Biosorption of Uranium, Am-241 and Cs-137 by Rice Husk – 15437

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ABSTRACT

New techniques involving the treatment of radioactive waste which combine simplicity and low cost have directed attention to biosorption. The biosorption term is used to describe the removal of metals, non-metals and/or radionuclides by a material from a biological source, regardless of its metabolic activity. Among the potential biomass, agricultural residues have very attractive features, as they allow for the removal of radionuclides present in the waste using a low cost biosorbent. The aim of this study was to evaluate the capacity of rice husk to remove uranium, Am-241 and Cs-137 in real radioactive liquid organic waste. This work was divided into two stages: i) Preparation and physical characterization of the rice husk and ii) Batch biosorption experiments. The parameters evaluated for physical characterization of biomass were morphological characteristics of rice husk, real and apparent density and surface area. The adopted contact times were 30 min, 1, 2 and 4 hours and the concentrations tested ranged between 10% and 100%. The results were evaluated by maximum experimental sorption capacity and isotherm and kinetics ternary models. The maximum capacity of the biosprtion for the rice husk with approximate values was of 0.5 mg/g of U (total), 14×10^{-6} mg/g of Am-241 and 20×10^{-9} mg/g of Cs-137. These results suggest that biosorption with rice husk can be applied in the treatment of radioactive liquid organic waste.

INTRODUCTION

The radioactive liquid wastes stored at Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP) are mainly generated from nuclear research centers. Several techniques can be employed to treat these wastes, such as precipitation, ion exchange resins and electrochemical processes. However, for removing low radionuclides ion concentrations in large solution volumes, these techniques are not effective for economic reasons [1, 2].

New techniques for the treatment of radioactive wastes which combine simplicity and low cost has directed attention to biosorption. This technique can be defined as the property of biomolecules or biomass bind to bind metals ions and reduce its concentration on aqueous solutions. It is a process which uses vegetable solid materials or microorganisms for retention, removal or recovery of heavy metals in a liquid environment [3].

In the field of biosorption, almost all researches have been conducted with metals and related elements, including actinides, lanthanides and metalloids. Among the biosorbents, agricultural residues stand out because they are a low-cost material beyond their sustainable use. The literature describes the efficiency of agricultural residues in biosorption [3, 4, 5, 6], including the rice husk [7, 8]. This residue is insoluble in water, has good chemical stability, high mechanical strength and functional groups in its structure such

as COOH, -OH, Si-OH, C-H, C=O, C=C, CH_2, CH_3, CO, Si-O-Si, C-C, Si-H, -O-CH_3, which confer quality as an absorbent material for heavy metal treatment in aqueous effluent [9, 10].

The biosorption capacity of rice husk can be improved modifying its structure by chemical treatments. Many authors have reported substantial increase in metals biosorption capacity by chemically modified biomasses, due to a greater active bond sites after the modification, an improvement of ion exchange properties and a formation of new functional groups, which promote the metals absorption [10, 11, 12].

The biosorption may be thus a method feasible, cheap, effective and easy to apply for the radioactive liquid waste treatment in the stored at Radioactive Waste Management Laboratory at IPEN/CNEN-SP. The aim of this study was to evaluate the rice husk capacity in removing uranium, Am-241 and Cs-137 from liquid radioactive wastes.

MATHERIALS AND METHODS

Biomass

The assessment of rice husk's ability to remove uranium in waste was performed using rice husk 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 rice husk; II) Physical characterization of the biomass, iii) Batch biosorption experiments.

Stage I: Preparation and Activation

The rice husk used was produced by Arroz Vale do Sul®. The husk 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 rice husk was activated (chemically modified) according to the procedure described by ROCHA et al [13]. 10 g of biomass was suspended in 50 mL 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.

Stage II: Physical Characterization

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

The morphological characteristics of rice husk 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].

Stage III: Biosorption Experiments

Biosorption experiments were performed using 0.2g of rice husk suspended in 10 ml 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. In the end of the experiment, the biomass was separated by filtration and concentration of radioisotope remaining in the filtrate was determined by ICP-OES and gamma spectrometry. All experiments were performed in triplicate.

Determination of U (Total) by ICP-OES

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.

Determination of Am-241 and Cs-137 by gamma spectrometry

Measurement of Cs-137 and Am-241 was accomplished through a Gamma Spectrometry (Canberra Industries, model GX4510) System (HPGe detector with beryllium window of 0.5 mm thickness). The detector shielding was composed of a lead wall (105 mm thickness), copper wall (2 mm), and lucite wall (4 mm). The activity concentration for Cs-137 and Am-241 was calculated through a specific energy photopeak of 661.66 and 59.54 KeV.

