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Synthesize Fe_3O_4-TiO_2 Composite for Methyl Orange Photocatalytic Degradation

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Abstract. The effect of Fe_3O_4 percentage on Fe_3O_4-TiO_2 composite for methyl orange photocatalytic degradation has been investigated. Hydrothermal was carried out on TiO_2 before being combined with Fe_3O_4 by precipitation method. The composites were characterized by means of Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and UV-Vis diffuse and reflectance spectroscopy (UV-Vis DRS). The photocatalytic activity of Fe_3O_4-TiO_2 composites were evaluated for methyl orange degradation. The addition of Fe_3O_4 to TiO_2 could reduce the bandgap energy. The lowest bandgap energy was obtained at 20% Fe_3O_4-TiO_2 composite. By using this composite, the degradation of methyl orange was 90%.

Introduction

Most of the textile industry uses synthetic dyes for reasons of cheap, durable, easy to obtain, and easy to use. The use of synthetic textile dyes poses some problems are the waste is still colored and difficult to degrade [1,2,3]. One of the dyes that are widely used in the dyeing process is methyl orange [4,5]. Several conventional ways of treating textile waste have been developed by researchers including chlorination, ozonation, biodegradation and adsorption. Some weaknesses of this method include high operational costs and relatively difficult to apply in Indonesia [6].

One alternative to treating textile waste is photocatalyst technology. According to International Union of Pure and Applied Chemistry (IUPAC), photocatalysts are defined as chemical reactions caused by light (photo-absorption) either ultraviolet, visible, or infrared by solid materials namely catalysts that have the ability to absorb photons and are generally owned by materials semiconductor material, the reaction on the semiconductor surface does not change during and after the reaction[7, 8].

The most frequently used and developed semiconductors is TiO_2. TiO_2 has an energy band of 3.2 eV [9]. The advantages of TiO_2 that have been widely applied include photocatalysts, biomaterials, pigments, solar cells, gas sensors, capacitors, anti-bacterial agents, self-cleaning, drug delivery, anticancer therapies, and in the environment, namely waste degradation [9-12].

Nanocomposites are nanomaterials that combine one or more components in order to obtain the best properties of each component. The result of nanocomposites can improve the properties that include mechanical strength, toughness, electrical conductivity, chemical resistance, thermal stability, and surface appearance [13].

The following are some types of TiO_2 nanocomposites, namely modification with charge transfer catalyst (Al_2O_3 and SiO_2), coating with photosensitizing dyes [3,14], noble metal deposition (Fe, Ag, Au, Pt), doping and grafting (CNT and MWCNT), coupling with semiconductors (semiconductor) CdS, ZnO, WO_3), and modification with polymers (Poly amide, poly-lactic acid, polypyrrole) [15]. To reduce the loss of catalysts and maintain performance during the separation and recycling process is by adding magnetic properties to the catalyst. Magnetic separation is considered faster and more

effective than traditional separation such as centrifugation and filtration. One material that has magnetic properties is Fe_3O_4 [16]. In this study we proposed the nanocomposite Fe_3O_4-TiO_2 by using combination sonication and hydrothermal treatment. The influence of Fe_3O_4 on the photoelectrochemical properties and photocatalytic activity evaluated by methyl orange degradation.

Methodology

Synthesis of TiO_2 for nanocomposite base was carried out by the hydrothermal-sonication method [10]. A total of 3 grams of Degussa P-25 TiO_2 was mixed with 150 ml of 10 M NaOH solution, followed by sonication for 1 hour (120 W). The solution put into an autoclave at 130^{o}C for 12 hours. The resulting sample is washed with a 0.2 N HCl solution to pH 2. Washing continued with water to pH 6 [10]. The next step, the sample was dried at 150^{o}C until the product is completely dry, then calcined for 1 hour at temperature of 500^{o}C. The Fe_3O_4-TiO_2 nanocomposite was obtained by the precipitation method. Solution A consists of $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ (2:1) dissolved in 20 ml distilled water to obtain a homogeneous solution. $FeSO_4.7H_2O$ and $FeCl_3.6H_2O$ as Fe^{2+} and Fe^{3+} precursors for Fe_3O_4 formation. Solution B consisted of TiO_2 prepared in a solution of distilled water and ethanol (1:1) and ultrasonic for 3 hours to obtain a uniform suspension. Solution A was dropped into solution B, then stirred in a water bath at 80^{o}C for 30 minutes to maintain the temperature. Then add ammonia and stir again for 5 minutes. The mixture transferred to the autoclave at 100^{o}C for 1 hour to form nanocomposite Fe_3O_4-TiO_2. The final product was washed with distilled water and dried in the oven. Morphological characterization using Scanning Electron Microscopy (SEM) at LIPI Physics, Serpong. The characterization of catalyst using X-Ray Diffraction (XRD) at the UIN Syarif Hidayatullah Integrated Laboratory Jakarta. To measure bandgap energy using UV-Vis Diffuse Reflectance Spectroscopy (UV-Vis DRS) at the Chemical Services Laboratory, Faculty of Mathematics and Natural Sciences, University of Indonesia. The photocatalytic activity test was carried out in a closed container using a 300 W mercury lamp for 1 hour with sampling intervals every 10 minutes, then to get a decrease in concentration carried out by testing with a spectrophotometer at the Basic Chemistry Laboratory of Sultan Ageng Tirtayasa University.

