



BIOSORPTION OF URANIUM BY HYDROXYAPATITE AND BONE MEAL

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ABSTRACT: One of the most important steps in radioactive liquid wastes management is the treatment. The employment of technique decides whether treatment will be successful or not, depending on wastes conditions. Biosorption is a technique that uses biological material in order to remove metals from aqueous solutions, which allies low cost and efficiency. The aim of this study is to evaluate the effect of contact time on the uranium contained in aqueous solutions by hydroxyapatite and bone meal. Batch biosorption experiments were performed to determine metal uptake of each adsorbent and then the solutions were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The results showed that bone meal maximum uptake is $28,27 \pm 0,16$ mg/g and hydroxyapatite maximum uptake is $20,75 \pm 1,02$ mg/g. These results show that both adsorbents can be used in the treatment of radioactive waste containing uranium.

KEYWORDS: biosorption; hydroxyapatite; bone meal.

1. INTRODUCTION

Heavy metals are usually put into the environment as wastes of industrial, mineral and agricultural processes, acting as pollution sources, which may bring risk to the environment and human life (ARAVINDHAN et al, 2007). Treatment of these metals by traditional techniques may not be viable, depending on their radioactive properties, chemical composition, concentration, among other features.

Traditional techniques, such as ion-exchange, precipitation, evaporation and eletrochemical methods are generally applied according to certain conditions, such as cost, time and efficiency. Sometimes, these conditions are not favorable, what might make treatment expensive and unsatisfactory, when the waste has low concentrations (DEANS & DIXON, 1992).

The research in finding new processes of managing of radioactive wastes has high importance and it is responsible for the evolution and development of new treatment techniques. Biosorption is the use of biological material on treatment of wastes and it is an alternative way that allies low cost, quickness, high sorption/desorption selectivity and remarkable efectiveness, that can be used when traditional modes of treatment do not behave well, in the case of low concentration wastes (DA SILVA, 2001). One of the advantages of biosorption use is that the biosorbent may be reutilized (DA SILVA, 2001). This technique is based on the uptake of metal species in solution by biosorbent materials through an array of mechanisms that are not clear, due to complexity of biological material.

The ability of removing heavy metal ions from solution by biomass can be applied to the



treatment of radionuclides in solution (GADD, 2009).

Some of the mechanisms in which biosorption occurs are adsorption, ion-exchange, complexation, coordination, microprecipitation, taking place at the same time or separately (BONIOLO, 2008). When equilibrium of such mechanisms is achieved, it is seen that the concentration of metal in solution decreases, what can ensure it as a reliable treatment.

An useful biosorbent needs to be inexpensive, easily found in nature, highly efficient and preferably able to be reutilized (BONIOLO, 2008). Some variables may change biosorption ability of the studied species, such as contact time between solution and biosorbent, concentration, temperature, pH, mass of biosorbent, stirring speed of the solution, among others (BONIOLO, 2008).

Hydroxyapatite belongs to the series of the mineral apatites which is given by the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, the main constituent of tooth enamel and bone core component (REIS, 2005; CAMPELL, 2003). Its synthetic form has high biocompatibility and is used in dental implants and prostheses as support for bone growth, bone cement for the construction of artificial joints, being a suitable substituent for bone (EANES, 1980), reason it is produced on large scale. This material is also used as coating metallic prostheses between the implanted material and living tissue (FULMER et al, 1992; SEPULVEDA et al, 1999).

Previous research has shown that hydroxyapatite is efficient in removing heavy metals from polluted soils due to their ability to adsorb molecules (BANDEIRA, 2007). A recent study has shown that hydroxyapatite can be used to remove uranium from aqueous solutions (LEYVA et al, 2000)

Hydroxyapatite has been used as adsorbent in liquid chromatography, thanks to its high affinity for proteins, being the most stable and less soluble calcium phosphate of all. The adsorptives/desorptives properties of hydroxyapatite also allow application on treatment of tumors by introducing anticancer drugs into blocks of ore, which are subsequently released into patient's body (FULMER et al, 1992; SEPULVEDA et al, 1999). Synthetic hydroxyapatite has been assessed as a sorbent in removal of radioactive and stable metals in synthetic solutions. Interest in its use is related to the high efficiency of exchanging cations and anions, availability and low cost (JEANJEAN et al,

1994).

Research involving use of synthetic hydroxyapatite on the sorption of metals is related in literature (JEANJEAN et al, 1994; LUSVARDI et al, 2002; MCGRELLIS, 2001). Presence of calcium ions and hydroxyl radicals are responsible for the mechanisms of sorption. For being the main constituent of bones, one of the aims of this work is to ascertain the biosorption of a metal of interest by natural bone material in their meal form (commercial bone meal), commonly used as fertilizer. The use of bone meal in the remediation of soils contaminated by metals and effluents is described in the literature (HODSON et al, 2001; DEYDIER et al, 2003; SNEDDON et al, 2006).

