*2011 International Nuclear Atlantic Conference - INAC 2011*
*Belo Horizonte,MG, Brazil, October 24-28, 2011*
*ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN*
*ISBN:* **978-85-99141-04-5**

# STUDY OF MOLYBDENUM ADSORPTION ISOTHERMS ON ACIDIC ALUMINA AND NEUTRAL ALUMINA

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## ABSTRACT

This work is part of the research of production technology of $^{99}$Mo from uranium targets, where acid and alkaline dissolutions are being investigated at the IPEN/CNEN-SP. In this study, the adsorption behaviour of molybdenum on acidic alumina and neutral alumina was evaluated. The adsorption studies were performed by batch assays with Mo solution, containing $^{99}$Mo tracer, in contact with 50 mg of alumina. The molybdenum concentration was varied in order to study the equilibrium adsorption isotherms. The isotherm models of Langmuir and Freundlich were investigated.

## 1. INTRODUCTION

Technetium-99m is the radioisotope more used in nuclear medicine, especially in cardiology and oncology diagnostics. Tc-99m is the decay product of Mo-99, which can be produced mainly by fission of $^{235}$U in the reactor in uranium targets. After irradiation in reactor, uranium targets are dissolved by acid or alkaline solutions, and the resulting solution goes through a series of chromatographic columns that allows a gradual decontamination of other components, yielding the $^{99}$Mo with high radiochemical and chemical purity for use in nuclear medicine as a generator of $^{99m}$Tc. This work, which started in 2010, is part of research of production technology of $^{99}$Mo from the low enriched uranium (LEU) targets, where acid and alkaline dissolutions and process of separation and purification were being investigated at the Environmental Chemistry Center (CQMA), IPEN/CNEN-SP. The first papers were presented on the 32nd International Meeting on Reduced Enrichment for Research and Test Reactors-RERTR 2010 [1, 2] and on the VII Congress of SBBN-2010 [3, 4]. In this paper, the adsorption behaviour of molybdenum(VI) on acidic and neutral aluminas was evaluated by batch aiming at their use in the process of separation and purification in chromatography columns. Equilibrium adsorption isotherms and the isotherm models of Langmuir and Freundlich were investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

Molybdenum stock solution was prepared by the dissolving of $Na_2MoO_4.2H_2O$ in distilled water. Mo(VI) solutions in the concentration range from 0.14 $g.L^{-1}$ to 600 $g.L^{-1}$ were prepared by the dilution from the Mo stock solution with nitric solution of pH 0.6-1.0. The acidic alumina and neutral alumina were provided by the Center of Radiopharmacy (CR), IPEN/CNEN-SP which no preconditioning was applied. The aluminas were worked as received. Other used chemical reagents were analytical grade. The used $^{99}$Mo samples as tracer were provided by the CR-IPEN/CNEN.

### 2.2. Batch Test

Adsorption experiments were conducted by the batch test. Fifty milligrams of each adsorbent (acidic alumina and neutral alumina) were placed in contact with 1 mL of Mo solution containing $^{99}$Mo tracer, in the stirring at 200 rpm, during 40 min on a shaker Q225M, Quimis. The shaking time of 40 min was used to guarantee the adsorption equilibrium at high concentrations of Mo. The study of adsorption equilibrium time of the Mo on the aluminas was determined and presented in the another paper [1]. After the contacting, a volume of the supernatant was removed and centrifuged on a Quimis 222T for separation of suspended particles. An aliquot of the supernatant 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 countings of the supernatant and the initial solution were correlated to the Mo concentrations.

