Synthesis of Magnetite/Volcanic Soil Composite from West of Java and Its Adsorption Properties

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Abstract. Adsorption is a cost-effective method that is successfully used to remove dyestuff from waste. However, this method requires filtering that takes a long time to separate the adsorbent medium. The Fe₃O₄/Volcanic soil composite was prepared to obtain adsorbates that can respond to the magnetic field so that the adsorbate is easily separated from the adsorbent medium after adsorption. The experimental results showed that physical mixing has adsorption capability better than composite. However, the physical mixing has weaker magnetic strength such that in the adsorbate separation process from the adsorbent medium can not be performed using a magnet. The composite has a homogeneous surface and can adsorb only one adsorbate molecule for each of its adsorbate molecules as evidenced by the obtained Langmuir isotherm.

Keywords: adsorption, volcanic soil, Fe₃O₄, composite, isotherm

1. Introduction

Synthetic dyes are more widely used than natural dyes in textile, plastics and cosmetics industries. It is due to their cost, stability, and color variations compared than natural dyes [1] However, some of these dyes were dangerous because they affect some diseases such as skin irritation, cancer, and liver damage [2]. The presence of reactive dyes which are deliberately discharged into the aquatic environment disrupt underwater life due to the reduced penetration of light is blocked. Therefore, removing dyes from wastewater become concern to improve the quality of environment.

The wastewater treatment can be carried out by several methods such as coagulation, flocculation, reverse osmosis, and adsorption [3]. Adsorption is one of the most successful methods used to remove dyes from wastewater because of its low cost, high efficiency, and easy to operate [4]. The adsorption process with natural materials such as volcanic soils can be used to wastewater treatment. Volcanic soil has high adsorbing ability based on their surface characteristic which contain Si/Al atom. Even volcanic soil can be used as adsorbent, practically it is difficult to separate between supernatant and adsorbent with short time.

To improve the capability of volcanic soil as adsorbent, it was modified by composting the volcanic soil with magnetite (Fe₃O₄). Magnetite is the strongest magnetism among other iron oxides that widely used in various fields. Some methods have been used in magnetite synthesizing (Fe₃O₄),
such as CVD (chemical vapor deposition), electrodeposition, hydrothermal, and solvothermal, co-precipitation, and decomposition of high temperature organometallic precursors [5]. The method used in this research is co-precipitation because it is simple, easy and low temperature [6]. The present study was focussed to synthesis of magnetite with volcanic soil as composite and its ability in separating with supernatant.

2. Experimental

2.1 Materials

Volcanic soil sample has been taken from Bubulak, Bogor, West of Java. Fe(NO$_3$)$_3$,9H$_2$O, FeCl$_2$.5H$_2$O, NaOH, methylene blue have been purchased from Nacalai Tesque Chemical with pa. quality.

2.2 Methods

2.2.1. Preparation of Magnetite (Fe$_3$O$_4$). Magnetite was prepared by mixing 1:2:10 mol ratio of Fe$^{2+}$, Fe$^{3+}$, and hydroxyl ions, respectively [7]. After stirring for 30 minutes, the black precipitate formed and the final pH was 12. The product was washed with distilled water until pH became 8 and dried in the oven at 80°C for 4 hours.

2.2.2. Preparation of Magnetite/Volcanic Soil Composite. The volcanic soil sample was dried and grained to obtain a size of 100 mesh. One gram of the volcanic soil sample was added into a mixture of iron ions contain 1:2 mol ratio of Fe$^{3+}$ and Fe$^{3+}$ and then stirred until homogeneous. Sodium hydroxide was added slowly into the mixture to increase the pH became 12 and formed a black precipitate. The product was washed with distilled water until pH became 8 and dried in the oven at 80°C for 4 hours. For comparison material, we used two kinds of samples. First, the volcanic soil sample treated with sodium hydroxide at pH of 12. The second sample was physical mixing by simple mixing between magnetite and volcanic soil sample treated with sodium hydroxide at pH of 12.