Metal uptake

The metal concentration in biosorbent was determined using the following equation:

$$q = \left(\frac{C_i - C_f}{m}\right) V$$

(Eq.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 dry mass of biosorbent (g).

**Mathematical modeling of the biosorption process**

The Langmuir and Freundlich models are commonly used in studies of biosorption with a single element but are not ideal for studying systems with more elements because they are not able to evaluate the combined effects of retaining two or more metals from biomass. This occurs because biosorption depends on the number of metals competing for sites of connections, associations between metal ions and the level of concentration of the metal [18].

In this work, the models used to represent the data of adsorption equilibrium in multicomponent systems were Langmuir ternary with two sites and Jain and Snowyink ternary obtained from modifications of the Langmuir isotherm model [19].

Langmuir ternary with two sites

In this model, it was assumed that the biosorbent has two types of sites, represented by B_U and B_C.

In B_U sites, adsorption occurs only with metal species M_1 and, thus, there is no competition for another species to occupy this site. In B_c sites there is competition among metal species (M_2, M_3) to occupy this sites. The kinetic equation for B_U sites can be written as:

$$B_U + M_1 \overset{k_1}{\underset{k_{-1}}{\leftrightarrow}} B_U - M_1 \quad K_1 = k_{-1}/k_1 \qquad \text{(Eq. 2)}$$
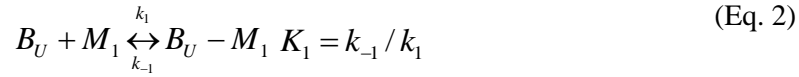
Assuming a system at equilibrium, the constant K_1 can be written as:

$$K_1 = \frac{[B_U - M_1]}{[M_1][B_U]} \qquad \text{(Eq. 3)}$$

The total number of sites is then the sum of free and occupied sites, represented as:

$$[B_{U0}] = [B_U - M_1] + [B_U] \qquad \text{(Eq. 4)}$$

where $[B_{U0}]$ is the total number of sites of the adsorbent without competition.

Applying equation (3) in equation (4) and isolating the term $[B_U - M1]$, obtains:

$$[B_U - M_1] = \frac{k[M_1][B_{U0}]}{[M_1]([B_{U0}] - [B_U - M_1])} \qquad \text{(Eq. 5)}$$

Isolating the term $[B_U - M_1]$ in the Equation (5) and dividing it by the molecular weight of the chemical species M_1, obtains:

$$q_{U1}^* = \frac{q_{mU}C_1^* b_{U1}}{1 + b_{U1}C_1^*} \qquad \text{(Eq. 6)}$$

where, q_{U1}^* is the amount of adsorbed species on B_U sites, q_{mU}, and $b_{U1} = 1/K_1$ are the Langmuir isotherm constants.

The kinetic equation for B_C sites can be written as:

$$B_C + M_2 \overset{k_2}{\underset{k_{-2}}{\leftrightarrow}} B_C - M_2 \quad K_2 = k_{-2}/k_2 \qquad \text{(Eq. 7)}$$

$$B_C + M_3 \overset{k_3}{\underset{k_{-3}}{\leftrightarrow}} B_C - M_3 \quad K_3 = k_{-3}/k_3 \qquad \text{(Eq. 8)}$$
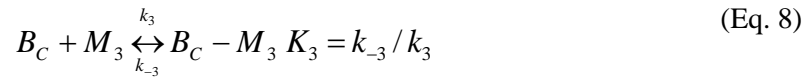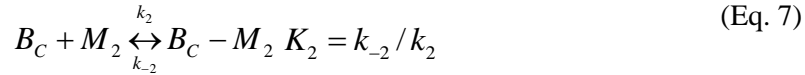
From the stoichiometric equations 7 and 8, we can obtain the following mathematical equations:

$$q_{C2}^* = \frac{q_{mC}C_2^* b_{C2}}{1 + b_{C2}C_2^* + b_{C3}C_3^*} \qquad \text{(Eq. 9)}$$

$$q_{C3}^* = \frac{q_{mC}C_3^* b_{C3}}{1 + b_{C2}C_2^* + b_{C3}C_3^*} \qquad \text{(Eq. 10)}$$

where, q_{C2}^* and q_{C3}^* are the amount of adsorbed species on B_C sites, q_{mC} and $b_{C2} = 1/K_2$, $b_{C3} = 1/K_3$

are constants of the model.

