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Uranium sorption on cork biomass

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Abstract

This work presents the effect of the pre-treatment of cork biomass with a hydrochloric acid solution on its sorption affinity towards uranium. The results show that the conversion of cork biomass into the H-form by the acid wash allowed to increase the sorption capacity towards uranium more than twice, due to the increase of the concentration of strong acidic and weak acidic groups on its surface. The optimum pH for uranium sorption was 5.0–5.2 for the original and 5.5–7.0 for the H-form biomass. The adsorption isotherms for uranyl ions on the natural and H-form cork biomass were determined. Finally, the kinetics of uranium adsorption on both biomasses was studied and a second-order model was fitted to the experimental data. It was found that the adsorption is faster for the H-form ($k = 0.196\,\mathrm{min}^{-1}$) than for the original biomass ($k = 0.057\,\mathrm{min}^{-1}$).

Keywords: Uranium; Biosorption; Cork biomass

1. Introduction

Due to the increasing environmental contamination caused by human technogenic activity (mining industry, enrichment factories, etc.) the removal of radionuclides, including uranium, from water solutions is an actual problem. On the other hand, the concentration of dissolved uranium in underground water can exceed the measured limited concentrations as uranium contained in some geological rocks, especially granites, can be easily dissolved by soil porous waters [1]. In Ukraine, the main source of radionuclides is the Chernobyl Power Station, where the concentration of uranium in the reservoirs of fourth block of the Chernobyl station ranges 0.1–23.0 mg/L [2].

It is known that sorption methods are very effective to solve ecological tasks on fine purification of water solutions from radionuclides. The main requirements for the use of an adsorbent for radionuclides removal are radiation, thermal, chemical and mechanical stability and low cost. There are many natural, organic and inorganic, adsorbents that have been used for uranium removal from water solutions [3–8]. For the last decade, biosorption of radionuclides by different biomasses, such as side products of wool production, rice and tea leafs, straw, coco shaving, peat, etc., has been increasingly studied due to the different type of functional groups that can take place in the biosorption reactions (carboxylic, sulfates, phosphates, and amino-groups) [9,10].

Within the scope of this work the use of cork as biosorbent for the removal of uranium was studied. Cork oak trees are very abundant in several Mediterranean countries that developed the production of, for example, bottle cork for wine industry. Portugal has a leading position in the cork industry due to the quality and quantity of bottle corks produced. Cork powder used as biosorbent in this work has no commercial value since it is rejected by the industry. Chemically, cork is composed of a complex mixture of fatty acids and heavy organic alcohol (∼45%, w/w), tannins (∼6%, w/w), polysaccharides (∼12%, w/w), lignin (∼27%) and alkanes. The mineral content is low (∼5%), the most abundant element being

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calcium (0.038–0.625%, w/w), followed by phosphorus, iron, magnesium and aluminium [11,12]. The high content of fatty acids makes of cork a promising biosorbent for heavy metals.

The removal of trivalent chromium [13] and copper, zinc and nickel [14–17] by biosorption in cork was presented elsewhere. The goal of the present work was to investigate the removal of uranium from aqueous solutions by biosorption in cork powder. Kinetics, pH effect and the isotherms of uranium sorption on cork were studied in batch conditions on both natural and converted to H-form of biomass.

2. Materials and methods

The cork powder was supplied by the Portuguese company CODICORK cortices LDA. Particle size fractions were obtained by sieving and all the experiments were carried out with the biomass size fraction 50–100 μm. The chemicals used were analytical grade and supplied by Merck. Uranium solutions were prepared from uranyl acetate. The cork biomass was converted into H-form by contacting 100 g of the biomass with 1 l of a solution 0.1 M HCl for 24 h. After contact, the mixture was filtered. The solid was washed with deionised water until a constant pH of the washing waters was measured and dried on air at room temperature.

