Biosorption of Uranium with *Sargassum filipendula* – Use in Treatment of Effluents of Laboratories

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Abstract. International and National Standards establish methodologies for the management of radioactive waste in order to comply with radiological protection principles. Thus, it is necessary to find alternatives with both low cost and effective results. This work studied the use of brown algae *Sargassum filipendula* in its ability to remove uranium in waste generated in the environmental analysis laboratories of the Institute of Radiation Protection and Dosimetry. At first, the kinetics of biosorption was studied. This experiment was conducted on a batch at concentrations of 1 mg/L and 100 mg/L. Mathematical models of the first and second order were used to fit the experimental results. In evaluating the maximum removal capacity by marine biomass on a batch, different uranium concentrations were analyzed, and isoterms of biosorption were plotted. The experimental results have been adjusted by Langmuir and Freundlich models. The Freundlich model presented the best correlation coefficients (0.99 and 0.94) for studies with an hour and three hours of contact, respectively. In order to determine the best conditions for removal of uranium using the *Sargassum filipendula*, it was necessary to hold experiments in a continuous flow. A study on the critical height of bed depth was carried out by filling a column with different masses of seaweed. It was obtained a lower outlet concentration of uranium (0.07 mg/L) in 40 cm bed depth. This best height of bed was applied to the waste treatment of SEANA laboratories. It was monitored the increase of retention in biomass for a known quantity of uranium. The results showed an excellent uptake of uranium (1.25 mg U/g of biomass) even in the presence of other metals and reagents. Decontamination of the effluent for uranium reached values below those set by CONAMA for water classes I and II, making it possible to reuse the water.

KEYWORDS: Uranium, biosorption, *Sargassum filipendula*, kinetics, equilibrium

1. Introduction

Worldwide, there is an increasing search for alternative techniques to reduce the final volume or suitable storage conditions for radioactive materials, before their final discharge.
Uranium, $_{92}U^{238}$, has an isotopic ratio equivalent to 99.27% and a half-life equal to 4.47×10^9 years, while $_{92}U^{235}$ has an isotopic ratio equivalent to 0.72% and a half-life equal to 7.04×10^8 years and $_{92}U^{234}$ an isotopic ratio equivalent to 0.0055% and a half-life to 2.45×10^5. This radioisotope can be enriched into its $_{92}U^{235}$ form, and be used as nuclear fuel. In the present work measurements of uranium are made, as well as on their chemically similar isotopes.
Among the available alternatives for the treatment of effluents containing this element there are ion-exchange, chemical precipitation, adsorption with activated carbon and membrane filtration. However, these techniques are frequently limited by technical and economic reasons [1, 2, 7, 8, 12]. From 1980, several studies started with the use of live or dead biomasses, a process that is directly affected by physico-chemical factors, such as pH, type and concentration of metal in solution, biomass concentration, temperature, kinetic and equilibrium between solid and liquid phases [5, 9, 11, 15, 17].
The effect of pH in the uranium uptake capacity by the seaweed *Cystoseira índica* was studied by KHANI *et al.* (2006) [9], indicating that it was maximized at pH 4.0. STRANDBERG *et al.* (1981) [16] also proved that microbial cells of *Saccharomyces cerevisiae* and *Pseudomonas aeruginosa* recovered uranium from solution at pH 4. Other types of biomass, such as *Leninist sajor-caju* [4], Cork biomass [14] and a cyanobacterial bloom [10] also proved to be suitable for the recovery of uranium.

The literature describes the ability of seaweeds to concentrate radionuclides at their surface, through biosorption [13]. This property is due to the presence of polysaccharides, mainly alginic acid and fucoidan, both present at the cell wall of brown seaweeds [6].

2. Material and Methods

2.1 Standard Uranium Solution

The uranium solution 1000 mg/L was prepared and the final concentration was determined through "Potentiometric Titration of Davies and Gray/NBL" [3]. This solution was used to prepared all solution used at the experiments.

2.1.1 Biomaterial

The biomass used in this work was the brown seaweed *Sargassum filipendula* obtained from the Northeastern Coast of Brazil, in the State of Pernambuco (8º 03' 17.48" South - 34º 52' 15.97" West). The classification of the biomass is presented: **Domain** *Eukarya*, **Kingdom** *Chromista*, **Sub-kingdom** *Chromobiota*, **Intra-kingdom** *Heterokonta*, **Phylum** *Ochrophyta*, **Sub-phylum** *Phaeista*, **Intra-phylum** *Chrysista*, **Superclass** *Phaeistia*, **Class** *Phaeophyceae*, **Order** *Fucales*, **Family** *Sargassaceae*, **Genus** *Sargassum*, **Species** *filipendula*.
The biomass was washed with tap water to remove sand and particulate materials from the surface. After washing, the biomass was exposed to the sun during 8 hours and later at 50 ºC for 24 hours.

