SYNTHESIS AND CHARACTERIZATION OF TiO$_2$/α-Fe$_2$O$_3$ COMPOSITE USING HEMATITE FROM IRON SAND FOR PHOTODEGRADATION REMOVAL OF DYE

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Abstract. In this paper, TiO$_2$/α-Fe$_2$O$_3$ composite with high photocatalytic activity was prepared by a mechanical milling using iron sand from Lampanan in Aceh Besar regency as hematite (α-Fe$_2$O$_3$) source. Hematite was extracted from iron sand by using hydrochloric acid followed by co-precipitating using ammonium hydroxide as co-precipitation agent. Hematite and TiO$_2$ powder were mixed and milled on a planetary ball mill without incorporating any solvent. The materials were characterized by using X-ray diffraction (XRD) and scanning electron microscopy energy dispersive x-ray spectroscopy (SEM-EDX). The XRD results showed that the iron (III) oxide synthesized was hematite (α-Fe$_2$O$_3$) phase with the average crystallite size 27.967 nm. SEM analysis showed that iron sand was on irregular form, while the hematite (α-Fe$_2$O$_3$) and TiO$_2$/α-Fe$_2$O$_3$ composite was on regular sphere. The TiO$_2$/α-Fe$_2$O$_3$ composite was evaluated on photodegradation of indigo carmine (IC) dye using UV light irradiation. The highest degradation efficiency of IC (100%) was obtained by initial pH of dye solution equal to 1, photocatalyst dosage of 0.2 g, initial dye concentration of 5 mg/L for 120 min irradiation time. The photocatalytic activity of TiO$_2$/α-Fe$_2$O$_3$ composites using UV light was almost the same as that of by solar light.

Keywords: Iron sand, α-Fe$_2$O$_3$/TiO$_2$ composite, mechanical milling, photocatalyst, indigo carmine

I INTRODUCTION

Iron sand is a type of sand with a significant concentration of iron that is usually dark gray or blackish in colour. Iron sand is one of an abundant natural resources in Aceh province and based on Department of Mines and Energy of Aceh data there are about 36,800.000 tons of iron sand deposits in Aceh Besar regency [1]. Iron sand from Aceh Besar regency is composed mainly of magnetite (Fe$_3$O$_4$) and small amount of TiO$_2$ and SiO$_2$ [2]. Iron sand was used as raw materials in the steel and cement industries. Hematite (α-Fe$_2$O$_3$) which can be extracted from iron sand is used in a wide range of applications such as in lithium ion batteries, gas sensors, fine ceramics, pigments, photo anode in photo-electrochemical cells, field effect transistor and catalysts [3,4]. Hematite is stable under ambient conditions, resistance to corrosion and the semiconductor properties of hematite with a band gap of 2.2 eV are highly beneficial in photocatalysis. The small band gap of hematite make it efficient absorption in the solar spectrum. However, the small band gap result in undesired recombination of photo-generated electron and hole that can reduce the photocatalytic activity [5]. Coupling with other semiconductor with higher band gap energy is one of efforts to solve the problem because it can help to separate its photo-generated charges and increase the photocatalytic activity. TiO$_2$ with high band energy gap (3.0 – 3.2 eV) is suitable for coupling with hematite. Fe$_2$O$_3$ doped TiO$_2$ nanoparticles has been synthesized by ultrasonic-assisted co-precipitation method and used on photocatalytic degradation of trichloroethylene under UV and visible light irradiation [6]. Hematite doped TiO$_2$ nanocomposite also has been fabricated and the obtained composites exhibited high photocatalytic activity on photocatalytic degradation of methyl orange [7]. Photocatalysis has been widely used to degrade organic pollutants such as aromatics, dyes and phenols [8] because it can convert pollutants into harmless substances, working at ambient condition, low cost and high efficiency [9]. Indigo carmine, an indigoid class of dye, is a synthetic dye which has been found in wastewater from textile industry. Wastewater
containing dyes may lead to environmental problem for human health and may have adverse effects on aquatic life because of toxicity and carcinogenic effect of this dye. In this work, hematite (α-Fe₂O₃) has been extracted from iron sand by co-precipitation method and modified with TiO₂ by mechanical milling. Crystallite size and surface morphologies of the extracted hematite (α-Fe₂O₃) and TiO₂/α-Fe₂O₃ composite were also investigated.