Result and Discussion

Scanning Electron Microscope Test Results. The sonication treatment causes the solution to appear more homogeneous by forming a white suspension, due to the breakdown of aggregates that exist to the molecular level. In addition, sonication helps break the chemical bonds of TiO_2 in the suspension into Ti-O-Ti bonds which will be easier to react with NaOH so that can be reduce hydrothermal time [4].

In the catalyst leaching process with 0.2 N HCl and distilled water, the Na element exchange from NaOH with hydrogen protons from H_2O that has a smaller atomic size [19]. To increase the crystallinity of the catalyst, calcination was carried out in the furnace at a temperature of 500^{o}C to obtain the anatase crystal structure.

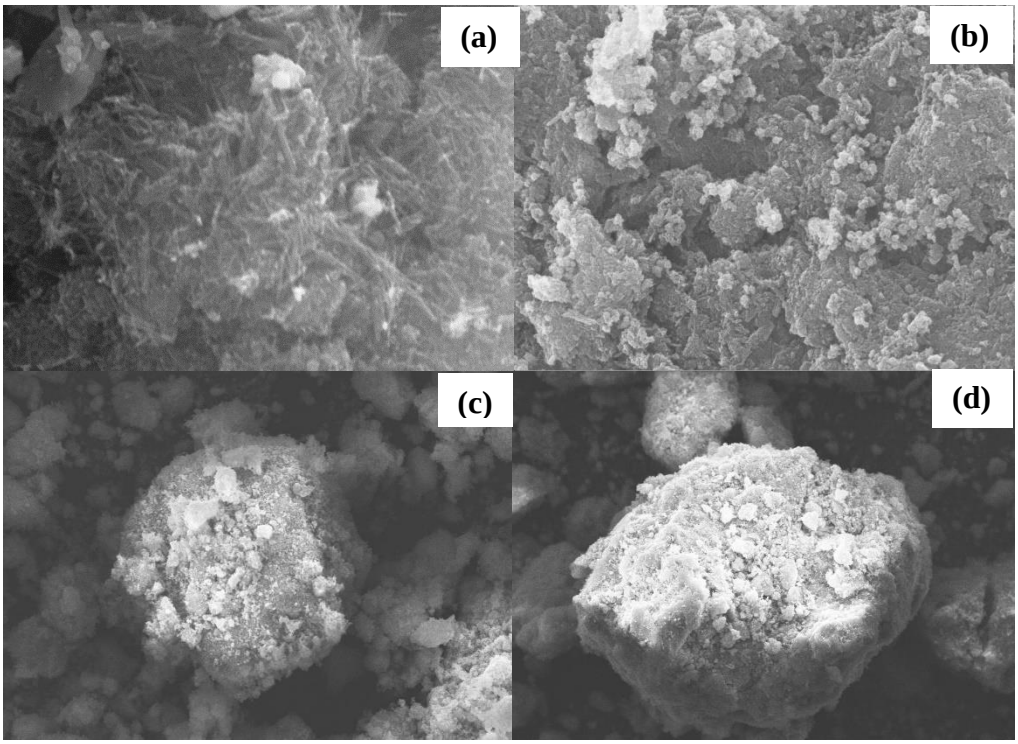

Figure 1. SEM Result of (a) TiO_2, (b) 10%Fe-TiO_2, (c) 15%Fe-TiO_2, and (d) 20%Fe-TiO_2

