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MOLYBDENUM ADSORPTION BY ALUMINA AND DOWEX 1x8 RESIN FOR THE SEPARATION AND 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-99m, a radioisotope used in over 80% of diagnostic tests. Since 2009, the production of generators ^{99}Mo/^{99m}Tc suffers a crisis of global supply. The raw material, the ^{99}Mo, is produced mainly by fission of ^{235}U in the reactor in uranium targets. Brazilian government invests in building of a research reactor suitable for the domestic production of ^{99}Mo from LEU (Low Enriched Uranium) targets and the IPEN/CNEN develops the production technology. This work is part of the research for the development of production technology of ^{99}Mo at the IPEN/CNEN-SP. The study has evaluated the adsorption behaviour of molybdenum from the alkaline dissolution of aluminum plates by the alumina and by the anionic resin Dowex 1x8 aiming at their use in the process of separation and purification in chromatography columns. Influences of pH and of aluminum concentration in the retention of molybdenum were investigated. Results showed high performance in the wide pH range. However in strongly acid solutions containing aluminum, alumina showed higher adsorption percentage than that achieved by the resin Dowex 1x8.

1. INTRODUCTION

Since 2009, availability of ^{99}Mo/^{99m}Tc generators suffers a worldwide crisis due to the reduction of production of its main raw material, the fission ^{99}Mo, which is obtained from the fission of U targets with High Enrichment of Uranium-235 (HEU) in the nuclear reactors. ^{99}Mo can also be obtained using Low Enriched Uranium (LEU) targets, a highly recommended practice by the IAEA with nuclear non-proliferation and security concerns [1]. The crisis was triggered after stopping reactors from Canada and the Netherlands by technical problems, which account for 64% of world production ^{99}Mo. Currently, Brazil has an expressive consumption and an increasing demand of ^{99m}Tc in the nuclear medicine industry with participation today of 4.4% of the world market [2]. This corresponds to over three millions medical procedures per year, this radiopharmaceutical is used in more than 80% of procedures adopted in medicine nuclear, whose role is fundamental in the diagnosis of diseases associated with heart, liver, kidney, brain, lung, stomach, thyroid and skeletal system, among other. To meet the demand, Brazil has imported the raw material from Argentina, South Africa and Israel. For long-term, Brazilian government invests in the construction of the first multipurpose reactor [3] suitable for the domestic production of ^{99}Mo from LEU targets in order to supply of fission ^{99}Mo in the coming decades.

This work is part of the research of production technology of ^{99}Mo that has been developed at the IPEN/CNEN-SP. The study evaluates the adsorption behaviour of molybdenum from the alkaline dissolution of aluminum plates on the aluminas and on the anionic resin Dowex 1x8 aiming at their use in the process of separation and purification in chromatography columns. Influences of pH and concentration of aluminum on the adsorption behavior of molybdenum were investigated.

2. EXPERIMENTAL

2.1. Materials

Molybdenum-98 stock solution was prepared by dissolving 3 $mol{\cdot}L^{-1}$ Na_2MoO_4 Merk, in distilled water. Aluminum plates (6061) were provided by Center of Nuclear Fuel, CCN-IPEN/CNEN. The acidic alumina (aluminum oxide active acid 90, 70-230 mesh, code 1.01078.1000) and neutral alumina (aluminum oxide neutral active 90, 70-230 mesh, code 1.01077.1000), Merck, and anionic resin Dowex 1x8 (50-100 mesh), Sigma-Aldrich, were worked as received, without a preconditioning. Other chemical reagents used were analytical grade. The ^{99}Mo samples used as tracer were provided by the Center of Radiopharmacy, CR-IPEN/CNEN.

Aluminum solutions were prepared by dissolution of an aluminum plate in boiling 3 $mol.L^{-1}$ NaOH solution. After the filtering process, the solutions were acidified with 10 $mol{\cdot}L^{-1}$ HNO_3 until total disappearance of precipitate of aluminum hydroxide, pH from 0.1 to 0.5. A pHmetro Metrohm E512 previously calibrated was used for pH reading.

