



Modified Humic Acid from Peat Soils with Magnetite (Ha-Fe₃O₄) by Using Sonochemical Technology for Gold Recovery

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Abstract

Sonochemical technology is a technology that involves ultrasonic waves in chemical reactions. In this study, humic acid isolated from peat soil has been successfully modified with magnetite (HA-Fe₃O₄) using sonochemical technology. Characterization of the physical and chemical properties of HA-Fe₃O₄ was carried out using FTIR, XRD, SEM and VSM. HA-Fe₃O₄ was used for recovery of gold from simulated gold waste (HAuCl₄). FTIR characterization showed that the interaction between HA and Fe₃O₄ was through hydrogen bonds. The crystal size of HA-Fe₃O₄ using the Debye-Scherrer equation based on the XRD diffractogram was 12.4 nm. The saturation magnetization value of HA-Fe₃O₄ obtained was 52.80 emu/g. Adsorption studies at various pH showed that HA-Fe₃O₄ has been successful in recovering of gold from simulated gold waste. The % recovery of gold was 99%. Gold recovery occurs through the adsorption process followed by reduction of Au (III) to Au(0).

INTRODUCTION

The organic compounds contained in the soil are divided into nonhumic and humic substances (Tan, 2014). Nonhumic substances include substances with recognizable chemical characteristics (eg polysaccharides, proteins, nucleic acids, lipids, etc.). Humic substances are considered to be modified materials that have lost the chemical characteristics of their precursors. However, operatively, it is difficult to distinguish between nonhumic and humic substances because once extracted from the soil. The humic fraction can be completely purified from the mixture by different procedures (solvent deposition, acid hydrolysis, resin adsorption, column or gel fractionation, etc.) (Aiken, 1985). Until now, the structure of humic acid is still hypothetical, but several studies have shown that the structure of

humic acid has 4 basic units as shown in Figure 1 (Picollo, 1996). Based on Figure 1, it can be seen that humic acid has functional groups such as carboxylic (-COOH), phenolic and hydroxyl (-OH), and ketone (C=O).

The wide variety of functional groups contained in the structure of humic acid makes humic acid one of the materials that is widely used for various applications. In recent years, humic acid has been widely applied for environmental remediation, such as for adsorption of phosphate (Xinga et al., 2020), adsorption of cadmium and copper ions from ground water (Faisal et al., 2020), adsorption of dyes in batik waste (Rahmayanti et al., 2020; Santi & Rahmayanti., 2019; Latifah & Rahmayanti, 2020), and adsorption of [AuCl₄]⁻ (Rahmayanti et al., 2019). Recent studies have shown that humic acid has begun to be modified using magnetite compounds with several purposes:

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1) facilitating the separation process between filtrate and solids using external magnetic fields, 2) producing smaller size adsorbents, and 3). increasing the stability of the adsorbent over a wide range of pH. In this study, humic acid from Kalimantan peat soil was modified using magnetite because magnetite was one of the iron oxide compounds which has the strongest magnetic properties compared to other iron oxide compounds. The novelty of this research was the use of sonochemical technology in the modification of humic acid and magnetite.

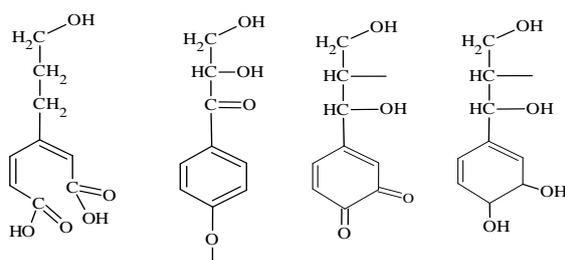


Figure 1. Basic units of humic acids.

Sonochemical technology is a technology that utilizes ultrasonic waves in chemical reactions. The use of ultrasonic waves in chemical reactions results the acoustic cavitation phenomenon. In this phenomenon, bubbles form, grow and burst in a liquid medium with very high temperature (5000 K) and pressure (20 MPa). This is followed by a very high cooling rate (more than 10^{10} Ks^{-1}) due to the bursting of the bubbles. This event resulted in extreme reaction conditions resulting in a microscopic mixing process (Rahmayanti et al., 2016). The phenomenon of acoustic cavitation produces materials with smaller crystal sizes and high stability (Jameel et al., 2020). The synthesized HA-Fe₃O₄ particles were characterized for their physical and chemical properties before and after being applied as adsorbents.

