Synthesis of polysulfone and nitrated polyeugenol based flat imprinted membrane for selective adsorption of gold

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Abstract. Gold (Au) is the most valuable metal compared to the other metals contained in electronic waste and adsorption is a promising method for its recovery. In this research, a flat ionic imprinted membrane (IIM) was synthesized utilizing polysulfone and nitrated polyeugenol (NPE) for the adsorption of Au. Nitration of polyeugenol was synthesized by dissolving polyeugenol in chloroform and adding it into a mixture of HNO3 and H2SO4. The evidence of a successful nitration process was marked by the appearance of NO2 spectra in the wavenumber area of 1533 cm⁻¹ and 1302 cm⁻¹. The resulted NPE was then contacted with Au and analyzed by XRD. IIM synthesis was done by using polysulfone as its base, NPE-Au as its functional polymer, and polyethylene glycol (PEG) as its crosslinker. Au was then released from the membrane by immersing the membrane in thiourea solution. The membrane was characterized by SEM-EDX to examine the surface morphology. It was then used as a selective adsorbent towards Au and the adsorption results were analyzed by AAS. The results showed that the IIM is more selective towards Au compared to the non-imprinted membrane (NIM) in a selectivity test towards Cd and Cu but not in Fe.

1. Introduction
Eugenol is a natural ingredient, commonly found in Indonesia that has been used for the separation of metal ions. Eugenol is also used as a starting material for the synthesis of a compound because of the presence of three functional groups attached to it. Through polymerization, the allyl group double bond in eugenol will undergo an addition reaction causing its reactivity to decrease, and the hydroxyl group will become easier to be modified [1]. The hydroxyl functional group in eugenol is reactive so it can be modified through an esterification process to produce a new compound that is more selective in an adsorption or permeation process. Eugenol ester derivatives have been made using the eugenol monomer, including the allyl-ether derivative eugenol, polyester, and eugenol methacrylate [3]. Eugenol is inexpensive and abundant, making it suitable to be used in many industries such as in the food industry, medicine, and even dentistry industries [4]. Electronic waste is a new problem in the era of globalization. Electronic waste consists of a metal : plastic : oxide ratio of 40 : 30 : 30, and Au is one of the elements contained in electronic waste among other metals [5]. Gold (Au) has the highest economic value when compared to other metals. When compared with the concentration of gold in the ore, the gold concentration in electronic waste is relatively higher at 200 grams per ton of electronic waste [6]. One of the superior characteristics of gold is that it is malleable so that it can be...
used in various ornaments, jewelry, electronic products, and also as a catalyst [7]. For that, we need a method to separate the Au from the waste. The adsorption method is an efficient method for gold recovery from electronic waste, and biosorbent-based adsorbents are an environmentally friendly choice [8]. So, this method needs to be developed for an optimum Au recovery from electronic waste. One of the environmentally friendly methods that are reported to be used for the recovery of gold metal from electronic waste is using a simple static adsorption method or permeation with an ionic imprinted membrane (IIM) which is a membrane made by imprinting template molecules (Au metal ions) that makes the membrane more selective towards the target molecule (Au metal ions) in a solution [9]. To produce ionic imprinted polymers, three important elements are needed, such as the target ion (template), a functional monomer, and a cross-linking agent (cross-linker) [10].

2. Methods

2.1. Materials
Eugenol p.a (Sigma Aldrich), BF$_3$-diethyl ether (Sigma Aldrich), methanol, anhydrous Na$_2$SO$_4$ (Merck), 0.1 M HCl (Merck), H$_2$SO$_4$ (Merck), HNO$_3$ (Merck), chloroform p.a (Merck), AIBN (2,2’, Azobis(2-methylpropionitrile)) (Sigma Aldrich), aquabidest, 1000 ppm Au solution, NMP (1-Methyl-2-pyrrolidone) (Merck), polyethylene glycol (Sigma Aldrich), thiourea (Merck), along with metals ions in the form of Cd(NO$_3$)$_2$, Cu(NO$_3$)$_2$, and Fe(NO$_3$)$_2$ (Merck).

2.2. Instruments
The tools used are laboratory glass equipment, analytical balance (pioneer), hotplate stirrer (LabTech Co. Ltd.), pH meter (Trans Instrument), reflux equipment, shaker (Tungtec Instruments TS-330A), AAS (Perkin Elmer Analyst 400), FTIR (Shimadzu Prestige 21), SEM-EDX (Jeol JSM 6510 La), and XRD (Shimadzu 7000).

