Synthesis, Characterization and Photocatalytic Activity of $\alpha$-Fe$_2$O$_3$/Bentonite Composite Prepared by Mechanical Milling

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Abstract. Preparation of $\alpha$-Fe$_2$O$_3$/bentonite composite has been carried out by solid state reaction method by using iron ore from Aceh Besar district, Aceh as hematite source and bentonite from Kuala Dewa, North Aceh. The $\alpha$-Fe$_2$O$_3$ was extracted from iron ore using hydrochloric acid and precipitated using ammonium hydroxide. The $\alpha$-Fe$_2$O$_3$/bentonite composite was prepared by mixing $\alpha$-Fe$_2$O$_3$ and bentonite at 4:1 ratio using ball mill for 2 h. The XRD results showed that the dominant phase of iron ore was magnetite (Fe$_3$O$_4$) and was converted to $\alpha$-Fe$_2$O$_3$ after extracting and calcined at 700 $^\circ$C. The photocatalytic activity of $\alpha$-Fe$_2$O$_3$/bentonite composite was evaluated on degradation of indigo carmine (IC) dye at various condition of pH, photocatalyst mass, initial dye concentration and irradiation time. The results showed that the highest photocatalytic activity of $\alpha$-Fe$_2$O$_3$/bentonite composite was obtained at an initial pH of 1, a photocatalyst mass of 250 mg and an initial dye concentration of 5 mg/L with UV irradiation time for 2 h. The photocatalytic activity of $\alpha$-Fe$_2$O$_3$/bentonite composite using solar light was higher than that of UV light.

1. Introduction
Hematite ($\alpha$-Fe$_2$O$_3$), a nontoxic semiconductor material, is often used as pigment, magnetic materials, sensors and photocatalyst. Hematite is a potential photocatalyst because of stability, low cost and narrow band gap energy (2.1 eV) that exhibits good visible light response. However, $\alpha$-Fe$_2$O$_3$ has drawback such as poor absorptivity and low electric conductivity which yields high charge recombination which implies low photoactivity [1, 2]. In addition, hydrophobic surface of iron oxide particles will result in hydrophobic interactions between particles which in turn will promote the agglomeration of particles and reduce the surface area [3]. Various efforts have been performed to overcome these limitations such as synthesis nanostructure and mesoporous $\alpha$-Fe$_2$O$_3$[4, 5], support or disperse nanoparticle $\alpha$-Fe$_2$O$_3$ within a porous matrix which has high specific surface area such as clay, bentonite and activated carbon and formation of composites. Bentonite, a low-cost material and abundant clay that is primarily composed of montmorillonite are often used as a good support to fabricate photocatalyst composites. These natural materials possess layered structure that consists of two silica tetrahedral sheets fused to one alumina octahedral sheet [6-7]. Synthesis of $\alpha$-Fe$_2$O$_3$ using montmorillonite matrix as a photocatalyst supported was used for oxidation of water has been reported [8].
Photocatalysis has become one of the alternative methods which can be used for environmental remediation and renewable energy. Photocatalysis is the acceleration of the rate of a chemical reaction by activating a catalyst by presence of light (ultraviolet (UV) or visible light). When photocatalyst absorbs light energy, transfer electron from the valence band (VB) to the conduction band (CB) take places and produce electron on CB and hole on VB. The resulting electron and hole can initiate redox reaction or react with oxygen (O\textsubscript{2}) and water (H\textsubscript{2}O) to form strong oxidizing agent superoxide anion (O\textsubscript{2}•\textsuperscript{-}) and hydroxyl radical (•OH), respectively [9-10]. Photocatalytic degradation of organic compounds such as dyes using semiconductor become an efficient method because it can be totally degraded these pollutant and mineralised into CO\textsubscript{2} and harmless inorganic anions [11-12].

Indigo carmine (IC) dye or acid blue 74, an indigoid class of synthetic dye is considered as highly toxic materials. IC can cause skin and eye irritation if contact with it and it has carcinogenic in nature. This dye is widely used in textile, paper and pharmaceutical industries. The discharge of this effluents into the ecosystem induced the environmental problems such as human health, esthetic pollution and perturbation of aquatic life [13].

