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BIOSORPTION OF URANIUM BY AZOLLA SP

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ABSTRACT

Radioactive liquid waste needs special attention and requires suitable treatment before deposition. Among the potential technologies under development for the treatment of liquid radioactive wastes the biosorption has been highlighted by being an efficient and low cost technique. Biosorption process involves the exchange of ions contained in the biomass matrix by others present in solution. There are many biomasses that could be applied in treatment of radioactive wastes, for example, agricultural residues and macrophytes. The aim of this study is evaluate the ability of the *Azolla sp.*, a floating aquatic plant, to absorb uranium in solution. *Azolla sp*. is a macrophyte that has been used to treat effluents containing heavy metals. The biosorption capacity of uranium by *Azolla sp.* was experimentally determined and modeled by isotherms. Experiments were performed to determine metal uptake, and then the solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The isotherms applied to model the data was Langmuir, Freundlich, Sips Toth, Redlich Peternson, Two-Site-Langmuir, Radke Prausnitz to develop a technique for the treatment of radioactive liquid waste generated at the Nuclear and Energy Research Institute – IPEN-CNEN/SP, Brazil.

Keywords: radioactive waste, biosorption, macrophyte, azolla sp., isotherms

1. INTRODUCTION

One important step in the management of liquid radioactive wastes is the chemical treatment, which usually requires many procedures when the chemical composition of the waste is complex. The objective of the treatment may be to achieve one or many the following results: reduce the volume by separating inactive components, modify chemically the materials present to facilitate the immobilization, separation of long- lived radionuclides, etc. Some of the common processes are evaporation, precipitation and ion exchange, which are used in the industry for the removal of heavy metal in wastewater.

Currently, the most efficient techniques used to treat radioactive waste are incineration and evaporation. However, they are expensive and unfeasible for low volume of radioactive waste. Consequently, biosorption may be an alternative in removing metals since low cost materials can be employed, for example, biomasses residues that do not require high technology for their production or acquisition [1]. There are several studies reporting the biosorption ability of different types of biomass to remove radionuclides from solution, such as banana peels [2], coconut fiber [3], *Padina sp.* algae [4] and *Catenella repens*, red algae [5].

Biosorption processes are a solid-liquid separation and occur when the ions of interest (adsorbate) migrate from the solution to the solid phase (sorbent). The biosorbent chosen in this process should have certain characteristics to be considered a good biosorbent, such as efficient and rapid sorption/desorption of the metal, high selectivity, reusability and easy separation from solutions [6]. Macrophytes may have all of these characteristics. They are aquatic plants with very wide geographical distribution that grow in submerged environments or water surface. Such plants showed high capacity for the removal of heavy metals such as Cu 2+, Cd 2+, Pb 2+, Ni 2+, in effluents [7]. One example is the macrophyte *Azolla sp*. commonly called as water bracken which is used as fertilizer and also in the treatment of industrial effluents for the removal of heavy metals.

The aim of this study is evaluate the ability of the *Azolla sp*., a floating aquatic plant, to absorb uranium in solution.

2. MATHERIALS AND METHODS

2.1. Biomass

The macrophyte *Azolla sp.* used in this research was provided by the State University of Western Paraná (UNIOESTE).
The *Azolla sp.*, was washed with distilled water, dried at 60 ° C for 24h, and then sterilized by UV radiation for about 30 minutes, to avoid deterioration by proliferation of fungi or bacteria. Then, the material was grinded and sieved to separate particle sizes between 0.297mm and 0.125mm for use in subsequent biosorption experiments. This range of particle size was selected in previous studies conducted to FERREIRA [8].

2.2. Preparation of Solution

The uranium solution used in biosorption experiments was prepared with uranium nitrate dissolved in distilled water, adjusted to pH 4.0 because this is the value of the radioactive liquid waste containing uranium stored at IPEN – CNEN/SP. In addition, there are several reports in the literature indicating that this pH favors the biosorption of uranium [9 and 10].

2.3. Biosorption Experiments

The biosorption assays were performed in batch system 0.2 g of biomass was added in vial containing 10 mL of solution. The samples were shaken in a mechanical stirrer at 130 rpm, at room temperature, for the time required to reach equilibrium. Then the solution was filtered to separate biomass and solution. The concentration of the solution was determined by atomic emission spectrometry with inductively coupled plasma (ICP-OES) model 7000DV Perkin Elmer, previously calibrated with standard uranium solutions. The wavelength used for the determination of uranium was 424.167 nm and the result is expressed as the mean of measurements in triplicate.

