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 behaviour of a metal ion in solution and the surface charge of an adsorbent. Fig. 3 shows a species distribution diagram, which has been calculated using literature data and assuming normal atmospheric conditions [22]. To study the effect of pH on the Eu(III) adsorption, samples of the three different biomass by-products were conducted with Eu(III) solutions at different pH values ($1 < pH < 8$).

The effect of pH on the relative adsorption of Eu (III) on the three different materials is shown in Fig. 4. Generally, the relative adsorption percentages are higher in the case of the chemically treated cactus fibres. In the case of the non-treated cactus fibres, the relative adsorption increases with increasing pH and reaches a maximum value (~90%) at pH > 6. For pH values below 6, the relative adsorption decreases almost linearly with pH and its value becomes about 50% at pH 1.5. At pH values below 6, Eu(III) is exclusively present in the form of positively charged species (Eu^{3+}) [11,21], thus the adsorption of the metal ion is solely governed by cation exchange reactions and hence the proton concentration in solution [10]. Because of its triple positive charge, a Eu^{3+} cation could replace one, two or even three protons according to Eq. (8). However, the concentration of the

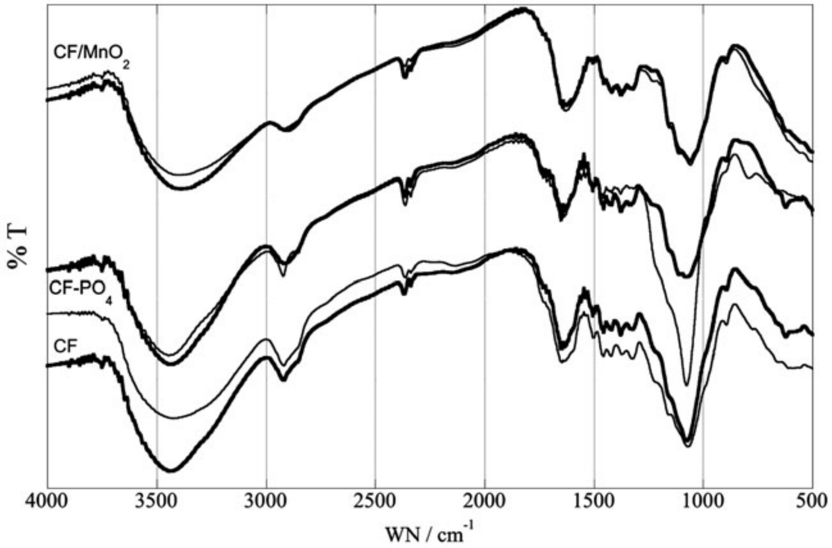

Fig. 2. FTIR (KBr) spectra of non-treated (CF) and chemically modified cactus fibres (CF-PO_4 and CF/MnO_2) prior (thin lines) and after (bold lines) Eu(III) sorption.

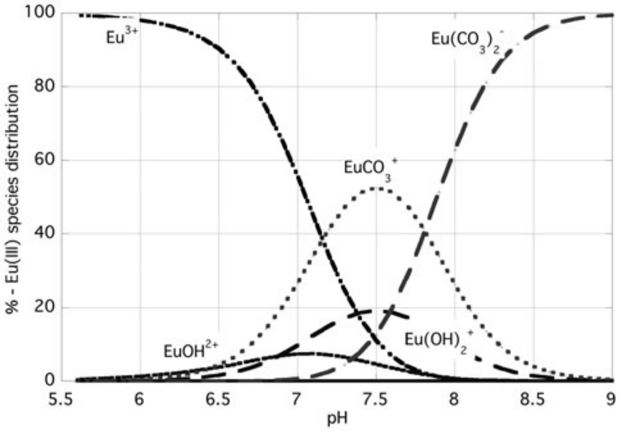

Fig. 3. Species distribution diagram for Eu(III) in aqueous solution under normal atmospheric conditions.

