Adsorption and decomposition of cationic dye by using goethite-polyacrylate composite

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Abstract. The adsorption of cationic dye has been widely carried out by using polyacrylate, but it has a low ability to degrade the dye. On other hand, goethite has the opposite properties. This study aims to synthesis the composite of goethite-polyacrylate and its application for adsorption and degradation of methylene blue dye. The composite was synthesized by aging goethite at 40 °C for 7 days, polyacrylate then was added to goethite and the aging process was continued until 21 days. The synthesized composite was characterized by using Fourier Transform Infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The result indicated that the composite has better adsorption capacity compared to goethite with the uptake of adsorbed methylene blue is 625 mg/g. The equilibrium data fit the Langmuir isotherm model correlation efficient higher than 0.99. Goethite-polyacrylate composite efficiently degraded the methylene blue compared to polyacrylate. The combination of goethite and polyacrylate improved the properties of the material which has good adsorption and degradation performance.

1. Introduction

Indonesia is one of the countries experiencing rapid development of the textile industry, reinforced by the award of batik as an intangible cultural heritage from the United Nations of Educational, Scientific, and Cultural Organization (UNESCO) [1]. Based on data, the total textile production continues to increase from 2012 to 2017, which amounted to IDR 116.56 trillion to IDR 150.43 trillion [2]. Even though the textile industry has a good economic impact on the country, the use of dyes in dyeing fabrics creates serious environmental problems as the number 2 producer of water pollutants after agriculture. This is because the textile industry uses a lot of chemicals and large amounts of water in various textile manufacturing processes including dyeing and printing. Daily water use in the textile fabric is around 1.6 million liters for the production of 8000 kg of cotton. This process contributed to about 15% of wastewater to the environment from the dyeing section [3].

The disposal of the dye, such as methylene blue to the environment causes some effects to the human being through the food chain, the ambient environment, fishes and sea life, and the plant life [4]. The impact of this damage was contributed by the dye molecules that are generally stable in the environment and are difficult to degrade by microorganisms in nature due to its large molecular size so that the
treatment of the dye is very important to do. The previous study has been conducted some methods to treat the dye through adsorption [5], coagulation [6], filtration [7], and flocculation [8]. The common method used is adsorption because it is effective and efficient [9,10]. The limitation of adsorption is its post handling where the dye waste is only transferred in the form of different phases without really remove the waste.

Various materials were used to adsorb methylene blue, but not all of them have the decomposition ability. So the development of adsorbent material is needed. Sodium polyacrylate is a good adsorbent for cationic pollutants due to its abundance of anionic carboxyl groups but it can not degrade the pollutant. On another hand, goethite has high decomposition capability even though has not good adsorption performance. The combination of these materials is expected to provide good adsorption and decomposition capability of cationic dye [11, 12].

2. Method

2.1 Materials
Materials used in this study were sodium polyacrylate (BM ~ 1200 g/mol) that purchased from Sumitomo Seika, Japan and methylene blue was purchased from Nacalai Tesque, Japan. \( \text{H}_2\text{O}_2, \text{FeCl}_3, \) and \( \text{NaOH} \) was purchased from Brataco Chemical, Indonesia.

2.2 Synthesis of goethite-polyacrylate composite
The composite of goethite-polyacrylate was prepared by adding 9 ml of \( \text{NaOH} \) 2.5 M solution to 5 ml of 0.5 M \( \text{FeCl}_3 \) in the polyethylene sampling cup then diluted to 100 mL using distilled water. The cup was capped to avoid evaporation and heated at 40 °C for 7 days [13]. As many as 300 mg polyacrylates were added to the goethite sample and the incubation process then continued until day 21. The mixture was shaken every day so that the sample mix well. The precipitate was rinsed until the pH reached near 7 and dried in an oven.

