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URANIUM REMOVAL BY CHITOSAN IMPREGNATED WITH MAGNETITE NANOPARTICLES: ADSORPTION AND DESORPTION

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ABSTRACT

A magnetic biosorbent composed of nanoparticles of magnetite covered with chitosan, denominated magnetic chitosan, was prepared. The magnetic chitosan has showed a magnetic response of intense attraction in the presence of a magnetic field without however to become magnetic, a typical behavior of superparamagnetic material. Its adsorption performance was evaluated by the adsorption isotherm models of Langmuir and Freundlich for uranium ions and the desorption behavior using carbonate and oxalate ions was investigated. The adsorption equilibrium data fitted well to the Langmuir model, being the maximum adsorption capacity equal 42 mg g^{-1}. In the desorption studies, 94% of recovered UO_2^{2+} with carbonate ion were verified under the conditions studied. The chitosan, available as a byproduct of marine food processing, is environmentally safe and can be a low cost adsorbent for U removal from waterwaste. The magnetic chitosan as adsorbent of U to treat radioactive waterwaste is a sustainable technology.

1. INTRODUCTION

Uranium is a naturally occurring radionuclide found at low levels in rocks, sediments and soils. The average U concentration in the earth crust is between 2 and 4 ppm. However, it can be enriched in soil and groundwater by several anthropogenic activities, such as by the release from uranium mill and milling, from agricultural application of phosphate fertilizers, which are often associated with U, as well as by release of radioactive wastewater from research and nuclear establishments. Due to its radioactivity and toxicity, U is a hazardous contaminant in the environment and the Worth Health Organization (WHO) recommends a drinking water limit of 0.015 mg L^{-1} [1]. The management of such wastewater is, therefore, an issue relevant and to reduce the release of radioactive substances into the environment requires constant improvement of processes and technologies for treatment of liquid radioactive waste.

In particular, application of magnetic nanoparticle technology had received considerable attention in recent years. This technology includes the adsorption process combined with magnetic separation and has been investigated in the processing of wastewater treatment and environmental application [2, 3, 4, 5].

The magnetic nanoparticles can be used to adsorb contaminants in wastewater and can subsequently be removed from the medium by a simple magnetic process because their superparamagnetic behavior [6]. After magnetic separation, the contaminants can be easily

removed from nanoparticles by the desorbent agent, and the recovered magnetic particles can be reused.

In this work, a conjugated chitosan-magnetite as magnetic particles was prepared and adsorption-desorption processes were investigated to uranyl ions as well as the magnetic separation technique was evaluated.

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2. EXPERIMENTAL

2.1. Materials

All chemicals used ($FeCl_2.4H_2O$, $FeCl_3.6H_2O$, Chitosan, NaOH, HNO_3, ArsenazoIII, Na_2CO_3 and $Na_2C_2O_4$) were analytical grade and purchased from Merck or Sigma-Aldrich. Standard solution of uranyl nitrate was prepared by dissolution of U_3O_8 nuclear pure obtained from Environment and Chemistry Centre at Nuclear and Energy Research Institute (IPEN), BR. Other U(VI) nitric solutions, pH 5, were prepared by diluting from standard solution in distilled water.

2.2. Preparation of Magnetic Chitosan

Magnetite particles were synthesized using chemical precipitation method according to the reference [7]. One gram of magnetite powder was added into 5 mL of chitosan 10 g L^{-1} in acetic acid solution. The mixture was homogenized under magnetic stirring. Afterwards, to form the coating layer of chitosan on the surface of magnetite particles, droplets of NaOH solution were mixed and stirred. The product was filtered, washed with distilled water until nearly neutral pH, dried at room temperature, stored, and was called magnetic chitosan.

2.3. Adsorption Isotherm of Uranyl Ions by Magnetic Chitosan

The adsorption experiments were carried out by batch assays in glass flasks of 15 mL. Ten milligrams of magnetic chitosan were contacted with 1.0 mL of U solution under shaking of 360 rpm for 40 min at room temperature of 27±1ºC. A shaking time of 40 min was used to guarantee the equilibrium at high concentrations of U. This time is higher that the required to reach the adsorption equilibrium which was determined in another work [7]. Afterwards, a permanent magnet was placed at the bottom of the tube for 2 min, and magnetic separation was carried out. The final concentration of uranium in the supernatant was measured at 650 nm using a spectrophotometer UV-Vis, mod. B582 Micronal, by arsenazo III method [9]. The adsorption equilibrium isotherm was obtained varying the U concentration from 50 to 500 mg L^{-1} at pH 5. All experiments were performed in duplicate and the averaged values were taken and all results represent measurements with an estimated standard deviation of 3%.

