

Sorption and desorption of molybdenum in alumina microspheres

F. M. S. Carvalho,* A. Abrão

Instituto de Pesquisas Energéticas e Nucleares-IPEN, Cidade Universitária "Armando de Salles Oliveira", Travessa R-400, CEP 05508-900, São Paulo, Brasil

(Received December 27, 1996)

The behavior of minor amount of molybdenum(VI) in the presence of large quantity of aluminum nitrate and separation of Mo(VI) from Al(III) with the aid of a chromatographic process onto an alumina column has been studied. The separation of both elements is in favor of the selective uptake of molybdenum by the alumina. The solution containing both elements is an acidified aluminum nitrate of high concentration in aluminum. The work envisage a future separation and purification of radiomolybdenum for the milking of technetium-99m.

Introduction

The ^{99m}Mo adsorbed on alumina is the most common source of ^{99m}Tc for nuclear medicine investigation.^{1–4} A number of studies have been made of the surface chemistry of molybdena-alumina catalysts.^{5–7}

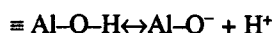
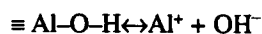
The alumina shows favorable ion exchange selectivities and exhibits both anion and cation exchange characteristics. It exhibits good thermal stability and good resistance toward strong oxidizing agents. Anion exchange capacity of alumina increases as the acidic pH decreases while its cation exchange capacity increases as the basic pH increases. In general, the change over from an anion exchanger to a cation exchanger is a gradual one and occurs in the vicinity of the isoelectric point (pH=8.5).⁸

The adsorption of molybdate ions onto alumina is strongly affected by pH due to changes in the chemical structure of the molybdate ion as shown in Fig. 1.^{9,10}

Then, alumina, like other hydrous oxides, has a very complex surface which is dependent on pretreatment and chemical environment.¹¹

The surface electrical charge of alumina is also strongly affected by pH changes. It is well-known that alumina is positively charged in an acidic medium and can adsorb the negatively charged molybdate ion. However, in the region of neutral to basic pH, the surface electrical charge is neutral or negative, and therefore it does not adsorb the molybdate ion, as depicted in Fig. 2.⁹

Embracing an ion exchange concept, the analyte ion is retained via the formation of an electrical double layer at the alumina surface. It is suggested that a surface charge appears due to dissociation at surface $\equiv\text{AlOH}$ groups and detachment of either H^+ or OH^- . As a result of the charge site, ions of opposite charge are attracted from the bulk of the solution with the resulting formation of two charged planes at the interface. In simplest term this can be represented by dissociation equilibria:⁸



Anion and cation exchange can then take place at these charge sites. The anion exchange takes place between added analyte anions and the alumina surface hydroxyl anions while cation exchange occurs between added analyte cations and the H^+ provided by dissociation of the alumina hydroxyl groups.

In acidic media, the number of molybdenum atoms in a molybdate ion increases with increasing acidity due to polymerization of monomeric molybdate ions.^{8,10–13} At pH greater than 6–7 the predominant species is MoO_4^{2-} . At intermediate pH values both $\text{Mo}_7\text{O}_{24}^{6-}$ and MoO_4^{2-} are observed.⁶ The alumina surface becomes positively charged at low pH and readily adsorbs the molybdena polyanions which are present in solution under these circumstances. At high pH, the surface takes on a net negative charge and tends not to adsorb the monomeric MoO_4^{2-} ions present in these solutions.

Accordingly, MoO_4^{2-} ions are adsorbed on distinct adsorption sites of the inner Helmholtz plane (IHP) of the electrical double layer developed between the surface of the solid particles of the adsorbent and the solution. In this plane, in alkaline medium, relatively weak lateral interactions are exercised between the adsorbent and the adsorbed MoO_4^{2-} ions, mainly attributed to the decrease in the concentration of the surface protonated hydroxyls, considered to be responsible for the creation of adsorption sites on I.H.P. Then, according to the pH increase, the superficial charge of alumina decreases, decreasing the molybdate anions attraction.⁶ In the very high acidic solutions a continuous transition via $\text{MoO}_2(\text{NO}_3)_2$ to the hydrated oxide $\text{MoO}_3 \cdot \text{H}_2\text{O}$ occurs, accompanied by decreasing adsorbability.¹⁴

LUTHRA and CHENG⁶ investigated the equilibrium between MoO_4^{2-} and MoO_4^{2-} the adsorption of molybdates on $\gamma\text{-Al}_2\text{O}_3$ at the pH range of 5.45 to 8.9 and the effects of molybdenum concentration.