This work is focused on the preparation and characterization of the α-Fe\textsubscript{2}O\textsubscript{3}/bentonite composite using mechanical process by milling of α-Fe\textsubscript{2}O\textsubscript{3} and bentonite at a certain time. Mechanical milling is a simple and free solvent method that involved the mechanical activation of solid-state chemical reactions displacement. The purpose of milling is to reduce the particle size and blending of particles in new phases [14-15]. α-Fe\textsubscript{2}O\textsubscript{3} can be found naturally as the mineral hematite which can be extracted from iron ore and iron sand. Therefore, α-Fe\textsubscript{2}O\textsubscript{3} used in this study was extracted from iron ore which is one of an abundant natural resources in Aceh province. Characterization of as-prepared materials was conducted by X-ray diffraction (XRD) and scanning electron microscopy energy dispersive X-ray spectroscopy (SEM EDS). Photocatalytic activity of the prepared composite was evaluated by means of photodegradation of indigo carmine (IC). Effect of conditions reaction such as pH of the reaction medium, photocatalyst mass, concentration of substrate and irradiation time on photocatalytic performance were also investigated.

2. Experimental

2.1. Materials

The raw iron ore was taken from PT. Lhoong Setia Mining in Aceh Besar district, Aceh province, Indonesia. Prior to treatment iron ore was separated manually using magnetic bar and was ground in a porcelain ball mill (Planetary mill, Fritch, P6) for 30 min using a rotational speed of 250 rpm to reduce the particle size up to 150 mesh sieve. Bentonite was obtained from Kuala Dewa, North Aceh. Hydrochloric acid (HCl), ammonium hydroxide (NH\textsubscript{4}OH), sodium hydroxide (NaOH) and indigo carmine (C\textsubscript{16}H\textsubscript{8}N\textsubscript{2}Na\textsubscript{2}O\textsubscript{8}S\textsubscript{2}, C.I. = 73015, MW = 466.36 g/mole) of analytical reagent grade were purchased from Merck and were used without further purification.

2.2. Extraction of α-Fe\textsubscript{2}O\textsubscript{3} from iron ore and synthesis of α-Fe\textsubscript{2}O\textsubscript{3}/Bentonite composite

Extraction and synthesis of hematite (α-Fe\textsubscript{2}O\textsubscript{3}) from iron ore using hydrochloric acid and precipitating agent was conducted according to previous works [16-17]. Iron ore sample (50 g) was dissolved in 280 mL of hydrochloric acid solution (6 M) with stirring and heating at 145°C for 30 min. The solution was filtered and ammonium hydroxide 25% was added to the filtrated solution until the pH reaches ~6 at which ferric hydroxide was obtained as a brown precipitate. The precipitate was filtered and washed with distilled water several times. The obtained sample was dried at 100°C for 3 h and calcined at 700°C for 5 h. The α-Fe\textsubscript{2}O\textsubscript{3} obtained was mixed with bentonite in the 4 : 1 weight ratio by mechanical milling method using Planetary mill for 2 h at the milling speed of 350 rpm with the balls to powder mass ratio was 10:1.

2.3 Characterization of materials

The chemical composition of iron ore was determined by X-ray fluorescence (PAN Analytical AXIOS Advance) and the results are represented in wt % of oxides. Phase identification of materials were
determined by powder X-ray diffraction (XRD) patterns recorded on an X-ray diffractometer (Shimadzu) using Cu-Kα radiation (λ = 0.154056 nm) at a scan speed 5 ° min⁻¹ with accelerating voltage and current were 40 kV and 30 mA, respectively and a monochromator at a 2θ angle between 10 to 80 degrees. Average crystallite sizes of materials were calculated by using the Scherrer’s formula (Equation 1), where D is the crystallite size, k is Scherrer’s constant (0.9), λ is the wavelength of X-ray diffraction radiation, FWHM is the full width at half maximum observed from XRD pattern and θ is the Bragg’s angle.

\[
D = \frac{k\lambda}{FWHM \cos \theta}
\]  

(1)

Morphological studies of materials were carried out using scanning electron microscopy (SEM; JEOL microscope model JSM6510LV) at an accelerating voltage of 15 kV, coupled with energy dispersive X-ray spectroscopy (EDS) for elemental analysis.