II METHODOLOGY

Iron sand taken from Lampanah Beach, Aceh Besar regency was ground in a porcelain ball mill for 30 min with a milling speed of 250 rpm until they completely passed through a 150 mesh standard sieve. Hematite (α-Fe₂O₃) was extracted from iron sand using hydrochloric acid followed by co-precipitation method according to previous works [10, 11]. A 50 g of iron sand sample was dissolved in 280 mL of 6M HCl solution with constant stirring and gently heating at 145°C for 30 min. The solution was filtered and ammonium hydroxide 25% was added by drops to the filtrated solution until the pH reaches 6 at which ferric hydroxide was obtained as a brown precipitate. The precipitate was filtered, washed with distilled water, dried at 100°C for 3 h and calcined at 700°C for 5 h. The crystal phase of the product was identified by X-ray diffraction (XRD) using Cu Kα radiation. A TiO₂/α-Fe₂O₃ composite was synthesized by mechanical milling method using ball mill with the mole ratio of TiO₂ to α-Fe₂O₃ 1:3. The powder were mixed and milled for 12 h at the milling speed of 300 rpm with the balls to powder mass ratio was 10:1. The mixture was calcined at 500°C for 5 h. The obtained composite was then characterized by using XRD and SEM-EDX. Average crystallite sizes of iron sand, hematite and TiO₂/α-Fe₂O₃ composite were calculated by the X-ray line broadening technique based on Scherrer’s formula (Eqs. (1)).

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

where D is the crystallite size, k is Scherrer’s constant (0.9), λ is the X-ray wavelength, θ is the Bragg’s angle and β (in radians) is the full width at half maximum (FWHM) intensity of the diffraction peak.

The photocatalytic activity of TiO₂/α-Fe₂O₃ composite was evaluated by the degradation of indigo carmine dye (IC) in an aqueous solution containing of 5, 10, 15, 20 and 25 mg/LIC as initial concentration; 1, 2 and 3 initial pH solution and 200, 400, 600, 800 and 1000 mg photocatalysts in 100 mL glass vessels. Indigo carmine, an anionic dye with the chemical formula C₁₅H₁₁N₄Na₂O₃S₂ (C.I. = 73015, MW = 466.36 g/mole) is a group of dark blue indigoid (Figure 1). The UV light source was a 6 W UV lamp (λ = 365 nm). The mixture was magnetically stirred in the dark for 30 min to establish adsorption-desorption equilibrium of IC and the composite surface before the irradiation. A 3 mL sample solution was drawn from the system at a certain time interval (0, 30, 60, 90, 120 and 180 min) during the experiment, and then was centrifuged and analyzed at 610 nm recording the characteristic absorption peak of IC with a UV-Vis spectrophotometer (Shimadzu UV mini 1240). The adsorption experiment was performed under the same condition without UV light irradiation. The degradation efficiency (%) of IC was calculated using the formula of Eqs. (2).

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

where C₀ and C_f referred to the concentration of the IC solution before and after irradiation.

![Figure 1 The structure of indigo carmine dye](image)

III RESULT AND DISCUSSION

The reaction of hematite (α-Fe₂O₃) formation extracted from the iron sand by using hydrochloric acid followed by ammonium hydroxide as co-precipitating agent were written in Eqs. (3) to (6) [12, 13].

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 6\text{HCl} & \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \\
\text{FeCl}_3 + 3\text{NH}_3\text{OH} & \rightarrow \text{Fe(OH)}_3 + 3\text{NH}_4\text{Cl} \\
\text{Fe(OH)}_3 & \rightarrow \text{FeOOH} + \text{H}_2\text{O} \\
2\text{FeOOH} & \rightarrow \alpha\text{-Fe}_2\text{O}_3 + \text{H}_2\text{O}
\end{align*}
\]

The structure of crystalline phase of hematite (α-Fe₂O₃) was studied via XRD analysis and was given in Figure 2.
The diffraction peaks found at 24.22°, 33.22°, 35.70°, 40.92°, 49.52°, 54.26°, 57.34°, 62.62°, 64.06°, 72.08° and 75.62° are consistent with those of hematite (α-Fe₂O₃) (Crystallography Open Database (COD) Inorganic Rev. 9015964). Hematite (α-Fe₂O₃) was used to synthesize TiO₂/α-Fe₂O₃ composite with the molar ratio of TiO₂ to α-Fe₂O₃ 1:3. Figure 3 presented the XRD patterns of iron sand, with diffraction peaks at 30.26°, 35.72°, 43.24°, 54.18°, 56.92° and 62.56°. These diffraction peaks are corresponding to the reflection planes of magnetite (Fe₃O₄) (Crystallography Open Database (COD) Inorganic Rev. 1537396). It can be deduced that the main component of iron sand taken from Lampanah Beach, Aceh Besar regency was magnetite (Fe₃O₄).

