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STUDIES ON MOLYBDENUM ELUTION STUDY IN DOWEX 1x8 RESIN APPLIED ON PURIFICATION PROCESS OF FISSION ^{99}Mo

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ABSTRACT

Molibdenum-99 is the most widely employed radioisotope in nuclear medicine, due to its decay product, Technetium-99, which is used in radio-pharmaceutical marking molecules for diagnostic examinations tumor diseases. Today Brazil imports ^{99}Mo from some countries, so the National Commission of Nuclear Energy (CNEN) is implementing a new research reactor RMB, currently in the conceptual design phase. The process of separation of fission ^{99}Mo begins with the dissolution of uranium targets after irradiation in reactor; the resulting solution goes through a series of chromatographic columns that allows a gradual decontamination of other components, yielding the ^{99}Mo with high radio-chemical and chemical purity for use in nuclear medicine as a generator of ^{99m}Tc. This work is part of the RMB research project to separate and purify the fission ^{99}Mo by chromatographic columns from alkaline dissolution of LEU UAl_x-Al targets. In the present study Mo removal by batch assays and glass column was investigated using anionic exchanger Dowex 1x8.
Different salts and its concentration, cations and temperature were evaluated on elution of molybdenum and iodine (contaminant) retained on resin Dowex 1x8, aiming at their use in the process of separation and purification in chromatography columns on Brazilian project. Results showed high recovery of Mo and low-level contamination by iodine using $NaHCO_3$ hot solution.

1. INTRODUCTION

Molybdenum-99 is the most widely employed radioisotope in nuclear medicine, due to its decay product, Technetium-99, which is used in radio-pharmaceutical marking molecules for diagnostic examinations and treating tumor diseases. But at the last years availability of ^{99}Mo/^{99m}Tc generators suffers a worldwide crisis on account of reduction of production of its main raw material Mo-99 [1, 2, 3], its supply is still uncertain because Brazil is not self-sufficient in production of ^{99}Mo radioisotope, being hardly dependent on international producer reactors. ^{99}Mo is produced mainly by ^{235}U fission of uranium targets in the reactor, and became scarce because of technical problems of old production reactors around world. Nowadays Brazil imports ^{99}Mo from some countries like Argentina, South Africa and Canada to meet partial demand. Brazil and Argentina recently signed a cooperation agreement for the construction of a nuclear reactor in Iperó-SP [4], in this context the National Commission of Nuclear Energy (CNEN) is in charge of implementing a new research reactor RMB, currently in the base design phase. This reactor will supply all need the radioisotopes production in Brazil for medicals and industrial applications. The process of separation of fission ^{99}Mo begins with the dissolution of uranium targets after irradiation in reactor. The resulting solution goes through a series of chromatographic columns that allows a gradual decontamination of other components, yielding the ^{99}Mo with high radio-chemical and chemical purity for use in

nuclear medicine as a generator of ^{99m}Tc. This work is part of the RMB research project to separate and purify the fission ^{99}Mo by chromatographic columns from alkaline dissolution of LEU (Low Enriched Uranium) UAl_x-Al targets. In the present study, anionic exchanger Dowex 1x8 was investigated on Mo removal by batch assays and glass column using some eluents. This resin is generally used in the production chemical processing of fission ^{99}Mo, e.g., in Argentina and on the ROMOL (Germany). Different salts were evaluated on elution of molybdenum and iodine (contaminant) retained on resin Dowex 1x8, aiming at their use on process of separation and purification in chromatographic columns in Brazilian project.
Initial tests were carried in batch by placing an aliquot of Mo solution, containing ^{99}Mo tracer, in contact with resin exchanger and after that the supernatant was separated. Another Mo solution was passed through the resin bed in the glass column and the eluted was collected. Both were submitted to counting on gamma ray spectrometer. Influences of type eluent, its concentration, and temperature on elution of molybdenum were investigated.

2. EXPERIMENTAL

2.1. Materials and Equipaments

A 10 mmol L^{-1} molybdenum stock solution and 1 mol L^{-1} eluent solutions were prepared by dissolving respective sodium salts, Merck, in distilled water. Aluminum solutions were prepared by dissolution of an aluminum plate 6061 (provided by Center of Nuclear Fuel, IPEN/CNEN) in boiling 3 mol L^{-1} NaOH solution and finally filtered at target dissolution laboratory, IPEN/CNEN.
The anionic resin Dowex 1x8 (50-100 mesh); Sigma-Aldrich and all other chemical reagents used were of analytical grade. The ^{99}Mo samples used as tracer were provided by the Center of Radio-pharmacy, IPEN/CNEN.
The instruments used throughout the work consisted of a gamma ray spectrometer HPGe connected to a multichannel analyzer (Canberra), a shaker (Q225M Quimis) and pH meter (Metrohm E512).