Experiments were performed to determine the time required for the system to reach equilibrium. Subsequently, biosorption was evaluated in function of the uranium concentration. Solutions with varying concentrations (from 6.30E-04 to 2.52E-03 mmol/L, increment of 2.10E-04 mmol/L) were prepared and all experiments were performed in quadruplicate.

2.4. Data Evaluation

The consumption of uranium biomass was determined by using the following equation:

$$q = \frac{(C_0 - C)V}{m} \quad (01)$$

Where **q** = equilibrium uranium absorption in mmol / g; **Co** = initial concentration of uranium in mmol / L; **C** = equilibrium concentration in mmol / L; **V** = volume of the solution L; biosorbent and **m** = mass in g.

The models isotherms were used to describe the uranium removal capacity in the solution when the system is in equilibrium. However, these models provide hypotheses that cannot be fully applied to the biosorption systems due to variety of structural components present in biomass [11]. They are useful, however to quantitatively describe sorption data in the range of concentrations studied.

3. RESULTS

3.1. Equilibration Time

The uptake of uranium species as a function of contact time is shown on Figure 1. The contact time between the biomass and the solution was varied from 5 minutes to 240 minutes.

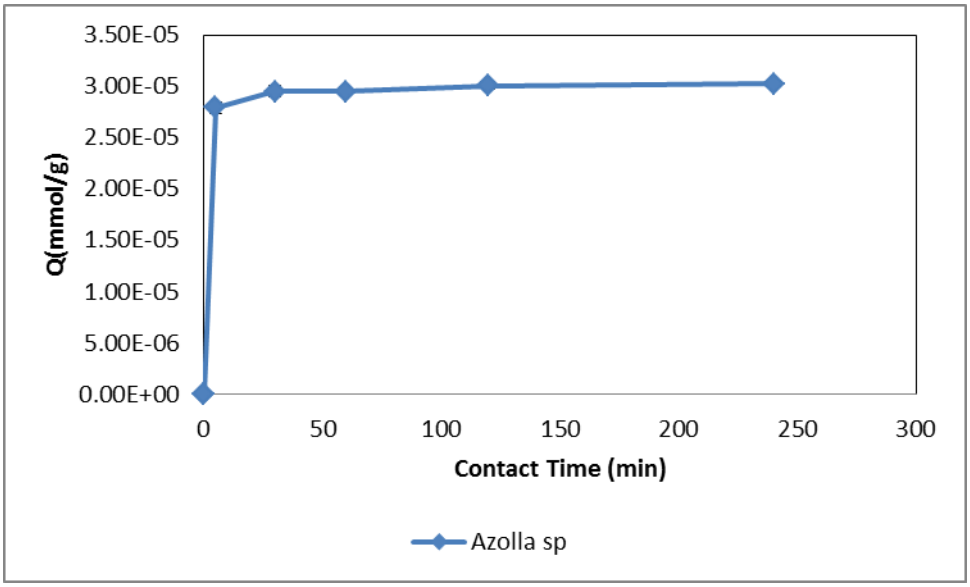

Figure 1. Uranium uptake by *Azolla sp.* as a function of time, initial metal concentration 6.05E-04 **mmol/L. The error bar represents the standard deviation amongst the results.**

Figure 1 shows that the metal concentration on biomass increases to reach equilibrium, That behavior is expected since as uranium accumulates in the biomass in the adsorption sites and occurring dynamic equilibrium the interaction between the ions and the biomass changes and the rate of desorption approaches the rate of biosorption.

Figure 1 shows that the metal concentration in the biomass increased as a function of time and the dynamic equilibrium is reached in about 30 minutes of contact of the solution with biomass. In other experiments the contact time was set at 30 minutes.

3.2. Concentration of solutions

The table 1 shows the results of biosorption experiments carried out to evaluate in function of the uranium concentration.

Table 1.Variation on concentrations of uranium in the solutions.

$C_{Theorical}$ **(mmol/L)**	C_0 **(mmol/L)**	C_f **(mmol/L)**	**q (mmol/g)**
6.30E-04	6.07E-04	3.49E-06	3.02E-05
8.40E-04	8.84E-04	4.83E-06	4.39E-05
1.05E-03	1.04E-03	6.64E-06	5.18E-05
1.26E-03	1.27E-03	6.00E-05	6.03E-05
1.47E-03	1.50E-03	6.20E-05	7.20E-05
1.68E-03	1.67E-03	7.07E-05	7.99E-05
1.89E-03	1.91E-03	1.12E-04	8.98E-05
2.10E-03	2.01E-03	1.00E-04	9.56E-05
2.31E-03	2.26E-03	1.36E-04	1.06E-04
2.52E-03	2.53E-03	1.68E-04	1.18E-04

$C_{Theorical}$ = theorical concentration; C_0= initial concentration; C_f = final concentration; q = equilibrium uranium absorption

3.3. Biosorption Isotherms

The adsorption isotherms represent the equilibrium between the biomass and the solution in a predetermined condition.