Jain and Snoeyink ternary model

Jain and Snoeyink [20] originally proposed isotherm model to predict the behavior of equilibrium sorption on activated carbon in binary systems. This model considers that there are two types of sites: one type is selective and adsorbs only one of the two metallic species and the other type adsorbs both species.

In this work, Jain and Snoeyink's model, adapted for the ternary model, considers two types of binding sites, represented by B_U and B_c. Thereby, in the B_U sites occurs adsorption only of the specie M_1 and in the B_c sites all species can be adsorbed. In addition, the binding adsorption between the metal species M_1 and sites B_U and B_C are distinct. From these considerations we can write the following mathematical equations:

$$q_1^* = \frac{q_{mU} C_1^* b_{U1}}{1 + b_{U1} C_1^*} + \frac{q_{mC} C_1^* b_1}{1 + b_1 C_1^* + b_2 C_2^* + b_3 C_3^*} \qquad \text{(Eq. 11)}$$

For the metal species M_2 and M_3 the equations are identical to previously developed model given by the following equations:

$$q_2^* = \frac{q_{mC} C_2^* b_{C2}}{1 + b_{C1} C_1^* + b_{C2} C_2^* + b_{C3} C_3^*} \qquad \text{(Eq. 12)}$$

$$q_3^* = \frac{q_{mC} C_3^* b_{C3}}{1 + b_{C1} C_1^* + b_{C2} C_2^* + b_{C3} C_3^*} \qquad \text{(Eq. 13)}$$

Where q_1^*, q_2^* and q_3^* are the amount of adsorbed species in the sites, q_{mC}, b_{U1}, q_{mC}, b_{C1}, b_{C2} and b_{C3} are constants of the model.

Estimation of parameters

The parameters of the model isotherms were estimated by using the simplex downhill algorithm to minimize the objective function, which gives

$$F = \sum_{j=1}^{n} \left(q_{1_j}^{EXP} - q_{1_j}^{MOD} \right)^2 + \left(q_{2_j}^{EXP} - q_{2_j}^{MOD} \right)^2 + \left(q_{3_j}^{EXP} - q_{3_j}^{MOD} \right)^2 \qquad \text{(Eq. 14)}$$

Where n is the number of experimental data, q_1^{EXP}, q_2^{EXP} and q_3^{EXP} represent respectively the experimental concentrations of ions in the biosorbent species M1,M2 and M3; q_1^{MOD}, q_2^{MOD} and q_3^{MOD} represent respectively the concentrations of ions species M_1, M_2 and M_3 in the biosorbent calculated by the model.

Normalization of data

With the objective to facilitate the construction and interpretation of the figures the concentrations were normalized using Eq. (15).

$$q_{norm_j} = \frac{q_j}{q_{\max_j}}$$

<div align="right">(Eq. 15)</div>

Where: q_{norm_j} is the concentration of the normalized element, q_j is the element concentration, $q_{\max_j}$ is the maximum concentration of the element and the index j represents the element which was being evaluated.