After going through the hydrothermal - sonication process and SEM analysis, TiO_2 was obtained for the base nanocomposite in the form of nanoparticles (Figure 1). In Figures 1b, 1c, and 1d are the results of SEM analysis of the Fe-TiO_2 nanocomposite photocatalyst. The Fe-TiO_2 nanocomposite was obtained from the second hydrothermal process from the first hydrothermal. From Fig 1, it can be seen that there are Fe_3O_4 nanoparticles attached to the surface of TiO_2. Figures 1b, 1c and 1d show the results of SEM characterization of nanocomposite photocatalysts with 10% Fe_3O_4 (10Fe-TiO_2), 15% (15-Fe-TiO_2) and 20% (20Fe-TiO_2) nanoparticle concentrations.

It can be seen in the figure 1 that when the concentration of Fe_3O_4 nanoparticles increases to 15%, more and more nanoparticles attach to the surface of TiO_2. However, when the concentration of Fe_3O_4 nanoparticles increases to 20%, there is an aggregation phenomenon and many nanoparticles form larger nanoparticles with rough surfaces. From Figure 1 it can be seen that the addition of Fe_3O_4 nanoparticles does not cause damage to the morphology of TiO_2 but that Fe_3O_4 nanoparticles adhere to and surround the surface of TiO_2 [20].

Characterization of X-Ray Diffraction (XRD). Based on Fig. 2 we can see the XRD pattern of TiO_2 material along with the characteristics of the peaks based on JCPDS card number 21-1272 which shows the diffractogram of TiO_2 obtained is an anatase phase. This can be seen from the value of 2θ obtained, namely 25.42º (101); 38.24º (112); 48.48º (200); 55.26º (211). Figures 2b, 2c and 2d are catalysts synthesized by Fe_3O_4 with different concentrations of 10%, 15% and 20%, in the three figures show that besides the anatase peaks there are also peaks of Fe_3O_4. Based on JCPDS card number 26-1136, the results of Fe-TiO_2 synthesis containing Fe_3O_4 compounds can be seen from the 2θ values obtained, namely 35.82º (311) and 63.04º (440). In Figures 2b, 2c, and 2d the peaks of Fe_3O_4 vary and show that the greater addition of quantity of a material in this case Fe_3O_4 can affect the peak of the added material will be higher. However, it should be noted also in the addition of quantities of Fe_3O_4 because if too much TiO_2 as a foundation will be covered by Fe_3O_4 and will affect the photocatalytic process.

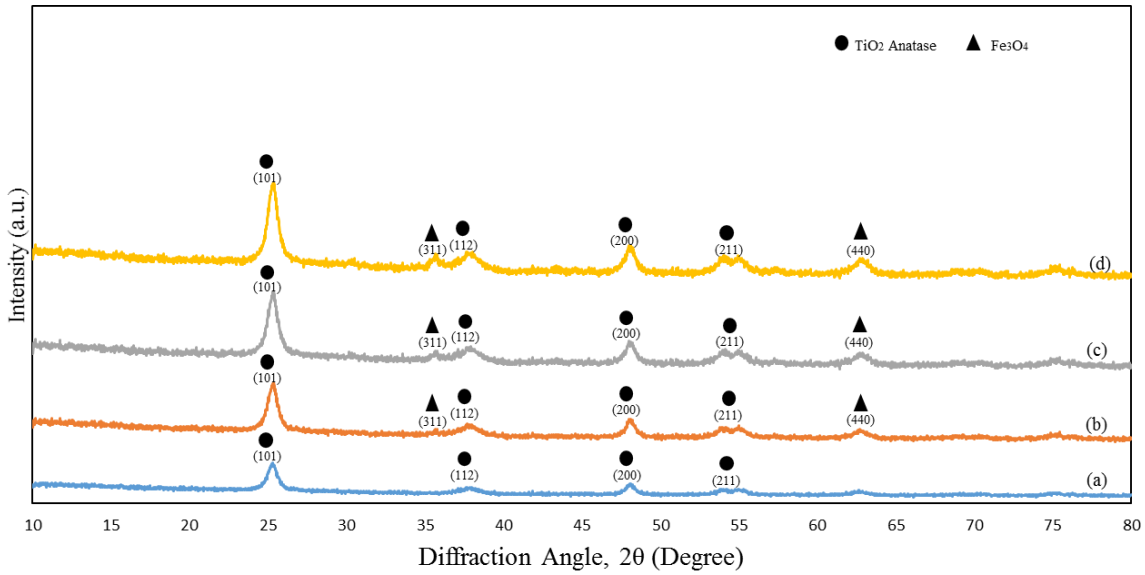

Figure 2. XRD Patters of catalysts (a) TiO_2, (b) 10%Fe-TiO_2, (c) 15%Fe-TiO_2, (d) 20%Fe-TiO_2

Determination of particle size is done using the Debye-Scherer equation as in equation (1).

