Adsorption of Methylene Blue onto a Low-Cost And Environmental Friendly Goethite

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Abstract. The commercial adsorbent has been widely used for dye removal, but it is non-economical. The objective of this study is to synthesize a low-cost and environmental friendly goethite as an adsorbent for methylene blue removal from aqueous solution using a batch-adsorption technique. Goethite was synthesized by adding sodium hydroxide to iron salt and aging at 40 °C for 7 and 21 days, then characterized by Infrared spectroscopy (FTIR) and x-ray diffraction (XRD). The results showed that the optimum concentration of adsorbed methylene blue was 300 mg/L with an adsorption capacity of 82.81 and 75.8 mg/g for GPA7 and GT7, respectively. The equilibrium data fit the Langmuir isotherm model with correlation efficient higher than 0.99. Based on cost analysis, GT7 was the cheapest adsorbent, compared to GPA7 and commercial goethite.

Keywords: adsorption, cationic, dye, economical, eco-friendly, waste.

1. Introduction
Methylene blue is one of the cationic thiazine dyes that is deep blue in the oxidized state. It often used in the textile industry because of its efficiency and easy to obtain. In coloring, this dye only used about 5%, while the remaining 95% will be disposed of as waste. This compound is so stable that it is difficult to degrade in nature and very dangerous for the environment. It can increase the value of chemical oxygen demand (COD), which can damage ecosystem balance [1]. The use of methylene blue can cause several effects, such as irritation of the digestive tract if swallowed, causes cyanosis by inhalation, and skin irritation if touched by skin [2]. Therefore, the use of methylene blue regulated in Kepmen LH No. KEP-51/MENLH/10/1995 concerning the establishment of a methylene blue maximum limit in waters is 10 ppm [3], so treatment efforts are needed waste methylene blue dye to reduce its concentration in the environment. Most dyes have a very aromatic molecular structure stable in the environment, and its large molecular size makes it difficult to biologically treated. Thus, the removal of dyes in liquid waste still a big problem. At present, the handling of dye waste is still not said to be useful due to a lack of awareness [4], technological limitations, and relatively expensive treatment costs [5].

Methylene blue removal had been conducted by several methods such as filtration[6], flocculation [7], decolorization [8], and adsorption [9]. Adsorption is one of the best ways to overcome dyestuff pollution. The adsorption method is often used for waste management because it is more efficient and...
easy to apply [10,11]. Adsorbents for textile dye adsorption are currently being developed. The use of synthesized goethite as an adsorbent material has been done to adsorb methylene blue as cationic waste because this material is stable and found in nature and easily synthesized [12,13]. Goethite can adsorb cations because it has positive and negative charges at a certain pH.

Some studies have switched from using synthetic materials to natural adsorbent materials to get cheap adsorbents on adsorption of dye wastes, such as peat, mud activated, banana juice, natural manganese minerals, oil ash flakes, natural zeolite, and a mixture of fly ash with soil [14]. But these adsorbents can be obtained only in a specific location while the synthetic materials can be easily synthesized. The commercial goethite is expensive compared to the natural one, so it was hard to apply in industrial-scale. Hence, this study aims to synthesis goethite using low-grade starting material as an economical and environmentally friendly adsorbent and its ability to remove methylene blue from aqueous solution. Adsorption isotherm and cost analysis were also analyzed and discussed in this paper.

2. Method

2.1. Synthesis of goethite
Goethite was prepared by adding 90 ml of 2.5 M NaOH solution with continuous stirring to 50 ml of 0.5 M FeNO₃·9H₂O solution in the beaker. The mixture was immediately diluted to 1 L with water and capped. The mixture solutions were aged at 40 °C for 7 and 21 days. After reaction time, the precipitates were formed and washed with distilled water until the supernatant pH reached neutral. Then the products were dried at 40 °C for 24 h. The synthesized product was namely GPA7 and GPA21. The same procedure was conducted using FeCl₃ as an iron ion source, and the products were namely GT7 and GT21.

2.2. Adsorption Analysis
A total of 10 ml of methylene blue solution with various concentrations was put into a test tube containing 0.03 g of adsorbent. The mixture was shaken and left for 24 hours. Then the mixture was centrifuged at 1792 G for 10 minutes. The supernatant obtained was determined using UV-Vis spectrophotometer Jenway 7300 at a maximum wavelength of 664 nm. The adsorption capacity was determined using the following equation (1).

\[ q_e = \frac{V(C_e - C_0)}{m} \]  \hspace{1cm} (1)

Where \( q_e \) is adsorption capacity (mg/g), \( V \) is the volume of solution (ml), \( C_0 \) is the initial of methylene blue concentration (mg/L), \( C_e \) is the equilibrium of methylene blue concentration (mg/L), and \( m \) is the weigh of goethite (g).

Adsorption isotherm data were determined by Langmuir isotherm: \( \frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \)

and

Freundlich isotherm: \( \log(q_e) = \frac{1}{n} \log(C_e) + \log(K_f) \)

Where \( K_L \) is Langmuir equilibrium constant (L/g), \( q_m \) is maximum adsorption capacity (mg/g), \( K_f \) is Freundlich equilibrium constant (L/g), and \( n \) is Freundlich exponent.