Magnetite-modified humic acid (HA-Fe₃O₄) was used as adsorbent-reducing agent of gold from simulated gold waste (HAuCl₄). This application was a preliminary research of gold recovery from electronic waste. The effect of acidity on [AuCl₄]⁻ adsorption onto HA-Fe₃O₄ were studied in this research.

MATERIALS AND METHODS

Equipment and Materials

The equipment used includes: a set of standard laboratory glassware, vacuum pump, 4800

Thermolyne oven, BP 110 Sartorius analytical balance, desiccator, sonicator type Leistungsfreq.generator 70VA, pH meter Orion 920A, shaker (Osk), Fourier Spectrophotometer Transform Infrared (FTIR), Shimadzu-8201 PC, X-Ray Diffraction (XRD) Shimadzu model XRD-6000, UV-Vis Spectrophotometer Double Beam 1601 PC Shimadzu, Atomic Absorption Spectrometer (AAS) Analytic Jena ContraAA 300, Scanning Electron Microscopy (SEM) JEOL type JED-2300 type, Vibrating Sample Magnetometer (VSM) type OXFORD VSM 1.2H, and the optical photomicroscope Ephitot + Nikon D60 type.

The chemicals used in this research were aquabides, HAuCl₄ solution prepared by the Analytical Chemistry Laboratory of UGM, and analytical grade materials made by E. Merck such as iron (II) sulfate heptahydrate (FeSO₄·7H₂O), iron (III) chloride hexahydrate (FeCl₃·6H₂O), sodium hydroxide (NaOH), and hydrochloric acid (HCl). Humic acid used was humic acid isolated from the peat soil of Kalimantan that has been purified (ready to use).

Methods

Preparation and Characterization of HA-Fe₃O₄

The Fe³⁺ solution (FeCl₃·6H₂O) was mixed with the Fe²⁺ (FeSO₄·7H₂O) solution with a mole ratio of = 2:1. The NaOH solution was stirred and heated to a temperature of 60°C in a three-neck flask with assisted ultrasonic waves. The mixture of Fe³⁺ and Fe²⁺ solutions was added dropwise into 0.5 M NaOH solution while stirring using a magnetic stirrer. After dropping the mixture of Fe³⁺ and Fe²⁺ solutions were complete, HA was added with the mole ratio of Fe²⁺/HA = 1:2 into the three neck flask and the pH of the mixture was measured. Stirring was carried out for 60 minutes and was still given ultrasonic waves. The reaction product was filtered with a buchner filter and dried in an oven for 12 hours at a temperature of 40°C, then characterized using FTIR, XRD, SEM, and VSM. The average crystal size of the synthesized product was calculated based on the XRD diffractogram, using the Debye-sherrer equation as presented in Equation (1). L is the crystal size (nm), λ is the x-ray wavelength (nm), β is the Full Width at Half Maximum (FWHM) of the reflection peak (rad) and θ is the diffraction angle (rad).

$$L = \frac{0,94 \lambda}{\beta \cos \theta} \quad (1)$$

Preparation of Simulated Gold Waste Solution

The simulated gold waste solution was prepared by diluting HAuCl_4 solution 1000 ppm to 25 ppm. HAuCl_4 solution prepared by the Analytical Chemistry Laboratory of UGM from 1 gram pure gold bullion.

Application of $\text{HA-Fe}_3\text{O}_4$ for Gold Recovery

A total of 10 mg of $\text{HA-Fe}_3\text{O}_4$ was put into an erlenmeyer which already contains 10 mL of 25 ppm HAuCl_4 solution with pH variations 2-7. The mixture was shaken for 18 hours at room temperature. The mixture was then filtered using Whatman 42 filter paper, the concentration of $[\text{AuCl}_4^-]$ in the filtrate was measured by AAS. The solid obtained was characterized using an optical photomicroscope.