Activated alumina in composition falls among various crystalline aluminium trihydroxides $[\text{Al}(\text{OH})_3]$ and the different crystalline aluminas (Al_2O_3) and is referred to as aluminum oxide hydroxide. The water content lies between $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 0.1 \text{H}_2\text{O}$.¹⁵

Unfortunately, alumina is usually supplied as a powder. Although it can be used as small columns, for preparative operation or work with greater volumes, powder alumina is not reliable, and does not perform well.

In this work a new type of chromatographic alumina was used specially prepared as microspheres. This material fitted well as the bed for chromatographic columns.

The alumina microspheres have been prepared by the sol-gel process, based on Reference 16. A colloidal solution prepared with aluminium nitrate, urea and hexamethylenetetramine as gelation agent is sprayed as droplets directly into a column with warmed oil (95 °C). The solid spheres are washed, dried and calcined at

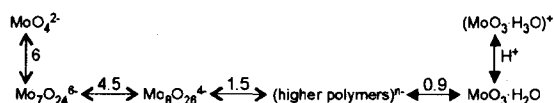


Fig. 1. Chemical structure changes in molybdate ion x pH

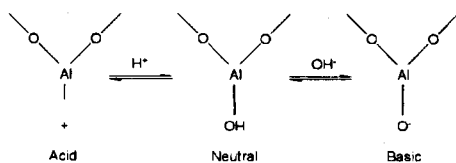


Fig. 2. Electric charge on alumina surface as function of pH

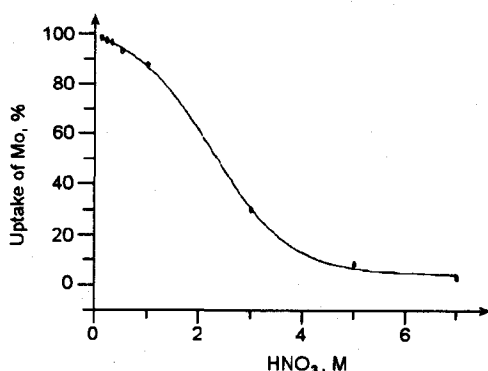


Fig. 3. Uptake of molybdenum by the alumina microspheres as function of nitric acid concentration

temperatures ranging from 300 to 850 °C and then characterized through sphericity, size classification and crystalline phases identification and behavior against acid and hydroxides as well.

As an inorganic ion exchanger the capacity of the alumina microspheres is assayed using Cu(II) in ammoniacal solution and ²³⁴Th tracer in hydrofluoric acid

media.¹⁷ The alumina exhibit an excellent performance as chromatographic material.

For the present work it was used alumina with microspheres diameter ranging from 0.50 to 0.80 mm.

Experimental

Inorganic and organic salts used for analytes were analytical reagent grade. For ion exchange experiments the columnar technique was employed with 2 g of alumina microspheres in the bed column. Determination of adsorption/desorption characteristics of this substrate for molybdenum was carried out under dynamic conditions. Glass columns were 8 mm in diam. and the volume of microspheres was 3.5 ml. After filling, the column was washed with 200 ml 1M HNO₃, 100 ml distilled water, 100 ml 1M NH₄OH and finally 200 ml H₂O. The column was conditioned with 200 ml 1M HNO₃. The adsorption and desorption velocities were maintained between 1 and 3 ml · min⁻¹ · cm⁻².

Molybdenum was assayed by hanging mercury dropping electrode voltammetry technique, with tartaric acid as electrolytic support. The electrolytical cell has a saturated calomel electrode as reference electrode. The auxiliary electrode was a platinum wire.

