

EVALUATION OF MAGNETITE NANOPARTICLES AS MOLYBDENUM IONS ADSORBENT

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ABSTRACT

Molybdenum-99 is the generator radionuclide of the most used radioisotope for preparation of radiopharmaceuticals with diagnostic purposes in nuclear medicine, technetium-99m (Tc-99m). One way of Mo-99 obtaining is as fission product of irradiated uranium targets in reactor. In this work, the potential application of magnetite particles in the separation of Mo-99 from a dissolution solution of U targets was evaluated. Synthetic magnetite nanoparticles were prepared by alkaline precipitation method from Fe²⁺ ions and heat-treated via microwave irradiation in a conventional household oven. Adsorption kinetics was studied. It was observed that the adsorption of Mo by magnetite nanoparticles is fast and followed the model of pseudo-second order.

1. INTRODUCTION

Molybdenum-99 is the generator radionuclide of the most used radioisotope for preparation of radiopharmaceuticals with diagnostic purposes in nuclear medicine, technetium-99m (Tc-99m). One way of obtaining of the Mo-99 is as fission product of irradiated uranium targets in reactor. The targets are dissolved by alkaline or acid process and the obtained solution is subjected to the stages of separation and purification of Mo-99 from other fission products.

In this work, magnetite nanoparticles as an adsorbent of Mo-99 from aqueous medium were investigated. Synthetic magnetite nanoparticles were prepared by alkaline precipitation method from Fe²⁺ ions and heat-treated via microwave irradiation in a conventional household oven. Adsorption kinetics was studied.

Magnetite, FeO.Fe₂O₃, is an iron oxide, soluble in acid and insoluble in water and in basic medium. It is a natural magnet found in iron deposits and one of the most used for obtaining iron and steel.

Due to the simple crystal structure, magnetite powder can be easily prepared in laboratory. In literature, several methods for the synthesis of magnetite are reported, such as by microemulsion, sol-gel process, alkaline hydrolysis of ferrous sulphate solution followed by heating at 100°C, reduction of hematite and others. These methods allow the synthesis of magnetite in various sizes and furthermore, spend much time and material to obtain the final product, which are decisive issues.

Alternative technological methods need to be developed to simplify existing ones or to improve on present methods. An alternative is microwave irradiation because it is easily generated.

Recent studies have shown that microwave synthesis implies a fast, simple and efficient method to prepare nanometer particles [1]. It has been found that in many cases reaction times can be reduced, in contrast to classical synthetic approaches, and the formation of undesired byproducts can be suppressed [2]. Microwave irradiation has been widely used in chemistry as an efficient heating method.

Compared with the conventional methods, the microwave synthesis has the advantages of rapid growth, small particle size and narrow particle size distribution due to fast homogenous nucleation [3].

In the laboratory at the Environmental Chemistry Center (CQMA)/IPEN-CNEN, magnetite has been synthesized by the microwave, characterized and evaluated as adsorbent of U ions from nitric medium [4, 5, 6]. Nanoparticles of magnetite have showed highly promising in the application of the process of treatment of wastewater for removal of metal ions due to its adsorptive property and superparamagnetic behaviour. The greater advantage this adsorbent over others is the superparamagnetism in which the solid-liquid magnetic separation technique can be applied. The nanoparticles can be separated from liquid medium when they are exposed in magnet field of a magnet. Due to these two essential properties, magnetite nanoparticles for removal of Mo was investigated in order to verify the potential as magnetic adsorbent, and in order to propose a alternative separation method for the fission Mo-99 from the dissolution solution of U targets by magnetic separation technique.

2. EXPERIMENTAL

2.1. Materials

A solution of molybdenum (VI) of concentration 0.96 mg L^{-1} , pH 3, was prepared by the dissolving of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ in distilled water. The pH was adjusted by addition of nitric solution. Other used chemical reagents were analytical grade. The used ^{99}Mo samples as tracer were provided by the Center of the Radiopharmacy (CR)-IPEN/CNEN.