RESULTS AND DISCUSSION

Characterization of $\text{HA-Fe}_3\text{O}_4$

Spectra of FTIR for $\text{HA-Fe}_3\text{O}_4$, HA and Fe_3O_4 were presented in Figure 2. The presence of magnetite was indicated by the appearance of wide absorption in the 578 cm^{-1} wavenumber which was the stretching vibration of Fe-O magnetite. In this study, $\text{HA-Fe}_3\text{O}_4$ FTIR spectra showed strong and wide absorption in the 578 cm^{-1} wavenumber. Several absorption peaks showing the HA functional group also continued to appear even at a lower intensity and experienced a shift in the wavenumber. The first shift occurred in the 3400 cm^{-1} absorption area which showed the absorption of the -OH group. Before modification, the absorption appeared in the area 3425.58 cm^{-1} , after the absorption modification shifted to the area 3417.86 cm^{-1} . The second shift occurred in the 1700 cm^{-1} and 1620 cm^{-1} wavenumbers showed the carbonyl groups of carboxylates. After modification the absorption shifted to the area 1581.63 cm^{-1} . This shift indicates that a carboxylate group (-COOH) and a phenolic group (-OH) play a role in interacting with magnetite. The presumed interaction was via hydrogen bonds between hydrogen atoms. If the interaction between iron oxide and organic compounds containing -OH groups was carried out at the pH of the medium below the pH_{ZPC} of magnetite, the interactions that occur between magnetite and these organic compounds were through hydrogen bonds, electrostatic interactions and ligand exchange. If the interaction was carried out at $\text{pH} > \text{pH}_{\text{ZPC}}$ of

magnetite, the interaction that occurs was hydrogen bonding and ligand exchange, while electrostatic interactions were not possible under these conditions (Zhou et al., 2015; Kazak et al., 2017; Rasoulzadeh et al., 2019).

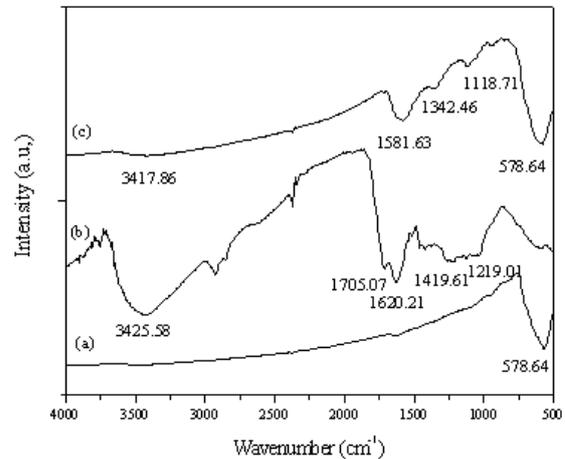


Figure 2. FTIR spectra (a). Fe_3O_4 ; (b) HA; (c) $\text{HA-Fe}_3\text{O}_4$.

In this study, HA was modified with magnetite at pH 10. This condition was above pH_{PZC} Mag (6-6,8), so the surface of the magnetite tends to be negative. Meanwhile, the -COOH and -OH groups in this condition were deprotonated to $-\text{COO}^-$ and $-\text{O}^-$ so that it was not possible to have electrostatic interactions between the surface of the magnetite and HA. It was suspected that the interaction occurs through hydrogen bonds between the oxygen atoms of the -OH phenolate and the undeprotonated hydrogen atoms. The reaction illustration between Fe_3O_4 particles and HA was shown in Figure 3.

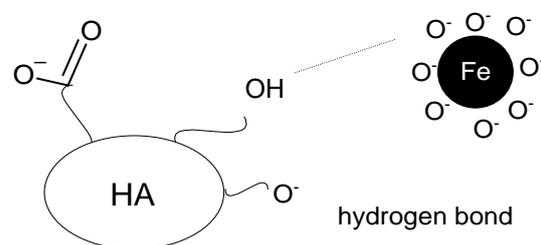


Figure 3. The reaction illustration between Fe_3O_4 particles with HA.

