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BIOSORPTION OF URANIUM BY *LIMNOBIUM LAEVIGATUM* AND *PISTIA STRATIOTES*.

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ABSTRACT: The aim of this work was to appraise uranium biosorption onto *Limnobium Laevigatum* and *Pistia Stratiotes*. Batch experiments were conducted using nonliving biomass and aqueous uranium solution of pH 4 to determine uranium uptake on both biomasses. Equilibrium between the biomasses and solution was reached within 1 hour. Adsorption isotherm models were used to evaluate equilibrium data. The best fit for the experimental data obtained by *Limnobium* and *Pistia* were the Radke-Prausnitz model and the Two-Site Langmuir model respectively. The highest uranium uptake was approximately 0.029 mmol/g (6,82 mg/g) for both biomasses when uranium concentration in solution was 0,64 mmol/L (150 mg/L).

KEYWORDS: Biosorption; Uranium; Aquatic plants

1. INTRODUCTION.

Treatment is a very important stage of the radioactive waste management. The treatment aims to reduce the volume of the waste and condition physically and chemically the waste in order to make it compatible with the immobilization matrix, reducing the costs of posterior phases. The processes adopted are the same commonly utilized on conventional industries, for instance, chemical precipitation, ion exchange and evaporation, with adjustments aiming radiological protection in cases where the risks of contamination are significant. (Hiromoto, et al., 1999). However, these techniques are inadequate to treat the waste under certain conditions. This may happen due to high implementation or maintenance costs or lack of efficiency when, for example, the concentration of ions is low and the volume of solution is high, or practical difficulties in the execution of the process.

The choice of the treatment method must consider viability, safety, cost and efficiency in the waste volume reduction.

The use of biological materials for the removal of substances in solution is known as biosorption, a process that stands out because of the low costs, abundance of the most biomass and the potential they have in removing the substance off solution.

The ability of biomass in removing heavy metal ions from solution can be applied to remove radionuclides in solution. Several studies on biosorption of radionuclides (Tsezos, Volesky, 1981; Tsezos, Keller, 1983; Boniolo, 2008; Dabbagh, et al., 2008), using different types of biomass, showed the potential existent in this method.

The mechanisms involved in the process of biosorption are not clear due to the complexity of biological materials. Adsorption, ion exchange and complexation/coordination may be important mechanisms in the removal of the substance from solution. (Gadd, 2009)

Some criteria may be used to investigate how well a biomass works. It is important, for example, that the biomass is available at cheap prices, and is fast and efficient in the removal of the substance from solution (Volesky, 1990).

Several biological materials have been studied as biosorbents, numerous of which possess these and other features favourable for the application of this process (Volesky, 2003).

Pistia Stratiotes is a floating aquatic macrophyte that proliferates in tropical aquatic ecosystems. This plant species is found on the north, northern, center-west, south and southeast regions of Brazil and it develops on all kinds of freshwater: pure, polluted, muddy or stagnant (Jardim Botânico do Rio de Janeiro, 2010; Cancian, et al., 2009). *Limnobium Laevigatum* is another floating aquatic macrophyte that grows easily and is also found on various regions of Brazil and the world (Jardim Botânico do Rio de Janeiro, 2010).

Both plants can be useful for treating radioactive liquid wastes, because they are easily acquired due to their natural abundance, and have a high growth rate which easily enables sustainable use.

In the present work we have studied the uptake of uranium in aqueous solution by *Limnobium Laevigatum* and *Pistia Stratiotes*.

2. MATHERIALS AND METHODS

2.1. Biomass

The Macrophytes *Limnobium Laevigatum* and *Pistia Stratiotes* were provided by Prof. Edson Antonio da Silva from Universidade Estadual do Oeste do Paraná (UNIOESTE). Both biomass were washed and dried at 60°C for 24 hours. Then they were chopped and sieved, to obtain particle size between 0.297 mm and 0.125 mm, finally they were stored for later use.

2.2. Preparation of Solution

The uranium solutions were prepared by dissolving uranium nitrate in distillate water with previously adjusted pH. The pH adjustments were made adding nitric acid and sodium hydroxide into solution. The solution pH was fixed at 4 because it is a common pH to be found in the radioactive wastes at IPEN. There are also evidences in the literature that this pH favours uranium biosorption as a great number of experiments reported this as the pH which uranium uptake was higher. Some studies indicate this is due to uranium speciation on water (Yang, Volesky, 1999).

2.3. Biosorption Experiments

The Biosorption experiments were conducted in a batch system. Exact 0.1 g of biomass was put into contact with 5 ml of solution. The system was stirred using a mechanic stirrer at room temperature (≈ 23 °C) for the necessary time to reach equilibrium, defined empirically. Next filter paper was used to separate the biomass from solution.

The solution concentration was determined by means of the Perkin Elmer model 7000DV Inductively Coupled Plasma Optical Emission Spectroscopy. A calibration curve was prepared through the dissolution of a standard uranium solution. The wavelength used in the determination of uranium was 424.167 nm and the result is expressed as the average of triplicate measurements.