RESULTS

Physical Characterization

Figure 1 presents the micrograph images of rice husk 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.
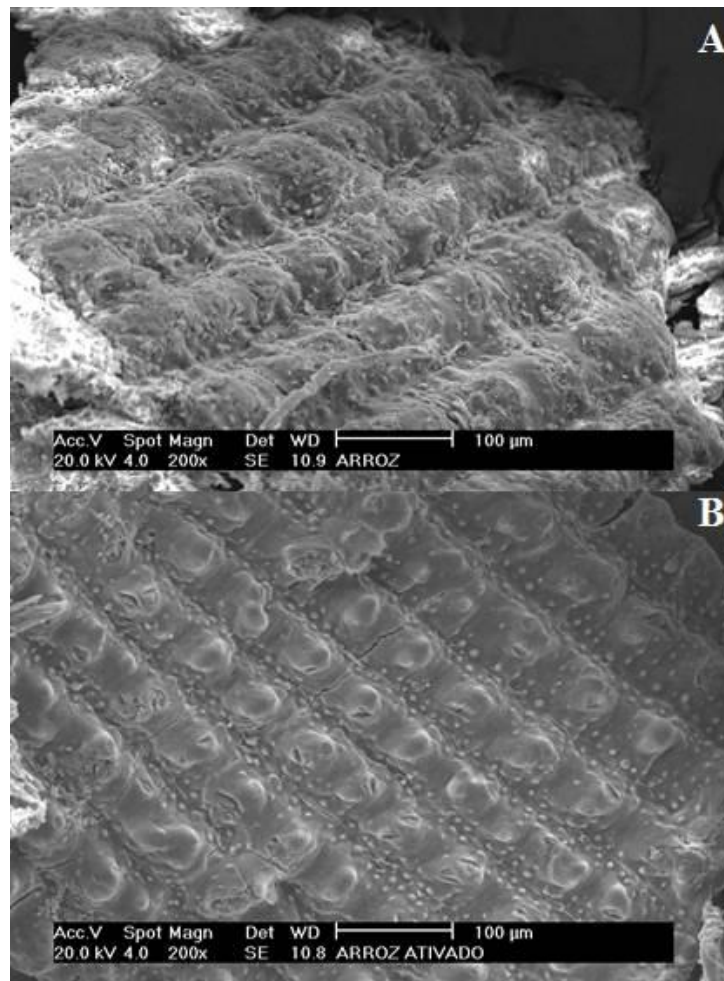
Fig. 1: Scanning electron microscopy of rice husk A (raw husk), B (activated husk).

Real Density, Apparent Density, and Surface Area

Table 1 shows the results of real and apparent densities and surface area of the rice husk. It can be observed the decrease of the values of all parameters in the activated forms of rice husks. This difference can be attributed to the changes caused by chemical treatment, which removed material from the surface of the biomass, as shown in Fig. 1.

TABLE 1: Real and apparent density and surface area for rice husk.

Biomass	Apparent density (g/cm³)	Real density (g/cm³)	Surface area (m²/g)
Raw husk	0.4	1.53	20.46
Activated husk	0.3	1.47	16.64

Biosorption Experiments

In Table 2, values of biosorption capacity at equilibrium observed within 2 hours of contact, for the U (total), Am-241 and Cs-137 are shown.

TABLE 2. Capacity values for biosorption in experimental equilibrium for the U (total), Am-241 e Cs-137.

Biomass	Uranium		Am-241		Cs-137	
	(mg/g)*	(mmol/g)*	(mg/g)*	(mmol/g)*	(mg/g)*	(mmol/g)*
Raw rice husk	0.47±0.13	(19.7 ± 5.5) $\times10^{-07}$	(14.4 ± 0.5) $\times10^{-6}$	(59.8 ± 2.0) $\times10^{-12}$	(19.8 ± 1.4) $\times10^{-9}$	(14.5 ± 1.0) $\times10^{-14}$
Activated rice husk	0.82±0.04	(34.5 ± 1.7) $\times10^{-07}$	(27.2 ± 1.5) $\times10^{-6}$	(11.3 ± 6.2) $\times10^{-11}$	(45.2 ± 8.9) $\times10^{-9}$	(33.0 ± 6.5) $\times10^{-14}$

* $\dot{x} \pm s$ (mean ± standard deviation)

In general, the best experimental sorption capacities were observed with rice husk activated being observed a difference in the sorption capacity between the two forms of approximately 100%.

The quantities removed from Am-241 and Cs-137 were much lower than uranium. This can be justified because their initial concentrations are much lower, making it impossible to conduct an analysis of the affinity between the elements and biomass. This is because the intermolecular forces acting in the sorption process are concentration dependent [21].

Sorption isotherms

The isotherm models of Langmuir ternary two sites and Jain and Snoeyink ternary were used to describe the equilibrium of the system. The parameter values obtained in models qmax1 (maximum biosorption capacity at site 1), b (rate of adsorption and desorption), qmax2 (maximum biosorption capacity at site 2), bb1 (rate adsorption and desorption of uranium in two sites), ADD (relative error) and ADD mean (mean relative error of the three metals) are presented in Table 3. The indices 1, 2 and 3 refer respectively to metals: uranium (total), Am-241 and Cs-137. Graphical representations of fit of all models are shown in Fig. 2 and 3.

TABLE 3. Isotherm parameters calculated to husk rice raw and activated.

