Synthesis Of Imprinted Ionic Material (SiO$_2$(BGS/RHA)-TMPDT-Im-Au) For Adsorption Of Ion Au(III)

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Abstract. Synthesis of imprinted ionic material SiO$_2$(BGS/RHA)-TMPDT-Im-Au) was successfully studied. Sodium silicate from a mixture of ash bagasse and rice husk (Na$_2$SiO$_3$(BGS/RHA)) were used as the precursors. Furthermore, Na$_2$SiO$_3$(BGS/RHA) is modified with the $N^1$-(3-Trimethoxysilylpropyl)diethylenetriamine (TMPDT) in which Au(III) ions are used as templates. The synthesis results were characterized by Fourier-transform infrared spectroscopy (FTIR), Surface area analyzers (SAA), Thermo Gravimetric analysis (TGA), Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX). The adsorption study was carried out using a batch system conducted in various pH and contact time. The adsorption process achieved a maximum pH of 3 in a 60-minute equilibrium time. Au(III) adsorption capacity of SiO$_2$(BGS/RHA)-TMPDT-Im-Au was 10.44 mg/g. The kinetic studies show that the adsorption of Au(III) on SiO$_2$(BGS/RHA)-TMPDT-Im-Au follows a pseudo-second-order with the reaction rate constant (k) of 76.7331 g mol$^{-1}$ min$^{-1}$.

1. Introduction

Gold is widely used in various fields, such as jewellery, catalysts and electronic fields. In the electronics field, gold is used for components such as ICs, contacts and cables. Mobile phones contain gold around 300-350 g/ton [1], while the ore is only around 5-30 g/ton [2]. Electronic waste will increase every year. To overcome this waste is to recover gold metal from waste. This also helps in providing gold raw materials.

Adsorption is one of the methods developed for gold extraction [1][3-6]. The adsorption method is the most suitable for extracting gold (III) metal ions at low concentrations. This is because of the low cost and high efficiency. Silica gel is a material developed for adsorbents. This material has several advantages such as good mechanical properties, high porosity, large surface area, no swelling, resistance to microbial attack and thermal stability [7-11]. One way to increase the ability of silica as an adsorbent is by surface modification using organic functional groups [11-14]. Imprinted ionic is a better method, because it combines modifications as well as the formation of templates that match the target metal ions [15-16]. Ionic imprinted material will increase capacity and selectivity of adsorption [16].

2. Experimental

2.1. Materials

The materials used are rice husk ash (RHA) and bagasse ash (BGS). In addition, chemicals are also used such as sodium hydroxide (NaOH), hydrochloric acid (HCl), HNO$_3$, thiourea from Merck. As a modifier is N1-(3-Trimethoxysilylpropyl)diethylenetriamine (TMPDT) from Aldrich. Whereas as a template is the solution of Au(III) 1000 ppm from analytical laboratory of UGM.

2.2. Physical measurements

Identification of functional groups was analyzed using FTIR (Fourier Transform Infra-Red Spectrophotometry) Shimadzu IR prestige 21. SEM-EDX (Scanning Electron Microscopy with...
Energy Dispersive X-ray Spectroscopy) was used to analyze the surface morphology and elemental composition of a material. Thermal stability of a material was analyzed using TGA (Thermo Gravimetric Analyzer) STA-PT-1600 TG-DSC / DTA lineis thermal analyzer. Porosity of material was analyzed using SAA (Surface Area Analyzer) Quantachrome Nova Analyzer 1100. AAS (Atomic Absorption Spectrophotometry) Shimadzu AA 6650 was used to determine the concentration of metal ions.

2.3. Synthesis of imprinted ionic Au(III) material
Synthesis of sodium silicate from rice husk ash Na$_2$SiO$_3$(RHA) and bagasse ash Na$_2$SiO$_3$(BGS) refers to research [16] with several changes. In the synthesis of imprinted material (SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Imp), 100 ml of a mixture of Na$_2$SiO$_3$(BGS)/Na$_2$SiO$_3$(RHA) with a volume ratio of 3:7 was added with 6 M HCl to almost forming a gel. After that the mixture was added with a mixture of 10 ml TMPDT and 10 ml Au(III) 1000 mgL$^{-1}$ which had been stirred for 1 hour, then added 6 M HCl to form a gel. The gel that formed is left for 24 hours, then dried at 70 °C until dry. Results in the form of dry solids of SiO$_2$(BGS-RHA)$^+$TMPDT-Au was mashed up to 200 mesh size. The Au(III) in SiO$_2$(BGS-RHA)$^+$TMPDT-Au was released with 7% thiourea in 1 M HCl. The result is imprinted ionic material (SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl). As a control, it was also synthesized of material SiO$_2$(BGS-RHA)$^+$TMPDT by adding a mixture (Na$_2$SiO$_3$(BGS)/Na$_2$SiO$_3$(RHA) =3:7) with TMPDT.

