Al-Kimia

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Development of Novel Alumina by Solid-State Reaction for 99Mo/99mTc Adsorbent Material

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Abstract: Technetium-99m (99mTc), a daughter radionuclide of molybdenum-99 (99Mo), is the most widely used radiodiagnostic agent due to its ideal characteristics. The separation of this radionuclide from 99Mo is commonly performed using alumina. However, a new production method of this radionuclide, which employs a low specific activity 99Mo, makes alumina no longer suitable as separation material. This study aims to develop novel alumina using a facile solid-state reaction for 99Mo/99mTc generator system. The SS-alumina was synthesized from aluminium nitrate nonahydrate and ammonium bicarbonate without solvent. The resulted SS-alumina was then analyzed by FTIR and BET method. 99Mo adsorption and 99mTc releasing study on a series of pH were also performed. FTIR study revealed that the resulting material was Al2O3 with a surface area of 237.65 m2/g. The adsorption capacity, 99mTc yield, 99Mo breakthrough, and alumina breakthrough were 76.06 mg Mo/g alumina, 80.31%, 56.5 µCi/µCi 99mTc, and less than 5 mg/mL, respectively. The elution profile shows a high activity of 99mTc in 2nd and 3rd fraction. It is concluded that the SS-alumina shows good performance as adsorbent material for separation of a 99Mo/99mTc and further work is now underway.

Keywords: alumina, 99Mo, 99mTc, column chromatography, radionuclide generator

1. INTRODUCTION

Technetium-99m (99mTc) is an ideal radiodiagnostic agent due to its pure gamma energy, low gamma energy (140 keV) and short half-life (6.02 h) (El-Absy et al., 2014). 99mTc can be radiolabeled with a variety of radiopharmaceutical kits for diagnostic purposes, for instance, cancer imaging, bone scan, cardiac perfusion, and renal scan (Jürgens et al., 2014). An unlabeled 99mTc or also known as pertechnetate (TcO4-) solution can be utilized for gastrointestinal and thyroid uptake study. 99mTc is available as TcO4- solution obtained from 99Mo/99mTc generator package containing column chromatography system. Alumina is used as column material to adsorb molybdenum-99 (99Mo), the parent radionuclide of 99mTc. 99Mo decays to 99mTc and can be eluted using saline solution every day. 99mTc is carried by the saline solution in TcO4- form, while 99Mo remains in alumina column (Guedes-Silva et al., 2016).

99Mo for a 99Mo/99mTc generator is mainly produced from fission of uranium-235 (235U), either high enriched or low enrich uranium form, which produces high specific
activity of $^{99}$Mo (~740 TBq/g) (Jo et al., 2014). The vulnerability of $^{99}$Mo supply has been indicated by its shortage in 2009 due to the shutdown of two main nuclear reactors producing $^{99}$Mo in Netherland and Canada. Other facilities, mainly research reactors, are relatively old so the crisis of $^{99}$Mo supply might be occurred again in the future (Welsh et al., 2015). Hence, alternative production routes of $^{99}$Mo have been developed to maintain the long-time stability of $^{99}$Mo supply for medical use. The alternative routes can be classified as neutron activation of natural molybdenum using research reactor and irradiation of high enriched molybdenum using cyclotron. The first method is mainly developed in developing countries possessing a research reactor without proper fission-$^{99}$Mo production facility (Blaauw et al., 2017; M Munir et al., 2019). The second method is mainly carried out in developed countries possessing a proper cyclotron for $^{99}$Mo production. The latter method is simpler because a research reactor is not required, however, the production cost is more expensive (Selivanova et al., 2016). Both methods produce lower specific activity $^{99}$Mo compared to that of production from fission uranium.

Alumina is material used as adsorbent material in commercial $^{99}$Mo/$^{99m}$Tc generator due to its ideal characteristics. Alumina is an inexpensive material and possessing sufficient hardness as a column filler. The main drawback of this material is its low adsorption capacity to molybdenum (20 mg Mo/g alumina) (Guedes-Silva et al., 2016). This adsorption capacity is enough for $^{99}$Mo/$^{99m}$Tc generator production using a high specific activity $^{99}$Mo, however it is inadequate for low specific activity $^{99}$Mo. In order to overcome this problem, many materials with better performance than alumina have been developed, for instance, zirconium-based material (Munir et al., 2018; Saptiama et al., 2016; Saptiama et al., 2015) and several metal oxides (Chakravarty et al., 2014; Marlina et al., 2017), however, their use bring up several drawbacks.