2.3 Adsorption Analysis
A 10 mg adsorbent was put into 8 centrifuged tubes and 2 ml of methylene blue solution was added for each tube with various concentrations, then the mixture was shaken. The adsorption process was conducted for 24 hours at room temperature. After that, the supernatant was determined its absorbance using Biochrome Libra S11 Visible spectrophotometer at 665 nm as maximum wavelength. The adsorption capacity was calculated by using equation (1). Where \( q_e \) represents adsorption capacity (mg/g), while \( V, C_0, C_e, \) and \( m \) are volume of cationic dye (ml), initial of methylene blue concentration (mg/L), the equilibrium of methylene blue concentration (mg/L), and the weigh of composite (g) respectively [14].

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

Furthermore, Langmuir and Freundlich adsorption isotherm was determined following equation (2) and (3) respectively [15].

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]

\[
\log (q_e) = \frac{1}{n} \log (C_e) + \log (K_f)
\]

2.4 Decomposition Process
The decomposition process was conducted after the adsorption analysis was done. The sample used was an adsorbent that had absorbed 200 ppm of methylene blue After 24 hours of adsorption, the supernatant and adsorbent were separated. A total of 2 drops of 30% \( \text{H}_2\text{O}_2 \) was added to the adsorbent then observed after 24 hours. The decomposition ability was known by the loss or decrease of methylene blue color.
3. Result and Discussion

3.1. Goethite-polyacrylate composite

Polyacrylate is a polymer that contains an abundance of the carboxyl group (–COO\(^-\)) that interacted with cationic solutes, such as dye and water but this polymer can not degrade the dye. On the other hand, goethite has good degradation ability and low adsorption capacity. The composting of these materials aims to get a composite that has good properties. The resulting sample of synthesized composite gave yellow-brownish gel-solid from brown (goethite) and white (sodium polyacrylate) solids (figure 1). The ferri chloride used in this study as goethite precursor was purchased in low-grade purity to get economically adsorbent. The use of low-grade material has no significant differentiation compare to pro analysis materials [16]. Besides, the used method of this study was different compared to the previous study [17] where the synthesis was conducted by adding polyacrylate on the seventh day of goethite formation then the incubation process was continued until 3 weeks. It aimed to get pure of the goethite-polyacrylate composite without the presence of a cross-linking agent so that it minimized the waste in the rinsing process. The composite was formed by hydrogen interaction and lewis acid-base bonding by sharing an electron pair between Fe atoms of goethite (Lewis acid) and carbonyl group of polyacrylate (Lewis base) (figure 2) [17].

![Figure 1. Synthesized sample of goethite-polyacrylate composite.](image1)

![Figure 2. Reaction of the formation of a goethite-polyacrylate composite.](image2)
3.2. Characterization of Materials

The formed composite and goethite were characterized using X-Ray Diffractometer (XRD) and Transform Infrared Spectrometer (FTIR). The XRD pattern of goethite (G7) and goethite-polyacrylate (K3) is shown in Figure 3. This data was collected using beam Cu Kα radiation and operated at 40 kV and 30 mA with a scanning speed of 2 degrees/min. The result showed that the goethite has specific diffractogram peaks at 2θ (d values) of 18° (4.98), 21° (4.20), 26° (3.37), 33° (2.69), 35° (2.45), 36°(2.44), 40°(2.25), 41° (2.19), 53° (1.72), 57° (1.57), 59° (1.56), 60° (1.53), 64° (1.46). All of these values followed the database in match tools. The intensity of these peaks decreased for composite because it contains polyacrylate which binds to goethite. The presence of short and small diffractogram peaks indicates the intermediate state in the form of amorphous goethite because the iron oxide has not transformed yet become goethite.

