Gold imprinted adsorption based on eugenol

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Abstract. Synthesis of Ionic Imprinted Polymer (IIP)-Au have been carried out using polyeugenoxy acetate (PA) as the base polymer. IIP is formed through the transfer of a basic polymer with a metal template which is then crosslinked with ethylene glycol dimethacrylate (EGDMA) and the release of the metal template using acid. Non Imprinted Polymers are also synthesized for use as a comparison. Polymerization of up to IIP and NIP was carried out using infrared spectrophotometers and SEM-EDX. IIP and NIP are used to determine the rate and capacity of adsorption through kinetics and adsorption isotherms studies. Adsorption selectivity tests were carried out on a mixed metal solution system Au(III)/Cd(II), Au(III)/Pb(II), and Au(III)/Fe(III). The amount of adsorbed metal ions is calculated based on the remaining metal ions in the solution measured using atomic absorption spectroscopy. The results of the adsorption of Au(III) metal ions in IIP and NIP followed the second-order pseudo and isotherm followed Langmuir. Adsorption capacity in IIP-PA is (28,305 mg/g), and NIP-PA adsorption capacity is (45,080 mg/g). IIP adsorption selectivity is greater than NIP in binary solutions in the order of Au(III)/Cd(II)> Au(III)/Pb(II)> Au(III)/Fe(III).

1. Introduction
Gold is a precious metal with high economic value. Very specific physical and chemical properties cause this gold metal is widely used in various fields. In addition to gold metal, jewelry is widely used in various fields. In addition to jewelry and investment, gold plays an increasingly important role in the world of industry. At present more than 300 tons of gold are used annually for electronic components such as ICs, contacts, and cables. After the end of its use, the electronic product has important potential to be recycled as the second gold supplier after gold ore. This makes the treatment of waste for gold metal more attractive than other metals. Also, taking gold from the water solution system also received very significant attention because of the high gold content in electronics and coatings. The content in electronic waste turns out to be greater than gold ore. For example, the gold content for cell phones is around 300-350 g / ton and the circuit board on a computer is 200-250 g / ton while the gold content in the ore is only around 5-30 g / ton. Various processes involving the use of gold can cause waste problems in the environment. One way to overcome the problem of waste is to recover gold metal from waste which also helps in providing gold raw materials. However, gold metal analysis and gold extraction from water solutions in sewage are not easy, because the concentration is very small, so it is necessary to develop better analysis methods, have a high sensitivity and selectivity and better separation and preconcentration technology. There are several methods for extracting gold (III) metal ions from aqueous solutions, including solvent extraction, ion exchange, and adsorption. The adsorption method is most suitable for the extraction of gold metal (III) ions in low concentrations due to low cost and high
efficiency [1]. One of the developments of the adsorption method is the adsorption method with high selectivity, namely IIP and IIM (Ionic Imprinted Membrane) because it involves the ion mold.

The mold ion selectivity is doubled by the IIP and IIM methods [2] developed the IIP and IIM Fe-based polyeugenol method with the result that the selective increase of Fe. The presence of OH-groups in polyeugenol facilitates this selectivity [3] inserting thiol groups (S-atoms) in silica to adsorb Au and Ag (Au and Ag are metals in the HSAB theory) [4] synthesize active group S polyeugenol to selectively transport Cd and Ag (Cd, Au, and Ag are a group of soft metals) [5-7] insert S atoms from different compounds to adsorb Au(III). By inserting S atoms in polyeugenol and with IIM / IIP selectivity Au is believed to be fully extracted.

2. Experimental

2.1. Synthesis of polieugenol

Polieugenol is synthesized from eugenol using a diethyl ether BF3 catalyst [8]. Polymer formation was analyzed using FTIR spectrophotometry.

2.2. Synthesis of polyeugenoxy acetate (PA)

Addition of acetate functional groups to polyeugenol using chloroacetic acid [9]. The results obtained were analyzed using FTIR.

2.3. Synthesis of IIP-PA

0.5 polyeugenoxy acetate (0.003 moles) was stirred with a certain concentration of Au(III) ions with a pH of 3 for 24 hours. Then the results were filtered with filter paper and dried with air to dry. Acetate (PA) -Au(III) polyeugenol produced 0.222 g crosslinked with 0.4 ml (5 mol) crosslinking agent EGDMA, mixed with 1.67 ml chloroform and added with 0.48 mL AIBN initiator. The mixture was refluxed. The precipitate was then dried. As much as 0.2 g of the resulting polymer precipitate was released by Au(III) ions which are bound to thiourea for 24 hours to produce IIP-PA resin.

