Synthesis of Ionic Imprinted Membrane (IIM) Based on Sulfonated Polyeugenol for Selective Transport of Gold (III) Metal Ions from Motherboard Waste

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Abstract

Ionic imprinted membrane (IIM) was successfully synthesized using sulfonated polyeugenol, a derivative of eugenol as a functional polymer, with PVA as a base membrane and PEGDE as a crosslinker. IIM Au(III) is a membrane with an Au(III) ion template. This study aimed to determine the pH effect of a feed phase for selective transport of IIM Au(III), comparing it with a non-imprinted membrane (NIM) against Au+ metal ions from motherboard waste. It also aimed to compare the membrane selectivity of Au+ metal ions to Cu2+ metal ions, which are also found in motherboard waste. Gold samples were prepared using H(AuCl4) standard and leaching solutions from motherboard waste. The leaching of the motherboard used aqua regia and the assistance of a microwave to accelerate the leaching process. The optimum transport of Au+ metal ions was when using IIM Au(III) at pH 3. This proved that the presence of a template affected IIM Au(III) to recognize Au(III) ions. IIM Au(III) showed higher selectivity than NIM, as evidenced by the percentage in the receiving phase of the Au+ metal ions, which was more significant than the Cu2+ metal ions from the motherboard leaching solution.

1. Introduction

Gold is a precious metal that can be applied in various fields, one of which is electronics. Gold is used as a coating for electronic goods because it has a very high electrical conductivity [1] and excellent corrosive resistance [2]. Electronic waste can be used as an alternative source of gold, such as motherboards with a gold content of around 80–100 ppm [3]. The costs and environmental impact appear from efforts to recover gold metal from electronic waste due to its complex composition. The chemicals that lead to environmental issues, such as cyanide and mercury, are still used in the amalgamation process [4].

The technique most frequently used to separate gold is leaching using cyanide solution. Cyanide is a leaching agent due to its high efficiency and cost-effectiveness, but it is highly toxic [5]. The gold separation technique requires an environmentally friendly and more affordable method. One method that meets these requirements is molecular imprinting. This method can result in a polymer with cavities due to the removal of the template, with the cavity serving to recognize molecules with the same size, structure, and physicochemical properties [6]. Molecular imprinting has been used in many fields, such as solid-phase extraction, membrane separation, and sensors [7].

The previous research conducted a synthesis of the ionic imprinted membrane (IIM) using polyeugenoxacytethyl thiophene methanol (PEATM) as the functional polymer, which showed that IIM PEATM was more...
selective than NIM towards Au(III) metal ions [8]. IIM was also synthesized using sulfonated polyethylene glycol (SPE) as a functional polymer and polysulfone as a membrane base for the selective separation of Au(III) metal ions. Another study revealed that the addition of SO₄⁻ during the sulfonation process gave excellent results because it was very suitable for the metal ion Au(III). This occurred based on the HSAB (Hard Soft Acid Base) theory, as evidenced by the membrane selectivity to a mixed solution of binary metal ions and the presence of imprinted ions in the IIM, causing the membrane to be more selective towards Au(III) [9].

In this study, synthesized IIM was applied as a selective transport membrane for Au⁺ metal ions from the leaching solution of the motherboard. Furthermore, when the feed phase was a leaching solution with a pH of 1.3 and 5, the influence of the pH of the feed phase would be examined. In addition, the selectivity of IIM Au(III) when transporting Au⁺ metal ions was compared with Cu²⁺ metal ions from the results of the leaching solution. IIM can be synthesized using sulfonated polyethylene glycol as a polymer and PVA (polyvinyl alcohol) in 1-Methyl-2-pyrrolidone (NMP) solvent as a membrane base. The synthesized IIM Au(III) transport performance was compared to that of the Non-Imprinting Membrane (NIM). This study will explain the function of IIM as a method for the recovery of Au(III) metal ions from motherboard waste.

2. Materials and Methods

2.1. Materials

Eugenol, polyvinyl alcohol, polyethylene glycol diglycidyl ether (Mv 500 g/mol), NMP (Sigma Aldrich), NaOH, KCl, HAuCl₄, chloroform. All those chemicals were analytical grade. BF₃-diethyl ether, anhydrous Na₂SO₄, methanol, H₂SO₄, HNO₃, HCl, and thiourea were purchased from Merck (Jakarta, Indonesia). The motherboard was purchased from e-commerce. Double-distilled water (ddH₂O) was purchased from Bratachem (Semarang, Indonesia).