In an attempt to develop an ideal adsorbent material, conventional alumina has been modified to increase its adsorption capacity. Various synthesis method has been performed to produce many derivative alumina, for instance, mesoporous alumina (Saptiama et al., 2017), mesoporous ordered alumina, and doped alumina. Saptiama, et al had developed nanosheet alumina (Saptiama et al., 2019), nanospheres alumina (Saptiama et al., 2018) and alumina embedded mesoporous silica (Saptiama et al., 2018) which has adsorption capacity to molybdenum greater than conventional alumina. However, adsorption study using $^{99}$Mo for these materials has not been performed and the synthesis route was quite sophisticated. Chakravarty et al had developed mesoporous alumina with a simple synthesis method which demonstrates adsorption capacity up to 225±10 mg Mo/g alumina and $^{99m}$Tc yield up to 89% (Chakravarty et al., 2013). The main drawback of this project was a double column system for $^{99}$Mo adsorption in the generator package which makes the assembly process more complicated. In order to obtain new alumina with a facile synthesis route and simple assembly on $^{99}$Mo/$^{99m}$Tc generator application, the reported synthesis method still needs to improve. In this work, new modified alumina was synthesized.
using a facile solid-state reaction. The modified alumina was then characterised and studied for its $^{99}$Mo adsorption, the yield of $^{99m}$Tc, $^{99}$Mo and alumina breakthrough.

2. METHOD

Material

Aluminum nitrate nonahydrate ($\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) and ammonium bicarbonate ($\text{NH}_4\text{HCO}_3$) were purchased from Sigma Aldrich and used without any further purification. Aquabidest was purchased from IPHA Laboratories, while a saline solution was purchased from Otsuka. A low specific activity $^{99}$Mo solution was produced by irradiating of natural MoO$_3$ in GA Siwabessy Multipurpose Reactor for 100 hours. The irradiated target was then further processed at the Center for Radioisotope and Radiopharmaceutical Technology, National Nuclear Energy Agency. The nuclear reaction for this production is $^{98}\text{Mo(n, γ)99Mo}$.

Instrument

The functional group of the SS-alumina was analysed using Alpha Fourier Transform Infrared (FTIR) Spectrometer (Bruker), while its surface area was measured using surface area analyser (Quadrasorb SI – Quantachrome Quadrawin). Radioactivity measurement was carried out using dose calibrator (Atomlab 100 plus), while $^{99}$Mo breakthrough was measured using multi-channel amplitude pulse analyser (MCA, Ortec GEM-30), High Purity Germanium (HPGe) detector.

Procedure

Material Synthesis

A 37.5 g of Al(NO$_3$)$_3$·9H$_2$O was placed in 100 mL beaker glass followed by addition of 11.85 g of NH$_4$HCO$_3$. The mixture heated at 100°C for 5 hours and stirred every 1 hour until a solid gel was formed. The solid was stored overnight and then calcinated at 700°C for 2 hours. The resulted material was sieved for obtaining a material with size of 300-700 µm.

Adsorption Study

A 0.5 g of the SS-alumina was soaked in a $^{99}$Mo solution with a series of pH (4, 5, and 6) for 3 hours. Filtrate and solid were separated and each of them was measured for its radioactivity. The solid was packed in a glass column and stored overnight. After stored, the column was eluted using a saline solution to release $^{99m}$Tc.

3. RESULT AND DISCUSSION

A high surface area alumina, which is denoted as SS-alumina, has been synthesized using a facile solid-state synthesis method. This synthesis route was carried out without solvent and considered as an inexpensive and simple method for SS-alumina production. The resulting SS-alumina was 9.195 g from the theoretical result of 10.2 g and the synthesis yield was 90.15%. It was considered as a high yield synthesis process due to its simple process without any sophisticated instrument and
The resulting SS-alumina was the white-colour grain with enough hardness for column material.

![Figure 1. FTIR spectra of synthesized the SS-alumina](image1.png)

The FTIR spectra showed in Figure 1 reveals the presence of Al$_2$O$_3$ in a spectral range of 435.13 - 515.81 cm$^{-1}$. The spectra showing the presence of elements from starting material, which should appear in 1000-1500 cm$^{-1}$ for C and N elements, was absent from the Figure 1. It is obvious that the absence of these elements was caused by the elimination during the calcination process. Al(NO$_3$)$_3$·9H$_2$O was chosen as starting material due to its ability to release N during the calcination process. AlCl$_3$, the other alumina starting material, remains Cl residue after calcination, so it is less preferable.

