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

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INTRODUCTION

To remove low radionuclides concentrations in large volumes of radioactive wastes, conventional techniques are not effective. New techniques which combine simplicity and low cost has directed attention to biosorption, a process which uses vegetable solid materials or microorganisms for retention, removal or recovery of metals in a liquid.

Rice husk can be used as an absorbent material for heavy metal treatment in aqueous effluent with success due to its characteristics. Chemical modifications can improve the biosorption capacity and the effectiveness of the process.

The biosorption may be a method feasible, cheap, effective and easy to apply for the radioactive liquid waste treatment. The aim of this study was to evaluate the rice husk capacity in removing uranium, Am-241 and Cs-137 from liquid radioactive wastes.

MATERIALS AND METHODS

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

Rice Husk → Washed (distilled water) → Dried for 24 hours (80°C) → Sterilized by UV radiation → Chopped and Sieved → particle size 0.297 to 0.500 mm

Stage I: Activation

Rice Husk (10g) + 50 mL of 0.5M HNO_3 solution → Stirred 240rpm - 1h - room temperature → Filtered and washed + 100 mL of 0.5M NaOH solution → Stirred 240rpm - 1h - room temperature → Filtered, Washed Neutralized → Dried at 40 °C → Activated rice husk

Stage II: Physical Characterization

Morphological Characteristics	Real Density	Apparent Density	Surface Area
Scanning Electron Microscopy (SEM)	Helium Picnometry	Filling a beaker and weighting	BET method Micromeritcs

Stage III: Biosorption Experiments

Rice husk Activated or not (0.2g) + Radioactive waste (10 mL) concentrations ranged from 10 to 100%. → Stirred - room temperature - 150rpm - 2h → Filtered

Filtered → Radionuclides determination; Uranium (Total) by ICP-OES; Am-241 and Cs-137 by gamma spectrometry → metal uptake

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

MATERIALS AND METHODS (cont.)

Mathematical modeling of the biosorption process

Langmuir ternary with two sites

Bu sites: adsorption occurs only with metal species M1 → **no competition for another species to occupy these sites**

$$q^*_{U1} = \frac{q_{mU} C^*_1 b_{U1}}{1 + b_{U1} C^*_1}$$

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.

Bc sites: adsorption occurs with two species (M2, M3) → **competition among metal species to occupy these sites**

$$q^*_{C2} = \frac{q_{mC} C^*_2 b_{C2}}{1 + b_{C2} C^*_2 + b_{C3} C^*_3}$$

$$q^*_{C3} = \frac{q_{mC} C^*_3 b_{C3}}{1 + b_{C2} C^*_2 + b_{C3} C^*_3}$$

where, q^*_{C2} and q^*_{C3} are the amount of adsorbed species on Bc sites, q_{mC} and $b_{C2} = 1/K_2$, $b_{C3} = 1/K_3$ are constants of the model.

Jain and Snowyink ternary (modified)

Bu sites: occurs adsorption only of the specie M1

$$q^*_1 = \frac{q_{mU} C^*_1 b_{U1}}{1 + b_{U1} C^*_1} + \frac{q_{mC} C^*_1 b_1}{1 + b_1 C^*_1 + b_2 C^*_2 + b_3 C^*_3}$$

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.

Bc sites: all species can be adsorbed

$$q^*_2 = \frac{q_{mC} C^*_2 b_{C2}}{1 + b_{C1} C^*_1 + b_{C2} C^*_2 + b_{C3} C^*_3}$$

$$q^*_3 = \frac{q_{mC} C^*_3 b_{C3}}{1 + b_{C1} C^*_1 + b_{C2} C^*_2 + b_{C3} C^*_3}$$

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.

RESULTS AND DISCUSSION

Physical Characterization

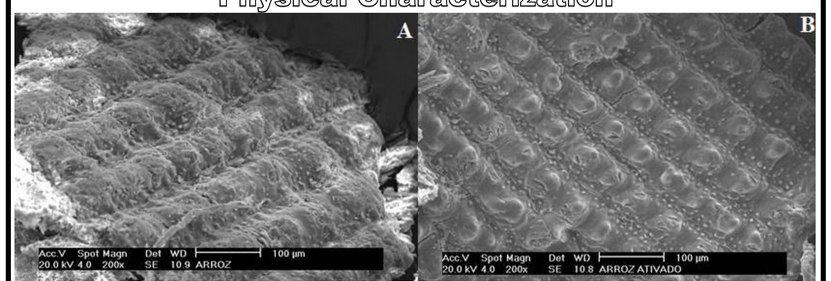

Fig. 1: SEM of rice husk A (raw husk), B (activated husk). HNO3/NaOH solutions were able to remove surface materials on the activated form.

RESULTS AND DISCUSSION (Cont.)

Real Density, Apparent Density, and Surface Area

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

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 SEM.

Biosorption Experiments

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) x10^{-07}	(14.4 ± 0.5) x10^{-6}	(59.8±2.0) x10^{-12}	(19.8±1.4) x10^{-9}	(14.5±1.0) x10^{-14}
Activated rice husk	0.82±0.04	(34.5±1.7) x10^{-07}	(27.2 ± 1.5) x10^{-6}	(11.3±6.2) x10^{-11}	(45.2±8.9) x10^{-9}	(33.0±6.5) x10^{-14}

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

Sorption isotherms

TABLE. 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)	9.62x10^{-04}	2.61x10^{-06}	1.92 x10^{-10}	5.74 x10^{-06}
b_1 (L/mmol)	-	2.79x10^{03}	-	8.16 x10^{03}
b_2 (L/mmol)	1.38x10	1.09 x10^{04}	3.63 x10^{08}	1.85 x10^{04}
b_3 (L/mmol)	5.19 x10	2.97x10^{04}	1.05 x10^{08}	4.53 x10^{03}
qmax2(mmol/g)	2.69 x10^{06}	1.21 x10^{-06}	3.69 x10^{-06}	6.85 x10^{-07}
bb_1 (L/mmol)	5.61x10^{03}	2.92 x10^{03}	4.10 x10^{04}	1.71 x10^{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

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.

CONCLUSION

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.