2.2. Polymerization of eugenol

In a three-necked flask, 5.8 g of eugenol was polymerized using BF₃-diethyl ether as a catalyst under stirring for 16 hours. The polymerization then ended by adding methanol. The result was dissolved with chloroform and neutralized by adding water. Afterward, anhydrous Na₂SO₄ was used to remove the water and then filtered. Chloroform was evaporated at room temperature. Polyethylene glycol was crushed, weighed, and then analyzed by FTIR.

2.3. Synthesis of sulfonated polyethylene glycol

Sulfonated polyethylene glycol (SPE) was synthesized by adding 0.5 g polyethylene glycol to 7.5 mL H₂SO₄ (99%) and 0.05 g PbSO₄, then heated under reflux condition for 15 minutes. The mixture was allowed to cool to room temperature. After that, 50 mL of H₂SO₄ 2 M (cold) was added to the mixture, then filtered and neutralized with distilled water. The resulting polymer was characterized by FTIR.

2.4. Synthesis of IIM Au(III) and NIM

IIM Au(III) and NIM were synthesized using the in-situ method by mixing 0.25 g SPE-Au(III) (for IIM Au(III) synthesis) and 0.25 g SPE (for NIM synthesis), 0.5 g PVA, 0.25 mL of NaOH 0.1 M, 0.3 mL PEGDE, and 2.5 mL NMP. The mixture was refluxed for 30 minutes at 110–130°C until a hydrogel formed. Once cooled, 1.75 g gel was mixed with 3 mL NMP, then refluxed for 30 minutes at 110–130°C. After homogenization, the mixture was poured into a mold and dried at 110°C in the oven. A 2 M KCl was poured into the membrane mold until the membrane was submerged and allowed to stand until it could be removed from the mold. The membrane was washed using distilled water to remove excess KCl and dried at room temperature afterward. The membrane was washed using a solution of 0.8 M thiourea in 0.1 M HCl for two days. The membranes were characterized by FTIR and SEM-EDX (JEOL Ltd., Tokyo, Japan).

2.5. Transport time optimization

The HAuCl₄ standard solution was used as the feed phase solution, while the receiving phase solution used was 0.8 M thiourea in 0.1 M HCl. Transport was conducted at pH 3 for 48 hours by taking the feed phase filtrate and receiving phase filtrate every 8 hours. The filtrate was analyzed using AAS to determine the Au⁺ concentration transported by the membrane.

2.6. Microwave-assisted leaching gold from motherboard waste

The yellowish pins of the motherboard were dissolved using aqua regia made by combining HCl and HNO₃ (3:1 v/v) solution, inserted into a hydrothermal tube, and heated using microwaves for different times (0, 5, 10, and 15 seconds). The leaching solution was then analyzed using AAS to determine the metal content of Au obtained.

2.7. Application of IIM Au(III) and NIM for Au⁺ transport from motherboard waste

The leaching solution with optimum yield was conditioned at pH 1.3 and 5, which were used as the transport feed phase for IIM Au(III) and NIM chronologically. The transport receiving phase was 0.8 M thiourea in 0.1 M HCl. The receiving phase filtrate was taken every 8 hours for 40 hours. The membrane selectivity can be determined by comparing the Au⁺ metal ions with the Cu²⁺ metal ions transported from the leaching solution. The receiving phase was measured.
using AAS to determine the concentration of transported metal ions.

3. Results and Discussion

3.1. Eugenol polymerization

Polyeugenol was made using BF$_3$-diethylether as a catalyst and 5.8 g of eugenol. The polymerization process was performed for 16 hours and stopped using methanol. The polymerization process begins with the initiation stage due to the presence of an initiator, BF$_3$-diethylether, which will add to the double bond to form a carbocation. The initiator can work effectively with vinyl monomers having an electron-donating group from a stable carbocation intermediate [10]. The second stage is propagation, forming bonds between eugenol monomers and carbocations. Lastly, the termination stage ends the polymerization process by removing protons, which was accomplished using methanol to add the nucleophilic side to the propagation side. Methanol also provides a methoxy group at the end of the polymer chain, allowing for polymerization at room temperature. Polyeugenol in a gel was dissolved using chloroform and washed using ddH$_2$O until neutral. The remaining ddH$_2$O in the polyeugenol was removed using anhydrous Na$_2$SO$_4$, and the polyeugenol was then left at room temperature for solvent evaporation. The resulting polyeugenol was a pink powder of 5.3 g (89.65%) with a 6578.32 g/mol molecular weight. Eugenol and polyeugenol that have been synthesized were analyzed using FTIR, and its result can be seen in Figure 1.

The absorption bands at 995 cm$^{-1}$ and 910 cm$^{-1}$ indicate a vinyl group owned by eugenol but not owned by polyeugenol because the vinyl group has undergone an addition reaction during the polymerization process. The absorption at 817 cm$^{-1}$ indicates the presence of ortho-substituted aromatic compounds, which are methoxy groups, and 753.61 cm$^{-1}$ indicates the presence of CH$_2$=CH-CH$_2-$ groups, thus strengthening the presence of aromatic compounds in polyeugenol and eugenol [9].

