OPTIMISATION $^{99}\text{MO}/^{99\text{m}}\text{TC}$ GENERATORS: CHARACTERIZATION OF α ALUMINAS SIMPLES AND KINETIC STUDY OF MOLYBDENUM ADSORPTION ON α ALUMINA

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ABSTRACT

In order to improve the efficiency of technetium generator manufacturing in the National Centre of Science, Energy and Nuclear Techniques (CNESTEN-Morocco), we evaluated the influence of different parameters of molybdenum adsorption by alumina. Firstly, samples in different conditions have been investigated to determine the intrinsic surface properties of $\alpha\text{-Al}_2\text{O}_3$, which is a point zero charge, isoelectric point and the number of active sites. These studies show that $\alpha\text{-Al}_2\text{O}_3$ with 63-200 μm of particles size, have the best intrinsic surface properties. On the other hand, several parameters have been studied to optimize the fixation of molybdenum on alumina involved for adsorption evaluation, such as pH, contact time, partial size of the oxide, chlorination, electrolyte concentration. Also, ATR-FTIR, UV-Vis and ICP-MS analytical techniques were used to investigate the molybdenum adsorption on the oxide. Finally, we have been able to define the molybdenum-alumina complex's behavior according to variations of pH and contact time.

Keywords: Adsorption, Technetium Generator, Specific Surface, Molybdenum, Alumina.

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INTRODUCTION

Currently, in Morocco, the demand for radioisotopes and radiolabeled compounds is steadily increasing with new nuclear medicine centers. To support this evolution, the National Center for Nuclear Energy, Sciences and Technologies (CNESTEN-Morocco). CNESTEN has placed an ambitious program for the development and manufacture of radioisotopes for medical purposes. The most important one is technetium-99m generators production. Because of its good physicochemical characteristics and its availability in the form of generators, technetium-99m ($^{99\text{m}}\text{Tc}$) is the radioisotope primarily used in

nuclear medicine, alone or as a radioactive tracer in radiopharmaceuticals¹. This artificial substance has a short physical period (about 6 hours) obtained by the decay of molydene-99². Molybdenum-99 can be produced by neutron flux bombardment of ⁹⁸Mo enriched natural or molybdenum targets; or with irradiating by neutron flux targets of uranium enriched by uranium ^{3,4}. After separation operations, the molybdenum- 99m is then fixed on a column of aluminum oxide. This column is placed in the system to constitute a technetium-99m generator called colloquially "technetium cow." This isotopic generator makes the extraction of technetium-99m solution very easy. The extraction called "elution" is performed with isotonic saline solution.

During the developing process, in Radiopharmaceutical Production Division (DPR-CNESTEN), the yield of technetium-99m generators is studied. The generator is calibrated according to the amount of radioactive molybdenum (^{99m}Tc-⁹⁹Mo) fixed on the column. The amount of technetium-99m available at the elution time depends on the delay before or after the calibration date (due to the decay of ⁹⁹Mo), the elapsed time since the last elution, and decay characteristics of ⁹⁹Mo (86.2% of ⁹⁹Mo decays yield ^{99m}Tc). The efficiency is calculated by comparing the estimated activity to the elution activity. Variation for the yield of the generator is observed from one generation to another. In theory, it is never less than 90% of the activity available in ^{99m}Tc. So, it depends on the column containing Al₂O₃, since W.D invented the technetium generator in 1957. Tucker's group at the Brookhaven National Laboratory, many studies have attempted to develop a new generator. They are trying to make it perform better by using other materials or by improving the characteristics of the oxide ^{5,7}.

In this study, we are trying to optimize the yield of the technetium generator. The characterization of alumina and the performing adsorption capacity of molybdenum can help. Different experiments are performed to evaluate the influence of different parameters such as pH, contact time, partial seize of the alumina, chlorination, and the concentration of the electrolytes on the molybdenum mechanism adsorption. Characterization of the starting material (alumina) goes through the monitoring of their surface charges. This monitoring is carried out experimentally by Potentiometric titrations or electrophoresis mobility. This study allowed the determination of a critical parameter called "the point of zero charges" (PZC) ^{8,9}. The influence of the mixture of partial sizes was carried out. The mechanism of adsorption of molybdenum is greatly influenced by pH modification. This investigation needs a huge number of experiences. For radioprotection, radioactive waste management and economics investment, the study was divided into two parts. In the first one, "cold investigation," we used stable molybdenum. In the second one "hot investigation," we reproduced the most relevant experiments in hot cells using radioactive molybdenum ^{99m}Mo solutions.