2.1. *Determination of the full static exchange capacity of cork biomass*

Static exchange capacity (SEC) (cation and anion exchange) of natural and H-form cork biomass has been studied by the Boehm method [18–20]. The Boehm method consists on a selective neutralization of the surface acidic groups with various strengths, using bases that have conjugate acids with a wide range of acid dissociation constants. According to Boehm, the acidic surface properties derive from the presence of different surface groups: both strong and weak carboxyl groups (–COOH), carbonyl, lactonic, enolic and phenolic groups (OH). These groups have different acidity: strong acidic (carboxylic groups), weak acidic (carboxylic, lactonic and enolic) and phenolic and can be differentiated by neutralization with solutions of $NaHCO_3$, Na_2CO_3 and NaOH. According to the protocol, the functional groups are determined considering that NaOH consumes all those groups (full cation exchange capacity), Na_2CO_3 reacts with weak acidic groups, while the $NaHCO_3$ uptake corresponds to the strong carboxylic acidity. Thus, for example, the difference between the NaOH and Na_2CO_3 consumption corresponds to the weakly acidic phenolic group.

In this work, to determine the concentration of the acidic groups on the surface of the cork biomass, 1 g of cork biomass was placed into an Erlenmeyer flask containing 0.1 L of 0.1 M $NaHCO_3$, Na_2CO_3 or NaOH and placed into the thermostated orbital shaker for 48 h, since it was found previously [15–17] that the sorption equilibrium is reached after 48 h. Blanks were also prepared. Afterwards, the suspensions were filtered and 0.01 L of the filtrate of each investigated solution ($NaHCO_3$, Na_2CO_3 and NaOH) were titrated with 0.1 M HCl down to pH 4.3 (pH was measured permanently). The static exchange capacity (SEC) on Na^+ from 0.1 M solutions of $NaHCO_3$, Na_2CO_3 and NaOH was then calculated as:

$$q = \frac{V(C_0 - C_{\text{eq.}})}{m} \qquad (1)$$

where q is the SEC (mequiv./g), C_0 the initial concentration of $NaHCO_3$, Na_2CO_3 or NaOH (mequiv./L), $C_{\text{eq.}}$ the equilibrium concentration of $NaHCO_3$, Na_2CO_3 or NaOH (mequiv./L) obtained by titration, V the volume of the initial solution in L (0.1 L in this case) and m the mass of cork biomass in g (1 g).

To determine the anion exchange capacity of cork biomass, 1 g of solid was shaked with 0.1 L of 0.1 M HCl solution for 48 h in a temperature controlled orbital shaker. Afterwards, an aliquot of the suspension was titrated with 0.1 M NaOH. The anion exchange capacity was calculated using Eq. (1), in which C_0 and $C_{\text{eq.}}$ are the initial and the equilibrium concentration of acid, respectively.

2.2. *Batch sorption experiments*

The removal of uranium from solutions of uranyl acetate containing 1.9×10^{-5} to 3.3×10^{-4} mol/L of U ions was studied in batch conditions. Tests were carried out in Erlenmeyer flasks placed in a temperature controlled orbital shaker (200 min^{-1}). Typically, the dried biomass was contacted with 0.05 L of the uranyl solutions at 25 °C using a solid/liquid ratio of 1 g/2 L. The pH of the solutions was established on the level of 5.2 ± 0.1 (for kinetic experiments and isotherms) or any other level (for a study of uranium sorption on pH), was periodically checked and kept constant during whole experiment by 0.1 M solutions of NaOH or CH_3COOH. After a pre-set contact time, the suspension was centrifuged and the filtrate was analyzed for uranium concentration by photometry on a LOMO-CF46 spectrophotometer (Sant-Petersburg, Russia), using arsenazo(III) as the complexing agent [21]. The error of a method of spectrophotometric determination of uranium(VI) with arsenazo III is 5%. The experiments were repeated three times and the average values were used for drawing the graphs. The uranium uptake was determined according to Eq. (1) where q is the amount of metal adsorbed per gram of dry cork (mg g^{-1}), C_0 the initial concentration of the metal in solution (mg/L), $C_{\text{eq.}}$ the final (or equilibrium) concentration of the metal in solution (mg/L), V the volume of the solution (L) and m the mass of the sorbent (g).

2.3. *Kinetic experiments*

The kinetic studies were carried out in a baffled stirred tank reactor (0.1 L) immersed in a temperature controlled water bath (22 ± 2 °C), pH = 5.2 and using a solid/liquid ratio of