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BIOSORPTION OF URANIUM IN RADIOACTIVE LIQUID ORGANIC WASTE BY COCONUT FIBER

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ABSTRACT

Radioactive liquid organic waste needs special attention because the available treatment processes are often expensive and difficult to be managed. Biosorption is a potential technique since it allies low cost with relatively high efficiency. Biosorption has been defined as the property of certain biomolecules to bind and remove selected ions or other molecules from aqueous solutions. Biosorption using vegetable biomass from agricultural waste has become a very attractive technique because it involves the removal of heavy metal ions by low cost biossorbent. This technique could be employed in the treatment of radioactive liquid wastes. Among the biosorbents reported in the literature, coconut fiber (Cocosnucifera L.) is highlighted due to the large number of functional groups in its composition. The aim of this study was to assess the potential of coconut fiber to remove uranium from radioactive liquid organic waste. This work was divided into three stages: i) Preparation and activation of the coconut fiber; II) Physical characterization of the biomass, iii) Batch biosorption experiments. Two forms of coconut fiber were tested, raw and activated. The activation was performed with dilute HNO3 and NaOH solutions. The parameters evaluated for physical characterization of biomass were morphological characteristics of coconut fiber, real and apparent density and surface area. The biomass was suspended in 10 m*l* of solutions prepared with distillate water and radioactive liquid waste for 2 hours in the proportion of 0.2% w/v. After the contact time, the coconut fiber was removed by filtration and the supernatant, analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES).The results were evaluated using Langmuir and Freundlich isotherms. The maximum capacity for the raw coconut fiber was lower than the activated one, removing only 1.14mg/g against 2.61mg/g. These results suggest that biosorption with coconut fiber in activated form can be applied in the treatment of radioactive liquid organic waste containing uranium.

1. INTRODUCTION

Treatment is an important stage in radioactive waste management to reduce the volume of the wastes and to enhance the safety and/or reduce the costs of further stages. Radioactive liquid waste streams may represent a challenge to treat, in general, as the physical properties and chemical composition vary widely. Conventional techniques as precipitation, ion exchange and electrochemical processes may be employed to treat these wastes depending on their characteristics; however, under certain conditions they are not efficient when, for example, the concentration of ions is low. New approaches and techniques are emerging that involve

the use of alternative materials such as biomass to remove pollutants from industrial waste streams. This technique combines simplicity and low cost and may be defined as the property of biomolecules or biomass to bind to metal ions thereby decreasing their concentration in aqueous solutions. It is a process which uses vegetable or microorganisms in the retention, removal or recovery of dissolved heavy metals [1].

Agricultural residues have been evaluated as biomass for biosorption processes to remove different types of pollutants from waste streams. The interest in using these residues is related to the low cost, high efficiency of heavy metal removal from dilute solutions, abundant availability, and the possibility of sustainable use [2]. There are several studies described in the literature involving the use of agricultural residues in biosorption processes [3,4,5,6], and among them, coconut fiber (Cocos nucifera L.) [7,8,9].Coconut fiber or coir is an attractive biosorbent because it is generated in large amount as by-product from coconut processing. This fiber is composed by several constituents including lignin and cellulose, which are the main constituents responsible for the metal-binding mechanisms [8]. This characteristic is related to its porous structure and the functional groups including carboxylic and phenolic acid groups [9]. The biosorption property may be enhanced by chemical treatment, which improves the ion exchange capacity by formation of new functional groups [10, 11, 12, 13].

Biosorption can be a viable, low cost, effective and easily applied treatment of liquid radioactive waste stored in IPEN-CNEN/SP. The objective of this study was to evaluate the capacity of Coconut fiber to remove uranium (total) in radioactive waste liquids.

2. MATERIALS AND METHODS

The assessment of coconut fiber ability to remove uranium in waste was performed using fibers in raw and activated forms. The radioactive liquid waste studied is composed of water, ethyl acetate (196 ppm), TBP (227 ppm) and total uranium (103 ppm) and pH value of 2.17.

