

# Thorium removal from acidic aqueous solutions by activated biochar derived from cactus fibres

LoukiaHadjittofi, IoannisPashalidis

Department of Chemistry, University of Cyprus, P.O. Box 20537, Cy-1678 Nicosia, Cyprus (E-mail: *pspasch@ucy.ac.cy*)

## Abstract

The removal of thorium from acidic aqueous solutions (pH 3) by activated biochar fibres obtained from *OpuntiaFicusIndica* has been investigated by batch experiments as a function of initial metal concentration, ionic strength and temperature, and FTIR spectroscopy. Activated biochar fibres possess increased sorption capacity for Th(IV) even in acidic solutions ( $q_{\max} = 81 \text{ g}\cdot\text{kg}^{-1}$ ), due to the formation of inner-sphere thorium complexes with the surface carboxylic moieties, indicating that the activated biochar fibres could be applied successfully for the removal of tetravalent metal ions from industrial process and waste waters.

## Keywords

*Thorium; acidic waters; activated biochar fibres; sorption capacity; FTIR spectra*

## 1. Introduction

Thorium is a naturally occurring, radioactive element, which is found in small amounts in most rocks and soils ( $6 \text{ mg kg}^{-1}$ ). Thorium is used in modern high-end optics and scientific instrumentation but its applications decrease in importance because of its radioactivity. On the other hand, its possible use as nuclear fuel through breeding to  $^{233}\text{U}$  is predicted to replace uranium in nuclear reactors[1]. Hence, removal and recycling of thorium from nuclear processes waters and wastewaters will be of particular interest. In addition, thorium could be used as an analogue for tetravalent metal ions such as Ti(IV), Zr(IV), Hf(IV), including lanthanides (e.g. Ce(IV)) and actinides (e.g. Pu(IV)) [2].

Wastewaters produced by industrial activities have usual complex compositions and contain increased amounts of toxic metal ions. Toxic metal ions in wastewaters are of major environmental concern and

contaminated waters, which may cause environmental and health problems, need to be treated prior to their disposal into environment. Removal of (radio)toxic metal ions from large volumes of wastewaters requires a cost effective remediation technology. Conventional technologies relying on mineral adsorbents or chemical flocculating agents are relatively expensive. Adsorption and ion exchange are among the most studied wastewater treatment technologies, which have been effectively applied using a wide range of different materials, including low-cost and highly available biomass by-products [3, 4].

Activated carbons and biochars are very good adsorbents for the removal of heavy metal ions and the treatment-purification of waters, because of their large surface area and the high affinity of their surface active groups for polyvalent metal ions and other pollutants [5-8]. On the other hand, relatively high production costs make the use of activated carbon impractical for the treatment of large quantities of wastewater by domestic use and industry. Biomass by-products could be viable sources because they are abundant in nature or are produced in large quantities as by-products or wastes from agricultural or industrial activities [3, 7].

The present study deals with the sorption of thorium (Th(IV)) by activated carbon/biochar prepared from a biomass by-product (*Opuntia Ficus Indica* cactus fibres). The fibrous structure of the precursor material, which is a biomass by-product is expected to result in relatively low-cost product (activated biochar) with increased separation efficiency because of its large external surface available for adsorption [9-11]. The main goal of the study is besides characterisation of the material, the investigation of various parameters (e.g. pH, thorium concentration, 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 the development of water treatment technologies related to toxic metal removal.

## **2. Materials and Methods**

All experiments were performed under normal atmospheric conditions in aqueous solutions. The preparation of the metal ion solutions was carried out using the nitrate salt of thorium ( $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , Merck). pH measurements were performed by a commercial glass electrode, which was calibrated using a series of buffer solutions (pH 2, 4, 7 and 10). The adsorbent used in this study was activated

biochar prepared from *OpuntiaFicusIndica* cactus fibres, which were separated from dried leaves and prepared as described elsewhere [14]. Characterisation of the material by Scanning Electron Microscopy (SEM, Vega TS5136LS-Tescan) and  $N_2$ -adsorption (ASAP 2000, micromeritics) for the determination of the specific surface area based on the Brunauer-Emmett-Teller-theory (BET measurements) is previously described [9 - 11]

The characterization of the activated after Th(IV) sorption was performed by Fourier Transform Infra Red Spectroscopy (FTIR spectrometer 8900, Shimadzu), and acid/base titrations. FTIR measurements were performed by means of translucent KBr disks including finely ground biomass, which was encapsulated at a 10:1 mass ratio. For the titrations, alkaline biosorbent suspensions (0.5 g in 15 ml of deionized water) of the product prior and after samarium sorption were titrated by 0.1 M  $HClO_4$  standard solutions (BDH Laboratory Supplies) under continuous magnetic stirring. After each addition of the titrant, the pH was allowed to reach equilibrium and finally measured by means of a pH-meter (Hanna Instruments).

