Preparation of Fe₂O₃-TiO₂/GO Composites as a Visible Light Oxidation Photocatalyst Material

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Abstract. Fe₂O₃-TiO₂/Graphene Oxide (Fe₂O₃-TiO₂/GO) has been synthesized through a step by step synthesized. Preparation of Fe₂O₃-TiO₂ composites from Sukabumi iron sand with high iron content. Meanwhile, preparation of GO separately from graphite on strong acid condition H₂SO₄ and addition oxidator KMnO₄ has been treated out. First composition analyzed Sukabumi iron sand shown content of iron about 50% and content of Ti about 10%. Fe₂O₃-TiO₂ composites prepared with addition TiO₂ powder thus obtained a ratio of Fe₂O₃-TiO₂ = 1:1(w/w). Fe₂O₃-TiO₂ composites were roasted at 400 °C, 500 °C, and 600°C shown optimal hematite formed at 600 °C. Formation of Fe₂O₃-TiO₂/GO composites were at Fe₂O₃-TiO₂:GO= 1:1, 1:2, and 1:3 (w/w), respectively. Fe₂O₃-TiO₂/GO composites (A, B, C) shown excellent photocatalyst activities. Fe₂O₃-TiO₂:GO (1:3) composites have the optimum ability for photocatalytic activity of Rhodamine B degradation achieved about 93.96% for 40 minutes illumination.

1. Introduction

Advanced oxidation processes (AOPs) have emerged as promising alternative strategies for water treatment, especially for persistent and nonbiodegradable contaminants. Oxidation process of organic pollutant will initiate by electron and hole production from photochemistry reaction in the photocatalytic oxidation reaction. Fe₂O₃, which is an abundant, cost-effective and environmentally benign n-type semiconductor with band-gap of 2.2 eV, has been extensively studied because of its peculiar and fascinating physicochemical properties and wide potential applications in diverse fields such as water splitting [1] and photocatalysis [2], [3]. TiO₂ in iron sand has benefits in the photocatalyst field and low cost natural materials. Raw materials for TiO₂ production are actually widely available in nature such as ilmenite (FeTiO₃) [4] and iron sand [5]. Magnetic particles in the form of Fe₂O₃ and Fe₃O₄ in iron sand content can be separated by magnetic separation method. The magnetic separation process will separate magnetic particles from iron sand approximately 99% [6]. Composite material of TiO₂ and Fe₂O₃ can absorb up to 550 nm wavelength adsorption edge, due to lower band gap energy of Fe₂O₃ that TiO₂. Fe₂O₃ are abundant, cost-effective and environmentally benign n-type semiconductor with band-gap of 2.2 eV, compare to TiO₂ with band gap of 3.2 eV. Composite of TiO₂-Fe₂O₃ has been extensively studied because of its peculiar and fascinating physicochemical properties and wide potential applications prospect.

Recently, Fe₂O₃ has been used to form hybrid materials with graphitic nanostructures for lithium ion batteries [7] and electrochemical detection of chromium [8]. However, there is still rarely found regarding the application of GO–Fe₂O₃ heterogeneous catalyst for photodegradation of organic contaminants to date. [9] claim that a reduced GO/TiO₂ composite will significantly increase the photovoltaic response and significantly prolongs the mean lifetime of electron–hole
pairs, compared with pure TiO$_2$ [10] suggests chemically bonded P25-graphene composite as a high performance photo-catalyst for degradation of methylene blue.

Graphene has unique and superior properties compared to other materials. In the visible energy range (1.5-3 eV) graphene is transparant [11]. Graphene compared to GO, GO sheets have more oxygen function groups due to exfoliation. There is an increase in photocatalytic activity factors that affect them, including structural properties (area width, grain size, morphology), optical properties (energy gap, electron recombination and holes) [12-15] and magnetic properties of the material [16]. GO can increase photocatalytic activity because it has a large surface area and acts as an electron transfer [17]. therefore, it is necessary to modify the properties of Fe$_2$O$_3$-TiO$_2$ material by adding GO [18] as a photocatalyst material for degradation photocatalyst of Rhodamine B.