2.4. Synthesis of NIP-PA

NIP-PA was synthesized in the same way as IIP-PA but without binding of Au(III) metal ions.

2.5. Material characterization

Characterization of IIP-PA and NIP-PA adsorbents was carried out using SEM-EDX.

2.6. Adsorption test

Adsorption test was carried out by batch method, at pH 3, 50 mg of IIP adsorbent and NIP of polyeugenoxy acetate (PA) 10 mg/L Au(III) solution of contact time variation (0-2160 minutes) was performed to determine the kinetics of adsorption. To determine the adsorption isotherm, adsorption study was carried out with concentrations of Au(III) metal ions from 50-20-10 mg / L. The mixture was filtered with fine filter paper and the concentration of Au(III) in the filtrate was analyzed using AAS.

2.7. Adsorption mechanism

To find out the type of interaction between Au(III) metal ions and adsorbents was carried out by elution using the desorption gradually Au(III) metal ions in a row using aquabidest, KNO3 (0.1 M), HCl (0.1 M) and Na2EDTA (0.1 M).

2.8. Adsorption selectivity test

The adsorption selectivity test was carried out by adding 50 mg of adsorbent to each of the 10 mL mixed metal solution consisting of a mixture of Au(III)/Cd(II), Au(III)/Pb(II), and Au(III)/Fe(III) with a concentration of 50 mg/L each ion. The adsorption test was carried out in a batch system using a magnetic stirrer at pH 3. This test was carried out on IIP-PA and NIP-PA as a comparison.
3. Results and discussion

3.1. Addition of function groups to polyeugenol

The eugenol polymerization process is a cationic addition polymerization process because the allyl group of eugenol undergoes an addition reaction. This addition reaction follows the Markovnikov law, where the stability of the carbonium ion determines reactivity for the subsequent monomers to occur.

Figure 1 displays a comparison of the FTIR spectra of eugenol and polyeugenol. Elimination of vinyl group spectra in wave numbers 995 cm\(^{-1}\), and 910 cm\(^{-1}\) sign of C=C bonding in the allyl group is interrupted and the polymerization process has taken place.

![Figure 1. Comparison of FTIR spectra eugenol, polieugenol and polieugenoxy acetate](image)

Polieugenoxy acetate (PA) is a polymer with an active group in the form of acid (COOH) which is expected to have a large affinity for various metal ions in the adsorption process. PA synthesis is carried out by adding NaOH solution and chloroacetic acid to the polyeugenol that has been produced. Polieugenol reacts with NaOH to form Na-polyeugenolate salt through its hydroxyl group. Protons in OH in polyeugenol will be easily released because their anions are stabilized by the resonance of the benzene ring Na-polyeugenolate that is formed reacted with chloroacetic acid to form PA compounds. FTIR Spectra at Figure 1 shows the appearance of carbonyl acid groups in the surrounding wave numbers 1739 cm\(^{-1}\) which indicates the occurrence of carboxylation reactions in polyeugenol which is
characterized by the formation of acetate groups [9]. PA compounds in the form of dark brown deposits with a yield of 91.09%.

3.2. Synthesis of IIP and NIP results
Formation of the template on polyeugenol was carried out by contacting Au(III) ions from H (AuCl) 4 50 ppm pH 3 solution for 24 hours which was then crosslinked using an EGDMA crosslinking agent. The cross-linking process is carried out to increase the adsorption capacity by increasing the number of active sites in polyeugenol, strengthening physical characteristics and stability to temperature, and decreasing solubility. Template Au(III) in PA-Au(III) -EGDMA that has been formed is released by acidification using a thiourea solution as in equation Error! Not a valid bookmark self-reference. [9]. Au(III) content in thiourea solution was then tested using an AAS spectrophotometer.

\[
\text{Au} + 2\text{CS(NH}_2\text{)}_2 \rightleftharpoons \text{Au(CS(NH}_2\text{)}_2)^{2+}
\]

Figure 2 shows the concentration of Au(III) in thiourea solution that has been contacted with PA-Au(III) -EGDMA on the first to fourth day. A decrease in Au(III) concentration in thiourea solution indicates the level of Au(III) template in PA-Au(III) -EGDMA decreases because it has been bound to thiourea solution until the template is completely released. The Au(III) free acetate polyeugenox is then dried after it is neutralized with aquabides and dried again, this stage ends the PA synthesis process into IIP.