2.2. Preparation of Magnetite Nanoparticles with Microwave Irradiation Heating

Magnetite nanoparticles were prepared by the precipitation method. Sample of 1.81 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 100 mL of distilled water. Then the system was brought to the homogenizer (6000-10000 rpm) and a solution of the 2 mol L^{-1} NaOH was slowly added until to reach pH 11 in order to obtain the precipitates of oxide and oxyhydroxide of iron. Subsequently, the system was placed under heating by microwave irradiation in a conventional household oven (280 W, 2450 MHz) during 1 min, under ambient pressure. After that, the system was placed on a magnet for 2 min, the supernatant was discarded and

the precipitate was washed several times with distilled water. The last washing was carried out with acetone and the precipitate was left to dry at room temperature.

2.3. Adsorption Assay

Adsorption experiments were conducted by the batch assay. Fifteen milligrams of the magnetite particles were placed in contact with 1 mL of Mo solution containing ^{99}Mo tracer, in the stirring at 200 rpm, during a time on a shaker Q225M, Quimis. After the contacting, the vial containing the magnetite and Mo solution was placed on a magnet for 2 min in order to separate the two phases and to remove an aliquot of the supernatant. The aliquot was subjected to the gamma counting at the energy of 739 keV using a HPGe detector, Canberra, at the CR/IPEN/CNEN. An aliquot of each initial solution of Mo was also subjected to the gamma counting. The counts of the supernatant and the initial solution were correlated to the Mo concentrations.

2.4. Kinetics

The adsorption kinetics was obtained varying the contact time of the magnetite particles with the Mo solution under agitation of 200 rpm. All experiments were performed at less in duplicate. The adsorbed quantity (q , mg g^{-1}) on the magnetite particles was calculated by the eq. (1) where the precision varied between 0.06% and 3% from lowest value to highest value of q , respectively.

$$q \text{ (mg g}^{-1}\text{)} = (C_0 - C_{\text{final}}) \times V/M \quad . \quad (1)$$

Where C_0 (mg L^{-1}) is the Mo concentration in the initial solution, C_{final} (mg L^{-1}) is the Mo concentration in the supernatant solution, V is the volume of solution (L) in contact with the magnetite and M is the mass (g) of the magnetite nanoparticles.

Three kinetics models were evaluated in order to investigate the adsorption process of Mo ions on magnetite nanoparticles pseudo-first-order, pseudo-second-order and intraparticle diffusion models with equations as follows, respectively.

$$\log(q_{\text{ex}} - q_t) = \log q_{\text{ex}} - k_1 t / 2.303 \quad . \quad (2)$$

$$t/q_t = 1/k_2 q_{\text{ex}}^2 + t/q_{\text{ex}} \quad . \quad (3)$$

$$q_t = k_{\text{id}} t^{1/2} + C \quad . \quad (4)$$

Where q_{ex} (mg g^{-1}) is the quantity of adsorbed Mo at equilibrium extrapolated to the infinite time t , q_t is the quantity of adsorbed Mo at time t (min), k_1 (min^{-1}) is the rate constant of the pseudo-first-order sorption, and k_2 (min g mg^{-1}) is the rate constant of the pseudo-second-

order kinetics. For intraparticle diffusion models, k_{id} ($\text{mg g}^{-1} \text{min}^{1/2}$) is the intraparticle diffusion rate constant. According to Eq. (4), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism follows the intraparticle diffusion process. Values of the C give an idea about the thickness of boundary layer, i.e., the larger the intercept is the greater the boundary layer effect.

3. RESULTS AND DISCUSSION

3.1. Adsorption Capacities of Magnetite Particles with the Contact Time

The effect of contact time on the adsorption capacity of magnetite particles for the Mo(VI) ions from nitric solution, pH 3, is showed in Fig.1. As can be seen the adsorption capacity increased rapidly in the initial stage of contact time from 10 min to 30 min. For the contact time higher than 30 min the adsorption equilibrium was reached.