2.2.3 Analysis of Methylene Blue Adsorption. Several concentrations of methylene blue were prepared from 0 to 300 ppm. Twenty-five mg of volcanic soil, volcanic soil treated with natrium hydroxide, and composite samples were added to methylene blue solution with different concentrations. After 24 hours shaking, centrifugation was carried out and the filtrate was determined using a 20D ± spectrophotometer at 668 nm. The obtained data were used to calculate their adsorption capacity and it was analyzed by using Freundlich and Langmuir equations.

3. Result and Discussion

3.1 Synthesis of Magnetite

The synthesis of magnetite in this study using co-precipitation method. The substance most commonly used as a precipitating agent in Fe$_3$O$_4$ co-precipitation is hydroxide ions. The present study used sodium hydroxide because of its ability to form magnetite, meanwhile weak base such as ammonia solution will produce hematite ($\alpha$-Fe$_2$O$_3$) [8]. Synthesis of magnetite with co-precipitation method has two reaction steps.

The first reaction was occurred at pH 2 to 4 and followed by the second reaction in pH 8 to 9. The addition of sodium hydroxide to the Fe$^{3+}$ and Fe$^{3+}$ mixture initially formed brown precipitate which indicated the formation of Fe(OH)$_3$ in the first reaction. The second reaction formed dark brown of Fe(OH)$_2$ precipitation. The addition of sodium hydroxide excess results the color of precipitation turned black with pH 12 indicating Fe$_3$O$_4$ was formed. Here, we used the excess of sodium hydroxide to make sure that all of iron ions reacted to form magnetite. The formation of magnetite reaction is shown by chemical reaction below.

$$\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe(OH)}_2 + 2\text{Fe(OH)}_3 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$
The simple method to know magnetite formed is used the neodymium magnetic bar. The black precipitate was attached strongly to this magnetic indicated the formation magnetite and shown in Figure 1. The strength of magnetic product obtained is to be paramagnetic because, with the small magnetic field, the magnetite can be attracted even though it is not directly with the magnet.

![Figure 1](image1.png)

**Figure 1** Synthetic product was attracted to the magnet

### 3.2 Magnetite/Volcanic Soil Composite

The formation of composites purpose to obtain materials that have new properties from their original samples. The preparation of composite was carried out with the similar procedure as magnetite synthesis. However, the color of product was not extensive compared to magnetite which has black color. Also, to reach the final pH became 12, it was needed the excess of sodium hydroxide than in magnetite synthesis. It is due to hydroxy ions not only react with Fe$^{2+}$ and Fe$^{3+}$ ions, but it also reacted with the surface of volcanic soil sample.

This process is very interesting because there is synergy between magnetite formation on the surface of volcanic soil, also the formation of new negative charge on the surface of volcanic soil. As been known that volcanic soil contains some amorphous material with negative charge namely silanol group in the surface. The negative charge on the surface has the possibility to react directly with Fe$^{2+}$ and Fe$^{3+}$ ions resulting magnetite bonded in the surface. The proposed mechanism of composite formation is shown in Figure 2.

Magnetite/volcanic soil composite sample can be attracted by the neodymium magnetic bar. However, the strength of magnetic composite products obtained was not so strong compare to magnetite. It is possible that interaction between magnetite with silanol group in the surface of volcanic soil caused decrease in the strength of magnetic.

![Figure 2](image2.png)

**Figure 2** Proposed mechanism of formation composite
Physical mixing was made by direct mixing between the volcanic soil treated with sodium hydroxide and magnetite obtained from the previous synthesis. The volcanic soil treated with sodium hydroxide and magnetite ratio were 1:1 by weight. This weight ratio is referred to the previous result which is the ratio of magnetite with volcanic soil composite was 1:1.

Figure 3 shows that the strength of magnetics of composite and physical mixing samples. The composite sample can be attracted to neodymium magnetic bar. On the other hand, magnetite and volcanic soil can be separated well on the physical sample. Here we can see that there are differences of properties between composite and physical mixing samples.