2.2. Batch and Chromatographic Column Experiments

Desorption experiment was conducted firstly by batch adsorption of Mo on the resin Dowex 1x8 and followed by a step of batch desorption of Mo from the resin onto solution. Batch adsorption was conducted with 50 milligrams of resin Dowex 1x8 placed in contact with 1 mL of molybdenum solution pH 5.3 containing natural Mo carrier (5 mg L^{-1}) and ^{99}Mo tracer, hereafter referred just Mo-feed solution, with stirring at 200 rpm for 40 min on shaker. After that the supernatant was separated and disposed, and the Mo-loaded resin particles washed with distilled water. The resin particles were measured for 180 sec at 739 keV by a gamma ray spectrometer. After that, a batch desorption was conducted to removal of adsorbed Mo on the resin. The Mo-loaded resin particles were placed in contact with 1 mL of desorption solution 1 mol L^{-1} stirring at 200 rpm for 40 min. The supernatant was separated, disposed and the resin particles washed with distilled water. The resin particles were counted for 180 sec at 739 keV by a gamma ray spectrometer.
Chromatography column experiments were carried out to evaluate the performance of desorption solution as eluent of Mo from a chromatographic bed packed with Dowex 1x8

resin. The chromatographic columns were made with a glass column, and were packed with 1.5 g of resin.
Aluminum solution (30 g L^{-1}) containing Mo carrier (5 mg L^{-1}), ^{99}Mo tracer, I carrier (0.5 mg L^{-1}) and ^{123}I tracer was passed through the chromatographic column.
After the column washing, Mo was eluted and collected in small vials each 5 mL, at last counts for 240 sec at 739 keV to Mo and 636 keV to I on gamma ray spectrometer were obtained.

2.3. Analysis

Desorption efficiency of each solution was evaluated based on the percentage value of removed Mo from Dowex 1x8 resin calculated according to the equation (1).

$$\text{Desorption } \% = (1 - (C_f / C_i)) \times 100 \qquad (1)$$

Where: C_f = gamma counting rate of the Mo-loaded resin after contact with desorption solution.

C_i = gamma counting rate of the Mo-loaded resin before contact with desorption solution.

3. RESULTS

3.1. Influence of Anion as desorbent of Mo ions

The ability of Mo desorption from the Dowex 1x8 resin with different salt solutions was investigated. Solutions of anions of carbonate, hydrogen carbonate, sulfite, sulfate, hydrogen sulfate, chloride and nitrate were used as desorption solutions. Fig. 1 shows the found results of desorption behavior of Mo. Nitrate and chloride anions revealed as very good desorbents which more of 80% of Mo were recovered while carbonate, hydrogen carbonate, sulfite, hydrogen sulfate and sulfate showed a lower recovery of Mo from the resin but still can be considered as good desorbents. Therefore, all studied anions revealed as desorbents of Mo being possible to elute it from a chromatographic column of Dowex 1x8.

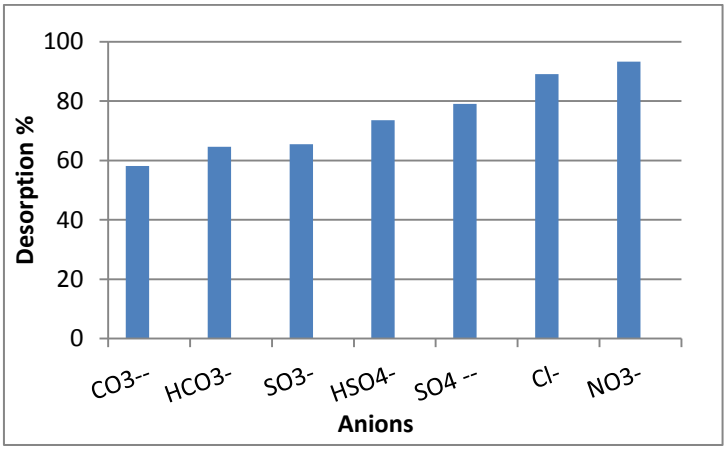

Figure 1. Molybdenum Desorption by Different Anions.