## 2.2 Sorption measurements

The sorption studies were performed by conducting batch-equilibrium experiments in 60 mL PE screw-cap vials. Generally, test solutions (30 mL) containing the metal ion, of known composition and concentration, were mixed with a given mass of the activated biochar (0.01 g) and the mixture was shaken in a thermostated orbital shaker (at 100 rpm) for 24 hours *to assure* that *equilibrium* had been reached. For studying the effect of initial Th(IV) concentration, the latter was varied between  $5 \times 10^{-6}$  M and  $5 \times 10^{-3}$  M in the test suspensions (0.01 g activated biochar in 30 mL solution) at pH 3. The effect of temperature was studied between 30 and 70 °C using test suspensions (0.01 g biochar in 30 mL solution,  $[Th(IV)]_0 = 5 \times 10^{-4}$  M) at pH 3. For kinetic studies certain amount of the activated biochar (0.033 g) was mixed with 100 ml of Th(IV) solutions ( $[Th(IV)]_0 = 5 \times 10^{-4}$  M,  $T=23$  °C) at pH 3 and the metal concentration was determined at regular time steps. For the thorium analysis aliquots withdrawn were centrifuged and filtered with membrane filters (pore size: 450 nm) and the thorium concentration was determined spectrophotometrically (UV 2401 PC Shimadzu) by means of arsenazo-III, according to a previously described method [12]. For each test solution, a corresponding reference solution was prepared and was similar to the test solution except that it didn't contain the adsorbent material.

For each test solution, a corresponding reference solution was prepared and was similar to the test solution except that it did not contain the adsorbent material. The relative amount of Th(IV) adsorbed was determined using the following equations:

$$\text{rel. adsorption (\%)} = 100 \times \frac{([\text{Th(IV)}]_o - [\text{Th(IV)}]_{\text{aq}})}{[\text{Th(IV)}]_o} \quad (1)$$

$$K_d = \frac{([\text{Th(IV)}]_o - [\text{Th(IV)}]_{\text{aq}})}{[\text{Th(IV)}]_{\text{aq}}} \times \frac{V}{m} \quad (\text{l kg}^{-1}) \quad (2)$$

where  $[\text{Th(IV)}]_o$  = the total actinide ion concentration ( $\text{mol l}^{-1}$ ) in the system or in the reference solution,  $[\text{Th(IV)}]_{\text{aq}}$  = actinide ion concentration ( $\text{mol l}^{-1}$ ) in the test solution after equilibrium,  $V$  (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 equation (3) and the Gibbs free energy isotherm equation (4) to estimate the corresponding thermodynamic data [13]

$$\ln K_d = -\frac{\Delta H^0}{R \times T} + \frac{\Delta S^0}{R} \quad (3)$$

$$\Delta G^0 = -R \times T \times \ln K_d \quad (4)$$

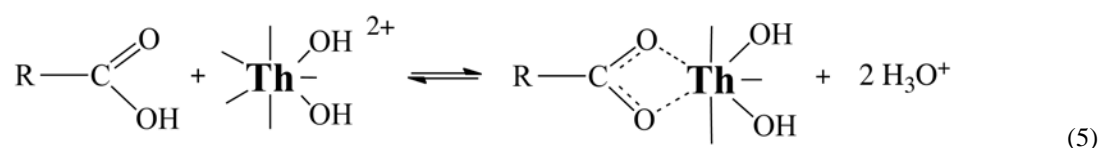
### 2.3 Statistical analysis

All experiments were performed in triplicate and the data are presented as mean  $\pm$  standard deviation. The uncertainty of the values was generally below 10% and is basically attributed to the error associated with analytical method used (e.g. spectrophotometry using arsenazo III). The analytical error was determined by the method calibration performed daily using seven reference solutions of various analyte concentrations. Differences between the means of two groups were analyzed by Student's t test at 95% confidence level. Generally, data analysis and plotting of diagram was performed using Kaleidagraph, a graphing and data analysis software.

