Adsorption of Gold(III), Copper(II), Nickel(II) on Amino Silica Hybrid Coated Magnetite

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Abstract. Selective adsorption of Au(III) in multimetal systems Au³⁺/Cu²⁺/Ni²⁺ on Amino-Silica Hybrid coated Magnetite (ASHM) has been studied. ASHM was synthesized via a sol-gel process using magnetite that was obtained through coprecipitation of Fe²⁺/Fe³⁺ salts mixture with NH₄OH as precipitating solution, sodium silicate solution of rice husk ash as a precursor and 3-aminopropyltrimethoxysilane (APTMS) as a source of amino. Adsorption kinetics was determined by pseudo-first-order and pseudo-second-order model, while the adsorption isotherm was analyzed studied by the Langmuir and Freundlich models. FTIR characterizations showed that ASHM has been successfully synthesized, indicated by the appearance of characteristic frequency at 570 cm⁻¹ was stretching vibrations of Fe-O-Si, and the frequency at 3424 cm⁻¹ was stretching vibrations of N-H. Adsorption kinetics studies showed that the adsorption of Au(III) on ASHM fit to pseudo-second-order model with adsorption rate constant was 1.21x10⁻³ g.mg⁻¹.min⁻¹. ASHM adsorbent showed a linear plot of the Langmuir isotherm model with the adsorption capacity of Au(III) was 102.04 mg/g. Adsorption on multimetal showed that Au(III), Cu(II), Ni(II) were adsorbed with chemical interaction on the ASHM with capacity adsorption of Au(III) was higher than that of Cu(II) and Ni(II). ASHM has high enough selectivity for Au(III) toward Cu(II) and Ni(II) ions.

1. Introduction
Areas of gold exploration in the world are found in Africa, South America, Asia, including Indonesia. For Indonesia itself, the potential for gold deposits is found in almost every region, such as in Sumatra, Kalimantan, Java, Sulawesi, Nusa Tenggara, Maluku, and Papua [1]. The relative abundance of gold in the earth's crust is estimated at 0.004 g/ton, including around 0.001 g/ton in marine waters [2].

Gold is mined or explored openly or closed mines in the depths of the earth. Gold in nature has never been found as a single material, but the presence of other metals always follows its existence. So that developing many gold isolation or extraction techniques such as the cyanide method [3] and the amalgamation method using mercury [4], have been used.

However, the isolation process produces dangerous substances, namely mercury (from the amalgamation process) and cyanide (from the cyanidation process). Therefore, both methods are not environmentally friendly. So we need another method that is more environmentally friendly. Another alternative method is the adsorption method. This method is inexpensive, easy to operate, simple, and has a large capacity [5]. Adsorption technique has advantages compared to other techniques, including
low cost and no side effects of toxic substances. Many materials can be used as adsorbents, including zeolite, silica, clay, bentonite, activated carbon, magnetite, and so on [6].

One of the adsorbents which have been developed is magnetite. Almost all of the above applications require magnetic particles to be chemically stable, not readily oxidized, and do not form aggregates. To overcome this, the magnetite particles must be coated or protected by other inert compounds [7]. One of the upholstery that can be considered is silica.

Silica particles can be used because they have silanol groups which can be activated by various functional groups, with a large surface area. Besides silica that coats the surface of magnetite can protect magnetite from leaching under acidic conditions. The negatively charged silica layer causes an increase in coulomb repulsion and magnetite dipole interactions coated so that the magnetite is stable [8].

Silica gel has a functional group of silanol (Si-OH) and siloxane (Si-O-Si) so that it can adsorb hard metal ions. To be more efficient, silica gel has been modified with various types of functional groups such as amines [9], thiols [10], and sulfonates [11] for the adsorption of various types of metal ions. The amino group was selected in this study so that the magnetite material was coated with a hybrid silica amino (ASHM).

In gold concentrates, the content of some by-products such as Cu and Ni can cause the ability of ASHM adsorbents to decrease and reduce the level of purity of the separated gold. For this reason, this paper reports the simultaneous adsorption study of a mixture of Au(III), Cu(II) and Ni(II) on ASHM adsorbents. The adsorption thermodynamics approximated by the Langmuir and Freundlich models for the determination of the capacity and the adsorption constant were evaluated and tested the selectivity of the ASHM.

