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Biosorption of Th(IV) in a fixed-bed column by Ca-pretreated *Cystoseira indica*

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ABSTRACT

Th(IV) biosorption from aqueous solutions by Ca-pretreated Cystoseira indica alga was studied by variations of bed height (3.5, 5.25 and 7 cm) and flow rate (1,2 and 4 ml/min) in a fixed-bed column. Favorable conditions were observed with the highest bed height and lowest flow rate. The maximum breakthrough time was 1450 min at flow rate 1 ml/min and bed height 3.5 cm. The experimental data were accurately described with the Belter model with R^2 0.99. In addition, the results obtained agreed entirely with the bed depth service time (BDST) model. The flow rate study and the BDST model led to the conclusion that the mass transfer in continuous mode of Th(IV) biosorption onto *C. indica* is governed by intra-particle diffusion. FTIR analysis confirmed that hydroxyl, carboxyl and amine are the main groups for Th(IV) biosorption. Calcium ion concentration measurement in the effluent solution and XRF analysis performed due to investigation on ion exchange process in biosorption.

1. Introduction

Heavy metals are the notorious environmental contaminants; many of them are toxic even at trace levels. Thorium(IV) is one of the most dangerous heavy metals not only in industrial applications but also in energy and environmental issues. Th(IV) in the environment originates from the nuclear industry and some human activities such as lignite burning in power stations, exploitation of ores with associated Th(IV) and the use of fertilizers. The effluents containing Th(IV) cause serious and irreversible environmental and biological damage. Therefore, it became important to recover Th(IV) from wastewaters [1–4].

For the separation and purification of Th(IV), liquid–liquid extraction has been widely used, but it is time-consuming. Other methods such as extraction chromatography, functionalized resins and different adsorbents have been extensively used for the separation and preconcentration of Th(IV) ions [2]. Biosorption which utilizes non-living biomass of algae, fungi, bacteria or agricultural wastes is a well-known method for the removal of heavy metals from wastewaters as it is cheaper and environmentally friendly [5]. The brown algae is among the most common biosorbents used for heavy metal biosorption. The cell wall of brown algae has different functional groups (such as carboxyl, hydroxyl, phosphate or amine) that can bind to metal ions [6].

Most biosorption experiments in the literature have been carried out in batch systems. Batch experiments were performed to study the effect of different operational factors such as pH, temperature, contact time, biomass dosage and initial metal concentration on the metal biosorption process. On the other hand, the practical application of heavy metal biosorption is most effectively performed in a fixed-bed column, as it efficiently uses the biosorbent capacity and results in a better quality of the effluent. Moreover, it can be easily scaled up from a laboratory scale [7–9].

The dynamic behavior of a fixed-bed column is described in terms of breakthrough curve (or the concentration–time profile). Different models have been applied to analyze and explain the experimental breakthrough curve and predict the effect of various operational factors on the efficiency of biosorption process. These models include Bohart–Adams, Thomas, modified dose-response, Yoon-nelson, Belter, Yan, Clark and convective-dispersive model [10–14]. In this study BDST (Bed Depth Service Time), Thomas, modified dose-response, Belter and convective-dispersive models have been used to predict the experimental data.

Cystoseira indica algae is abundant in the Persian Gulf on the coast of Qeshm, Iran. In our previous study the equilibrium and kinetic data of Th (IV) biosorption onto Ca-pretreated *C. indica* were obtained [15]. Also, we investigated Th(IV) biosorption by the Ca-pretreated *C. indica* alga biomass in a fixed-bed column. The effect

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of Th(IV) influent concentration on performance of fixed-bed column studied and the breakthrough curves described by Clark model and a mass transfer model including convection-dispersion terms. Also, the equilibrium biosorption data of Th(IV) at different pH modeled using Langmuir, Freundlich, Dubinin-Radushkevich, Redlich-Peterson, Sips and Toth isotherm models [10]. Therefore, in this work biosorption of Th(IV) by the Ca-pretreated *C. indica* algae was investigated in a fixed-bed column. The effect of design parameters such as bed height and flow rate on the Th(IV) biosorption was examined. In addition, the Th(IV)-binding process onto the biosorbent were also investigated by Fourier-transform infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and monitoring of Ca^{2+} ions in effluent solution.