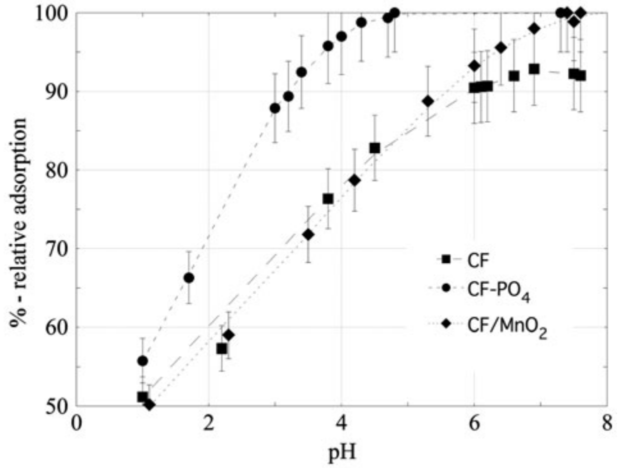

Fig. 4. Adsorption of Eu(III) onto non-treated (CF), phosphorylated (CF-PO_4) and MnO_2-coated (CF/MnO_2) cactus fibres, as a function of pH (0.01 g of biomass, $[Eu(III)]_{tot} = 1 \times 10^{-5}$ mol l^{-1}, $I = 0.1$ mol l^{-1} $NaClO_4$, $T = 23 \pm 2$°C, 24 h of reaction time).

different species formed depends on various parameters such as the pH, Eu(III) concentration and surface texture.

$$n\text{R-CH}_2\text{OH} + \text{Eu}^{3+} \leftrightarrow (\text{R-CH}_2\text{O}-)_n\text{Eu}^{(3-n)+} + n\text{H}^+ \quad (8)$$

Above pH 6, $EuCO_3^+$ becomes predominant in solution favouring the formation of the Eu(III)-carbonato surface complex as described by the following equation:

$$\text{R-CH}_2\text{OH} + \text{EuCO}_3^+ \leftrightarrow \text{R-CH}_2\text{O} - \text{EuCO}_3 + \text{H}^+ \quad (9)$$

On the other hand, the phosphorylated cactus fibres present even at low pH values (pH ~3) the highest adsorption capacity (80%) for Eu(III) and the optimum pH value for maximum adsorption percentage (100%) is about 4, which is lower compared to the adsorption on the non-treated material. This result can be attributed to lower pK (pK ~ 3) values of the organophosphate moieties present on the cactus fibres surface. The presence of the phosphate groups on the cactus surface allows adsorption of positively charged europium ions even in the acidic pH area. The protonation of the organo-phosphate moieties results in the gradual decreasing of relative adsorption of Eu(III) at lower pH values (<3). The corresponding reaction is described by the following equation:

$$\text{R-CH}_2 - \text{OPO}_3\text{H}_2 + \text{Eu}^{3+} \leftrightarrow \text{R-CH}_2 - \text{OPO}_3\text{Eu}^{+} + 2\text{H}^{+} \tag{10}$$

In the case of MnO_2-coated cactus fibres, the highest values of the relative adsorption (100%) are observed at pH values higher than 6. Assuming that the adsorption of $EuCO_3^+$ on the neutral MnO_2 surface takes place, the chemical reaction at the solid–liquid interface can be described by the following equation:

$$\equiv \text{MnOH} + \text{EuCO}_3^{+} \leftrightarrow \equiv \text{MnO–EuCO}_3^{+} + \text{H}^{+} \tag{11}$$

3.2.2. *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 Eu(III) adsorption, experiments have been performed at room temperature (23 ± 2˚C) and $I = 0.1$ M in which pH was varied between 1 and 8. According to Fig. 5, the K_d values 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 Eu(III) for a wide pH range, especially in the case of the phosphorylated cactus fibres. Specifically, the K_d values evaluated at the optimum pH for each cactus fibres type are 9.0×10^4 l kg^{-1} (pH 6.0), 2.4×10^5 l kg^{-1} (pH 4) and 1.2×10^5 l kg^{-1} (pH 6) for the non-treated, phosphorylated and MnO_2-coated cactus fibres, 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 [23–25], 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. Moreover, according to SEM images, the cactus fibres are composed of highly oriented series of lamellar structures giving the material a strong and tough structure that also provides microchannels and extended surface for rapid fluid exchange [14,15]. K_d values corresponding to Eu(III) adsorption on biomass by-product of plant origin are of particular interest for the development of water treatment technologies based on adsorption.