Characterization of magnetite-modified XRD HA was intended to see how the differences in crystallinity and crystal size resulted from the modification. Based on the Figure 4, the peaks that appear on the modified results were the characteristic peaks of magnetite such as peaks that

appear at the diffraction angles of about 30, 35, 43, 57 and 62° with the Miller index, respectively [220], [311], [400], [511], and [440], however the crystallinity of magnetite after modification has decreased. This indicates that HA modification of magnetite has occurred. The results of calculating the crystal size using the Debye-sherrer equation (Table 1) showed the modified crystal size was higher than the Fe₃O₄ crystal size. This showed that HA modification with Fe₃O₄ has been successfully carried out.

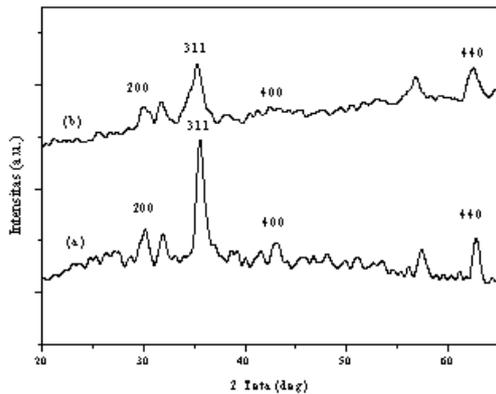


Figure 4. XRD Patterns of (a). Fe₃O₄; (b) HA-Fe₃O₄.

Table 1. Distribution of the average crystal size of the HA-Fe₃O₄.

| Material | The average crystal size (nm) |
|-----------------------------------|-------------------------------|
| Fe ₃ O ₄ | 9.0 |
| HA-Fe ₃ O ₄ | 12.4 |

The saturation magnetization value of HA-Fe₃O₄ can be known through material characterization using VSM. Based on the Figure 5, it can be seen that the saturation magnetization (Ms) value has decreased after the modification process. After HA modified with magnetite, the Ms was reduced from 84.00 to 52.80 emu g⁻¹. The decrease of Ms occurs because Fe₃O₄ has interacted with HA which was a non-magnetic compound so that it can reduce the magnetic interaction between particles. The HA coating on magnetite can reduce the surface moment of the magnetite which in turn can reduce the magnetic moment in the particles. The saturation magnetization value was inversely proportional to the particle size.

SEM images for HA-Fe₃O₄ were presented in Figure 6. From the images, it can be seen that the magnetite has been coated with HA, but the SEM images produced in this study were not very sharp.

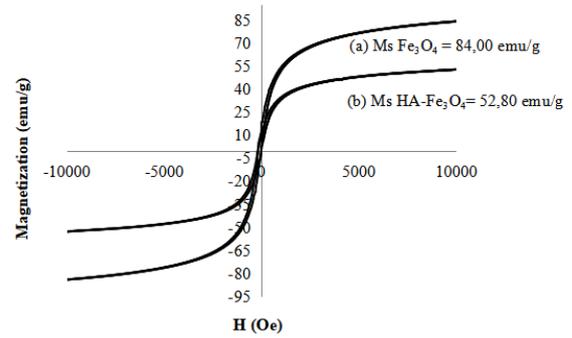


Figure 5. Magnetization curve at room temperature.

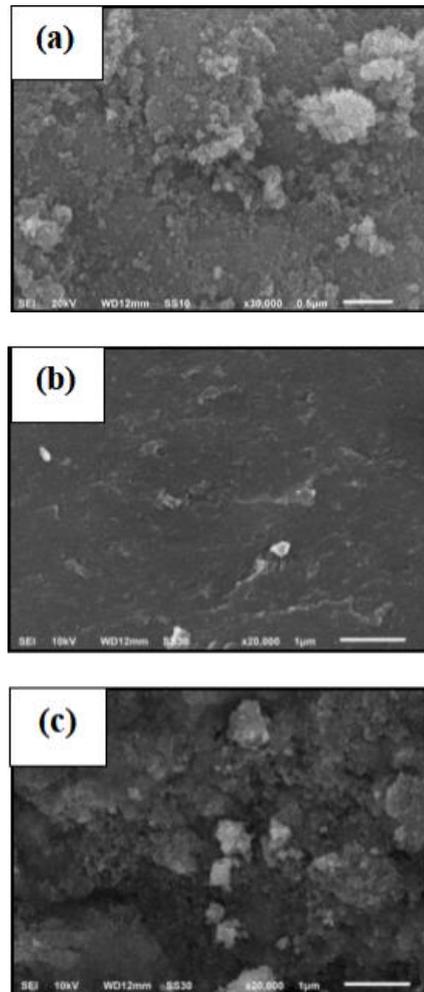


Figure 6. SEM image of (a) Fe₃O₄; (b) HA; (c) HA-Fe₃O₄.