EXPERIMENTAL

Laboratory Temperature

All experiments for charge determination were carried out under ambient laboratory conditions temperature T= 22 ± 3 °C.

All experiments of determinations of molybdenum concentrations in solutions were carried out under ambient laboratory conditions temperature = 20°C ± 3°C.

Preparation of Alumina

The physicochemical characteristics of α-alumina are mentioned in Table-1. Activated alumina has prepared from a simple of alumina, so the material was dried at 180 °C during 4 hours, then cooled to room temperature in a desiccator. When the sample got the room temperature, 2g of the oxide is adding in suspension with 0.02N clorhydric acid solution (HCl) at different times of contact: 15 min, 30 min, 45 min, 60 min, 75 min, 90 min, 105 min, 120 min and 24 h.

Table-1:α-alumina Characteristics

Alumina	pH Value	Particle Size Distribution	Specific Surface
MP Alumina (N, Akt.I)	7.4 ± 0.4	10% < 63µm 5% > 200µm	150 m ² /g
MP Alumina (N 32-63)	7.0 ± 0.1	D ₁₀ (%) 25-35 µm D ₅₀ (%) 45-50 µm D ₉₀ (%) 60-75 µm	200 m ² /g when properly activated

MP Alumina (N 18-32)	7.4 ± 0.4	18-32 μm	About 200 m ² /g
MP Alumina (N 7-12)	7.4 ± 0.4	7-12 μm	About 200 m ² /g when properly activated
MP Alumina (N 3-6)	7.4 ± 0.4	7-12 μm	200 m ² /g when propel activated

Water used in this study is fresh demineralized water with characteristics:
Resistivity > 10 MΩ .cm and TCO < 30 ppm .

Potentiometric Titrations

All potentiometric titrations of α-Al₂O₃ suspensions were performed using a titrator from Mettler Toledo type DL53. Before using this material, a performance qualification was approved. Verification is also required to confirm the requirements specified in GMP's and European pharmacopeia.^{10,11} Dally calibration of the sensor is performed too. The addition mode of reagents during acid-base titrations is the dynamic one. This mode allows an optimal calculation of the increment to be added during the dynamic titration. The volume increment added by the titrator changes within the defined smallest and largest increment: ΔV(min) and ΔV(max). This should lead to a constant potential difference ΔE per increment: ΔE = 0.5 mV ; ΔV (min) = 0.02 ml and ΔV (max) = 0.1 ml .

In this condition, the equilibrium is installed in the suspension before the titrator adds the next increment, the value of the measurement must be stable.

IRTF-ATR Spectrometric Investigations

The IRTF measurements were carried out with a Perkin Elmer Fourier-Transform spectrometer. Type spectrum tow with universal ATR sampling accessories. Before using this material, a performance qualification with polystyrenes standards films was approved.

UV-Visible Spectrophotometer Method

UV-VIS spectrometric measurements realized molybdate quantifications. Solutions absorbencies were measured with a Perkin Elmer spectrophotometer from Perkin Elmer (Lambda 25). Before using this material, a performance qualification with standards filters was approved. To achieve the spectrophotometer dosing of molybdenum ion, an initial solution molybdenum concentration of 4.1310⁻³ M was prepared from the suitable mass of (Na₂MoO₄, 2H₂O). Then 7 Standards solutions are obtained by dilutions with demineralized water of this initial solution: adding 5 ml to 50 ml flasks contained previously and 10 ml of sulfuric acid (H₂SO₄ 2M), and 1.5 ml of hydrogen peroxide (H₂O₂ 0.2M), then completed with demineralized water. The reaction used is:

A yellow color appears, indicating complex formation (MoO₃, H₂O₂). These solutions are left in the absence of light for 15min. The maximum adsorption of this solution was the wavelength λ_{max} = 327nm. The blank was a flask without adding (Na₂MoO₄, 2H₂O).

Determination of Sites Adsorption Density

Experimentally, site actives number N_s are determined by comparing suspended oxides titration isotherms and blanks titration isotherms. Blanks used as references to calculate sites actives numbers are results of acid-base titrations: potassium hydroxide 0.1N by nitric acid 0.1N (KOH-HNO₃) under the same experimental conditions.

