

## STUDY ON OPTIMUM CONDITIONS FOR MO-99 ADSORPTION BY MAGNETITE NANOPARTICLES

Helber Holland<sup>1</sup>, Mitiko Yamaura<sup>2</sup>, Marcos O. Damasceno<sup>3</sup> and Jacinete L. Santos<sup>4</sup>

<sup>1,2,3,4</sup> Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)

Av. Professor Lineu Prestes 2242

05508-000 São Paulo, SP

<sup>1</sup> [helberholland@yahoo.com.br](mailto:helberholland@yahoo.com.br)

<sup>2</sup> [myamaura@ipen.br](mailto:myamaura@ipen.br)

<sup>3</sup> [marcos956@bol.com.br](mailto:marcos956@bol.com.br)

<sup>4</sup> [jlsantos@ipen.br](mailto:jlsantos@ipen.br)

### ABSTRACT

Radioisotopes play an important role in the peaceful uses of atomic energy. Technetium-99m is the most used radioisotope for diagnosis imaging in nuclear medicine and it is the decay product of Mo-99. One route to obtaining Mo-99 is in the form of fission product from Uranium targets irradiated in reactor. Uranium targets are dissolved by alkaline or acid process and the obtained solution is submitted to separation and purification steps of Mo-99 from the other fission products. Traditional separation techniques are inadequate for removing large volumes containing low concentrations metals due to the low operating efficiency and high costs processes. Therefore, alternative methods are being investigated as adsorption. Adsorption advantages over other techniques is low waste generation, easy metals recovery and reusability of adsorbents. Inorganic oxides are known for their ability to bind to metal ions in solution. At nanoscale range, this characteristic is highly potentialized. Thus, the use of nanoparticles has attracted attention for metal ions recovery by adsorption. Magnetite, Fe<sub>3</sub>O<sub>4</sub>, is an oxide formed by iron ions of valence 2+ and 3+. Due to the superparamagnetic behavior that arises in this material at nanoscale and crystal structure itself which favors surface adsorption, magnetite can be used as an adsorber agent to remove metal ions in solution. In this work, adsorption studies were performed to investigate best conditions for Mo-99 removal in solution. Influence of pH, stirring speed, contact time and initial concentration of Mo were studied.

### 1. INTRODUCTION

Technetium-99m is a radionuclide which has suitable physical characteristics for diagnostic use because its low energy gamma monoemissor, physical half-life relatively short and does not emit particulate radiation. Radiopharmaceuticals are used in trace amounts (radioactive tracer) for the purpose of diagnosing diseases and disorders of the body [1].

The <sup>99</sup>Mo is generally produced either by irradiation of <sup>98</sup>Mo or by <sup>235</sup>U fission in a reactor. However, <sup>99</sup>Mo obtained as a byproduct of the fission <sup>235</sup>U has greater stability and emission intensity compared to that obtained by <sup>98</sup>Mo irradiation. Allied to this, the low availability of mineral Mo hinders their production as would be necessary assessed amounts and at the end

of the process it still would present low intensity and lifetime radioactive too brief to be used efficiently, not to mention the high cost process [2].

IPEN is the only Brazilian institution that has a prepared radiopharmacy with a suitable production process and is in compliance with 100% of the national demand for over 10 years. Brazil consumes about 5% of  $^{99}\text{Mo}$  world production [3].

Magnetic nanoparticles with controlled size and shape are of great interest for fundamental science and technological applications due to their chemical, physical and especially, magnetic properties [4]. Among magnetic nanoparticles, ferrites, which stands magnetite -  $\text{Fe}_3\text{O}_4$  - constitute a group of materials with high permeability and saturation magnetization [5]. Below a critical diameter at which the particles start to have magnetic monodomains, magnetite nanoparticles exhibit superparamagnetic behavior, characterized by spontaneous magnetization in the presence of magnetic field.

In this work, application of magnetite nanoparticles synthesized from  $\text{Fe}^{2+}$  and heat treated by microwave irradiation in a conventional oven for  $^{99}\text{Mo}$  removing was studied. Reaction parameters was investigated to provide the best adsorption conditions.

## **2. EXPERIMENTAL**

### **2.1. Reagents e Materials**

All chemical reagents used in this study were of analytical grade and purchased from Merck, Aldrich and Vetec. Mo solution was prepared by dissolving  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in distilled water and the pH was adjusted to 3 by addition of nitric solution. The loading solution, which was placed in contact with the magnetite nanoparticles, was prepared by the addition of the Mo-99 tracer to the natural Mo solution, provided by the Center of Radiopharmacy (CR) of IPEN/CNEN.

