

MAGNETIC BIOSORBENT FOR REMOVAL OF URANYL IONS

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ABSTRACT

In this work magnetic biosorbent, which consisted of sugarcane bagasse as polymeric matrix with magnetite nanoparticles, was prepared. This magnetic composite has the purpose to remove uranyl ions from aqueous effluents. The magnetite was synthesized by simultaneous precipitation by addition a solution of NaOH to the aqueous solution containing Fe^{2+} and Fe^{3+} . This magnetic bagasse biosorbent have presented superparamagnetic properties, that is, it have showed a high magnetization of saturation without hysteresis. The magnetic biosorbent was utilized to remove uranyl ions from water. Radioactive uranium waste is generated in hospitals, universities and it is used as fuel for nuclear power plants. Variables of adsorption process of uranyl ions by magnetic biosorbent in nitric solutions were investigated, such as, time required for the uranium-magnetic bagasse biosorbent equilibrium in the interval from 20 to 90 min, pH in the intervals from 2 to 5 and 10, stirring speed from 240 to 500 r.p.m. and biosorbent dose from 2 to 25 g.L^{-1} were investigated. Equilibrium isotherm was verified according to the Langmuir and Freundlich adsorption isotherm models. The highest adsorption capacity reached 17 mg.g^{-1} . The Gibbs free energy indicated to be spontaneous adsorption. This work updates the paper was presented on the 2007 INAC.

1. INTRODUCTION

Effluent treatment is nowadays one of the most important targets for industry and others institutions. The presence of toxic elements such as heavy metals in the aquatic environment has been of great concern because they are toxic at low concentrations, carcinogen, absorbed cumulatively and stored in animal and vegetable tissues. Radioactive uranium, for instance, it is a waste generated at hospitals and universities. Furthermore uranium is used as fuel for nuclear power plants.

There are some methods available for the removal of metal ions from aqueous solutions, such as ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption. The last one, adsorption, has directed the research to new materials with good removal capacity, for example, the magnetic biosorbents.

Magnetic biosorbent becomes possible the use of two separation techniques for metal removal: the adsorption separation and the magnetic separation. The first one occurs when molecules of a fluid are sorbed onto a solid surface of biosorbent. Once loaded, the magnetic biosorbent can be retired from the aqueous effluents using a magnet.

In this paper, the magnetic biosorbent, which consisted of sugarcane bagasse as polymeric matrix with magnetite nanoparticles was prepared. The magnetite was synthesized by simultaneous precipitation by addition a solution of NaOH to the aqueous solution containing Fe^{2+} and Fe^{3+} .

Sugar cane bagasse is a residue from the sugarcane agroindustry. It is a biodegradable material, with low cost and presents affinity for organic compounds and toxic metals. All over of the world, Brazil is the major producer of sugarcane, producing about 24% of total amount. From the sugarcane industry come the bagasse which represent between 25% and 30% of the sugarcane mass. Bagasse is a biodegradable material, of low cost (R\$ 20.00 per ton - 2009) and presents affinity to sorb the organic compounds and toxic metals.

Variables of adsorption process of uranyl ions by magnetic biosorbent in nitric solutions were investigated and the equilibrium isotherm was verified according to the Langmuir and Freundlich adsorption isotherm models. The Gibbs free energy indicated to be spontaneous adsorption. This work updates the paper was presented on the 2007 INAC.

1.1. Equilibrium Adsorption Isotherm

The equilibrium adsorption isotherm describes the equilibrium relationships between biosorbent and adsorbate at a constant temperature. There're various models describing the experimental dates. Two adsorption isotherm models more considered are Langmuir and Freundlich.

1.1.1. Langmuir isotherm model

In the Langmuir model, adsorption increases with increasing solute concentration at low concentration values and approaches a constant value at high concentrations because there are a limited number of adsorption sites in the biosorbent. The linear Langmuir isotherm is represented by Eq. 1 [3].

$$C_{eq}/Q_{eq} = 1/(Q \times K_L) + C_{eq}/Q \quad (1)$$

Where:

Q_{eq} = amount of metallic ions adsorbed [mg.g^{-1}];
 C_{eq} = equilibrium concentration [mg.L^{-1}];
 Q_m = adsorption maximum capacity [mg.g^{-1}];
 K_L = sorption equilibrium constant [L.mg^{-1}];

1.1.2. Freundlich isotherm model

The model is based on the assumption that ions are accumulated infinitely on the sorbent surface. The linear Freundlich isotherm is represented by Eq. 2 [4].

$$\log Q_{eq} = \log K_f + 1/n \times \log C_{eq} \quad (2)$$

Where:

K_f = adsorption capacity [$(\text{mg.g}^{-1}).(\text{L.mg}^{-1})^{1/n}$];
 n = adsorption intensity.