2. Materials and Methods

2.1 Research Materials

Silica sourced from rice husk destruction (Na$_2$SiO$_3$ solution). Manufacture of magnetite silica using FeCl$_3$.6H$_2$O (Merck), FeCl$_2$.4H$_2$O (Merck), NH$_3$ 25% (Merck) and HCl 37% (alba). Making amino-modified silica magnetite using 3-Amino Propyl Tri Methoxysilane (APTMS) (Merck), Fe$_3$O$_4$, Na$_2$SiO$_3$, and HCl (alba) and aqua demineralization (UGM Food and Nutrition Laboratory).

For the process of adsorption and selectivity of multimetal used HAuCl$_4$ (UGM Analytical Chemistry Analytical laboratory), CuCl$_2$.2H$_2$O (Merck), NiCl$_2$.6H$_2$O (Merck) and to adjust the pH used a standard pH three buffer solution and universal indicator paper.

2.2 Research Tools

Equipment used includes: analytical equipment and supporting equipment. Analysis equipment includes an X-ray diffractometer (Shimadzu XRD 6000) for the identification of crystal size and structure; infrared spectrometer (Shimadzu FT-IR Prestige21) for identification of functional groups, atomic absorption spectrophotometers (AAS AnalyticJena 300 series) for analysis of gold, copper and nickel content.

Supporting equipment includes external magnets (Niobium), centrifuges (OSK 6474B centrifuge), sonicators (Bransonik 220 with a frequency of 48 kHz), analytical scales (GR-200 XND), heating ovens (Fischer Scientific), porcelain cups, grinding tools, desiccators glassware and plastic tools.

2.3 Manufacture and Characterization of Magnetite

5.2 g of FeCl$_3$ and 2 g of FeCl$_2$ and added 1 mL of HCl 37% was dissolved with 200 mL of aqua demineralization and then drained with N$_2$ while sonication was also performed. Then added 15 mL 25% NH$_3$ drop by drop then continued N$_2$ drainage and sonication for up to 1 hour. The solution was treated for 24 hours in a closed condition. Then the solution was washed using aqua demineralization that has been bubbled with N$_2$ for 5 minutes. This was done three times. Then separated between the settling with the solution using an external magnet. The precipitate obtained was dried in an oven at 70-
80°C and obtained magnetite. The magnetite (Fe₃O₄) obtained was characterized by FTIR and XRD spectrophotometers.

2.4 Coating and Characterization of Magnetite with Amino Silica Hybrids
0.5 gram magnetite (Fe₃O₄) was added 0.606 mL APTMS then 3 mL sodium silicate was added and finally with 2.39 mL aqua demineralization. The mixture was transferred to a cup and then dropped with 1 M HCl until gel was formed and then maintained until pH 7 (neutral), then dried in an oven with a temperature range of 70-80°C. After drying, rewash it with aqua demineralization until the pH shows the same pH as aqua demineralization itself (about 5-6). Then dried again in the oven at 70-80°C. After drying, it is crushed and separated between uncoated silica with magnetite, then weighed and then characterized by XRD and FTIR. ASHM was further tested as an adsorbent in monometal and multimetal systems.

2.5 Multimetal Adsorption
Adsorption is carried out under optimum conditions, at pH was 3, and optimum adsorption time at 60 minutes. A total of 10 mg of ASHM is placed in a plastic bottle. Adsorption is done in a batch system by adding 10 mL of Au(III), Cu(II), and Ni(II) multimetal with the same concentrations of 25, 50, 100, 150, 200, 300 mg/L at pH was 3 and contact time 60 minutes. Thermodynamic adsorption of multimetal is assessed based on the Langmuir and Freundlich adsorption isotherm equations.

2.6 Effect of Cu(II) and Ni(II) Metal Ions on the Adsorption of Au(III) on ASHM
Selective adsorption is performed by making a constant ratio of Au(III) concentration of 0.5 mmol/L while concentrations of Cu(II) and Ni(II) are varied, 0.5: 1.0: 2.0 mmol/L.

3. Results and Discussion

3.1 Material Characteristics

3.1.1 FTIR Spectrum
The FTIR spectrum is used to identify functional groups contained in the adsorbent. In figure 1, spectra (a) is a spectrum for commercial magnetite, while (b) is magnetite synthesis. The results of the IR spectra characterization for commercial magnetite have an active absorption band at 586 cm⁻¹, as well as on the magnetite synthesized, and this shows the vibrations of Fe-O bonds. The absorption band at 1635 cm⁻¹ in both commercial magnetite and synthesis results shows the presence of H₂O vibrations, and the material is slightly moist because of its hygroscopic properties. The absorption band at 3448 cm⁻¹ shows the presence of O-H stretching vibrations on the surface of the magnetite. FTIR spectra show that magnetite has formed.