### 2.3. Isotherm

The adsorption equilibrium isotherm was obtained varying the Mo(VI) concentration from 0.14 mg $L^{-1}$ to 600 mg $L^{-1}$ in pH 0.6-1.0. All experiments were performed at less in duplicate and all results represent measurements with an estimated experimental erro between 10% and 4% in the concentration range from 0.14 $mg.L^{-1}$ to 600 $mg.L^{-1}$, respectively. The adsorbed quantity on the alumina ($q_{eq}$, mg $g^{-1}$), in the equilibrium, was calculated by the equation (1).

$$q_{eq}\ (mg\ g^{-1}) = (C_0 - C_{eq}) \times V/M \quad . \tag{1}$$

Where $C_0$ (mg $L^{-1}$) is the Mo concentration in the initial solution, $C_{eq}$ (mg $L^{-1}$) is the Mo concentration in the supernatant solution, V is the volume of solution (L) in contact with the alumina and M is the mass (g) of the alumina.

The adsorption equilibrium isotherm data were evaluated by Langmuir and Freundlich adsorption isotherm equations [5]. Langmuir isotherm model represented by the equation 2 assumes monolayer adsorption. The equation [3] describes its linear form used to calculated the absorption parameters of Langmuir.

$$\text{Langmuir model: } q_{eq} = Q_{max} * K_L * C_{eq}/(1+K_L*C_{eq}) \quad (2)$$

$$\text{Langmuir model in linear form: } C_{eq}/q_{eq} = 1/(Q_{max}*K_L) + 1/\, Q_{max} *C_{eq} \quad (3)$$

Where $q_{eq}$ is the metal amount adsorbed per unit mass of adsorbent (mg $g^{-1}$), $C_{eq}$ is the equilibrium concentration of metal in the supernatant solution (mg $L^{-1}$), $Q_{max}$ is the maximum adsorption capacity (mg $g^{-1}$), and $K_L$ is the constant related to the free energy of adsorption. A straight line is obtained by plotting $C_{eq}/q_{eq}$ against $C_{eq}$ and the slope and intercept are used to calculate the $Q_{max}$ and $K_L$, respectively.

The Freundlich model is represented by the equation 4, which indicates that the surface of adsorbent is heterogeneous. The equation (5) describes its linear form used to calculate the Freundlich parameters.

$$\text{Freundlich model: } q_{eq} = K_F *C_{eq}^{\ 1/n} \quad (4)$$

$$\text{Freundlich model in linear form: } \log q_{eq} = \log K_F + 1/n * \log C_{eq} \quad (5)$$

Where $K_F$ is a parameter of relative adsorption capacity of the adsorbent related to the temperature and n is a characteristic constant for the adsorption system. A plot of log $q_{eq}$ against log $C_{eq}$ gives a straight line and the slope and intercept correspond to 1/n and log $K_F$, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Adsorption with the Concentration of Mo(VI) Ions

In this study the values of adsorption percentage were determined to each Mo concentration in the range from 0.14 mg.$L^{-1}$ to 600 mg.$L^{-1}$ and were illustrated in Fig. 1. It shows that the adsorption decreased from 100% to 60% with the increasing of the Mo concentration until 200 mg.$L^{-1}$ and stabilized around of 60% to higher concentrations, on the acidic alumina. The adsorption decreased from 90% to 55% with the increasing of the Mo concentration until 100 mg.$L^{-1}$; in higher concentration increased slightly until 200 mg.$L^{-1}$ and stabilized around 60% to higher concentrations, on the neutral alumina. Between the two aluminas, the acidic alumina shows higher affinity by the Mo ions until to concentration of 200 mg.$L^{-1}$.

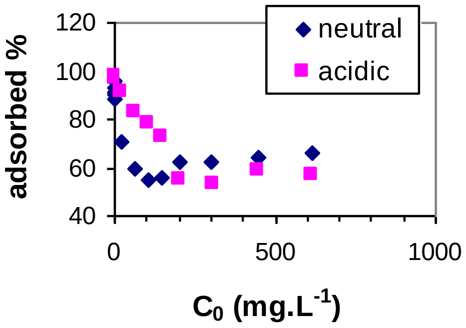

**Figure 1. Adsorption of the Mo(VI) ions from the nitric solutions, pH 0.6-1.0, on the acidic alumina and neutral alumina at 27±1ºC. $C_0$ = initial concentration of Mo.**