### **2.2. Synthesis of Magnetite Nanoparticles**

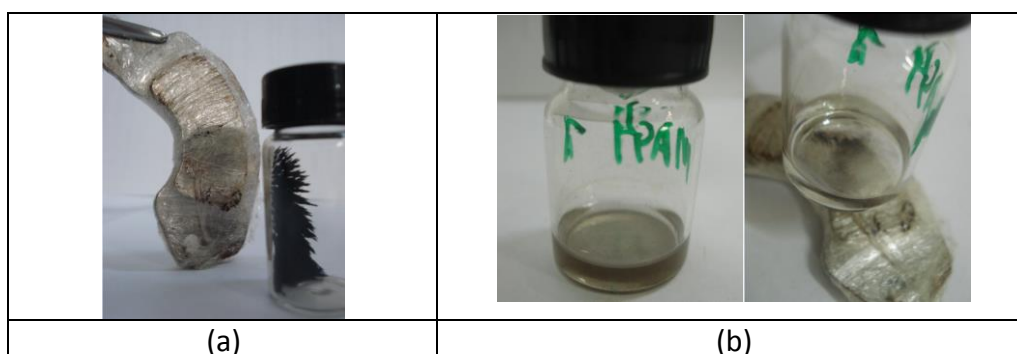
Magnetite nanoparticles were prepared by the precipitation method. Samples of 1.81 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in 150 mL of distilled water. In the homogenizer (6000-10000 rpm), a volume of 5 mL  $\text{NaOH}$   $2,5 \text{ mol.L}^{-1}$  was slowly added at  $250 \mu\text{L}/30\text{s}$  rate until the solution reached pH 11. After successive addition of  $\text{NaOH}$ , the solution color changed from light yellow to dark green, indicating the hydrated iron complexes formation. 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 Studies

Adsorption experiments were conducted by batch assay. Fifteen milligrams of the magnetite particles were placed in contact with 1 mL of Mo solution containing  $^{99}\text{Mo}$  tracer, under stirring at 200 rpm, during a determined time on a shaker Q225M, Quimis. After the contact, 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.

### 3. RESULTS AND DISCUSSION

Fig. 1 (a) presents magnetite synthesized in this work. In the presence of an external magnetic field, magnetite nanoparticles exhibit superparamagnetic behavior. In (b), vial used for adsorption experiments with the suspension of magnetite.



**Figure 1. In (a), magnetite nanoparticles in the presence of a magnet. In (b), magnetic separation solid-liquid suspension containing magnetite nanoparticles.**

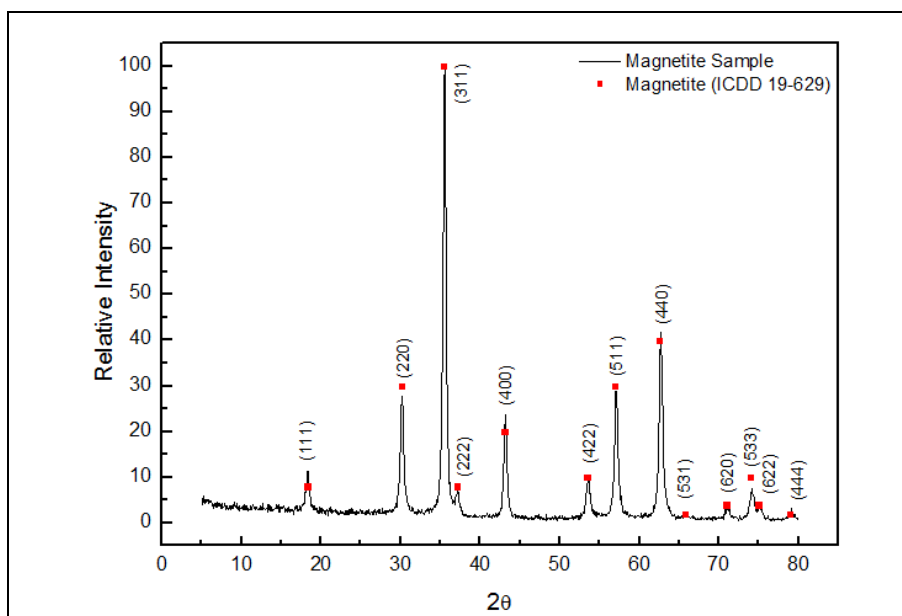
The amount of  $^{99}\text{Mo}$  adsorbed by magnetite was evaluated by equation (1a), where  $q_{eq}$  is the amount adsorbed ( $\text{mg.g}^{-1}$ ),  $C_0$  and  $C_{eq}$  are concentrations at the beginning and at equilibrium ( $\text{mg.L}^{-1}$ ),  $m$  is the mass of adsorbent (g) and  $V$  is the volume of the solution (L). The reaction efficiency was calculated by the equation (1b), where  $C_0$  and  $C_f$  are the initial and final concentrations.

$$q_{eq} = \frac{(C_0 - C_{eq})}{m} \times V \quad (1a)$$

$$R(\%) = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (1b)$$

### 3.1. Characterization

Magnetite nanoparticles were characterized by X-ray diffractometry recorded in a Rigaku Diffractometer model Miniflex II using CuK $\alpha$  (30KV and 15mA) radiation.