![Figure 2. Data release of Au(III) template](image)

The process of NIP synthesis is the same as IIP without contacting Au(III) ions from H (AuCl) 4 solution. PA NIP is used as a comparison of the ability of adsorption selectivity with PA IIP.

3.3. Morphological characteristics of adsorbents
SEM results in Figure 3 show different morphological forms between IIP (a) and PA-Au-EGDMA (b). Cavities that have IIP change shape and size, this is estimated to result from the formation of a template where the adsorbent has adjusted the shape of the cavity to the target metal. [11] explain the change in shape as the role of the template where in this study it is Au(III) which causes the formation of functional group bonds in the polymer.

EDX results in

Table 1 for IIP and PA-Au-EGDMA shows the composition of elements C, O, and Au. The difference in the composition of elements in IIP and PA-Au-EGDMA explains the role of the Au(III) template already formed in the polymer used. Au metal not found in IIP shows the role of the Au(III) release step in PA-Au-EGDMA.
Figure 3 Form of surface morphology results of 8000x magnification a) IIP b) PA-Au-EGDMA

Table 1 Results of EDX IIPP and PA-Au-EGDMA compounds

| Atomic number | Element symbol | Element name | Concentration percentage | Certainty |
|---------------|----------------|--------------|--------------------------|-----------|
|               | IIP            | PA-Au-EGDMA  | IIP                      | PA-Au-EGDMA |
| 6             | C              | Carbon       | 73.4                     | 0.99       |
| 8             | O              | Oxygen       | 26.6                     | 0.98       |
| 26            | Au             | Gold         | -                        | 0.37       |

3.4. Au(III) metal ion adsorption capability

3.4.1. Adsorption kinetics. The adsorption of Au(III) metal ions (efficiency) increases rapidly because most of the active sites in the adsorbent have not been filled with Au(III) metal ions. Figure 4 shows the IIP-PA adsorption equilibrium is reached at 1440 minutes (24 hours of stirring) and NIP-PA is reached at 2160 minutes (36 hours of stirring) and the longer the adsorption that occurs tends to be constant, it is possible that under these conditions IIP-PA and NIP-PA have arrived at the saturation point. Under these conditions, the two samples were unable to absorb more Au(III) metal ions in water. A slight decrease in adsorbed ions occurs since a small portion of Au(III) metal ions that have been absorbed in the sample are released again due to stirring [12].

Adsorption kinetics is studied by modeling the data into first-order and second-order kinetics equations. The pseudo-first level kinetic equation is formulated as follows [13].

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

where \( q_e \) and \( q_t \) are the adsorption capacity (mg g\(^{-1}\)) at equilibrium and at time \( t \) (minute), and \( k \) is the apparent first-rate rate constant (L min\(^{-1}\)).
Figure 4 Adsorption of Au(III) metal ions with variations in adsorption time

Pseudo second level kinetic equations are formulated as follows [14]

\[ \frac{t}{qt} = \frac{1}{kq_e^2} + \frac{1}{qe} \]

Table 2 shows the adsorption kinetics parameters for Au(III) metal ions in IIP-PA and NIP-PA. All adsorbents give a very low correlation coefficient for log plots (qe-qt) vs t in pseudo order 1 equations while plots t / qt vs t provide very high correlations (> 0.96), it can be assumed that apart from being influenced by the adsorbent properties, also influenced by the nature of adsorbate (its metal ions) [12]. The rate constant value (k2) in NIP-PA is higher than the k2 value in IIP-PA. The greater the value of k2, the smaller the level of adsorption [15].

| Parameter                  | Adsorbent | IIP  | NIP  |
|---------------------------|-----------|------|------|
| Pseudo Orde 1 (log (qe-qt) vs t) | qe (mg/g) | 0.8653 | 0.7090 |
|                           | k1 (L/men) | 0.0002 | 0.0002 |
|                           | R²        | 0.0603 | 0.2376 |
| Pseudo Orde 2 (t/qt vs t)  | qe (mg/g) | 0.1218 | 0.1219 |
|                           | k2 (g/mg men) x 10⁻² | 1.4184 | 4.9182 |
|                           | R²        | 0.9699 | 0.9773 |