### 3.2. Equilibrium Adsorption Isotherms

The equilibrium adsorption isotherms were obtained and can be seen by plotting the quantity of sorbed Mo on the acidic and neutral aluminas ($q_{eq}$) against equilibrium concentration ($C_{eq}$) in the solution in Fig. 2. For acidic alumina, the Figure shows that the quantity of sorbed Mo increased with the increasing of the equilibrium concentration until to reach a constant value around 2 $mg.g^{-1}$ between the concentrations 40 $mg.L^{-1}$ and 100 $mg.L^{-1}$. After this, again the sorbed quantity increased with the increasing of the equilibrium concentration.

There are many factors that may influence the adsorption behaviour, such as the ionic species of adsorbate, adsorbent surface properties, protonation reaction and hydrogen bonding. The range, which the sorbed quantity is constant, suggests that the adsorption of Mo(VI) ions onto acidic alumina occurred through a combination of electrostatic forces where after the formation of the step of saturation with formation of a monolayer, more adsorption was possible under the experimental condition. It can be explained by a possible reaction of protonation. With the increasing of the Mo concentration, the monolayer underwent protonation by the $H^+$ ions of the acid medium. The phenomenon started a new process of adsorption of the Mo ions.

For neutral alumina, the quantity of sorbed Mo increased with the increasing of the equilibrium concentration under the studied experimental condition. In this case, the adsorption behaviour suggests that the protonation on the alumina surfaces by the $H^+$ ions was continuous, so the adsorption was also continuous.

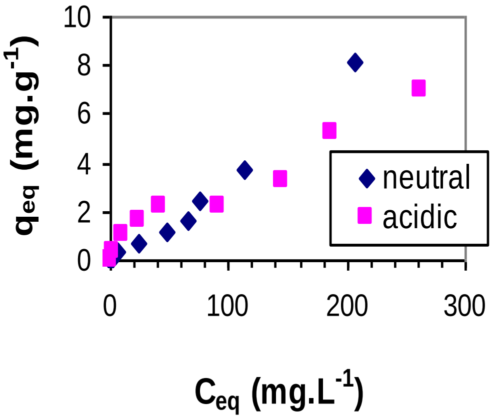

**Figure 2. Equilibrium adsorption isotherm for Mo(VI) ions from the nitric solutions, pH 0.6-1.0, on the acidic alumina and neutral alumina at 27±1ºC.**

The Langmuir and Freundlich isotherm models were evaluated for the equilibrium adsorption isotherms of Mo, and the values of the parameters and the related correlation coefficients ($R^2$) are presented in Table 1 and 2. It can be observed that the best-fit isotherm model was the Freundlich isotherm model confirmed by greater $R^2$ value closer to unity (0.99) for both aluminas. The value of 1/n, which is lower than unity, indicated that Mo ions are favourably adsorbed on the aluminas.

The Langmuir model did not describe well the equilibrium adsorption isotherm, the values of correlation coefficients were so far to unity.

**Table 1. Parameter values of the Langmuir and Freundlich isotherms for adsorption of the Mo(VI) ions on the acidic alumina from nitric solutions, pH 0.6-0.1.**

| Isotherm model | $Q_{max}$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | 1/n | $K_F$ (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$ | correlation coefficient, $R^2$ |
|---|---|---|---|---|---|
| Langmuir | 5.8 | 0.0281 | ----- | ----- | 0.746 |
| Freundlich | ----- | ------ | 0.653 | 0.176 | 0.992 |

**Table 2. Parameter values of the Langmuir and Freundlich isotherms for adsorption of the Mo(VI) ions on the neutral alumina from nitric solutions, pH 0.6-1.0.**

| Isotherm model | $Q_{max}$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | 1/n | $K_F$ (mg g$^{-1}$)(L mg$^{-1}$)$^{1/n}$ | correlation coefficient, $r^2$ |
|---|---|---|---|---|---|
| Langmuir | 7.5 | 0.0099 | ----- | ----- | 0.311 |
| Freundlich | ----- | ------ | 0.720 | 0.100 | 0.992 |

In Fig. 3 and 4 the isotherm models are plotted together with the experimental data points. As can be seen the Freundlich isotherm model fit well the experimental isotherm of the Mo(VI) ions for both aluminas.

