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# Synthesis of Nano-α-$Al_2O_3$ for $^{99}$Mo Adsorbent

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## ABSTRACT

The fission-product $^{99}$Mo, having a high specific activity, is commonly used in alumina-based $^{99}$Mo/$^{99m}$Tc generator. Due to the limitation on the use of fission-product $^{99}$Mo, an alternative route for $^{99}$Mo production, namely activation of natural molybdenum using thermal neutron, has been explored. Unfortunately, this neutron-activated $^{99}$Mo has a low specific activity. Therefore, $^{99}$Mo/$^{99m}$Tc generator based on neutron-activated $^{99}$Mo requires a column with higher capacity absorbent. Thus, in this study, the nanomaterial of alumina (nano-α-$Al_2O_3$) was synthesized which was expected to have a higher $^{99}$Mo adsorption capacity, so that nano-α-$Al_2O_3$ could be potentially used as a matrix of column for $^{99}$Mo/$^{99m}$Tc generator based on neutron-activated $^{99}$Mo. Nano-α-$Al_2O_3$ was synthesized by using sol-gel method and characterized using FTIR spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM). In addition, the Scherrer method was used to determine the size of the crystals. To determine the $^{99}$Mo adsorption capacity of the synthesized nanoalumina, the nano-α-alumina was soaked in nitric acid solution for one hour at room temperature followed by removing the filtrate. Then, the nano-α-alumina was soaked in $^{99}$Mo solution ($Na_2{}^{99}MoO_4$) at certain conditions. The FTIR spectra for nano-α-alumina showed adsorption peak at 450-500 $cm^{-1}$ which indicated the presence of Al-O bond. The XRD patterns of nanoalumina crystals showed peaks at 2θ region of 25.8°, 35.9°, 38°, 52.8°, and 57.7°, indicating that the synthesized alumina had an α-phase with an average crystal size of ~5.5 nm. The average $^{99}$Mo adsorption capacity of the synthesized alumina was 47.55 ± 12.3 mg Mo/g nano-α-$Al_2O_3$.

## INTRODUCTION

Generally, a high specific activity of $^{99}$Mo radionuclide obtained from high- or low-enriched uranium-235 ($^{235}$U, ~95 % and ≤ 20 % respectively) is required as precursor for $^{99}$Mo/$^{99m}$Tc radioisotope generator. However, in the last decade, there have been three main problems related to $^{99}$Mo supply and technical process. These are: (1) most of the reactor used to produce $^{99}$Mo have entered the end of operational period, (2) due to safety issues, there has beena restriction which was proposed by the United Stated through the Global Threat Reduction Initiative for Highly Enriched Uranium (HEU) $^{235}$U usage for radioisotope production such as $^{99}$Mo, (3) Numerous radioactive by products resulting from a fission reaction require a complex separation technique for obtaining $^{99}$Mo [1,2]. Consequently, other methods needed to be explored in order to obtain $^{99}$Mo that does not use uranium, whether HEU or LEU, its precursor.

Production of $^{99}$Mo by neutron activation reaction [$^{98}$Mo (n, γ) $^{99}$Mo] using natural molybdenum target could be an alternative method for facing the aforementioned issues. However, production via this reaction produces $^{99}$Mo of low specific activity. Therefore, obtaining $^{99m}$Tc from this type of $^{99}$Mo requires a $^{99}$Mo adsorbent system or material that is capable of separating clinical-grade $^{99m}$Tc from $^{99}$Mo. Various methods and materials have been developed by many researchers. These include Chattopadhyay *et al.* who investigated an extraction methods using methyl ethyl ketone (MEK) as solvent to produce $^{99m}$Tc from low specific activity $^{99}$Mo [3]. Indeed, this