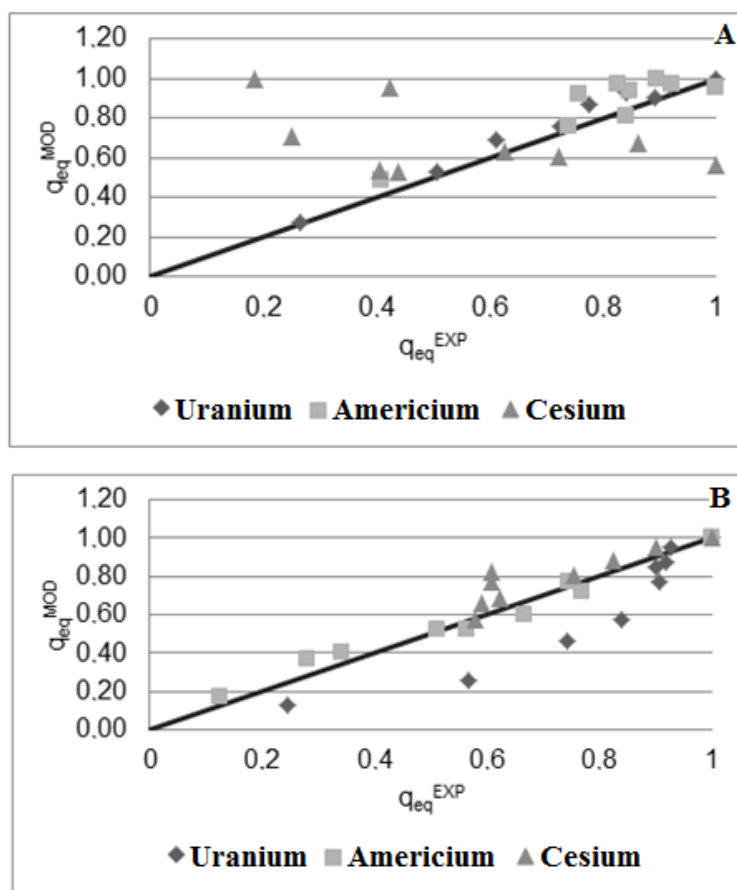| Parameters	Biomass			
	Raw rice husk		Activated rice husk	
	Langmuir ternary two sites	Modified Jain and Snoeyink ternary	Langmuir ternary two sites	Modified Jain and Snoeyink ternary
qmax1(mmol/g)	9.62×10^{-04}	2.61×10^{-06}	1.92×10^{-10}	5.74×10^{-06}
b_1 (L/mmol)	-	2.79×10^{03}	-	8.16×10^{03}
b_2 (L/mmol)	1.38×10	1.09×10^{04}	3.63×10^{08}	1.85×10^{04}
b_3 (L/mmol)	5.19×10	2.97×10^{04}	$1.05E+08$	4.53×10^{03}
qmax2(mmol/g)	2.69×10^{06}	1.21×10^{-06}	3.69×10^{-06}	6.85×10^{-07}
bb_1 (L/mmol)	5.61×10^{03}	2.92×10^{03}	4.10×10^{04}	1.71×10^{04}
ADD_1	3.14	7.38	7.70	15.94
ADD_2	41.91	32.81	12.75	11.49
ADD_3	0.17	17.53	7.97	8.55
ADD (mean)	15.07	19.24	9.47	11.99

