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**STUDIES ON THE SEPARATION OF <sup>99</sup>MO FROM NITRIC ACID  
MEDIUM BY ALUMINA**

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**ABSTRACT**

<sup>99m</sup>Tc, the product of radioactive decay of <sup>99</sup>Mo, is one of the most used radioisotopes in nuclear medicine. The <sup>99</sup>Mo is produced mainly by fission of <sup>235</sup>U targets HEU or LEU. After the dissolution of uranium targets, chemical process for the separation and purification is performed in chromatographic columns. This work presents a study on the behavior of <sup>99</sup>Mo removal by adsorption on acid and neutral alumina from nitric acid, which is the dissolution reagent for LEU targets in the Modified Cintichem Process. Adsorption kinetics in solution of HNO<sub>3</sub> and the influence of pH were investigated. It was also evaluated the adsorption of <sup>99</sup>Mo from nitric solutions containing uranyl ions.

**1. Introduction**

Technetium-99m, the product of radioactive decay of <sup>99</sup>Mo, is the most widely used radioisotope in nuclear medicine, which is used in over 80% of diagnostic tests, especially cardiology and oncology. Since 2009, the production of Tc-99m generators suffers a global crisis of supply. The raw material, the <sup>99</sup>Mo, is produced mainly by fission of <sup>235</sup>U in the reactor and became scarce after the shutdown of the NRU reactor in Canada and HFR in The Netherlands due to technical problems, triggering the crisis. The two reactors account for 64% of world production. To meet demand, even in part, currently, Brazil imports the <sup>99</sup>Mo Argentina [1], South Africa and Israel. Therefore, the Brazilian government invests in domestic production with the construction of a research reactor suitable for the production of fission <sup>99</sup>Mo [2] and the Institute for Energy and Nuclear Research/National Commission of Nuclear Energy (IPEN/CNEN) develops the production technology of <sup>99</sup>Mo from uranium LEU (low enriched uranium) targets (UAl<sub>x</sub>/Al or metallic uranium). After irradiation of the U targets in the reactor, the process of separation of <sup>99</sup>Mo from fission products begins with the acidic (metallic uranium) or alkaline (UAl<sub>x</sub>/Al) dissolution of the targets. The resulting solution goes through a series of chromatographic

columns that allows a gradual decontamination of other components, yielding the  $^{99}\text{Mo}$  with high radiochemical and chemical purity for use as generator of Tc-99m in nuclear medicine.

Due to its high selectivity for  $^{99}\text{Mo}$ , alumina,  $\text{Al}_2\text{O}_3$ , is widely used as adsorbent in chromatographic purification step in the alkaline dissolution process. Alumina is also used in the separation of  $^{99}\text{Mo}$  from uranium and fission products in the dissolution of HEU targets (high-enrichment uranium) in nitric acid [3, 4].

In 1996, an acid dissolution of metallic uranium LEU targets, in the process called Modified Cintichem, was successfully demonstrated by Leonard et al. [5], who used nitric acid as a dissolution reagent instead of a mixture of acids. The main advantage in using only nitric acid is related to the treatment and disposal of radioactive waste, showing a significant reduction of the total cost of processing [6].

This work is part of a research for the development of  $^{99}\text{Mo}$  production process from uranium targets where all the steps, from dissolution throughout separation and purification, are being investigated. The aim of this study is to evaluate the adsorption behavior of molybdenum by acid and neutral alumina from the acid dissolution of metallic uranium LEU targets with  $\text{HNO}_3$  as the first separation step. The kinetics of adsorption, the influence of pH and the adsorption of Mo (VI) from nitric solutions containing uranyl ions were investigated.

## 2. Materials and methods

The Mo solution was prepared from the dissolution of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  in distilled water. The  $^{99}\text{Mo}$  tracer and acidic and neutral alumina were provided by the Center for Radiopharmacy (CR/IPEN). The alumina was used without any pretreatment or conditioning. The uranyl ion solutions were obtained dissolving pure  $\text{U}_3\text{O}_8$  with  $\text{HNO}_3$ . Ammonium hydroxide p.a. and nitric acid p.a. were used in the experiments.