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method have been made a automatic system in order to reduce radiation exposure to operators. Many materials have also developed as molybdenum adsorbent in $^{99}$Mo/$^{99m}$Tc generator column. Guzman *et al*. developed and used zirconium molybdate gel material as molybdenum adsorbent. Briefly, the material was synthesized through sol-gel reaction using zirconyl solution as precursor and then mixed with molybdate [$^{99}$Mo] solution and dried at a certain time and temperature. Pertechnetate ($^{99m}TcO_4^-$) obtained from this material has been found fulfilling all pharmacopoeia regulations [4]. Another material, alumina molybdate gel, has also been studied as a column matrix for $^{99}$Mo/$^{99m}$Tc generator. This material has been reported to have potentialsas $^{99}$Mo adsorbent in preparation of $^{99m}$Tc radiopaharmaceuticals [5]. However, all the aforementioned materials have yet tobe improved their properties so they can be used in the $^{99}$Mo/$^{99m}$Tc generator based on neutron-activated natural molibdenum.

Meanwhile, the Centre for Radioisotopes and Radiopharmaceutical Technology- National Nuclear Energy Agency (PTRR-BATAN) has also developed a zirconium-based material (ZBM) for use as $^{99}$Mo adsorbent [6-9]. This material has been succesfully synthesized and used as $^{99}$Mo adsorbent in $^{99}$Mo/$^{99m}$Tc generator. The $^{99m}$Tc prepared from this generator meet the quality standard of pertechnetate for clinical use [10]. However, there are many condition yet to be improved such as yield of $^{99m}$Tc (<75 %) and adsorption capacity (<200 mg/g adsorbent). In addition, the use of NaOCl for increasing the $^{99m}$Tc yield could affect the labelling of some radiopharmaceuticals. Hence, other techniques and materials have to be explored in obtaining ideal column matrix for $^{99}$Mo/$^{99m}$Tc generator based on neutron-activated natural molybdenum.

Basically, the previous inorganic sorbents have poor adsorption capacity toward Mo due to the limited active sites and surface areas of those sorbents. An alternative solution for the aforementioned problems is probably the use of nanomaterials, as they have high porosities and large surface areas. Several nanomaterials such as mixed phasenano-zirconia (nano-$ZrO_2$)/ tetragonal nano-zirconia (t-$ZrO_2$), polymer embedded nanocrysrtalline titania (TiP), nanocrystalline alumina ($\gamma$-$Al_2O_3$), and nano-ceria-polyacrylonitrile composite ($CeO_2$-PAN) had been developed as effective adsorbent for several radionuclide generator such as $^{99}$Mo/$^{99m}$Tc, $^{188}$W/$^{188}$Re and $^{68}$Ge/$^{68}$Ga generators [11]. Therefore, nano-α-alumina could also be considered as molybdenum adsorbent for $^{99}$Mo/$^{99m}$Tc generator.

Alumina is a ceramic material that is widely used as catalysts, catalyst supports, and adsorbents. Some alumina-based materials are reported to have been used for $^{99}$Mo adsorbent, including nano-$\gamma$-$Al_2O_3$ [2] and alumina $^{99}$Mo-molybdate (VI) gel [5]. Their nano-form has been reported to have improved physical properties. Therefore, this form of alumina might be very potential to be used as adsorbent of low-specific-activity $^{99}$Mo. Nanoparticles can be produced through several methods such as sol-gel, hydrothermal, co-precipitation, mechanical grinding, vapor phase reactions, and combustion methods. However, it's nanopowder alpha-alumina ($\alpha$-$Al_2O_3$) form is difficult to obtain. This is due to: (1) $\alpha$-$Al_2O_3$ being in a stable phase after calcination at high temperature, and (2) $\alpha$-$Al_2O_3$ particles, which are prepared by wet chemical method, tend to aggregate during their dehydration process. Therefore, it is necessary to develop new methods to overcome this problem. The sol-gel synthesis provides a relatively inexpensive and simple process. In this study, we report the synthesis and characterization of nano-α-alumina as a molybdenum adsorbent using sol-gel method.

## EXPERIMENTAL METHODS

In this study, the nano-$\alpha$-$Al_2O_3$ was synthesized by using sol-gel method. The characterization of the synthesized nano-$\alpha$-$Al_2O_3$ was carried out by using Fourier Transform Infrared Spectroscopy (FT-IR), powder X-Ray Diffraction (XRD), and Transmission Electron Microscopy (TEM). HighScore Plus software was employed for crystallographic analysis.