In 0.5M tartaric acid medium two characteristics peaks are obtained, with potential peak about -0.20 and -0.50 V. The current passing through the cell is recorded as a function of the voltage. There is a linear relation between the current and the concentration of Mo(VI) for both waves, which was exploited in analytical measurements for molybdenum with satisfactory results.¹⁸

Results and discussion

Adsorption of molybdenum onto alumina microspheres

Figure 3 depict the adsorption of Mo as a function of acidity of the influent solution. Optimal adsorption was attained at 0.1-0.2M HNO₃.

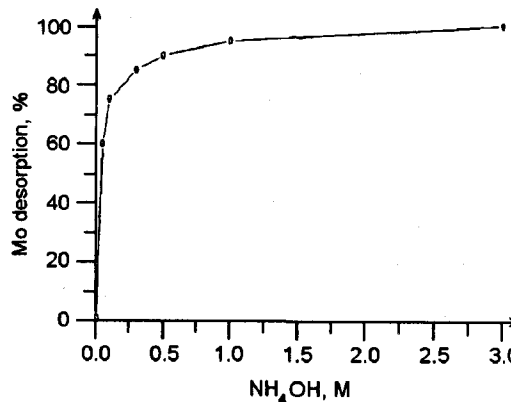


Fig. 4. Desorption of molybdenum from the alumina column as function of ammonium hydroxide concentration

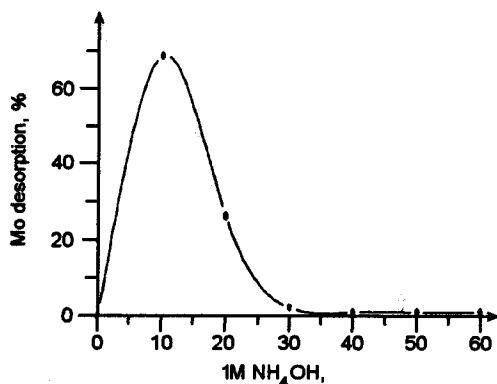


Fig. 5. Molybdenum elution curve from the alumina microspheres using 1M NH_4OH

Desorption of molybdenum from alumina microspheres

The desorption of molybdenum was carried out after washing the column with 0.1M HNO_3 and distilled water. Molybdenum was then eluted with 1M NH_4OH . The elution volume was 100 ml. Figure 4 depicts the results of the desorption of molybdenum from the alumina column.

As observed from Fig. 4 the desorption of molybdenum is better with ammonium hydroxide solution higher than 1M.

Optimal volume of ammonium hydroxide solution for the desorption of molybdenum

Figure 5 depicts the optimal volume of ammonium hydroxide for the elution of molybdenum from alumina microspheres column.

Temperature influence on adsorption and desorption of molybdenum

The temperature of molybdenum solution was raised before the percolation. Between 25–100 °C the uptake of molybdenum did not varied more than 0.7%. It was observed a lower retention at lower temperature. The desorption of molybdenum from the alumina achieved using 100 ml of 1M NH_4OH at 25 °C. The results are shown in Figs 6 and 7.

The experiments allowed to conclude that when the uptake of molybdenum by the alumina occurred at higher temperature, the molybdenum elution was more difficult.

The polymerization of the Mo(VI) is effective at $\text{pH} < 7.0$. As depicted from Fig. 4, the increasing of the acidity above 0.2M HNO_3 decreases the retention of the molybdate ion. This effect can be observed from Fig. 1 by the formation of the $\text{MoO}_3 \cdot \text{H}_2\text{O}$ and $(\text{MoO}_3 \cdot \text{H}_3\text{O})^+$ species.