The adsorption assays of Mo ions from aqueous medium by alumina was performed by placing 1.0 mL of solution containing Mo and  $^{99}\text{Mo}$  tracer in contact with 50.0 mg of alumina, at room temperature (Shaker mod. Q225M, and a tube centrifuge, Quimis). Mo solutions were prepared varying pH and uranyl ions concentration. After shaking at 200 rpm, the supernatant was separated and centrifuged for 3-5 min. A volume was removed and separated into another bottle to gamma counting at the energy of 739 keV in a Ge detector (Canberra). The experiments were performed in duplicate or triplicate and showed reproducibility greater than 90%.

The adsorption process was evaluated by distribution coefficient,  $K_d$ , defined in Equation 1.

$$K_d = ((A_i - A_f)/W)/(A_f/V) \quad (1)$$

Where  $A_i$  and  $A_f$  represent the activity (cpm) of the aqueous phase before and after contact, respectively,  $W$  is the dry mass of alumina (g) and  $V$  is the volume of the aqueous phase (mL).

### 3. Results and discussion

Figure 1 shows the adsorption kinetics of Mo (VI) at concentration of  $0.07 \text{ g.L}^{-1}$  in nitric acid solution with pH 1.1, represented by the variation of  $K_d$  with the contact time in acidic and neutral alumina in the range from 5 to 60 min. The higher the value of  $K_d$ , the greater the amount of ions of Mo (VI) adsorbed. A  $K_d$  greater than 2,000 means an adsorption of Mo greater than 99%. According to the kinetics, the adsorption increased with time to achieve equilibrium from 20 min, which is characterized by the curve plateau. The amount adsorbed is in equilibrium with the amount desorbed. The adsorption of Mo (VI) on alumina showed fast kinetics, which is a fundamental feature for chromatography in columns.

In subsequent studies, all adsorption experiments were performed using a contact time of 40 min to ensure the equilibrium time of Mo adsorption. The equilibrium time may vary due to the Mo concentration, temperature, adsorbent quantity or other assay conditions.

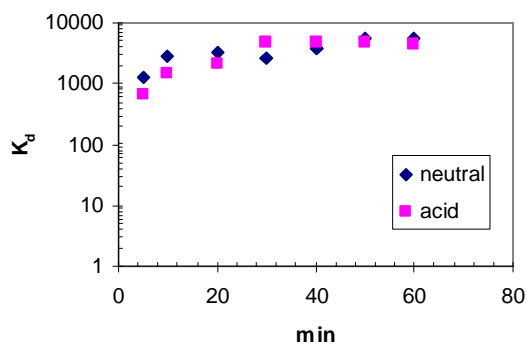


Figure 1. Adsorption kinetics of Mo (VI) ( $0.07 \text{ g L}^{-1}$ ) in acidic and neutral alumina from nitric acid medium, pH 1.1, at room temperature.

The adsorption of Mo (VI) in function of pH, in equilibrium, was evaluated and the result is illustrated in Figure 2. In acidic alumina, the existence of a pH range between 0.4 and 10.0, where the  $K_d$  value is greater than 479, peaking at 53,860, was verified. On neutral alumina, the maximum adsorption was found at pH 1.1 with  $K_d$  value equals to 3,742. At pH lower and higher than 1.1, adsorption decreased rapidly, but below pH 0.4 a  $K_d$  greater than in acidic alumina was observed. Mo (VI) in aqueous medium has several ionic species according to pH. At pH < 1.0, in which the concentration of  $\text{H}^+$  is high, they form the neutral and cationic species. According to Olazabal et al. [7], the species existing in equilibrium are  $\text{H}_6\text{Mo}_2\text{O}_8^{2+}$ ,  $\text{H}_3\text{MoO}_4^+$  and  $\text{H}_2\text{MoO}_4$ . Tangri et al. [8] suggest the predominance of  $\text{MoO}_2^{2+}$  and  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ . The low  $K_d$  value observed in Figure 2 at pH < 1.0 (acidic medium) indicates that the cationic species and neutral Mo (VI) have lower affinity for adsorption on acidic and neutral alumina.

