Preparation of magnetite coated humic acid (Fe₃O₄-HA) as malachite green dye adsorbent

T Sulistyaningsih¹*, S Ariyani², and W Astuti²

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Semarang, Indonesia
²Department of Chemical Engineering, Faculty of Engineering, Universitas Negeri Semarang, Indonesia

*Corresponding author: triastuti.s@mail.unnes.ac.id

Abstract. Magnetite (Fe₃O₄) coating using humic acid (HA) to form Fe₃O₄/HA as malachite green dye adsorbent has been carried out. Humic acid was obtained from the isolation of peat soil from Rawa Pening, Ambarawa, Central Java, using the conventional alkaline extraction method. Synthesis of magnetite and Fe₃O₄/HA by coprecipitation method under alkaline conditions using NaOH. The characterization using Fourier Transform Infrared (FTIR) shows a bond between carboxylate groups in HA and Fe on magnetite, which proves that HA coating on magnetite surfaces has been successfully carried out. The characterization results using X-Ray Diffraction (XRD) showed that the coating of HA on magnetite did not change its phase shape but decreased its peak intensity. The results of characterization using a Surface Area Analyzer (SAA) showed that HA coating increased the surface area of Fe₃O₄. The optimum adsorption of malachite green by HA occurred at pH 3 for 60 minutes, with a concentration of 96.95 mg/L. Magnetite adsorbs optimally at pH 7 for 90 minutes and a concentration of 83.48 mg/L, while Fe₃O₄/HA occurs at pH 3 for 90 minutes with 104.15 mg/L.

1. Introduction

The textile industry is one type of industry in Indonesia that produces much waste in dyes. Malachite green is a triphenylmethane cation dye most commonly used in the textile industry and biocides in aquaculture [1]. In humans, malachite green can irritate the respiratory tract if inhaled and irritate the gastrointestinal tract after ingestion. If it comes into contact with the skin, it will cause redness irritation, and if it gets into the eye, it will cause permanent injury to the human eye [2]. Besides, the release of malachite green into the hydrosphere can cause environmental degradation because it gives water an unwanted colour and reduces sunlight penetration [1]. Therefore, it is crucial to remove malachite green from wastewater before being discharged into the environment.

Magnetite (Fe₃O₄) is a type of iron oxide with large magnetic properties and black colour. Fe₃O₄, with its magnetic properties, has been widely used as an adsorbent for the adsorption of dyes and heavy metals. For example, magnetite nanoparticles modified by activated carbon for cationic and anionic dyes adsorbent in aqueous solutions [3], modification of the surface of magnetite nanoparticles to remove methyl violet (MV) from aqueous solutions [4], synthesis of propyl aminopyridine modified nanoparticles magnetic for adsorption of cadmium (II) in aqueous solution [5], and adsorption of methylene blue (MB) with a controlled size of magnetite nanoparticles [6].
According to Sulistyaningsih et al. [7], the Fe₃O₄ adsorbent has a large surface area, a large adsorption capacity and is easy to separate because an external magnetic field can attract it. However, this adsorbent's weakness is that it is easily oxidized and experiences clumping in an aqueous solution, which can affect its adsorption capacity [1]. The coating of natural organic matter on magnetite surfaces can make magnetite less toxic and more environmentally friendly. This layer can also inhibit autoxidation and agglomeration, which are the weaknesses of magnetite adsorbents [8]. One of the natural organic ingredients is HA. Humic acid is a macromolecule with a complex structure with large functional groups, especially -COOH, -OH phenolics, -OH alcohulates, enolates and -C = O [9]. The presence of HA functional groups is useful in the coating process on an adsorbent solid. HA, the coating on Fe₃O₄, can stabilize the active surface site, increase the adsorption capacity and prevent clumping in aqueous solution systems. The stability of the HA and Fe₃O₄ interaction is due to electrostatic and steric interactions [10]. Based on the description above, Fe₃O₄ coated with HA is expected to be the right choice as an adsorbent for adsorbing malachite green dye.

2. Methods

The equipment used in this study included the vision hot plate and magnetic stirrer, furnace, centrifuge, Bionex oven, Fourier Transform Infrared Spectroscopy (FT-IR) Perkin Elmer Spectrum Version 10.4.00, Surface Area Analyzer (SAA) Quantachrom 1200c, X-ray diffraction (XRD), and Thermo Scientific Uv-Vis Spectrophotometer. The materials used in this research include; peat soil originating from the Rawa Pening area, NaOH 99% (Merck), HCl 37 %, HF pa Merck, AgNO₃ 99% (Merck), FeCl₃·6H₂O pa Mercck, FeSO₄·7H₂O pa Merck, Whatman 42 filter paper, distilled water, pH indicator, pH buffer and malachite green dye. Isolation of HA was carried out using the alkaline extraction method recommended by the International Humic Substances Society (IHSS).

