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Synthesis of Fe-TiO₂ Composite as a Photocatalyst for Degradation of Methylene Blue

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Abstract

Synthesis and characterization of Fe-TiO₂ composite as a photocatalyst in the photodegradation of methylene blue on visible light irradiation in a closed reactor have been carried out. Synthesis was conducted by the sol-gel method at room temperature using titanium tetraisopropoxide (TTiP) and iron (III) chloride as a precursor, followed by thermal treatment at a temperature of 500 °C. The characterizations were performed using X-ray diffraction (XRD), FT-IR spectrometry, UV-Vis diffuse reflectance spectrophotometry and fluorescence X-rays. The results showed that the Fe-TiO₂ composite could be synthesized by sol-gel method at room temperature, followed by thermal treatment with the concentration of iron was 6% wt. Degradation of methylene blue have been carried out at pH 10 with the percentage degradation of 36% without irradiation and 99.5% under visible light irradiation for 3 hours.

Keywords: Fe-TiO₂ composite; photocatalyst; photodegradation; methylene blue

1. Introduction

Dyes are one of the larger groups of pollutants in wastewater from textile and other industrial processes. About 15% of the total world production of dyes are lost during the dyeing process¹. These waste water are highly colored. Dyes can be converted to the toxic or carcinogenic compounds. The dyes are toxic in certain concentration, so that the release of dyes into the environment can damage our health. The dyes could also damage the environment because as colored materials they can prevent the penetration of light into the waters.

Dyes can be degraded naturally by the sun light, but it is slow. It causes faster accumulation than degradation process, so dyes concentration gets increase. Most of dyes have a stable aromatic molecules structure, large molecular size and difficult to be degraded by biological process, methods of removal of dyes such as physical and chemical methods were required.

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The researches of dye removal have been studied. The object of research is dye removal of textile industry wastewater using chemical and physical methods such as adsorption technique. Degradation of dyes are chemically can be done by oxidation and photodegradation. The degradation of dye through an oxidation process using the ozone oxidant and H_2O_2 is very effective for breaking the benzene ring, but it was required a lot of oxidants and resulted other waste chemicals. So this study, methylene blue removal by the photodegradation method using modified TiO_2 photocatalyst has been done.

Photocatalyst is a material that can be increase the rate of oxidation and reduction reactions induced by light. Photodegradation method was first introduced in 1972², through the decomposition of water into hydrogen and oxygen by titanium electrodes. Photocatalytic considered as an efficient process for toxic organic compounds degradation and disinfectant bacteria by hydroxyl radical ($\cdot OH$) is a strong oxidizing agent³. Mechanisms of Semiconductor Photocatalysis⁴ are shown in Figure 1.

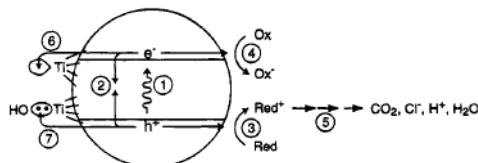


Fig. 1. Mechanisms of Semiconductor Photocatalysis

Primary steps in the photoelectrochemical mechanism: (1) formation of charge carriers by a photon; (2) charge carrier recombination to liberate heat; (3) initiation of an oxidative pathway by a valence-band hole; (4) initiation of a reductive pathway by a conduction-band electron; (5) further thermal (hydrolysis or reaction with active oxygen species) and photocatalytic reactions to yield mineralization products; (6) trapping of a conduction band electron in a dangling surficial bond to yield $Ti(III)$; (7) trapping of a valence-band hole at a surficial titanol group.

TiO_2 has the energy of band gap in the UV light, so the light absorption capability in the visible region is still relatively low. The use of the sun as an energy source becomes less efficient in the TiO_2 photocatalytic process, because the composition UV light in the sun is only 5-7%, thus it is required to modify to modifications TiO_2 photocatalysts to absorb the light in the visible light region.

The photocatalytic of metal ion doped TiO_2 is used to extended the photocatalyst response into the visible region⁵. $Fe-TiO_2$ composite is expected to be an effective and efficient photocatalyst to degraded methylen blue dye under UV and visible light irradiation.

2. Materials And Method

Materials used in this research were titanium tetraisopropoxide (TTiP) 97% (Merck), ethanol 99.99% pa, hydrochloric acid 37% (Merck), sodium hydroxide (Merck), iron (III) chloride (Merck), Metylen blue (Aldrich).

Fourier transform infrared spectrophotometer (Model 8201 PC Shimadzu FTIR) was used to analyze the functional groups in the photocatalyst. X-ray Diffractometer Perkin Elmer 3110 (Shimadzu XRD 6000), UV-Vis spectrophotometer (Genesys 20), UV-Vis spectrophotometer Diffuse Reflectance (UV 1700) and XRF (Analytical MiniPal4 UM Malang), reactor with a source of visible light with $\lambda > 400$ nm (Philips) were used in this research.