**Figure 2. Magnetite nanoparticles diffraction peaks. Analysis made in 0.05°/s step from 2θ = 5 to 80 ° and with 1s for data collection.**

The x-ray diffractogram of Fig. 2 showed that the samples prepared by the method used in this work presented only the magnetite phase and no intermediate phases formation. All diffraction peaks were perfectly indexed to the magnetite standard diffractogram. Average size of magnetite crystals were calculated using Scherrer equation [5] applied to the measure

of the width from the half height of the peaks of diffraction of plan (hkl) 311:

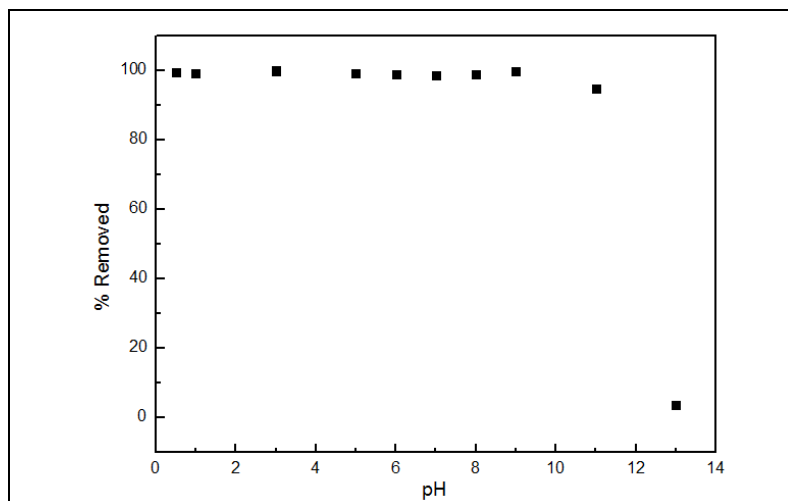
$$D_{rx} = \frac{0,89\lambda}{\Delta\theta \cos \theta}$$

Where:  $\lambda$  is the wavelength (1.5406 ) of CuK $\alpha$  radiation,  $\Delta\theta$  is the width from the half height,  $\theta$  is the Bragg angle and 0.89 is a constant related approximately to the shape of magnetite crystallite. It was estimated crystallite size of 20 nm. Particle size in this region have high surface reactivity which provide a great applicability in adsorption studies.

### 3.2. pH Effect

The effect of pH on the adsorption of Mo was studied in values between 0.5 and 13. In the graph of Fig. 3 was observed that magnetite nanoparticles had a high percentage removal of  $^{99}\text{Mo}$  in a broad pH range, maintaining close to 100% removal between pH values 0.5 and 10. For very high values of pH the percentage removed decreased. Mo exhibits ionic species with oxidation states from 2+ to 6+, predominantly in the states Mo(IV) and Mo(VI) [6]. For low

pH, prevalent cation species of  $MoO_2^{2+}$ ; for higher pH values, the predominant anionic species is  $MoO_4^{2-}$ ; intermediate pH values exhibit a mixer of different species. Molybdenum ionic state is strongly affected not only by the acidity of the solution but also because the concentration of Mo [7]. Magnetite shows amphoteric behavior: in neutral pH, aqueous surrounding Fe-OH sites are formed at the crystal surface. In alkaline, H atoms dissociate into solution and the Fe-O-sites are generated [8].



