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Thorium removal from acidic aqueous solutions by activated biochar derived from cactus fibers

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ABSTRACT

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

Keywords: Thorium; Acidic waters; Activated biochar fibers; Adsorption capacity; FTIR spectra

1. Introduction

Thorium is a naturally occurring radioactive element, which is found in small amounts in most rocks and soils (6 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}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 analog for tetravalent metal ions such as Ti(IV), Zr(IV), and 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

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different materials, including low-cost and highly available biomass byproducts [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 byproducts could be viable sources because they are abundant in nature or are produced in large quantities as byproducts or wastes from agricultural or industrial activities [3,7].

Regarding the adsorption of thorium from aqueous solutions by biochar, there are only few studies reported in the literature and are basically related to activated carbon prepared from olive stones and olive pulp [9,10], and reduced graphene oxide [11]. The corresponding experiments are performed in the acidic pH region ($3 < \text{pH} < 4$) due to the hydrolysis of tetravalent thorium (Th(IV)) and the very low solubility of $Th(OH)_4$ ($K_{sp} = -44.5$ [12]), which limits the performance of adsorption experiments at increased concentrations. According to the adsorption data, the equilibrium is reached within 48 h and the maximum capacity determined varies between 0.09 and 1.2 mol kg^{-1}. In addition, thermodynamic data indicate the formation of inner-sphere complexes [9,13] and specific interaction between Th(VI) and the carboxylic moieties on the surface of the activated carbons.

The present study deals with the adsorption of thorium (Th(IV)) by activated carbon/biochar prepared from a biomass byproduct (Opuntia ficus-indica cactus fibers). The fibrous structure of the precursor material, which is a biomass byproduct is expected to result in relatively low-cost product (activated biochar) with increased separation efficiency because of its large external surface available for adsorption [14–16]. The main goal of the study is besides characterization 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, ΔG, ΔH, and ΔS), 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 ambient conditions in aqueous solutions. The preparation of the metal ion solutions was carried out using the nitrate salt of thorium ($Th(NO_3)_4 \cdot 6H_2O$, Merck). pH measurements were performed by a pH meter (Hanna Instruments, HI 8424) attached to a commercial a glass electrode (Sentek, P12), 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 Opuntia ficus-indica cactus fibers, which were separated from dried cladode leaves. The carbonization of the material was carried out by thermal treatment under oxygen-restricted conditions and the chemical activation by means of boiling, concentrated nitric acid as described elsewhere [16–18]. Characterization 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 [16]. The surface analysis by BET measurements indicated that there is no internal mesoporous surface (BET surface $< 5\ m^2\ g^{-1}$ and pore volume $< 0.3\ cm^3\ g^{-1}$) and the internal surface of the activated biochar consists mainly of micropores ($d < 2$ nm), which are of minor importance for the Th (IV) adsorption from aqueous systems [16–18].

The characterization of the activated after Th(IV) adsorption was performed by Fourier transform infrared 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 before and after thorium adsorption 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).

2.1. Adsorption measurements

The adsorption 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 h to ensure that equilibrium had been reached. Preliminary kinetic experiments have shown that the system reaches steady-state equilibrium after 24 h contact time. For studying the effect of initial Th(IV) concentration, the latter was varied between 5×10^{-6} and 5×10^{-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, $[\mathrm{Th(IV)}]_o = 5 \times 10^{-4}$ 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 ($[\mathrm{Th(IV)}]_o$ 5×10^{-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 [19]. For each test solution, a corresponding reference solution was prepared and was similar to the test solution expect that it did not contain the adsorbent material.