1.1.3. Standard Gibbs energy of the reaction

The Langmuir constant is related to the standard Gibbs energy of the reaction by Eq. 3 [5,6].

$$\Delta_r G^\ominus = - R.T.\ln k_L \quad (3)$$

Where:

$\Delta_r G^\ominus$ = Standard Gibbs Energy of the reaction [J.mol^{-1}];

R = ideal gas constant [$\text{J.K}^{-1}.\text{mol}^{-1}$];

T = temperature [K];

k_L = Langmuir constant [L.mol^{-1}] [6].

If:

$\Delta_r G^\ominus < 0 \rightarrow$ favorable adsorption

$\Delta_r G^\ominus > 0 \rightarrow$ unfavorable adsorption

2. EXPERIMENTAL

2.1. Preparation of Magnetic Biosorbent

The sugarcane used in this study was obtained from the market fair in São Paulo. Initially sugarcane bagasse was washed with water and was sundried (27 ± 2)°C, cutted and screened through of sieves. It was thermically treated in muffle at 300°C during 30min. The material sieved was stored. A solution of 0.25 mol.L⁻¹ ferrous chloride and 0.5 mol.L⁻¹ ferric chloride (molar ratio 1:2) was prepared and added to the material stored. Magnetic biosorbent was prepared by precipitation method, by adding 5 mol.L⁻¹ NaOH solution into the solution until to reach the pH 11 at room temperature. This system was stirring during 1 h. The biosorbent was washed until to reach pH ~7. The precipitation process was repeated. It was dried in a hot-plate and used for adsorption experiments. This material was called magnetic biosorbent.

2.2. Adsorption Process

Batch adsorption experiments were conducted at (27 ± 2)°C by agitation with 2 mL uranyl nitrate solution and an amount of magnetic biosorbent. After stirring at specified speed and time, the supernatant was separated by a magnet. It was analyzed to determinate the U concentration by arsenazo III method [1], using a spectrophotometer UV-Vis, mod. B582 Micronal. The removal percentage was determined by the Eq. 4.

$$\text{Removal \%} = (C_0 - C) \times 100/C_0 \quad (4)$$

where:

C_0 = concentration of U ions (mg.L^{-1}), before of the contact;

C = concentration of U ions (mg.L^{-1}), after the contact.

The uranium mass adsorbed per gram of magnetic biosorbent was calculated by difference between the U concentration of the solution before equilibrium and in the equilibrium,

multiplied by the uranium volume used in batch experiment and divided by magnetic biosorbent mass. The adsorption capacity was determined by the Eq. 5 [2].

$$\text{Capacity of adsorption (mg.g}^{-1}\text{)} = (C_0 - C) \times V/M \quad (5)$$

where:

V = volume of uranyl ions solution (L) in contact with the magnetic biosorbent;
M = mass (g) of the magnetic biosorbent.

3. RESULTS AND DISCUSSION

3.1. Influence of Contact Time

The adsorption experiments were carried out for different contact times with fixed biosorbent dose at 12.5 g.L⁻¹, pH 3.5, stirring speed 400 r.p.m. and concentration initial 100 mg.L⁻¹. The results were plotted in Fig. 1, which indicates that the equilibrium for uranium adsorption was attained in 20 min of contact with 98% adsorption.