Adsorption models used to describe the data within the range of concentrations are given in Table 2, and Table 3 shows the parameters of the models and how they relate to the experimental data.

Table 2. Adsorption isotherm models used to describe data.

Model 1	Equation
Langmuir [12]	$q_e = \frac{\mathrm{QbC_e}}{1 + \mathrm{bC_e}}$
Freundlich [12]	$q_e = K_f {C_e}^{1/n}$
Sips [12]	$q_e = \frac{\mathrm{K_s} {C_e}^{\beta s}}{1 + \mathrm{a_s} {C_e}^{\beta s}}$
Toth [12]	$q_e = \frac{\mathrm{K_T C_e}}{(\mathrm{a_T} + C_e)^{1/t}}$
Redlich Peterson [12]	$q_e = \frac{\mathrm{K_r C_e}}{1 + \mathrm{a_r} {C_e}^{g}}$
Two – Site Langmuir [13]	$q_e = \frac{\mathrm{Q_1 b_1 C_e}}{1 + \mathrm{b_1 C_e}} + \frac{\mathrm{Q_2 b_2 C_e}}{1 + \mathrm{b_2 C_e}}$
Radke – Prausnitz [12]	$q_e = \frac{\mathrm{a_{RP}} r_R {C_e}^{\beta R}}{\mathrm{a_{RP}} + \mathrm{r_R} {C_e}^{\beta R - 1}}$

Qe= amount of adsorbate in the adsorbent at equilibrium (mg/); Q = maximum monolayer coverage capacities (mg/g); Ce= equilibrium concentration (mg/L); b = Langmuir isotherm constant (dm3/mg); KF = Freundlich isotherm constant (mg/g) (dm3/g)n related to adsorption capacity; Ks = Sips isotherm model constant (L/g); n = adsorption intensity; aS = Sips isotherm model constant (L/mg); βS = Sips isotherm model exponent; KT = Toth isotherm constant (mg/g); aT = Toth isotherm constant ; (L/mg); t = Toth isotherm constant; KR = Redlich–Peterson isotherm constant (L/g); b1 and b2 = affinity coefficients for sites 1and 2 in the two-site Langmuir isotherm (mg^{-1}); Q1 and Q2 = maximum adsorption capacity of sites 1 and 2 on the adsorbents ($mg\ g^{-1}$), aR Redlich–Peterson isotherm constant (1/mg); g = Redlich–Peterson isotherm exponent; aRP Radke–

Prausnitz isotherm model constant; rR = Radke–Prausnitz isotherm model constant; βR = Radke–Prausnitz isotherm model exponent.

Table 3. Parameters of isotherm models for uranium biosorption Azolla sp. and coefficient of correlation with experimental data.

Biomass	Model	Parameters				
Azolla sp.	Langmuir	Q 1.035E-04	b 1.265E+05			R^2 0.920
	Freundlich	K 1.457E-03	1/n 2.961E-01			R^2 0.975
	Sips	K_S 1.246E+01	a_S 1.170E-04	β_S 2.961E-01		R^2 0.975
	Toth	K_T 1.058E-08	a_T 9.970E-01	1/t 1.579E-04		R^2 0.952
	Redlich Peternson	K_R 1.433E-03	a_R 6.328E+05	g 7.058E-01		R^2 0.975
	Two-Site Langmuir	Q_1 6.543E-05	Q_2 5.042E+01	b_1 2.719E+05	b_2 6.066E-03	R^2 0.986
	Radke - Prausnitz	a_{RP} 1.002E-03	r_R 1.768E+02	β_R 1.134E+00		R^2 0.969

According to the R^2 values found on Table 3, the Two- Site Langmuir isotherm model was the best fit for uranium biosorption on *Azolla sp.*. Further experimentation and characterization of the biomass would be necessary to understand the mechanisms occurring in the biosorption system. Therefore theoretical assumptions based on the isotherm models theory would not be correct.