The adsorption equilibrium isotherm data were evaluated by Langmuir and Freundlich adsorption isotherm equations [10]. Langmuir isotherm model represented by the Eq. 1 and 2 assumes monolayer adsorption.

$$\text{Langmuir model: } q_{eq} = Q_{max} * K_L * C_{eq} / (1 + K_L * C_{eq}) \quad (1)$$

$$\text{Langmuir model in linear form: } C_{eq}/q_{eq} = 1/(Q_{max} * K_L) + 1/ Q_{max} * C_{eq} \quad (2)$$

Where q_{eq} is the metal amount adsorbed per unit mass of adsorbent (mg g^{-1}), C_{eq} is the equilibrium concentration of metal in the solution (mg L^{-1}), Q_{max} is the maximum adsorption capacity (mg g^{-1}), and K_L is the constant related to the free energy of adsorption. A straight line is obtained by plotting C_{eq}/q_{eq} against C_{eq} and the slope and intercept are used to calculate the Q_{max} and K_L, respectively.

The Freundlich model is represented by the Eq. 3 and 4, which indicates that the surface of adsorbent is heterogeneous.

$$\text{Freundlich model: } q_{eq} = K_F * C_{eq}^{\ 1/n} \quad (3)$$

$$\text{Freundlich model in linear form: } \log q_{eq} = \log K_F + 1/n * \log C_{eq} \quad (4)$$

Where K_F is a parameter of relative adsorption capacity of the adsorbent related to the temperature and n is a characteristic constant for the adsorption system. A plot of log q_{eq} against log C_{eq} gives a straight line and the slope and intercept correspond to 1/n and log K_F, respectively.

2.4. Desorption of U from Magnetic Chitosan

After the U adsorption process, the U loaded-magnetic chitosan was resuspended in 1 mL of distilled water and was shaken for 10 min at room temperature to remove the U ions contained in the intra-particle liquid. The distilled water was separated by magnetic separation and discarded. Then, one milliliter of desorbing solution was added for the U desorption from magnetic chitosan. The system was shaken for 40 min, and the U concentration of the supernatant was determined by arsenazo III method. The desorption process was repeated twice more. The amount of desorbed U in 3 supernatants was combined and used for the determination of the recovered amount. The percentage of recovered U was defined by the Eq. 5. The solutions of 1.1 g L^{-1} sodium carbonate and 1.4 g L^{-1} sodium oxalate were studied as desorbing solutions.

$$\text{Recovered } \% = \{(U_{ads} - U_{des})/U_{ads}\} * 100 \quad . \quad (5)$$

Where U_{ads} is the amount (mg g^{-1}) of adsorbed U onto the magnetic chitosan and U_{des} is the amount (mg g^{-1}) of desorbed U to the desorbent solution.

3. RESULTS AND DISCUSSION

The magnetic chitosan prepared in this work is formed of magnetite nanoparticles and chitosan molecules which its characterization was presented in another work by Stopa [7]. Superparamagnetic properties were observed [8]. Due to the superparamagnetic properties, the magnetic separation technique was employed with success in separating the two phases in the batch assays. An effective magnetic separation was carried out with a small magnet placed at the bottom of the batch flask for 2 min, only. The separating the two phases by magnetic separation technique was faster than the conventional method of centrifugation.

3.1. Equilibrium Adsorption Isotherm

The equilibrium adsorption isotherm was obtained by plotting the amount of U sorbed on magnetic chitosan (q_{eq}) against equilibrium concentration (C_{eq}) in the solution, and was presented in Fig. 1. The Figure shows that the amount of sorbed U increases with the increase of the equilibrium concentration until to reach a maximum value which is related to the maximum adsorption capacity of the magnetic chitosan. These data were evaluated by equations of Langmuir and Freundlich adsorption isotherms and were, respectively, shown in Fig. 2 and 3, and the parameter values were calculated and presented in Table 1.

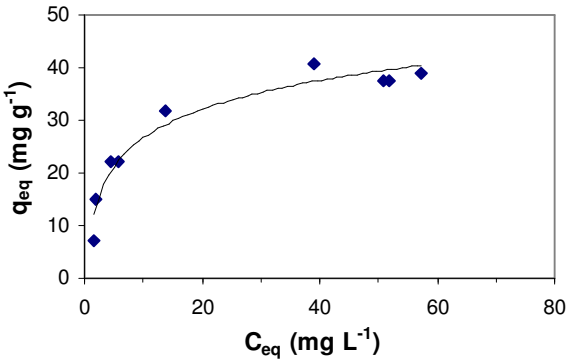

Figure 1. Equilibrium adsorption isotherm for UO_2^{2+} adsorption onto magnetic chitosan at 27±1°C.

