STUDY OF ADSORPTION OF MOLYBDATE ION BY ALUMINA

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Received November 24, 2016

Accepted March 3, 2017

ABSTRACT

The study of the molybdenum by alumina adsorption was studied for the improvement of technetium generators CNESTEN used for the manufacture of radiopharmaceuticals products. The molybdenum concentrations used vary between 330μM and 1.7mM, distribution of Mo between the aqueous phase and the organic phase was characterized by the percentage of adsorption (P) and the distribution coefficient (D). The optimal conditions for adsorption are in the pH range between 3-5. Followed by the adsorption of this radiosotope depending on contact time between the adsorbent and the adsorbat showed some significant effect, however the concentration of molybdenum used may change the adsorption mechanism.

Key Words: Adsorption, Molybdenum, Alumina, Distribution, Spectrophotometry

INTRODUCTION

Molybdenum adsorption by the oxide aluminum was studied by Goldberg et al. It presents a maximum for low pH and up to about (pH 3-5). Above pH= 5 the adsorption decreases rapidly. The Mo adsorption mechanism of alumina is proposed to be a ligand exchange with hydroxyl ions surface.1-4 The ligand exchange is a mechanism by which ions become specifically adsorbed by forming complexes of spheres inner surface.5 The inner surface Complexes do not contain water molecules between the oxide adsorbent and the surface functional group. The point of zero charge (PZC) of minerals is shifted to an acid pH value after the specific adsorption of anions.6-10 The adsorption of molybdenum reduces the PZC of alumina, which favors the specific adsorption. Furthermore by studying the effects of ionic strength on the anion adsorption were able to distinguish between the inner and outer surface complexes. The external sphere surface complexes contain at least one molecule of water between the oxide adsorbent and the surface functional group.11

AIMS AND OBJECTIVES

The objective of this study is to determine mechanisms of adsorption molybdate by alumina in order to develop new technetium generators. During our work we examined the adsorption of molybdate by alumina α-Al₂O₃. The sharing of this molybdate between the organic and aqueous phases is characterized by the distribution coefficient D and percentage P. The variations log D=f (pH) study for a concentration of molybdate. Although sets at different time of contact. The exploitation of data log D=f (pH) allow initially defined the adsorption mechanism involved in this case.

MATERIAL AND METHODS

Study of the adsorption of molybdate ion by α-Al₂O₃ alumina having a granulometry between 63-200μm and a specific surface area 150m²/g. A specific volume of a molybdate solution is range contacted with alumina α-Al₂O₃ with a mass of 8g/L, the adsorption ion molybdate is between about 2 and 10. After a well defined
time, we realize a sampling 250mL. The dosage of the ion molybdate is affected by \( \text{H}_2\text{O}_2 \). The partition coefficient of the Mo between the aqueous and organic phases is means used by the distribution coefficient D, the value of D is obtained by comparing the content of the ion molybdate before and after adsorption.

\[
D = \frac{[\text{MoO}_4^{2-}]_{\text{org}}}{[\text{MoO}_4^{2-}]_{\text{aq}}}
\]

\([\text{MoO}_4^{2-}]_{\text{org}}\): amount of molybdate determined by the solid phase.
\([\text{MoO}_4^{2-}]_{\text{aq}}\): concentration of molybdate in the aqueous phase after a contact time.

\([\text{MoO}_4^{2-}]_{\text{org}} = [\text{MoO}_4^{2-}]_{\text{aq}} - [\text{MoO}_4^{2-}]_{\text{aq}}\)

If \( P \) designates the percentage of binding of the ion molybdate on the solid phase then, we have.

\[
P = \frac{[\text{MoO}_4^{2-}]_{\text{org}}}{[\text{MoO}_4^{2-}]_{\text{aq}} + [\text{MoO}_4^{2-}]_{\text{aq}} - [\text{MoO}_4^{2-}]_{\text{aq}}}
= \frac{1}{1 + \frac{[\text{MoO}_4^{2-}]_{\text{org}}}{[\text{MoO}_4^{2-}]_{\text{aq}}}}
\]

And the dosage of the ion molybdate in the aqueous medium before and after adsorption allows determining the percentage \( P \) and the distribution coefficient D.