Effects of solution pH on [AuCl₄]⁻ adsorption onto HA-Fe₃O₄

The acidity parameter (pH) is an important factor in the adsorption process of [AuCl₄]⁻ onto HA-Fe₃O₄ because the change in acidity in the solution causes a change in the species of the metal solution. The species [AuCl₄]⁻ is in its maximum concentration at pH 3, and decreases with

increasing pH (Wojnicki et al., 2012; Paclawski & Fitzner., 2004). After pH 7 the species $[\text{AuCl}_4]^-$ is not present in the solution. In addition, changes in acidity can cause changes in the surface charge of HA- Fe_3O_4 .

Adsorption of $[\text{AuCl}_4]^-$ on HA- Fe_3O_4 was influenced by the surface charge of HA- Fe_3O_4 . The presence of the -COOH group and the -OH group affected the surface charge of HA- Fe_3O_4 . When the system pH=3, the HA- Fe_3O_4 surface was positive due to the protonated -OH phenolate group to $-\text{OH}_2^+$, so it was possible to have an interaction between HA- Fe_3O_4 and $[\text{AuCl}_4]^-$ through electrostatic (dipole-ion) interactions and hydrogen bonds between H (from $-\text{OH}_2^+$) with Cl from $[\text{AuCl}_4]^-$. This interaction through hydrogen bonds has also been reported by Rahmayanti et al. (2019). Above pH 3, the species $[\text{AuCl}_4]^-$ decreases due to the exchange of $-\text{Cl}^-$ with $-\text{OH}^-$, this causes increasing the species $[\text{AuCl}_{4-n}(\text{OH})_n]$ so that the interaction of $[\text{AuCl}_4]^-$ with HA- Fe_3O_4 decreases. This was evidenced in Figure 7, where the amount of $[\text{AuCl}_4]^-$ adsorbed on HA- Fe_3O_4 decreases after pH 3 which was caused by the HA- Fe_3O_4 phenolic group starting to ionize to $-\text{O}^-$ so that the interaction of HA- Fe_3O_4 with $[\text{AuCl}_4]^-$ decreases. However, in this study, the amount of $[\text{AuCl}_4]^-$ adsorbed at pH>5 was still above 85%. This reinforces the notion that the interaction that occurs between HA- Fe_3O_4 and $[\text{AuCl}_4]^-$ was not only through electrostatic interactions. If only through electrostatic interactions, increasing pH makes it more difficult for HA- Fe_3O_4 to interact with $[\text{AuCl}_4]^-$, because the HA- Fe_3O_4 surface becomes negative.

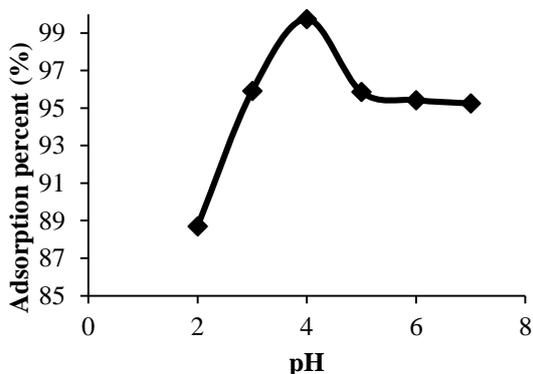


Figure 7. Adsorption of $[\text{AuCl}_4]^-$ onto HA- Fe_3O_4 at various pH.

Adsorbent Characterization After the Adsorption Process

According to Stevenson (1994), HA was a macromolecule that has various active sites, such as -COOH, -OH, -C=O and -NH. The presence of these various groups allows HA to interact with $[\text{AuCl}_4]^-$ in various ways. Phenolic -OH groups have been reported to reduce Au(III) to Au(0). The number of phenolic -OH groups present in the HA structure according to Rahmayanti et al. (2016) was thought to increase the ability to reduce Au(III) to Au(0).