Combinations between the valence and polarity of desorbent anions allow exchanging them with the adsorbed Mo anions by different efficiency on the Dowex 1x8 which is an ion exchange resin, and as result releasing the adsorbed Mo anions. On the other hand, these ions strongly attracted can also release along with Mo unwanted elements (contaminants) of the ion exchange resin.

3.2. Elution Profile of Molybdenum and Iodine

In order to assess the elution profile of Mo from the Dowex 1x8 column two desorbent were studied, the very good desorbent NO_3^- and good desorbent HCO_3^- anions. The elution profile of iodine was also investigated in order to compare the Mo-I separation from the Dowex 1x8 column. In chemical processing of fission Mo-99, the radioactive iodine, another fission product, is present in the dissolution alkaline solution and is retained on the column together with the Mo. So, it is very important to obtain the elution profiles of Mo and I, and to evaluate the desorbent performance in separation process between the two fission products. Fig.2 shows the elution profiles of a typical separation of Mo and Iodine using NO_3^- and HCO_3^- anions, where Na was used as cation.

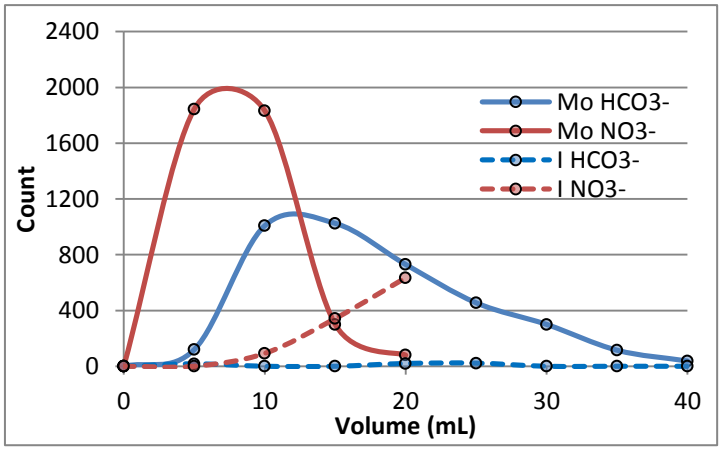

Figure 2. Elution Profiles of Molybdenum and Iodine.

The elution curve depends strongly on the chromatographic system characterized by the diameter and bed height, the eluent flow, size and shape of the resin beads, and depends especially of chemical equilibrium between eluent and adsorbed compound, and hence the concentration of the eluent, pH, temperature, competition between the adsorbed compound, and other factors too.

Elution profile of the Mo by nitrate was excellent showing fine peak and short tail while the bicarbonate profile is broad band with a long tail increasing greatly the volume eluted. In other hand, none iodine contamination throughout in the HCO_3^- elution was observed unlike NO_3^- elution where the iodine contamination was high.

It is possible that the sum of the forces of HCO_3^- ion allowed a more selective elution of molybdenum, keeping iodine retained on resin [5]. Probably the same behavior will be observed for other contaminants present in the loading solution, thus impeding the use of nitrate ion as eluent anion of molybdenum.

3.3. Effect of the Cation on the Mo Elution with HCO_3^-

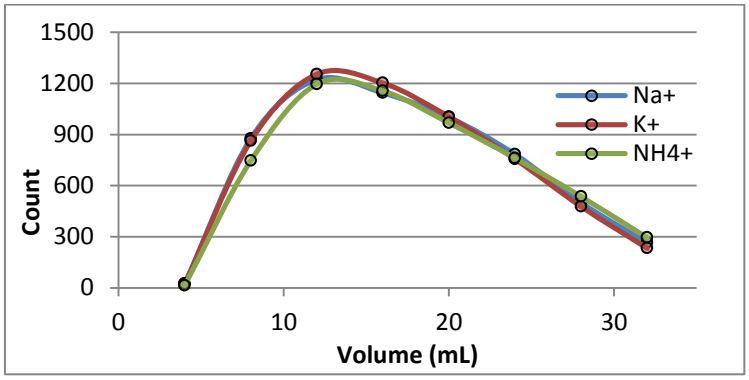

Figure 3. Elution Profiles of Molybdenum by different cations.

Taking the appropriate HCO_3^- as eluent anion, the effect of the cation ion in the elution profile was investigated. The cations Na^+, K^+ and NH_4^+ were studied with concentration 1 mol L^{-1}, at room temperature. Fig. 3 shows that the difference of intensity of the polarity among the cations did not result in significant difference in the elution profiles of Mo.