2.3. Synthesis of polyeugenol (PE)
In a three-necked flask, 5.8 g of eugenol is added with 0.25 mL of BF$_3$-diethyl ether every one hour for four hours while being stirred continuously. The polymerization reaction was done for 12-16 hours and 1 mL of methanol was then added to stop the polymerization. A gel was then formed and then dissolved with chloroform and washed with aquabidest until it reached a neutral pH. The solution was then dried from any water left in it by using anhydrous Na$_2$SO$_4$. While the solvent, chloroform, was evaporated at room temperature. The formed precipitate was weighed and analyzed with FTIR.

2.4. Synthesis of nitrated polyeugenol (NPE)
As much as 2 mL of HNO$_3$ and 1 mL of H$_2$SO$_4$ is mixed with a magnetic stirrer for 5 minutes. Into it, 3 g of polyeugenol dissolved in 50 mL of chloroform was added little by little and then stirred at room temperature for 2 hours. The solution was then washed with aquabidest until it reached a neutral pH and then filtered. The formed precipitate was weighed and analyzed by FTIR.

2.5. Nitrated polyeugenol (NPE) contact with Au
The synthesized nitrated polyeugenol was contacted with a standard Au solution from Merck in the form of H(AuCl$_4$) 1000 mg/L in 2 mol/L HCl to make a membrane printed with Au (template Au). Contacting is carried out by stirring 1 g of NPE and 20 mL of Au solution with a concentration of 500 ppm for 24 hours. It was then filtered and dried. Contacting was carried out at pH 3. The result was then characterized by AAS.

2.6. Synthesis of IIM (Ionic Imprinted Membrane) and NIM (Non-imprinted Membrane)
A total of 0.833 g of NPE was added with 4.17 g of polysulfone, 0.833 g of PEG as a crosslinking agent, and 12 mL of NMP in a two-neck flask then refluxed for 10 hours at the temperature of 90-110°C until
the mixture began to thicken. The heating variations used were 1 hour, 5 hours, and 10 hours. After that, the mixture was let stand at room temperature. After 24 hours, it will change into a gel shape. The mixture results of the synthesis were then cast on a glass surface and quickly immersed into water to form a membrane. The membrane was then washed with thiourea for 14 days to release the template. The membrane was then removed and then analyzed by SEM-EDX. NIM synthesis was done in the same way as the IIM but without the contact process between nitrated polyeugenol and Au(III).

2.7. Adsorption of Au(III) using IIM and NIM
IIM and NIM were used for adsorption of 25 ppm of Au(III) standard solution using a shaker. The solution condition was set to pH 3. Each IIM and NIM was put in the 250 mL Erlenmeyer tube with 25 mL of adsorbate. Using a shaker, the adsorption was carried out for 6 hours and sampling was done by taking 2 mL of the sample every 90 minutes. Then, AAS was used to determine the concentration of Au(III) metal adsorbed by the membrane. The adsorption of Au(III) on NIM was carried out in the same way as IIM but without contacting and releasing of Au(III) ions.

2.8. Selectivity test of IIM towards Au(III) in a binary metal mixture
The selectivity test used 25 mL of a mixture of 10 ppm Au/Cu, Au/Cd, Au/Fe with a pH of 3 which was then used as an adsorbate in the adsorption process. Each IIM was placed on the Erlenmeyer tube, then added with 25 mL of adsorbate. Next, the Erlenmeyer tube was placed in a 100 rpm shaker. Adsorption was carried out for 6 hours (360 minutes) and sampling was done by taking 2 mL of each adsorbate every 90 minutes. Then the sample was analyzed using AAS to determine the concentration of metals Au(III), Cu(III), Cd(II), and Fe(III) adsorbed by the membrane.

