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### Mechanisms of Gold Recovery From Aqueous Solutions Using Gallic acid-modified Magnetite Particles Synthesized Via Reverse Co-precipitation Method

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Abstract: Gallic acid-modified magnetite particles (Mag-GA) were synthesized via reverse coprecipitation method. The obtained Mag-GA were characterized by Fourier Transform Infrared spectroscopy and X-Ray diffraction. FTIR characterization for Mag-HA after modification indicated the presence of specific absorption bands for functional groups of humic acid and Fe-O bonds, though with lower intensity than before modification. The XRD patterns showed that the crystalinity of magnetite before modification were higher than after modification with gallic acid. The mechanism of synthesis was assumed to occur through electrostatic bonding between the surface of magnetite and gallic acid. The Mag-GA particles were applied for AuCl<sub>4</sub>adsorption and results showed that the optimum adsorption of [AuCl<sub>4</sub>]<sup>-</sup> onto Mag-GA was found at pH 3. 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 oxidization of the hydroxyl groups of gallic acid. This assumption was supported by FTIR spectra, XRD chromatogram and photo-optical microscope that showed the presence of metallic gold on Mag-GA after adsorption. Keywords : Gallic acid-modified magnetite particles, the reverse co-precipitation, the synthesis mechanism, the mechanism of gold adsorption onto Mag-GA particles.

Introduction

Gold is one of the most useful metals and has been used in many fields of modern society, such as electronics and medicine. During the last three decades, substantial quantities of gold have been used by the electronic industry because of its excellent electrical conductivity and resistence to corrosion. This ensures high demand in electronics industry, but over a period of time gets obsolete and redundant. Thus, the recovery of gold from secondary sources, such as electronic waste is a very important technology to develop. Gold-containing waste can be effectively leached in acid solutions, which provides a resource of gold recovery. Therefore, it is essentially important to find an effective method for the recovery of gold from aqueous solution.

Conventional methods for the recovery of gold from aquoeus solutions include precipitation<sup>1</sup>, ions exhange<sup>2</sup>, and solvent extraction<sup>3</sup>. Nevertheless, these methods are not effective and economical because gold is usually present at very low concentrations (1-100 ppm) in solutions, especially in liquid waste, so the use of an adsorbent with the following characteristics is desirable: high efficacy, low environmental impact, and simpel

method of synthesis. Compared with conventional methods, adsorption offers distinct advantages for metal ions recovery, including high efficiency, low operating costs, and minimal volume of sludge.<sup>4</sup>

Recovery of gold via adsorption method using macromolecular compounds with phenolic and carboxylic groups have also been developed. The use of persimmon peel gel for the recovery of gold from aquoeus chloride medium was investigated by Parajuli et al.<sup>5</sup>. The reduction of Au(III) is accompanied by the exchange of ligands between AuCl<sub>4</sub><sup>-</sup> and polyphenolic groups of substrates followed by reduction of Au(III) to Au(0). Similarly, Santosa et al.<sup>6</sup> pointed out that humin had the ability to remove  $[AuCl_4]^-$  from the aqueous solution. They also claimed that the role of -COOH functional group in removing  $[AuCl_4]^-$  through hydrogen bonding is more significant for the purified humin, while that of -OH group in removing  $AuCl_4^-$  through reduction to Au metal is better for the crude (unpurified) humin. Other researchers showed that Bayberry tannin-immobilized on mesoporous silica (BT-SiO<sub>2</sub>) was highly effective and selective for the adsorptive recovery of Au(III) from diluted aqueous solutions<sup>7</sup>. The study also showed that the adsorption of Au(III) on BT-SiO<sub>2</sub> was a reductive adsorption process, in which Au(III) was reduced to its elemental form while the phenolic group of tannins was oxidized to quinone.

Based on the above mentioned, in the present study, the gallic acid-modified magnetite were synthesized through the reverse co-precipitation method. The gallic acid-modified magnetite particles (Mag-GA) were developed for recovery of gold in aqueous solution. The mechanisms of reaction between magnetite particles and gallic acid and the mechanism of gold recovery using Mag-GA particles were investigated in this study.

Gallic acid has a –COOH group and three –OH groups. In addition, magnetic separation has been applied recently in various fields. From an environmental point of view, magnetic separation offers advantages due to easy recovery of the adsorbent without filtration or centrifugation. Several studies have reported magnetic separation using modified magnetite ( $Fe_3O_4$ ) as an environmental friendly approach to remove heavy metal ions<sup>8</sup> and organic pollutants<sup>9</sup>. Rahmayanti et al.<sup>10</sup> have succesfully prepared the gallic acid-modified magnetite via sonochemical co-precipitation synthesis. According to FTIR spectrum, the binding of gallat anions to surface of magnetite particles by chemisorptions of carboxylate groups.