The magnetite coating process using silica through the sol-gel method produces sharp absorption at 1080 cm⁻¹, which are characteristic of Si-O-Si stretching vibrations. There is also a widening absorption at 3425 cm⁻¹ is the stretching vibration of the -OH group, while 1635 cm⁻¹ is an H₂O vibration. The vibration of Si-O stretching from silanol can be shown by weak absorption at 956 cm⁻¹, but in silica-coated magnetite, the absorption band is not observed because it overlaps with the absorption bandwidth of the Si-O-Si stretching vibration. 563 cm⁻¹ is also absorption, which is a stretching vibration of Fe-O-Si. Observation of siloxane (Si-O-Si) and Fe-O-Si absorption in FTIR spectra indicates that magnetite has been coated with silica.
Figure 1. Commercial Infrared Magnetite Spectra (a), Synthesis Magnetite (b), Silica Magnetite (c) and ASHM (d)

Figure 2. Model of Bonding on the Surface of ASHM

Spectra (d) is a spectrum of ammonite-modified magnetite silica (NH$_2$) showing changes in the specific absorption band of the APTMS group. N-H vibrations in modified silica are shown by absorption at 3500-3100 cm$^{-1}$[12]. N-H may overlap with the OH of Si-OH at 3424 cm$^{-1}$. The presence is supported by the shift in the siloxane group. The absorption band also appears at 2939 cm$^{-1}$, which is the CH$_2$ asymmetric stretching vibration. 1527 cm$^{-1}$ an absorption appears, which is the N-H buckling vibrations of the primary amine. Primary amine uptake is in the area around 1640-1560 cm$^{-1}$ [13].

Estimates of possible variations of the bonding model that occur on the surface of ASHM are shown in Figure 2. It is seen that magnetite coated A1 and B1, can still undergo hydrolysis reaction resulting in coated magnetite A2 and B2. In A2 coated magnetite, the sol-gel transition that occurs involves the condensation of one -Si-O- group and methoxy (-OCH$_3$) to produce two silanol groups (Si-OH) and one amino group (-NH$_2$) thereby increasing the type and number of active sites on magnetite. In magnetite B2 coated, it shows that the sol-gel transition does not affect the number of active sites that exist, but only varies the type of active site, whereas in magnetite C coated, the sol-gel transition will reduce the number of active sites that exist. This is due to the modification of 3 hydroxyl groups (O-H) with one amine group (-NH$_2$).

Figure 3. ASHM X-ray Diffractogram. Inset; Commercial Magnetite Diffractogram

3.1.2 X-ray Diffraction

The XRD method provides information about the stable structure analyzed in the form of diffraction by the level of crystallinity. The adsorbent diffractogram pattern can be seen in Figure 3 that there are six peaks in the diffraction pattern with high intensity. Of the six peaks, five peaks show the character of magnetite, which is at the diffraction angle (20) 30.2°; 35.56°; 43.4°; 57.2°; 62.8° on [hkl]: [220], [311], [111], [200], and [222].
The pattern shown by ASHM is not much different from the pattern shown by commercial magnetites. This means that the addition of an amino group does not cause a significant change in the crystallinity of the magnetite.

### 3.2 Adsorption Thermodynamics

The study of ASHM adsorption thermodynamics in multimetal systems is done by calculating the value of the adsorption capacity, the equilibrium constant and the adsorption energy of each metal based on the Langmuir adsorption isotherm equation and Freundlich [14-15].

The Langmuir adsorption isotherm model assumes that the surface of the adsorbent has a certain number of adsorption sites that are proportional to the surface area of the adsorbent and that the adsorption occurs only in the monolayer. Adsorption is not possible in the adsorbent that has been filled by adsorbate species but occurs in the blank. If the active adsorption site is saturated with adsorbate species, the increase in adsorbate concentration does not relatively increase the amount of adsorbed metal, or even adsorption tends to decrease [16]. The Langmuir adsorption isotherm model is expressed by Equation 1.

\[
\frac{C}{m} = \frac{1}{bK} + \frac{1}{b}C \quad \text{………… (1)}
\]

Where \(C\) is the equilibrium concentration, \(m\) is the amount of substance adsorbed per gram of adsorbent, \(b\) is the adsorption capacity, and \(K\) is the equilibrium adsorption constant. From the linear curve of the relationship between \(C/m\) versus \(C\), we can determine the value of \(b\) of the slope and \(K\) of the curve intercept.