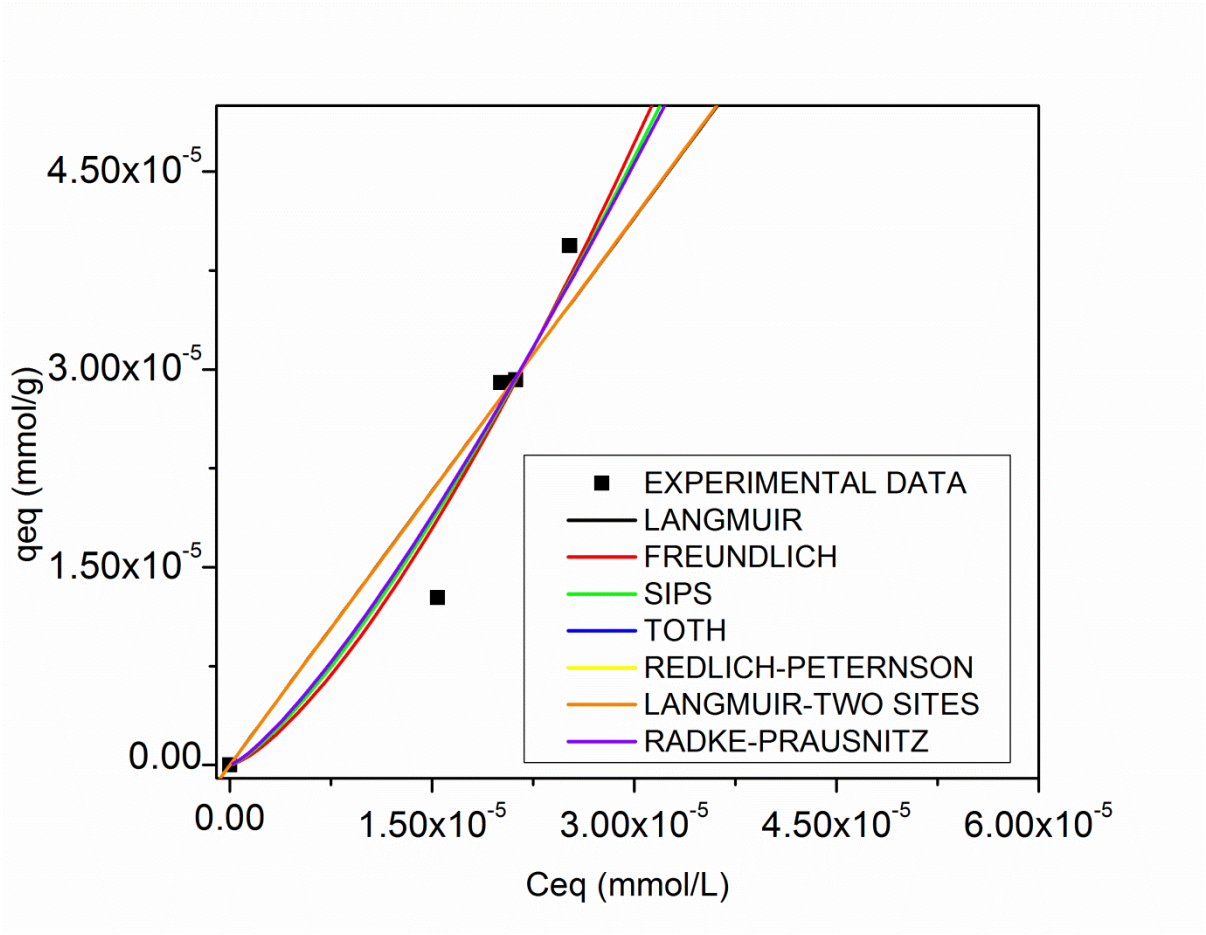

Figure 2: biosorption isotherms of uranium biosorption by Azolla sp .

Evaluating the figure 2 is possible to note that the best fit to the experimental data was Two-site Langmuir and the worst fit was Langmuir. The highest uranium uptake approximately 50 mmol/g .

This study showed superior results in the maximum biosorption capacity when compared with the macrophyte *Pistia Stratiotes* and *Limnobium Laevigatum* [14], *Padina sp*. algae [4], *Catenella repens* [5], and *Cystoseria Indica algae* [15].

4. CONCLUSIONS

The results showed that uptake of uranium by *Azolla sp*. is quick and reached the maximum in 30 minutes. Two-site Langmuir model was the best fit for uranium biosorption onto *Azolla sp*.. This study shows us that biomass is potentially applicable in the treatment of aqueous uranium solution.

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