### Materials and equipment

The materials used in this study included $AlCl_3$, ethanol, 32 % ammonia solution, $HNO_3$, NaOH, and HCl, all of which were purchased from Merck, and $MoO_3$ purchased from Sigma-Aldrich. The equipment used were glass beaker, hot plate stirrer, evaporation dish, thermometer, and furnace (Raypa®). Characterizations were carried out by using Bruker Alpha FTIR (Fourier-transform infrared) spectrometer, JEOL JEM-1400 TEM (transmission electron microscope), MiniFex 600 XRD (X-ray diffraction), and Atomlab 100 Plusdose calibrator.

### Synthesis of nano-$\alpha$-$Al_2O_3$

A total of 13.5 g of $AlCl_3$ was dissolved in 1000 mL ethanol, and 37 ml of 32 % ammonium hydroxide solution was then added. The mixture was stirred to form a gel. The gel was left for

30 hours at room temperature then followed by drying process at 100 ºC for 24 hours. The dried gel was then calcined at 1000 ºC for 2 hours.

## Characterization of nano-α-$Al_2O_3$

Characterization of nano-α-$Al_2O_3$ was performed by FTIR, 120-kV TEM,and XRD. The FTIR analysis was conducted at the Center for Radioisotope and Radiopharmaceutical Technology, BATAN.

## Optimization of $^{99}$Mo adsorption capacity of the nano-crystalline α-$Al_2O_3$

### *Method I*

A set of three samples, each containing 250 mg, was prepared. Each sample was put into 0.28 mL of $^{99}$Mo solution, and water was then added until the total volume reached 2 mL. The samples were left for 30 minutes at room temperature and were shaken occasionally. The filtrate was then removed from the nano-α-$Al_2O_3$. The $^{99}$Mo radioactivity of the filtrate and the nano-α-$Al_2O_3$ were measured by using dose calibrator.

### *Method II*

A set of six samples, each containing 100 mg was prepared. Each sample was put into 1 mL $HNO_3$ solution with various pH ranging from 1 to 6. Each sample was left for 1 hour at room temperature, followed by removing the filtrate. Into each sample, containing nano-α-$Al_2O_3$, was added 0.12 mL of $^{99}$Mo solution, and then water was added until the total volume reached 1 mL. Samples were left for 30 minutes at room temperature. The filtrate was separated from nano-α-$Al_2O_3$. The $^{99}$Mo radioactivity of the filtrate and the nano-α-$Al_2O_3$ were measured by using dose calibrator.

## RESULTS AND DISCUSSION

The synthesis of nano-α-$Al_2O_3$ was started with 0.01 mol of $AlCl_3$. The addition of ammonium hydroxide solution into aluminum chloride solution resulted in a white gel. The gel was then dried at a temperature of 100 ºC. At this stage, the gel was presumed of $Al(OH)_3$. It is estimated that chemical reaction occurs as follows:

$$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl \quad (1)$$

After calcination (1000 ºC, 2 h), the gel turned into a white powder. At this stage, a white powder formed that was presumed as $Al_2O_3$. It is estimated that chemical reaction occurred as follows:

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 2H_2O \quad (2)$$

The average yield of synthesized nano-α-alumina (three experiment runs) was found to be 80 %. Characterization of the synthesized alumina by using FTIR spectroscopy was carried out by comparing the FTIR spectra of the $AlCl_3$ reagent, dried gel, and white calcined powder.

Figure 1 shows the FTIR spectrum of $AlCl_3$. It can be seen that there are adsorptions at the wave number of 1615 $cm^{-1}$, indicating stretching vibration from the Al-Cl group, and 693 $cm^{-1}$, which indicate a bending vibration from the Al-Cl group.