**Sodium molybdate dosing by UV-visible spectrophotometry**

To achieve the spectrophotometry dosing of molybdenum ion, we prepare an initial solution molybdenum concentration of \( 4.13 \times 10^{-3} \text{ M} \), by the dissolution of a suitable mass of \((\text{Na}_2\text{MoO}_4,2\text{H}_2\text{O})\). Different standard solutions are obtained by adding a volume \( V = (0, 1, 2, 4 \) and \( 5 \text{ mL} \)) of this initial solution into 50ml volumetric flasks which previously contain 10 mL of sulfuric acid (2M), and 1.5 mL of hydrogen peroxide (0.2M). These volumetric flasks are then completed with distilled water.

A yellow color appears, indicating complex formation \((\text{MoO}_3, \text{H}_2\text{O})\). These solutions are left in the absence of light, for 15min, then subjected to dosing by spectrophotometry at the wavelength \( \lambda = 327\text{nm} \), which corresponds to the maximum molybdenum absorption.

It should be noted that the complexing reaction to be used in this dosing is:

\[
\text{MoO}_4^{2-} + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow (\text{MoO}_3, \text{H}_2\text{O}_2) + \text{SO}_4^{2-} + \text{H}_2\text{O}
\]

\( \text{(1)} \)

The complex \((\text{MoO}_3, \text{H}_2\text{O}_2)\) is characterized by a yellow color and an absorption maximum at 327nm. To perform the spectrophotometry dosing of molybdenum, the sampled volume (10 mL) was introduced into a 50 mL flask, to which is added 10 mL of 2M sulfuric acid and 1.5 mL of hydrogen peroxide (0.2M). This mixture is left to rest for 15 min protected from light before the analysis.

**RESULTS AND DISCUSSION**

The percentage variations \( (P) \) of adsorption depending on the pH and the contact time

The results obtained are represented in the form of curves representing the changes in the adsorption percentage \( (P) \), depending on the pH and the contact time \((t)\). The adsorption behavior of molybdenum is examined as a function of pH, contact time, and concentration of the molybdenum ion. The suspension of alumina used in this review contains an amount of \( 8 \text{ g/L} \) of \( \alpha-\text{Al}_2\text{O}_3 \). In the upcoming figure we give the variations \( P=f (\text{pH}) \) obtained for fixed time contact and for concentrations of Molybdate respectively equal to 330 \( \mu\text{M} \) and 496 \( \mu\text{M} \). These results show that the adsorption mechanism is fast and does not depend much on the contact time in the explored experimental conditions \((\text{Fig.1})\). In addition, the shape of the curves \( P=f (\text{pH}) \) indicate that the sorption of molybdenum ion is governed in this case by multiple adsorption mechanisms. The optimal adsorption conditions are in the range \( 3 \leq \text{pH} \leq 5 \).

It should be noted that the optimal adsorption pH coincides with the PCN value of alumina previously determined and is of the order of 5, the charge carried by the sorbent surface is positive, while it is negative when the pH becomes greater than 5. Therefore, It appears that the molybdenum is dominant in the experimental conditions explored in the forms \( \text{HMoO}_4, \text{H}_2\text{MoO}_4 \) and \( \text{MoO}_4^{2-} \) in which the sorption is favored on solid surfaces positively charged. As a result, when the pH is greater
than 5, the alumina becomes negatively charged, which leads to a reduction in the adsorption of molybdenum ion in these conditions.

Fig. 1: Variations of P = f (pH) obtained for Mo 330.46μM and Mo 496,03μM, in the range 15 min ≤ t ≤ 135 min.