The calculation of contents of sites actives number per alumina mass by the formula:

$$N_s = \frac{C_a (V_{ei} - V_{eb})}{1000 m}$$

Were, m: Mass of alumina by grams (g), N_s: The content by mass of primary alumina sites (mol/g), V_{eb}: The volume equivalence of the blank (ml), V_{ei}: The neutralization volume of suspensions of various contact times (ml), C_a: The initial concentration of the acid.

RESULTS AND DISCUSSION

Determination of PZC

The main parameters characterizing any oxide are the point of zero charges (PZC) and the isoelectric point (IEP). These terms are used to define the surface state of a dispersed solid phase at a solid-electrolyte solution interface. The point of zero charges is the pH value where negative ($[\text{MO}^-]$) and positive ($[\text{MOH}^{+2}]$) surface concentrations are equal.^{12,13} The surface charge is negative at $\text{pH} > \text{pH}_{\text{pzc}}$, and positive at $\text{pH} < \text{pH}_{\text{pzc}}$.

Experimentally, PZC is determined at the intersection of the suspension titration curves with the blank curve (Figure1). The isoelectric point (IPE) is determined at the intersection point between the titration curves suspension. Figure-4 is an example of the isotherms curve of acid-base titration of α -aluminas used in this study.

Fig.-1: Isotherms of Potentiometric Titration of α -alumina in Different Contact time with HCl.

The most exciting results carried in this study concern sites actives numbers on aluminas surfaces samples. Results are gathered in Fig.-2. The first graph in this figure shows variations of numbers of sites actives of aluminas samples which have particles sizes 3-6 μm , 7-12 μm , 18-31 μm , 32-63 μm , 50-200 μm and 63-200 μm by time (min) and on acid environments. The second one shows the variation of sites actives numbers of aluminas samples which have particles sizes 3-6 μm , 7-12 μm , 18-31 μm , 32-63 μm , 50-200 μm and 63-200 μm by time and on basic environments. The values of PZC and IEP in the acidic and essential medium are shown, respectively, in Table-2.

Graph-1: numbers of sites actives of alumina samples with different particles sizes (3-6 μm , 7-12 μm , 18-31 μm , 32-63 μm , 50-200 μm and 63-200 μm) on acid environments

Graph-2: numbers of sites actives of alumina sample with different particles sizes (3-6 μm , 7-12 μm , 18-31 μm , 32-63 μm , 50-200 μm and 63-200 μm) on basic environments.

Fig.-2: Sites Actives Numbers of Aluminas Samples with Different Particles Sizes (3-6 μm , 7-12 μm , 18-31 μm , 32-63 μm , 50-200 μm .-63-200 μm) on Acid and Basic Environments

Table-2: PZC and IEP of Alumina.

Basic Environment		
Alumia's particles size (μm)	IEP	PZC
63-200	9.6	3.68
50-200	9.1	3.35
42-72	9.2	3.92

32-63	9.6	4.58
18-32	5.5	6.34
7-12	7.12	6.34
Acid Environment		
Alumina's particles size	PIE	PCN
63-200	4.5	9.61
63-200	4.3	9.96
32-63	4.2	9.25
18-32	4.8	7.73
7-12	6.7	5.36

In both environments, we observe that the alumina with big particles sizes always have the highest sites activity numbers. We can observe this in mixtures 63-200 μ m and 50-200 μ m particles sizes. For all aluminas mixtures, a maximum peak is observed at 75 min in all the granulometric fractions. It is the optimum contact time. And site's actives numbers are much highest in the primary environment than in acid one. Actually, this result is affected by the influence of dissolved aluminum basic solution. It is manifested by upward shifts in pH in the suspension, as the overall dissolution equation:

For each aluminum dissolved, three protons are consumed. These upward mechanism shifts have been observed in addition to proton adsorption, so more volume acid adds in titration. Brunelle et al. studied the solubility of alumina in different pH range. This study concludes that alumina has high solubility zone at firm basic suspension. Dissolution of aluminum above pH=4 is negligible^{14,15}.

Acidification

Addressing the question of the impact of chlorine on the reactivity of α - Al_2O_3 , the first answer was clearly observed in Fig.-2 and it is clearly demonstrated that acidification increase the number of N_s on α -alumina surfaces. For more answers, spectroscopic measurements were done using an ATR-FTIR. Spectra of pure alumina before and after activation were acquired Fig.-3.