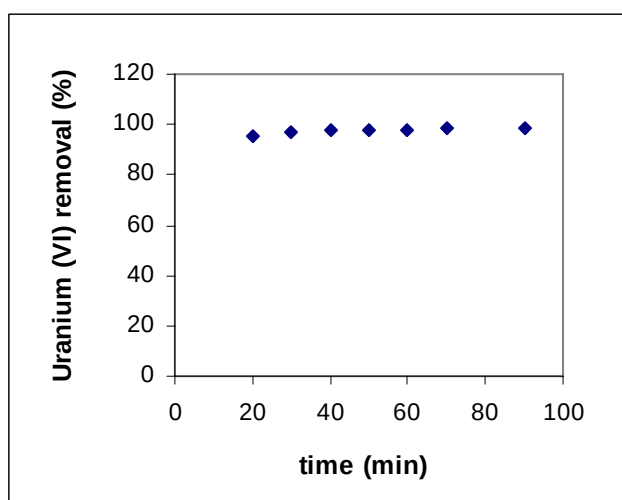


Figure 1. Influence of contact time on uranium (VI) removal (%). Variables fixed: biosorbent dose at 12.5 g.L⁻¹, pH 3.5, stirring speed 400 r.p.m. and initial concentration 100 mg.L⁻¹.

3.2. Influence of Solution pH

The pH is one of the most important parameters on adsorption of metal ions from aqueous solutions [3]. The contact time between solution's uranium and magnetic biosorbent was fixed at 50 min. The results are illustrated in Fig. 2. Uranium removal by magnetic biosorbent increased varying pH from 2 to 5. The H⁺ competition with uranyl ions at lower pH and the

formation of $\text{UO}_2(\text{OH})_3^-$ uranium species at higher pH explain the lower adsorption on the biosorbent surface which is negatively charged.

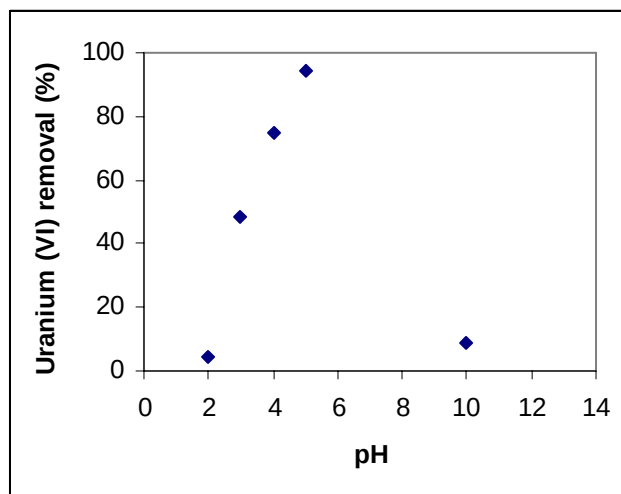


Figure 2. Influence of pH on uranium (VI) removal (%). Variables fixed: time at 50 min, biosorbent dose 12.5 g.L^{-1} , stirring speed 400 r.p.m. and initial concentration 100 mg.L^{-1} .

3.3. Influence of Stirring Speed

The stirring speed is essentially required to maximize the interactions between metal ion and adsorption sites of biosorbent in the solution. The effect of stirring speed on uranium adsorption was investigated with 100 mg.L^{-1} U solution, pH 5 and 40 min agitation. The result was plotted in Fig. 3 and it shows that the adsorption equilibrium was obtained at stirring speed 300 r.p.m..

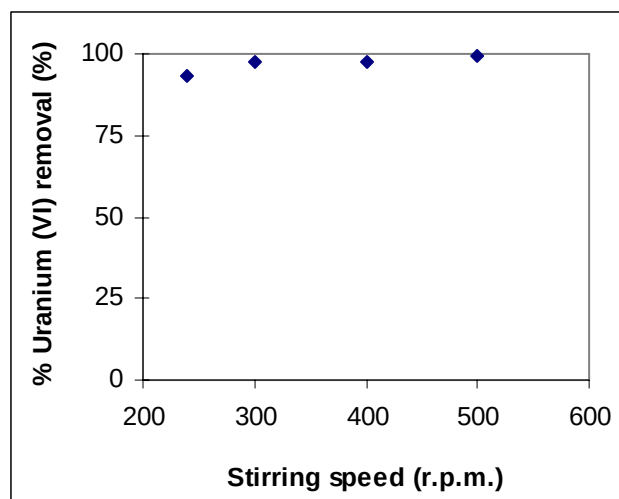


Figure. 3. Influence of stirring speed on uranium (VI) removal (%). Variables fixed: biosorbent dose at 12.5 g.L^{-1} , pH 5 and initial concentration 100 mg.L^{-1} .

