Increasing the performance of silica modified quaternary triammine for sorption of Gold(III) Ion

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Abstract. Synthesis Silica Modified Quaternary Ammines (SMQA) and its application has been carried out on the adsorption of gold(III) ions in a batch system. SMQA material is synthesized through the SMA methylation reaction. SMA material is synthesized from Na₂SiO₃ and 3-Aminopropyltrimethoxysilane (3-APTMS). Furthermore, the replacement of the methyl group in [-N(CH₃)₃]⁺ will change to [-N⁺CH₃{(CH₂)₃N⁺(CH₃)₃}₂] called Silica Modified Quaternary Triammines (SMQT). SMQT is synthesized by watching SMA with 3-APTMS become SMT which is then refluxed for methylation process to form SMQT. Material characterization is carried out through identification of functional groups, surface morphological analysis, elemental composition and metal ion concentration. Adsorption process of metal anion [AuCl₄]⁻ obtained optimum results at pH 5 with a contact time of 100 minutes with an adsorption capacity of 77.58 mg/g and an efficiency value of 96.975%.

1. Introduction

Indonesia is known as a country that has abundant natural resources (SDA) and one of them is gold. Gold mining can be carried out on a small scale through the panning of people's gold like in Sarolangun, Jambi [1], and on a large scale such as in Tembagapura, Papua conducted by PT. Freeport Indonesia. The largest potential gold mine on the island of Sulawesi is in Bombana Regency at 165,000.00 tons [2].

Gold extraction based on the results of amalgamation of sand beach concentrate on the beachfront around the Bayah beach obtained 6-71 ppb gold (Au) bullion and the following, silver 4-47 ppb [3]. The amalgamation process can cause problems namely environmental pollution. In the adsorption process using adsorbents, it was shown to increase the concentration of Au(III) ions to be detected. Gold(III) in the form of anion [AuCl₄]⁻ optimally adsorbed by SMA at pH 3. At pH 3 the ammonium group is protonated into an ammonium cation group, so that it is able to interact with the anion [4]. The amine group (-NH₂) can be converted to a quaternary ammonium cation [-N(CH₃)₃]⁺ by methylation reaction with methyl iodide [5]. Although stable in various acidities, SMQA still has a relatively low gold(III) adsorption capacity [6], so it is necessary to re-modify the SMQA.

For this reason, the SMQA modification will be done by replacing the methyl group in [-N(CH₃)₃]⁺ to [-N⁺CH₃{(CH₂)₃N⁺(CH₃)₃}₂] which will be called Silica Modified Quaternary Triammine (SMQT)). New material is very potential and promising as an adsorbent that has an adsorption capacity and as a catalyst material candidate.
2. Materials and methods

2.1. Materials

The ingredients used in this study are as follows. Chemicals include NaOH, HCl, 3-aminopropyltrimethoxysilane (3-APTMS), dimethyl formamide (DMF), toluene, acetonitrile, sodium chloride, pro analysis. Au(III) or H[AuClO₄] ion solution - from the FMIPA UGM analytical chemistry laboratory. Aqua demineralization from PAU UGM, KSCN, Tiourea, Na₂S₂O₃. Acetate buffer, ethanol, ether, sodium bicarbonate, metal ion solution from AgNO₃, CuCl₂·2H₂O, K₃[PtCl₆], K₂CrO₄ (Merck). Other materials are used rice husks and soil samples from traditional gold mining sites in the Sarolangun, Jambi.

Standard glassware used 1 mL, 10 mL, 50 mL pipette volume, 10 mL, 100 mL, 250 mL, 1 L measuring flask, 50 mL glass beaker, 100 mL, 250 mL, 500 mL, 1 L, 250 mL erlenmeyer flask mL, 500 mL and 50 mL burettes. Equipment for the synthesis of adsorbents used is 1 set of reflux apparatus (3 neck flasks and coolers), a set of vacuum filtering devices (buchner). Magnetic stirrer, 200 mesh size sieve, analytical balance and equipment for batch adsorption including film bottles, shakers, filter paper, cartridge, vacuum pump, whatman 42, aluminum foil, black duct tape, universal indicator, porcelain cup, watch glass and pH meter (Orion 4 Star). Grinder is used mortar and mortar porcelain.

The main instruments are Infra-Red Spectrometer (Shimadzu Fourier Transform Infra-Red, FTIR, 8201PC), Scanning Electron Microscopy (SEM JEOL JSM 6063 LA Zeiss), Energy Disperive X-Ray (EDX), Atomic Absorption Spectrophotometer (SSA, Perkin Elmer, 3110).

