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ADSORPTION BEHAVIOR OF ^{99}Mo USING AG1-X8 ANIONIC RESIN

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ABSTRACT

The significant growth in demand of ^{99}Mo in developed and developing countries, like Brazil, requires large production capacity and availability of this radioisotope. With the global crisis on its supply to Brazil rethought the need to become independent in their production and the solution was to start the Brazilian Multipurpose Reactor (RMB) project, which aims to meet the national demand of ^{99}Mo for the medical field. This work aims to study the ^{99}Mo adsorption in AG1-X8 strong anion resin, which is one of the intermediate steps of separation and purification, retaining it in the form of molybdate ions. In process evaluated the resin properties with respect to pH and concentration of ^{99}Mo in the solution. The adsorbed amount of ^{99}Mo was determined indirectly by the amount in the supernatant after adsorption and the data fitted to the Langmuir and Freundlich isotherms. Among the models, the Langmuir showed a closer relationship with the experimentally obtained data. This suggests the occurrence of monolayer adsorption and heterogeneous conditions at the surface, where both phenomena can coexist in the experimental conditions tested.

1. INTRODUCTION

Radioisotopes play an important role among the peaceful uses of nuclear energy. In nuclear medicine, radioisotopes are used to conduct assessments of anatomical and/or physiological, diagnostic, treatment of relevant diseases, such as cancer and medical research.

The supply of ^{99}Mo, the main isotope used in medicine, is increasingly scarce because few reactors in the world are under repair, as the National Research Universal (NRU) reactor in Canada and the High Flux Reactor (HFR) in the Netherlands, responsible for approximately 70% of the world [1].

The dependence of Brazil with the importation of radioisotopes became evident in 2009, when the Canadian NRU reactor, which was the main supplier of Brazil, had ma unscheduled stop, while the reactors in Belgium and the Netherlands were also disconnected. Despite the problem be mitigated by purchasing the surplus from Argentina and South Africa, it was not enough to prevent the supply crisis that year.

Each year, nuclear medicine is dependent on new reactors under construction or development of new technologies, and the Brazilian government's main objective is to make Brazil to become self-sufficient in the production of radioisotopes. And for that, in 2008, the Brazilian Multipurpose Reactor (RMB) project was established as a government target.

The process of obtaining ^{99}Mo fission via ^{235}U the from UAl_x targets, which uses one primary winding and subsequent steps of separation and purification of ^{99}Mo involving the use of chromatographic columns, so as alumina exchange resins ion to reach the pharmaceutical specifications needed for their use in the diagnosis of diseases.

Studies of the group responsible for the stages of dissolution, separation/purification of ^{99}Mo at Nuclear and Energy Research Institute (IPEN-CNEN/SP) began by dissolving alkaline UAl_x targets via fission process of ^{235}U.

After irradiation targets also other fission products are formed, which are considered contaminants. Some of them decay in the early hours, due to the short half-life, but others may have a half-life of hundreds of years, and high toxicity to humans, hence the great importance of the separation / purification of ^{99}Mo.

The subsequent steps of separation and purification of ^{99}Mo involve the use of chromatographic columns, both of alumina as ion exchange resins, to reach the specifications needed for use in disease diagnostics. ^{99}Mo and ^{99m}Tc form radioactive pair in equilibrium transient time since the physical half-life of the parent is about ten times greater than that of the child. This balance enables the manufacture of the radionuclide generator system of ^{99}Mo–^{99m}Tc [2].

The main objective of this study was to investigate the effects of pH, equilibration time, and other parameters in the process of separation and purification of ^{99}Mo in AG1-X8 resin in order to determine the factors that influence the retention of this radioisotope.

2. MATERIALS AND METHODS

2.1. Reagents and Solutions

All reagents and solvents were of analytical reagent grade.

^{99}Mo tracer obtained from the production of IPEN and used with the addition of carrier in the form Na_2MoO_4 $2H_2O$.

The pHs of the solutions were adjusted with a nitric acid and sodium hydroxide.

AG1®-X8 anionic resin from Bio-Rad (analytical grade, 50-100 mesh size, chloride form and 8% cross linkage) [3] was used in the experiments.