3.4. Influence of Biosorbent Dose

In this paper the magnetic biosorbent dose was defined as the amount of magnetic biosorbent in contact with a determined volume of uranium solution. The biosorbent amount varied from 4 mg to 50 mg in 2 mL of the uranium solution 0.1 g.L^{-1} , pH 5. The stirring time was fixed at 50 min and the speed at 400 r.p.m. The results of 97% removal and the adsorption capacity of 17 mg.g^{-1} are in Fig. 4 and Fig. 5, respectively.

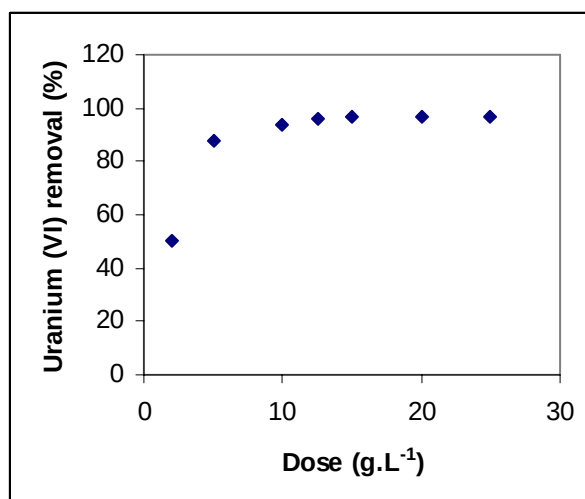


Figure. 4. Influence of dose on uranium (VI) removal (%). Variables fixed: pH 5, stirring speed 400 r.p.m. and initial concentration 100 mg.L^{-1} .

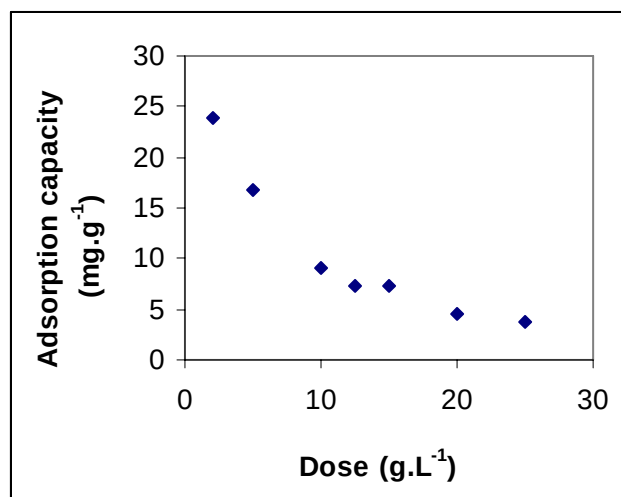


Figure. 5. Influence of pH on adsorption capacity (mg.g⁻¹). Variables fixed: biosorbent pH 5, stirring speed 400 r.p.m. and initial concentration 100 mg.L⁻¹.

The increase in the removal percentage with the increase in the adsorbent dose is due to the increase in the number of adsorption sites. The adsorption capacity was smaller at higher adsorbent doses, according with the Fig. 5. This can be attributed to overlapping or aggregation of adsorption sites resulting in decrease in total adsorbent surface area available to metallic ions and an increase in diffusion path length [7].

3.5. Adsorption Isotherms Models

The models of Langmuir and Freundlich isotherms were studied for the equilibrium adsorption isotherm for the uranium varying the concentration from 50 to 400 mg.L⁻¹. Firstly, the sorption data were analyzed according to the linear form of the Langmuir isotherm described in equation 3.

Plot of specific sorption, C_{eq}/Q_{eq} versus equilibrium concentration, C_{eq} for uranium is shown in Fig. 6. The Langmuir isotherm was found to be linear over the entire concentration range studied with high r^2 value, which suggest being a good model for this sorption system. The values of Q_m and K_L were determined from the slope and intercept of the linear plots of C_{eq}/Q_{eq} versus C_{eq} and presented in table 1.