2.4. Determination of the optimum pH of adsorption
A 10 mL solution of Au(III) 15 mgL$^{-1}$ in a variety of pH 1-6 was contacted at 10 mg SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl for 1 hour. The mixture was stirred for 1 hour then filtered. Au(III) in filtrate was analyzed by AAS. Eq. 1 was used to calculate the percentage of Au(III) adsorbed.

$$ P = 100 \times \frac{(C_0-C_e)}{C_0} \quad (1) $$

where $P$ represents the amount of the metal ions adsorbed (%); $C_0$ and $C_e$ represent the initial and the final concentration of the metal ions (mgL$^{-1}$).

2.5. The adsorption contact time
As much as 10 mL of Au(III) 15 mgL$^{-1}$ at pH 3 was contacted with 10 mg SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl at a time variation of 0, 5, 10, 20, 30, 40, 50, 60, 90, 120 minutes. The mixture was stirred for 1 hour then filtered. The same treatment was carried out on SiO$_2$(BGS-RHA)$^+$TMPDT.

3. Result and Discussion
3.1. Synthesis material imprinted ionic Au(III) (SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl)
The mechanism for the formation of imprinted ionic Au(III) material (SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl) can be explained in Figure 1. Reaction I (Figure 1.) shows the formation of orthosilicic acid (compound 1). Reaction II (Figure 1.) is the binding of AuCl$_4^-$ by TMPDT (compound 2). The release of the methoxy group from TMPDT is shown in reaction III (Figure 1). Then compound 1 reacts with compound 2 to form polymerization as shown in reaction IV (Figure 1). The reaction of V (Figure 1.) is the release of AuCl$_4^-$ ions to produce SiO$_2$(BGS-RHA)$^+$TMPDT-Au-Impl (compound 5).

In the release process AuCl$_4^-$, it was used thiourea 7% in 1M HCl solution. The release AuCl$_4^-$ was carried out 3 times then washed with distilled water (Figure 2). Thiourea is used for desorption of Au(III) because thiourea will reduce to Au(I) and then Au(I) forms a stable complex [16]:

$$ \text{Au}^{3+}(aq) + 2 \text{SC(NH$_2$)$_2$}(aq) \rightleftharpoons \text{Au[SC(NH$_2$)$_2$]$_2$}^{+}(aq) $$
Figure 1. Mechanism of formation of SiO$_2$(BGS-RHA)-TMPDT-Au-Imp

Figure 2. Au(III) ions released in each wash (mgL$^{-1}$)

3.2. Characterization of Material
3.2.1. FTIR Analysis. Functional groups contained in the material was analyzed using FTIR. Based on Figure 3 that the SiO$_2$(BGS-RHA)$^3$-TMPDT, SiO$_2$(BGS-RHA)$^3$-TMPDT-Au and SiO$_2$(BGS-RHA)$^3$-TMPDT-Au-Imp appeared a peak of around 1480 cm$^{-1}$ indicating a bond = C-NH- [17]. This proves that the
TMPDT modifier has been bound to silica. The Au(III) bound to the N atom will reduce the vibration intensity of the N-H bond in the compound [18].

![Figure 3. FTIR Spectra of SiO$_2$ (BGS-RHA) (a), SiO$_2$(BGS-RHA)-TMPDT (b), SiO$_2$(BGS-RHA)-TMPDT-Au (c) and SiO$_2$(BGS-RHA)\textsuperscript{\textdagger}$\textdagger$-TMPDT-Au-Imp (d)\[a\] ]

3.2.2. TGA Analysis. Thermal stability of SiO$_2$(BGS-RHA)-TMPDT-Au-Imp was analyzed by TGA shown in Figure 4. The results show that there are two stages of weight loss. The first stage, the loss of H$_2$O molecules is 11.9% at a temperature of 35.4°C - 128.8°C. The second stage, lost the organic group of TMPDT by 39.4% in 187.4°C - 899.9°C.

![Figure 4. Curve of TGA of SiO$_2$(BGS-RHA)$\textsuperscript{\textdagger}$-TMPDT-Au-Imp\[b\] ]

3.2.3. SEM-EDX analysis. To determine surface morphology and elements in SiO$_2$(BGS-RHA)$\textsuperscript{\textdagger}$-TMPDT-Au-Imp was analyzed using SEM-EDX. The results are shown in Figure 5 and Table 1. The SEM image indicate that SiO$_2$(BGS-RHA)$\textsuperscript{\textdagger}$-TMPDT-Au-Imp have irregular shapes [16].