Fig.-3: ATR-FTIR Spectrum of Pure α -alumina and Chlorinated α -alumina.

Some theoretical and experimental works from Digne et al., Hind et al and Markus et al. helps to interpret this FTIR spectrum^{16,18}. In the chlorinated α -alumina spectrum, the broad infrared feature between 3700 and 2600 cm^{-1} is attributed to the O-H stretching vibrations of hydrogen-bonded AlOH species and adsorbed H_2O . The O-H stretching vibrations of isolated AlOH species are observed at different wavelengths depending on their position on the alumina surface^{19,20}. The region of 3450 cm^{-1} indicates continuing interaction between chlorides and hydroxyl groups¹⁸. Hydroxyls ions are preferentially substituted by chlorides. The region of 1028 cm^{-1} may be due to O-Al-Cl vibrations. The bending vibration of H-O for physisorbed water that is not coordinated with an aluminum ion occurs at 1650-1630 cm^{-1} . Hind et al indicate that the hydrated alumina surface is oxygen terminated. The structure is an intermediate between α - Al_2O_3 and γ - $Al(OH)_3$, with the surface terminated by a monolayer of OH under ambient conditions. Water can then molecularly adsorb in a partly ordered overlayer on top of the

OH- terminated surface. In conclusion, the acidity of the oxide increases with chlorination. α -alumina owes its acidic character to surface hydroxyls whose acidity Bronsted is exalted by the attracting inductive effect of adjacent chlorides by a simple treatment with aqueous hydrochloric acid.

Evaluation of Molybdenum Adsorption Capacity on α -alumina

To understand the molybdenum adsorption mechanism on ^{99m}Tc generators columns, influences of different parameters on molybdenum adsorption were studied. Principally: pH, contact time (t_c), surface oxide and chlorination. The alumina, which has 63-200 μm particles size, was used in these (have the highest N_s) investigations. The molybdenum-alumina interaction modes are expected to be varied by modifying the acid-base properties of suspensions, contact time and initial concentration of the electrolyte. The molybdenum adsorption capacity was measured by slow stirring suspensions containing 1 g of the oxide and 100 ml of sodium molybdate solution with different concentrations (330, 496, 800 and 1650 $\mu\text{mol/l}$) in different values of (pH 2 to 10). After different times (15, 30, 45, 60, 75, 90, 105, 120 and 135 minutes) under stirring, the suspension was filtered and analyzed by UV-VIS spectrophotometer. Percentages of adsorbed molybdenum %P were evaluated from the Mo concentration in the suspension and initial concentration of Na_2MoO_4 ratio ²¹.

Adsorptions equilibriums isotherms of %P were obtained by varying Mo initial concentrations, pH and contacts times are represented in Figs.-4, 5 and 6.

Fig.-4: Isotherms of Molybdenum (initial concentration 330 $\mu\text{mol/l}$) Adsorption on α -alumina in the Different Ranger of pH and in Different Contacts Times.

Fig.-5: Isotherms of Molybdenum (Initial Concentration 800 and 1650 $\mu\text{mol/l}$) Adsorption Different Ranger ($t_c=15\text{ min}$).

Fig.-6: Isotherms of Molybdenum (Initial Concentration 330 μmol/l) Adsorption on α-alumina in the Different Ranger of pH and Different Contacts Times.

Figure-7 present the adsorption isotherms of molybdenum with initial concentrations of 330 μmol/L and 496 μmol/L on α-alumina. From this figure, it's carried out that isotherms of molybdenum adsorption bellowing ph 5 have the same behaviors according to the time. At low concentration (330 μmol/l), adsorption of molybdenum around pH 6 range is not stable: at first 90 min it's fluctuating around 50%, then he stabilizes at 40%. On the other hand, with $C_i = 496 \mu\text{mol/l}$, the adsorption of molybdenum is low at first 30 min, but he grows up over time. Infirm basic suspensions, the molybdenum adsorption remains negligible. For both Concentrations, maximums of adsorptions were observed at pH value equal to 4. In other to compare molybdenum adsorption capacities; during the time, at different pH ranges, relative parameter %PR was calculated:

$$RP = \frac{\% P_{pHi} - \% P_{pH4}}{\% P_{pH4}} \times 100$$

Were, $\%P_{pHi}$ is the adsorption percentage of molybdenum adsorbed at different values of pH at i, $\%P_{pH4}$ is the adsorption percentage of molybdenum adsorbed at pH=4 in the same i. Figure-8 shows isotherms of %PR on α alumina during contact time.