The diffraction peaks of TiO₂ and hematite (α-Fe₂O₃) can be observed in XRD patterns of TiO₂/α-Fe₂O₃ composite. The peaks at 20° are 25.27°, 38.54°, 48.01°, 53.85°, 62.65°, 68.72°, 75.01° and 76.02° correspond to the crystal planes of anatase (ICPDF file No.04-0477). Other observable difference in the XRD patterns of TiO₂/α-Fe₂O₃ composite is the decrease intensity of the main peaks of hematite (α-Fe₂O₃) due to the coorporation of two semiconductors.

The average crystallite size of as-prepared materials calculated from XRD data by using Debye-Scherer equation were given in Table 1. It can be seen that the average crystallite size of TiO₂/α-Fe₂O₃ composite was higher than that of iron sand and hematite. This is probably due to high-energy impact between milling balls and the mixture of TiO₂ and α-Fe₂O₃ leading to the formation of agglomerate of TiO₂/α-Fe₂O₃ composite.

Table 1: Average crystallite size of iron sand, hematite, TiO₂ and TiO₂/α-Fe₂O₃ composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron sand</td>
<td>33.144</td>
</tr>
<tr>
<td>Hematite</td>
<td>27.967</td>
</tr>
<tr>
<td>TiO₂</td>
<td>45.361</td>
</tr>
<tr>
<td>TiO₂/α-Fe₂O₃ Composite</td>
<td>40.616</td>
</tr>
</tbody>
</table>

The morphologies of the sample were investigated by SEM observation equipped with EDX. It can be seen from Figure 4a that iron
sand was irregular in shape while hematite obtained from iron sand (Figure 4b) was in spherical regular and almost uniform particle size. TiO$_2$/α-Fe$_2$O$_3$ composite (Figure 4c) was in spherical form and slightly agglomerated probably due to the formation of high heat energy during the mechanical milling process. Energy dispersive X-ray spectroscopy (EDX) was used to determine the Fe to Ti mass ratio. The result exhibited that Fe and Ti was 53.72% and 33.51% (weight %) and thus the mass ratio of Fe to Ti was about 3:2.

Figure 4 SEM images of (a) Iron sand (b) α- Fe$_2$O$_3$ (c) TiO$_2$/α-Fe$_2$O$_3$ composite

Photocatalytic Activity of TiO$_2$/α-Fe$_2$O$_3$

The effect of pH on the photocatalytic degradation of indigo carmine (IC) over TiO$_2$/α-Fe$_2$O$_3$ composite studied in the range of pH 1-3 as a function of time is presented in Figure 5. It was exhibited that degradation efficiency of IC significantly improved on the lower pH and IC was degraded up to 99% at pH 1. This may be due to the fact that the pH of dye solution affects the surface properties of photocatalyst. In the acidic solutions, the surface charge properties of α-Fe$_2$O$_3$ change to the positive charge (FeOH$^+$), while in the basic solution the surface is negative charge. On the other hand, the surface of the TiO$_2$ is positive potential in the range of pH<3, and the surface is negatively charged under pH>3 [14]. The lower the pH the more FeOH$^+$ and TiOH$_2^+$ will be formed.

Figure 5 Effect of pH on IC degradation efficiency over TiO$_2$/α-Fe$_2$O$_3$ composite. Initial dye concentration of 15 mg/L and photocatalyst dosage 0.2 g

IC molecule has negative site and electrostatic attraction between anionic dye and the positive site of α-Fe$_2$O$_3$ or TiO$_2$ occurred (Figure 6). Thus IC molecule can easily adsorb on the photocatalyst surface and react with the holes or *OH radical generated on the surface of TiO$_2$/α-Fe$_2$O$_3$ composite when irradiated by UV light. With increasing pH, the negative charges on TiO$_2$ and α-Fe$_2$O$_3$ repel the dye molecule and decrease the efficiency of photodegradation.

\[
\text{(acidic side) } \quad \text{Ti} - \text{OH}^+ \quad \text{OH}^- \quad \text{Ti} - \text{OH}^- \quad \text{Ti} - \text{O}^-
\]

Figure 6 Surface properties of TiO$_2$ under different condition

Effect of photocatalyst dosage

Figure 7 shows the degradation efficiency of IC dye over TiO$_2$/α-Fe$_2$O$_3$ composite in the range of 0.2–1.0 g. It was found that the amount of photocatalyst 0.2 g gave the highest degradation efficiency of IC (99%) compare to other dosage. More photocatalyst dosage result in degradation efficiency reduction due to increased scattering and turbidity effects that prevented the penetration of UV light into the surface of photocatalyst [15]. Thus the quantity of generated electron, holes, *OH or O$_2$* that can react with IC molecule decrease.
Thus, it can be catalyzed by species involved in the photocatalytic process. When \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite has almost the same photocatalytic activity under UV irradiation and solar light. On the other hand, in the dark condition only 52% of IC can remove from the solution. Thus, it can be concluded that IC removal over \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite was a result of synergistic effect of adsorption and photodegradation process.