The Freundlich adsorption isotherm model is used to explain the non-ideal adsorption process on heterogeneous surfaces. Heterogeneity can be caused by differences in functional groups on the surface of the adsorbent [15]. Empirically, the Freundlich isotherm equation is expressed by Equation 2.

\[
\ln Q = \ln K_F + \left(\frac{\ln C_e}{n}\right) \quad \text{………… (2)}
\]

Where \(Q\) is the number of adsorbed metal ions (mmol/g), \(C_e\) is the concentration of Au(III) at equilibrium (mmol/ml), \(n\) is the Freundlich constant, and \(K_F\) is the constant indicating the affinity or adsorption capacity of the adsorbent towards the adsorbate. Based on the thermodynamic study of monometal adsorption on magnetite, silica magnetite and ASHM are shown in table 1, while multimetal adsorption on ASHM shown in table 2 is obtained by Langmuir and Freundlich constant values, and adsorption capacity.

Based on Table 1 it can be seen that the adsorption of Au(III) with adsorbents M, SM, and ASHM follows the Langmuir isotherm model. Thus it can be concluded that the adsorption of Au(III) on M, SM, and ASHM is monolayer adsorption on similar active sites. The \(q_{\text{max}}\) parameter determined the adsorption capacity of Au(III) by magnetite and coated magnetite in the Langmuir isotherm model. Positive and Au(III) complexes with negative ions, but these electrostatic interactions are unstable and selective. The large adsorption capacity of ASHM shows that the modification of the amine group (-NH\(_2\)) on the surface of the magnetite silica has succeeded in increasing the adsorption ability of the metal Au(III) ions.

### Table 1. Langmuir and Freundlich M, SM and ASHM Isothermal Adsorption Parameters

| Material | Langmuir Adsorption Parameters | Freundlich Adsorption Parameters |
|----------|--------------------------------|---------------------------------|
|          | \(R^2\) | \(q_{\text{max}}\) | \(K_L\) | \(E_{\text{ads}}\) | \(R^2\) | \(K_F\) | \(n\) |
| M        | 0.995  | 36.4   | 0.054 | 37.670 | 0.847  | 10.301 | 4.242 |
| SM       | 0.958  | 19.3   | 0.073 | 36.927 | 0.711  | 0.138  | 0.809 |
| ASHM     | 0.986  | 102    | 0.085 | 36.555 | 0.334  | 4.567  | 4.440 |

### Table 2. Langmuir Parameters of Multilateral Adsorption on (ASHM)
In table 2, it is seen that the pattern of adsorption of gold metal ions in all multimetal systems follows the Langmuir adsorption isotherm model, which is monolayer adsorption at similar active sites. When viewed from the adsorption energy, adsorption of Au(III) in all multimetal systems involves the energy of about 33-37 kJ/mol, exceeding the adsorption energy of Cu(II) and Ni(II). Energy adsorption > 20 kJ/mol indicates that the adsorption that occurs is chemisorption or chemical adsorption; the bond between adsorbate and adsorbent involves chemical interactions such as covalent bonds or electrostatic interactions.

### 3.3 Adsorption Capacity

Multimetal adsorption on ASHM is an adsorption system that is carried out simultaneously so that during the interaction, there will be competition between the metal ions in occupying the active sites on the adsorbent. A high adsorption capacity value for Au(III) adsorption indicates that the metal Au(III) ions can compete with other metals (Table 3).

**Table 3. Comparison of Au(III) Adsorption in Monometal and Multimetal Systems**

| Multimetal System | Metal   | Adsorption Capacity (mg/g) | E_{ads} (kJ/mol) | R^2  |
|------------------|---------|----------------------------|------------------|------|
|                  |         | Adsorption Capacity         |                  |      |
|                  |         | mmol/g                      | mg/g             |      |
| Au-Cu            | Au(III) | 0.169                       | 33.444           | 37.829 | 0.991 |
|                  | Cu(II)  | 0.060                       | 11.876           | 38.701 | 0.962 |
| Au-Ni            | Au(III) | 0.119                       | 23.584           | 31.026 | 0.968 |
|                  | Ni(II)  | 0.052                       | 10.288           | 36.252 | 0.988 |
| Au-Cu-Ni         | Au(III) | 0.132                       | 26.041           | 34.458 | 0.993 |
|                  | Cu(II)  | 0.107                       | 21.142           | 33.206 | 0.995 |
|                  | Ni(II)  | 0.066                       | 13.089           | 34.055 | 0.942 |

