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

Maya Rahmayanti¹,², Sri Juari Santosa², Sutarno²

DOI: https://doi.org/10.15294/jbat.v9i2.26131

¹ Department of Chemistry, State Islamic University of Sunan Kalijaga, Jl. Marsda Adi Sucipto Yogyakarta, Indonesia
² Department of Chemistry, Universitas Gadjah Mada, Jl. Sekip Utara, Yogyakarta 55281, Indonesia

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 (e.g., 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 keto (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:
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.

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 1010 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., 2016). The synthesized HA-Fe\(_3\)O\(_4\) particles were characterized for their physical and chemical properties before and after being applied as adsorbents.

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 ContrAA 300, Scanning Electron Microscopy (SEM) JEOL type JED-2300 type, Vibrating Sample Magnetometer (VSM) type OXFORD VSM 1.2H, and the optical photomicroscope Epifhot + Nikon D60 type.

The chemicals used in this research were aquabides, HAuCl\(_4\) solution prepared by the Analytical Chemistry Laboratory of UGM, and analytical grade materials made by E. Merck such as iron (II) sulfate heptahydrate (FeSO\(_4\)·7H\(_2\)O), iron (III) chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O), 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-Fe\(_3\)O\(_4\)

The Fe\(^{3+}\) solution (FeCl\(_3\)·6H\(_2\)O) was mixed with the Fe\(^{2+}\) (FeSO\(_4\)·7H\(_2\)O) 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 Fe\(^{3+}\) and Fe\(^{2+}\) solutions was added dropwise into 0.5 M NaOH solution while stirring using a magnetic stirrer. After dropping the mixture of Fe\(^{3+}\) and Fe\(^{2+}\) solutions were complete, HA was added with the mole ratio of Fe\(^{2+}\)/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), \(\lambda\) is the x-ray wavelength (nm), \(\beta\) is the Full Width at Half Maximum (FWHM) of the reflection peak (rad) and \(\theta\) is the diffraction angle (rad).

\[
L = \frac{0.94 \lambda}{\beta \cos \theta}
\]
**Preparation of Simulated Gold Waste Solution**

The simulated gold waste solution was prepared by diluting HAuCl₄ solution 1000 ppm to 25 ppm. HAuCl₄ solution prepared by the Analytical Chemistry Laboratory of UGM from 1 gram pure gold bullion.

**Application of HA-Fe₃O₄ for Gold Recovery**

A total of 10 mg of HA-Fe₃O₄ was put into an erlenmeyer which already contains 10 mL of 25 ppm HAuCl₄ 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 [AuCl₄]⁻ in the filtrate was measured by AAS. The solid obtained was characterized using an optical photomicroscope.

**RESULTS AND DISCUSSION**

**Characterization of HA-Fe₃O₄**

Spectra of FTIR for HA-Fe₃O₄, HA and Fe₃O₄ 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, HA-Fe₃O₄ 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 3400cm⁻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_pzc 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 pH > pH_pzc 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](image)

**Figure 2.** FTIR spectra (a). Fe₃O₄; (b) HA; (c) HA-Fe₃O₄.

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 –COO⁻ and –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 deprotonated hydrogen atoms. The reaction illustration between Fe₃O₄ particles and HA was shown in Figure 3.

![Figure 3](image)

**Figure 3.** The reaction illustration between Fe₃O₄ 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) |
|-------------|------------------------------|
| Fe₃O₄       | 9.0                          |
| HA-Fe₃O₄    | 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\(_2\)O\(_4\).

Adsorption of \([\text{AuCl}_4^-]\) on HA-Fe\(_2\)O\(_4\) was influenced by the surface charge of HA-Fe\(_2\)O\(_4\). The presence of the -COOH group and the -OH group affected the surface charge of HA-Fe\(_2\)O\(_4\). When the system pH=3, the HA-Fe\(_2\)O\(_4\) surface was positive due to the protonated –OH phenolate group to –OH\(^2+\), so it was possible to have an interaction between HA-Fe\(_2\)O\(_4\) and \([\text{AuCl}_4^-]\) through electrostatic (dipole-ion) interactions and hydrogen bonds between H (from –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 –Cl with –OH, this causes increasing the species \([\text{AuCl}_4^-(\text{OH})_2]\) so that the interaction of \([\text{AuCl}_4^-]\) with HA-Fe\(_2\)O\(_4\) decreases. This was evidenced in Figure 7, where the amount of \([\text{AuCl}_4^-]\) adsorbed on HA-Fe\(_2\)O\(_4\) decreases after pH 3 which was caused by the HA-Fe\(_2\)O\(_4\) phenolic group starting to ionize to –O so that the interaction of HA-Fe\(_2\)O\(_4\) 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\(_2\)O\(_4\) and \([\text{AuCl}_4^-]\) was not only through electrostatic interactions. If only through electrostatic interactions, increasing pH makes it more difficult for HA-Fe\(_2\)O\(_4\) to interact with \([\text{AuCl}_4^-]\), because the HA-Fe\(_2\)O\(_4\) surface becomes negative.