Magnetite synthesis was carried out using the coprecipitation method. 1.525 grams of FeCl₃·6H₂O was dissolved in 25 mL of distilled water, and 1.05 grams of FeSO₄·7H₂O was dissolved in 25 mL of distilled water [11]. The solution is then mixed, stirred and heated to 55 °C [12]. After reaching a 55 °C, the solution is dripped with 5M NaOH [11] little by little until it reaches pH 12. Stirring is continued for 1 hour [13] at 55 °C, then cooled overnight at room temperature. The Fe₃O₄ particles formed were then dried by oven at 60 °C [14] for 24 hours.

The synthesis of Fe₃O₄-HA was carried out using the coprecipitation method. The synthesis was initiated by mixing FeCl₃·6H₂O with FeSO₄·7H₂O, like magnetite synthesis. However, before reaching pH 12, a 0.025 g HA solution that had been dissolved in 10 mL of distilled water was added quickly [11]. Stirring was continued for 1 hour [13] at 55 °C, then cooled overnight at room temperature. The Fe₃O₄-HA particles formed were then dried in an oven at 60 °C [14] for 24 hours. The functional group and surface area characteristics of HA, magnetite and Fe₃O₄-HA were analyzed using FT-IR, XRD and Brunauer–Emmett–Teller (BET).

Determination of the optimum conditions for the adsorption of malachite green was carried out using a pH variation of 1 to 8 in a 50 mg/L solution of malachite green dye. The interaction was carried out for 30 minutes. Optimization of contact time was carried out in the optimum pH 50 mg/L malachite green solutions with variations in contact time. The concentration optimization was carried out in the malachite green solutions, up to 250 mg/L, at the optimum pH with the optimum contact time.

3. Results and Discussion

3.1. Characterization of Fe₃O₄, HA and Fe₃O₄-HA

In this study, synthetic Fe₃O₄ and Fe₃O₄-HA use the coprecipitation method in an alkaline state because Fe₃O₄ is amphoteric. When the pH is above pHₚZC (pH <6.8), the surface charge of the Fe₃O₄ is negative so that the HA coating on Fe₃O₄ occurs with a ligand change reaction [15]. The reaction can be seen from equation 1.

\[
\text{Fe-OH} + R-\text{COO}^- \rightarrow \text{Fe-OOC-R} + \text{OH}^-
\]  

(1)
The FT-IR spectra of HA (Fig. 1) reported strong and broad absorption in the 3337 cm\(^{-1}\) regions, indicated the abundance of –OH groups, and was strengthened by absorption in the 3694 cm\(^{-1}\) regions. The small absorption at wavenumber 2925 cm\(^{-1}\) identifies the presence of aliphatic C-H stretching vibrations. The stretching vibration of –C=O from the –COOH group is indicated by absorption in the region of wavenumber 1704 cm\(^{-1}\). The absorption at wavenumber 1620 cm\(^{-1}\) identifies the presence of –C=C– aromatic and aromatic rings formed by hydrogen bonds of –OH groups and C=O quinone groups. The -OH bending vibration and the C-O stretching vibration of COOH are indicated by absorption at the wavenumber 1212 cm\(^{-1}\). The aliphatic C-H bond is also shown by the absorption band's appearance in the 1436 cm\(^{-1}\) area. The absorption at the wavenumber 1030 cm\(^{-1}\) is the C-O stretching vibration of the polysaccharide compound or a silicate Si-O impurity that usually appears at the wavenumber 830-1100 cm\(^{-1}\). The FT-IR spectra of HA resulted from the research showing characteristic peaks around the wavenumbers 3400, 2900, 1600, and 1200 cm\(^{-1}\) [16].

Figure 1. (a) FT-IR spectra of adsorbent and (b) diffractogram X-Ray Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)-HA

FT-IR characterization results from Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)-HA have the main absorption band that occurs in the area of wave numbers 586 and 582 cm\(^{-1}\), which are tetrahedral Fe-O bonds [11]. The success of coating HA on magnetite was shown in the absorption in the 1617 cm\(^{-1}\) wavenumber, which came from the stretching vibration of C = O, which showed the interaction between carboxylic anions and metal oxide surfaces [17]. This interaction indicates that the carboxylic group plays an important role in bonding HA to the surface of the magnetite. The difference in FT-IR spectra between magnetite and Fe\(_3\)O\(_4\)-HA is seen in the wavenumber 1364 cm\(^{-1}\) for stretching vibrations -CH\(_2\) of HA, which is not found in magnetite [18].