Based on the gold metal ion adsorption capacity in monometal and multimetal systems, it can be seen that the ability of gold adsorption is powerful under a single condition in solution. Unlike the case when there are already other metal ions in the solution, the competition will occur so that the adsorption capacity is decreased compared to when it was still single. According to Sakti, the amine group in the adsorbent will be dominantly positively charged under acidic conditions (the pH used in the study was 3) [17]. This is related to the protonation to form primary ammonium ions (-NH$_3^+$). This is what drives the adsorption of Au(III), which is in the pH of the dominant acid in the form of species [AuCl$_4$]$^-$, through strong electrostatic interactions.

### 3.4 ASHM Selectivity to Au(III)

ASHM absorbent selectivity to Au(III) in multimetal (Au-Cu-Ni) systems is done by varying the concentration of a multimetal solution with a constant concentration of Au(III) (0.5 mmol/L) while Cu(II) and Ni(II)) varies from 0.5-1-2 (in mmol/L). ASHM selectivity parameters for Au(III) can be seen from the coefficient of distribution of metals based on the equation:
D = Q/Ce
\[ \alpha_{Au} = \frac{D_{Au}}{D_{M}} \]

D is the distribution coefficient (L/g), Q is the adsorption capacity (mg/g), Ce is the final concentration (mg/L), \( \alpha \) is the coefficient of selectivity, \( D_{Au} \) and \( D_{M} \) are the coefficients of the distribution of Au(III) against Cu(II) and Ni(II). The ASHM selectivity data for Au(III) is presented in table 4.

**Table 4. The ASHM selectivity**

| Solvent system | Initial Concentration (mmol/L) | D(L/g) |
|---------------|-------------------------------|--------|
| Au-Cu         | Au  | Cu  | Au  | Cu  | \( \alpha_{Au-Cu} \) |
| 0.5           | 0.5 | 1.73| 0.10| 16.04|
| 0.5           | 1   | 3.51| 0.27| 12.96|
| 0.5           | 2   | 3.78| 0.45| 8.31 |
| Au-Ni         | Au  | Ni  | Au  | Ni  | \( \alpha_{Au-Ni} \) |
| 0.5           | 0.5 | 2.71| 0.14| 18.40|
| 0.5           | 1   | 3.45| 0.19| 17.90|
| 0.5           | 2   | 2.88| 0.30| 9.51 |
| Au-Cu-Ni      | Au  | Cu  | Ni  | Au  | Cu  | Ni  | \( \alpha_{Au-Cu} \) | \( \alpha_{Au-Ni} \) |
| 0.5           | 0.5 | 0.5 | 2.94| 0.16| 0.21| 17.67| 13.95|
| 0.5           | 1   | 1   | 0.85| 0.10| 0.51| 7.97 | 1.68 |
| 0.5           | 2   | 2   | 0.90| 0.01| 0.05| 4.98 | 1.65 |

Based on table 4, it can be seen that ASHM has a high selectivity to Au(III) than metal ions Cu(II) and Ni(II) in all three multimetal systems, which is shown from the value of \( \alpha \) which is much higher than 1. The value of \( \alpha_{Au} > 1 \) shows that Au(III) is preferred or has a higher affinity than Cu(II) and Ni(II). This can occur because, at pH was 3, the surface of the adsorbent is positively charged, related to the protonation of the amine group to the \( \text{-NH}_3^+ \) group. Therefore, electrostatic interactions between Au(III) adsorbents, which at pH 3 are in AuCl₄⁻ species - are more likely to occur. Whereas in Cu(II) and Ni(II), electrostatic repulsion occurs. The increase in selectivity is mostly determined by the metal ion charge and the size of the metal [10].

4. Conclusion

The results showed that in simultaneous multi-metal adsorption (Au, Cu, and Ni), ASHM adsorbents from rice husk ash tended to follow the Langmuir isotherm model, where adsorption took place in a monolayer, by giving adsorption capacity to Au(III) much higher than Cu(II) and Ni(II). This difference in capacity makes the prospective ASHM to be developed as an absorber of gold in a homogeneous solution.

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