Fig.-7: Adsorption Isotherms of Molybdenum with Initial Concentrations equals to 330 μmol/L and 496 μmol/L on α-alumina.

Fig.-8: Relative Molybdenum's Adsorptions on α alumina according to the Time.

It emerges from this study that the adsorption of molybdenum is significant and instantaneous in an acid medium. At the same time, it remains very weak and even negligible in basic environments.

However, in neutral or slightly acidic environments, the adsorption of molybdenum is at 50% relative to the maximum adsorption and it remains dependent on the contact time. This comportment explains the yield fluctuation of some technetium-generators according to time.

However, this result is conflicting because the optimal adsorption conditions are around of range of PZC. Before any conclusion, others experiences were realized. Actually, during UV-VIS spectrophotometric dosage of molybdenum, a specific volume of a molybdate solution is contacted with alumina α -Al₂O₃, 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 H₂O₂. Adjustments of pH were realized using 0.1M HCl or 0.1 M NaOH solutions. Suspicions of errors, contaminations made during sampling collection, or eventual influence of species added in the medium on absorbance measurements. The second set of solutions were prepared from the same stock solution. ICP-MS realized this time molybdenum quantification(Fig.-9).

In this experience, we can see that the adsorption of molybdenum is always interesting at pH 4 but it's not as much as the first result at pH 4. Curious about this result, Molybdenum adsorption of the others aluminas witch had different particles sizes were studied at pH. %P of every simple is represented in Fig.-10.

Fig.-9: Adsorption Isotherm of Mo in a Different Range of pH.

Fig.-10: Percentage of Molybdenum of aluminas which had Different Particles Sizes at pH 4.

We have observed that molybdenum adsorption is lower than the results obtained by the UV-VIS spectrophotometer method. This difference may be due to the presence of dissolved alumina species under these pH conditions ($\text{pH} < 4$). In addition to molybdenum dosage on the liquid phase, spectroscopic measurements were done using an ATR-FTIR on the solid phase. α -aluminas were in suspensions with $800 \mu\text{mol/l}$ Na_2MoO_4 solutions. Spectra of aluminas were acquired in different pH after 30 min of contact with an electrolyte (Fig.-11).

FTIR bands that appeared at 1630 and 2150 cm^{-1} were related to physisorbed water and OH group free from the interaction of H bonding, respectively. Also, the band's appearance around 1050 cm^{-1} was typical for alumina due to Al-O vibration mode. ATR-FTIR band at 900 cm^{-1} was due to the Mo-O stretching mode of the molybdenum-oxide complex bonded to the alumina surface. Bands due to microcrystallites MoO_3 appeared at 518 and 870 cm^{-1} . The increase in the intensity of this band with MoO_3 loading indicated the growth of polymolybdate species. These bands were associated with Mo-O-Al and Mo=O bond vibration in aluminum molybdate and crystalline MoO_3 phases. The signal of complex Al-Mo in suspension with pH 5 is more intense than the other.

Fig.-11: ATR-FTIR Spectra of Mo- α alumina Complex formed at Molybden Solution at pH 3,4, 5, 6 and 8.5 for the Same Initial Concentration of Mo.

Fig.-12: ATR-FTIR Specters of Molybdenum Solution at pH 6, alumina- Mo Complex and Pure alumina.

CONCLUSION

This study allowed the influence of several physicochemical parameters on the charge density of alumina used in the solid phase of technetium generators; to characterize its surface and optimize its pretreatment. On the other hand, by understanding the molybdenum adsorption mechanism, we have been able to define the behavior of the molybdenum-alumina complex according to the variations of pH and contact time. Until today we believed that the adsorption of molybdenum on alumina is instantaneous and time-independent. It turns out that this is not the case in a neutral and slightly acidic medium. In this environment, adsorption and desorption phenomena occur. In conclusion, the conditioning of the technetium column in a neutral medium disturbs the system and thus seeks a new state of equilibrium. However, the second step using radioactive molybdenum is to be realized.

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