3.4.2. Adsorption isotherms. The adsorption isotherms describe concentrations that depend on the equilibrium distribution of metal ions between the solution and the solid phase [16]. The commonly used adsorption isotherm equation is the Langmuir and Freundlich equation. The Langmuir isotherm is adsorption that occurs in the homogeneous monolayer layer [17]. The Langmuir equation forms as follows [16]

\[ \frac{Ce}{qe} = \frac{1}{Qmb} + \frac{Ce}{Qm} \]
where \( C_e \) is the equilibrium concentration (mg L\(^{-1}\)), \( q_e \) the amount of adsorbate adsorbed at equilibrium (mg g\(^{-1}\)), \( Q_m \) adsorption capacity (mg g\(^{-1}\)), and \( b \) is the adsorption intensity or known as the Langmuir constant (L mg\(^{-1}\)).

The Freundlich equation assumes that adsorption occurs multi-layer on the surface of the adsorbent and adsorption increases with increasing concentration [18]. The shape of the Freundlich isotherm equation according to [19]

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \( K_f \) is the relative adsorption capacity or known as the Freundlich constant, and \( 1/n \) is the adsorption intensity.

Table 3 it can be seen that IIP and NIP have the same adsorption properties, namely following the Langmuir adsorption model. It shows that the adsorption occurs on the surface of the homogeneous monolayer as a whole with a large adsorption capacity in IIP-PA that is (28.305 mg / g), and the NIP-PA adsorption capacity is (45.080 mg / g). The IIP adsorption capacity is smaller than the NIP estimated due to the treatment of template formation so that the pore contained in the PA is adjusted to the target metal ion.

The adsorption energy of an adsorbate on the surface of the adsorbent can be formulated as follows:

\[
E = \Delta G^0 = -RT \ln K
\]

where \( \Delta G^0 \) is the change in Gibbs energy (J mol\(^{-1}\)), \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \( T \) the temperature (K), and \( K \) the adsorption equilibrium constant (L mol\(^{-1}\)).

The amount of energy released in physical adsorption is around -20 kJ / mol and the energy released in chemical adsorption ranges from -40 to -800 kJ / mol [17]. \( \Delta G^0 \) IIP and NIP have values of -25,634 kJ / mol and -28,502 kJ / mol respectively. This shows that the adsorption of Au(III) metal ions in IIP and NIP is a combination of physical and chemical adsorption, this also shows that the molding process increases the interaction strength between Au(III) metal ions with adsorbents [20]

| Parameter         | Adsorbent | IIP     | NIP     |
|-------------------|-----------|---------|---------|
| Isoterm Langmuir  | \( Q_m \) (mg/g) | 28.305  | 45.080  |
|                   | \( b \) (L/mg)  | 0.158   | 0.503   |
|                   | \( B \) (L/mol) \times 10^2 | 31.141  | 99.093  |
|                   | \( R^2 \)     | 0.962   | 0.981   |
| Isoterm Freundlich| \( n \)     | 1.087   | 1.307   |
|                   | \( K_f \)     | 2.966   | 2.766   |
|                   | \( R^2 \)     | 0.928   | 2.766   |
| \( \Delta G \) (kJ/mol) |       | -25.634 | -28.502 |

3.5. Au(III) metal ion adsorption selectivity in binary metal ion mixes

Determination of adsorption selectivity is done by adding 50 mg of adsorbent to 10 mL of solution containing metal pairs Au(III) / Cd(II), Au(III) / Pb(II), and Au(III) / Fe (III) respectively each ion concentration of 50 mg / L. Adsorption is carried out in a batch system at pH 3 for 24 hours.

The coefficient of selectivity (\( \alpha \)) is determined using the equation [21], a selectivity coefficient, \( M_c \) is a competing metal ion:
The selectivity of adsorbents for metal ions is influenced by one of them the competition of metal ions [22]. Data on the comparison of selectivity values between IIP and NIP against each of the different metal ions are shown in Table 4.

| Selectivity       | IIP PA | NIP PA |
|-------------------|--------|--------|
| Au(III)/Cd(II)    | ~      | 10.193 |
| Au(III)/Pb(II)    | 6.046  | 3.578  |
| Au(III)/Fe(III)   | 1.348  | 1.127  |

The highest selectivity of Au(III) metal ion adsorption is Au(III)/Cd(II), indicating that the adsorbent formed has characteristics that match the metal ion template used during the printing process [23], so that the adsorbent is only suitable for metal Au(III) ions even though the metal ion Cd(II) has the size of the ionic radius which is almost the same as the radius of the Au(III) metal ion which is 109 pm for Cd(II) and 99 pm for Au(III), but the mold factor of the adsorbent is very selective against the metal ion Au(III).