2.2. Batch Tests

Adsorption tests were conducted by batch tests employing 50 milligrams of adsorbents (acidic alumina, neutral alumina and anionic resin Dowex 1x8) placed in contact with 1 mL of aluminum solution (varying concentrations) containing natural Mo carrier (0.25 $mg.L^{-1}$) and ^{99}Mo tracer, hereafter referred just Mo, stirring at 200 rpm, during 40 minutes on a shaker Q225M, Quimis. After the contacting, 800 µL of supernatant were centrifuged on a Quimis 222T for separation of suspended particles, and then a 500 µL aliquot of the supernatant was subjected to gamma counting during 180 seconds at the energy of 739 keV using a HPGe detector, Canberra, at the CR/IPEN/CNEN. Also, Mo adsorption tests were conducted at pH range from 0.1 to 13 in solutions without aluminum.

The pH values in the aluminum solutions were fixed at the start of the experiments using solutions 10 $mol{\cdot}L^{-1}$ HNO_3 and 1 $mol.L^{-1}$ NaOH. A pHmetro Metrohm E512 previously calibrated was used for pH reading. All trials were conducted in duplicate at room temperature of 25 ± 3° C.

2.3. Analysis of Batch Tests

Adsorption efficiency of adsorbents was calculated on the basis of percentage values of removed Mo from aqueous phase, using the equation (1).

$$\text{Adsorption \%} = (1- (C_a / C_b)) \times 100 \qquad (1)$$

Being: C_a = gamma counting rate of the sample after contact (final solution = supernatant)
C_b = gamma counting rate of the sample before contact (initial solution)

3. RESULTS

Adsorption performance of molybdenum on the acidic and neutral aluminas and resin Dowex 1 x 8 in pH range from 0.1 to 13 and in the presence of Al^{3+} ions from 1.2 to 20 g. L^{-1} was investigated.

3.1. Influence of pH

The formation of ionic species of Mo(VI) by the hydrolysis depends of pH of aqueous medium [4, 5], and each species has a different adsorption behavior. Fig. 1 illustrates the result of Mo adsorption on the neutral and acidic aluminas and Dowex 1x8 at studied pH values.

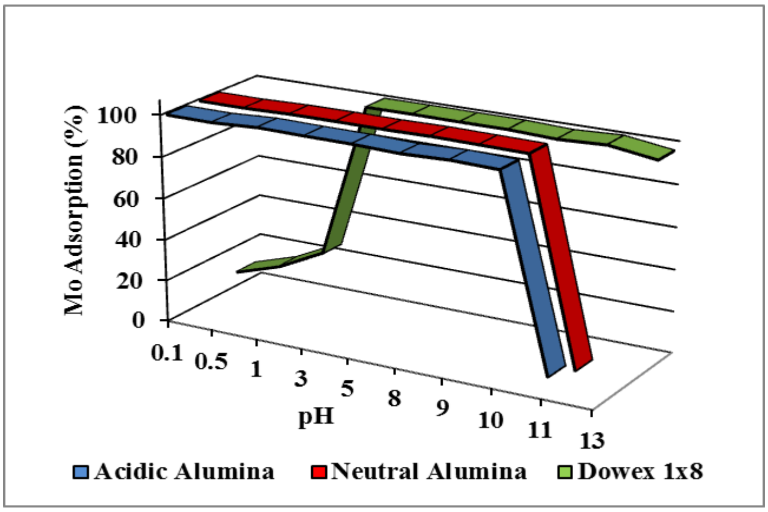

Figure 1. Performance of the adsorbents for Mo ions from aqueous medium.

In pH range from 3 to 10 both aluminas and Dowex 1x8 exhibit high values of Mo adsorption (greater than 99%). In pH from 10 to 13, high adsorption was observed for dowex only. Between the acidic alumina and neutral alumina no difference in Mo adsorption behavior was observed.

For Dowex 1x8, the adsorption efficiency in an acid medium is low, but increases significantly from pH 2 to reach a value > 99% at pH 3 and remains constant until pH 13. For pH ≤ 2, the adsorption gradually decreased, such behavior can be attributed to forming of the several polymeric ionic species of Mo(VI) with low affinity by the Dowex 1x8. In strong acid (pH < 1), molybdenum is mostly as cation without any affinity for anionic resin, whereas the Mo is still adsorbed on aluminas probably by affinity to cationic species of Mo.