The research was initiated by synthesis of TiO_2 sol. Preparation of TiO_2 sol was made by mixing TTiP: H_2O : ethanol: HCl with a mole ratio of 1: 4: 3: 0.01. Synthesis was conducted by the sol-gel method at room temperature and followed by thermal treatment at 500°C. $Fe-TiO_2$ composite sol prepared by mixing $FeCl_3$ and TiO_2 sol, then they were characterized using X-ray diffractometer, FTIR spectrophotometer, UV-Vis spectrophotometer DR, and X-ray Fluorescence (XRF). Test composite photocatalytic activity of $Fe-TiO_2$ was performed on degradation of methylen blue dye under visible light irradiation.

3. Results And Discussion

3.1. X-ray diffraction

Fe-TiO₂ composites synthesized were characterized using X-ray diffractometer to determine the degree of crystallinity, and identify the immobilization of metal ions Fe (III) on TiO₂. Fe-TiO₂ X-ray diffraction pattern are shown in Figure 2. Figure 2 (a) shows the TiO₂ composite X-ray diffraction pattern with 3 major peaks at $2\theta = 25.2078^\circ$, 47.9916° , and 22.7109° with $d = 3.53009$, 1.89417 , 3.91224 Å as a peak of anatase TiO₂ character in accordance with anatase standard JCPDS (12-1276) at $d = 3.520$ Å.

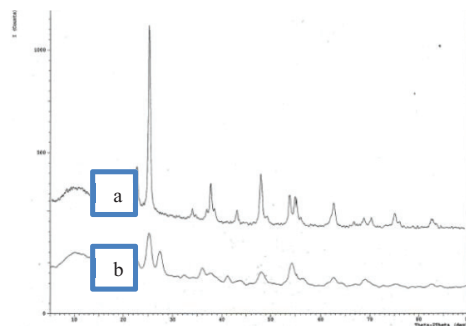


Fig. 2. XRD patterns of Fe-TiO₂

Figure 2 (b) shows the Fe-TiO₂ composite X-ray diffraction pattern with 3 major peaks at $2\theta = 25.1741^\circ$, 27.3975° , 54.2850° and 35.9800° at $d = 2.49408$ Å as the Fe₂O₃ character in accordance with the reports by Pecchi et al. (2002) at $2\theta = 35.87^\circ$ as the Fe₂O₃ character. Peak at $2\theta = 35.9800^\circ$ indicates that Fe metal ions have been immobilized on the surface of TiO₂.

3.2. Infrared Spectroscopy

Fe-TiO₂ composites synthesized were characterized using infrared spectroscopy to determine its functional group. Its Characterization performed on the wavenumber range of 400-4000 cm⁻¹. Figure 3 shows the result of the infrared spectra of Fe-TiO₂ composites.

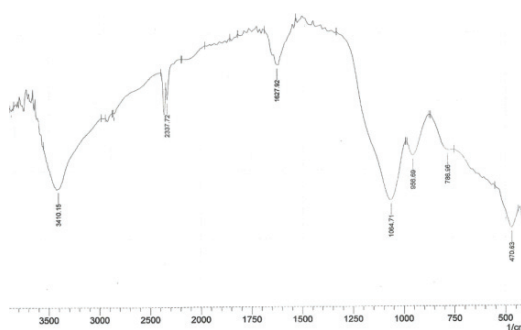


Fig. 3. FT-IR Spectra of Fe-TiO₂ composite

Figure 3 shows strong and broad absorption infrared spectra in the wavenumber of 3410 cm^{-1} and 1627 cm^{-1} , characterized as the OH stretching and bending vibrational of H₂O molecules.

Absorption at wavenumber of 2337 cm^{-1} is characterized as Ti-O absorption of TiO₂, which are reported by Nyquist, 1997⁶. Absorption at wavenumber of 2291 cm^{-1} in Figure 3 is characterized as a vibration of Ti-O-Fe bonding. Luu et al., 2010⁷, reported that the absorption at wavenumber of 2200 cm^{-1} indicates the vibrational bonds

Ti-O-Fe. Based on above data, it can be concluded that Fe (III) has been immobilized in a TiO₂.

3.3. UV-Vis diffuse reflectance Spectrophotometer

The Fe-TiO₂ composites synthesized were characterized using UV-Vis diffuse reflectance spectrophotometry to identify metal ions Fe (III) contained within the framework of the Fe-TiO₂ composite.

In the ultraviolet wavelength range between 200–400 nm, TiO₂ composite gave greater absorbance than Fe-TiO₂ composite, whereas in the visible wavelength region between 400–800 nm, Fe-TiO₂ composite gave greater absorbance than composite TiO₂.

The emerge of new absorption in the UV-Vis diffuse reflectance absorbance spectra of Fe-TiO₂ composite, caused immobilized metal ions Fe (III) into the structure of TiO₂, resulting in overlapping the conduction band. The orbitals of atomic T from TiO₂ and the orbitals d from the metal ions. Fe can reduce the energy band gap of Fe-TiO₂ that causes the TiO₂ in absorbing the visible light.

Spectrum data of UV-Vis diffuse reflectance can also be used to determine Fe-TiO₂ composite of band gap energy (E_g). Spectrum data UV-Vis diffuse reflectance were processed using the Kubelka-Munk equation then made into wavelength and K/S relationship curve.