2.2 Kinetic Study of Uranium Biosorption

This study was performed in order to determine the time needed to reach equilibrium between the biomass and the radionuclide solution. This was performed with different uranium standard solution, at pH 4, using acetate buffer solution, 0.17M ammonium acetate and 1M acetic acid solution, with a final volume of 50 mL and 0.1 g of *Sargassum filipendula*.

2.3 Equilibrium Study of Uranium Biosorption

In this study, several uranium solutions were prepared, at different concentrations (0.02 to 1.0 mg/L). The objective of these experiments was to determine the maximum uranium uptake capacity by the biomass (0.1 g) in 1 h and 3 h of contact between the biomass and uranium solution, at 25 ^{o}C.

These experiments were also conducted in triplicate and values reported correspond to average values. Experimental values were fit to classical Langmuir and Freundlich adsorption equations.

3. Results and Discussion

3.1 Kinetic Study of Uranium Biosorption

Figure 1 presents the results obtained from the kinetic study of the biosorption of uranium by *Sargassum filipendula* biomass using the secondary standard Uranium solutions of 1 mg/L and 100 mg/L uranium.

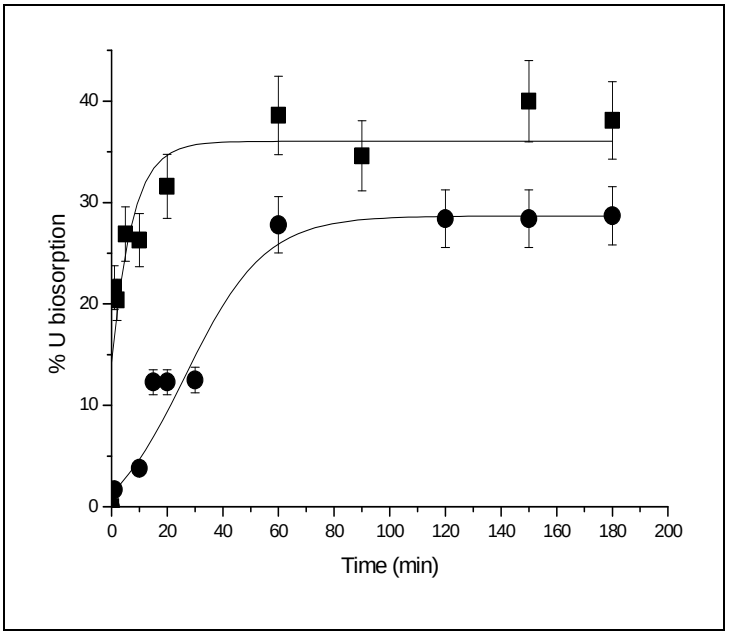

Figure 1 – Kinetic behavior during the biosorption of uranium by the brown seaweed *Sargassum filipendula*. ■ 1 mg/L, ● 100 mg/L.

Figure 2 shows the results observed for the kinetic modeling of the experimental data obtained for the less concentrated solution, according to the second-order model. The figure representing the fit of experimental data to first-order model was not presented due to the less favorable fit to the model. However, the mathematical data from both models are presented in Table 1.

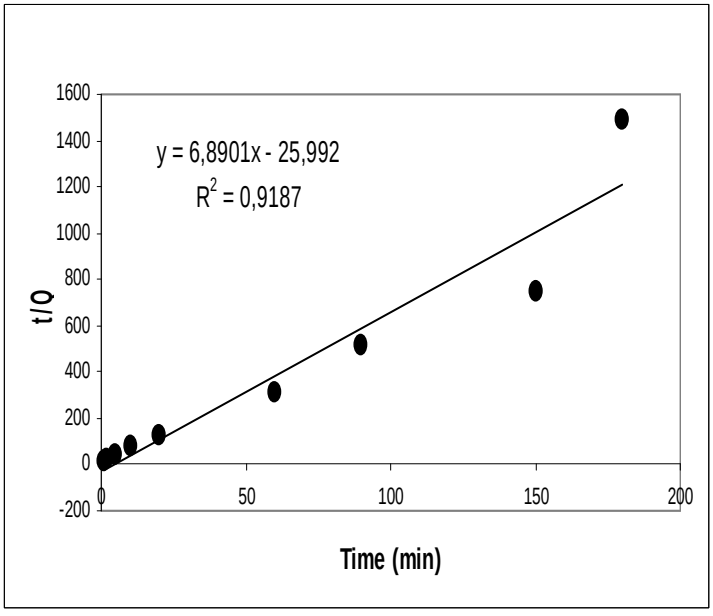

Figure 2 – Kinetic modeling of the results from the biosorption of uranium by the brown seaweed *Sargassum filipendula* with the second-order model - 1 mg/L.

