Photoelectrocatalytic performance of ilmenite(FeTiO$_3$) doped TiO$_2$/Ti electrode for reactive green 19 degradation in the UV-visible region

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Abstract. FeTiO$_3$ doped TiO$_2$/Ti electrode synthesized through a sol-gel and dip-coating methods for Reactive Green 19 (RG-19) degradation under UV-Visible irradiation. The electrode was characterized by Scanning Electron Microscope (SEM), Linear Sweep Voltammetry (LSV), and Multi Pulse Amperometry (MPA). The electrode surface show that a FeTiO$_3$ layer is quite thin and evenly distributed on the surface of the TiO$_2$/Ti electrode. The photocurrent responses of TiO$_2$/Ti and FeTiO$_3$ doped TiO$_2$/Ti showed the TiO$_2$/Ti electrode was active in UV light, while FeTiO$_3$ doped TiO$_2$/Ti was active in the visible light. The optimum condition show that the TiO$_2$/Ti dopedFeTiO$_3$ provided RG-19 degradation activity of 95%.

1. Introduction

Dyes made from Azo compounds and their derivatives such as the benzene group are very difficult to degrade in nature. Where, azo compounds are very dangerous if they accumulate in the environment due to their carcinogenic and mutagenic properties[1–3]. One of these harmful dyes is Reactive Green 19 (RG-19). RG-19 has toxic, carcinogenic and mutagenic effects on the environment and organisms[4,5], so prevention of waste pollution is required by using the photodegradation method[6–8].

The use of TiO$_2$ semiconductor with the photodegradation method received attention by researchers because of the advantages of TiO$_2$, including good optical, environmentally friendly, high activity, more stable, inexpensive and abundant, but has a large band gap of about 3.2 eV or proportional to the length wave 350-380 nm [9–14]. So for wide applications, TiO$_2$ cannot be applied in sunlight because the intensity of UV entering the earth is only around 3-5%[15–21].

Efforts made in improving the performance of TiO$_2$ photocatalysts are by combining the process of photocatalysis with electrochemistry known as photoelectrocatalysis. The metal dopant reported in this study was ilmenite (FeTiO$_3$). FeTiO$_3$ mineral contains iron and titanium with a high percentage so it is being used as a heterogeneous catalyst for the oxidation process against pollutants in wastewater [22]. The focus of this research is to test the use of FeTiO$_3$ which is doped on the surface of TiO$_2$/Ti electrodes by hydrothermal and anodizing methods, and test its photoelectrocatalysis activity in RG-19 degradation.
2. Experimental Methods

2.1. Preparation of Titanium (Ti) Plate
Preparation of TiO$_2$ Plate carried out by cutting Ti foil (99.7%) with a size of 4 × 0.3 cm and cleaned using sandpaper with a size of 1200 cc. Preparation of TiO$_2$ plate is done by cutting Ti foil (99.7%) with a size of 4 × 0.3 cm and cleaned using sandpaper with a size of 1200 cc. TiO$_2$ foil is washed with detergent and rinse with distilled water. Next, the Ti plate was echoed with a mixtures of HF, HNO$_3$ and distilled water in a ratio of 1: 3: 6 in a row for 2 minutes. The Ti plate is then rinsed with distilled water and then dried[23].

2.2. Fabrication of TiO$_2$/Ti by Anodizing
The Ti plate was prepared into a probe that contain of electrolyte solution mixtures NH$_4$F 0.27 M and distilled water in glycerol 98%. The anodizing process carried out by placing the Ti plate as anode and Cu plate as a cathode by giving a potential difference of 25 volts for 4 hours and Ti Plate was calcined for 90 minutes at a temperature of 500°C[17].

2.3 Synthesis of Ilmenite (FeTiO$_3$)
FeTiO$_3$ is synthesized by refluxing a mixture of 4 mL TTIP, 0.5 mL acetyl acetate, 30 mL ethanol, 2 mL distilled water, 1 mL acetic acid 0.1 M and 1 mL Fe (NO$_3$)$_3$ 0.5 M for 3 hours at 50°C to form sol. FeTiO$_3$ sol were stored at room temperature for 48 hours then heated at 500 °C for 30 minutes.[24].

2.4 TiO$_2$/Ti plate coating with FeTiO$_3$ sol-gel
TiO$_2$/Ti plates were stored in a 25 mL beaker containing FeTiO$_3$ sol-gel for 5 minutes and then heated at 150°C for 15 minutes.

