Biosorption of Thorium by Bone Meal – 15435

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ABSTRACT

In the recent years, there is an increasing interest in the application of biological materials for the removal of heavy metal ions from aqueous solutions. There are a variety of biological materials that have been proven efficient biosorbents such as agriculture residues, plants, algae, etc. The use of these materials is attractive and advantageous because they are inexpensive in comparison with commercial adsorbents. Bone meal is a biological material that reunites low cost and efficiency. It is a natural material that contains large amount of calcium phosphate in the form of hydroxyapatite. Studies with hydroxyapatite showed that this material is efficient in removing heavy metals from polluted soils due to their ability to adsorb molecules and can be used to remove radionuclides from liquid aqueous solutions, as liquid radioactive wastes generated in many activities. Bone meal was purchased in local market and chopped and sieved to obtain particle size between 0.297 mm and 0.125 mm. Batch biosorption experiments were performed to determine the metal uptake capacity and equilibrium time. Fixed concentrations of thorium solutions were prepared by dissolving thorium nitrate in distillate water. The bone meal was suspended in 5 mL of thorium solutions in a ratio of 0.2% w/v and left in contact during different times. The contact times adopted were 30 min, 1, 2 and 4 hours. After the contact time, the bone meal was removed by filtration and the supernatant, analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). The results were evaluated using isotherms and kinetics models. The maximum capacity for the bone meal was 11.5 mg/g in 2 h. These results suggest that biosorption with bone meal can be applied in the treatment of aqueous solutions and liquid radioactive wastes containing thorium.

INTRODUCTION

The rapid development of industrial activities and the increasing consumption of different sorts of products in the last decades have caused serious environmental problems. Waste waters containing heavy metals are usually discharged into the environment as by-products of industrial, mineral and agricultural processes, acting as pollution sources, which may offer risks to the environment and human life [1]. Conciliating industrial development and the environment preservation has been a challenge and for this reason it is necessary that new techniques to treat the residues are investigated.

Radioactive properties, chemical composition and especially the concentration of solutions set if traditional treatment techniques are practicable or not. The so-called traditional techniques, ion-exchange, precipitation, evaporation and eletrochemical methods are applied according to certain conditions, such as cost, time and efficiency. When the waste has low concentrations, the treatment by these techniques may not be favorable and, consequently, be expensive and unsatisfactory [2].

The evolution and development of new aqueous waste treatment techniques are built through research in finding out different processes of managing these residues and it is of high importance to environmental protection. The use of biological material, plant or animal biomass on treatment of wastes is an alternative way that brings together low cost, quickness, high sorption/desorption selectivity and remarkable effectiveness, and may be used when traditional methods of treatment do not behave well, as in case of low concentration wastes [3]. This is a physico-chemical method called biosorption [4]. The binding of the metal species in solution on the surface of the biosorbent is the basis of this technique. The biomass requires little processing and is usually a by-product of other industries. These features explain the low cost and availability of biosorbent materials. Biosorption can be a new treatment technique because all biological materials have affinity for metals and the biosorbent material may be reused after the process [4, 5]. However, due to the complexity of biological material, all the mechanisms involved in the biosorption process are not clear yet.

The capacity of removing heavy metal ions from solution by biomass can be applied to the treatment of radionuclides in solution [5]. Some mechanisms in which biosorption occur are the same as traditional techniques, such as adsorption, ion-exchange, complexation, coordination, microprecipitation, occurring at the same time or separately [6]. Biosorption is a reliable treatment because after the procedure, the equilibrium between biosorbent and biosorbate is achieved and the metal concentration decreases. As main characteristics, a biosorbent needs to be inexpensive, easily found in nature, highly efficient and preferably able to be reutilized, that is, the metal attached to the biomass should be easily recovered. [6]. Some variables may change biossorption ability of the species studied, as contact time between solution and biosorbent, concentration of the metal, temperature, pH, mass of biosorbent, stirring speed of the solution [6].