In fact, the distribution diagram of different molybdenum species shows that the anionic species HMoO₄⁻ and MoO₄²⁻ predominate in the field 4≤pH, these are species that are fixed in the optimal conditions defined by 3≤pH≤5 (Fig. 2). It should be noted that the pKa of the first and second acidity of the molybdenum diacid H₂MoO₄ are: pKₐ₁= 2.5 and pKₐ₂= 3.9 the acid-base properties of molybdenum were described assuming the protonation and deprotonation reactions:

\[ \text{H}_2\text{MoO}_4 \rightarrow \text{H}^+ + \text{HMoO}_4^- \]
\[ \text{HMoO}_4^- \rightarrow \text{H}^+ + \text{MoO}_4^{2-} \]

Fig. 3 shows the logD=f (pH) fluctuations obtained for the fixe contact time and for concentrations of molybdenum ion respectively equal to 330 μM and 496 μM.
The distribution coefficient variations (D) of adsorption depending on the pH and the contact time

Note that the electrostatic attraction model does not explain two important points: first, the fact that the adsorption of $\text{H}_2\text{MoO}_4$ is over riding in acid environment, the second one is that anionic species are dominant for pH $>$ 5 where the alumina surface charge is negative (Fig. 3). That is why it is generally called the surface complexation model. According to this model which is similar to the complexation of a given element by a chelate, the gradient

$$\frac{\delta \log D}{\delta \text{pH}}$$

is equal to the average number of protons $\text{H}_2\text{O}^+$ or OH$^-$ hydroxyl groups exchanged with surface active sites. Then we have

$$\frac{\delta \log D}{\delta \text{pH}} > 0 ; \text{pH} \leq 5 \quad \frac{\delta \log D}{\delta \text{pH}} = 0 ; 6 \leq \text{pH} \leq 7 \quad \frac{\delta \log D}{\delta \text{pH}} < 0 ; \text{pH} > 7$$

This allows us to conclude that the adsorption of molybdenum by $\alpha$-$\text{Al}_2\text{O}_3$ is caused by cation exchange ($\text{H}_2\text{MoO}_4$) in the conditions of pH$<$3, and also by dehydration or elimination of $\text{H}_2\text{O}$ for $6 \leq \text{pH} \leq 7$ on the one hand, and by anion exchange hydroxides to pH $>$ 7 on the other hand. However, the latter reaction is not possible because the predominant entity in this case is the $\text{MoO}_2^{2-}$ anion, which is dehydrogenated and whose adsorption may not lead to the elimination of $\text{H}_2\text{O}$ Fig. 3. Therefore, the sorption mechanism employed in this case is an anion exchange mechanism involving the Cl or Na$^+$ in the pH region of the IEP and is of type :

$$\text{SOH} + \text{Na}^+ \rightarrow \text{SO}^-\text{Na}^+ + \text{H}^+ \quad (1)$$
$$\text{SOH} + \text{H}^+ + \text{Cl}^- \rightarrow \text{SOH}_2^+ + \text{Cl}^- \quad (2)$$
$$\text{SCl}^- + \text{MoO}_4^{2-} \rightarrow \text{SO}^-\text{MoO}_4^{2-} + \text{Cl}^- \quad (3)$$
Fig. 3: The Variations logD = f (pH), obtained for Mo 330 µM and Mo 496 µM in the range 15 min ≤ t ≤ 135 min.

The effect of the adsorbent concentration
The adsorption of molybdenum ion is investigated at t=30 min depending on the concentration of this element and the pH (Fig. 4). These results show that the adsorption mechanism, involved in acidic environments, changes when the concentration of molybdenum becomes high and equal to 1.7 mM. The bearing LogD=f(pH) obtained in this case, indicates a predominance of the adsorption mechanism by removing a H₂O molecule.

Taking into account the variations logD=f(pH), and the distribution of molybdenum species as a function of pH (Fig. 2), the sorption mechanisms may predominate depending on pH as follow:

pH ≤ 1

> SOH + H₂MoO₄⁺ → SOH− H₂MoO₄+ H⁺  

2 ≤ pH ≤ 4

> SOH + H₂MoO₄ → SOH₂− HMoO₄⁻  

> SOH + H₂MoO₄ → SOH₂− H₂O  

> SOH + H₂MoO₄ → SHMoO₄⁻ + H₂O  

3 ≤ pH ≤ 5

> SOH + H₂MoO₄ → SOH⁺ MoO₄₂⁻  

> SOH + H₂MoO₄ → SOH⁺ + H₂O  

> SOH + H₂MoO₄ → SOHMO₄ + H⁺  

pH > 6.5

> SOH + MoO₄²⁻ → SMoO₄⁻ + OH⁻
Fig. 4: The variations $\log D = f(pH)$ obtained at different concentrations of the molybdenum ion for $t = 30$ min.