3. Result and Discussion

3.1. Goethite
Goethite (α-FeOOH) can be found in nature in the form of sediments and also be synthesized in the laboratory by reacting iron ion with a base. The hydroxylation, olation, and oxolation reactions involved in the formation of goethite. The goethite can be synthesized by using pro analysis chemicals (p.a) or low-grade chemicals. The pro analysis chemicals have high purity and more expensive than low-grade materials. The synthesis of goethite can be conducted by incubating the sample at the 40 °C for 3 weeks [15]. In this study, the incubation was carried out for 7 and 21 days (3 weeks). Figure 1 shows the
difference in the color of the products, where the goethite synthesized using pro analysis material has a lighter color than the low-grade goethite. Goethite formed by the pro analysis chemicals has a yellow-brownish color, while low-grade chemical was black. The impurities contained in the low-grade chemical has affected in the color product. However, the longer the synthesis time, the color of the goethite formed becomes brighter (figure 1).

Figure 1. Synthesized powder of pro analysis (GP) and low grade (GT) goethite a) GT21 b) GT7 c) GPA21 dan d) GPA7.

3.2. Characterization of Goethite
The XRD diffractogram peaks of all analyzed samples were following pure goethite based on the database in the match application. According to the database, goethite has a typical diffractogram peak with 20 values (ca. 18°, 21°, 26°, 33°, 35°, 37°, 40°, 41°, 53°, 57°, 59°, 59°, 61°, 64°). The analysis showed that the goethite synthesized for 7 and 21 days had the same diffractogram peak (figure 2), but the degree of crystallinity was significantly different (table 1). These results are also consistent with previous studies [16,17,18]. The degree of goethite crystallinity increases with the increasing time of the incubation sample (table 1). The existence of small diffractogram peaks in XRD analysis indicates that the product contains not only goethite but also amorphous materials. This amorphous form can exist in the precipitation phase because there are some steps to form goethite. Therefore, even starting material in low-grade used is not so affect in goethite formation because amorphous peaks are formed either on the p.a goethite pro analysis or low-grade goethite.

Table 1. The percentage of goethite’s crystallinity degree.

| Sample | Crystallinity Degree (%) |
|--------|--------------------------|
| GPA21  | 65.69                    |
| GT21   | 56.03                    |
| GPA7   | 54.20                    |
| GT7    | 45.26                    |

Figure 2. Diffractogram peaks of pro analysis goethite and low-grade goethite.
Characterization of goethite using FTIR was carried out to see the functional groups in goethite. The peaks found in the range 621-632 cm\(^{-1}\) indicate the presence of FeO octahedral lattice. The peak at 786-791 indicates the presence of Fe-O-H vibrations. There is a broad peak centered around 3101-3118, indicating to the goethite hydroxyl group. In goethite pro analysis (GPA7 and GPA21) samples, the presence of NO\(_3^-\) residues from washing was detected at wave number 1400 cm\(^{-1}\) (Figure 3). The spectra of GT7 and GT21 showed wave numbers around 1300-1570 and 1575-1650, which indicate the possibility of the -C-NO\(_2\) and amine groups as the following materials [18]. This is because the material used to form goethite has a low purity level (figure 3).

3.3. The adsorption capacity of methylene blue
The determination of adsorption capacity was carried out by varying the concentration of methylene blue from 50-500 mg/L. There was no significant difference between the adsorption capacity of the pro analysis goethite and the low-grade goethite synthesized for 7 days with a difference in the degree of crystallinity of ~ 10% (figure 4). There was a significant increase at the beginning of the curve because the increase in the concentration of adsorbate during adsorption caused the interaction of methylene blue cation with goethite was high. The interactions between goethite and methylene blue occurred on many sides, thus accelerating the adsorption of methylene blue on goethite surfaces.

![Figure 3. FTIR spectra of low-grade a) and pro analysis goethite b).](image1)

![Figure 4. The adsorption capacity of goethite.](image2)
The adsorption of methylene blue was conducted in isoelectric point, pH 7, where goethite negatively charge. Goethite electrostatically attracted the methylene blue, which has an opposite charge to the carrier surface [19]. The mechanism of the adsorption is proposed in figure 5.

![Figure 5](image)

Figure 5. Goethite polyhedral framework (blue line represents unit cell) a) and methylene blue adsorption onto goethite surface b).