In this work, we report an easy and scalable way of synthesizing Fe$_2$O$_3$-TiO$_2$/GO composite through a step by step synthesized. Preparation of Fe$_2$O$_3$-TiO$_2$ composites was conducted from Sukabumi iron sand with high iron content. While, the preparation of GO was carried out from graphite on strong acid condition H$_2$SO$_4$ and addition oxidator KMnO$_4$. Fe$_2$O$_3$-TiO$_2$ composites prepared with addition TiO$_2$ powder to gain a ratio of Fe$_2$O$_3$-TiO$_2$ =1:1(w/w).

2. Experimental

2.1 Material and Equipment

The materials used was iron sand from Sukabumi, sulphuric acid 95-98% (Merck), ammonia (NH$_4$OH) 25%, TiO$_2$ anatase powder, graphite, KMnO$_4$, H$_2$O$_2$, aquadest, and Rhodamine B. The equipment that require in this research was ultrasonic cleaner, platenary ball miller, oven, sentrifuge, thermometer. The materials characterization both before and after treatment were carried out by Scanning Electron Microscopy (Quanta 250), Fourier Transform Infra Red (Shimadzu PC 8201), X-Ray Fluorescence (Bruker S2 Ranger), X-Ray Difraction and Uv-Vis Spectrometry Double Beam (Shimadzu PC 1601).

2.2 Preparation of Iron Sand

The Sukabumi iron sand was analyzed by XRF (X-Ray Fluorescence) and XRD (X-Ray Difraction). The magnetic and non magnetic particles was separated by magnet field. Then, the separated particles were milled by platenary ball milling (300 rpm) for 5 hours. Milling process was conducted in ratio w/w (10:1) (130 gram : 13 gram).

2.3 Fe$_2$O$_3$-TiO$_2$

10 gram of iron sand was leached with an addition 100 ml H$_2$SO$_4$ 98% (9 M) for 5 hours under reflux 90 °C. Then, the liquor of iron sand was hydrolyzed using NH$_4$OH (6M) until solid precipitate was apparanced. The precipitate was analyzed by XRF (X-Ray Fluorescence).

2.4 GO

2.5 gram of Graphite oxidized with addition KMnO$_4$ (8 gram) and H$_2$SO$_4$ 98% (150 ml). Then, added 200 ml aquadest and 5 ml of H$_2$O$_2$ and stirred for 30 minutes. After that, 200 ml of aquadest were slowly added until pH 7. Solid powder was dried at 80 °C for 8 hours.

2.5 Composites Fe$_2$O$_3$-TiO$_2$/GO

Composites Fe$_2$O$_3$-TiO$_2$/GO synthesized with ratio 1:1, 1:2, and 1:3 (w/w). GO (0.5 gram, 1 gram and 1.5 gram) was mixed with 60 ml aquadest and 0.5 gram of crystal composites Fe$_2$O$_3$-TiO$_2$ of iron sand. Then, the solution mixture was sonicated for 1 hours and hydrothermal process at 150 °C for 3 hours.

2.6 Photocatalytic activity of Fe$_2$O$_3$-TiO$_2$/GO composites

0.01 gram composites Fe$_2$O$_3$/TiO$_2$/GO (1:1; 1:2; and 1:3) added 10 ml Rhodamine B 10 ppm. Then, mixed solution is irradiated 10, 20 and 40 minutes. Finally, degradation results characterized by UV-Vis.
3. Results and Discussion
Firstly, the pretreatment Sukabumi iron sand was analysed by XRF. The result in Figure 1 and Table 1 shown that Sukabumi iron sand contains Fe 50.48%, Ti 8.65%, and other elements under 5%.