2.2. Method

Synthesis of SMQT from SMT was carried out by adding to the round neck flask 3 which was covered with black duct tape and filled with 12 gram SMT, added 20 mL DMF, 20 mL acetonitrile, 20 mL toluene and 20 mL methyl iodide. The mixture is refluxed for 6 hours continuously at 70°C while adding dropwise drops of methyl iodide to a total volume of methyl iodide 4 mL. The mixture is filtered, the solid product is washed with distilled water, 2% NaHCO₃ solution and washed again with distilled water.

The adsorbent material is dried at 80°C for 6 hours.

3. Results and discussion

3.1. Stages of SMQT synthesis

The synthesis of SMA material begins with 60 grams of RHA which is destined using NaOH. The next process, carried out the process of modification of silica-gel (SG) with an amino group (-NH₂) using 3-aminopropyltrimethoxysilane solution (3-APTMS). The result of white solid is STA material. This material is neutralized by soaking repeatedly, using 2 L of distilled water for 24 hours. The material is characterized by FTIR, XRD, morphology and elemental composition with SEM-EDX and TEM images and determined by BET adsorption-desorption of the material against N₂ gas. The methylation process is carried out by mixing 12 g of SMA with 10 mL of toluene, 20 DMF and 20 mL of acetonitrile and 4 mL of CH₃I in stages. At this stage the addition of methyl iodide is added drop by drop, while continuing to stir with magnetic stirrer, so that the methylation reaction occurs.

3.2. Characterization

3.2.1. FT-IR Analysis. From the analysis using infrared spectra on SMQT (figure 1), it can be observed that there are qualitatively significant differences in functional groups in the adsorbent material.

The functional group contained in SG, namely the absorption band at wave number 455,20 cm⁻¹ which is the Si-O bending vibration of the siloxane (Si-O-Si) group, 786,96 cm⁻¹ symmetry stretching vibration 1087,85 cm⁻¹ asymmetric stretching vibration Si-O, 1635,64 cm⁻¹ vibration of the Si-O buckling of the silanol group [7]. C-H stretching vibration of the methyl group (-CH₃) occurs at wave
number 2931.80 cm\(^{-1}\). O-H stretching vibrations from water molecules occur at wave number 3448.72 cm\(^{-1}\) [8]. Specifically, infrared spectra analysis is presented in table 1.

### Table 1. Analysis spectra infrared SG, STA and SMAK.

| Types of vibrations in functional groups | SMQT Wave Number (cm\(^{-1}\)) |
|-----------------------------------------|-------------------------------|
| Vibration of buckling Si-O on siloxane (Si-O-Si) | 455.20 |
| Vibratory stretching of Si-O symmetry in siloxane (Si-O-Si) | 786.96 |
| Vibratory asymmetry of Si-O in siloxane (Si-O-Si) | 1087.85 |
| Vibration of buckling N-H from primary amine (-NH\(_2\)) | 1512.19 |
| Vibratory buckling Si-O from silanol (Si-OH) | 1635.64 |
| C-H stretching vibration of methylene (-CH\(_2\)) | 2931.80 |
| Vibratory Si-O from silanol (Si-OH) | 3448.72 |

**Figure 1.** FTIR spectra of SMQT and Fe\(_3\)O\(_4\). **Table 2.** Infrared spectra analysis of Fe\(_3\)O\(_4\) dan SMQT.

| Functional Groups | Fe\(_3\)O\(_4\) Wave number (cm\(^{-1}\)) | SG | Fe\(_3\)O\(_4\)—STT |
|-------------------|----------------------------------------|----|------------------|
| Vibration buckling Fe — O of Fe—OH | 628.43 | - | - |
| Vibration stretching —OH of Fe—OH | 3419.73 | - | - |
| Vibration buckling —OH from Fe—OH | 1630.35 | - | - |
| Vibratory buckling Si—O—Si | - | 421.72 | 423.39 |
| Stretching vibration of Fe — O from Fe—O—Si | - | - | 631.96 |
| Stalling vibration Si — O of Si—O—Si | - | 798.36 | 798.08 |
| Stalling vibration Si — O of Si—OH | - | 956.84 | 960.11 |
| Vibration buckling —OH from Si—OH | - | 1638.69 | 1643.84 |
| Stretching vibration —OH from Si—OH | - | 3451.80 | 3439.31 |

The FTIR results show the presence of the Fe-O-Si group in the wave number 631.96 cm\(^{-1}\) [9]. The appearance of the functional group Fe-O-Si indicates that Fe\(_3\)O\(_4\) has bind to SMQT. The addition of Fe\(_3\)O\(_4\) to SMQT aims to make SMQT magnetic properties so that it will be easier at the recycling stage of using SMQT adsorbents.