Moreover, according to Olazabal et al. [7] and Tangri et al. [8], in pH > 1.0 anionic species are formed, such as  $\text{Mo}_7\text{O}_{21}(\text{OH})_3^{3-}$ ,  $\text{Mo}_7\text{O}_{23}(\text{OH})_5^{5-}$ ,  $\text{Mo}_8\text{O}_{26}^{4-}$ , with predominance of  $\text{MoO}_4^{2-}$  at pH > 6.

Figure 2 shows that in the pH range from 1.0 to 10.0, the acidic alumina has high adsorptivity for the anionic species of Mo (VI). At pH  $\times$  10.0, the  $K_d$  values decreased markedly. In this case, it is suggested that the anions  $\text{MoO}_4^{2-}$  compete with the high concentration of  $\text{OH}^-$  ions by acidic alumina sites, resulting in low adsorption. This behavior suggests a process of desorption of molybdate ions from acidic alumina in an alkaline solution of pH  $>$  11.0. For neutral alumina, Figure 2, the anionic species of Mo (VI), present at pH 2.8, showed a  $K_d$  value  $<$  3 and, therefore, low adsorptivity. This confirms the same behavior observed by Bakel et al. (2006), where the  $K_d$  decreased with decreasing acidity from 0.1 to 0.01 mol.L $^{-1}$ .

The acidic and neutral alumina showed high adsorption yield of Mo (VI) at acidic pH. However, the acidic alumina is applicable to both acidic and alkaline solution of  $^{99}\text{Mo}$  between pH 0.4 and 10.0. The acidic alumina can be used for adsorption of  $^{99}\text{Mo}$  when an alkaline dissolution of LEU targets is used. Neutral alumina can only be applied in acidic solutions, about pH 1.1.

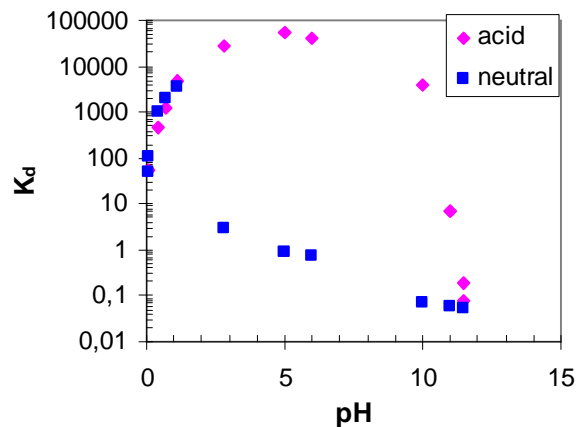


Figure 2. Adsorption behavior of Mo (VI) on acidic and neutral alumina from nitric acid medium at various pH. Equilibration time of 40 min.

To complement the study of Figure 2, the adsorption in the range of  $\text{HNO}_3$  concentration from 0.5 to 2.0 mol.L $^{-1}$ , i.e., below pH 0.1, was investigated. The results (Figure 3) show that the  $K_d$  value of Mo is low for  $\text{HNO}_3$  concentration  $>$ 1.0 mol.L $^{-1}$ . The results confirm that the neutral alumina has a small advantage over the acidic alumina with respect to adsorption of Mo in the range from 0.5 to 1.0 mol.L $^{-1}$   $\text{HNO}_3$ . Despite the low  $K_d$  value at 1.0 mol.L $^{-1}$   $\text{HNO}_3$ , the adsorption of Mo is feasible in chromatographic columns for both adsorbents.