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

$$\text{rel. adsorption } (\%) = 100 \cdot \frac{\left([\mathrm{Th(IV)}]_o - [\mathrm{Th(IV)}]_{aq}\right)}{[\mathrm{Th(IV)}]_o} \tag{1}$$

$$K_d = \frac{\left([\mathrm{Th(IV)}]_o - [\mathrm{Th(IV)}]_{aq}\right)}{[\mathrm{Th(IV)}]_{aq}} \cdot \frac{V}{m} \ (1 \cdot \mathrm{kg}^{-1}) \tag{2}$$

where $[\mathrm{Th(IV)}_o$ = the total actinide ion concentration ($\mathrm{mol\,l^{-1}}$) in the system or in the reference solution, $[\mathrm{Th(IV)}]_{aq}$ = actinide ion concentration ($\mathrm{mol\,l^{-1}}$) 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 Eq. (3) and the Gibbs free energy isotherm Eq. (4) to estimate the corresponding thermodynamic data [20]:

$$\ln K_d = -\frac{\Delta H^\circ}{R \cdot T} + \frac{\Delta S^\circ}{R} \tag{3}$$

$$\Delta G^\circ = -R \cdot T \cdot \ln K_d \tag{4}$$

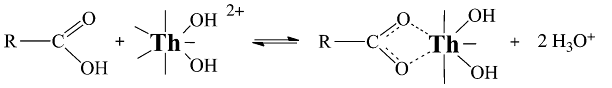
2.2. Statistical analysis

All experiments were performed in triplicate and the data are presented as mean ± 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 as chromophore [19]). 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 were 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 (1,713 $\mathrm{cm^{-1}}$) and carboxylic bending (1,248 $\mathrm{cm^{-1}}$) vibrations [21]. The relative decrease in the band at 1,713 and 1,248 $\mathrm{cm^{-1}}$ 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 adsorption of monomeric species on the biochar surface and taking into account the species distribution of tetravalent actinides under the given conditions [12,22], the adsorption reaction can be described schematically by Eq. (5):



(5)

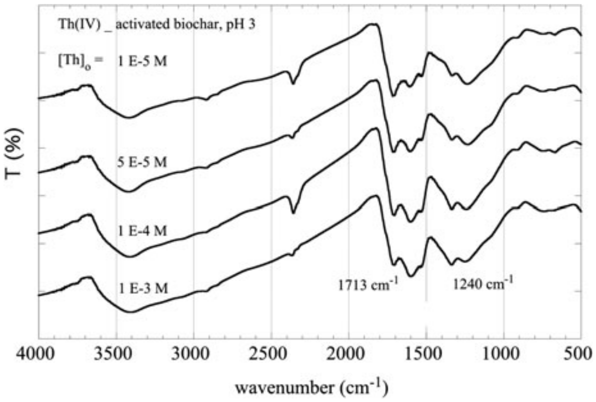


Fig. 1. IR spectra of the activated biochar before and after Th(IV) adsorption at pH 3 and varying thorium concentration.

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

3.2. Adsorption studies

3.2.1. Adsorption isotherm

According to the FTIR spectra adsorption of Th(IV) occurs through complexation of the metal by the carboxylic moieties found on the activated biochar surface. Hence, the relative adsorption depends on both the chemical behavior of Th(IV) in solution and the surface charge of the adsorbent. The solution pH is one of the most important parameters affecting adsorption 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 pH > 3, the adsorption studies have been performed only at pH 3.

In order to evaluate the maximum adsorption capacity ($q_{\max}$), adsorption experiments with varying Th(IV) concentrations have been performed at pH. The corresponding isotherm is graphically shown in Fig. 2 and indicates that activated biochar derived from cactus fibers presents increased adsorption capacity for Th(IV) even in the acidic pH range. The surface saturation is reached for pH 3 at 0.35 mol kg^{-1} ($q_{\max}$ = 81 g kg^{-1}) and above a certain concentration (8 × 10^{-4} mol l^{-1}, Fig. 2) the relative adsorption/removal increases dramatically suggesting surface polymerization or surface precipitation on the surface. Comparison of the experimental data with the corresponding literature data clearly shows that the activated biochar derived from cactus fibers presents significantly increased adsorption capacity compared to activated carbon and biochars (0.09 mol kg^{-1} < $q_{\max}$ < 1.2 mol kg^{-1}) [9,10], and modified graphene oxide ($q_{\max}$ = 0.21 mol kg^{-1}) [11]. This enormous adsorption capacity of the activated biochar derived from cactus fibers is attributed to highly oriented series of lamellar structures, which provide the sorbent microchannels and extended surface relatively rapid fluid exchange and increased adsorption capacity [16]. Nevertheless, the adsorption capacity is significantly lower than the adsorption capacity for hexavalent uranium (0.9 mol kg^{-1}) at the corresponding pH [17] and this is attributed to the formation of the hydrolysis products of thorium (e.g. $\mathrm{Th(OH)}_2^{2+}$ and $\mathrm{Th(OH)}_3^{+}$), which are the predominant Th(IV) species [22], and stabilize Th(IV) in solution.