For aluminas, the adsorption of Mo was greater than 99% in pH from 0.1 to 10. In pH > 10, the adsorption decreased significantly. The MoO_4^{2-} anions, predominantly present in basic medium, probably compete with OH^- ions present in greater quantity by adsorption on the aluminas. Moreover, the adsorption of OH^- promotes the formation of a negative charge on surface, decreasing Mo adsorption by electrostatic repulsion. Another existing factor which can have contributed to the reduction of adsorption of Mo in basic pH is the reaction between the alumina and ions OH^-, becoming the alumina in a cationic exchanger [6].

It is important to report herein that the used Merck aluminas in this experiment showed an adsorption behavior of Mo very different from the aluminas provided by the CR/IPEN, in all studied pH range. This can be associated to the existence of different structures for both acidic and neutral alumina. The work with the aluminas from the CR/IPEN was presented at the RERTR 2010 [7].

3.2. Influence of Aluminum Ions from Acid Medium

The solutions from the alkaline dissolution (pH 13.5) of Al plates exhibited considerable amount of Al^{3+} ions which caused the formation of a flocculating precipitate of aluminum hydrate during the acidification step. This precipitate hinders the adsorption of Mo ions on alumina and Dowex 1x8. So, the solution of Al was acidified to total disappearance of precipitate and then the adsorption of Mo ions was investigated. Fig. 2 shows the results found for adsorption of Mo ions in various concentrations of Al^{3+} ions in pH between 0.1 and 0.5.

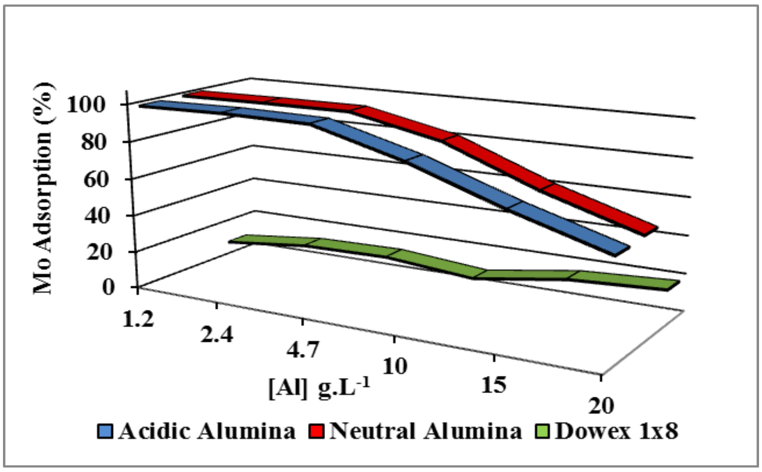

Figure 2. Performance of the adsorbents for Mo ions from the acid medium containing Al^{3+} ions.

The values of Mo adsorption on the aluminas are greater than 98% until the concentration of Al 4.7 $g.L^{-1}$. This value indicates high performance of aluminas in small chromatographic columns and the possibility to use high flow-rates as the main advantages for separation of Mo from solution containing Al^{3+} ions. At larger concentrations of Al, a decreasing of adsorption was observed due to the influence of Al. This can be explained by the competition between the Mo and Al ions for adsorption, which turns in favor of Al ions on the acidic alumina and neutral alumina.

For Dowex 1x8, Al ions have no significant influence in the adsorption of Mo which remained in value between 10% and 20%, an equal value found in the study of pH < 0.5 (Fig. 1). This performance of the Dowex 1x8 shows that probably, with a height column greater than the alumina column it is possible to remove Mo from solutions of pH< 0.5 containing Al, with the same efficiency of alumina.

4. CONCLUSIONS

Acidic alumina, neutral alumina and the anionic resin Dowex 1x8 were investigated by the batch studies for retention of Mo ions from the alkaline dissolution of Al plates. In the acidified dissolution solutions containing Al^{3+} ions, the aluminas are good adsorbents of Mo. The adsorption of Mo on the Dowex 1x8 was low, but was noted no influence of Al^{3+} ions.

Among the adsorbents studied, the two aluminas provided greater retention of Mo in acid solutions containing Al. So, its chromatographic column will be more efficient with less processing time than the column of Dowex 1x8 in separation process of fission ^{99}Mo. However, a Dowex 1x8 column can be as efficient as the alumina column at pH ≥ 3 without Al ions. The next experiments will be conducted in chromatography columns also will be investigated the influence of the fission products present in dissolution solution of LEU targets such as Te, Ru and Iodine.

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