First were conducted the experiments to determine the necessary time for the system to reach equilibrium. Then experiments were carried out to evaluate the behavior of the system when there was a change at the concentration of uranium ions in solution. All experiments were performed in triplicate

2.4. Data Evaluation

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

$$q = (Co - C)\frac{V}{M} \qquad (01)$$

Where q = uptake of uranium at equilibrium in mmol/g; Co = initial uranium concentration in mmol/L; C = equilibrium concentration in mmol/L; V = volume of solution in L; and M = mass of biosorbent in g.

Adsorption isotherm models were utilized to describe the equilibrium between the biomass and the solution. These models contain several theoretical assumptions that cannot be fully accredited to biosorption systems because of the complex chemical structure of biological materials (Gadd, 2009). They are useful however to describe quantitatively the sorption data in the range of concentrations studied. Also qualitative experiments can be conducted to reveal some of the mechanisms of the biosorption system and prove or disprove those theoretical assumptions.

Recently, it has been pointed out that there may be errors inherent in the use of linear methods to estimate isotherm parameters (El-Khaiary, Malash, 2011; Kumar, Sivanesan, 2007; Foo,

Hameed, 2010). For this reason, the parameters of the isotherm models were estimated by applying the downhill Simplex optimization method to the experimental data. The objective function used in this method is given by Equation 02, where q^{EXP} and q^{MOD} are, respectively, the experimentally determined and the model calculated equilibrium amounts of uranium sequestered per mass of biomass and n is the number of experimental data.

$$F_{obj} = \sum_{j=1}^{n}(q^{EXP} - q^{MOD})^2 \qquad (02)$$

The coefficient of correlation (R^2) was used to measure how well experimental data fit the isotherm models.

3. RESULTS AND DISCUSSION

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 15 minutes to 240 minutes.

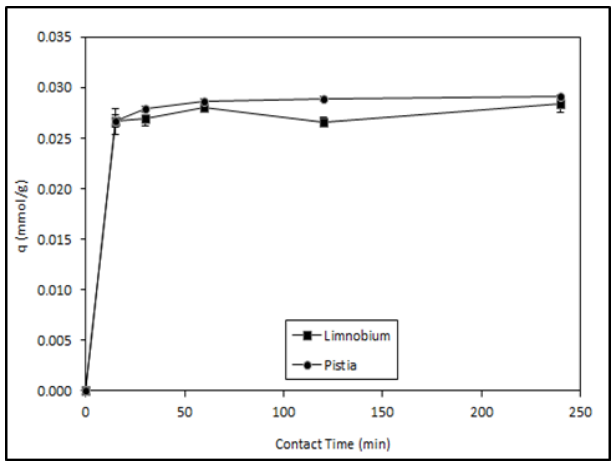

Figure 1. Uranium uptake by *Limnobium Laevigatum* and *Pistia Stratiotes* as a function of time, initial metal concentration 0.64 mmol/L. The error bar represents the standard deviation amongst the results.

Figure 1 shows that the metal concentration on biomass raises more slowly until equilibrium is reached. That behavior is expected since as uranium accumulates in the biomass less adsorption sites are avaiable, the interaction between the ions and the biomass changes and the rate of desorption approaches the rate of biosorption.

Figure 1 reveals a quick rate of biosorption. In 15 minutes the biomasses had removed most of the uranium species present in solution and in 1 hour the uptake of uranium by both biomasses remain constant, therefore dynamic equilibrium between biomass and solution is established.

On the following experiments the contact time was fixed at 1 hour.

3.2. Biosorption Isotherms

The biosorption isotherm represents the equilibrium existent between the biomass and the solution at a given condition. It reveals how biosorption behaves as the metal concentration in solution varies.

The adsorption isotherm models used to describe the data in the range of concentrations studied are given on Table 1, and Table 2 shows the models parameters and how they relate with experimental data.

Table 1. Adsorption isotherm models used to describe data.

Model	Equation
Langmuir (Foo, Hameed, 2010)	$q_e = \frac{QbC_e}{1+bC_e}$
Freundlich (Foo, Hameed, 2010)	$q_e = K_f {C_e}^{1/n}$
Sips (Foo, Hameed, 2010)	$q_e = \frac{K_s {C_e}^{\beta_S}}{1+a_S {C_e}^{\beta_S}}$
Toth (Foo, Hameed, 2010)	$q_e = \frac{K_T C_e}{{(a_T + C_{e)}}^{1/t}}$
Redlich Peterson (Foo, Hameed, 2010)	$q_e = \frac{K_R C_e}{1+a_R {C_e}^{g}}$
Two-Site Langmuir (Hinz, 2001)	$q_e = \left(\frac{Q_1 b_1 C_e}{1+b_1 C_e} + \frac{Q_2 b_2 C_e}{1+b_2 C_e}\right)$
Radke-Prausnitz (Foo, Hameed, 2010)	$q_e = \frac{a_{RP} r_R {C_e}^{\beta_R}}{a_{RP} + r_R {C_e}^{\beta_R - 1}}$

Table 2. Parameters of isotherm models for uranium biosorption onto *Limnobium Laevigatum* and *Pistia Stratiotes*, and coefficient of correlation with experimental data.