2.4 Photocatalytic evaluation of α-Fe₂O₃/bentonite composite

The photocatalytic activity of α-Fe₂O₃/bentonite composite was evaluated according to the removal of indigo carmine (IC), a group of dark blue indigoid dye, from solution in various initial pH, photocatalyst mass, initial dye concentration and UV irradiation time. The UV light source was a 6 W UV lamp (λ= 365 nm) and was located 10 cm from the Pyrex glass vessel. The pH of dye solution was adjusted by addition of either 0.1 M HCl or 0.1 M NaOH solutions using a pH meter (HANNA instruments pHep). A mixture of 25 mL of IC solution and photocatalyst with the appropriate amount was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium of IC in the photocatalyst surface before the irradiation. The suspensions were exposed to UV light irradiation for another 2 h and a small aliquot was taken from the system within 0.5 h at different time intervals (0.5, 1.0, 1.5 and 2 h) during the experiment and centrifuged. The remaining IC dye in the filtrate was determined using UV-Vis spectrophotometer (Shimadzu UV mini 1240) at λ_max of 610 nm. The experiment was also conducted without UV irradiation (dark condition) under the same parameter with UV irradiation. All experiments were repeated twice. The removal efficiency (%) of IC was calculated using the formula of Equation (2).

\[
IC\text{ Removal }\% = \left(\frac{C_0-C_t}{C_0}\right) \times 100\%
\]  

(2)

3. Results and Discussion

3.1 Materials Characterization

The chemical analysis of iron ore was obtained from XRF analysis. The results show that iron ore from Aceh Besar district is composed mainly of iron (III) oxide (89.69%), SiO₂ (2.25%) with small amount of MnO₂ (1.41%), CuO (1.01), CaO (0.59%), ZnO (0.12%), MgO (0.12%) and TiO₂ (0.03%) as impurities. Iron (III) oxide in iron ore was extracted by using hydrochloric acid followed by ammonium hydroxide as precipitation agent. The ferric (III) hydroxide obtained was dried and calcined at high temperature (700 °C) in order to convert it into hematite (α-Fe₂O₃) [18-19]. Hematite was mixed with natural bentonite by mechanical milling to produce α-Fe₂O₃/bentonite composite. The phase identification of materials determined by XRD analysis was given in Figure 1. X-ray diffraction patterns of natural iron ore at 2θ = 30.14°, 35.48°, 37.12°, 43.10°, 53.44°, 56.96° and 62.55° represented in Fig 1a attributed to magnetite phase (Fe₃O₄) (Crystallography Open Database (COD) Inorganic 1537396). XRD diffraction peaks indicated at 2θ = 24.22°, 33.24°, 35.70°, 40.94°, 49.56°, 54.16°, 62.66°, 64.16° and 72.04° (Fig 1b) was in accordance with hematite (α-Fe₂O₃) (COD Inorganic 9015964). XRD pattern of natural bentonite (Fig 1d) shows that the reflections corresponding to quartz (SiO₂) are present at 2θ = 20.96°, 23.76°, 26.74°, 36.66° and 60.06° (JCPDS file no. 96-710-3015). This results was confirmed to the chemical analysis that the main constituents of bentonite are SiO₂ (55.76%), Al₂O₃ (25.36%), Fe₂O₃ (10.29%), ZnO (3.89%) and some traces of MgO (1.86), K₂O (1.25%), CaO (1.23%) and TiO₂ (0.36%) [20]. The diffraction peaks of hematite (α-Fe₂O₃) and bentonite can be observed in XRD patterns of α-Fe₂O₃/bentonite composite (Fig 1c) but with the lower
intensity of the main peaks of bentonite due to coorporation of two materials in which bentonite only 25 wt%.

An estimation of the average crystallite size using Scherer’s equation and the full width at half maximum (FWHM) peaks of all samples were listed in Table 1. Hematite (α-Fe₂O₃) has the smallest crystallite size compare to others, while the particle size of α-Fe₂O₃/bentonite composite was slightly higher than that of extracted α-Fe₂O₃. This is probably because of the combination of α-Fe₂O₃ with a higher crystallite size of material (natural bentonite = 72.59 nm) and agglomeration of α-Fe₂O₃/bentonite composite due to the high-energy impact between miling balls and the mixture.

