Application of Humic Acid Isolated From Kalimatan Peat Soil Modifying Magnetite for Recovery of Gold

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INTRODUCTION

The cyanidation process is one method used in gold recovery wherein finely ground ore is agitated in vats of 0.1% sodium cyanide solution. This process recovers over 85% of the gold. Although this method has been used commercially for the past 100 years, there are ores that are not amenable to treatment by cyanide. Other methods that have been used for the recovery of gold from aqueous solutions include precipitation, ions exchange, and solvent extraction. Nevertheless, these methods are not effective (incomplete metal removal) or economical (high cost, high reagent and/or energy requirement) because gold-containing wastewater is often characterized by low concentration (<100 mg/L). Compared with conventional methods, adsorption offers distinct advantages for recovery of metals, including high efficiency and low operating costs (Huang et al., 2010). On the other hand, it has been frequently pointed out that organic matter which is rich in both −COOH and phenolic −OH functional groups can serve as adsorbents of metal ions and/or as reducers of adsorbed metal ions. Santosa et al. (2011) reported that the role of the −COOH functional group in removing [AuCl4]− ions through hydrogen bonding was more significant for the purified humin, while that of the −OH group in removing [AuCl4]− ions through reduction to Au metal was better for the crude (unpurified) humin. Gallic acid-modified magnetite particles have been reported as adsorbents of AuCl4− by Rahmayanti et al. (2016a). The mechanism of gold recovery using Mag-GA particles takes place through the formation of hydrogen bonding followed by reduction of trivalent gold ions to metallic gold, which is
accompanied by simultaneous oxidation of the hydroxyl groups of gallic acid. Support for this approach can be traced to the work of Rahmayanti et al. (2016b). They reported that the adsorption of \([\text{AuCl}_4^-]\) on both salicylic acid and gallic acid-modified magnetite was found to allow the pseudo-second order. The isotherm adsorption equation of \([\text{AuCl}_4^-]\) onto salicylic acid modified magnetite was better described by the Langmuir model, while that onto gallic acid-modified magnetite fitted better to the Freundlich model.

For the easy recovery of the adsorbent from the solution with external magnetic field without additional filtration or centrifugation, the adsorbent can be modified using magnetic compounds. Magnetic supports are commonly prepared by organic/inorganic compounds modification in presence of magnetite. Magnetite \((\text{Fe}_3\text{O}_4)\) is a common magnetic iron oxide with a cubic inverse spinel structure having face-centered cubic close packed oxygen anions and Fe cations occupying interstitial tetrahedral and octahedral sites. The magnetite particles are superparamagnetic, that is, they do not become permanently magnetized after aggregate formation. Hence, the particles may be reused. Stability of the polymeric coating and the covalent attachment of molecules also contribute to the reuse ability of the particles.

Recent research indicated that the modification of magnetite with organic compounds is usually used to load the surface with some donor atom such as oxygen, nitrogen, sulfur and phosphorus (Liu et al., 2008). The adsorption of organic compound onto the \(\text{Fe}_3\text{O}_4\) is reported to happen through ligand exchange (Tan, 2014), electrostatic interaction (Tan, 2014), and hydrogen bonding (Rahmayanti, 2016a), and so on. Humic acid (HA) has a skeleton of alkyl and aromatic units which attach to carboxylic acid, phenolic hydroxyl, and quinone functional groups (Aiken et al., 1985). Therefore, it is suspected that humic acid can also play a role in the recovery of gold from chloride solution.

In this study, a magnetic sorbent material prepared by modifying \(\text{Fe}_3\text{O}_4\) particles with HA was developed for the recovery of gold from chloride solution. The physical and chemical properties of the synthesized HA-modified \(\text{Fe}_3\text{O}_4\) particles (Mag-HA) were characterized, and the applicability of Mag-HA in \([\text{AuCl}_4^-]\) removal was evaluated in view of the sorption kinetics and sorption isotherms.