### 3. Results and Discussion

#### 3.1 FTIR Spectroscopic Measurements

Fig. 1 shows FTIR spectra of the activated biochar with increasing Th(IV) sorbed on the material at pH 3. According to Fig. 1 there is a significant change in the IR spectra and particularly at wavenumbers corresponding to carbonyl stretching ( $1713\text{ cm}^{-1}$ ) and carboxylic bending ( $1248\text{ cm}^{-1}$ ) vibrations [15]. The relative decrease of the band at  $1713\text{ cm}^{-1}$  and  $1248\text{ cm}^{-1}$  with increasing Th(IV) concentration indicates direct interaction between Th(IV) and the carboxylic group, and the formation of inner-sphere chelate complexes. Assuming only sorption of monomeric species on the biochar surface and taking into account the species distribution of tetravalent actinides under the given conditions [16, 17], the sorption reaction can be described schematically by equation (8):



The formation of the neutral species, which is favoured at pH 3, is expected to be more stable than charged Th(IV) surface species.

**Fig. 1:** IR spectra of the activated biochar prior and after Th(IV) sorption at pH 3 and varying thorium concentration.

#### 3.2 Sorption Studies

##### 3.2.1 Sorption Isotherm

According to the FTIR spectra sorption of Th(IV) occurs through ion-exchange and complexation of the metal by the carboxylic moieties found on the activated biochar surface. Hence, the relative adsorption depends on both the chemical behaviour of Th(IV) in solution and the surface charge of the adsorbent. The solution pH is one of the most important parameters affecting sorption on surfaces, because pH governs both the chemical behavior of the metal ion in solution and the surface charge of the adsorbent. To avoid colloid formation and surface precipitation, which become dominant for  $\text{pH} > 3$ , the sorption studies have been performed only at pH 3.

In order to evaluate the maximum sorption capacity ( $q_{\max}$ ), sorption experiments with varying Th(IV) concentrations have been performed at pH 3. The corresponding isotherms graphically shown in Fig. 2 and indicates that activated biochar derived from cactus fibres presents increased sorption capacity for Th(IV) even in the acidic pH range. The surface saturation is reached for pH 3 at  $0.35 \text{ mol}\cdot\text{kg}^{-1}$  ( $q_{\max} = 81 \text{ g}\cdot\text{kg}^{-1}$ ) and above a certain concentration the relative sorption/removal increases dramatically suggesting surface polymerization or surface precipitation on the surface. Comparison of the experimental data with corresponding literature data clearly shows that the activated biochar derived from cactus fibres presents significantly increased sorption capacity compared to activated carbon and biochars ( $0.09 \text{ mol}\cdot\text{kg}^{-1} < q_{\max} < 1.2 \text{ mol}\cdot\text{kg}^{-1}$ ) [18, 19], and modified graphene oxide ( $q_{\max} = 0.21 \text{ mol}\cdot\text{kg}^{-1}$ ) [20]. This enormous sorption capacity of the activated biochar derived from cactus fibres is attributed to highly oriented series of lamellar structures, which provide to the sorbent microchannels and extended surface for relatively rapid fluid exchange and increased sorption capacity [11]. Nevertheless, the sorption capacity is significantly lower than the sorption capacity for hexavalent uranium ( $0.9 \text{ mol}\cdot\text{kg}^{-1}$ ) at the corresponding pH [15] and this is attributed to the formation of the hydrolysis products of thorium (e.g.  $\text{Th}(\text{OH})_2^{2+}$  and  $\text{Th}(\text{OH})_3^+$ ), which are the predominant Th(IV) species [17] and stabilize Th(IV) in solution.

**Fig. 2:** Sorption isotherm of the Th(IV) sorption on activated biochar at pH 3 (0.01 g of biochar  $[\text{Th}(\text{IV})]_{\text{tot}} = 5 \times 10^{-6} - 5 \times 10^{-3} \text{ mol}\cdot\text{l}^{-1}$ ,  $I = 0.1 \text{ mol}\cdot\text{l}^{-1} \text{ NaClO}_4$ ,  $T = 23 \pm 2 \text{ }^\circ\text{C}$ , 24 hours of reaction time).

### 3.2.3 Thermodynamics of the Th(IV) Sorption on Activated Biochar

The effect of temperature on Th(IV) sorption on the activated biochar cactus fibres was investigated to estimate the corresponding thermodynamic data based on the linear form of the van't Hoff equation [13]. Evaluation of the data shows that the sorption of Th(IV) at pH 3.0 is favoured with increasing temperature (endothermic process) and corresponding values of the thermodynamic parameters are  $\Delta H^\circ = 28 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta S^\circ = 145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . This is similar to the thermodynamic behaviour of the Th(IV) sorption on biochars described in literature [18].