| Table 1. Analysis of pretreatment Sukabumi sand |
|-----------------------------------------------|
| **Element** | **Concentration (%)** |
| Fe         | 50.48               |
| Ti         | 8.65                |
| Si         | 3.07                |
| Al         | 1.16                |
| Ca         | 0.78                |

Figure 1. XRF analysis of pretreatment Sukabumi sand

Figure 2. X-ray diffractogram a) Sukabumi iron sand b) Sukabumi iron sand (magnetic separation)

Sukabumi iron sand (magnetic separation) shown new peaks indicated that $\gamma$-$\text{Fe}_2\text{O}_3$ is starting to form and other peaks are indicated $\text{Fe}_2\text{O}_4$.

The process for extracted $\text{Fe}_2\text{O}_3$ and $\text{TiO}_2$ in iron sand used hydrometallurgy method, the dissolution process by using concentrated sulfuric acid solution to obtain Titanyl Sulphate ($\text{TiOSO}_4$) and Ferro Sulfate ($\text{FeSO}_4$). The materials was leached under reflux with $\text{H}_2\text{SO}_4$ 9 M. The mechanism reaction that may occur during the leaching process is in equation 1 and equation 2.

\[
\text{FeTiO}_3(s) + 2 \text{H}_2\text{SO}_4(aq) \rightarrow \text{FeSO}_4(aq) + \text{TiOSO}_4(aq) + 2\text{H}_2\text{O}(l) \quad (1) \\
\text{TiO}_2(s) + \text{Fe}_2\text{O}_3(s) + 4 \text{H}_2\text{SO}_4(aq) \rightarrow \text{TiOSO}_4(aq) + 2\text{Fe}_2(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O}(aq) \quad (2)
\]
The filtrate from the leaching was precipitation with the addition of NH₄OH 6 M to produce Fe₂O₃/TiO₂. This process could dissolve sediment Fe₂O₃-TiO₂ obtained the ratio between the content of Fe₂O₃ and TiO₂ is 4.46:1.

**Table 2. XRF result precipitation**

| Compound | Concentration (%) | Element | Concentration (%) |
|----------|------------------|---------|------------------|
| Fe₂O₃    | 75.19            | Fe      | 52.59            |
| TiO₂     | 16.84            | O       | 32.80            |
| Al₂O₃    | 1.33             | Ti      | 10.09            |
| SiO₂     | 1.24             | Al      | 0.71             |
| P₂O₅     | 0.68             | Si      | 0.58             |

**Figure 3. Analysis XRF of Fe₂O₃-TiO₂ sediment**

Fe₂O₃/TiO₂ composites that have dried up and after adding TiO₂ anatase are carried out calcination variations of 400 °C, 500 °C, and 600 °C to obtain Fe₂O₃-TiO₂ composites crystals. From the results of X-Ray Diffraction (XRD) analysis shows specific differences in the diffractogram pattern of calcination results shown in Figure 4.

**Figure 4. Diffractogram XRD of Fe₂O₃-TiO₂ composites at a) 400 °C, b) 500 °C, and c) 600 °C (**= α-Fe₂O₃)**

Calcination 400 °C and 500 °C still form the same diffractogram that is the peaks that indicate TiO₂ anatase. XRD diffractogram at 600 °C calcination shows α-Fe₂O₃(ICSD No. 15840) pada
$\theta = 24.2156^\circ, 33.2436^\circ, 35.7482^\circ, 41.0043^\circ, 49.6522^\circ, 54.0104^\circ, 62.7409^\circ, 64.1241^\circ, 70.3294^\circ, 75.0640^\circ$, TiO$_2$ anatase (JCPDS No. 78-2486) at $\theta = 25.3113^\circ, 48.1137^\circ, 55.1844^\circ, 68.8008^\circ$, $\gamma$-Fe$_2$O$_3$ (ICSD No. 172905), Fe$_3$O$_4$ (ICSD No. 49549) at $\theta = 35.7482^\circ, 70.3294^\circ$, Cr$_2$O$_3$ (ICSD No. 250078) at $\theta = 33.2436^\circ$, MnO (ICSD No. 657304) at $\theta = 38.6735^\circ$ and 68.8008$^\circ$