This work was divided into three stages: i) Preparation and activation of the coconut fiber; II) Physical characterization of the biomass, iii) Batch biosorption experiments.

2.1. Preparation and Activation

The coconut fiber used was produced by West Garden® obtained in local commerce. The fiber was washed with distilled water, oven dried at 80 °C for 24 hours, sterilized by UV radiation, chopped and sieved to obtain particle size between 0.297 mm and 0.500 mm.

The Coconut fiber was activated (chemically modified) according to the procedure described by ROCHA et al [11]. 10 g of biomass was suspended in 50 m*l* of 0.5 M HNO_3 solution and mechanically stirred at 240 rpm for 1h at room temperature. The biomass was filtered and washed with water to remove the excess of acid. Then, the material was dispersed in 100 mL of 0.5M NaOH solution and mechanically stirred at 240 rpm for 1 h at room temperature. Finally, the biomass was separated by filtration, washed with deionized water, neutralized and dried at 40 °C.

2.2. Physical Characterization

The parameters evaluated for physical characterization of biomass were morphological characteristics of coconut fiber, real and apparent density and surface area.

The morphological characteristics of coconut fiber were evaluated by scanning electron microscopy performed using a Philips model XL30 scanning electron microscope. The samples were coated with a thin, electric conductive gold film.

The real density of biosorbent was determined by helium picnometry (Micromeritcs, Moldel 1330) [14]. The apparent density was determined by filling a measuring beaker with a defined volume of the specimen and weighing it according to the method described in the EMBRAPA standard [15].

The surface area of the biosorbent was determined by BET method (Micromeritcs, ASAP 2010 apparatus), based on nitrogen adsorption–desorption isotherms at 77 K [16,17].

2.3. Biosorption Experiments

Biosorption experiments were performed using 0.2g of Coconut fiber suspended in 10 m*l* of solutions prepared with distillate water and radioactive liquid waste. The concentrations ranged from 10 to 100%. The suspensions were shaken (150 rpm) at room temperature for 2 hours, filtered and the concentrations of uranium were determined in the free aqueous fraction of biomass. All experiments were performed in triplicate.

The uranium (total) in the samples was quantified by inductively coupled plasma optical emission spectrometry (ICP-OES), model 7000DV (PerkinElmer). A calibration curve was prepared using a standard uranium solution (Matthey Johnson Company) to perform the analysis. The wavelength (λ) used in the determination of the uranium was 385.466 nm and the result is expressed as the average of triplicate measurements.

The uranium uptake was determined using the equation showed in eq. 1:

$$q=\left(\frac{C_i-C_f}{m}\right)v \quad (1)$$

where, C_i and C_f are the initial and final concentration of metal in solution (mg/*l*), v is the volume of solution (L) and m is the mass of biosorbent (g). Langmuir and Freundlich isotherms were applied to describe the adsorption of uranium by coconut fibers. The equations that represent these isotherms are given respectively by e. (2) and (3):

$$q=\frac{q_{max}K_LCeq}{1+K_LCeq} \quad (2)$$

$$q=K_FC_{eq}^{1/n} \quad (3)$$

where q is the amount adsorbed in mg/*l*; q_{max} is the maximum amount adsorbed in mg/L; K_L is Langmuir equation constant, which represents ratio of adsorption and desorption rates in

l/mg; K_f is the Freundlich adsorption coefficient in mg/*l* and 1/n is a measure of the sorption intensity (7,18, 19).

The parameters of the isotherm models were estimated by applying the downhill Simplex optimization method [20] to the experimental data. The objective function used in this method is given by Eq.4, where q_{eq}^{EXP} and q_{eq}^{MOD} are, respectively, the experimentally determined and the model calculated equilibrium amounts of dye adsorbed per unit mass of adsorbent and n is the number of experimental data.

$$F_{obj} = \sum_{j=1}^{n} (q_{eq}^{EXP} - q_{eq}^{MOD})^2 \quad (4)$$

3. RESULTS

3.1. Physical Characterization

Figure 1 presents the micrograph images of coconut fibers before and after activation by scanning electron microscopy. In Figure 1, it is possible to see that HNO_3/NaOH solutions were able to remove surface materials on the activated form, exposing clearly open and closed pores.