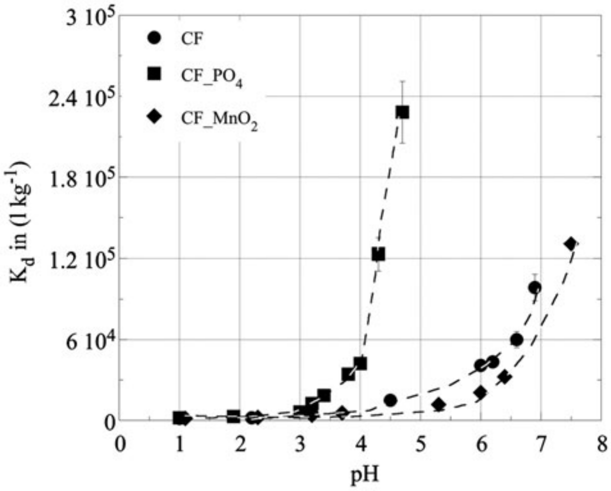

Fig. 5. Effect of pH on the distribution coefficient (K_d values) of the Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO_4) and MnO_2-coated (CF/MnO_2) cactus fibres (0.01 g of biomass, $[\text{Eu(III)}]_{\text{tot}} = 1 \times 10^{-5}$ mol l^{-1}, $I = 0.1$ mol l^{-1} $NaClO_4$, T =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

3.2.3. *Effect of europium concentration*

In order to evaluate the maximum adsorption capacity ($q_{\max}$), adsorption experiments with varying europium concentrations have been performed at the optimum pH for each cactus biomass adsorbent. The corresponding isotherms are graphically shown in Fig. 6 and indicate that the cactus fibres coated with MnO_2, present the highest adsorption capacity (0.47 mol kg^{-1} or 72 mg g^{-1}) for Eu(III). Further, the $q_{\max}$ values of the MnO_2- coated adsorbent clearly show that chemical modification of the material improves its adsorption capacity. Because of their increased adsorption capacity, MnO_2 cactus fibres could be used as an alternative instead of MnO_2 resins [13]. In addition to this, the maximum adsorption capacity of the oxide-coated material is higher than capacity values for similar systems reported in literature [23,24,26]. Further, the $q_{\max}$ values of the non-treated and phosphorylated cactus fibres are approximately 0.13 mol kg^{-1} or 20 mg g^{-1} and 0.07 mol kg^{-1} or 11 mg g^{-1}, respectively. In order to obtain further information, the adsorption data have been fitted by three different isotherm models (Langmuir, Freundlich and Dubinin–Radushkevich), and the corresponding parameters and goodness of fits of the three models are summarized in Table 1. The best fits of the data correspond to the Langmuir isotherm model [27] and

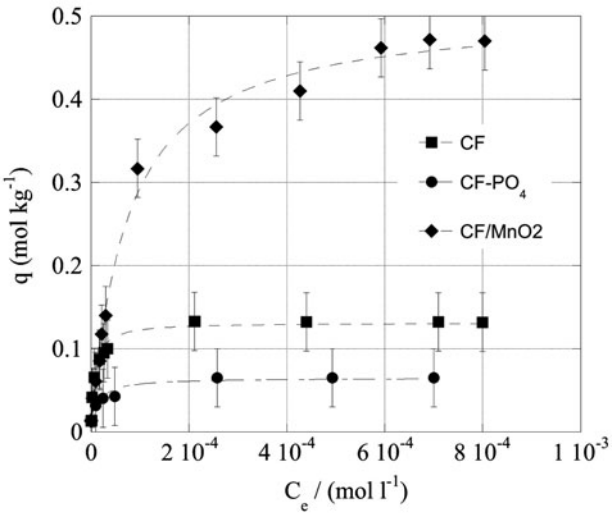

Fig. 6. Adsorption isotherms of the Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO$_4$) and MnO$_2$-coated (CF/MnO$_2$) cactus fibres (0.01 g of biomass, $[\mathrm{Eu(III)}]_{\mathrm{tot}} = 9 \times 10^{-6}$ to 9×10^{-4} mol l^{-1}, pH = optimum pH value, $I = 0.1$ mol l^{-1} NaClO$_4$, $T = 23 \pm$ °C, 24 h of reaction time).

the average adsorption energy value obtained from the Dubinin–Radushkevich isotherm model is above the critical value $E > 8$ kJ mol^{-1}, indicating chemisorption of Eu(III) on the non-treated and chemically modified fibres.