**MATERIALS AND METHODS**

**Materials**

All reagents employed, i.e. Iron (II) sulfate heptahydrate \((\text{FeSO}_4 \cdot 7\text{H}_2\text{O})\), ferric chloride hexahydrate \((\text{FeCl}_3 \cdot 6\text{H}_2\text{O})\), sodium hydroxide \((\text{NaOH})\), hydrochloric acid \((\text{HCl})\), hydrofluoric acid \((\text{HF})\), barium hydroxyde \((\text{Ba(OH)}_2)\), and calcium acetate \((\text{Ca(CH}_3\text{COO)}_2)\) were purchased from Merck (Germany) and used without further purification. \(\text{HAuCl}_4\) solution was prepared by Analytical Chemistry Laboratory of Universitas Gadjah Mada. The removal studies for \(\text{AuCl}_4^-\) ions were carried out with fresh solutions prepared from a 1000 mg/L stock solution. Carbonate-free distilled water was used for preparation of the solution and for rinsing the products.

**Methods**

**Preparation of Humic Acid (HA)**

The peat soil used as the source of HA was taken from South Kalimantan, Indonesia. The method for isolating humic acids from the peat soil sample was adapted from the recommended procedure of the International Humic Substances Society (IHSS) (http://www.ihss.gatech.edu). The peat soil was first dried under a flow of nitrogen gas in a container having no direct contact with sunlight, and then crushed and sieved to pass through a 200-mesh sieving apparatus. The dry peat soil powder was shaken for 24 h in 0.1 M NaOH solution under a nitrogen atmosphere employing a soil sample weight (g)/NaOH volume (mL) ratio of 1:10. After such treatment, the mixture was centrifuged at the rate of 2000 rpm for 20 min to separate the suspended material from the supernatant. Next, 0.1M HCl was added to the supernatant until pH 1. Then the suspended material separated from the supernatant with centrifugation at 2000 rpm for 20 min. This suspended material was purified by immersion in a solution containing 0.1 M HCl and 0.3 M HF with shaking at room temperature for 24 h. The resulting mixture was centrifuged at 2000 rpm for 10 min to separate the suspended material from the supernatant. This purification procedure was repeated until a clear transparent supernatant was
obtained. The purified suspended material was intensively rinsed with water until the supernatant wash liquid was neutral, after which it was dried at 40°C and subsequently crushed and sieved to pass through a 200-mesh sieving apparatus to obtain purified HA powder. The quality of the purified HA used was monitored by characterization using Fourier-transform infrared (FT-IR) spectrophotometer.

**Preparation and Characterization of Humic Acid-Modified Magnetite Particles (Mag-HA)**

Aqueous solutions of Fe²⁺, Fe³⁺ and HA were separately prepared by dissolving the respective amounts of FeCl₂·6H₂O (10 mL, 1.1 M), FeSO₄·7H₂O (10 mL, 0.55 M) and HA (20 mL, 1 M) in distilled water. An aqueous solution of NaOH of pH 13 was also prepared by dissolving the corresponding amount of NaOH in distilled water (100 mL). A mixture containing equal volumes of Fe²⁺ and Fe³⁺ was added drop by drop in to the NaOH solution with vigorous stirring at temperature 60°C. Once the mixture of Fe²⁺ and Fe³⁺ was completely added, HA solution was added quickly to the reaction. The mixture was stirred at 60°C for 1 h until significant amount of precipitate was visible. The precipitate was then separated from the aqueous solution by external magnetic decantation, followed by repeated washing with distilled water and drying at 50°C for 3 h. The dried powders were then characterized for its functional groups by a FTIR spectrophotometer (Shimadzu FTIR-820 IPC) in the transmission mode using spectroscopic grade KBr pellets. The crystallinity of the samples was determined by X-Ray diffraction analysis using Shimadzu XRD-6000 diffractometer with Ni-filtered Cu Kα radiation (λ=0.15406 nm) at voltage 40 kV and current 30 Ma. The samples were scanned in steps of 0.02° (2θ) in the range from 0 to 70° with a count time of 4 s per step. VSM (OXPORD VSM 1.2H) was used for magnetization measurements. These measurements were taken from 0 to 10 kOe field. From these field versus magnetization curve patterns, saturation magnetization values of the samples were measured.