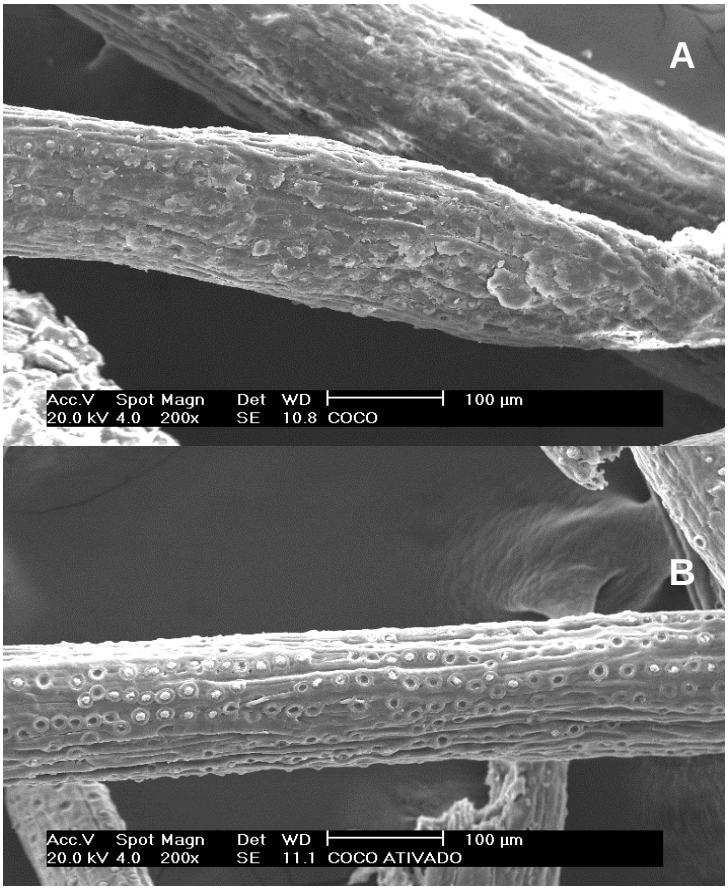

Figure 1: Scanning electron microscopy of coconut fiber A (raw fiber), B (activated fiber).

3.2. Real Density, Apparent Density, and Surface Area

Table 1 shows the results of real and apparent densities and surface area of the coconut fiber. It can be observed that the real and apparent densities of activated fiber were lower than that of raw fiber. However, the surface area of the activated fiber was approximately 28.0% higher than the raw one, this difference can be attributed to the changes caused chemical treatment, shown in Fig. 1.

Table 1: Values real, apparent density and surface area for coconut fiber.

Biomass	Apparent density (g/cm^3)	Real density (g/cm^3)	Surface area (m^2/g)
Raw fiber	0.29	1.67	6.23
Activated fiber	0.19	1.56	8.63

3.3. Biosorption Experiments

Uranium uptake data showed that there was removal by raw and activated coconut fiber. The experimental adsorption capacities were 0.66 ± 0.10 mg/g and 1.82 ± 0.04 mg/g for raw and activated fiber, respectively. The adjusting of the Langmuir and Freundlich model to experimental data are shown in Figure 2. Table 2 shows the parameters q_{max}, KL and R^2calculated for these two models.