To determine the stoichiometric coefficients of $H^+$ and $OH^-$ involved in the exchange reactions (4); (6); (11) and (12), we have plotted the variations curves $\log D = f(pH)$ obtained for concentrations between 330 and 800 $\mu$M.

It appears from these results that the $\log D=f(pH)$ are lines of directing coefficient equal to about $0.5 (2 \leq pH \leq 4.5)$; Mo (330-800$\mu$M) (Fig. 5), $-0.5 (5 \leq pH \leq 6.6)$; Mo (330 to 800 $\mu$M) (Fig. 6) $-0.2 (6.5 \leq pH \leq 11)$; (330 to 800 $\mu$M) (Fig. 7) and $-0.14 (2.5 \leq pH \leq 11)$ for and Mo concentration equal to 1.7 mm (Fig. 8). The tendency curve of $\log D = f(pH)$ is a straight line for every pH range explored. The gradient $\frac{\delta \log D}{\delta pH}$ equals -0.14. Then it can be concluded that the reactions (4) and (8) interferes with almost similar percentages in the sorption of Mo (330 and 800 $\mu$M) in acid environments. This is also the case of reactions (7) and (9) in the case where the environment is neutral to basic.

Fig. 5: $\log D = f(pH)$ in the range $2 \leq pH \leq 4.5$ obtained for a concentration of 330, 800 and 496 $\mu$M
Fig. 6: \( \log D = f(\text{pH}) \) in the range 4.5 ≤ pH ≤ 6.6 obtained for a concentration of 330, 800 and 496 µM

\[
y = -0.4675x + 3.411 \\
R^2 = 0.3763
\]

Fig. 7: \( \log D = f(\text{pH}) \) in the range 6.6 ≤ pH ≤ 11 obtained for a concentration of 330, 800 and 496 µM

\[
y = -0.2226x + 1.2134 \\
R^2 = 0.5366
\]

Fig. 8: \( \log D = f(\text{pH}) \) in the range 2.5 ≤ pH ≤ 11 obtained for a concentration of Mo 1.7 mM

\[
y = -0.1384x + 0.9997 \\
R^2 = 0.9215
\]
However the dominant mechanisms, for molybdenum ion of 1.7mM concentration, are characterized by:

\[
\frac{\delta \log D}{\delta \text{pH}} = -0.14
\]

It indicates that we have an essentially predominance of reaction (7). The reaction (9) also interfere but at very low percentages. However, the existence of the mechanism is paradoxical since the species HMoO$_4^-$ is not predominant in basic pH. The adsorption of molybdenum (1.7mM) in a buffer environment at pH = 4 We examined the effect of contact time on the adsorption of molybdenum

![Graph of P% vs t(min)](image)

**Fig. 9 : Curve of P = f (pH) variation obtained at pH =4, for 1.7 mM**

**CONCLUSION**

The adsorption of molybdenum ions by alumina is examined as a function of the contact time and the concentration of the adsorbate, the results obtained show that the adsorption of molybdenum ions MoO$_4^{2-}$ is almost stable in the pH range 2-5, and then decreases rapidly as the pH continues to increase, the study of this adsorption according to the concentration of the adsorbate shows an insignificant effect which is also the case of the contact time. The exploitation of experimental results P=f(pH) and log=f(pH) enable us to conclude that the adsorption processes employed involves complex mechanisms that involves by their turn dehydration ion exchange reactions where the H$_3$O$^+$ and OH play an important role. However, a preliminary analysis suggests that the dehydration is the predominant mechanism in acidic media. When the pH of the suspension media is next to PIE = 6, the Mo is then adsorbed by an anion exchange mechanism involving the chloride and sodium ions. Note that when the molybdenum fixation is performed under these conditions, the technetium source may be of high radiochemical purity. The study of the effect of molybdenum concentration on the adsorption shows the possibility of the existence of the polymerization phenomenon that leads to a decrease in the fixation efficiency of Mo.

**REFERENCES**

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