![X-ray diffraction patterns](image)

**Figure 1** X-ray diffraction patterns of a) Iron ore b) Extracted α-Fe₂O₃ c) α-Fe₂O₃/bentonite composite and d) Bentonite

**Table 1** Crystallite size and elemental analysis of studied materials

| Sample                          | Particle size (nm) | Element (wt%) |
|---------------------------------|--------------------|---------------|
|                                 |                    | Fe  | Si  |
| Iron ore                        | 51.02              | 77.16 | 2.25 |
| Hematite                        | 44.37              | 90.93 | 0.48 |
| Bentonite                       | 72.59              | 3.84  | 62.01 |
| α-Fe₂O₃/bentonite composite     | 47.32              | 73.05 | 11.42 |
3.2 Photocatalytic activity measurement

Photocatalytic activity is determined by two mechanisms that rely on each other (i.e. the effect of photocatalytic surface and the interaction between light and the photocatalyst leads to generate electron (e\(^-\)) and hole (h\(^+\)) pairs [21]. The electron or hole will be trapped and migrated to the photocatalyst surfaces where it will play a role in reduction and oxidation reaction with the adsorbed molecules, which inhibits the recombination of electron and hole and increases the photodegradation efficiency [22-23]. The photocatalytic activity is also influenced by conditions reaction such as pH of the reaction medium, photocatalyst mass and concentration of dye [24].

Effect of initial pH of dye solution and Photocatalyst Mass

The effect of pH on the photocatalytic degradation of IC over α-Fe\(_2\)O\(_3\)/bentonite composite was evaluated by varying the initial pH equal to 1-5. Fig 3a exhibited that the lower the pH of initial solution the greater the removal efficiency of IC. As can be seen, the maximum removal efficiency of IC was achieved at pH equal to 1. This may be due to the fact that the pH of dye solution not only affects the surface charge of photocatalyst but also the degree of ionization of dye molecule [25]. In the acidic solutions, the surface charge properties of α-Fe\(_2\)O\(_3\) change to the positive charge (FeOH\(^+\)). IC is anionic dye due to the negatively charged of sulphonate (SO\(_3\)\(^-\)) group [26] which can easily adsorbed on the positively charge of α-Fe\(_2\)O\(_3\). In addition, bentonite has a net negative surface charge due to the isomorphous substitution of Al\(^{3+}\) for Si\(^{4+}\) in the tetrahedral sheet and Mg\(^{2+}\), Fe\(^{2+}\) and other cations for Al\(^{3+}\) in the octahedral sheet [27], but at a lower pH (< 2) the surface of bentonite tend to positively charged increase in adsorption takes place for IC molecule. Increasing of IC molecule on the photocatalyst surface lead to increase of photodegradation of IC. It has been reported that dye adsorption process on the photocatalyst surface is an important step in photodegradation [28]. The greater the molecule adsorbed, the greater amount of IC molecule will react with •OH, hole, electron or O\(_2\)•\(^-\) in photocatalysis. At higher pH values the adsorption decrease due to repulsion between the anionic dye molecules and negatively charged surface, as the result the removal efficiency of IC due to photodegradation process decrease.
Figure 3 Degradation of IC over α-Fe₂O₃/bentonite composite as a function of UV irradiation time. 
  a) Effect of initial pH solution and b) Effect of photocatalyst mass

Fig 3b shows the effect of photocatalyst mass on removal efficiency of IC. As denote in Fig 3b, the removal efficiency of IC increased with the photocatalyst mass increasing from 50 to 250 mg. The maximum removal efficiency of IC was achieved by using 250 mg of α-Fe₂O₃/bentonite composite. This is because the fact that increasing in photocatalyst mass leads to increase the number of photogenerated electron and holes. The greatly increased of electron and holes is in favor to the formation of *OH and superoxide ion (O₂⁻) and the photodegradation of IC increase.