#### Experimental

#### Materials

All reagents employed, i.e. Iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O), ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), sodium hydroxide (NaOH), gallic acid, hydrochloric acid (HCl), barium hydroxydewere purchased from Merck (Germany) and used without further purification. HAuCl<sub>4</sub> solution was prepared by Analytical Chemistry Laboratory of Universitas Gadjah Mada. The removal studies for [AuCl<sub>4</sub>]<sup>-</sup> were carried out with fresh solutions prepared from a 1000 mg/L stock solution. Carbonate-free distilled water was used to prepare the solutions and rinse the products.

#### Synthesis of magnetite powder

Aqueous solutions of  $Fe^{3+}$ ,  $Fe^{2+}$  were separately synthesized by dissolving the respective amounts of  $FeCl_3 \cdot 6H_2O$  (10 mL, 1,1 M),  $FeSO_4 \cdot 7H_2O$  (10 mL, 0,55 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  $Fe^{3+}$  and  $Fe^{2+}$  was added drop by drop into the NaOH solution with vigorous stirring at 60 °C. The mixture was continuously 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.

#### Synthesis of gallic acid-modified magnetite particles (Mag-GA)

The magnetite powder was added to gallic acid solution with the molar ratio of 1Mag:2GA. This mixture was then stirred at 60°C for 1 h until significant amount of precipitate was visible. The procedures of separating, washing and drying was done the same as magnetite powder synthesis.

#### **Characterization of materials**

The magnetite and Mag-GA powders were then characterized for its functional groups by a FTIR spectrophotometer (Shimadzu FTIR-820 IPC) in the transmission mode using spectrocopic grade KBr pellets. The crystallinity of the samples was determined by X-Ray diffraction using Shimadzu XRD-6000 diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda$ =0.15406 nm) at voltage 40 kV and current 30 mA. The samples were scanned in steps of 0.02° (2 $\Theta$ ) in the range from 0 to 70° with a count time of 4 s per step.

#### Experimental procedure for gold recovery

A series of  $[AuCl_4]^-$  solutions (10 mL, 25 mg/L) were adjusted to pH 2, 3, 4, 5, 6, and 7 by adding either HCl or NaOH solution. Ten miligrams of Mag-GA was added then to the  $[AuCl_4]^-$  solutions with various pH, shaken at 125 rpm for 60 min, followed by phase separation using an external magnet. The residual concentration of  $[AuCl_4]^-$  in the solution was determined with Atomic Adsorption Spectroscopy (AAS). The amount of  $[AuCl_4]^-$  ions removed from the solutions was considered to be the difference between the initial and remaining amounts of  $[AuCl_4]^-$  ions in the solution each time a sample was analyzed. The Mag-GA after adsorption of gold were characterized by FTIR spectrophotometer,X-Ray diffractometer and photo-optical microscope (Ephitot + Nikon D60).

#### **Results and discussion**

#### Characterization of Mag-GA (before and after adsorption of gold)

Fig. 1 shows the typical FTIR spectra of Mag, GA, Mag-GA before and after adsorption. The spectra for Mag, Mag-GA before and after adsorption showed the characteristic vibration modes of magnetite particles. The strong and broad absorption band centered at around 580 cm<sup>-1</sup> corresponds to the Fe-O bonds in the spinel structure of Fe<sub>3</sub>O<sub>4</sub>. FTIR spectra for GA (Fig. 1b) presents a broad band at around 3400 cm<sup>-1</sup> which can be ascribed to free phenolic O-H stretching and a band at around 3400 cm<sup>-1</sup> is due to acidic O-H stretching. Several bands at 2400-3100 cm<sup>-1</sup> correspond to C-H stretching mode. The absorption bands at 1700 and 1450 cm<sup>-1</sup>, can be attributed to asymmetric and symmetric vibrations of COOH, recpectively. The FTIR spectra of Mag-GA before adsorption (Fig. 1c) are generally comprised of combined spectral band features of gallic acid and magnetite. In the spectra, the band of carboxylate group C=O at 1700 and 1450 cm<sup>-1</sup> was absent, which indicates that the binding of gallat anions to surface of magnetite particles happens by chemisorptions of carboxylate groups. Based on FTIR spectra of Mag-GA after adsorption (Fig. 1d), it appears that an absorption shift also occurs for the absorption band of around 1620 cm<sup>-1</sup> to 1650 cm<sup>-1</sup> which supposedly came from the - C=O quinone group. This shows that Au(III) was reduced to Au(0) by phenolic group.



Fig. 1. FTIR spectra (a). Mag; (b) GA; (c) Mag-GA before adsorption and (d). Mag-GA after adsorption

Crystaline phases present in the magnetite before and after modification with gallic acid were identified by X-Ray diffractometer and the resulted patterns are shown in Fig. 2b which indicates that the product are magnetite. All of the observed diffraction peaks are indexed as the cubic structure of Fe<sub>3</sub>O<sub>4</sub> (JCPDS no. 89.069). The XRD patterns comparison between the magnetite particles (Fig. 2a) and the Mag-GA (Fig. 2b) demonstrates that the peaks of Mag are sharper than that of Mag-GA which indicates that the crystalinity of magnetite before modification were higher than after modification with gallic acid. Figure 2c is the XRD patterns of Mag-GA after the adsorption of Au<sup>3+</sup>. Figure 2c also shows that the intensive characteristic peaks of elemental Au are located at  $2\theta = 37.97^{\circ}$ ; 44.16°; 64.44° (JCPDS-4784) although with low intensity, which confirms the reductive adsorption of Au<sup>3+</sup> on Mag-GA adsorbent. This result confirms that the adsorption ofAu<sup>3+</sup> by Mag-GA is accompanied by the formation of elemental gold, which was further confirmed by the observation of gold particles in the photo-optical microscope as shown in Fig. 3.