3.2.4. Effect of mass adsorbent

The dependence of Eu(III) adsorption on dose was studied by varying the amount of adsorbents while keeping the other parameters constant. The relative adsorption of Eu(III) on the investigated biomass by-products as a function of mass adsorbent is shown in Fig. 7. According to the results, in the case of the non-treated cactus fibres, the relative amount of adsorbed Eu(III) decreases with increasing biomass dose, probably due to partial aggregation and a screening effect on the biomass surface, which results in decreasing the number of active sites available for Eu (III) adsorption and hence in lower europium uptake per unit mass of biosorbent. On the other hand, the relative adsorption of Eu(III) increases with increasing the amount of the chemically modified biomasses until europium is quantitatively removed from solution.

3.2.5. The effect of ionic strength/salinity on the adsorption efficiency

Moreover, the effect of ionic strength ([NaClO$_4$] = 0.001, 0.01, 0.1, 0.5, 0.7 and 1 M) on the relative adsorption of Eu(III) was investigated, in order to understand the interaction mechanisms on which Eu(III) 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. 8, showing clearly that the relative adsorption of CF-PO$_4$ (phosphorylated cactus fibres) 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 cactus fibres surface and Eu(III) is affected by electrostatic interactions. On the other hand, the relative adsorption on non-treated and MnO$_2$-coated cactus fibres (CF-MnO$_2$) is almost not affected by increasing salinity and indicates specific interactions between Eu (III) and the hydroxy-groups of the CF and CF-MnO$_2$ surface. The specific interactions could be attributed to the formation of inner-sphere complexes, which are only little affected by salinity changes [28]. In addition to this, while increasing salinity, a slight increase of the relative adsorption is observed and can be attributed to activity changes of the ionic species in solution.

Table 1
Fitting parameters and goodness of fits for three different isotherm models (e.g. Langmuir, Freundlich and Dubinin–Radushkevich) applied to the experimental adsorption data

Isotherm model								
Langmuir			Freundlich			Dubinin–Radushkevich		
$q_{\max}$ (mol kg^{-1})	K_L	R^2	K_f	n	R^2	$q_{\max}$ (mol kg^{-1})	E (kJ mol^{-1})	R^2
Non-treated cactus fibres								
0.16	1.25×10^5	0.97	5.76	2.5	0.91	0.35	14.7	0.90
Phosphorylated cactus fibres								
0.045	1.11×10^6	0.92	0.39	4.5	0.98	0.12	17.7	0.99
MnO$_2$-coated cactus fibres								
0.46	1.28×10^5	0.99	20.42	2	0.98	1.67	11.5	0.97

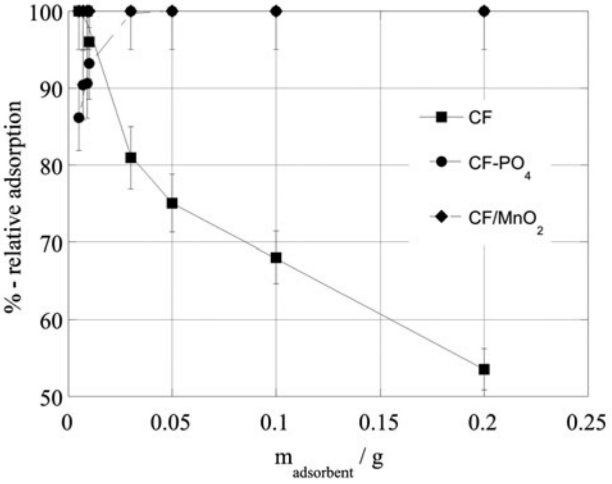

Fig. 7. Effect of the adsorbent dose on the Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO_4) and MnO_2-coated (CF/MnO_2) cactus fibres (0.005–0.2 g of biomass, $[Eu(III)]_{tot} = 1 \times 10^{-5}$ mol l^{-1}, pH = optimum pH value, $I = 0.1$ mol l^{-1} $NaClO_4$, $T = 23 \pm 2$°C, 24 h of reaction time).