**Effects of Solution pH on [AuCl₄] Adsorption onto Mag-HA Particles**

A series of [AuCl₄] solutions (10 mL, 25 ppm) were adjusted to pH 2, 3, 4, 5, 6, and 7 by adding either HCl or NaOH solution. Ten milligrams of Mag-HA was added to the [AuCl₄] solution with various pH, shaken at 125 rpm for 60 min, and followed by phase separation using an external magnet. The residual concentration of [AuCl₄] in the solution was determined with Atomic Adsorption Spectroscopy (AAS). The amount of [AuCl₄] ions removed from the solution was considered to be the difference between the initial and remaining amounts of [AuCl₄] ions in the solution each time a sample was analyzed.

**Adsorption kinetics**

The adsorption kinetics were carried out in batch adsorption mode. Into a series [AuCl₄] solution (10 mL, 25 ppm) at optimum pH, 10 mg of Mag-SA was added, shaken at 125 rpm for various contact times and followed by the phase separation using an external magnet. The residual [AuCl₄] in every solution was determined with AAS.

Santosa’s first order (Santosa et al., 2007) and Ho’s pseudo second-order were employed to perform the kinetic study. The linier form of the first order rate expression was given as shown in Eq. (1).

\[
\ln \frac{C_0}{C_A} = \frac{kt}{C_A} + K
\]

where C₀ is the initial concentrations of adsorbate (mol/L), Cₐ is the remaining concentrations of adsorbate in solution after adsorption at equilibrium (mol/L), k is the Santosa’s first order rate constant, K is the equilibrium adsorption constant and t is the interaction time.

The pseudo-second order equation was applied to the same sorption data, it was represented as shown in Eq. (2) (Ho, 2006), where k is the pseudo-second order sorption rate constant, qₑ is the amount of adsorbate adsorbed (mol/g) at equilibrium and qₜ is the amount of adsorbate adsorbed (mol/g) at time t. If the plot of \(\frac{t}{q_t}\) versus t is linier, then k can be determined from the intercept, while the qₑ is the slope of the plot.

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t
\]

**Adsorption Isotherms**

The adsorption isotherms experiments were conducted using a series of 10 mL [AuCl₄] solution with various concentration at optimum
pH. Into every AuCl$_4^-$ solution, 10 mg Mag-HA was added and the mixture was shaken at 125 rpm for optimum contact time, followed by phase separation using an external magnet. The residual [AuCl$_4^-$] concentration in the solution was determined with AAS.

Adsorption isotherm data were further analyzed by the Freundlich and Langmuir isotherm models. The Freundlich isotherm is an empirical model, which is widely used to describe the adsorption occurs on a heterogeneous surface. Meanwhile, the Langmuir isotherm model is established on the assumption that the adsorption occurs on a homogeneous mono layer surface with identical adsorption sites, and there is no lateral interaction between the adsorbed sites. The general forms of the Freundlich (1906) and Langmuir (1916) models are expressed as Eq. (3) and (4).

$$q_e = kC_e^{1/n}$$  \hspace{1cm} (3)
$$q_e = \frac{q_{max}bC_e}{1 + b C_e}$$  \hspace{1cm} (4)

Where $C_e$ is the equilibrium concentration (mol/L), $q_e$ is the equilibrium adsorption capacity (mol/g), $q_{max}$ is the maximum adsorption capacity (mol/g), $k$ and $b$ are the Freundlich constant and the Langmuir constant, respectively.

RESULTS AND DISCUSSION

Characterization of Mag and Mag-HA

The FTIR spectra show a successful modifying of HA on the magnetite surface. Figure 1 shows the strong and broad absorption band centered at ~578 cm$^{-1}$ which corresponds to the Fe-O bonds in the spinel structure of magnetite (Figure 1a), and after the modification the absorption band in this area was still evident (Figure 1c). The C=O stretches of Mag-HA at ~1651 cm$^{-1}$ (Figure 1c), indicates that the carboxylic acid has been ionized as the C=O stretches in free carboxylic acid should be above 1700 cm$^{-1}$ (Figure 1b). This may be explained by pH of reactions when modification occurred. Modification of Mag with HA was occurred at pH of 9-10 which is higher than the pH$_{PZC}$ of Mag (8.2). Magnetite surfaces tend to be negative, while the –COOH and –OH groups of HA were ionized, so that the interaction between the surface of the magnetite and -COO$^-$ and -OH is difficult to occur due to electrostatic interaction. This is what causes the wavenumber of around 3400 cm$^{-1}$ still appear after modification. Therefore, it can be suggested that the interactions between the Mag and HA occur through hydrogen bonds between phenolic groups which were not ionized and the surface of magnetite. Based on FTIR spectra of Mag-HA after adsorption (Figure 1d), it appears that an absorption shift also occurs for the wavenumber of around 1651 cm$^{-1}$ to 1620 cm$^{-1}$ which supposedly came from the -C=O quinone group. This shows that Au(III) was reduced to Au(0) by phenolic group.