Previous research has shown that bone meal, commonly used as a fertilizer, can adsorb metals in aqueous solutions and binds to an array of ions, such as Pb^{2+}, Co^{2+}, Cu^{2+} and Ni^{2+}. The great amount of low soluble calcium phosphate on bone meal is responsible for its high affinity for metals. The use of bone meal as biosorbent was describes in literature for the remediation of metal-contaminated soils [7], on the removal of lead from aqueous effluent [8] and nickel and copper from synthetic solutions [9]. According to Haddad et al, bone meal can be used as an alternative adsorbent in the removal of dyes from aqueous solution and wastewater [10].

In this study, synthetic aqueous solution containing thorium was prepared in order to evaluate the biosorption of this metal by a commercial bone meal. The biosorption capacity was evaluated through batch experiments and analysis of contact time.

MATERIALS AND METHODS

The biosorbent material, bone meal, was purchased in local market. The bone meal was chopped and sieved to obtain particle size between 0.125mm and 0.297mm. Then, it was stored at laboratory for later use. The morphological characteristics of bone meal were evaluated by scanning electron microscopy performed using a Philips model XL30 scanning electron microscope. The samples were coated with a thin, electric conductive gold film.

The thorium solutions were prepared by dissolving thorium nitrate pentahydrate in distillate water with pH 4 adjusted by adding nitric acid and sodium hydroxide. This value of pH was chosen because it is a common pH found in real radioactive wastes stored at Radioactive Waste Management Laboratory of Nuclear and Energy Research Institute (IPEN-CNEN/SP) and the interest is based on investigating how bone meal behaves under real wastes conditions. The literature describes that pH 4 favors the biosorption of a great number of species.

The biosorption experiments were performed in a batch system. Amounts of 5 mL thorium solutions with fixed concentration of 230 ppm were kept within vials. 0.1g of bone meal was added in each of these vials. The vials containing the solution and the biosorbent were stirred by a mechanic stirrer (130 rpm) at room temperature (22°C) controlled by air conditioner system. The stirring varied between 15 and 240 minutes. The experiments were carried out in quadruplicate. After the stirring, bone meal was separated from the solutions by simple filtration. The filtered thorium solutions were diluted ten times and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) Perkin Elmer model 7000DV to determine their concentrations and time required to the system thorium-bone meal to reach the equilibrium. A calibration curve was prepared using a standard thorium solution to perform the analysis. The concentration results were expressed as the average of three measurements. The wavelengths utilized at ICP-OES to determine thorium concentration in all experiments were 283.730 nm, 339.204 nm and 401.913 nm.

The uptake of thorium in solution by bone meal in was determined using the equation 1 (GADD, 2009):

$$q = \frac{V(C - C_0)}{M} \qquad \text{(Eq. 1)}$$

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.

RESULTS

Fig. 1 shows the micrograph image of chopped and sieved bone meal with particle size between 0.125 mm and 0.297 mm before batch experiments. It is possible to see surface materials of raw form and open and close pores.