3.2.2. Thermodynamics of the Th(IV) adsorption on activated biochar

The effect of temperature on Th(IV) adsorption on the activated biochar cactus fibers was investigated to estimate the corresponding thermodynamic data based on the linear form of the van't Hoff equation [20]. Evaluation of the data, which is graphically presented in Fig. 3, shows that the adsorption of Th(IV) at pH 3.0 is favoured with increasing temperature (endothermic process) and corresponding values of the thermodynamic parameters are $\Delta H^\circ = 28$ kJ mol^{-1} and $\Delta S^\circ = 145$ J K^{-1} mol^{-1}. These thermodynamic data

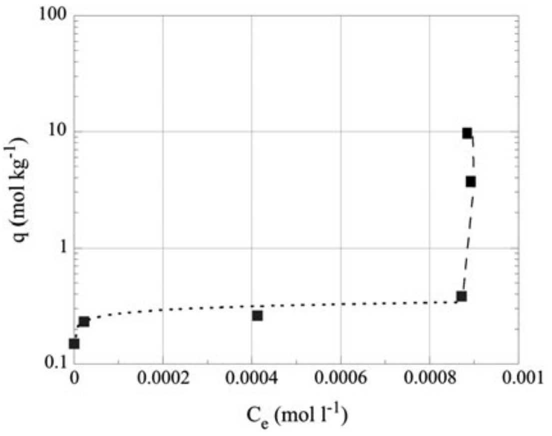


Fig. 2. Isotherm of the Th(IV) adsorption on activated biochar at pH 3 (0.01 g of biochar $[\mathrm{Th(IV)}]_{\mathrm{tot}} = 5 \times 10^{-6} - 5 \times 10^{-3}$ mol l^{-1}, $I = 0.1$ mol l^{-1} NaClO$_4$, $T = 23 \pm 2$°C, 24 h of reaction time).

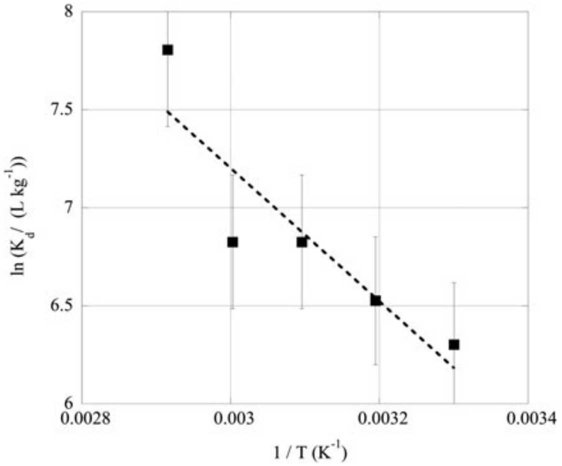


Fig. 3. ln $K_d = f(1/T)$ plots corresponding to Th(IV) adsorption on activated biochar at pH 3 (0.01 g of biomass, $[\mathrm{Th(IV)}]_{\mathrm{tot}} = 5 \times 10^{-4}$ mol l^{-1}, $I = 0.1$ mol l^{-1} NaClO$_4$, $T = 23 \pm 2$°C).

indicate that the adsorption reaction is an entropy-driven process related to the release of water molecules from the coordination sphere of the metal ion. The release of water molecules occurs upon surface complexation and corroborates the formation of inner-sphere complexes. This behavior is similar to the thermodynamic behavior of the Th(IV) adsorption on biochars described in literature [9].

4. Conclusions

Activated biochar produced from *Opuntia ficus-indica* cactus fibers has been used to remove Th(IV) from aqueous solutions. The material presents increased adsorption capacity in acidic solutions the adsorption capacity is remarkable ($q_{\max} = 81\ \mathrm{g\ kg}^{-1}$; 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.

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