Fig. 2. Adsorption capacity in experimental equilibrium and predicted for raw rice husk in accordance with the models (A) Langmuir ternary two sites; (B) Jain and Snoeyink ternary
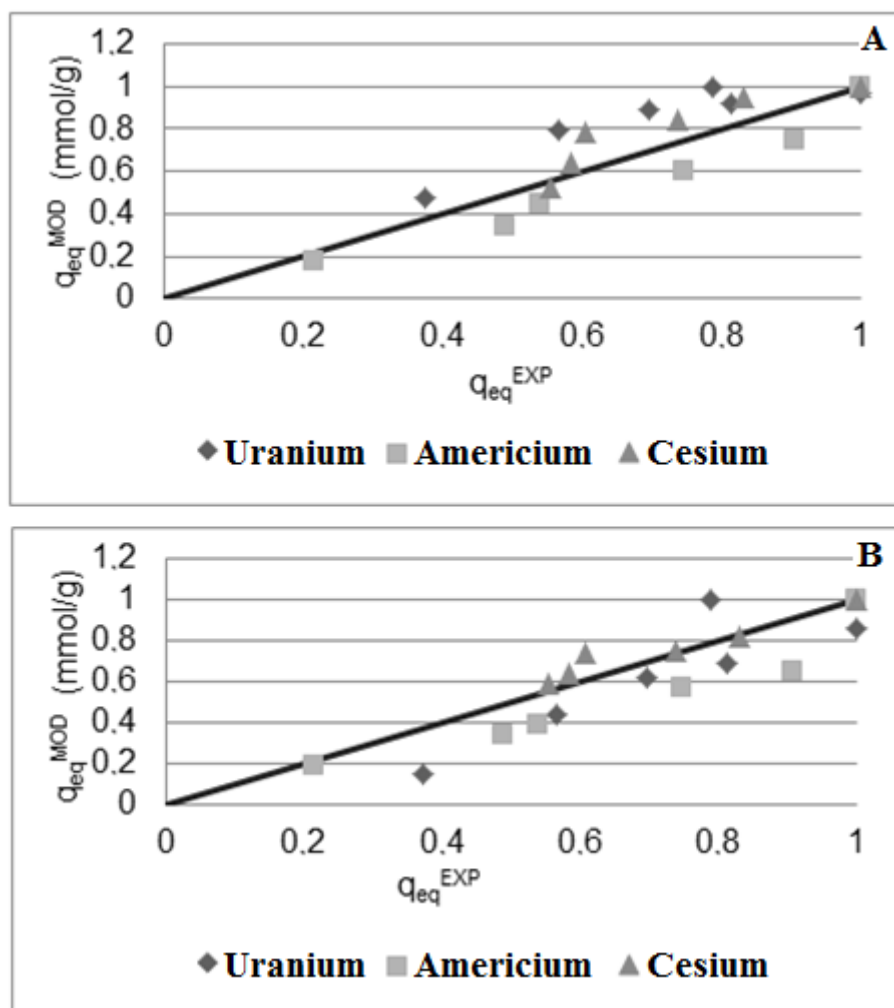
Fig. 3. Adsorption capacity in experimental equilibrium and predicted for activated rice husk in accordance with the models (A) Langmuir ternary two sites; (B) Jain and Snoeyink ternary

Considering the mean relative error values (TAB 3) the biosorption process for raw and activated rice husk was best represented by the model isotherm Langmuir ternary with two sites, indicating that the adsorption of uranium occurs at different a site of Am-241 and Cs-137.

The parameter values of b in the isotherms are related to the affinity of the metal sites of the adsorbent material. The values of these parameters when compared with the raw and activated biomass were distinct, showing that the chemical treatment modified the properties of the adsorbent and hence influence its adsorption capacity.

For all biomass and all models evaluated, the parameter values b, showed the same affinity sequence, or b2 (Am-241)> b1 (U)> b3 (Cs-137). This behavior shows that the models are consistent for evaluation of experimental data.

There were no reports in the literature describing the biosorption of a ternary system (U, Am-241 and C-137) by rice husk, which does not allow a direct comparison of the results obtained in this work. However, a survey of papers that used U, Am-241 and C-137 in isolation, simulating the radioactive

waste was conducted.

The biosorption of uranium obtained in this study was lower than that observed by KAUSAR et al [22] who reported a sorption capacity of around 40 mg/g for raw rice husk subjected to different treatments. The low biosorption observed in this work can be caused by tributyl phosphate presence in the waste, which is a known uranium extractant.

There are no reports in the literature describing the biosorption of americium by rice husk. When compared to other biosorbents, the rice husk showed a lower removal capacity, for example, Rhizopus arrihizus [7], Saccharomyces cerevisiae [8] and Candida sp [9] remove practically 100% of Am-241 in solution. However, variations in experimental conditions such as time, temperature and biosorbent/waste ratio should be tested to make a better comparison between the biosorbents and determining the mechanisms of Am-241 removal.

The biosorption capacity of Cs-137 observed in this study was similar to that obtained by Mishra et al [11] who observed a removal of approximately 40×10^{-9} mg/g of Cs-134 by rice husk. This low sorption capacity for cesium could be explained by a high concentration of hydrogen ions in the medium (pH = 4), which compete with the binding sites for Cs present in the rice husk [11].

CONCLUSIONS

The results showed that the rice husk in activated form removes more uranium than the raw one. The treatment appears to expose more metal binding sites, increasing adsorption capacity.

The models of ternary isotherm were effective for the evaluation of simultaneous biosorption of uranium, cesium and americium in organic liquid radioactive waste.

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 rice husk form showed good potential for the treatment of radioactive liquid waste stored at the Radioactive Waste Management Laboratory of IPEN-CNEN/SP.

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