In this research, the optical photomicroscope of HA- Fe_3O_4 was presented in Figure 8. From the images, it can be seen that there was a shiny yellow deposit on the adsorbent (8(a)) and after being separated by an external magnet, it can be seen that the shiny yellow solid was separated even in very small amounts (8(b)). Thus the interaction between $[\text{AuCl}_4]^-$ and HA- Fe_3O_4 was not only through the adsorption process but also accompanied the reduction of Au(III) to Au(0). Thus it can be described that the interaction mechanism occurs in two stages, (1). $[\text{AuCl}_4]^-$ adsorbed on HA- Fe_3O_4 through electrostatic interactions and (2) followed by the reduction process of Au(III) to Au(0). That is, $[\text{AuCl}_4]^-$ was not only adsorbed on HA- Fe_3O_4 but also accompanied by a reduction process that produces gold metal. This adsorption-reduction process has

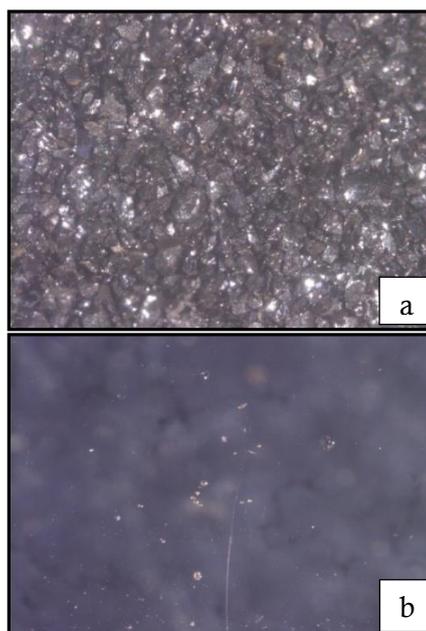


Figure 8. (a) The image of HA- Fe_3O_4 using the optical photomicroscope after adsorption. (b) The Au metal that has been separated

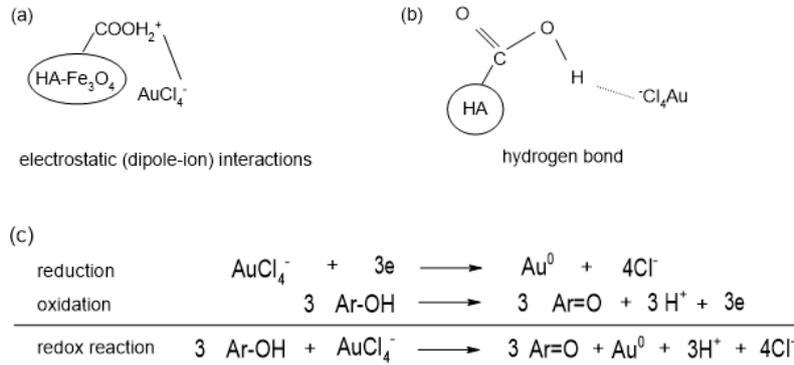


Figure 9. Illustration of gold recovery by HA-Fe₃O₄.

also been reported by Yi et al. (2016), Santosa et al. (2020) and Hadi et al. (2015). An illustration of gold recovery from simulated gold waste (HAuCl₄) by HA-Fe₃O₄ was presented in Figure 9.

CONCLUSION

Humic acid isolated from peat soils has been successfully modified with magnetite using sonochemical technology. FTIR characterization showed that the interaction between HA and Fe₃O₄ was through hydrogen bonds. The results of calculating the crystal size using the Debye-scherrer equation based on the XRD diffractogram of HA-Fe₃O₄ was 12.4 nm. The saturation magnetization value of HA-Fe₃O₄ obtained was 52.80 emu/g. This value was lower than the Ms Fe₃O₄ value. That was, the magnetic strength of HA-Fe₃O₄ was lower than that of Fe₃O₄. Adsorption studies at various pH showed that HA-Fe₃O₄ has been successful in recovering gold from simulated gold waste.

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