3. Result and Discussion

3.1. Synthesis of polyeugenol and nitrated polyeugenol
Eugenol was polymerized to synthesize polyeugenol with a yield of 96.4% in the form of a pink powder. Polyeugenol nitration produced nitrated polyeugenol in the form of a powder with a yield of 91%. The results of the molecular weight measurement of polyeugenol using ubbehlohde viscometer are 6081.51 g/mol and the molecular weight of the nitrated polyeugenol was 7394.65 g/mol. The FTIR spectra shows the synthesis of polyeugenol and nitrated polyeugenol is proven to be successful by the FTIR analysis results which showed that there was a disappearance of the vinyl group spectra at wavenumbers 995 cm⁻¹ and 910 cm⁻¹. This indicates that the C=C bond in the allyl group is broken and the polymerization process has occurred. Meanwhile, the results of the FTIR analysis of polyeugenol and nitrated polyeugenol showed that there was an addition of NO₂ group spectra at wavenumbers of 1533 cm⁻¹ and 1302 cm⁻¹. The nitration reaction is a reaction that adds a nitrate functional group into a molecule. The nitration reaction mechanism occurs through an electrophilic substitution reaction. The nitration reaction uses nitric acid as the source of nitronium ions and sulfuric acid as a catalyst. The function of sulfuric acid is to convert nitric acid into nitronium ion, NO₂, which is highly reactive and electrophilic [11].

3.2. NPE contacting with Au(III)
The contacting of NPE with Au(III) metal derived from the standard 1000 ppm AuCl₄ solution that aims to make a template of Au(III) metal ions mold on NPE which will be used as a functional polymer in the synthesis of ionic imprinted membranes (IIM). The pH condition of pH 3 was chosen for contacting because the Au(III) species in the form of [AuCl₄]⁻ is in the maximum distribution condition (distribution = 100%). In pH 3 conditions, the stability of the complex [AuCl₄]⁻ will likely be disturbed by the presence of hydroxyl ligands (-OH), aqua (H₂O), and other ligands that can interfere with the contacting process [12]. The filtrate was analyzed with XRD and the residue was analyzed with AAS. The concentrations of Au before and after contacting that have been analyzed using AAS. The result showed that 99.55% of Au was contacted with the nitrated polyeugenol.
Then, XRD analysis was performed to determine the form of crystallinity of the sample compounds and to determine whether the sample contains Au or not. The standard Au compound from RRUFF with the ID number of R070279 has several peaks on 2theta. All peaks present in the standard compound are present in the sample. This proves that the sample contains standard compounds which are the Au compounds and it is in the form of crystalline because it produces peaks from the diffractogram graph on XRD. When AuCl₄⁻ in pH 3 condition is reacted with polymer, Au(III) will be adsorbed on the surface of the nitrated polyeugenol through an electrostatic bond, Au(III) will gain three electrons for it to be reduced into Au(0) so, the standard spectra used was Au(0) [13].

3.3. IIM and NIM characterization by SEM-EDX

IIM is a membrane that owns molecular recognizing site by firstly introducing the template molecule (in this case Au) to the membrane, afterward, the template molecule was released, leaving cavities that able to recognize the template molecule in a solution, which is expected to make the membrane work more selectively during the adsorption process [14]. The NIM is a membrane that is not imprinted with target metal ions, NIM only contains carrier and plasticizer compounds. The purpose of IIM and NIM synthesis is to determine the difference in their adsorption performance. Synthesis of IIM and NIM is carried out in the same process, except that in NIM, there is no contact with Au(III) solution. Template molecule (in this case Au) will take role in changing the shape of the template in the membrane by causing the formation of functional group bonds [15]. The adsorption membrane is created by connecting functional polymer to the surface and pore walls of polymer membranes, the target pollutants are selectively absorbed into the functional polymer [16].

In the membrane synthesis process, polysulfone and the functional polymer will be crosslinked with PEG. Synthesis of IIM with heating variations of 1 hour, 5 hours, and 10 hours were analyze using SEM-EDX to determine the porous membrane morphology with the average pore size of IIM pores after template release for IIM-1 hour, IIM-5 hours, and IIM-10 hours were 0.809 µm, 0.714 µm, and 0.537 µm, respectively. The SEM images of IIM variations can be seen in figure 1. From these results, it can be concluded that the pore size of IIM-1 hour is greater than IIM-5 hours and IIM-10 hours.

![Figure 1](image1.png)

**Figure 1.** Surface morphology of (a) IIM-1 hour, (b) IIM-5 hours, and (c) IIM-10 hours

Figure 2 showed the NIM surface morphology with the average pore size of NIM-1 hour, NIM-5 hours, and NIM-10 hours are 1.459 µm, 1.167 µm, and 0.949 µm respectively.