Fig. 2. XRD patterns of (a) Mag; (b) Mag-GA before (c) and after adsorption



# Fig. 3. Gold aggregates distinctly observed in the photo-optical microscope of Mag-GA after adsorption of [AuCl<sub>4</sub>]<sup>-</sup>

#### The mechanisms of reaction between magnetite particles and gallic acid

The gallic acid-modified magnetite were synthesized through reverse co-precipitation method with twostep reaction. The two-step reaction included the formation of magnetite powder and the mixing of the magnetite powder with gallic acid solution. This synthesis was conducted at pH 4-5, which was lower than  $pH_{PZC}$  of magnetite (6 to 6.8)<sup>11</sup> so that the surface of the magnetite tend to be positive due to protonation. On the other hand the -COOH group of GA at this pH has been ionized to -COO<sup>-</sup> since the pK<sub>a1</sub> GA is 4,4. Based on the pK<sub>a2</sub> of GA (8,5), -OH group of GA should not have been ionized at this pH, so that the interaction between the surface of the magnetite with -O<sup>-</sup> group will be difficult to occur. Therefore, it can be suggested that the interactions between the Mag and GA occur through electrostatic interaction between -COO<sup>-</sup> group and the surface of magnetite. The reaction mechanism is presented in Fig. 4.



Fig. 4. The reaction mechanism between magnetite particles and gallic acid

#### Mechanism of reaction between gold and Mag-GA particles

The Mag-GA particles were more effective in adsorbing  $[AuCl_4]^-$  from aqueous solution under highly acidic conditions rather than in slightly acidic ones (Fig. 5). The maximum adsorption of  $[AuCl_4]^-$  by the Mag-GA particles occurred at pH 3. Above pH 3, the –OH group are ionized so that the surface of Mag-GA was more negative. Hence, the interaction between  $[AuCl_4]^-$  with the surface of Mag-GA will be weaker. Consequently, the amount of  $[AuCl_4]^-$  being adsorbed decreases with increasing pH. Accordingly, it is reasonable to assume that the adsorption of  $[AuCl_4]^-$  by the –OH group in Mag-GA occurred through the formation of hydrogen bonding. When the acidity of the medium decreases, more H<sup>+</sup> will be released from the – OH groups, which in turn will cause more hydrogen bonding to be broken and, hence, the adsorption of  $[AuCl_4]^-$  will be suppressed.



## Fig. 5. Effects of pH on the adsorption of [AuCl<sub>4</sub>]<sup>-</sup> onto Mag-GA (initial [AuCl<sub>4</sub>]<sup>-</sup> concentration 25 mg/L; solution volume 10 mL; adsorbent dose 0.01 g).

The Mag-GA particles after adsorption were characterized by FTIR spectrophotometer and X-Ray diffractometer. Both the result of X-Ray patterns (Fig. 2c) and FTIR spectra (Fig.1d) indicate that the redox reaction takes place between Mag-GA and [AuCl<sub>4</sub>]<sup>-</sup>. This result is supported byphoto-optical microscope (Fig.

3).When viewed from the standard potentials of  $[AuCl_4]^-$  and phenolic groups of GA, it is known that the standard reduction potential of  $[AuCl_4]^-$  is +1.0 V<sup>5</sup> and the standard potential of phenolic group of GA is +0.309 V<sup>12</sup>. The standard potential of  $[AuCl_4]^-$  is higher than phenolic group of GA, hence,  $[AuCl_4]^-$  can be reduced on the surface of GA. Therefore, we propose that the mechanism of gold adsorption onto Mag-GAtakes place through the formation of hydrogen bonding followed by the reduction of trivalent gold ions to metallic gold, accompanied by simultaneous oxidization of the hydroxyl groups of gallic acid. The proposed reaction mechanisms is presented in Fig. 6a and Fig. 6b.



Fig. 6. The mechanism of gold recovery using Mag-GA particles

#### Conclusions

Gallic acid-modified magnetite particles were synthesized at pH 4-5 through reverse co-precipitation method. The mechanism of gold adsorption onto Mag-GA was elucidatedthrough electrostatic interaction between -COO<sup>-</sup> group and the surface of magnetite. In order to develop a material for effective recovery of gold utilizing Mag-GA particles, the mechanism of gold adsorption onto Mag-GA was clarified to happen via the formation of hydrogen bonding followed by the reduction of trivalent gold ions to metallic gold, which is accompanied by simultaneous oxidization of the hydroxyl groups of gallic acid.

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