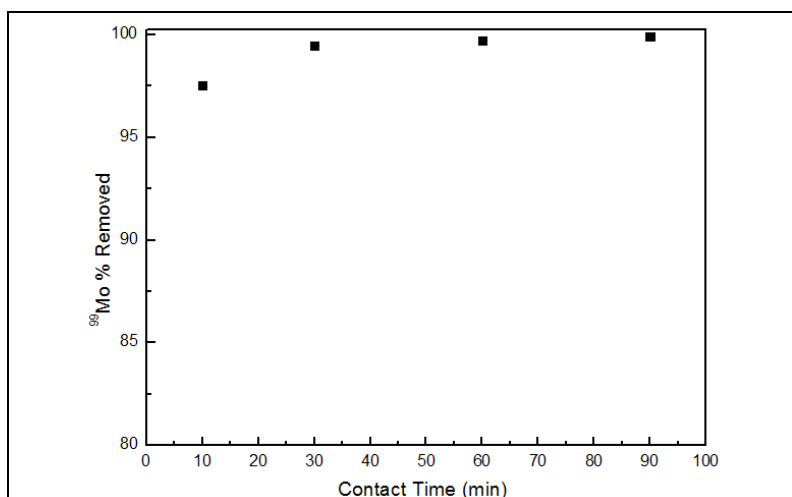
**Figure 3. Removed  $^{99}Mo$  variation in function of pH. It was used 15 mg of magnetite, stirring speed 200 rpm, volume 1 mL, contact time of 40 min, Mo concentration of  $0.5\text{ mg.L}^{-1}$ ,  $25\pm 2^\circ\text{C}$ .**

For pH above 11, the high concentration of negative charges on the surface of the magnetite is not favorable to Mo anions binding due to the high repulsion. At low pH, besides high removal rate, results emphasized magnetite nanoparticles resistance to degradation during the long period of contact. Considering all the features presented, nanoparticles proved to be a great alternative for use in removing Mo.

### 3.3. Contact Time Effect

Contact time for Mo solution with concentrations of  $1\text{ mg.L}^{-1}$  in the range of 10-90 min was studied. The results from  $^{99}Mo$  removal are shown in Fig. 4.

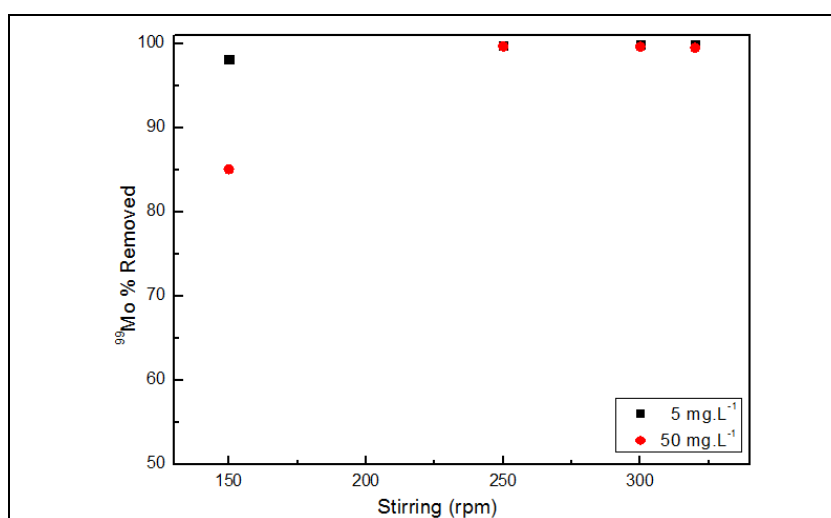
It can be seen that the rate of Mo uptake was high and in only 10 min a quantity higher than 90% was adsorbed by magnetite. At about 20 min, Mo adsorption reached 100%. These result showed that Mo adsorption by magnetite nanoparticles is quite rapid.



**Figure 4. <sup>99</sup>Mo removal due to the contact time effect. It was used 15 mg of magnetite, stirring speed of 200 rpm, volume 1 mL, pH 3, Mo concentration of 1 mg.L<sup>-1</sup>, 25±2°C.**

### 3.4. Agitation Speed Effect

The effect of stirring speed is shown in Fig. 5. Agitation speed of 150, 250, 300 and 320 rpm and solutions with Mo initial concentration 5 and 50 mg.L<sup>-1</sup> were investigated. It was observed that removal rate is high for both concentrations and at all speeds used. At low speed, Mo removal was higher for the solution of lower concentration, showing that magnetite nanoparticles performs better results at low concentrations.