Biomass	Model	Parameters				
Limnobium	Langmuir	Q	b			R^2
		0.02606	63.08910			0.9486
	Freundlich	K	1/n			R^2
		0.05093	0.324303			0.9769
	Sips	K_s	a_s	β_s		R^2
		0.06441	0.37944	0.36197		0.9764
	Toth	K_T	a_T	1/t		R^2
		0.00601	0.59238	0.10402		0.9135
	Redlich Peternson	K_R	a_R	g		R^2
		13.664	279.65	0.69927		0.9759
	Two-Site Langmuir	Q_1	Q_2	b_1	b_2	R^2
		0.01416	0.01259	38.161	99.866	0.9530
	Radke-Prausnitz	a_{RP}	r_R	β_R		R^2
		0.00188	0.05288	0.33407		0.9771
Pistia	Langmuir	Q	b			R^2
		0.027317	50.58834			0.9127
	Freundlich	K	1/n			R^2
		0.060798	0.38389			0.9553
	Sips	K_s	a_s	β_s		R^2
		0.06982	0.24825	0.40661		0.9538
	Toth	K_T	a_T	1/t		R^2
		0.00432	0.53316	0.11860		0.8762
	Redlich Peternson	K_R	a_R	g		R^2
		6.6403	117.74	0.66146		0.9512
	Two-Site Langmuir	Q_1	Q_2	b_1	b_2	R^2
		0.16906	0.01372	0.83960	176.02	0.9618
	Radke-Prausnitz	a_{RP}	r_R	β_R		R^2
		0.05822	49.634	1.1995		0.9533

According to the R^2 values showed in Table 2 the Radke Prausnitz isotherm model was the best fit for uranium biosorption on *Limnobium Laevigatum*, and the Two-Site Langmuir model was the best fit for uranium biosorption on *Pistia Stratiotes*. For both set of experimental data the Toth isotherm was the worst fit.

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 and 3 show biosorption isotherms of uranium biosorption by *Limnobium Laevigatum* and *Pistia Stratiotes* respectively. The best and worst fit to the experimental data were represented on each figure.

Initial concentration of uranium in solution was varied from 0.253 mmol/L to 0.640 mmol/L.

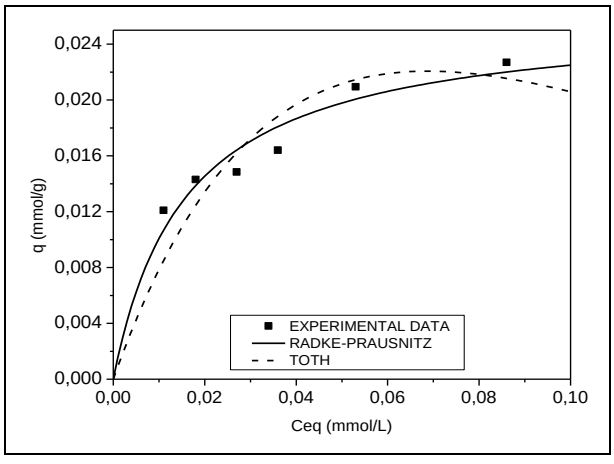

Figure 2. Adjusting of the best and worst isotherm fit to the experimental data of uranium biosorption by *Limnobium Laevigatum*.

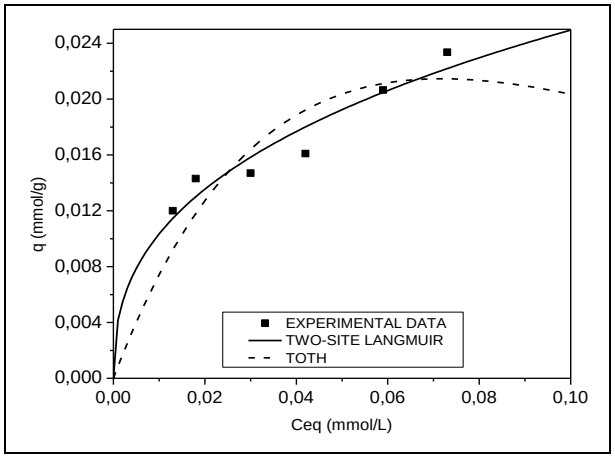

Figure 3. Adjusting of the best and worst isotherm fit to the experimental data of uranium biosorption by *Pistia Stratiotes*.

The highest uptake of uranium was 0.028 mmol/g and 0.029 mmol/g for *Limnobium* and *Pistia* respectively when initial concentration was 0.640 mmol/L. It is not possible to verify significant differences between the two tested biomasses. This result is similar to that obtained by Ferreira (2013) in his work with biosorption of uranium in radioactive liquid waste by coconut fiber.

4. CONCLUSIONS

The results showed that uptake of uranium by both biomasses is quick and in 1 hour equilibrium was reached. Radke-Prausnitz model was the best fit for uranium biosorption onto *Limnobium Laevigatum* and Two-Site Langmuir Model was the best fit for uranium biosorption onto *Pistia Stratiotes*.

This study shows us that both biomasses are potentially applicable in the treatment of aqueous uranium solution.

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