The aim of this study is to evaluate the sorption capacity of uranium by natural bone material (bone meal) and by synthetic hydroxyapatite, through batch experiments followed by spectrometric analysis.

2. MATERIALS AND METHODS

2.1. Adsorbents

The synthetic hydroxyapatite was produced at Centro de Ciência e Tecnologia de Materiais of Instituto de Pesquisas Energéticas e Nucleares (CCTM – IPEN). It was calcined at 800°C for 24 hours. Bone meal was purchased in local market. Both adsorbents 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 favors uranium biosorption, a great number of experiments reported this as the pH which uranium uptake was higher.

2.3. Biosorption Experiments

The biosorption experiments were carried out through a batch system. 5 ml of uranium solutions were placed in vials and exact 0,1g of adsorbent was put in each vial containing the solutions. The system was stirred using a mechanic stirrer at room temperature ($\approx 23^\circ\text{C}$). After the



experiment, the adsorbents were separated from the solutions through a filter paper.

The experiments were based on previous research to determine how much time it was necessary for the system to reach the equilibrium, that is, to know when the system has its maximum uptake of uranium by hydroxyapatite and bone meal.

The solution concentration was determined by means of the Perkin Elmer model 7000DV Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A calibration curve was prepared through the dissolution of standard uranium solution. The experiments were performed in quadruplicate. The wavelength used in the determination of uranium was 424.167 nm and the result is expressed as the average of three measurements.

2.4. Data Evaluation

The uptake of uranium by both hydroxyapatite and bone meal was determined using the following equation (GADD, 2009):

$$q = (C_0 - C) \frac{V}{M} \quad (1)$$

Where q is the uptake of uranium at equilibrium in mg/g; C_0 is the initial uranium concentration in mg/L; C is the equilibrium concentration in mg/L; V is the volume of solution in L; and M is the mass of biosorbent in g.

3. RESULTS AND DISCUSSION

3.1. Contact time

The uptake of uranium species as a function of contact time is shown in Figure 1. The contact time between uranium and the adsorbents varied from 15 minutes to 360 minutes..

Figure 1 shows that as time passes, the uptake of uranium by the adsorbents is higher, i.e. the uranium species accumulate on the adsorbents. The concentration of uranium on the biosorbents increases until the equilibrium is reached, that is, when the rate of adsorption and desorption are equal. Both systems presented effective biosorptions.

The removal of uranium by bone meal is greater than the one by hydroxyapatite. At the end of the experiment, the bone meal had removed most of the uranium from the solution, as well as

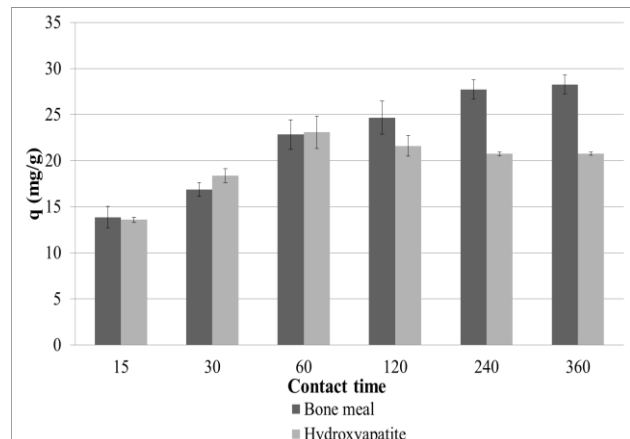


Figure 1. Differences between sorption capacities of uranium by bone meal and uranium by hydroxyapatite with their respective standard deviations.

the hydroxyapatite, but in this second system, it removed little more than half of the initial quantity of uranium. The biosorption of uranium by bone meal has a higher uptake than by hydroxyapatite ($28,27 \pm 0,169$ mg/g against $20,75 \pm 1,022$ mg/g, respectively) and almost achieves its complete equilibrium in 2 hours, being necessary 2 additional hours to get to it.

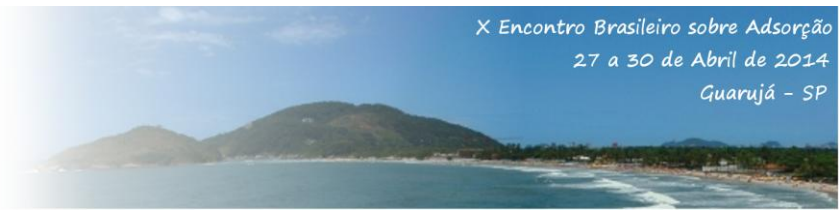
The bone meal system takes more time to establish its dynamic equilibrium, 4 hours, whereas the hydroxyapatite system needs 1 hour in the conditions both experiments were carried out.