![Figure 5. SEM image of SiO$_2$(BGS-RHA)-TMPDT-Au-Imp\[c\] ]
The presence of N and C elements in SiO$_2$(BGS-RHA)-TMPDT-Au-Imp (Table 1) indicates the presence of TMPDT in the material. Total 0% Au showed the release of Au (III) from the adsorbent to form Au (III) template.

### Table 1. Elements of the material SiO$_2$(BGS-RHA)-TMPDT-Au-Imp

| Element | % mass |
|---------|--------|
| C       | 18.68  |
| N       | 14.02  |
| O       | 39.73  |
| Si      | 18.52  |
| Cl      | 8.25   |
| Cu      | 0.08   |
| Au      | -      |

The presence of N and C elements in SiO$_2$(BGS-RHA)-TMPDT-Au-Imp (Table 1) indicates the presence of TMPDT in the material. Total 0% Au showed the release of Au (III) from the adsorbent to form Au (III) template.

### 3.2.4. SAA analysis

The porosity of adsorbent such as surface area and pore volume in SiO$_2$(BGS-RHA)-TMPDT-Au-Imp were 16,361 m$^2$/g, and 0.050 cc/g, respectively. While the surface area and pore volume for SiO$_2$(RHA) are 296.387 m$^2$/g and 0.833 cc/g, respectively. Surface area of SiO$_2$(BGS-RHA)-TMPDT-Au-Imp is smaller than SiO$_2$. This is due to pore closure by TMPDT compounds [8].

### 3.3. Adsorption of Au(III) on SiO$_2$(BGS-RHA)-TMPDT-Au-Imp

#### 3.3.1. The effect of pH

The effect of pH on the adsorption of Au (III) in SiO$_2$(BGS-RHA)-TMPDT-Au-Imp is shown in Figure 6. The optimum conditions were achieved at pH 3 of SiO$_2$(BGS-RHA)-TMPDT and SiO$_2$(BGS-RHA)-TMPDT-Au-Imp. In general at pH 1-6 the adsorption ability of SiO$_2$(BGS-RHA)-TMPDT-Au-Imp is greater than SiO$_2$(BGS-RHA)-TMPDT. The existence of templates on imprinted material allows Au(III) to be adsorbed more. At pH 1-2, percent adsorption is decreases. This is because AuCl$_4^-$ ions at low pH tend to form HAuCl$_4$ which is difficult to interact with adsorbents which positively charged [12]. Similarly at pH 4-6, it also tends to decrease. It is possible to occur the deposition of Au(III) ions into gold hydroxide (Au(OH)$_3$)[16].
3.3.2. Kinetics of Adsorption

Figure 6 shows the effect of pH on adsorption of Au(III) in SiO$_2$-TMPDT and SiO$_2$-TMPDT-Au-Imp. The balance time is achieved starting at 60 minutes for SiO$_2$-TMPDT and SiO$_2$-TMPDT-Au-Imp. The value of $q_e$ on SiO$_2$-TMPDT and SiO$_2$-TMPDT-Au-Imp are 10.05 mg/g; 10.44 mg/g, respectively.

To determine the reaction kinetics that control the adsorption process, the reaction kinetics were tested for First order (Eq. 2) [19], second order (Eq. 3), pseudo-first order (Eq. 4) [20] and pseudo-second order (Eq. 5) [21]. They were applied to evaluate the experimental data of contact time. Kinetic model and parameters for Au(III) adsorption are presented in Table 2.
\[
\ln C_e = -k_1 t + \ln C_0
\]

\[
\frac{1}{C_e} = k_2 t + \frac{1}{C_0}
\]

\[
\log(q_e - q_t) = \log q_e - \frac{k_3}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{k_4 q_0^2} + \frac{t}{q_e}
\]

where \(C_e\) represents Au(III) concentration at equilibrium (mM); \(C_0\) represents Au(III) initial concentration (mM); \(q_e\) and \(q_t\) represent the amounts of Au(III) adsorbed at equilibrium (mol g\(^{-1}\)) and at any time \(t\) (mol g\(^{-1}\)); \(k_1\), \(k_2\), \(k_3\), and \(k_4\) represent the adsorption rate constant of first order (min\(^{-1}\)), second order (mM \(^{-1}\) min\(^{-1}\)), pseudo-first order (min\(^{-1}\)), and pseudo-second order (g mol\(^{-1}\) min\(^{-1}\)), respectively. The results of the calculation of \(k\) and \(R^2\) values are shown in the Table 2.