K/S indicates the coefficient of light absorbed by the Fe-TiO₂ composite compared to the scattered light. Wavelength edge which gives maximum absorption can be determined from the wavelength and K/S relationship curve. Its wavelength is an absorption edge (λ_g) which can be used to calculate the band gap energy with the formula:

$$E_g = \frac{hc}{\lambda_g} = \frac{1240}{\lambda_g} \text{ eV}$$

Based on the data from UV-Vis diffuse reflectance and processed by the Kubelka-Munk equation, was obtained the value of Fe-TiO₂ composite band gap energy (E_g) at 1.45 eV. The value of Fe-TiO₂ composite band gap energy (E_g) is smaller than TiO₂ composite, at 3,2 eV⁸.

This can be explained due to red shift to a higher wavelength, in other words, the Fe-TiO₂ composite can provide a greater uptake in the region of visible light than TiO₂.

TiO₂ photocatalysts which doped with Fe (III) is a n-type semiconductor. Doping of metal ions Fe (III) on TiO₂ provide a new energy level in the TiO₂, which was under the conduction band, so the electrons were excited from the valence band to the conduction band becomes easier because of closer distance. Fe³⁺ metal ions have more valence electrons than Ti⁴⁺, so it can fill the new energy level. Figure 4 shows the new energy levels of n-type semiconductor.

3.4. X-ray Fluorescence

X-ray fluorescence analysis is used to determine the concentration of Fe atom in the Fe-TiO₂ composite. The results of X-ray fluorescence analysis showed that Fe content for calculating weight percent of 6% is 6.85%. Based on these data, it can be concluded that the synthesis of Fe-TiO₂ composite is relatively successful with the desired composition or percentage.

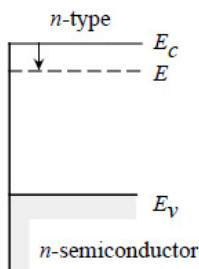


Fig. 4. The new energy level of n-type

3.5. Photodegradation of methylene blue catalyzed by Fe-TiO₂ synthesized

Photodegradation reaction of methylene blue has been conducted for 3 hours, under alkaline conditions (pH = 10). Pecchi, 2002⁹, showed that photodegradation cationic dye optimum under alkaline conditions, this is due to the ease of formation of [•]OH radicals on the surface of the photocatalyst TiO₂.

At alkaline conditions, TiO₂ was instrumental in the formation of [•]OH radicals, such as >TiO⁻ and >TiOH, so that methylene blue can interact strongly on Fe-TiO₂ surface through electrostatic interactions between the negative charge of TiO⁻ and positive charge of cationic dye methylene blue.

Photodegradation of methylene blue was catalyzed by Fe-TiO₂ synthesized and was performed without irradiation (dark reaction) and irradiation visible light. Fe-TiO₂ acted as a photocatalyst that could degrade methylene blue after absorbing the photon energy (hν) provided by visible light.

The effectiveness of photodegradation indicated by the concentration of methylene blue degraded, which is calculated based on the difference between the initial and final concentration of methylene blue.

From the research, it is find the percent degradation with visible light irradiation is higher than without irradiation (dark reaction) Table 1.

Table 1. Effect of irradiation on the degradation of methylene blue

Reaction condition	% Degradation
without irradiation	36.0
visible light irradiation	99.5

In dark conditions, the degradation was influenced by the character of porous TiO₂ which able to act as an adsorbent, and the presence of Fe³⁺ ions as oxidator that is capable to oxidize methylene blue dye. Fe³⁺ ion has a standard reduction potential positive. Fe³⁺ ions can capture electrons on the surface of TiO₂ so it is susceptible to have reduction and prevent recombination. The oxidation reaction methylene blue dye runs slowly, making it less effective in degrading methylene blue with percentage of degradation is 36%. Photodegradation of methylene blue under visible light exposure by Fe-TiO₂ photocatalyst is more effective than the dark reaction, with the percentage of 99.5%. Immobilization of metal ions Fe (III) affected the performance of TiO₂ photocatalysts by forming a new energy level that lied between the valence band and conduction band, it was below the conduction band. It caused a decrease of band gap energy (*E_g*) of Fe-TiO₂ composite. The shift in energy levels was characterized by reducing the value of band gap energy into 1.45 eV. It caused a new absorption at a wavelength of visible light region, so TiO₂ photocatalysts became active under visible light irradiation. When the band gap energy of composite was suitable to the photon energy (*hν*) of visible light, the [•]OH radicals would be formed. [•]OH radicals oxidized the methylene blue into simpler compounds.

Conclusion

Synthesis of Fe-TiO₂ composites have been successfully carried out based on the characterization result, and applied to degrade methylene blue dye on visible light irradiation. The addition of metal ions Fe (III), decrease the band gap energy of Fe-TiO₂ composite to 1.45 eV, resulting in an increase in the absorption spectrum toward the visible light wavelengths. Photocatalytic activity test was carried out at pH 10. Percentage degradation of 36% without irradiation has been obtained and 99.5% under visible light irradiation for 3 hours.

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