The results obtained show that bone meal has better uptake capacity when compared to synthetic hydroxyapatite, however, it takes more time for bone meal to reach equilibrium with uranium solution.

In the first 60 minutes of contact, both sorbents have similar uptake velocities. In fifteen minutes of contact, bone meal had reached 49,02% of total uptake capacity, and hydroxyapatite had achieved 65,54% of its maximum uptake. These data show that biosorption acts quickly in the first minutes under the conditions given. A previous study shows that the uptake of uranium by hydroxyapatite increases similarly to the uptake revealed in this study in the first fifteen minutes of contact time (LEYVA et al, 2000).

4. CONCLUSIONS

Both systems have high velocities of biosorption in the beginning, becoming slower until both systems reach dynamic equilibrium.



This study also shows that these biosorbents can be used as low cost alternatives and can be part of a viable technique of radioactive wastes treatment.

Future studies could verify how other variables affect the biosorption behavior, such as uranium concentration and temperature, for instance.

5. REFERENCES

ARAVINDHAN, R.; RAO, J.R.; NAIR, B.U., et al. Removal of basic yellow dye from aqueous solution by sorption on green alga *Caulerpa racemosa*. *J. Hazard. Mater.* 142, p. 68-76, 2007.

BANDEIRA, L.F.M. Remoção de metal pesado de efluentes aquosos através da combinação dos processos de osmose inversa e adsorção. *Dissertação de Mestrado* - Universidade Federal do Rio de Janeiro, COPPE, 2007

BONIOLO, M.R. Biossorção de Urânio nas cascas de banana. *Dissertação de Mestrado* - Instituto de Pesquisas Energéticas e Nucleares, São Paulo - SP, 2008.

CAMPBELL, A. A. *Mater. Today.*, 26, 2003.

DA SILVA, E.A. Estudo de remoção dos íons Cromo(III) e Cobre(II) em coluna de leito fixo pela alga marinha *Sargassum sp.* *Tese de Doutorado* - Universidade Estadual de Campinas, 2001.

DEANS, R. J.; DIXON, B. G. Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers, *Water Res.*, 26, p. 469-472, 1992.

DEYDIER, E; GUILLET, R; SHARROCK, P., et al. Beneficial use of meat and bone meal combustion residue: "An efficient low cost material to remove lead from aqueous effluent". *Journal Of Hazardous Materials*, v. 101. p. 55-64, 2003.

EANES, E. D. *Program Crystal Growth Characteristics*. vol. 3, p. 3-15, 1980.

FULMER, M. T.; MARTIN, R. I.; BROWN, P. W., et al. Formation of calcium deficient hydroxyapatite at near-physiological temperature. *Journal of Materials Science: Materials in Medicine*, v. 3, p. 299-305, 1992.

GADD, G.M. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J Chem Technol Biotechnol*, v. 84, p.13-28, 2009.

JEANJEAN, J.; VICENT, U.; FEDOROFF, M., et al. Structural Modification of Calcium Hydroxyapatite Induced by Sorption of Cadmium Ions. *Journal of Solid State Chemistry*, v. 108, p. 68-72, 1994.

LEYVA, A.G.; MARRERO, J.; PÉREZ ARISNABARRETA, S; DI NANNO, M.P.; SMICHOWSKI, P., et al. Uranium retention in aqueous hydroxyapatite suspensions. *Comisión Nacional de Energía Atómica*. p. 1-3, 2000.

LUSVARDI, G.; MALAVASI, G.; MENABUE, L., et al. Removal of Cadmium Ion by Means of Synthetic Hydroxyapatite, *Waste Management*, v. 22, p. 853-857, 2002.

MCGRELLIS, S.; SERAFINI, J.; JEANJEAN, J., et al., Influence of Sorption Protocol on the Uptake of Cadmium Ions in Calcium Hydroxyapatite, *Separation Purification Technology*, v. 24, p. 129-138, 2001.

REIS, P. C. Desenvolvimento de Adsorventes Específicos para Remoção de Mercúrio em Petróleo, *Exame de Qualificação ao Doutorado*, COPPE/UFRJ, Rio de Janeiro - RJ, 2005.

SEPÚLVEDA, P.; PANDOLFELLI, V. C.; ROGERO, S. O.; HIGA, O. Z.; BRESSIANI, J. C., et al. *Hidroxiapatita porosa produzida através do gelcasting de espumas visando aplicações biomédicas*. *Cerâmica*, v. 45, n. 296, p.6-15, 1999.

SNEDDON, I.R.; ORUEETXEBARRIA, M; HODSON, M; SCHODIELD, P; VALSAMI-JONES, P., et al. Use of bone meal amendments to immobilise Pb, Zn and Cd in soil: A leaching column study. *Environmental Pollution*, v. 144. p.816-825, 2006.

6. ACKNOWLEDGEMENTS

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