STUDY OF ADSORPTION-DESORPTION Au(III) USING IMPRINTED IONIC MATERIAL (SiO$_2$ (RHA-BGS) -TMPDT-Au-Imp)

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Abstract. Research on the adsorption of desorption of Au (III) metal using imprinted ionic SiO$_2$ (RHA-BGS) -TMPDT-Au-Imp material has been carried out. In this research, silica source (SiO$_2$) from rice husk ash (RHA) and bagasse (BGS) was modified through imprinted ionic technique. Adsorption studies include variations in concentration and selectivity while desorption studies include time variations. Furthermore, the adsorption and desorption processes were characterized using FTIR. The results of the adsorption process followed the Freundlich isotherm model with an adsorption capacity of 981.672 mg/g. The adsorption selectivity shows that the imprinted ionic material (SiO$_2$ (RHA-BGS) -TMPDT-Au-Imp) is more selective than the material without imprinted ionic (SiO$_2$ (RHA-BGS) -TMPDT). The order of selectivity is Au(III)/Zn(II) > Au(III)/Fe(III) > Au(III)/Cu(II). Study of desorption kinetics Au(III) followed the zero order kinetics. The results of the FTIR show that there are still O-H, C-H and -NH groups. This indicates the imprinted ionic material (SiO$_2$ (RHA-BGS) -TMPDT-Au-Imp) is not damaged.

1. Introduction

Gold reserves on earth are decreasing, while market demand continues to increase. This condition is encouraging to move on by finding a second source other than gold ore. In the electronics industry, gold is widely used because it has quite high electrical conductivity and is not easily corroded [1]. At present more than 300 tons of gold are used annually for electronic components such as ICs, contacts and cables. At the end of the use of electronic goods such as computers, mobile phones become waste that has not been used optimally. It is reported that the cellphone contains 300-350 g/ton gold [2]. This encourages efforts to recover gold from electronic waste while helping to provide gold raw materials. Gold extraction from electronic waste has been carried out, among others, the process of precipitation, ion exchange, solvent extraction and adsorption. Adsorption is one method of extracting gold metal ions which is more effective, simple, and inexpensive. The gold metal recovery process requires high selectivity from the adsorbent material so that it can produce pure gold. According to Sakti et al. (2013) [3] the selectivity of adsorption from silica adsorbents (SiO$_2$) can be improved by adding imprinted ionic techniques. The imprinted ionic method is judged to have very high selectivity compared to just ordinary modifications. This is because at the time of polymer synthesis there are metal ions which act as templates and monomers that contain functional groups. The release of ions as
a template from the polymer matrix will cause the formation of imprinted ionic cavities and the arrangement of imprinted ionic materials which will selectively adsorb target ions [4-6]. This research will study about the selectivity of Au(III) adsorption on ionic imprinted materials (SiO$_2$(RHA-BGS)-TMPDT-Au-Imp). In addition, Au(III) desorption process was studied to determine the stability of the adsorbent during the desorption process.

2. Experimental

2.1. Materials

The materials used in this study include: sodium hydroxide (NaOH), hydrochloric acid (HCl) (pa), from Merck. The standard solution is Cu(II) 100 ppm, Fe(III) 100 ppm, Zn(II) (pa) 100 ppm from merck. A solution of gold(III) 1000 mgL$^{-1}$ was prepared in our laboratory by dissolving gold in an aquaregia solution.

2.2. Physical measurement

The tools used include glassware, pH meters, AAS (Atomic Absorption Spectrophotometry) Shimadzu AA 6650, FTIR (Fourier Transform Infra-Red Spectrophotometry) Shimadzu IR prestige 21.

2.3. Effect of concentration on the adsorption ability of SiO$_2$ (RHA-BGS) -TMPDT-Au-Imp

SiO$_2$(RHA-BGS)-TMPDT-Au-Imp (10 mg) is contacted with 10 mL Au(III) with variations in concentration 0 - 40 (0, 5, 10, 15, 20, 25, 30, 35, and 40) mgL$^{-1}$ at pH 3. Then it is stirred for 60 minutes then filtered. The filtrate was analyzed using SAA. The results are evaluated using the Freundlich (1) and Langmuir (2) equations. From the Freundlich equation obtained $K_F$ (maximum capacity) and $N$. From the Langmuir equation obtained the values of $K$ and $Q_m$. Furthermore, from the KL value adsorption energy can be calculated by calculating Gibbs free energy (3).

\[
\log q_e = \log K_F + 1/n \log C_e \tag{1}
\]

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{C_e}{Q_m} \tag{2}
\]

where: $C_e$ and $q_e$ masing masing adalah konsentrasi dan kapasitas adsorpsi pada saat kestimbangan. $K_F$ adalah konstanta Freundlich yang menunjukkan kapasitas adsorpsinya. The $q_m$ and $K_L$ are the maximum adsorption capacity and constant of the Langmuir isotherm, respectively. The Free energy ($\Delta G^\circ$) can be calculated from the Langmuir equilibrium constant ($K_L$) using equation (4).

\[
\Delta G^\circ = -RT \ln K_L \tag{3}
\]

where: $R$ (8.314 J K$^{-1}$mol$^{-1}$) is a gas constant, $T$ (K) is the adsorption temperature.