Adsortent 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) 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\(_2\)O\(_4\) but also accompanied by a reduction process that produces gold metal. This adsorption-reduction process has

![Figure 7](image7.png)

Figure 7. Adsorption of \([\text{AuCl}_4^-]\) onto HA-Fe\(_2\)O\(_4\) at various pH.

![Figure 8](image8.png)

Figure 8. (a) The image of HA-Fe\(_2\)O\(_4\) using the optical photomicroscope after adsorption. (b) The Au metal that has been separated.
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.

ACKNOWLEDGEMENT

The researchers would like to thank the Chemistry, Physics and Biology Laboratory of UIN Sunan Kalijaga and LPPT UGM for the services and facilities provided.

REFERENCES

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

Faisal, A. A. H., Abdul - Kareem, M. B., Mohammed, A. K., Naushad, M., Ghfar, A. A., Ahamad, T. 2020. Humic Acid Coated Sand as a Novel Sorbent in Permeable Reactive Barrier for Environmental Remediation of Groundwater Polluted with Copper and Cadmium Ions. Journal of Water Process Engineering. 36: 101373.

Hadi, P., Xu, M., Lin, Hui, C-W., McKay, G. 2015. Waste Printed Circuit Board Recycling Techniques and Product Utilization, a Review. Journal of Hazardous Material. 283: 234–243.

Jameel, M.S., Aziz, A.A., Dheyab, M. A. 2020. Comparative Analysis of Platinum Nanoparticles Synthesized Using Sonochemical-assisted andKonventional Green Methods. Nano-Structures & Nano-Objects. 23: 100484.

Kazak, O., Eker, Y. R., Akin, I., Bingol, H., Tor, A. 2017. A Novel Red Mud@Sucrose Based Carbon Composite: Preparation, Characterization and Its Adsorption Performance Toward Methylene Blue in Aqueous Solution. Journal of Environmental Chemical Engineering. 5(3): 2639 – 2647.

Latifah, W. N., Rahmayanti, M. 2020. Desorption of Indigosol Blue from Humic Acid Coated Fe₃O₄ Particles. Proceeding International Conference Science and Engineering. 3: 169-170.

Paclawski, J., Fitzner, K. 2004. Kinetics of gold(III) chloride complex reduction using sulfur(IV). Metallurgical and Materials Transactions B. 35: 1071–1085

Piccolo, A. 1996. Humic Substances In Terrestrial Ecosystems Ecosystems. The Netherlands: Elsevier. 1996.

Rahmayanti, M., Abdillah, G., Santosa, S. J., Sutarno. 2019. Application of Humic Acid Isolated From Kalimatan Peat Soil Modifying Magnetite for Recovery of
Gold. Jurnal Bahan Alam Terbarukan. 8 (2): 77-83.

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

Rahmayanti, M., Yunita, E., Putri, N. F. Y. 2020. Study of Adsorption-Desorption on Batik Industrial Dyes (Naphthol Blue Black) on Magnetite Modified Humic Acid (HA-FeO4). Jurnal Kimia Sains dan Aplikasi. 23(7): 244-248.

Rahmayanti, M., Santosa, S.J., Sutarno. 2016. 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.

Rasoulzadeh, H., Mohseni-Bandpei, A., Hosseini, M. and Safari, M. 2019. Mechanistic Investigation of Ciprofloxacin Recovery by Magnetite–Imprinted Chitosan Nanocomposite: Isotherm, Kinetic, Thermodynamic and Reusability Studies. International Journal of Biological Macromolecules. 133: 712–721.

Santi G.C., Rahmayanti, M. 2019. Effect of Solution pH to Indigosol Blue Adsorption on Humic Acid Isolated from Kalimantan Peat Oil. Proceeding International Conference Science and Engineering. 2: 193-195.

Santosa, S. J., Fitriani, D., Aprilita, N. H., Rusdiarso, B. 2020. Gallic and Salicylic Acid-Functionalized Mg/Al Hydrotalcite as Highly Effective Materials for Reductive Adsorption of AuCl−. Applied Surface Science. 507: 145115.

Stevenson, F. J. 1994. Humus Chemistry Genesis, Composition, Reaction. 2nd Edition. John Wiley, New York.

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

Xinga, B., Ouyang, M., Graham, N., Yu, W. 2020. Enhancement of Phosphate Adsorption During Mineral Transformation of Natural Siderite Induced by Humic Acid: Mechanism and Application. Chemical Engineering Journal. 393: 124730.

Zhou, Y., Zhang, Y., Li, G. and Jiang, T. 2015. A Further Study on Adsorption Interaction of Humic Acid on Natural Magnetite, Hematite and Quartz in Iron Ore Pelletizing Process: Effect of The Solution pH Value. Powder Technology. 271: 155-166.