**Table 3.** XRF results in hematite formation at 600 $^\circ$C calcination temperature

| Element | Concentration (%) |
|---------|-------------------|
| O       | 35.07             |
| Fe      | 32.17             |
| Ti      | 29.33             |
| La      | 1.44              |
| S       | 0.44              |

**Figure 5.** XRF of hematite calcination temperature at 600 $^\circ$C

The results of the analysis of iron sand in the formation of Fe$_2$O$_3$-TiO$_2$ composites crystal shown a decreased in Fe and an increase in TiO$_2$ due to the addition of TiO$_2$ anatase powder, so it is obtained ratio of Fe$_2$O$_3$-TiO$_2$ is 1:1 (w/w)

Graphene Oxide was characterized by XRD and FTIR shown in Figure 6, 7, and 8. In Figure 6 it shown that the peak was intense in graphite (ICSD No. 76767) $\theta = 26.42^\circ$, become lost and replaced with a peak on GO $\theta = 10.77^\circ$ and 42.47$^\circ$. Graphene Oxide has increased $d_{\text{spacing}}(\text{Å}) = 8.22$ Å from $d_{\text{spacing}}$ grafit $3.37$ Å.

**Figure 6.** Diffractogram of a) Graphene Oxide b) Graphite
Figure 7. Diffractogram of a) GO b) Fe$_2$O$_3$-TiO$_2$ composites crystal c) Fe$_2$O$_3$-TiO$_2$-GO (1:1) d) Fe$_2$O$_3$-TiO$_2$-GO (1:2) and e) Fe$_3$O$_3$-TiO$_2$-GO (1:3)

The peak intensity increases with the addition of GO in Fe$_2$O$_3$/TiO$_2$ composites crystal. However, the peak intensity on Fe$_2$O$_3$-TiO$_2$/GO (1:3) composites decreases and the width of the peak widen because the GO number increases. Thus, the composites formation is optimal in Fe$_2$O$_3$-TiO$_2$/GO (1:2). This was shown the interaction of GO in composites formation. Spectra (C) is formed uptake of –OH, C=C, C-OH and Fe-O which has been successfully formed on Fe$_2$O$_3$ - TiO$_2$/GO composites.

Figure 8. FTIR of a) Fe$_2$O$_3$-TiO$_2$ composites crystal b) GO c) Fe$_2$O$_3$-TiO$_2$-GO (1:1; 1:2; and 1:3)

Decrease in concentration (Figure 9) shown the optimization of photocatalytic activity of Fe$_2$O$_3$-TiO$_2$/GO composites. The degradation of Fe$_2$O$_3$-TiO$_2$/GO composites increased significantly with increasing GO content in composites from 1:1 variations, 1:2 variations to 1:3 variations. Therefore, the composite Fe$_2$O$_3$-TiO$_2$/GO (1:3) shown the best photocatalytic activity.
Figure 9. Results of photocatalytic degradation of Rhodamine B of (a) Fe$_2$O$_3$/TiO$_2$ (b) Fe$_2$O$_3$-TiO$_2$/GO (1:2) (c) Fe$_2$O$_3$-TiO$_2$/GO (1:1) and (d) Fe$_2$O$_3$-TiO$_2$/GO (1:3)

4. Conclusion
In conclusion, Preparation of Fe$_2$O$_3$-TiO$_2$ composites through magnetic separation, hydrometallurgy and by addition of TiO$_2$ anatase powder to obtained a ratio of Fe$_2$O$_3$-TiO$_2$= 1:1 (w/w). The amount of Graphene Oxide added to the of on Fe$_2$O$_3$-TiO$_2$/GO composites crystal gives a large change in photocatalytic activity.

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