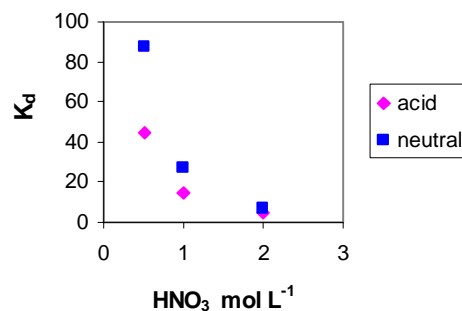


Figure 3. Adsorption behavior of Mo (VI) in acidic and neutral alumina with the concentration of nitric acid medium

In the Modified Cintichem process, the acid solution from the dissolution of LEU targets with HNO<sub>3</sub> contains uranyl ions, whose concentration is limited by the solubility of uranium, approximately 500 g.L<sup>-1</sup> [9].

The effectiveness of both alumina to adsorb Mo (VI) from uranyl nitrate solution, pH 0.4 and 2.8, was studied by varying the concentration of uranyl ions. The result is shown in Figure 4. At pH 0.4, it was found that the distribution coefficient K<sub>d</sub> decreased sharply with increasing concentration of uranyl ions, significantly affecting the adsorption of Mo (VI) for both alumina. Considering only the value of K<sub>d</sub> = 40 found in the studied conditions in a single equilibrium stage, the separation of Mo (VI) by adsorption on alumina proved to be viable in a maximum concentration of uranyl ions of 113.1 g.L<sup>-1</sup>, when performed in chromatographic columns of several equilibrium stages. To confirm this assertion, it is necessary a detailed study on the adsorption behavior of Mo in the presence of uranyl ions in chromatographic column.

At pH 2.8 and absence of uranyl ions, where the adsorption of Mo reaches a K<sub>d</sub> value equals to 27,380 on acidic alumina (a value much greater than on neutral alumina), in the presence of a increasing concentration of uranyl ions, K<sub>d</sub> values decreased markedly. Above 26 g.L<sup>-1</sup> of uranyl ions, the K<sub>d</sub> values were lower than those at pH 0.4. Therefore, separation of Mo (VI) in high concentrations of uranyl ions is better at pH 0.4 than at pH 2.8.

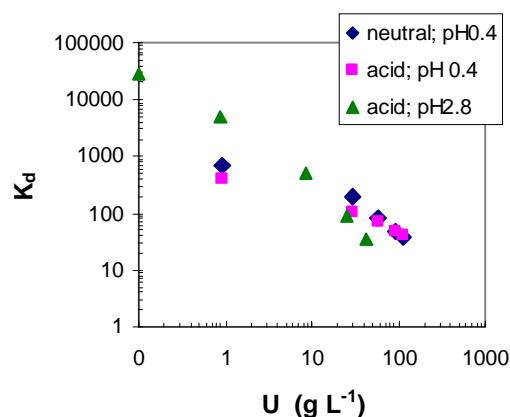


Figure 4. Influence of the concentration of U ions in the adsorption of Mo (VI) by means of alumina oxide at pH 0.4 and 2.8.

#### 4. Conclusions

Under the conditions studied in this work, both acidic and neutral alumina can be used to adsorb <sup>99</sup>Mo depending on pH of nitric solution. The acidic alumina showed higher adsorption performance of Mo (VI) from nitric acid medium at a higher pH range, from 1.0 to 10.0, than neutral alumina. The neutral alumina showed high adsorption efficiency at pH near 1.0. The presence of uranium affects the adsorption of Mo by alumina, however, the  $K_d$  values indicate a possible separation of Mo at concentrations below 113 g.L<sup>-1</sup> of uranyl ions in chromatographic columns. Future work for the separation of Mo from U solutions in chromatographic columns is programmed with the acidic and neutral alumina.

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