3.3 Adsorption Capacity

The determination of adsorption ability can be known from its adsorbent capacity. Generally, for all samples have the same trend for adsorption patterns. The adsorption curve shows a significant increasing early stage adsorption and then the curve begins constant after reaching equilibrium concentration as shown in Figure 4.

In the initial stage, the methylene blue as cations can interact with the surface of adsorbent easily. The active site is available and easily access for methylene blue attached to it. Therefore, the amount of methylene blue adsorbed increase sharply. After almost active sites on the samples have already occupied, the capability of methylene blue to bind on the surface became decrease. In other words, the equilibrium between adsorption and desorption occurred.

Results showed that the adsorption capacity on the volcanic soil and magnetite samples is similar and lower than composite sample. The adsorption capacity was 15 and 18 mg/g for magnetite and volcanic soil, respectively. Methylene blue has the positive charge in the structure and interacts to the negative charge of the surface on volcanic soil.

![Figure 4 Adsorption capacity of Bubulak volcanic soil](image-url)
Magnetite has also the ability to adsorb methylene blue. The adsorption of magnetite depends on the pH of solution [7]. Higher pH induced the formation of FeO\(^+\) ions on the surface of magnetite. This negative charge will undergo electrostatic interaction with a positive charge on methylene blue. However, the capability of composite has increased two times on the composite sample compared to magnetite and volcanic soil samples. It is possible to form a new negative charge on the surface of composite during synthesis.

On the other hand, volcanic soil treated sodium hydroxide has higher capacity to adsorb methylene blue. Once again, the reaction of volcanic soil with sodium hydroxide has facilitated for the formation of active site on the surface. If we compared between composite and volcanic soil treated sodium hydroxide samples have different behavior on adsorption. Volcanic soil with sodium hydroxide has the capability to adsorb methylene blue fastly. It means methylene blue easily interacted to the active sites. Meanwhile, methylene blue molecule gradually adsorbed on the surface of composite sample. This surface not so easily accessed by methylene blue molecule.

For physical mixing sample, the capability of adsorption of methylene blue was highest compared for all samples used. This capability was contributed almost from volcanic soil treated sodium hydroxide and magnetite samples. However, physical mixing sample is just simple mixing and difficult used it for the application. Even the capability adsorption of composite is lower than physical mixing, it seems easily used for application as shown in Figure 5.

**Table 1** Linearity of Freundlich and Langmuir isotherms of volcanic soil, magnetite, volcanic soil treated sodium hydroxide, composite and physical mixing

| Samples                      | \(R^2\)          | \(R^2\)          |
|------------------------------|------------------|------------------|
|                              | Freundlich       | Langmuir         |
| Volcanic soil                | 0.7715           | 0.9986           |
| Volcanic soil + NaOH         | 0.8975           | 0.9994           |
| Magnetite                    | 0.7509           | 0.9988           |
| Composite (chemical)         | 0.8737           | 0.9989           |
| Physical mixing              | 0.9038           | 0.9998           |

The adsorption of the liquid-solid phase generally refers to Freundlich and Langmuir isotherms [9]. The results showed that volcanic soil, magnetite, volcanic soil treated sodium hydroxide, composite and physical mixing samples followed Langmuir isotherm type. This is indicated by the linearity value of the Langmuir isotherms higher than the Freundlich isotherm linearity (Table 1). Langmuir's isotherm type indicated that the bonding between the methylene blue and the adsorbent surface is a chemical interaction. This interaction also has a homogeneous surface, so it can adsorb only one adsorbate molecule for each of its adsorbent molecules.
4. Conclusion
Magnetite/volcanic soil composite can be synthesized using Fe$^{2+}$ and Fe$^{3+}$ ions by co-precipitation method. Composite can be attracted by the neodymium magnetic bar. The strength of magnetic composite is lower than magnetite. Composite has higher adsorption capacity than original volcanic soil. The adsorption isotherm of composite followed Langmuir isotherm. Composite which adsorbed methylene blue can be easily separated by using the neodymium magnetic bar for the supernatant.

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