2.5 Characterization of FeTiO$_3$ doped TiO$_2$/Ti
FeTiO$_3$ doped TiO$_2$/Ti electrode were characterized using a Scanning Electron Microscope (SEM) and Linear Sweep Voltammetry (LSV).

2.3. Testing of photoelectrocatalyst Activity
The photo electro catalyst activity test was carried out using RG-19 dyes with a concentration of 0.5: 1.0: 2.0: 3.0 ppm in a 0.1 M NaNO$_3$ solution performed by the Multi pulse Amperometry (MPA) method with a duration of 10 minutes and a potential difference 0.5 Volts in the variations of UV lamps and Visible lamps. Every time span of 10 minutes in 1 hour, absorbance measurements were taken using a UV-Vis spectrophotometer to determine the decrease in the concentration of the dye. Measurements were made on FeTiO$_3$-TiO$_2$/Ti electrodes. The results obtained are plotted against the rate of degradation of RG-19 compounds.

3. Results and Discussion

3.1. SEM Characterization
The results of the characterization using SEM provide information about the surface morphology of the TiO$_2$/Ti and FeTiO$_3$-TiO$_2$/Ti layers. The formation of TiO$_2$/Ti on titanium plates is characterized by the distribution of small particles but does not cover the entire surface homogeneously, irregularly so that there are still empty spaces on the surface of the titanium plate as shown in Figure 1B. The surface of the FeTiO$_3$-TiO$_2$/Ti electrode showed a layer of FeTiO$_3$ gel sol which was quite thin and evenly distributed on the surface of the TiO$_2$/Ti electrode (Figure 1B). The role of TiO$_2$/Ti as a template is very good for the sol-gel coating process and provides information on the small possibility of surface covering of TiO$_2$/Ti nanotubes[25–29].
3.2. Electrode activity test using LSV

Figure 2A shows the working electrodes of TiO$_2$/Ti irradiated using UV light have better activity than when irradiated using visible light and without irradiation (dark). This is consistent with the theory that TiO$_2$/Ti with anatase crystal structure is only able to be active under UV light with a wavelength ($\lambda$) < 388 nm[30–35]. While irradiation using visible light and without irradiation (dark) does not show good activity in a good measurement process.

Figure 2B shows the performance of FeTiO$_3$ doped TiO$_2$/Ti electrode in visible light radiation is better than of TiO$_2$/Ti electrode. Photocurrent of FeTiO$_3$ doped TiO$_2$/Ti electrode in visible light is very high when compared radiation using UV rays or in the dark condition. The high performance of the electrode in Visible rays is due to the presence of FeTiO$_3$ dopants. where, the dopant shift the absorption area of the working electrode so that it can work optimum in the Visible light. When electrons move from the valence band to the conduction band, the FeTiO$_3$ will trap electrons so that the possibility of recombination is very small even with little energy[5,36,37].
3.3. Photoelectrocatalysis degradation test

3.3.1. Determination of maximum wavelength ($\lambda_{\text{max}}$) of RG-19
Based on measurements using a UV-Vis spectrophotometer, it is known that the maximum wavelength of RG-19 is 530 nm (Figure 3). This result has previously been reported by [36,38]. Based on this wavelength, the line equation $y = 0.094x + 0.025$ is obtained for the concentration range of 0.5 - 3 ppm (Figure 4).

![Figure 3. Maximum wavelength of RG-19](image)

3.3.2. Photoelectrocatalysis degradation test using FeTiO$_3$ doped TiO$_2$/Ti electrode
Based on this test, FeTiO$_3$ doped TiO$_2$/Ti electrode showed excellent photoelectrocatalysis performance, both in UV and Visible radiation. The RG-19 concentration decreases with increasing degradation time, as shown in Figure 4A. FeTiO$_3$ doping can prevent recombination in the hole, so the degradation process becomes more optimal. The slow recombination rate gives the opportunity of the hole to produce large quantities of hydroxyl radicals. The degradation ability of FeTiO$_3$ doped TiO$_2$/Ti electrode can be seen in Figure 4B, where the highest % degradation is 95%.

![Figure 4. (A)Photoelectrocatalysis performance of FeTiO$_3$ doped TiO$_2$/Ti electrode on RG-19 compounds (B) % degradation](image)

4. Conclusion
TiO$_2$/Ti doped FeTiO$_3$ electrode synthesized using the dip-coating method succeeded in expanding their photoelectrocatalysis performance in the UV-Visible region. FeTiO$_3$ is doped thinly and evenly on the surface of TiO$_2$/Ti. Based on the photoelectrocatalysis performance test, the electrode had excellent performance with 95% degradation for RG-19 by 95%.
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