**Table 2.** Constant rate and linear coefficient of Au(III) adsorption in various kinetics models on (A). SiO\(_2\)(BGS-RHA)-TMPDT and (B). SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp

| Kinetic model            | Constant rate (k)   | \(R^2\) |
|--------------------------|---------------------|---------|
|                          | A       | B       | A       | B       |
| First order              | 0.0082  | min\(^{-1}\) | 0.0047  | min\(^{-1}\) | 0.6643  | 0.2000 |
| Second order             | 0.2639  | mM \(^{-1}\) min\(^{-1}\) | 0.1396  | mM \(^{-1}\) min\(^{-1}\) | 0.8052  | 0.2166 |
| Pseudo-first order       | 0.0408  | min\(^{-1}\) | 0.0249  | min\(^{-1}\) | 0.7519  | 0.1144 |
| Pseudo-second order      | 3.3961  | g mol\(^{-1}\) min\(^{-1}\) | 76.7331 | g mol\(^{-1}\) min\(^{-1}\) | 0.9911  | 0.9996 |

Based on the \(R^2\) value, the adsorption kinetics of Au(III) on SiO\(_2\)(BGS-RHA)-TMPDT and SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp tend to follow pseudo-second order kinetics model. This is because the values for both adsorbents in pseudo-second order are close to 1. The pseudo-second order kinetics model illustrates that adsorption occurs chemically [3-4][12][22].

**4. Conclusion**

Synthesis of SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp can be done using SiO\(_2\)(BGS-RHA) as a precursor, TMPDT as a modifier and Au(III) as a template. Formation of the template was done by desorption of Au(III) using 7% thiourea solution in 1M HCl for 3 repetitions. The process of maximum adsorption of Au(III) by SiO\(_2\)(BGS-RHA)-TMPDT and SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp occur at pH 3. Adsorption capacity (\(q_e\)) on SiO\(_2\)(BGS-RHA)-TMPDT and SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp are 10.05 mg/g; 10.44 mg/g, respectively. Constant rate (k) for SiO\(_2\)(BGS-RHA)-TMPDT and SiO\(_2\)(BGS-RHA)-TMPDT-Au-Imp are 3.3961; 76.7331 g mol\(^{-1}\) min\(^{-1}\), respectively. Adsorption kinetics follow pseudo-second order kinetics model.

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**References**
[1] Hagelüken C and Corti C W 2010 *Gold Bull.* 43 209.
[2] Ogata T and Nakano Y 2005 *Water Res.* 39 4281.
[3] Fujiwara K, Ramesh A, Maki T, Hasegawa H and Ueda K 2007 *J. Hazard. Mater.* 146 39.
[4] Ramesh A, Hasegawa H, Sugimoto W, Maki T and Ueda K 2008 *Bioresour. Technol.* 99 3801.
[5] Shamsipur T and Mostafavi A 2009 *J. Hazard. Mater.* 168 1548.
[6] Bozkurt S and Merdivan M 2009 *Environ. Monit. Assess.* 158 15.
[7] Xie F, Lin X, Wu X and Xie Z 2008 *Talanta* 74 836.
[8] Jal PK, Patel S and Mishra BK 2004 Talanta 62 1005.
[9] Zougagh M, Pavon J M and de Torres AG 2005 Anal Bioanal Chem. 381 1103.
[10] Mahmoud M, Maximous N and Masoud M 2004 Microchim Acta 147 111.
[11] Tong A, Akama Y and Tanaka S 1990 Anal. Chim. Act. 230 179.
[12] Hastuti S, Nuryono and Kuncaka A 2015 Indones. J. Chem. 17(2)108.
[13] Istiningrum R B, Tiwow C D, Nuryono and Narsito 2015 Procedia Chemistry 17 132.
[14] Rubcumintara T 2015 Inter. J. Chem Eng and Appl. 6(2) 95.
[15] Buhani, Narsito, Nuryono and Kunarti, E S 2010 Desalin 251 83.
[16] Sakti S C W, Siswanta D and Nuryono 2013 Pure Appl. Chem. 85 211.
[17] Chan C C P, Choudhurya N R and Peter P 2011 Colloids and Surfaces A: Physicochem. Eng. Aspects 377 20
[18] Wu Y, Zuo F, Lin Y, Zhou Y, Zheng Z And Ding X 2014 Journal of Macromolecular Science, Part A: Pure Appl. Chem. 51, 441
[19] Singh S, Verma L K, Sambi S S and Sharma S K 2008 Proceedings of the World Congress on Engineering and Computer Science, San Francisco, USA, 112.
[20] Lagergren S 1898 Kungliga Svenska Vetenskapsakademiens Handlingar 24 1.
[21] Ho Y U S H 2004 Scientometrics 59 171.
[22] Wang H, Bao C, Li F, Kong X and Xu J 2010 Microchim. Acta. 168 99.