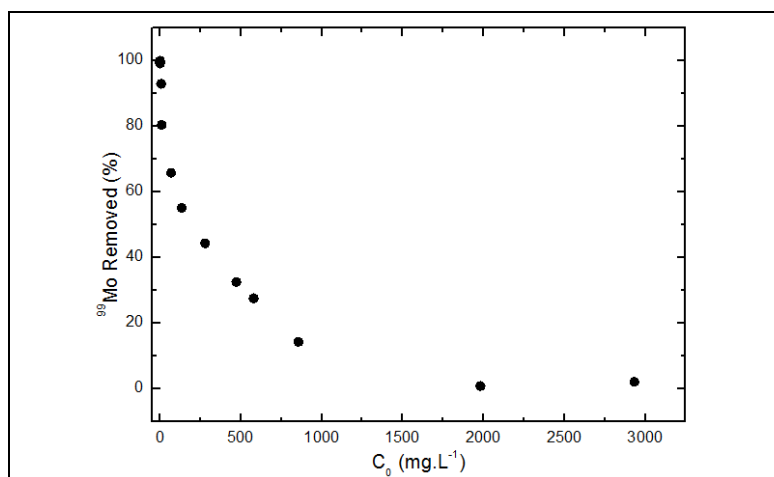


**Figure 5. Influence of stirring speed on the <sup>99</sup>Mo removal. It was studied solutions with concentration of 5-50 mg.L<sup>-1</sup>. Speeds of 150, 250, 300 and 320 rpm were analyzed. It was used 15 mg of magnetite, contact time of 30 min, 1 mL volume, pH 3, 25±2°C**

It was found that to obtain the best performance of the system it must be taken into consideration the volume of solution and the amount of adsorbent so contact with the adsorbate is facilitated. High agitation speeds make a turbulent system which interferes with the binding between the adsorbate and adsorbent.

### 3.5. Initial Concentration Effect

Effect of initial concentration on  $^{99}\text{Mo}$  adsorption for 0.5 to 3000  $\text{mg.L}^{-1}$  solutions was studied. It was observed that for higher concentrations the amount of  $^{99}\text{Mo}$  removed drops drastically. For solutions at low concentrations the nanoparticles proved to have wide applicability. Whereas in real situations the concentrations of radioisotopes are small, the method can be a low cost alternative for separation of radionuclides.



**Figure 6.  $^{99}\text{Mo}$  removal due to initial concentrations variation. It was used 15 mg of magnetite, stirring speed of 200 rpm, volume 1 ml, pH 3,  $25\pm 2^\circ\text{C}$ .**

## 4. CONCLUSIONS

The synthesis method used in this work to obtain magnetite nanoparticles proved to be highly reproducible with excellent results. The use of magnetite nanoparticles for removal of Mo-99 showed a promising alternative method. Adsorption reached maximum at acid pH, sustaining about 99% until values close to 11. Contact time study demonstrated that the reaction is rapid and reached equilibrium at 20 min in solutions up to 10  $\text{mg.L}^{-1}$ . Stirring speed was investigated between 150 and 320 rpm and there were no significant differences in the amounts removed in conditions analyzed in this work. Initial concentration study showed that adsorption of  $^{99}\text{Mo}$  is more efficient for lower concentration solutions. Studies involving temperature variation during the separation are underway to determine its influence on magnetite binding with the molybdenum species. In order to study the efficiency of the proposed method for real applications, chromatographic columns will be applied for the process of contact between the magnetite nanoparticles and radioisotope.

## ACKNOWLEDGMENTS

The support of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Radiopharmacy Center/IPEN, is gratefully acknowledged.

## REFERENCES

1. Marques N. L., Fabio, Okamoto, M. R. Y., Buchpiguel, C. A., “Alguns aspectos sobre geradores e radiofármacos de Tecnécio-99m e seus controles de qualidade,” *Radiologia Brasileira*, **34**, pp.233-239 (2001).
2. Sameh, A. A., Hans, J. A., “Production Techniques of Fission Molybdenum-99,” *Radiochimica Acta*, **41**, pp.65-72 (1987).
3. “MCT investe na construção de reator para produzir tecnécio,” <https://www.ipen.br/sitio/?idc=5844> (2009).
4. Heuser, J. A., Spendel, W. U., Pisarenko, A. N., “Formation of surface magnetite nanoparticles from iron-exchange zeolite using microwave radiation,” *Journal of Materials Science*, **42**, pp. 9057-9062 (2007).
5. Cullity, B. D. *Elements of X-ray Diffraction*, Addison-Wesley Publishing Co., New York (1972).
6. D. Malinovsky, *et al*, “Molybdenum isotope ratio measurements on geological samples by MC-ICPMS,” *Journal of Mass Spectrometry*, **245**, pp. 94–107 (2005).
7. V. M. Ivanov *et al*, “Methods for Determining Molybdenum,” *Journal of Analytical Chemistry*, **57**, pp. 758–772 (2002).
8. Qiao, R., Yang, C., Gao, M., “Superparamagnetic iron oxide nanoparticles: from preparations to in vivo MRI applications,” *Journal of Material Chemistry*, **19**, pp. 6274–6293 (2009).