2.4. Determination of competing adsorption (selectivity) of Au (III) metal ions with other metal ions

SiO$_2$(RHA-BGS)-TMPDT-Au-Imp (10 mg) is contacted with 10 mL Au(III) 35 mgL$^{-1}$ with other metal ion pairs such as: Cu(II), Zn(II) and Fe(III) with concentration variations of 5, 10 and 15 mgL$^{-1}$. The same thing is done for SiO$_2$(RHA-BGS)-TMPDT. Then selectivity is calculated using the equation.

\[
q = \frac{(C_0-C_e)}{V/M} \tag{4}
\]

\[
D = \frac{q}{C_e} \tag{5}
\]

\[
\alpha = \frac{D_{M_1}}{D_{M_2}} \tag{6}
\]

where $q$ is the adsorption capacity (mg/g), $C_0$ and $C_e$ are the concentration of the initial metal ion and concentration at equilibrium (mg/L), $M$ is the mass of the adsorbent (g), $V$ is the volume of solution, $D_M$ is the distribution ratio (L/g), and $\alpha$ is the coefficient of selectivity (Sakti et al., 2013).
2.5. Determination of Optimum Desorption Time

500 mg SiO$_2$(RHA-BGS)-TMPDT-Au-Imp was contacted with 500 mL Au(III) 350 mgL$^{-1}$ at pH 3, then stirred in 60 minutes. Then filtered, then the precipitate was roasted at 60 °C to dry. 10 mg of sludge that has absorbed Au(III) was desorbed using a thiourea-HCl solvent with time variations of 0, 15, 30, 45, 60, 90, 120 and 150 minutes. From the time variation data then evaluated using 0,1 and 2. order kinetics models. The results before desorption and after desorption are then analyzed using infrared spectroscopy (FTIR).

3. Result and Discussion

3.1. SiO$_2$(RHA-BGS)-TMPDT-Au-Imp Adsorption Performance Test on Au (III) Metal Ion Model Solution.

Figure 1. Adsorption Curve in a. SiO$_2$(RHA-BGS)-TMPDT and b. SiO$_2$(RHA-BGS)-TMPDT-Au-Imp on the Concentration of Au (III) Metal Ion Solution.

Figure 1 shows that imprinted (SiO$_2$(RHA-BGS)-TMPDT-Au-Imp) material absorbs Au(III) more than without imprinted (SiO$_2$(RHA-BGS)-TMPDT). Furthermore, the time variation data is used to study the adsorption isotherm model. The results are shown in Table 1.

Table 1. Langmuir and Freundlich Isotherm Data.

| Adsorption Isotherms | SiO$_2$(RHA-BGS)-TMPDT | SiO$_2$(RHA-BGS)-TMPDT-Au-Imp |
|----------------------|------------------------|-----------------------------|
| Langmuir             |                        |                             |
| qm (mg/g)            | 139,341                | 299,256                     |
| R$^2$                | 0,0471                 | 0,1266                      |
| B                    | 3,10112                | 2,21277                     |
| ΔG                   | 20,0522 kJ/mol         | 19,9026 kJ/mol              |
| Freundlich           |                        |                             |
| K_f (mg/g)           | 473,006                | 981,672                     |
From Table 1 shows that the adsorption of Au(III) on SiO$_2$ (RHA-BGS)-TMPDT and SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp tend to follow the Freundlich isotherm model. It is shown that the value ($R^2$) for the Freundlich isotherm model is greater than Langmuir. The Freundlich model illustrates that the adsorption process occurs multilayer$^{[7]}$. The adsorption process is not only on the surface of the adsorbent but also enters the adsorbent pore. The interactions that occur are very heterogeneous involving various active sites in the adsorbent. Maximum adsorption capacity ($K_f$) in SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp (981.672 mg/g) is greater than SiO$_2$ (RHA-BGS)-TMPDT (473.006 mg/g). This is due to the formation of imprinted cavities in the adsorbent so Au(III) is adsorbed more.

From the Langmuir isotherm model the adsorption energy ($\Delta G$) can be estimated. The magnitude $\Delta G$ represents the adsorption energy between Au(III) and the active site in the adsorbent. According to the table 1 $\Delta G$ above 20 kJ/mol indicates the interaction between Au(III) and the active site of the adsorbent occurs chemically. $\Delta G$ on SiO$_2$ (RHA-BGS)-TMPDT and SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp material is approaching 20 KJ/mol so the interaction is estimated to occur chemically.

3.2. Adsorption Selectivity of Au(III) Metal Ions with Other Metal ions in SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp.

Au(III) adsorption Selectivity with other metal ions in SiO$_2$ (RHA-BGS)-TMPDT and SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp materials shown in table 2.