2.2. Apparatus

The analytical control has been done by gamma rays spectrometry of High Purity Germanium (HPGe) detector, Canberra. For ^{99}Mo, the gamma energy counted for adsorption studies is 739.5 keV.

2.3. Procedure for Adsorption Experiments

The experiments were carried out using the batch method. Batch adsorption were conducted using 50 mg of resin with 1.5 mL of solutions containing molybdenum ions of desired concentrations at constant temperature (298± 2 K) on a shaker (200 rpm) with each experiment performed in duplicate.

After the specified time 500 μL of the supernatant solution was separated and ^{99}Mo activity was measured in the gamma detector. The concentration of molybdenum in the resin was obtained by mass balance using the equation below:

$$\text{Percentage adsorption} = (A_i - A_f)/A_i \times 100 \quad (1)$$

where A_i and A_f are the activities of the molybdenum in initial and final solutions, respectively.

The amount of adsorbed Mo (q_{eq}) was calculated using the equation 2 described below:

$$\text{Adsorption capacity, } q_{eq} = (C_i - C_f) \times \frac{V}{m} \quad (2)$$

Where, C_i and C_f = initial and final concentrations (mg L^{-1}) of the molybdenum, respectively, V = volume of molybdenum solution (L), and m = weight of AG1-X8 (g).

2.4. Effect of pH on Adsorption

The effect of pH on ^{99}Mo adsorption was studied over the range 0.5–14.0 using HNO_3 (1 mol L^{-1}) or NaOH (1 or 3 mol L^{-1}) solutions. Resin was equilibrated at the desired pH for about 30 min using an initial molybdenum 30 mg L^{-1}.

2.5. Effect of Contac Time

The experiments were conducted to quantify the effect of contact time on the molybdenum adsorption. The contact time interval was from 10 to 120 min, the solution pH was 11 and the molybdenum concentration was 20 mg L^{-1}.

2.6. Adsorption Isotherms

The adsorption isotherms are curves that show how effectively the adsorbent adsorbs the solute and if required the purification can be obtained; gives an estimate of the maximum amount of solute which the adsorbent adsorbs and if it is economically feasible to purify the solution.

Generally, the concentration is expressed ion adsorbed (mg g^{-1}) versus remaining concentration in the solution (g mL^{-1}) at a constant temperature. The adsorption isotherms are commonly used: the Langmuir, Freundlich (4, 5).

Molybdenum solutions (1.5 mL) with concentrations varying from 10 to 200 mg L^{-1}, pH 11, were contacted with 50 mg of resin during 60 min for determining the adsorption capacity of

the AG1-X8 resin for molybdenum. The data were evaluated by adsorption isotherm models of Langmuir and Freundlich to describe the adsorption data.

2.6.1. Langmuir isotherm

It is derived from the following theoretical considerations: assume that the surfaces are homogeneous, all active sites are equal affinity for the adsorbate, and therefore, adsorption of a site will not affect the adsorption site adjacent to this. The Langmuir adsorption isotherm is defined from the following expression:

$$q_{eq} = \frac{Q_{max} * K_L * C_{eq}}{(1 + K_L * C_{eq})} \quad (3)$$

The Langmuir equation can be rearranged to linear form:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_{max} * K_L} + \frac{1}{Q_{max} * C_{eq}} \quad (4)$$

where, q_{eq} is the mass of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}); C_{eq} is the equilibrium concentration of the adsorbate in solution after adsorption (mg L^{-1}); Q_{max} is the empirical constant that indicates the monolayer adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant related to the adsorption.

The constants Q_{max} and K_L can be determined by the slope and the linear coefficient of the linear equation.

2.6.2. Freundlich isotherm

The Freundlich isotherm is represented by the equation:

$$q = K_F \, C_{eq}^{\,1/n} \quad (5)$$

where, C_{eq} is the equilibrium concentration (mg L^{-1}), q is the amount adsorbed (mg g^{-1}) and K_F and *n* are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity, respectively. The linearised form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_F + \frac{1}{n} \ln C_{eq} \quad (6)$$

3. RESULTS AND DISCUSSION

3.1. Effect of pH

pH is considered as an important parameter in the adsorption studies of metals as it controls the adsorption at the adsorbent-solution interface. It affects both the resin and the molybdenum ions present in the solution. Experiments were conducted varying the solution pH from 0.5–14 while rest of the factors were kept constant. The maximum removal of

molybdenum was observed at pH range 3–13 as illustrated in Figure 1. The maximum removal efficiency 99.9 at pH range 9–12.5.