Adsorption and desorption velocities has a decisive effect on the retention and elution of the element. Greater velocities produces a lost of significant amount of

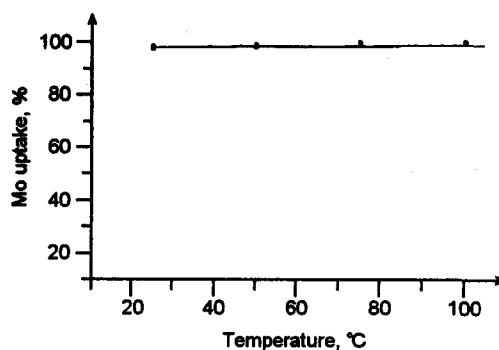


Fig. 6. Molybdenum uptake by the alumina microspheres as function of the temperature of the loading solution

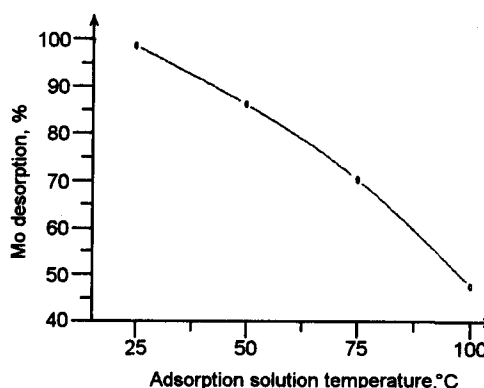


Fig. 7. Elution of molybdenum with 1M NH_4OH at 25 °C as function of the temperature of the loading solution

molybdenum uptake and increases the necessary volume of ammonium hydroxide for the elution.

The molybdenum solution retention temperature is important because its desorption is better when the uptake is made at ambient temperature. With retention at 75 °C, for example, only approximately 62% of the element was eluted with the ammonium 1M hydroxide solution at 25°C. The effect of the temperature is very important because when the irradiated material is dissolved, the temperature of the resultant solution is high. Then it is necessary to slow down the temperature of the loading solution prior the percolation. Then, it was concluded that molybdenum solution was better purified, and decontaminated from aluminium, when it was adsorbed onto alumina microspheres from a 0.1M HNO_3 solution and, after washing the column with water, it was desorbed with 1M NH_4OH at 25 °C.

References

1. A. MUSTAQ, J. Radioanal. Nucl. Chem., 199 (1995) 89.
2. L. G. STANG JR., P. RICHARDS, Nucleonics, 22 (1964) 46.
3. W. D. TUCKER, M. W. GREENE, M. P. MURRENHOFF, Atompraxis, 5 (1962) 163.

4. S. M. MILENKOVIC, J. L. VUCINA, L. M. JACIMOVIC, E. S. KARANFILOV, T. V. MEMEDOVIC, *Isotopenpraxis*, 19 (1982) 85.
5. LI WANG, W. K. HALL, *J. Catalysis*, 77 (1982) 232.
6. N. P. LUTHRA, W. C. CHENG, *J. Catalysis*, 107 (1987) 154.
7. L. WANG, W. K. HALL, *J. Catalysis*, 66 (1980) 251.
8. G. L. SCHMITT, D. J. PIETRZYK, *Anal. Chem.* 57 (1985) 2247.
9. M.T. EL-KOLAHY, L. F. MAUSNER, S. C. SRIVASTAVA, *Nucl. Med. Biol.*, 17 (1990) 229.
10. H. ARINO, H. H. KRAMER, *Intern. J. Appl. Radiation Isotope*, 26 (1975) 301.
11. I. LINDVIST, *Acta Chim. Scand.*, 5 (1951) 568.
12. E. PUNGOR, A. HALÁSZ, *J. Inorg. Nucl. Chem.*, 32 (1970) 1187.
13. K. H. TYTKO, O. GLEMSER, *Adv. Inorg. Chem. Radiochem.*, 19 (1976) 239.
14. S. E. BAYOUMI, O. HADLIK, R. MÜNZE, *Isotopenpraxis*, 9 (1973) 131.
15. J. STEIGMAN, *Intern. J. Appl. Radiation Isotope*, 33 (1982) 829.
16. W. R. SANTOS, A. ABRÃO, *Publicação IPEN*, No. 22, April 1981.
17. A. ABRÃO, *Publicação IEA*, No. 217, June 1970.
18. F. M. S. CARVALHO, *Três Novas Reações Seletivas para a Precipitação de Mo(VI), Processo Alternativo para a Separação e Purificação de Molibdênio*, Doctor Thesis, IQUSP, 1995.