In order to understand the above mentioned result, X-Ray diffraction analysis of the Mag-HA before and after adsorption of Au(III) was performed. As shown in Figure 2, the diffraction peaks of [220], [311], [400], [511], and [440] reflect the magnetite crystal. They correspond to the standard data for Fe$_3$O$_4$ (JCPDS no. 89.0691). The XRD patterns showed the peaks of Mag (Figure 2a) were sharper than those of...
Mag-HA (Figure 2b) which indicated that crystallinity magnetite before modification were higher than after modification with HA. After modification, 2θ of the characteristic peaks of Mag did not change significantly. Characteristic peaks of gold metal appear at 2θ = 37.97°; 44.16°; 64.44° although with low intensity (Figure 2c) for the reflection field [111], [200], and [220], respectively. These three peaks were equal to the peak pattern of gold diffractogram obtained by Huang et al. (2010) and Rahmayanti (2016a; 2016b). This result confirms that the adsorption of Au(III) by Mag-HA was accompanied by the formation of elemental gold.

As shown in Figure 3, the respective saturation magnetizations of Mag-HA and Mag were 93.90 emu/g to 66.99 emu/g. The value of saturation magnetization of Mag decreased after the modification process because HA is a non magnetic compound which is able to reduce the magnetic interaction between the particles. Humic acid on Mag layer can reduce surface moment of magnetite and ultimately reduce the magnetic moment in the particles. This result confirms that the modification of humic acid on magnetite have been successfully carried out.

Effects of solution pH on [AuCl₄]⁻ adsorption onto Mag-HA particles

The effects of pH on the adsorption of [AuCl₄]⁻ onto Mag-HA is shown in Figure 4. The figure shows that the highest removal efficiency of AuCl₄⁻ was 96.26% at pH 3. Figure 4 also shows that the adsorption of [AuCl₄]⁻ on the surface of the Mag-HA was significantly influenced by pH. It was proposed that a change in pH of the solution will result in the formation of different ionic species and different surface charge of Mag-HA. When the pH of the system was lower than the pHₚ𝑺 of Mag-HA (2-3), –COOH group is unionized, while the charge of [AuCl₄]⁻ was negative. Therefore, it was possible to form hydrogen bonding between the surface of Mag-HA and [AuCl₄]⁻. Lower adsorption of [AuCl₄]⁻ at pH 2 was caused by fact that Mag in Mag-HA was not stable at this pH. Above pH 3, the –COOH group has begun to ionize so that the surface of Mag-HA was more negative. Hence, the interaction between [AuCl₄]⁻ with the surface of Mag-HA was getting weaker. Consequently, the amount of [AuCl₄]⁻ being adsorbed decreases with increasing pH. the results of this study show the same pattern as the results of Rahmayanti’s et al. (2016a; 2016b) study which reported the effects of pH on the adsorption of [AuCl₄]⁻ onto Mag-GA (gallic acid) and Mag-SA (salicylic acid).

Adsorption kinetics

Adsorption kinetics of [AuCl₄]⁻ on Mag-HA is presented in Figure 5 and Table 1.
Table 1. Calculated values of parameters in the first order equation and pseudo-second order equation of Mag-HA.

| Adsorbents | First order equation | Pseudo-second order equation |
|------------|----------------------|------------------------------|
|            | $r^2$    | $k$ (min$^{-1}$) | $K$ (L/mol) | $r^2$ | $q_e$ (mmol/g) | $h$ (mmol/g.min) | $k$ (g/mmol.min) |
| Mag-HA     | 0.892   | 0.014          | 12905      | 0.999 | 0.073          | 0.0045           | 0.052           |

Accordingly as shown in Figure 5 and Table 1, the adsorption of [AuCl$_4$]$^{-}$ on Mag-HA perfectly fits pseudo-second order model rather than first order one. The extremely high correlation coefficient ($r^2=0.999$) for a pseudo-second order equation implied that the adsorption of [AuCl$_4$]$^{-}$ by Mag-HA was closer to chemisorptions.