Table 1: Theoretical and experimental values obtained for the kinetic study of uranium biosorption by *Sargassum filipendula* biomass for a diluted uranium solution - 1 mg/L uranium (0.050 mg) and a concentrated uranium solution - 100 mg/L (5 mg) uranium.

Kinetic Model	k_{ads}	Theoretical Q_e (mg/g)	Experimental Q_e (mg/g)	R^2
1 mg/L Uranium				
First-order	0.0023	0.034	0.200	0.0316
Second-order	0.0008	0.145	0.200	0.9187
100 mg/L Uranium				
First-order	0.0239	12.38	14.60	0.9364
Second-order	144.19	18.38	14.60	0.9163

The results from Figure 2 and Table 1 indicate a better fit of the experimental data to the second-order model, in comparison to the first-order model, for the less concentrated uranium solution. This conclusion could be reached due to the good correlation coefficient obtained for this model. To corroborate this conclusion, the theoretical Q_e value predicted from the second-order model (0.145 mg/g) is closer to the experimental Q_e value (0.200 mg/g), in comparison to the value predicted by the first-order model (0.034 mg/g).

3.1 Equilibrium Study of Uranium Biosorption

The table 2 presents the constants, as well as the correlation coefficients calculated, obtained from the fit of experimental data to both models during the biosorption of uranium by the seaweed *Sargassum filipendula*, at 1 and 3 hours of contact between the biomass and the radionuclide solution.

Table 2 – Parameters from the Langmuir and Freundlich models – Biosorption of Uranium by *Sargassum filipendula* at 1 h and 3 h of contact times.

Langmuir			**Freundlich**		
1 h contact					
Q_0 (mg/g)	K_L (L/mg)	R	n	K_f	R
262.4 x 10^{-3}	0.06	0.8329	1.08	10.23	0.8562
3 h contact					
Q_0 (mg/g)	K_L (L/mg)	R	n	K_f	R
252.5 x 10^{-3}	0.05	0.7007	1.10	9.51	0.8509

The correlation coefficients obtained indicate that the experimental data fit well to the Freundlich model, in comparison to the Langmuir model, in both cases (Table 2).

The most important parameter from the Freundlich model is ***n*,** a parameter that is related to the distribution of ions onto the active binding sites on the biomass. The values of *n* were 1.08 and 1.10, for 1h and 3h of contact time between the biomass and the radionuclide solution, respectively. Values of n higher than 1.00 indicate a favorable condition for the uptake of the radionuclide, under the experimental conditions used.

KHANI *et al.* (2006) [9] described the Freundlich equation as the best model to describe the biosorption of uranium by the seaweed *Cystoseira indica*. The present results, however, are distinct from the ones obtained by PICARDO *et al.* (2006) [13] with the radionuclide Thorium. Even though the work of PICARDO *et al.* (2006) [13] indicated a similar kinetic behavior between Thorium and Uranium (present work), this similarity was not true for equilibrium studies.

In that work [13] it was observed a saturation of the reaction sites available for the uptake of Thorium, a fact clearly observed due to the stabilization of the loading capacity of *Sargassum filipendula*

biomass, indicating a good fit to Langmuir model. In the present work, however, data were fit to Freundlich model, representing an increasing uptake of uranium, probably with the formation of polychains during biosorption.

3.2 Equilibrium Study of Uranium Biosorption in Continue Model

Experiments were conducted to determine the critical amount (or minimum) biomass, *Sargassum filipendula*, to be used in the decontamination treatment of effluents produced in the laboratories of environmental analyses of SEANA (Office of Environmental Analysis).

To determine the amount of biomass critical need for greater absorption of uranium, was calculated the mass of uranium removed by the biomass and the mass of uranium waste in different quantities used in various experiments performed. The experiments were made with standard solution of uranium by adjusting the pH to 4 with buffer solution and then used a real effluent from the laboratory only adding to a known amount of standard uranium so that it could do a control experiment.

4. Conclusions

- The kinetic behavior observed during uranium biosorption by *Sargassum filipendula* biomass indicated a good fit between the experimental data and a second-order kinetic model, both for dilute and concentrated uranium solutions.
- Equilibrium between the biomass and Uranium solutions, was reached after 60 minutes, indicating a rapid uptake process, both for dilute and concentrated uranium solutions.
- Experimental data fit well to Freundlich model, both for 1h contact time and 3h contact time, indicating a possible polychain biosorption.
- The capture of uranium in the treatment of real effluent, on a continuous, was a mean of 1.25 mg/g of biomass, slightly higher than the value obtained when using only standard solution of uranium (1.05 mg/g). The system showed stability in the treatment of the standard solution of uranium and the real effluent.
- The use of aquatic plants dead and dried for removal of metals, have significant advantages over the use of microorganisms, due to high efficiency in capturing the metal, minimizing the volume of mud chemical or biological for further deposition. Moreover, there is no need for nutrients for growth, low cost associated with its recovery, storage, transport and handling.

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