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

In the equation (1), λ is the wavelength of the X-Ray (0.1540 nm), β is FWHM (full width at half maximum), θ represents the diffraction angle and D indicates the size of a particle. The value of crystal size calculated using the Debye-Scherer (equation (1)) is shown in Table 1.

Table 1. Crystallite size of anatase

Catalyst	Anatase Diameter [nm]
TiO_2	92.91
10% Fe-TiO_2	109.122
15% Fe-TiO_2	108.534
20% Fe-TiO_2	104.236

Characterization of UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). The UV-Vis DRS for can be seen in Fig. 3. Fig. 3 shows that the wavelength for TiO_2 is 383 nm, Fe_3O_4-TiO_2 with a concentration of 10% by 363 nm, Fe_3O_4-TiO_2 with a concentration of 15% by 365 nm, Fe_3O_4-TiO_2 with a concentration of 20% is 366 nm.

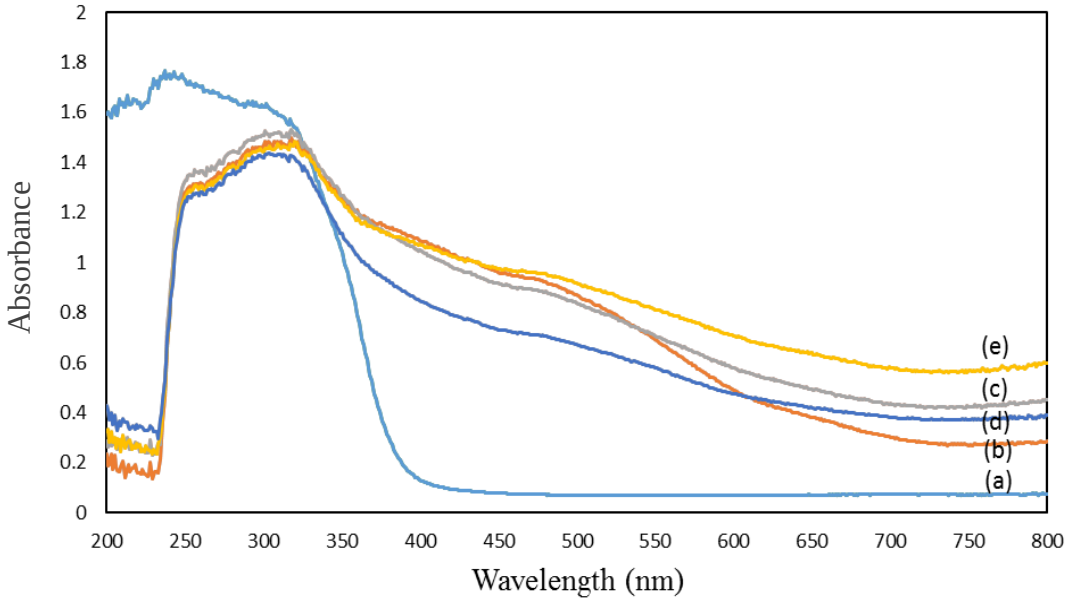

Figure 3. UV-Visible absorbtion spectra of the catalysts (a) TiO_2 (b) 10%Fe-TiO_2, (c) 15%Fe-TiO_2, (d) 20%Fe-TiO_2, (e) Cu@Fe-TiO_2

From these data it can be seen that TiO_2 and Fe_3O_4-TiO_2 photocatalysts with concentrations of 10%, 15% and 20% have similar response characteristics to rays, all of which can respond to rays with wavelengths <400 nm. Based on the UV-Vis DRS pattern, it can also be determined the bandgap energy level of the photocatalyst using the Tauc's relation formula. The bandgap energy of samples are shown in Table 2.