**Effect of initial dye concentration**

Figure 8 shows the effect of initial IC concentration on the photocatalytic activity of \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite. The results revealed that degradation efficiency of IC decreased with the increase of initial dye concentration. It was found that IC degradation efficiency 100% was achieved by using 5 mg/L initial dye concentration for 120 min irradiation time. On the other hand, IC degradation efficiency 98 and 99% was achieved by applying 10 and 15 mg/L initial dye concentration for 180 min irradiation time. When the initial dye concentration increases, more particles of dye are adsorbed on the photocatalyst active surfaces, however the reactive species quantities such as electron, holes, \( ^\bullet \text{OH} \) and \( \text{O}_2^- \) which will react with dye molecule are not enough for high IC concentration. It may be due to the dosage of photocatalyst that was applied are constant 0.2 g.

**Effect of light source**

The effect of light source on degradation efficiency of IC over \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite was also studied (Figure 9). It was observed that on the same condition of initial pH solution, photocatalyst dosage and initial IC concentration, \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite has the same photocatalytic activity under UV irradiation and solar light. Therefore, it can be concluded that IC removal over \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite was a result of synergistic effect of adsorption and photodegradation process.

**Proposed degradation mechanism of IC**

When the \( \text{TiO}_2/\alpha-\text{Fe}_2\text{O}_3 \) composite irradiated by UV light, \( \text{TiO}_2 \) was activated and generated electron-hole pairs. The electron transfers from the valence band to the conduction band in \( \text{TiO}_2 \), then to the conduction band of \( \alpha-\text{Fe}_2\text{O}_3 \), while the hole still remains in the valence band of \( \text{TiO}_2 \). Because the difference between conduction bands of \( \alpha-\text{Fe}_2\text{O}_3 \) and \( \text{TiO}_2 \) (2.2 and 3.2 eV, respectively), electrons generated in \( \text{TiO}_2 \) were easily transferred to the conduction band of \( \alpha-\text{Fe}_2\text{O}_3 \) [16, 17]. As the results, the recombination of electrons and holes is inhibited and the electron in conduction band of \( \alpha-\text{Fe}_2\text{O}_3 \) will react with \( \text{O}_2 \) to produce the superoxide anion \( \text{O}_2^- \). On the other hand, holes in valence band of \( \text{TiO}_2 \) will react with \( \text{OH}^- \) to generate reactive \( \text{OH}^* \). Further, the \( \text{OH}^* \) will react and decompose IC molecule [18]. The proposed mechanism is shown in Eqs. (7) to (11).

\[
\begin{align*}
\text{TiO}_2 + h\nu &\rightarrow e_{\text{CB}}^- + h^+_{\text{VB}} \quad \text{(7)} \\
\text{Fe}^{3+} + e_{\text{CB}}^- &\rightarrow \text{Fe}^{2+} \quad \text{(8)} \\
\text{Fe}^{2+} + \text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{O}_2^- \quad \text{(9)} \\
\text{TiO}_2(h^+_{\text{VB}}) + \text{OH}_{\text{ads}} &\rightarrow \text{TiO}_2 + \text{OH}^* \quad \text{(10)} \\
\text{O}_2^*/\text{OH}^- + \text{IC} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{degraded products} \quad \text{(11)}
\end{align*}
\]

**CONCLUSION**

Synthesis and characterization of hematite (\( \alpha-\text{Fe}_2\text{O}_3 \)) extracted from Lampanan Beach, Leungang district in Aceh Besar regency and modification with TiO\(_2\) to produce TiO\(_2/\alpha-\text{Fe}_2\text{O}_3\) composite by mechanical milling has
been successfully performed. The TiO$_2$/α-Fe$_2$O$_3$ composite has a high photocatalytic activity on photodegradation of indigo carmine (IC) dye. The maximum degradation efficiency of IC was achieved on the initial pH solution 1, photocatalyst dosage 0.2 g, initial IC concentration 5 mg/L for 120 min irradiation time. TiO$_2$/α-Fe$_2$O$_3$ composite has almost the same photocatalytic activity under UV irradiation and solar light.

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