![Figure 3. Diffractogram peaks of goethite (G7) and goethite-polyacrylate composite (K3).](image)

FTIR spectroscopy was applied in the characterization of goethite and its composite to know the functional group of the surface of the materials. This process was conducted by grinding the dried sample with KBr (ratio 1:100) then scanned at a wavenumber of 4000 – 500 cm\(^{-1}\). The spectra of goethite and its composite was depicted in Figure 4. The broad peak around 3101-3200 cm\(^{-1}\) originated from the
hydroxyl group-bonded of goethite, while the peak that observed around 621-632 cm\(^{-1}\) corresponded to the octahedral lattice of FeO. The vibration Fe-O-H was observed at wavenumber of 786-791 cm\(^{-1}\) [18]. The formation of the goethite-polyacrylate composite was signed by the presence of the carbonyl group (C-O) that was observed at region 1559 cm\(^{-1}\) and C-C vibration at region 1324 cm\(^{-1}\) [19]. The presence of the C-O band along with the decreasing intensity of Fe-O. So, the spectra proved that the composite consists of goethite and polyacrylate (figure 4).

3.3. The Adsorption Capacity of Methylene Blue

The adsorption capacity was determined by measuring the absorbance of the supernatant of the adsorbed methylene blue with various concentrations from 25–1000 mg/L for 24 hours. The result of this measurement is depicted in figure 5. The adsorption of methylene blue is supported by the presence of Fe–OH (iron hydroxide) on goethite and carboxyl group (–COO\(^{-}\)) on polyacrylate. The curve showed that polyacrylate has the highest adsorption capacity, indicated with the increasing of the curve compared to others that had reached equilibrium condition. The adsorption capacity of polyacrylate is higher than goethite because it has a more active side of the carboxyl group (–COO\(^{-}\)) while the composite has fewer active sites of the carboxyl group because some of them has bound to the goethite [20]. The rapid increase of the curve along with the increasing concentration of adsorbate indicate that the interaction of adsorbent and methylene blue was high where the active site that has strong energy will be easily bound [21].

![Figure 5. The adsorption capacity of adsorbents.](image)

To understand the adsorption phenomena on the surface of composite, the conventional isotherm model of Langmuir and Freundlich isotherm was used in this study. The data table 1 showed that the goethite-polyacrylate fitted the Langmuir isotherm with a correlation value of \(R^2 > 0.99\). It means the molecule of methylene blue is adsorbed on the monolayer and homogeneous composite surface with the same activation energy [22].

| Isoterm  | Parameter (\(R^2\)) |
|----------|---------------------|
| Langmuir | 0.9969              |
| Freundlich | 0.8225            |
3.4 Decomposition of Methylene Blue

The decomposition reaction was carried out using the Advanced Oxidation Processes (AOP) method after the adsorption process was conducted. AOP method is a method used to decompose organic compounds in liquid waste through oxidation reactions with a hydroxy radical attack using ozone, hydrogen peroxide, and ultraviolet light. Synthesized materials were tested in the MB degradation reaction using hydrogen peroxide as an oxidizing agent in the Fenton reaction. The Fenton reaction can occur because of the iron content in the sample. The resulting hydroxyl radical will decompose the methylene blue dye which has been absorbed on the surface of the adsorbent [23].

The decomposition results showed that goethite had better catalytic abilities than composite in decomposing methylene blue because of its abundance of iron. Degradation of the methylene blue dye by using composite is much longer because composite contains polyacrylate as an organic compound. So, the hydroxyl radicals produced by the Fenton reaction first react with polyacrylate in composite and are followed by degradation of the absorbing dyes. Therefore, the decomposition of methylene blue that occurs in the soil is longer than that of synthetic products (figure 6).

Figure 6. The decomposition of methylene blue through Fenton-like reaction.

4. Conclusion

Goethite and goethite/polyacrylate composites successfully synthesized using iron and base precursors based on characterization using XRD pattern and FTIR spectra. Composite has good adsorption capacity compared to goethite but lower than polyacrylate. Goethite has the highest decomposition ability because of its abundant Fe(II)/Fe(III) and can be regenerated while the composite cannot be regenerated because the polyacrylate that acts as its content is destroyed through the decomposition process.

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