To avoid precipitation of aluminum hydroxides, from the U-Al_x alloy in alkaline dissolution process, the experiments were carried in pH above 11.

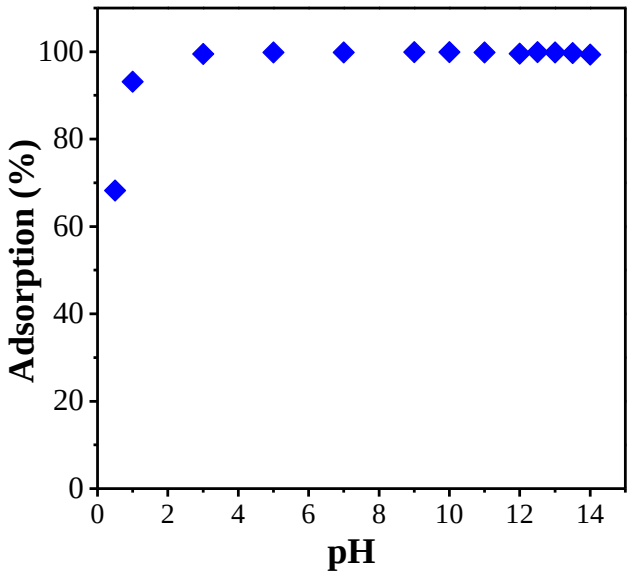

Figure 1: Effect of pH on the molybdenum adsorption by AG1-X8 resin.

3.2. Effect of Contact Time

Contact time shows a marked influence on the adsorption efficiency and is used to elucidate the kinetics of the adsorption process. The adsorption of molybdenum by resin was very rapid for 20 mg L^{-1} solutions and the equilibrium was achieved within 10 min and the percentage of molybdenum adsorbed was 98% (Figure 2), reaching values of the order of 99.9% in 20 min and maintained until 120 min.

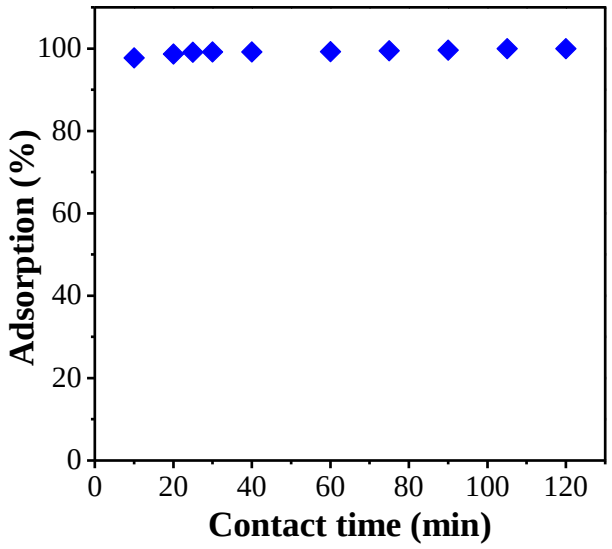

Figure 2: Effect of contact time on the molybdenum adsorption by AG1-X8 resin.

According to the results, the agitation/equilibrium time was fixed at 60 min for the rest of the experiments so that equilibrium is reached.

3.3. Adsorption Equilibria Studies

To evaluate the adsorptive capacity of resin for Mo ions from the solution of pH 11, the adsorption isotherm was fitted (Figure 3).