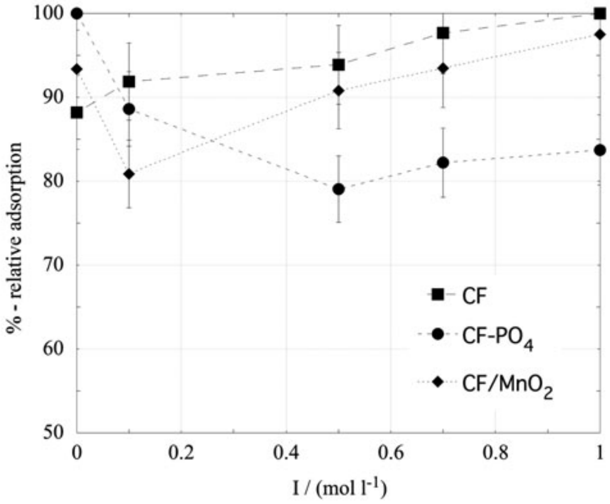

Fig. 8. Effect of the ionic strength/salinity ([$NaClO_4$]) on the Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO_4) and MnO_2-coated (CF/MnO_2) cactus fibres (0.01 g of biomass, $[Eu(III)]_{tot} = 1 \times 10^{-5}$ mol l^{-1}, pH = optimum pH value, $I = 0.001$–1 mol l^{-1} $NaClO_4$, $T = 23 \pm$ °C, 24 h of reaction time).

3.2.6. The effect of temperature on the adsorption efficiency

The effect of temperature on europium adsorption on cactus fibres was investigated to estimate the corresponding thermodynamical data based on the van't Hoff equation. Evaluation of the data revealed that adsorption of Eu(III) on cactus fibres is an endothermic, entropy-driven spontaneous process. The corresponding thermodynamic values, which are summarized in Table 2 and graphically presented in Fig. 9, indicate clearly that the phosphorylated and MnO_2-coated products present higher chemical affinity for Eu(III) ($\Delta H^o = 80.9$ and 73.6 kJ mol^{-1}, respectively) than the non-treated cactus fibres. Generally, the values of the thermodynamic parameters evaluated are similar or higher than corresponding values reported in literature for similar systems [29,30].

3.2.7. Kinetic measurements

According to Fig. 10, which shows the relative amount of adsorbed Eu(III) as a function of time, the adsorption of Eu(III) on the three different biomass products is relatively fast but differs from one another. The adsorption on the non-treated cactus biomass seems to be the fastest, whereas the adsorption on the phosphorylated biomass is the lowest indicating different adsorption mechanisms for Eu(III) binding on the phosphorylated biomass. The lower adsorption rate is attributed on the possible formation of a double layer by Na^+ ions from the background electrolyte and PO_4^{3-} ions from the adsorbent surface, which intervenes in europium adsorption on the phosphorylated surface. Evaluation of corresponding data by the first order rate expression described by Lagergren [31]

Table 2
Thermodynamic parameters (log K_d, ΔH^o, ΔS^o and ΔG^o) for the formation of surface complexes of europium with non-treated cactus fibres (CF), phosphorylated (CF-PO_4) and MnO_2-coated (CF/MnO_2) cactus fibres, obtained from varying temperature experiments

Complex	log K_d(25°C)	ΔH^o(kJ/mol)	ΔS^o(J/mol)	ΔG^o(kJ/mol) 283 K	ΔG^o(kJ/mol) 298 K	ΔG^o(kJ/mol) 313 K	ΔG^o(kJ/mol) 323 K	ΔG^o(kJ/mol) 333 K
Eu(III)-CF	5.5	39.7	237	−28.5	−31.1	−32.0	−33.0	−34.4
Eu(III)-CF_PO_4	6.3	80.9	397	−31.8	−38.2	−40.5	−42.5	−44.5
Eu(III)-CF_MnO_2	5.4	73.6	342	−22.7	−29.5	−32.3	−35.4	−38.4