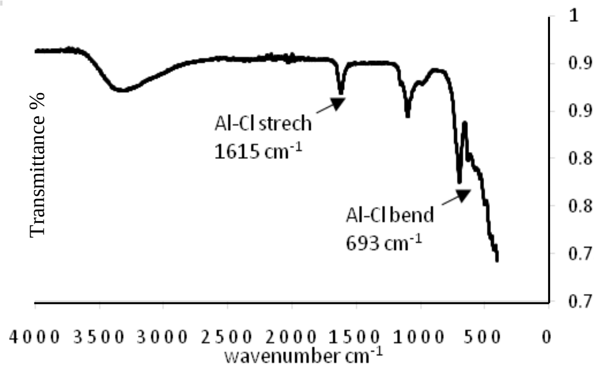

**Fig. 1**. FTIR spectra of $AlCl_3$.

Figure 2 is the FTIR spectra of the dried gel. It can be seen that there are adsorption at wave number of 3000-3200 $cm^{-1}$ (broad) which shows the stretching vibration of O-H group, as well as the adsorption at 1397 $cm^{-1}$ indicate the presence of vibration from the Al-O group. Based on the FTIR spectrum, it can be concluded that the dried gel consisted of $Al(OH)_3$.

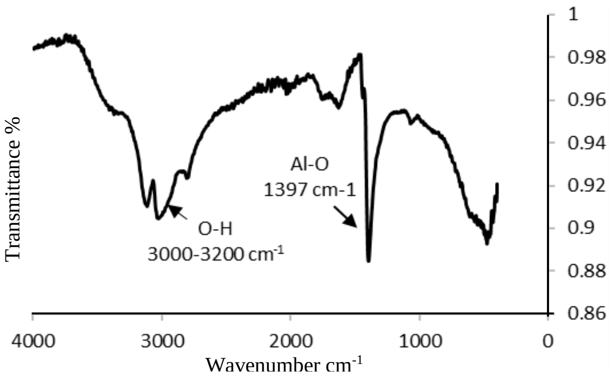

**Fig. 2.** FTIR spectra of dried gel of Al $(OH)_3$.

Based on Fig. 1 and Fig. 2, it can be presumed that the aluminum chloride has reacted with $NH_4OH$ to produce aluminum hydroxide. This result is in accordance with (1).

Figure 3 (a) is the FTIR spectrum of calcinated white powder. This figure shows adsorption peak at 439-514 $cm^{-1}$. The FTIR spectrum was then compared with the FTIR spectrum of standard $Al_2O_3$ at Fig. 3 (b). Figure 3 (b) shows an adsorption at 410-510 $cm^{-1}$. These two spectra show similar adsorption spectra patterns. Therefore, it can be suggested that the synthesized white powder contained $Al_2O_3$.

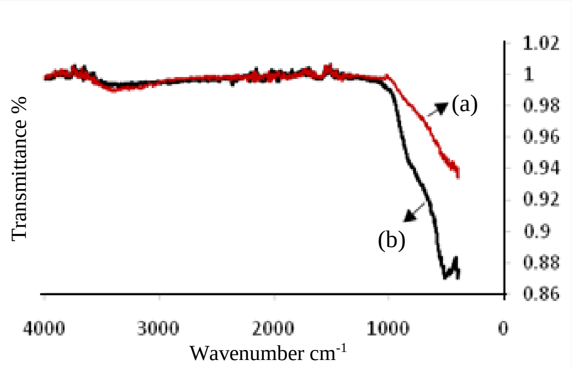

**Fig. 3**. FTIR spectra of (a) the synthesized $Al_2O_3$, (b) the standard $Al_2O_3$.

The TEM micrographs of synthesized alumina are shown in Fig. 4. The TEM micrographs indicate that the synthesized alumina had a crystalline form. It can also be observed that the nanoparticles of alumina had a uniform particle shape and size with an average particle size of less than 20 nm.