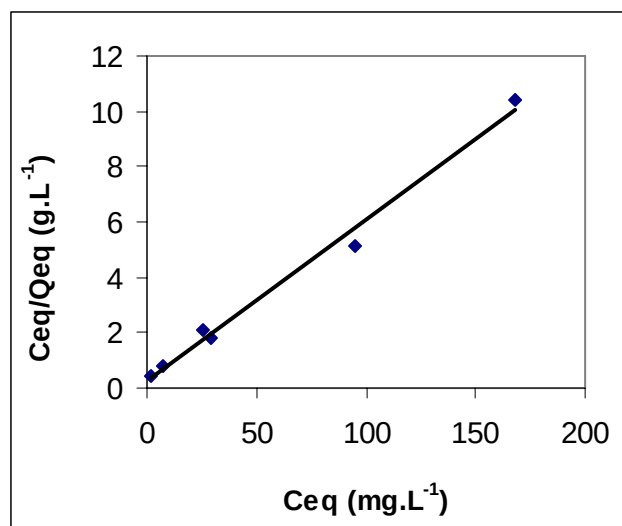


Figure. 6. Linear Langmuir isotherm for uranium adsorption process by magnetic biosorbent.

The linear Freundlich isotherm for the sorption of the uranium on magnetic biosorbent is presented in Fig. 7. The values of k_f and $1/n$ were determined from the slope and intercept of the linear plot of $\ln Q_{eq}$ versus $\ln C_{eq}$, (equation 4) and shown in table 1.

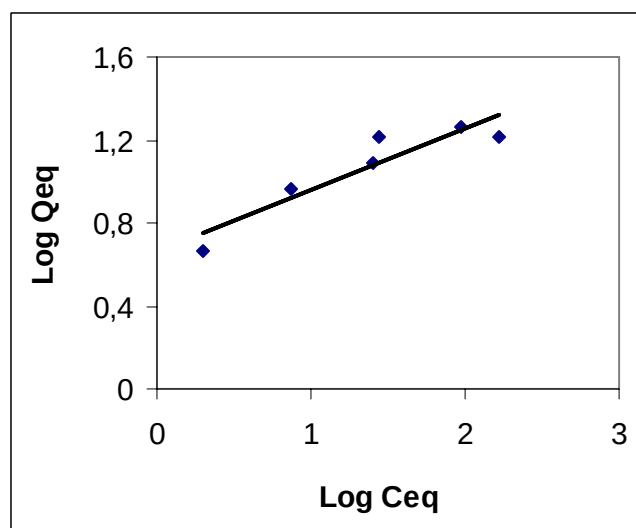


Figure 7. Linear Freundlich isotherm for uranium adsorption process by magnetic biosorbent.

The better fit occurred with the Langmuir linear isotherm, with high r^2 value, 0.9901, which can be observed in Tab. 1. The values of r^2 are regarded as a measure of the goodness-of-fit of experimental data on the isotherms models.

Table 1 – Langmuir and Freundlich constants uranium adsorption.

	r^2	K_L (L.mg ⁻¹)	Q (mg.g ⁻¹)	K_F [(mg.g ⁻¹). (L.mg ⁻¹) ^{1/n}]	1/n
Langmuir	0.9901	0.212	17.15	-	-
Freundlich	0.8483	-	-	4.61	0.295

The K_L was utilized to obtain the standard free energy of adsorption ($\Delta_r G^\ominus$) by equation 5. The value of K_L used in this equation was expressed in L.mg⁻¹. The value for standard Gibbs energy of reaction obtained was -27 kJ.mol⁻¹, showing favorable adsorption.

4. CONCLUSION

Adsorption of uranium (VI) by magnetic biosorbent was highly pH dependent. The better adsorption occurred in pH 5. Besides, was verified the equilibrium for uranium adsorption was attained in 20 min of contact. The uranium adsorption at dose 12.5 g.L⁻¹ was of 97% under studied conditions.

The equilibrium isotherm correlated better to the Langmuir isotherm model, being found adsorption maximum capacity of 17 mg of U per g biosorbent and $\Delta G^\ominus$ of valor -27 kJ.mol⁻¹ indicated that biosorption process was spontaneous.

Thus, the U biosorption by magnetic biosorbent can be considered a potential technology of treatment process for U removal.

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