Table 2. Selectivity of Au(III) Metals to Cu(II), Zn(II), and Fe(III) Metals.

| Variations [Cu(II)] | Selectivity | | Selectivity |
|-------------------|-------------|-------------------|
|                   | SiO$_2$ (RHA-BGS)-TMPDT | SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp |
| 5 ppm             | 3,20        | 37,49             |
| 10 ppm            | 153,12      | 30,46             |
| 15 ppm            | 5,85        | 114,30            |

| Variations [Zn(II)] | Selectivity | | Selectivity |
|-------------------|-------------|-------------------|
|                   | SiO$_2$ (RHA-BGS)-TMPDT | SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp |
| 5 ppm             | 3,36        | 372.77            |
| 10 ppm            | 4,24        | 128,96            |
| 15 ppm            | 0.92        | 1252,12           |

| Variations [Fe(III)] | Selectivity | | Selectivity |
|---------------------|-------------|-------------------|
|                     | SiO$_2$ (RHA-BGS)-TMPDT | SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp |
| 5 ppm               | 0           | 261,93            |
| 10 ppm              | 0           | 21,19             |
| 15 ppm              | 0           | 680,71            |

Au(III) selectivity in SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp is higher than SiO$_2$ (RHA-BGS)-TMPDT. This is due to the formation of imprinted cavities that match their size with Au(III). At pH 3 the adsorbent active group becomes -NH$_3^+$, so it is expected that the cationic ion Zn(II), Cu(II), Fe(III) is not adsorbed. Part of the metal ion is in fact also distorted. This is due to the adsorption process does not only involve the active site -NH$_3^+$, but also from the pores and s-OH groups of silanol on silica. The order of selectivity in SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp is Au/Zn > Au/Fe > Au/Cu.

3.3. Adsorbent Material Desorption Performance Test.

Table 3. Au(III) Metal Desorption on SiO$_2$ (RHA-BGS)-TMPDT and SiO$_2$ (RHA-BGS)-TMPDT-Au-Imp material.
From the desorption results, it is necessary to know the kinetic model that occurs in the desorption. Determination of the rate of desorption reaction of Au(III) metal ions from each adsorbent is carried out by the kinetic model plot of the desorption with the kinetic model that can be applied to the desorption process is the reaction equation of order 0, order 1, and order 2. From the results of the linear kinetics regression equation the desorption rate will then be determined the coefficient of determination ($R^2$) of each reaction order equation which is then compared, where the reaction order equation that has the closest $R^2$ is 1 which best describes the desorption process that occurs.

Table 4. Kinetic Desorption SiO$_2$-TMPDT and SiO$_2$-(RHA-BGS)-TMPDT-Au-Imp.

| Time (minutes) | Desorption Au(III)(mg/g) | SiO$_2$-TMPDT | SiO$_2$-(RHA-BGS)-TMPDT-Au-Imp |
|---------------|-------------------------|---------------|-------------------------------|
| 0             | 0                       | 0             | 0                             |
| 30            | 0.78348                 | 0.4279        |                               |
| 60            | 0.64782                 | 0.41824       |                               |
| 90            | 0.64313                 | 0.33258       |                               |
| 150           | 0.52709                 | 0.51107       |                               |
| 200           | 0.77215                 | 0.6898        |                               |

The results obtained from the linear regression equation show that the kinetic model that is suitable for the desorption reaction of the Au (III) metal ion from the SiO$_2$-TMPDT adsorbent is 2nd order while in the SiO$_2$-(RHA-BGS)-TMPDT-Au-Imp adsorbent is zero order.

Functional group analysis on the desorption performance of SiO$_2$-(RHA-BGS)-TMPDT and SiO$_2$-(RHA-BGS)-TMPDT-Au-Imp material is needed to determine the differences that occur in the two materials before and after desorption using the FTIR (Fourier Transform Infra Red) instrument with the following results:
Figure 2. FTIR spectra of a. SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp before desorption, b. SiO$_2$(RHA-BGS)$^*$-TMPDT-Imp after Desorption, c. SiO$_2$(RHA-BGS)$^*$-TMPDT-Au before desorption, and d. SiO$_2$(RHA-BGS)$^*$-TMPDT after desorption.

Based on Figure 2. above it can be seen that the results of the FTIR spectra of the two adsorbents have peaks that are almost the same as the literature. From the figure it can also be seen that the absorption at wavelengths of absorption –OH, N-H, and C-H is still visible which shows that the SiO$_2$(RHA-BGS)$^*$-TMPDT and SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp material has no damage when desorption.

4. Conclusion
The results of the adsorption process followed the Freundlich isotherm model with an adsorption capacity of 981.672 mg/g for SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp and 473.006 mg/g for SiO$_2$(RHA-BGS)$^*$-TMPDT. The adsorption selectivity shows that the imprinted ionic SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp material is more selective than the material without imprinted ionic SiO$_2$(RHA-BGS)$^*$-TMPDT. The order of selectivity is Au(III)/Zn(II)$>$ Au(III)/Fe(III)$>$ Au(III)/Cu(II). Study of desorption kinetics Au(III) followed the zero order kinetics for SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp and second order for SiO$_2$(RHA-BGS)$^*$-TMPDT. The results of the FTIR show that there are still O-H, C-H and -NH groups. This indicates the imprinted ionic material (SiO$_2$(RHA-BGS)$^*$-TMPDT-Au-Imp) and SiO$_2$(RHA-BGS)$^*$-TMPDT is not damaged.

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