Adsorption capacity is carried out over 24 hours when the adsorption is in equilibrium conditions. The equilibrium model used in this study is the Langmuir and Freundlich. Langmuir's equilibrium shows that the adsorption monolayer in which the adsorbate molecule is absorbed has the same adsorption activation energy on the monolayer adsorbent surface. Freundlich's equilibrium applies to multilayer adsorbents with heterogeneous surfaces in which adsorbates are absorbed on the adsorbent through interactions and occur physically. Based on table 2, the results of the synthesis of goethite using pro analysis and low-grade materials follow Langmuir's equilibrium with a correlation value of $R^2 > 0.99$. The saturation capacity value and the Langmuir are GT7 higher than GPA7.

| Isoterm   | Parameter      | Adsorbent | GPA7  |
|-----------|----------------|-----------|-------|
|           | Adsorbed       | GT7       | GPA7  |
| Langmuir  | $K_L$ (L/g)    | 0.0125    | 0.0115|
|           | $Q_{max}$ (mg/g) | 76.2800   | 83.8500|
|           | $R^2$          | 0.9988    | 0.9997|
| Freundlich| $K_L$ (L/g)    | 0.2977    | 0.2583|
|           | $R^2$          | 0.8713    | 0.9204|

### 3.4. Cost analysis of adsorbents

This study analyzed the cost of synthesized goethite as an adsorbent and compared it with commercial goethite [20]. The total cost for the preparation of each adsorbent is given in table 3. To produce 1 kg of adsorbent, the total cost required is IDR 8,437,319 and 205,000 for the GPA and GT7, while the price of 1 kg of commercial goethite is IDR 1,724,710/kg. Based on the adsorption capacity obtained for all adsorbents, the price for removing 1 kg of methylene blue in the water is IDR 2,531,196 and 61,500 for GPA7 and GT7, respectively. This shows that the cost of GT7 is the cheapest compared to GPA7 and commercial goethite. Hence, GT7 can be chosen as the lowest cost of adsorbent to better adsorb methylene blue and replace commercial goethite.
Table 3. Cost of the adsorbent for the removal of 1 kg of methylene blue from the water

| Adsorbent           | Adsorption capacity (mg/g) | Cost of chemical used for synthesis/kg (IDR) | Cost of goethite (kg/IDR) | Cost of the adsorbent for removal of 1kg of Metblue (IDR) |
|---------------------|---------------------------|---------------------------------------------|---------------------------|---------------------------------------------------------|
| GPA7                | 82.81                     | 1,774,234                                   | 8,437,319                 | 2,531,196                                               |
| GT7                 | 75.8                      | 35,000                                      | 205,000                   | 61,500                                                  |
| Commercial goethite |                           |                                             |                           |                                                         |

4. Conclusion
Goethite was successfully synthesized by using iron salt and base compound confirmed by FTIR dan XRD results. The adsorption capacity of GPA7 and GT7 were 82.81 and 75.8 mg/g respectively. The synthesized of low-grade goethite has the lowest economic cost for adsorbent which is GT7 is 8 times cheaper than commercial goethite and 41 times cheaper than GPA7. Hence, GT7 can be applied for adsorption on a big scale.

5. References
[1] Riyanto, Sidiq N Y and Hidayah N 2017 AIP Conference Proceeding 1911.
[2] Hamdaoui O and Chiha M 2006 Acta Chim. Slov. 54.
[3] Kepmen LH No. KEP-51/MENLH/10/1995, Tanggal 23 Oktober 1995 Tentang Baku Mutu Limbah Cair Bagi Kegiatan Industri
[4] Rahmawati D and Alpiana 2018 Jurnal Ulul Albab 22 1.
[5] Kusumadewi R Y and Bagastyo A Y 2016 Jurnal Teknik ITS 5 2.
[6] He S, Fang H and Xu X 2016 Korean Journal of Chemical Engineering 33 4.
[7] Yie Lau Y, Shian Wong Y, Tow Teng T, Morad N, Rafatullah M and An Ong S 2015 Royal Society of Chemistry Advance 5.
[8] Ogino C, Dadjou M F, Iida Y and Shimizu N 2008 Hazardous Material 153.
[9] Abidin Z, Triawati AH, Sugirti S, Fahmi AG, Prapajutra V and Kharisma D 2018 IOP Conference Series: Earth and Environmental Science 187.
[10] Samiey B, Cheng C H and Wu J 2014 Materials 7.
[11] Liang T, Yan C, Li X, Zhou S and Wang H 2018 Water Science and Technology.
[12] Jaiswal A, Banerjee S, Mani R and Chattopadhyaya M C 2013 Journal of Environmental Chemical Engineering. 1.
[13] Zhong Y, Sheng D, Xie D, Li G, Li H, Han X, Xie W and Oh W C 2019 Journal of the Korean Ceramic Society 56 2.
[14] Yavuz O and Aydin A H 2006 Polish Journal of Environmental Studies 15 1.
[15] Kugbe J, Matsu N and Henmi T 2009 Journal of Hazardous Materials 164.
[16] Thies-Weesie D M E, Hoog J P, Mendiola M H H, Petukhov A V and Vroege G J 2007 Chemical Material 19.
[17] Shou Q, Cheng J, Zhang L, Nelson B J, and Zhang X 2012 Journal of Solid State Chemistry 185.
[18] Garcia M V, Arzate M U, Escobar K V, Villalobos M, Zanella R and Villegas N M 2015 Sociedad Geologica Mexicana 67 3.
[19] Gayathri K and Palanisamy N 2019 Separation Science and Technology
[20] Gupta M, Gupta H and Kharat D S 2018 Environmental Technology & Innovation. 10.

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