**Fig. 3:**  $\ln K_d = f(1/T)$  plots corresponding to Th(IV) sorption on activated biochar at pH 3 (0.01 g of biomass,  $[\text{Th}(\text{IV})]_{\text{tot}} = 5 \times 10^{-4} \text{ mol}\cdot\text{l}^{-1}$ ,  $I = 0.1 \text{ mol}\cdot\text{l}^{-1} \text{ NaClO}_4$ ,  $T = 23 \pm 2 \text{ }^\circ\text{C}$ ).

#### 4. Conclusions

Activated biochar produced from *OpuntiaFicusIndica* cactus fibres has been used to remove Th(IV) from aqueous solutions. The material presents increased sorption capacity in acidic solutions the sorption capacity is remarkable ( $q_{\max} = 81 \text{ g}\cdot\text{kg}^{-1}$ ; pH 3.0), indicating that the material could be a very attractive candidate for the effective removal of tetravalent actinides and other metals from industrial process waters and wastewaters. The formation of the Th(IV) inner-sphere complexes on the biochar surface is confirmed by FTIR spectroscopic measurements.

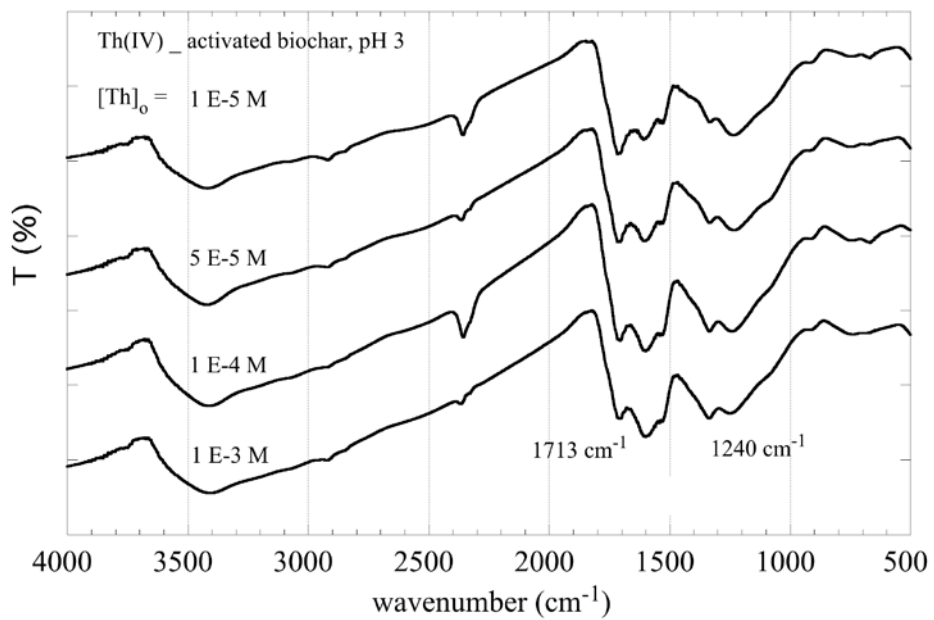
#### 6. References

1. Jeong, C. J., Park, C. J., Ko, W. I.: Dynamic analysis of a thorium fuel cycle in CANDU reactors. *Ann Nucl Energy* 35, 1842-1848 (2008)
2. Antoniou, S., Pashalidis, I.: The effect of natural organic matter on the formation and solubility of  $M(\text{OH})_4$  solid phases. *J. Radioanal. Nucl. Chem.* 299, 791–795 (2014)
3. Hernandez-Ramirez, O., Holmes, S.M.: Novel and modified materials for wastewater treatment applications. *J. Mater. Chem.* 18, 2751–2761 (2008)
4. Zhao, G., Wu, X., Tan, X., Wang, X.: Sorption of Heavy Metal Ions from Aqueous Solutions: A Review. *J. Open Colloid Sci.* 4, 19-31 (2011)
5. Ioannidou, O., Zabaniotou, A., 2007. Agricultural residues as precursors for activated carbon production-A review. *Renew. Sust. Energ. Rev.* 11, 1966–2005.
6. Sud, D., Mahajan, G., Kaur, M.P.: Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresour. Technol.* 99, 6017–6027 (2008)
7. Hubbe, M.A., Hasan, S.H., Ducoste, J.J.: Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals. *BioResources* 6, 2161-2287 (2011)
8. Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J., Sánchez-Polo, M.: Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *J. Environ. Manage.* 85, 833-846 (2007)