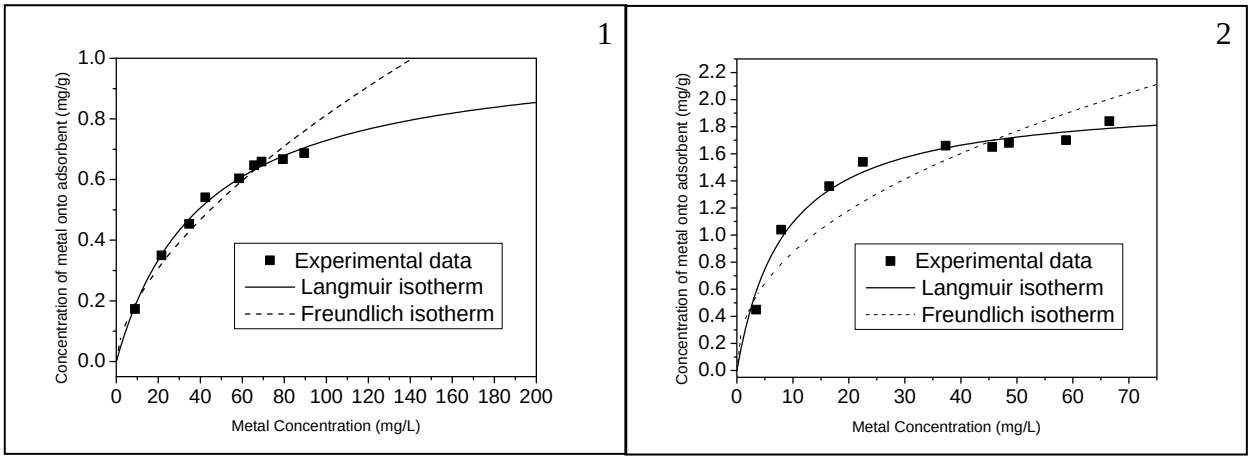

Figure 2: Adjusting of the Langmuir and Freundlich models to experimental data and equilibrium adsorption of uranium by raw coconut fiber (1) and activated coconut fiber (2).

Table 2: Adsorption Parameters for Uranium on Coconut Fiber

Biomass	Model	Parameters		
Coconut fiber	Langmuir	q_{max} (mg/g)	K_L (*l*/mg)	R^2
		1.03	0.02	0.99
	Freundlich	K_f (mg/g)	1/n	R^2
		0.050	0.60	0.94
Activated Coconut fiber	Langmuir	q_{max} (mg/g)	K_L (*l*/mg)	R^2
		2.01	0.12	0.97
	Freundlich	K_f (mg/g)	1/n	R^2
		0.32	0.43	0.79

In view of the adjusting of the isotherm model (Figure 2) and correlation regression coefficients (Table 2), the process of biosorption for both forms can be well described by Langmuir isotherm model. This model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules, assuming that the process occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface [18].

The maximum capacity q_{max} determined from the Langmuir isotherm defines the total capacity of the adsorbent as 1.03 mg/g and 2.01 mg/g by raw and activated biomass, respectively. The higher values of q_{max} for activated fiber show greater affinity of uranium for this form, which agrees with the values of KL obtained. The KL values are related to the energy of adsorption through the Arrhenius equation. The higher KL, the higher is the affinity of the sorbent for the sorbate [21].

Results of th total adsorption capacity obtained in this study was lower than those obtained by Parab et al (235.27 mg/g) [7] and Monteiro & Yamaura (27.00 mg/g) [22] who studied the uranium adsorption by coconut fiber in solutions prepared with deionized water at different pH . This difference coud be caused by the pH and chemical composition of the radioactive waste solution, which affected negatively the biosorption in this study.

4. CONCLUSIONS

The results showed that the coconut fiber in activated form removes more uranium than the raw one. The treatment appears to expose more metal binding sites, increasing the power of adsorption.

The pH value and presence of organic compounds in the waste affects the capacity of biosorption, additional studies are needed to understand the mechanisms involved.

The activated coconut fiber form can be used to remove uranium from liquid radioactive waste stored at the Radioactive Waste Management Laboratory IPEN-CNEN/SP.

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