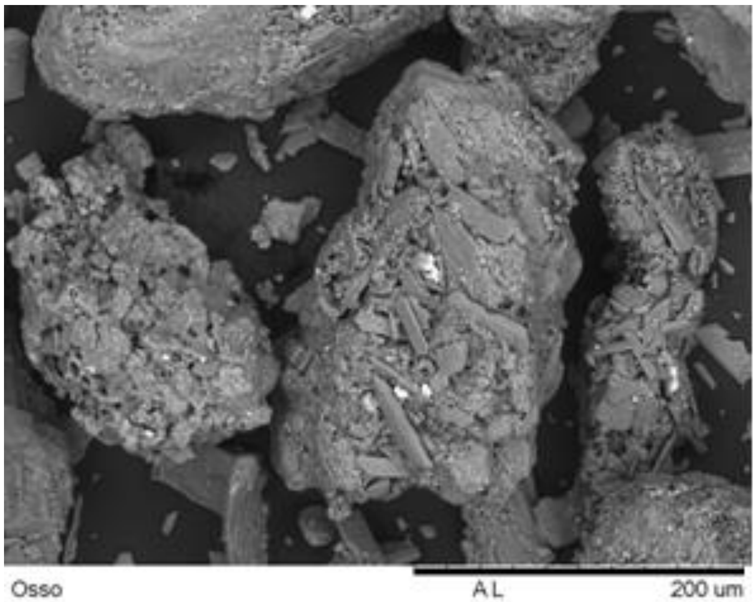

Fig. 1. Scanning electron microscopy of bone meal

The uptake of thorium by bone meal as function of contact time is shown in Fig. 2. The concentration of thorium on the biosorbents increases until the equilibrium is reached, that is, when the rate of adsorption and desorption are equal.

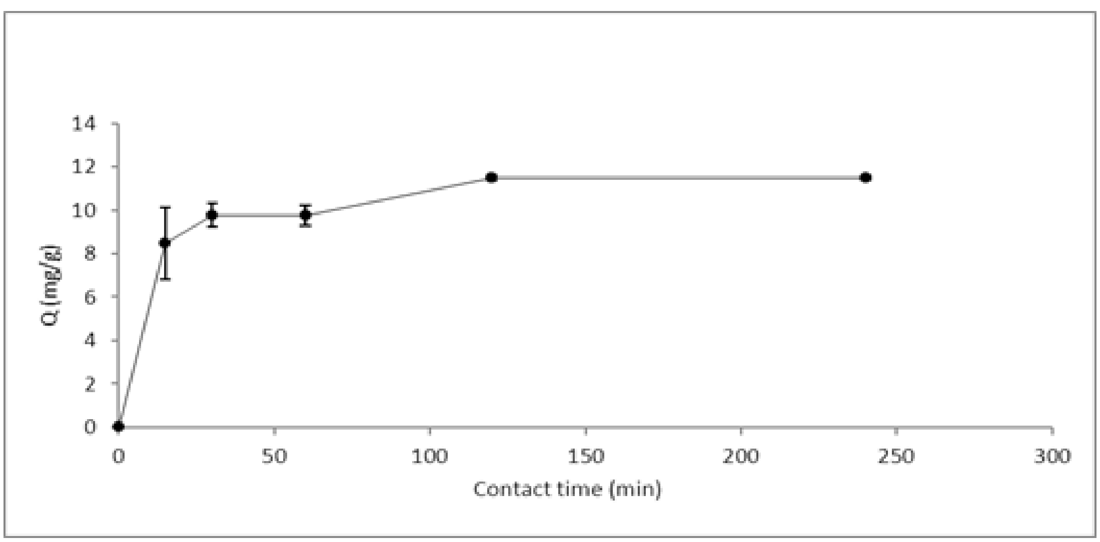

Fig. 2. Effect of contact time on thorium uptake by bone meal

Figure 2 shows that with the passage of time, the uptake of thorium by the biosorbent is higher, i.e. thorium is accumulated on the adsorbent. The biosorption equilibrium was established in 120 minutes, when the biosorption capacity reached 11.48 ± 0.08 mg/g. In fifteen minutes of contact, the system achieves 73.7% of the total uptake, showing that the biosorption becomes slower as time goes by.

The equilibrium can also be analyzed by the ratio between initial and final thorium concentrations. Table 1 shows the amount of thorium removed as function of time.

Table 1. Influence of time on the total concentration of thorium

Contact time (minutes)	Thorium removed (%)
15	72.5
30	83.7
60	83.7
120	98.6
240	98.5

The results showed that almost all thorium of aqueous solution was removed by bone meal. In 240 minutes, there is a decrease in this rate, that can be caused by a little desorption in the solution after the achievement of equilibrium.

CONCLUSIONS

The biosorption assays carried out by batch system showed two distinct behaviors, a high uptake velocity in the beginning and slower as equilibrium approaches. Bone meal can be used as a low cost alternative to remove thorium, being part of a viable waste treatment technique. Next studies may be useful to ascertain the biosorption analyzing other variables, such as initial concentration, pH and temperature.

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