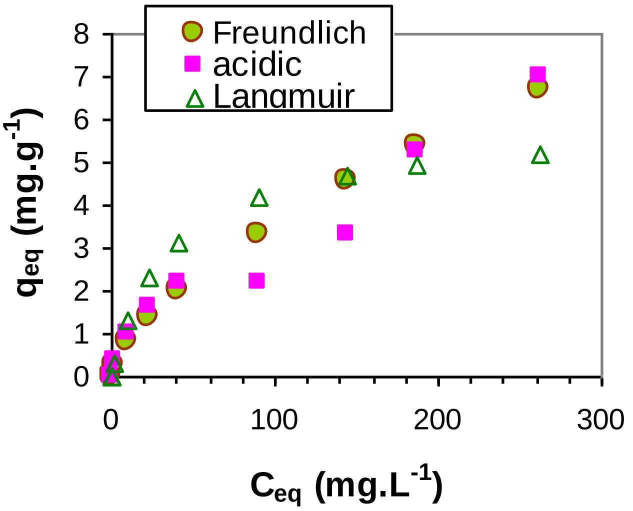

**Figure 3. Comparison between the experimental equilibrium adsorption isotherm of the Mo(VI) ions from the nitric solutions, pH 0.6-1.0, on the acidic alumina and the isotherm models. 27±2ºC.**

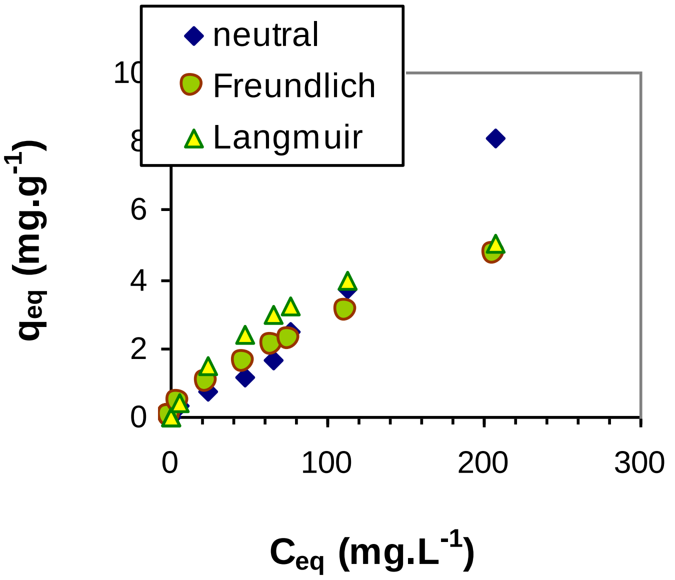

**Figure 4. Comparison between the experimental equilibrium adsorption isotherm for Mo(VI) ions from the nitric solutions, pH 0.6-1.0, on the neutral alumina and the isotherm models. 27±2ºC.**

## 4. CONCLUSIONS

Acidic alumina and neutral alumina were investigated by the batch studies for retention of Mo(VI) ions from nitric medium. Both aluminas provided high retention of Mo in acid solutions where an adsorption > 90% was found for concentration of 0.14 $mg.L^{-1}$. In the studied conditions, the two aluminas were very efficient indicating that can be applicated in chromatographic columns of the process of separation and purification of fission Mo.

## ACKNOWLEDGMENTS

The authors thank to the Center of Radiopharmacy – CR/IPEN/CNEN.

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