**3.2.2. Analysis SEM-EDX.** The results of the SEM-EDX analysis to determine the surface morphology of the base material (SG) with after the methylation process (SMQT) is presented in figure 2.
From SEM analysis, it can be observed that in SMQT the surface morphology becomes more heterogeneous, which shows the cavity of the methylation process. This is supported by EDX spectra in SMQT containing carbon, silicon, nitrogen and iodine. Silica composition is obtained relatively high compared to other elements [10]. The percentage of element C in SMQT is higher, due to the binding of C to the quaternary group. The results of the quantitative elemental composition analysis using EDX in SMQT are presented in table 3.

![Figure 2. SEM–EDX SMQT.](image)

| Element | Mass (%) | Atom (%) |
|---------|----------|----------|
| C       | 50.51    | 63.93    |
| O       | -        | -        |
| N       | 18.78    | 20.34    |
| Na      | -        | -        |
| Si      | 28.70    | 15.50    |
| I       | 1.90     | 0.23     |

Table 3 shows that in the SMQT material there is an element of iodine mass of 1.90% and an atomic mass of 0.23%. This shows that SMQT has formed and the composition of its elements, iodine.

3.2.3. **TEM Analysis.** TEM analysis results to determine the surface morphology of the SMQT after the adsorption process is performed are presented in Figure 3, the black part is gold and the white part is the adsorbent material.
3.2.4. Reaction mechanisms for the formation of SMQT. Rice husk ash will be isolated by Na-silicate which is then reacted with 3-APTMS to form SMA. SMA then reacted again with 3-APTMS to form Silica Modified Triaminine (SMT). SMT is refluxed for the methylation process to form SMQT. Hypothetical structure of the above process reaction equation can be seen in figure 4.

![Figure 4. Rute hipotetik sintesis SMQT.](image)

3.3. Adsorption

3.3.1. Effect of pH on gold adsorption. The pH parameter is important in the adsorption process, because pH can affect ionization. Changes in pH can cause changes in the charge on the surface of the material or species of metal ions in solution. The pH range chosen is in the pH range from 2 to 6. For adsorption efficiency can be seen in figure 5.

![Figure 5. The curve of the effect of pH on the adsorption of gold.](image)
Based on figure 5 which shows a graph of the relationship between adsorption efficiency and pH, it can be seen that the optimum efficiency value is at pH 3, which is 13.116%. This is because at pH 3, species \([\text{AuCl}_4^-]\) are in the maximum amount.

**Figure 6.** The curve of the effect of pH on the gold adsorption capacity.

Adsorption capacity is the amount of adsorbate that is adsorbed per adsorbent weight, so the value is influenced by the weight of the adsorbent. In this result, an optimum adsorption capacity value of 1.4712 mg / g was obtained with an adsorption efficiency value of 13.116% which means that the adsorbent can adsorb as much as 1.4712 mg / g of metal anion \([\text{AuCl}_4^-]\) with a percentage decrease in concentration of 13.116% of Initial concentration is at pH 3.

3.3.2. **Effect of time on gold adsorption.** Contact time is the time needed by the adsorbent to absorb the adsorbate. Longer contact time will allow the process of diffusion and adhesion of the adsorbent molecules to take place better. The longer the contact time between adsorbent and adsorbate, the adsorption power will increase. The contact time to reach the equilibrium state in the process of metal absorption by the adsorbent ranges from a few minutes to several hours.

**Figure 7.** The time relationship curve and the gold adsorption efficiency.

Based on Figure 6 which shows the efficiency of adsorption, in the range of 20 to 80 minutes the adsorption process increases slowly, this is because the active site of the adsorbent has not been saturated by metal anions [AuCl₄]⁻.
In this result the optimum adsorption capacity was obtained at 77.58 mg / g with an adsorption efficiency value of 96.975%. Which means that the adsorbent can adsorb 77.588 mg / g of metal anion [AuCl₄⁻] with a percentage decrease in concentration of 96.975% from the initial concentration at the 100th minute. But at 120 minutes there was no change in the adsorption process. This indicates that the surface of the adsorbent has been saturated and an equilibrium has been reached between the concentration of gold in the adsorbent and its environment so that the adsorption process does not occur again at the contact time above 100 minutes.

4. Conclusion
Synthesis of Silica Modified Quaternary Triamine (SMQT) material has been successfully carried out through several stages, namely the formation of SMA, followed by the formation of SMQT. The FTIR results show the existence of functional groups of the constituent compounds of SMQT.

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