The X-ray diffractogram showed Fe\(_3\)O\(_4\) peaks at 2θ: 30.29, 35.71, 43.52, 57.30, 62.98, and 74.11° (Fig. 2). These results are following JCPDS No.19-0629. X-ray diffractogram results on Fe\(_3\)O\(_4\)-HA showed peaks at 2θ: 30.12, 35.61, 43.01, 57.39, and 62.64°. These peaks are following the Miller Index on JCPDS number 00-019-0629, which has the values (hkl): (220), (311), (400), (511) and (440). Based on the characterization results, it is known that Fe\(_3\)O\(_4\)-HA has the same peaks as Fe\(_3\)O\(_4\), but has decreased in intensity. The decrease in the crystallinity of Fe\(_3\)O\(_4\) in Fe\(_3\)O\(_4\)-HA indicates that the surface of Fe\(_3\)O\(_4\) is bound with HA. This bonding indicates that HA immobilization by Fe\(_3\)O\(_4\) has been successfully carried out. BET analysis has been carried out to determine surface area. BET analysis showed that the coating of HA on Fe\(_3\)O\(_4\) increased surface area but decreased pore size (Table 1). This phenomenon is possible because of the dense structure of HA that blocks the interactions between particles due to the interaction of the well-known HA molecules on magnetite surfaces [19].
Table 1. Adsorbent Surface Characteristics

| Adsorbent          | Surface area \(m^2/g\) | Pore radius \(nm\) | Total pore volume \(cc/g\) |
|--------------------|-------------------------|--------------------|----------------------------|
| Humic acid (HA)    | 11.31                   | 2.78               | \(1.578 \times 10^{-2}\)   |
| Magnetite \(Fe_3O_4\) | 81.12                 | 8.02               | \(3.256 \times 10^{-1}\)   |
| \(Fe_3O_4\)–HA    | 98.67                   | 6.69               | \(3.299 \times 10^{-1}\)   |

3.2. Sorption studies of malachite green on \(Fe_3O_4\) and \(Fe_3O_4\)-HA

In this study, the influence of solution pH, contact time, and concentration on the adsorption of malachite green was investigated. The pH investigations of the solution were carried out at pH 1-8 (Fig. 2a). The results showed that the adsorption of malachite green by HA was optimum at pH 3 with an absorption capacity of 4,847 mg/g. Humic acid has functional groups that are hydrophilic and hydrophobic. Interaction of MG dye with HA is possible because MG can break through to hydrophobic AH [20]. In \(Fe_3O_4\), the optimum pH for the adsorption of malachite green dye occurred at pH 7 with an absorption capacity of 3.704 mg/g. This phenomenon was caused when the pH is lower than pHpzc \(Fe_3O_4\) (pHpzc \(Fe_3O_4\) = 6.4), the \(Fe_3O_4\) surface is positively charged due to protonation so that it can react with anions. Otherwise, at a higher pH than pHpzc, \(Fe_3O_4\) is negatively charged due to deprotonation [15].

![Figure 2](image)

**Figure 2.** (a) Effect of pH, (b) Effect contact time on the adsorption of MG on adsorbent (initial MG concentration 50 mg L\(^{-1}\); solution volume 10 mL; adsorbent dose 0.01 g)

The optimum adsorption of malachite green dye by \(Fe_3O_4\)-HA occurred at pH 3 with an absorption capacity of 3.491 mg/g. Plating HA on magnetite changes the surface charge of magnetite. Humic acid has functional groups, namely carboxylic (-COOH) and phenolic (-OH), which will bind to the active group on the surface of the magnetite, which results in a change in charge on the particle surface. When the pH is lower than pHpzc (pHpzc \(Fe_3O_4\)–HA ~ 2.3), \(Fe_3O_4\)–HA is positively charged, so that it has a weak interaction with the green malachite cation. However, when the pH is higher than pHpzc, \(Fe_3O_4\)–HA is negatively charged because of the carboxylic acids in HA form carboxylic ions, which increase the absorption of the malachite green dye [15]. This negative charge will reduce the agglomeration of \(Fe_3O_4\)–HA and help attract positively charged dye molecules.