2. Experimental

2.1. Materials

C. indica algae was washed with distilled water to remove sand and other impurities and later on it was sun-dried for 48 h. The biomass was crushed and sieved to a particle size of 1–2 mm and then washed with distilled water and dried in an oven at 70 °C overnight. In this study the biomass was treated by calcium solution as follows: *C. indica* algae was treated in the solution of 0.1 M $CaCl_2$ (10 g biomass with 1 L of solution) for 3 h at agitation rate of 150 rpm and constant temperature of 25 °C in an incubator shaker (INFOR Smultitron, Switzerland). Then, the Ca-pretreated algae was washed several times with distilled water in order to remove excess calcium ions. Finally, The Ca-pretreated biomass was dried in an oven at 70 °C for 24 h.

2.2. Biosorbent characterization studies

The unloaded and Th(IV) loaded biomasses were characterized by Fourier transform infrared spectroscopy (FTIR) (Vector22-Bruker Company) in the range of 400–4000 cm^{-1}. Also unloaded and Th(IV) loaded biomasses were analyzed by means of a X-ray fluorescence analyzer (XRF) (Model ED 2000 Oxford Instruments corporation). FTIR and XRF analyses were performed to find the main biosorption mechanism. In addition, the morphological analysis of the biosorbent were performed using scanning electron microscopy (SEM, JEOL JSM-6380).

2.3. Biosorption experiment

The experiments were carried out in a glass column of 10 cm length and 1.5 cm inside diameter (Fig. 1) that packed with different quantities of the *C. indica* algae. Two plastic sieves both with the pore size of 0.5 mm were sealed with cap holders and installed at the top and bottom of this glass column. The Th(IV) solution (prepared by the use of deionized water and analytical grade salts of Th $(NO_3)_4 \cdot 6H_2O$ (Merck supplied) was pumped at the ambient temperature in the up-flow mode to avoid possible short-circuiting and channeling, utilizing a peristaltic pump (Watson Marlow, Model 205U). The pH of influent solutions was measured with a pH meter (Metrohm, Model 780) and adjusted by addition of negligible volumes 0.1 M HCl and/or 0.1 M NaOH solutions. In all cases, pH of the influent metal solutions was adjusted to 3.5. The column effluent samples were collected periodically and were analyzed for the remaining Th(IV) ion concentration by an inductively coupled plasma spectroscopy (ICP, Varian, Model Liberty 150 AX Turbo). After the system reached saturation (the effluent concentration was the same as the feed solution), it was brought to a standstill.

2.4. Analysis of column data

The breakthrough curve showed the performance of the fixed-bed column. Total adsorbed Th(IV) ions, q_{total} (mg), in the fixed-bed column can be written in the following form:

$$q_{total} = \frac{Q}{1000} \int_{0}^{t_{total}} C_{ad} dt \quad (1)$$

where $C_{ad} = C_0 - C$ (mg/L), C_0 and C are the influent and effluent concentrations, respectively, t_{total} is the total flow time (min), Q is the flow rate (mL/min). The biosorption column capacity (mg/g),

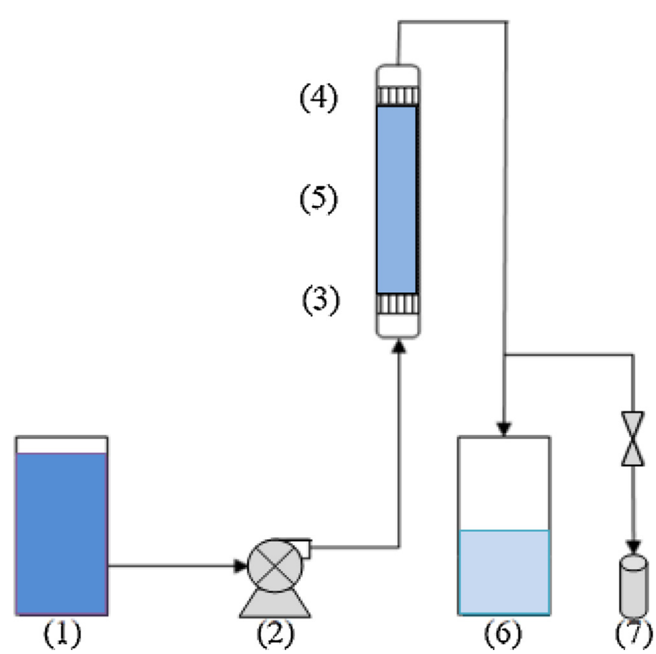

Fig 1. Experimental arrangement of the biosorption fixed-bed column: 1-feed storage, 2-peristaltic pump, 3-bottom holder, 4-top holder, 5-column, 6-effluent, and 7-sampling vessel.