4. Conclusion
The formation of polyeugenoxo acetate compounds is proven by changes in the FTIR spectra by the carboxylation reaction of polyeugenol. IIP and NIP compounds are shown by differences in surface morphology and adsorption results. The adsorption of Au(III) metal ions in IIP and NIP follows pseudo-order 2 and the isotherm both follow Langmuir. The adsorption capacity of IIP-PA is (28,305 mg / g), and the adsorption capacity of NIP-PA is (45,080 mg/g). IIP adsorption selectivity is greater than NIP in binary solutions in the order Au(III)/Cd(II) > Au(III)/Pb(II) > Au(III)/Fe(III).

References
[1] Hastuti S 2017 Sintesis Silika Termodifikasi L-Arginin Secara Sol-Gel Untuk Sorpsi Au(III) Universitas Sebelas Maret
[2] Djunaidi M C, Jumina, Siswanta D, Ulbricht M 2015 AIP Conference Proceedings 060001
[3] Indriyanti N, Manuhutu J, Shunitz T 2013 Malaysian Journal of Analytical Sciences 17 (2) 244-54
[4] Djunaidi M C, Khabibi K, Trisna D 2010 Jurnal Kimia Sains dan Aplikasi 13(1) 12-7
[5] Prado A G, Sales J A, Carvalho R M, Rubim J C, Airoldi C 2004 Journal of Non-Crystalline Solids 333(1) 61-7
[6] Donia A M, Atia A A, Elwakeel K Z 2007 Hydrometallurgy 87(3-4) 197-206
[7] Bozkurt S S, Merdivan M 2009 Environmental monitoring and assessment 158(1-4) 15
[8] Djunaidi M C, Jumina J, Siswanta D, Ulbricht M 2015 Indones J Chem 15(3) 305-14.
[9] Djunaidi M C, Ulumudin I 2017 IOP Conference Series: Materials Science and Engineering 012032
[10] Groenewald T 1977 Journal of the Southern African Institute of Mining and Metallurgy 77(11) 217-23
[11] Rao T P, Daniel S, Gladis J M 2004 Trends in Analytical Chemistry 23(1) 28-35
[12] Nafsiyah N, Shofiyani A, Syahbanu I 2017 Jurnal Kimia Khatulistiwa 6(1)
[13] Ho Y, McKay G 1998 Process safety and environmental protection 76(4) 332-40
[14] Ho Y S 2006 Journal of hazardous materials 136(3) 681-9
[15] Fan H T, Sun T 2012 Korean Journal of Chemical Engineering 29(6) 798-803
[16] Filipović-Kovačević Ž, Sipos L, Briški F 2000 Food Technology and Biotechnology 38(3) 211-6
[17] Foo K Y, Hameed B H 2010 Chemical engineering journal 156(1) 2-10
[18] Namasivayam C, Radhika R, Suba S 2001 Waste management 21(4) 381-7
[19] Panneerselvam P, Bala V S S, Thiruvengadaravi K, Nandagopal J, Palanichamy M, Sivanesan S 2009 Indian Journal of Science and Technology 2(2) 63-6
[20] Djunaidi M C 2016 Adsorpsi dan Transpor Selektif Fe(III) dan Fenol Menggunakan Polieugenol sebagai Polimer Tercetak Ion dan Molekul Universitas Gadjah Mada
[21] Liu H, Kong D, Sun W, Li Q, Zhou Z, Ren Z 2016 Chemical Engineering Journal 303 348-58
[22] Shofiyani A, Narsoito N, Santosa S J, Noegrohati S, Zahara T A, Sayekti E 2015 Indonesian Journal of Chemistry 15(2) 163-71
[23] Ningrum I P, Shofiyani A, Zaharrah T A 2017 Jurnal Kimia Khatulistiwa 6(4)