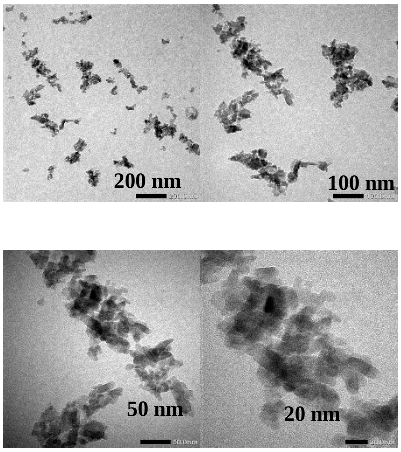

**Fig. 4**. TEM micrographs of synthesized nano-α-$Al_2O_3$.

The XRD characterization was used to determine the phases of the synthesized alumina, whether it was alpha or gamma phase alumina. The result of XRD characterization of the synthesized $Al_2O_3$ is shown in Fig. 5. The quantitative analysis of the synthesized $Al_2O_3$ using HighScore Plus software confirmed that it consisted of aluminum oxide and corundum phases. In aluminum oxide phase - $Al_8O_{12}$ (78.4 %), crystal peaks appeared in the region of $2\theta = 31.2°$, 33.1°, 37°, 39.1°, 45.2°, and 67°. This type of XRD pattern is typical for nanocrystalline alumina with monoclinic crystal structure. In the corundum phase, $Al_{12}O_{18}$ (21.6 %), crystal peaks appear in the region of $2\theta = 25.8°$, 35.9°, 38°, 52.8°, and 57.7°. This type of XRD pattern is typical for nanocrystalline alumina with a hexagonal crystal structure. The analysis of crystallite size (grain size) by using Scherrer method resulted in average crystallite size of 5.5 nm. The corundum is also one of the example of α-phase of $Al_2O_3$. The standard of α-phase of $Al_2O_3$ has XRD crystal peaks pattern of $2\theta = 25.8°$, 35.3°, 38.2°, 43.5°, 52.3°, and 57.1° [12]. By comparing of the XRD pattern of synthesized nano-α-$Al_2O_3$ and the standard α-phase of $Al_2O_3$, it can be suggested that synthesized $Al_2O_3$ has an α-phase.

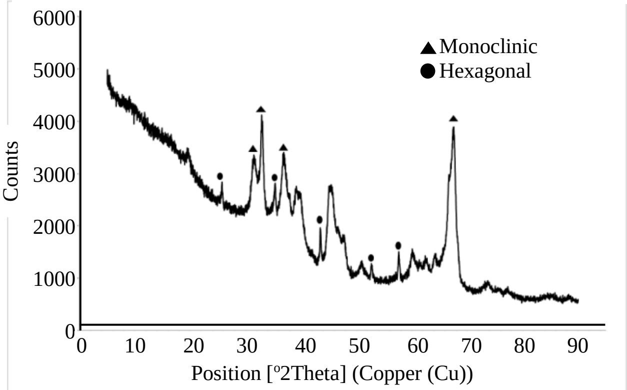

**Fig. 5**. XRD patterns of nano-α-$Al_2O_3$.

## Optimization of $^{99}$Mo adsorption capacity of the nanocrystalline α-$Al_2O_3$

The results of the optimization of $^{99}$Mo adsorption capacity of the nanoalumina using Method I is shown in Fig. 6. The average of $^{99}$Mo adsorption capacity was found to be 11.55 ± 4.1 mg Mo/g nano-α-$Al_2O_3$. In order to increase the adsorption capacity of this nanoalumina toward $^{99}$Mo, another method was used, namely Method II. Six samples of nano-α-$Al_2O_3$ were soaked with nitric acid solution with concentrations between $10^{-1}$ - $10^{-6}$ M with pH between 1 and 6. By using Method II, the average of the $^{99}$Mo adsorption capacity was found to be 47.55 ± 12.3 mg Mo/g nano-α-$Al_2O_3$, as shown in Fig. 7. The optimum condition for the $^{99}$Mo adsorption was achieved when nano-α-$Al_2O_3$ was soaked in 0.1 M nitric acid solution at pH 1. This condition resulted in an adsorption capacity of 68.5 mg Mo/g nano-α-$Al_2O_3$.