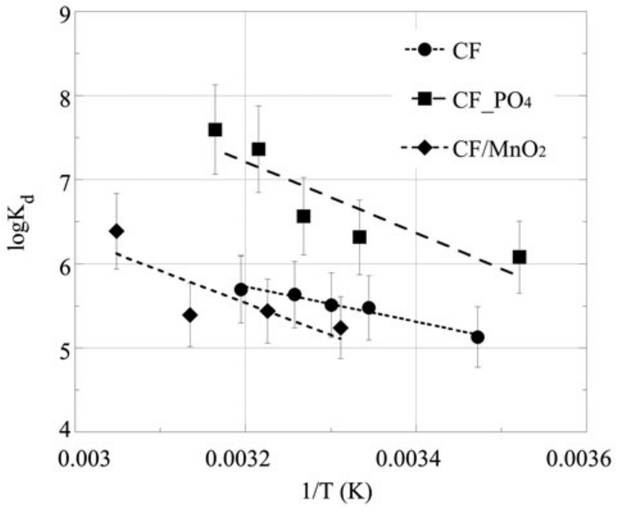

Fig. 9. log K_d as a function of temperature for the Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO$_4$) and MnO$_2$-coated (CF/MnO$_2$) cactus fibres (0.01 g of biomass at optimum pH, $[\text{Eu(III)}]_{tot} = 1 \times 10^{-5}$ mol l^{-1}, $I = 0.001$ mol l^{-1} NaClO$_4$, 24 h of reaction time).

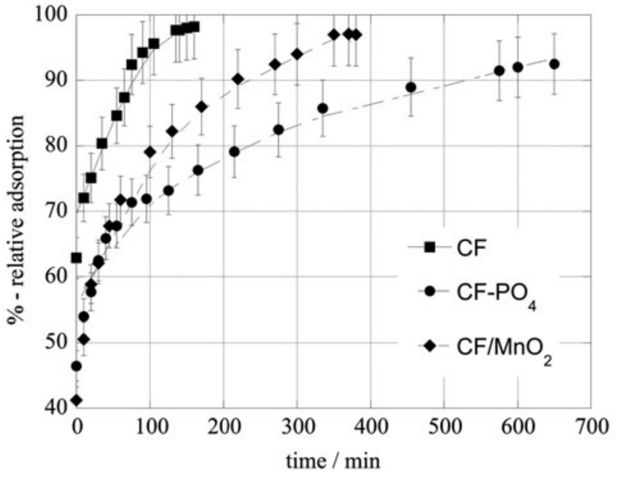

Fig. 10. Relative adsorption as a function of time corresponding to Eu(III) adsorption onto non-treated (CF), phosphorylated (CF-PO$_4$) and MnO$_2$-coated (CF/MnO$_2$) cactus fibres (0.04 g of biomass in 60 ml Eu(III) solution, $[\text{Eu(III)}]_{tot} = 1 \times 10^{-5}$ mol l^{-1}, $I = 0.1$ mol l^{-1} NaClO$_4$, pH = optimum pH value, $T = 23 \pm 2$°C).

results in values for the reaction rate constant (k_{ad}), which are 0.024 min^{-1} ($R = 0.99$), 0.005 min^{-1} ($R = 0.98$) and 0.012 min^{-1} ($R = 0.99$), for the non-treated (CF), the phosphorylated (CF-PO$_4$) and MnO$_2$-coated cactus fibres (CF-MnO$_2$). The k_{ad} for the adsorption of Eu(III) on cactus fibres is similar to corresponding values reported in literature for similar systems [27,32,33].

4. Conclusions

In this study, non-treated and chemically modified *Opuntia ficus indica* cactus fibres were used to adsorb Eu(III) ions from aqueous solutions. The results indicate that the non-treated *opuntia* cactus fibres show increased affinity for Eu(III), which is further improved by chemical modification of the biomasses. Eu(III) adsorption is strongly dependent on pH and differs significantly from one product to another, indicating that the phosphorylated product presents the highest relative adsorption even in the acidic pH area, followed by the MnO$_2$-coated product and non-teated product. Increasing temperature affects positively the adsorption capacity, and the corresponding data evaluation indicates that ΔS favours biosorption. The equilibrium data were best described by the Langmuir isotherm, while the Dubinin–Radushkevich fitting data indicate chemisorption of Eu(III) on the non-treated and chemically modified fibres. Moreover, the biosorption of Eu(III) ions on the three cactus biomasses follows a pseudo-first order kinetics, which is described by the Lagergren equation. Cactus fibres are very effective biosorbents basically because of the relative high surface of the primary and secondary fibres constituting this biomaterial.

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