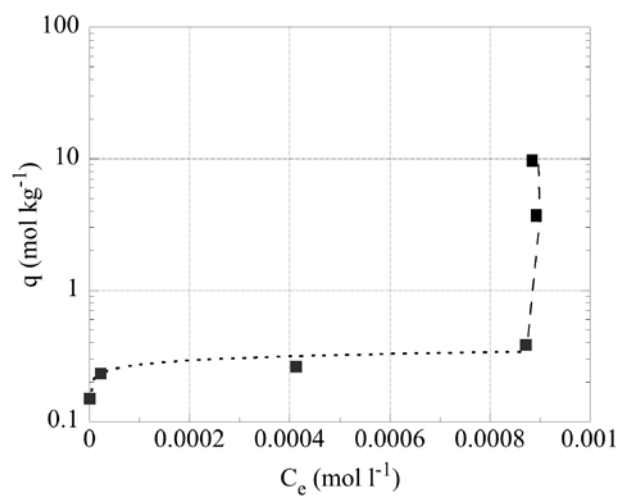
9. Prodromou, M., Pashalidis, I.: Uranium adsorption by non-treated and chemically modified cactus fibres in aqueous solutions. *J. Radioanal. Nucl. Chem.* 298, 1587–1595 (2013)
10. Prodromou, M., Pashalidis, I.: Copper(II) removal from aqueous solutions by adsorption on non-treated and chemically modified cactus fibres. *Water Sci. Technol.* 68, 2497-2504 (2013)
11. Hadjittofi, L., Prodromou, M., Pashalidis, I.: Activated biochar derived from cactus fibres--preparation, characterization and application on Cu(II) removal from aqueous solutions, *Bioresour. Technol.* 159, 460-464 (2014)
12. Hosten, E., Rohwer, H., Interactions of uranium and thorium with arsenazo III in an aqueous medium. *Anal. Chim. Acta*, 341, 263–268 (1997)
13. Atkins, P.W.: *Physical Chemistry*. Oxford University Press, Oxford (1978)
14. Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G.: Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresour. Technol.* 102, 8877– 8884 (2011)
15. Hadjittofi, L., Pashalidis, I. Uranium sorption from aqueous solutions by activated biochar fibres investigated by FTIR spectroscopy and batch experiments. *J. Radioanal. Nucl. Chem.* (2014). DOI 10.1007/s10967-014-3868-5
16. Baes, C. F., Mesmer, R. E.: *The Hydrolysis of Cations*. John Wiley & Sons, New York (1976)
17. Moulin, C., Amekraz, B., Hubert, S., Moulin V.: Study of thorium hydrolysis species by electrospray-ionization mass spectrometry. *Anal. Chim. Acta* 441, 269–279 (2001)
18. Kutahyalı, C., Eral, M.: Sorption studies of uranium and thorium on activated carbon prepared from olive stones: Kinetic and thermodynamic aspects. *J. Nucl. Mater.* 396, 251-256 (2010)
19. Metaxas, M., Kasselouri-Rigopoulou, V., Galiatsatou, P., Konstantopoulou, C., Oikonomou, D.: Thorium removal by different adsorbents”, *J. of Hazard. Mater.* 97, 71-82, (2003)
20. Pan, N., Jianguo Deng, J., Guan, D., Jin, Y., Xia, C.: Adsorption characteristics of Th(IV) ions on reduced graphene oxide from aqueous solutions”, *Appl. Surf. Sci.* 287, 478-483 (2013)



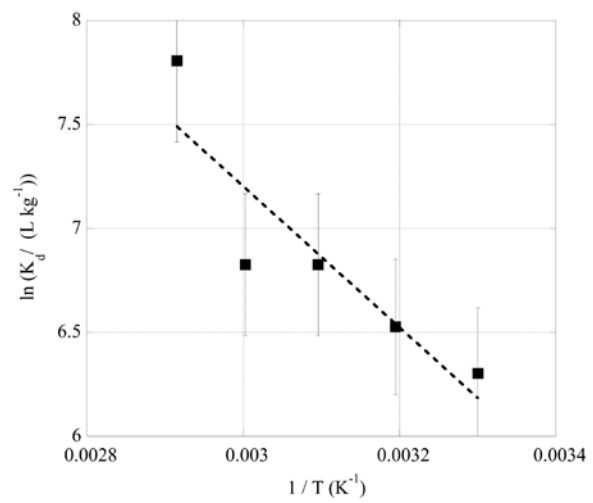
## Figures



**Fig. 1:**



**Fig. 2:**



**Fig. 3:**