![Figure 2](image2.png)

**Figure 2.** Surface morphology of (a) NIM-1 hour, (b) NIM-5 hours, and (c) NIM-10 hours

The pore size is notably smaller in the increase of heating duration, it is also supported by the FTIR results that showed an increase in C-O group intensity correlates with the lowering intensity of the O-H group. The FTIR result can be seen in figure 3.
3.4. Ionic imprinted membrane template release
Membrane washing was done to release the template molecule (Au) inside the membrane so that only a mold of Au(III) metal ions is formed in the membrane. Thiourea in acidic pH conditions was chosen as a washing solution according to the previous research which used thiourea solution in acidic conditions as a solution for gold washing [17]. It is used because thiourea is a desorption agent for Au(III) metal ions [18]. To determine whether the Au(III) metal ions had been released from IIM after washing, the thiourea solution that was used as a washing solution was analyzed using AAS. The results are 97.747%, 57.888% and 48.929% for IIM-1 hour, IIM-5 hours and IIM-10 hours respectively.

3.5. Membrane adsorption and selectivity towards Au
An adsorption test was done to determine the content of Au(III) metal ions that have been adsorbed by the membrane with heating variations of 1, 5 and 10 hours. In the adsorption process there is a solute called the adsorbate and the material providing the surface is called the adsorbent [19]. During the adsorption process, the condition was set to pH 3 because Au(III) metal ions have shown maximum adsorption results at that pH [20]. To determine the percentage of adsorption, AAS was used for analyzing the metal ion solutions before and after the adsorption process. The results for the average adsorption of IIM 1, 5 and 10 hours are 50.25%, 50.50% and 44% respectively. The best adsorption result was achieved with the IIM-5 hours.

The pore size of the IIM-5 hours is the most similar to the adsorbate, so it will be more likely to show the most optimum adsorption. The IIM-1 hour pore size is too big that the adsorbate will be easily adsorbed but also easily released again. While the IIM-10 hours’ pore was too small that it caused the adsorbate to only sit on the surface. The adsorbate could not enter the membrane and is more easily released that way. The average adsorption of Au using NIM results are 72, 74 and 90 % for NIM 1, 5 and 10 hours respectively. The results above showed that the increased duration of heating will optimize the adsorption percentage because PEG will be more strongly crosslinked. It is supported by the FTIR results that showed the C-O wavelength area of around 1000-1300 cm\(^{-1}\) showed a peak sharpening that indicates the increasing intensity. The smaller pore size also indicates the same thing, it is due to the crosslinking between O-H, resulting in the strengthening of the C-O group. Then, the membrane that has been successfully synthesized is tested for its selectivity in a binary metal ions mixture. AAS was used to determine Au, Cd, Cu, and Fe quantitatively based on the absorption of radiation with a certain wavelength by atoms in the free state of the element [21].

Separation using a membrane is possible because the membrane could selectively separate particles from the mixture due to the particle size that is larger than the pore size [22]. The mixture of metal ions used to determine IIM selectivity in this research are Au/Cd, Au/Cu, and Au/Fe. According to the HSAB theory, Cd metal ions are classified as soft acids, Cu metal ions are classified as borderline acids, and Fe metal ions are classified as hard acids [23]. The adsorbents selectivity for metal ions adsorption is influenced by the competition of the metal ions [24]. The results of IIM selectivity are Au/Cd 28.756;
Au/Cu 8.694; Au/Fe 3.804 while NIM selectivity of Au/Cd 17.012; Au/Cu 2.020; Au/Fe 9.850. It can be concluded that the membrane showed good selectivity towards Au in the adsorption of Au/Cd and Au/Cu binary metal mixture, while the membrane is not selective towards Au in a binary mixture of Au/Fe because the porosity of the membrane was too small [25].

4. Conclusion
Synthesis of polyeugenol has been successfully conducted with a yield of 96.4%, while the yield of nitrated polyeugenol is 91%. Ionic imprinted membrane (IIM) and non-imprinted membrane (NIM) have been successfully synthesized with a thickness of 0.05 – 0.07 mm. IIM adsorption selectivity on Au/Cd and Au/Cu is greater than NIM, but IIM adsorption selectivity on Au/Fe is lower than NIM.

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