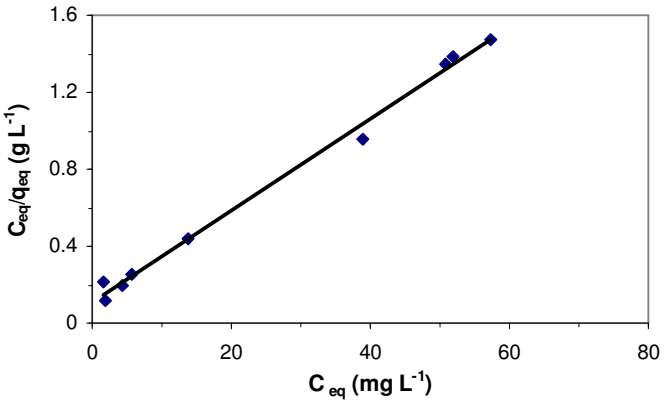

Figure 2. Linearized Langmuir isotherm for UO_2^{2+} adsorption onto magnetic chitosan at 27±1ºC.

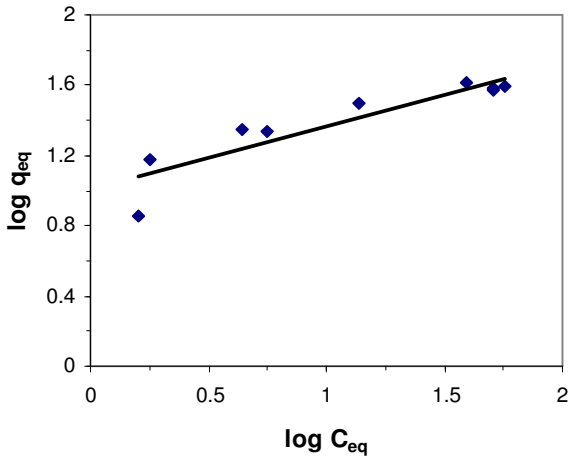

Figure 3. Linearized Freundlich isotherm for UO_2^{2+} adsorption onto magnetic chitosan at 27±1ºC.

Table 1 shows that the correlation coefficient (r^2) for the Freundlich plot is 0.829, which suggests a low validity of the Freundlich isotherm over the entire range of studied concentration. The Freundlich isotherm does not predict a sorbent finite capacity for sorption at high concentrations, but it often describes sorption of trace amounts of sorbing species satisfactorily. The Freundlich plot gave a slope less than 1, indicating a nonlinear sorption behaviour with the concentration of U in the concentration range studied. The observed values of K_F as 10.33 (mg g^{-1})(L mg^{-1})$^{1/n}$ confirms a significant affinity of the uranyl ions by magnetic chitosan.

The value of the correlation coefficient equal to 0.994 of the Langmuir model is higher than of the Freundlich model. This shows that the adsorption of U ions onto magnetic chitosan was best described by Langmuir model, indicating a monolayer type adsorption with a maximum adsorption capacity of 42 mg g^{-1} corroborating with the plot in Fig.1.

Table 1. Parameter values of the Langmuir and Freundlich isotherms for UO_2^{2+} removal by magnetic chitosan at 27±1ºC, from nitric solutions in pH5. Magnetic chitosan dose = 10 g L^{-1}.

Isotherm model	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	1/n	K_F (mg g^{-1})(L mg^{-1})$^{1/n}$	r^2
Langmuir	42	0.216	-----	-----	0.994
Freundlich	-----	------	0.354	10.33	0.829

3.2. Desorption Efficiency of U Ions from Magnetic Chitosan

The desorption of U ions from magnetic chitosan was investigated with solutions of carbonate and oxalate as desorbents. The recovered amount is the accumulated in the 3 desorption batch assays as previously described, and the result of recovery percentage was presented in Table 2.

From this result, 1.1 g L^{-1} Na_2CO_3 solution was found to be effective for desorption of 94% uranyl ions from magnetic chitosan with three desorption stages. This indicates that is possible to obtain a total recovery of U from magnetic chitosan using column method.

Table 2. Desorption efficiency of the UO_2^{2+} ions from magnetic chitosan by carbonate and oxalate solutions at 27±1ºC.

Desorbing solution	$U_{adsorbed}$ (mg g^{-1})	$U_{desorbed}$ (mg g^{-1})	$U_{recovered}$ (%)
1.1 g L^{-1} sodium carbonate	114.5	107.8	94
1.4 g L^{-1} sodium oxalate	147.7	73.3	50

4. CONCLUSIONS

A magnetic biosorbent denominated magnetic chitosan was prepared and investigated as an economically feasible alternative adsorbent for U removal from radioactive waterwaste.

The magnetic chitosan exhibed a strong magnetization being easily attracted and separated from the aqueous solutions using a magnet, indicating the possibility of application in magnetic separation process. Maximum adsorption capacity of 42 mg U per g of magnetic chitosan was found. Three desorption-batch assays with carbonate solutions recovered 94% of U from the magnetic chitosan.

The results demonstrated that the magnetic chitosan particles are effective for the recovering of UO_2^{2+} ions by adsorption-desorption processes, so they present good perspectives of application for the processes of uranium liquid waste treatment.

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