![Figure 2. The plot of 1/[W((W(Po/P)-1)] and relative pressure for surface area calculation](image2.png)
A surface area is an important parameter for adsorbent material, where the adsorption process occurs. The higher the surface area, the higher the adsorption capacity (Indra Saptiama, Kaneti, Suzuki, et al., 2018). The plot of $1/[W((W(Po/P)-1)]$ and relative pressure can be seen in Figure 2, which is used for the surface area calculation. The calculated $S_{BET}$ was 237.65 $m^2/g$, similar with most alumina $S_{BET}$ which is ranging from 200-450 $m^2/g$ (Chakravarty et al., 2013; Saptiama et al., 2017, 2019; Saptiama et al., 2018). Even though the surface area is an important parameter for the adsorption process, the other parameter, for instance, crystal phase and acidity, might also play an important role (Sulaiman et al., 2018).

![Figure 3. 99Mo/99mTc generator column design](image)

The synthesized SS-alumina was packed in a glass column with frit as seen in Figure 2. A glass frit and glass wool were used for material holding, and material filter, respectively. The top and bottom of glass column were covered with rubber septa and aluminium cap. The output needle was used for releasing the column eluate. This column chromatography design is adapted from a commercial 99Mo/99mTc generator. This is the simplest design which is expected to reduce the possibility of failure in generator assembly. The result of 99Mo adsorption and 99mTc releasing test for the SS-alumina can be seen in Table 1.

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<th>pH 5</th>
<th>pH 6</th>
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<td>Loaded $^{99}$Mo activity (MBq)</td>
<td>987.90</td>
<td>987.90</td>
<td>976.80</td>
</tr>
<tr>
<td>Adsorption yield (%)</td>
<td>37.68</td>
<td>36.75</td>
<td>19.95</td>
</tr>
<tr>
<td>Adsorption capacity (mg Mo/g alumina)</td>
<td>76.06</td>
<td>74.18</td>
<td>40.28</td>
</tr>
<tr>
<td>Obtained $^{99m}$Tc Activity (MBq)</td>
<td>215.12</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>$^{99m}$Tc Yield (%)</td>
<td>80.31</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>$^{99}$Mo breakthrough (µCi/mCi $^{99m}$Tc)</td>
<td>56.5</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Alumina breakthrough</td>
<td>&lt; 5 mg/mL</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 1. The performance of SS-Alumina for $^{99}$Mo/$^{99m}$Tc generator material
Table 1 reveals that the adsorption capacity of the SS-alumina in pH 4 and 5 was almost similar, while the one in pH 6 was much lower. In high acidity solution, molybdenum tends to form polymolybdate, for instance, heptamolybdate (Mo$_7$O$_{24}^{6-}$) which possesses a more negative charge (Figure 4). While in the lower acidity, molybdate (MoO$_4^{2-}$) is more preferable. This might increase the affinity of $^{99}$Mo species to bind alumina. The higher the pH value, the lower the adsorption capacity of alumina (Sulaiman et al., 2018). Table 1 also shows that in pH 4, the column can release the eluate, while in pH 5 and 6 cannot. This might be caused by either the material’s particle size was too small or its hardness was not sufficient (Sholikhah et al., 2016). It is not clear, whether the pH influences the physical properties of the material or not. The resulting $^{99m}$Tc yield was 80.31%, slightly lower than commercial $^{99}$Mo/$^{99m}$Tc generator possessing $^{99m}$Tc yield more than 90%. The alumina breakthrough was found less than 5 mg/mL which conform to the required specification. The $^{99}$Mo breakthrough was of 56.5 µCi/mCi $^{99m}$Tc which is much higher than the required specification (0.15 µCi/mCi $^{99m}$Tc) (Uzunov et al., 2018). Hence, the alumina tandem column is required to reduce the $^{99}$Mo breakthrough (Marlina et al., 2016).

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**Figure 4.** Structure of molybdate (left) and heptamolybdate (right) (Damjanović et al., 2019)

**Figure 5.** Elution profile of $^{99m}$TcO$_4$ solution from the SS-alumina column
Figure 5 shows that the highest $^{99m}$Tc yield was found in 2nd and 3rd fraction, while 4th to 7th fraction remain the lower one. This is very promising for $^{99}$Mo/$^{99m}$Tc generator utilization because the radioactive concentration can be adjusted. In order to obtain high radioactive concentration, the generator can be eluted with 3 mL only.

4. CONCLUSION
The SS-alumina has been synthesized using solid-state method and its adsorption capacity has been studied. This material possesses higher $^{99}$Mo adsorption capacity than ordinary commercialized alumina. It demonstrated a good profile as adsorbent material for $^{99}$Mo/$^{99m}$Tc generator system, however, the $^{99}$Mo breakthrough was out of specification, so the alumina tandem column is required.

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