3.2. Sulfonated polyeugenol synthesis

SPE was made using concentrated H$_2$SO$_4$ and 0.5 g of polyeugenol, producing SPE in a black powder of 0.4 grams (80%) with a molecular weight of 8385.4 g/mol. Sulfonated polyeugenol will have a $-$SO$_3$H group, thereby increasing the selectivity of the polymer against Au(III) based on the HSAB (Hard Soft Acid Base) theory. The synthesized sulfonated polyeugenol was analyzed using FTIR, as shown in Figure 2.

Figure 2 reveals the presence of a novel group $-$SO$_3$H on sulfonated polyeugenol, which was not present in polyeugenol. In sulfonated polyeugenol, the $-$SO$_3$H group exhibits absorptions at 1036.01 cm$^{-1}$ and 1209.06 cm$^{-1}$, indicating a vibration from the S=O range, while wavenumber 626.75 cm$^{-1}$ suggests an absorption from the C-S group. The results show minor differences from previous studies, the absorption of the C-S group is depicted at 632.75 cm$^{-1}$, the absorption band at 1213.59 cm$^{-1}$, and 1036.41 cm$^{-1}$ is a vibration of S=O from $-$SO$_3$H [9].

![Figure 2. FTIR graphs of polyeugenol and sulfonated polyeugenol](image)

3.3. Synthesis of IIM Au(III) and NIM

IIM Au(III) and NIM synthesis used the in-situ technique. The template ion-bound functional polymer was refluxed with the base membrane, crosslinker, and solvent until thickened and chilled to form a gel [11]. The membrane that has been successfully synthesized has a black color with an average thickness of 0.185 mm (NIM) and 0.187 mm (IIM Au(III)).
from RRUFF with ID number R070279, proving that SPE chemical stability, hydrophilic, non-toxic, and similar to the standard Au(o) diffractogram obtained to synthesize IIM Au(III), while SPE was used for NIM. The electron boosters. Therefore, the bond between agent and a plasticizer that increases the membrane mechanical strength [8].

The results of SPE-Au can be proven using the XRD analysis of Figure 3. The contact between Au(III) has a concentration of 300 ppm. Polyethylene sulfonate can occur because the –SO3H acts as an electron-withdrawing group, compared to the –OH and –OCH3 groups, which are electron boosters. Therefore, the bond between O in the –SO3H group is easier to interact with Au(III) [9]. Several new peaks of ztheta 38.26, 44.46, 64.52, and 77.78 appeared in the SPE-Au diffractogram. These peaks are similar to the standard Au(o) diffractogram obtained from RRUFF with ID number R070279, proving that SPE has successfully contacted Au(III).

The data acquired from the FTIR proved the success of the IIM Au(III) dan NIM synthesis process, as shown in Figure 4. According to Figure 4, the OH group absorption band is broadening on NIM and IIM Au(III). Based on the estimated structure (Figure 5), −OH plays a role in cross-linking by PEGDE during the formation of NIM and IIM Au(III). The wavenumbers in the S=O absorption region at SPE, SPE-Au, NIM, and IIM Au(III) are 1207.18 cm⁻¹, 1209.95 cm⁻¹, 1320.99 cm⁻¹, and 1328.24 cm⁻¹ respectively. The wavenumbers of NIM and IIM Au(III) in the S=O absorption region experience a shift that is assumed to be caused by the interaction of SPE cross-links with PEGDE. The presence of cross-links causes the S=O group to require significant energy to experience vibrations. According to the Planck constant, energy is inversely proportional to the wavelength, while the wavenumber is proportional to the energy. Therefore increasing the energy leads to an increase in wavenumber [13].

SEM–EDX results (Figure 6) revealed a broad percentage difference between NIM and IIM Au(III). IIM Au(III) had a more significant percentage of the area than NIM, indicating the influence of template ions in the synthesis process of IIM Au(III) (Table 1). Therefore, a larger area was obtained, and the ability to detect Au(III) ions was improved over NIM. The difference between NIM and IIM Au(III) was also identified from the elemental composition of C, O, and S, as shown in Table 2.

PVA was used as a base membrane because of its chemical stability, hydrophilic, non-toxic, and biodegradable [12]. The PEGDE has a role as a cross peanut agent and a plasticizer that increases the membrane’s mechanical strength [8].