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Adsorptions isotherms

The adsorption isotherms and fitting results are shown in Figure 6 and Table 2. It is found that the correlation coefficients are satisfactory ($r^2>0.95$) for both equations, and the data are better fitted by Langmuir model. It can therefore be assumed that the adsorption of [AuCl$_4$]$^{-}$ onto Mag-HA occurs in a monolayer, or the adsorption may only occur at a fixed number of localized sites on a surface in which all adsorption sites are identical and energetically equivalent.

CONCLUSION

Recovery of gold from chloride solution was studied using humic acid-modified magnetite particles. The model of interaction between magnetite and humic acid was also clarified. The recovery of gold strongly depended on pH. The kinetic studies indicated that the adsorption reaction follows the pseudo-second order kinetics. The adsorption isotherm of Mag-HA particles agreed well with Langmuir isotherm model, and the maximum adsorption amount at given conditions was 0.62 mmol/g. The model of interaction between the surface of Mag-HA and [AuCl$_4$]$^{-}$ occurred through hydrogen bonding.
Table 2. Calculated values of parameters in Langmuir and Freundlich equations

| Adsorbents       | Langmuir equation | Freundlich equation |
|------------------|-------------------|---------------------|
|                  | \( q_{\text{max}} \) (mol/g) | \( K_L \) (L/mol) | \( E_{ads} \) (kJ/mol) | \( r^2 \) | \( K_F \) (mol/g) | \( n \) | \( r^2 \) |
| Mag-HA           | 0.00062           | 1608               | 18.60                | 0.992   | 0.000102         | 4.695 | 0.956 |
| Mag-GA (Rahmayanti, 2016a) | 0.00060 | 17851 | 24.66 | 0.994 | 0.019000 | 2.330 | 0.968 |
| Mag-SA (Rahmayanti, 2016b) | 0.00047 | 82423 | 78.516 | 0.991 | 0.022000 | 2.370 | 0.887 |

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REFERENCES

Aiken, G.R., Mcknight, D.M., Wershaw, R.L. 1985. Humic Substances In Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization. John Wiley & Sons. New York.

Freundlich, H.M.F. 1906. Tiber die adsorption in losungen. Zeitschrift für Physikalische Chemie. 57: 385-490.

Huang, X., Wang Y., Liao X., Shi, B. 2010. Adsorptive recovery of Au\(^3+\) from aqueous solutions using bayberry tannin-immobilized mesoporous silica. Journal of Hazardous Material. 183(1-3): 793-798.

Ho, Y.S. 2006. Review of second-order models for adsorption system. Journal of Hazardous Material. 136(3): 681-689.

Langmuir, I. 1916. The constitution and fundamental properties of solids and liquids. Journal of The American Chemical Society. 38(11): 2221-2295.

Liu, J.F., Zhao, Z.S., Jiang, G.B. 2008. Coating Fe\(_3\)O\(_4\) magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. 42(18): 6949-6854.

Rahmayanti, M., Santosa, S.J., Sutarno. 2016a. Mechanisms of Gold Recovery From Aqueous Solutions Using Gallic acid-modified Magnetite Particles Synthesized Via Reverse Co-precipitation Method. International Journal of ChemTech Research. 9(4): 446-452.

Rahmayanti, M., Santosa, S.J., Sutarno. 2016b. Comparative Study on the Adsorption of [AuCl\(_4\)]\(^-\) onto Salicylic Acid and Gallic Acid Modified Magnetite Particles. Indonesian Journal of Chemistry. 16(3): 329-337.

Santosa, S.J., Narso, Ratna. 2007. Adsorption kinetics of Cu(II) species on silica gel in the presence of humic acid. Journal of Ion Exchange. 18(4): 168-173.

Santosa, S.J., Sudiono, S., Siwanta, D., Kunarti, E.S., Dewi, S.R. 2011. Mechanism of AuCl\(_4\) removal from aqueous solution by means of peat soil humin. Adsorption Science & Technology. 29: 733-746.

Tan, K.H. 2014. Humic Matter in Soil and the Environment (Principles and Controversies). Tylor and Francis Group. Boca Raton, Florida.