Effect of Initial IC concentration and different light source
Influence of initial concentration on the removal efficiency of IC is evaluated over the concentration range of 5 mg/L to 25 mg/L. Results showed in Fig. 4a indicate that as the initial IC concentration increases, the removal efficiency decreases. When the initial IC concentration increased, more IC molecule will adsorbed on the photocatalyst surface while the photogenerated electron, hole and the active species remained the same because the photocatalyst mass is fixed. Fig 4a also shows that the removal efficiency of IC is very high at low concentrations (5 mg/L) which IC dye almost completely degraded after irradiating with UV light for 2 h. In all measurement of photocatalytic activities studied in this report, the removal efficiency of IC molecules increases with irradiation time.

Figure 4 Degradation of IC over α-Fe₂O₃/bentonite composite as a function of UV irradiation time. 
  a) Effect of initial IC concentration b) Effect of different light source and condition

Photocatalytic activities of α-Fe₂O₃/bentonite composite and extracted α-Fe₂O₃ on photodegradation of IC using UV irradiation were compared to solar light irradiation and without UV irradiation (dark condition) (Fig 4b). The results indicated that the removal efficiency of IC could be enhanced effectively by the fabrication of α-Fe₂O₃/bentonite composite. Fig 4b also shows that photocatalytic activity of α-Fe₂O₃/bentonite composite under solar light irradiation was higher than
that of UV irradiation. All of IC molecule was completely degraded after irradiating with solar light for 2 h.

Photodegradation Mechanism of IC

Photocatalytic activity of the $\alpha$-Fe$_2$O$_3$/bentonite composites was attributed to the presence of $\alpha$-Fe$_2$O$_3$ and bentonite. The higher removal efficiency of IC over $\alpha$-Fe$_2$O$_3$/bentonite composite compare to $\alpha$-Fe$_2$O$_3$ probably due to increase in dye adsorption on the photocatalyst surface which will react with active species in photocatalysis process. When $\alpha$-Fe$_2$O$_3$/bentonite composite was irradiated by UV or solar light, electron and hole pair was generated on the conduction band (CB) and valence band (VB) of photocatalyst (equation 3). Hole on the VB allows the oxidation of IC to degradation products (equation 4). In addition, hole also can react with hydroxyl group from water to produce $^\cdot$OH (equation 5), a strong oxidant that can oxidize IC molecule (equation 6). On the other hand, electron in CB on $\alpha$-Fe$_2$O$_3$ surface will reduce O$_2$ into O$_2^-$ (superoxide ion) (equation 7). Superoxide ion will react with water to generate $^\cdot$OH [29-31].

$$\begin{align*}
\alpha$-Fe$_2$O$_3$ + h\nu & \rightarrow Fe$_2$O$_3$ + h^\prime_{VB} + e^-_{CB} \\
h^\prime_{VB} + IC & \rightarrow \text{degradation product of IC} \\
h^\prime_{VB} + \text{OH} & \rightarrow ^\cdot\text{OH} \\
^\cdot\text{OH} + IC & \rightarrow \text{degradation product of IC} \\
e^-_{CB} + \text{O}_2 & \rightarrow \text{O}_2^- \\
2\text{O}_2^- + 2\text{H}_2\text{O} & \rightarrow ^\cdot\text{OH} + 2\text{OH}^- + \text{O}_2 \\
^\cdot\text{OH} + IC & \rightarrow \text{degradation product of IC} \\
& \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{other degradation product of IC}
\end{align*}$$

(3) (4) (5) (6) (7) (8) (9) (10)

4. Conclusion

Synthesis of $\alpha$-Fe$_2$O$_3$/bentonite composite using $\alpha$-Fe$_2$O$_3$ extracted from iron ore has been successfully performed by mechanical milling method. The $\alpha$-Fe$_2$O$_3$/bentonite composite has a high photocatalytic activity on removal of indigo carmine (IC) dye compare to extracted $\alpha$-Fe$_2$O$_3$. The maximum removal efficiency of IC was achieved on the initial pH solution 1, photocatalyst mass 250 mg, initial dye concentration 5 mg/L for 2 h UV irradiation time. Photocatalytic activity of $\alpha$-Fe$_2$O$_3$/bentonite composite under solar light was higher than that of UV irradiation.

Acknowledgement

The authors kindly acknowledge for the assistance and encouragement from colleagues for scientific and technical support.

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