### Table 2. EDX results of NIM and IIM Au(III)

| Element | NIM (%) | IIM Au(III) (%) |
|---------|---------|-----------------|
| C       | 62.35   | 59.75           |
| O       | 35.7    | 36.87           |
| S       | 0.76    | 2.60            |

The obtained SEM–EDX images were further analyzed using the ImageJ software. The difference in the percentage area results indicated the influence of the template ion in the synthesis process of IIM Au(III). Therefore, a larger area was obtained, and the ability to detect Au(III) ions was improved over NIM.
3.4. Transport time optimization

The optimization of transport time results can be seen in Figure 7. The optimum transport time was reached at 40 hours, as evidenced by the receiving phase transport percentage and the remaining feed phase transport percentage being at one point (overlapping). The percentage of Au{}^{3+} metal ion transport increases when measured against the value of the receiving phase but decreases when measured against the value of the feed phase. This indicates that the concentration of transported Au{}^{3+} metal ions increases with increased transport time. The IIM reveals that Au{}^{3+} metal ion transport is more rapid than NIM, as seen by the gap between the residual percentage of feed phase transport and the denser percentage of receiving phase transport at each time variation. This demonstrates that imprinted-Au{}^{3+} metal ions in IIM Au(III) promote more efficient Au{}^{3+} metal ion transport.
with the standard at 2theta 31.73, 45.46, 56.47, 66.25, 75.28, and 83.99. The standard diffractogram was NaCl obtained from RRUFF with ID number R070292. The white precipitate can be identified as NaCl salt based on the resemblance of the peaks. Because the pH of the solution was very acidic, excess NaOH caused the formation of NaCl salt. The following reactions may occur.

\[ \text{HCl}_\text{(aq)} + \text{NaOH} \rightarrow \text{NaCl}_\text{(s)} + \text{H}_2\text{O} \]

Figure 8. XRD analysis of NaCl salt

According to Figure 9, the optimum condition of Au\(^{3+}\) transport was formed by the IIM Au(III) membrane at pH 3. The concentration transported in the receiving phase was the highest, 58.68%, within 40 hours. The transport performance of the IIM Au(III) membrane was more excellent than NIM, indicating that the template influences IIM's ability to detect Au\(^{3+}\) ions. The pH conditions also affected the transport performance.

Figure 9. Percentage of ion Au\(^{3+}\) transport with variation pH

In the presence of competitor metal ions in the leaching solution, selectivity comparisons of IIM Au(III) and NIM membranes for transporting Au\(^{3+}\) metal ions were performed. According to the HSAB hypothesis, none of the metals on the motherboard have the same characteristics as the metal ion Au(III); hence the selectivity is compared to the most abundant metal on the motherboard. Cu\(^{2+}\) was chosen as a comparative metal ion.
since it had the greatest concentration in the waste motherboard.

Figure 10. Comparison graph of IIM and NIM selectivity

Figure 10 shows that IIM Au(III) has a higher selectivity than NIM at pH 1, 3, and 5, with the highest selectivity at pH 3. This indicates that the IIM Au(III) membrane transports Au$^{3+}$ metal ions more efficiently than Cu$^{2+}$ metal ions. It also proves that the presence of an Au$^{2+}$ template on the IIM Au(III) membrane allows the membrane to detect Au$^{3+}$ metal ions rather than Cu$^{2+}$ metal ions. Meanwhile, the selectivity of the NIM membrane, which does not contain an Au$^{2+}$ metal ion template, is lower because the NIM membrane is unable to detect Au$^{3+}$ metal ions efficiently.

The selectivity of IIM Au(III) and NIM is similarly affected by pH, with pH 3 being the optimal condition for transporting Au$^{3+}$ metal ions and IIM Au(III) at pH 3 having the most excellent selectivity value. In addition, according to the HSAB theory, the Cu$^{2+}$ metal ion is an intermediate acid, and the Au$^{2+}$ metal ion is a soft acid, as it is known that soft acids tend to form bonds easily with sulfur or nitrogen-containing groups [13]. The -SO$_4$H group in sulfonated polyeugenol allows the membrane to be more selective for metal ions Au$^{3+}$ than for Cu$^{2+}$.

4. Conclusion

Polegenol with a molecular weight of 6578.32 g/mol was successfully synthesized, whereas sulfonated polyeugenol had an 8358.4 g/mol molecular weight. The synthesized membranes had an average thickness of 0.185 mm (NIM) and 0.187 mm (IIM Au(III)). This study proves that the presence of SO$_4$H groups caused by polyeugenol sulfonation leads NIM and IIM Au(III) to be more selective for Au$^{3+}$ following the HSAB theory. IIM Au(III) has a higher selectivity for Au$^{3+}$ ions than NIM due to the presence of template ions in the synthesis process. The most effective condition for Au$^{3+}$ metal transport was at pH 3, and the most optimum transport time was 40 hours.

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