Thus, this condition (under Method II) can be applied for the best adsorption of $^{99}$Mo.

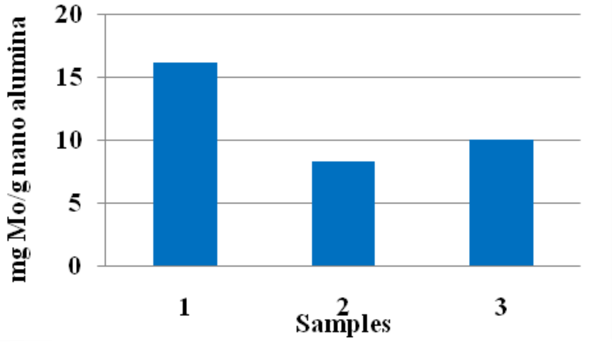

**Fig. 6**. $^{99}$Mo adsorption capacity of nano-$\alpha$-$Al_2O_3$ (Method I).

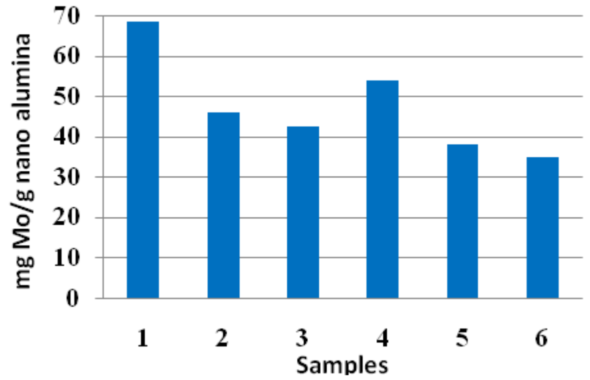

**Fig. 7.** $^{99}$Mo adsorption capacity of nano-$\alpha$-$Al_2O_3$ (Method II).

Alumina has many crystalline structure forms, namely $\alpha$, $\chi$, $\eta$, $\delta$, $\kappa$, $\theta$, $\gamma$, and $\rho$-$Al_2O_3$. Among those forms, $\alpha$-$Al_2O_3$ is the most stable form of the compounds formed between aluminum and oxygen. A study of the application of $\alpha$-$Al_2O_3$ as neutron-activated $^{99}$Mo adsorbent has never been reported.

Chakravarty *et al.* have synthesized $\gamma$-$Al_2O_3$ and determined the adsorption capacity of $\gamma$-$Al_2O_3$. The synthesized $\gamma$-$Al_2O_3$ has static and dynamic adsorption capacities of 205±10 mg Mo/g adsorbent and 148±3 mg Mo/g adsorbent, respectively [2]. Another study of alumina that was functionalized with a sulfate moiety found it to have a $^{99}$Mo adsorption capacity of 217 mg Mo/g adsorbent [2].

In this study, the average of the $^{99}$Mo adsorption capacity was found to be 47.55 ± 12.3 mg Mo/g nano-$\alpha$-$Al_2O_3$. Although $\alpha$-$Al_2O_3$ is the most stable form of the alumina, it has a lower $^{99}$Mo adsorption capacity compared to $\gamma$-$Al_2O_3$ and sulfate-functionalized alumina. It is due to the crystalline form of $\alpha$-$Al_2O_3$ that it has more difficulties to adsorb by $^{99}$Mo. The different results might also be caused by the difference of the amount of materials used, the specific activity of the $^{99}$Mo bulk solution, or the duration of the $^{99}$Mo adsorption toward the material.

## CONCLUSION

This study has succeeded to synthesis nano-$\alpha$-$Al_2O_3$, with an average $^{99}$Mo adsorption capacity of 47.55 ± 12.3 mg Mo/g nano-$\alpha$-$Al_2O_3$. This result is still lower than what was attained by $\gamma$-$Al_2O_3$ and sulfate-functionalized alumina.

Based on this result, we can conclude that nano-$\alpha$-$Al_2O_3$ is not good enough as an adsorbent for neutron-irradiated natural molybdenum.

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