Table 2. Catalyst Energy Bandgap

Catalyst	Bandgap Energy [eV]
TiO_2	3.26
10% Fe-TiO_2	2.92
15% Fe-TiO_2	2.85
20% Fe-TiO_2	2.81

Photocatalytic Activity. The methyl orange degradation was carried out by irradiation using a 300 W mercury lamp for 1 hour at intervals every 10 minutes. The initial concentration of methyl orange tested was 4 ppm and a wavelength of 464 nm was obtained which was tested with a UV-Vis Spectrophotometer. The result of methyl orange degradation can be seen at Fig. 4.

The photocatalytic activity of methyl orange degradation results obtained were 20% Fe-TiO_2 (44.23%) > 15% Fe-TiO_2 (24.13%) > TiO_2 (18.40%) > 10% Fe-TiO_2 (17.01%). Figure 4 shows most of the maximum degradation is achieved in 40 minutes. After going through the maximum catalyst time to degrade there is no significant decrease even some have increased again because the absorption of the catalyst was saturated and the catalyst quantity also decreases due to sampling every minute because the sample is in the form of powder and can easily be carried away when taking which sample proven by the moment of separation with a centrifuge there are catalyst deposits. While TiO_2 degradation process still takes place within 60 minutes and is likely to be able to degrade but requires a relatively long time. In the first 10 minutes can be seen from Figure 4 shows that most of the catalyst is working optimally to degrade in the first 10 minutes this is shown by the drastic reduction of some catalysts such as 15% Fe-TiO_2 and 20% Fe-TiO_2.

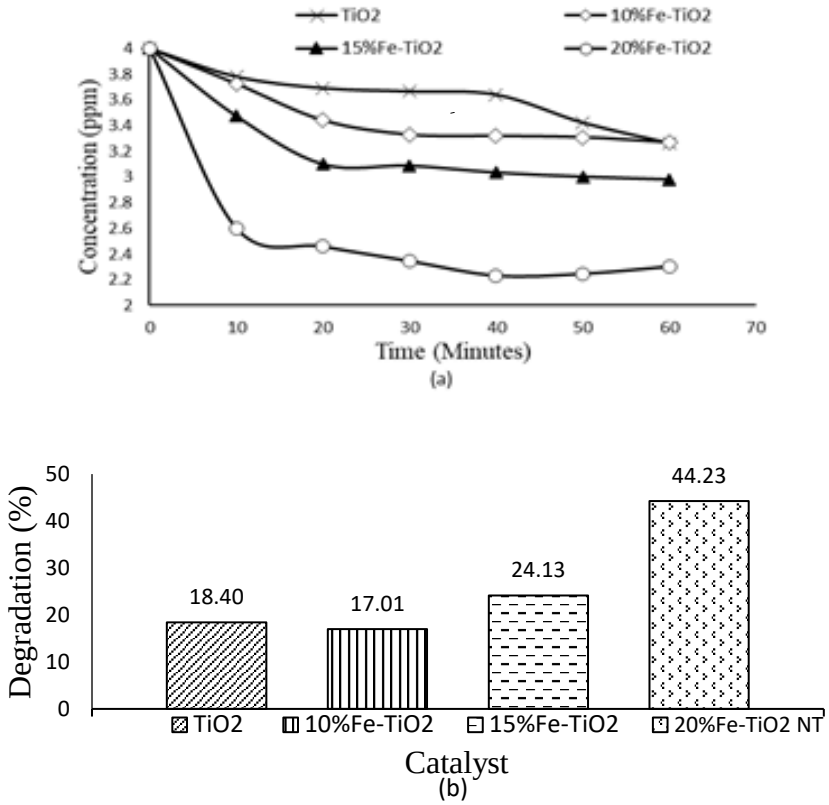

Figure 4. Degradation of methyl orange using the samples (a) for 60 minutes (b) % Degradation of methyl orange

Conclusion

In this study TiO_2 photocatalysts for nanocomposite bases were obtained by sonication - hydrothermal method. Fe-TiO_2 nanocomposite photocatalyst in the form of nanoparticles and nanocomposite photocatalyst has magnetic properties. Bandgap energy of TiO_2, 10% Fe-TiO_2, 15% Fe-TiO_2, 20% Fe-TiO_2, respectively is 3.26 eV; 2.92 eV; 2.85 eV; 2.81 eV. This photocatalyst has a high enough activity to degrade color waste by 44.23% for 60 minutes.

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