The optimum contact time for the adsorption of malachite green dye by HA occurred at 60 minutes, while for magnetite and \(Fe_3O_4\)–HA at 90 minutes (Fig. 2b). At optimum conditions, the active sites available from each adsorbent are filled or saturated so that the absorbed green malachite dye does not experience a significant increase or runs slowly. Fig. 3 shows the amount of adsorbed malachite green on the adsorbent surface versus the concentration of this anion in the aqueous equilibrium phase (effect of adsorbate concentration). At the beginning of the malachite green concentration, there was an increase in adsorption drastically in line with the enhance in the adsorbate's concentration caused by the
adsorbent's active sites, which were still widely available. However, at the HA concentration values above 96.95 mg/L, 83.48 mg/L for Fe₃O₄ and 104.15 mg/L Fe₃O₄–HA with the adsorbate increase concentration, small changes occurred in the amount of adsorbed. This shows that the adsorption ability of Fe₃O₄–HA is much higher than both Fe₃O₄ and HA.

![Figure 3](image-url)  
**Figure 3.** Effect adsorbate concentration on the adsorption of MG on adsorbent (initial MG concentration 10 mg L; solution volume 10 mL; adsorbent dose 0.01 g)

4. Conclusion
Magnetite (Fe₃O₄) coating HA to form Fe₃O₄-HA adsorbent for the adsorption of malachite green dye has been successfully prepared through coprecipitation method. The coating of HA on Fe₃O₄ increased surface area, and maximum concentration adsorbate malachite green. The optimum adsorption of malachite green by HA occurred at pH 3 for 60 minutes, with a concentration of 96.95 mg/L. Magnetite adsorbs optimally at pH 7 for 90 minutes and a concentration of 83.48 mg/L. Fe₃O₄-HA adsorbs optimally occurs at pH 3 for 90 minutes with a concentration of 104.15 mg/L.

Acknowledgement
The authors would like to thank Universitas Negeri Semarang Indonesia for providing financial support through a basic research grant, contract number SP DIPA-023.17.2.677507/2020

References
[1] Raval NP, Shah PU, Shah NK 2016 *Water Conserv Sci Eng.* 1 69.
[2] Zhou Y, Min Y, Qiao H, Huang Q, Wang E, Ma T 2015 *Int J Biol Macromol.* 74 271
[3] Madrakian T, Afkhami A, Ahmadi M, Mondal P, Anweshan A, Purkait MK 2020 *Chemosphere* 152 106
[4] Keyhanian F, Shariati S. 2016 *Arab J Chem.* 9 S348
[5] Tajali Rad F, Kefayati H, Shariati S 2019 *Appl Organomet Chem.* 33
[6] Khan MY, Mangrich AS, Schultz J, Grasel FS, Mattoso N, Mosca DH 2015 *J Anal Appl Pyrolysis* 116 42
[7] Sulistyaningsih T, Santosa SJ, Siswanta D, Rusdiarso B 2017 *Int J Mater Mech Manuf.* 5 16.
[8] Rashid M, Price NT, Gracia Pinilla MA, O’Shea KE 2017 *Water Res.* 123 353.
[9] Faisal AAH, Abdul-Kareem MB, Mohammed AK, Naushad M, Ghfar AA, Ahamad T 2020 *J Water Process Eng* 36 101373.
[10] Tang Z, Zhao X, Zhao T, Wang H, Wang P, Wu F 2016 *Environ Sci Technol*.
[11] Koesnarpadi S, Santosa SJ, Siswanta D, Rusdiarso B 2017 *Indones J Chem* 17 274
[12] Sulistyaningsih T, Santosa SJ, Siswanta D, Rusdiarso B 2016 *Indones J Chem.* 16
[13] Mert EH, Yildirim H, Üzümçü AT, Kavas H *React Funct Polym.* 2013 73 175
[14] Azhar U, Huyan C, Wan X, Zong C, Xu A, Liu J. *Arab J Chem*. 2019 **12** 559-572.
[15] Gautam RK, Tiwari I. 2020 *Chemosphere* **245** 125553.
[16] Machado W, Franchini JC, de Fátima Guimarães M, Filho JT. 2020 *Heliyon* **6**.
[17] Chen Q, Yin D, Li J, Hu X. 2014 *Environ Toxicol Chem.* **33** 1090-1097
[18] Peng L, Qin P, Lei M, Zeng Q, Song H, Yang J. 2012 *J Hazard Mater* **209** 193.
[19] Singhal P, Jha SK, Pandey SP, Neogy S. 2017 *J Hazard Mater* **335** 152.
[20] Zhang H, Yin M, Shi J, Wang Y. 2015 *J Mol Struct* **1081** 268.