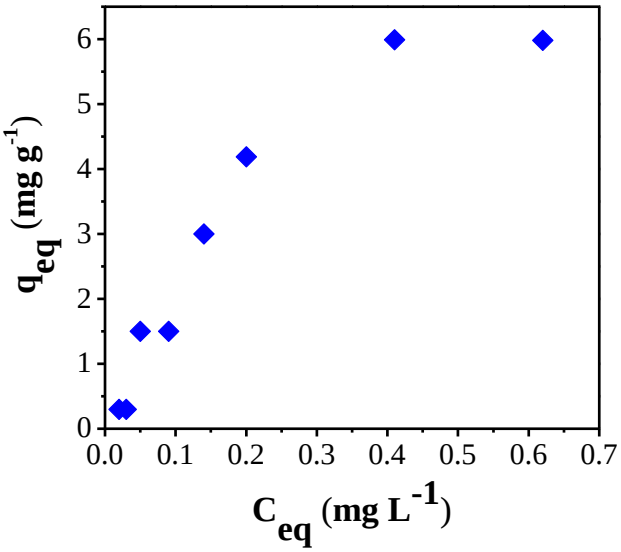

Figure 3: Adsorption isotherm of Mo ion by the AG1-X8 resin.

It is noted that the adsorbed amount has evolved rapidly with increasing equilibrium concentration up to 0.2 mg L^{-1} and the second stage at equilibrium concentrations above 0.4 mg L^{-1}, the increase of the amount adsorbed was lower tending to stabilize, indicating a possible saturation of the resin under the conditions of this study.

Figure 4 represent the plot of the experimental data based on Langmuir and Freundlich models. In this study, a Chi-square analysis [6, 7] of two isotherms, Langmuir and Freundlich, have been applied to the experiment of molybdenum adsorption.

The Chi-square test was used in all isotherms on the same abscissa and ordinate. The equivalent mathematical statement was:

$$\chi^2 = \sum \frac{(q_{eq} - q_{e,m})}{q_{e,m}} \quad (7)$$

where q_e, m equilibrium capacity obtained by calculated from models (mg g^{-1}) and that was the equilibrium capacity (mg g^{-1}) from the experimental data. If data from model were similar to the experimental data, χ^2 would be a small number and vice versa.

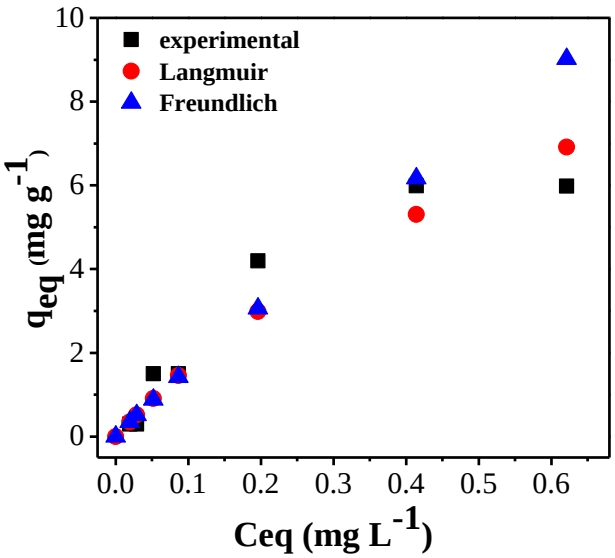

Figure 4: Theoretical isotherms and experimental data

Correspondingly, the linear regression showed very different results. The chi-square test for each model are shown in Table 1. In this study, the Chi-square of the Langmuir isotherm showed values lower than the Freundlich isotherm and was statistically confirmed to be a better fit.

Table 1. **Langmuir and Freundlich parameters for the adsorption of molybdenum**

Langmuir			
Q_{max} (mg g^{-1})	**b (L mg $^{-1}$)**	**R**	**χ^2**
17.575	0.0545	0.2486	1.18
Freundlich			
K_F [(mg g^{-1}) (L mg^{-1})$^{1/n}$]	***n***	**R**	**χ^2**
14.103	1.0651	0.9087	1.99

This suggests the occurrence of monolayer adsorption and heterogeneous conditions at the surface, where both phenomena can coexist in the experimental conditions tested.

4. CONCLUSION

The results obtained using AG1-X8 resin as adsorbent, showed a high percentage of molybdenum ion adsorption. Among the analyzed models, the Langmuir model is a good fit for the set of adsorption data.

The maximum adsorption capacity of the resin for molybdenum ions through the Langmuir model, is equal to 17.575 mg g-1. Thus, this resin was satisfactory for use in the step of separation and purification of molybdenum.

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