3.4. Influence of the Concentration of Eluent

In this study, the temperature of 40 ^oC was used in order to prepare high concentrations of $NaHCO_3$ solutions. Fig. 4 shows that concentrations of 1.0 mol L^{-1} and 1.5 mol L^{-1} provided best elution profiles characterized by a rapid extraction into the lower eluent volume, and less time elution. On the other hand, the 0.5 mol L^{-1} concentration provided a broad band profile, increasing the eluted volume and the time required for extract all Mo. The recovery of Mo was higher than 98% in three concentrations.

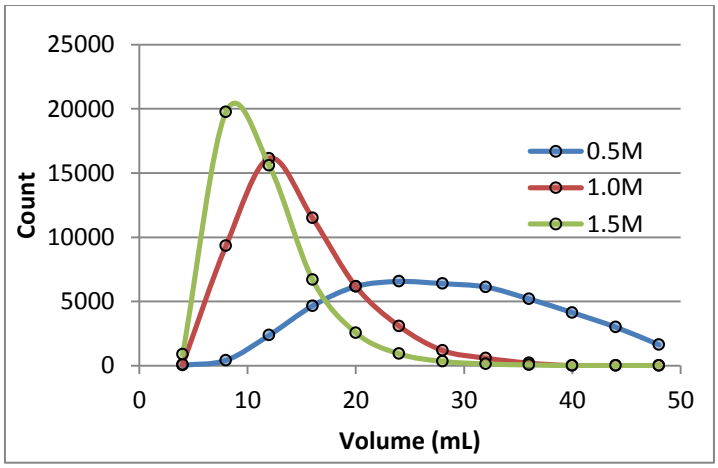

Figure 4. Elution Profiles of Molybdenum on different concentrations of $NaHCO_3$.

3.5. Influence of Temperature in Elution

In this study, the Mo was eluted from Dowex 1x8 column with 1.0 mol L^{-1} $NaHCO_3$ at different temperatures, and the results are showed in Fig.5.

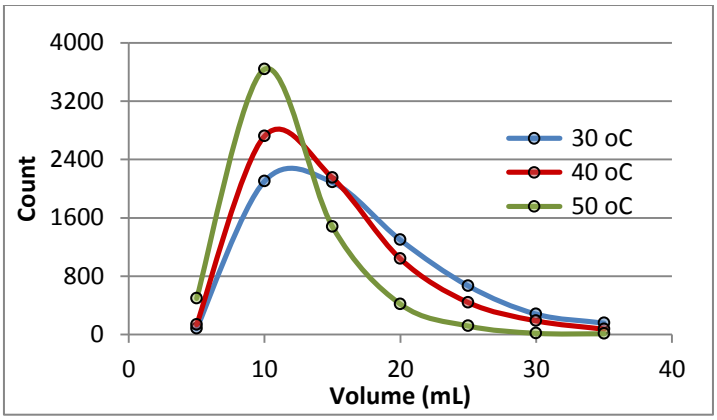

Figure 5. Elution Profiles of Molybdenum with $NaHCO_3$ at different temperatures.

Fig.5 shows that the Mo elution profiles from the Dowex 1x8 column with 1.0 mol L^{-1} $NaHCO_3$ improved with the increasing of temperature. Lesser spent time and lesser eluted volume were observed at 50 ^oC than at 30 ^oC. This elution profile reduces the processing time, and a concentrated final product in smaller volume is obtained. Such characteristics are recommendable for a separation process by chromatographic column.

4. CONCLUSIONS

Among the investigated desorbents, the nitrate revealed the best elution profile of Mo from the Dowex 1x8 resin column. The strong interaction between the nitrate anions and ion exchange resin produces effective desorption of molybdate ions. However, this same strong inter action of nitrate on the resin releases also the adsorbed iodide ions contaminating the eluted Mo.

On the other hand, moderate interaction between the hydrogen carbonate and the exchanger was observed, and preferential desorption of molybdate ions without iodide ions was obtained.

From studies of eluent concentration and the temperature was verified that these can improve the elution profile of Mo. The increasing both concentration and temperature reduce the elution time and eluted volume.

Based on the results in this work, a simple separation process of Mo-I by chromatographic column can be suggested using 1.0 mol L^{-1} $NaHCO_3$ as eluent at 50 ^oC. In these conditions, the Mo recovery is higher that 98% with the minimal contamination of iodide. In future works, a systematic retention-elution study of Mo for Dowex 1x8 column of the suggested separation process will be investigated, in presence of other contaminants like I, Te, Ru and Zr.

ACKNOWLEDGMENTS

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