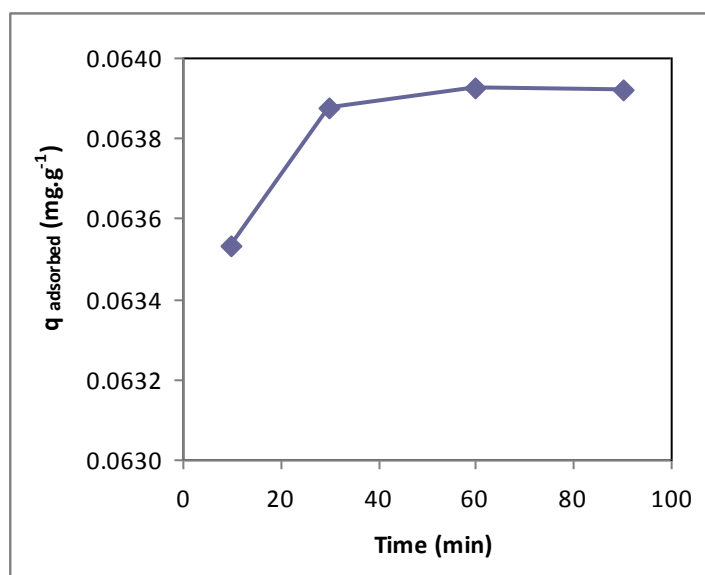


Figure 1. Effect of contact time on the adsorption capacity of the magnetite particles for the Mo ions from nitric solution, pH 3, at $27\pm 1^\circ\text{C}$. C_0 = initial Mo concentration of 0.96 mg L^{-1}

3.2. Kinetics

In order to investigate the adsorption process the Eq. 2, 3 and 4 were applied to adsorption kinetics showed in Fig.1, where the extrapolated value of q_{ex} was equal to $0.06393 \text{ mg g}^{-1}$.

All the parameters were calculated as well as the linear regression correlation for each linear curve, and are given in Table 1. The pseudo-second-order kinetic model better described the adsorption process according to the correlation coefficient, $R = 1.0000$, than those other models. In addition, the extrapolated adsorption capacity, q_{ex} , was very close to the calculated adsorption capacity, q_{calc} , confirming the high correlation to the pseudo-second-order model. On the other hand, the value of q_{calc} of the pseudo-first-order is so far distant from the value of q_{ex} , so, the pseudo-first-order is not good model to describe the adsorption kinetics of Mo(VI) ions on the magnetite nanoparticles although the coefficient is very close to one unity. The intraparticle diffusion model showed low linearity to the data, indicating that the adsorption mechanism did not follow the intraparticle diffusion process.

Table 1. Kinetics parameters for the adsorption of Mo(VI) ions on the magnetite nanoparticles

Pseudo-first-order	k^1 (min^{-1})	q_{calc} (mg g^{-1})	R_1
	0.0241	3.9E-4	0.927
Pseudo-second-order	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	q_{calc} (mg g^{-1})	R_2
	130.48	0.06396	1.000
Intraparticle diffusion	k_i ($\text{mg g}^{-1} \text{min}^{1/2}$)	C (mg g^{-1})	R_i
	5.9E-4	0.0205	0.775

4. CONCLUSIONS

The adsorption kinetics of the Mo (VI) ions from nitric medium, pH 3, on the magnetite nanoparticles was investigated. The adsorption is very fast, being the equilibrium time from 30 min. Among the studied kinetics models, the pseudo-second-order described well the adsorption mechanism. In this study conditions, the magnetite showed high adsorption efficient indicating that is a good adsorbent for Mo (VI). However, more studies are necessary as the desorption behavior and the effect of Al ions and fission products from the dissolution alkaline solutions of $\text{UAl}_x\text{-Al}$ targets in order to ensure as an alternative separation method of the process of obtaining of fission ^{99}Mo using the magnetic and adsorption separation technique.

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