Degradation test of organic congo red compounds using Mn-TiO$_2$/Ti electrode by photocatalytic under the uv-visible irradiation

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Abstract. Preparation of TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes was successfully carried out. The purpose of this study was to effect the addition of manganese (Mn) to TiO$_2$ which will be used to degrade congo red organic compounds by photocatalysis. TiO$_2$ is made through an anodic oxidation process. Mn coating is done by doping using the electrodeposition method. The results of the characterization using XRD showed that the TiO$_2$/Ti electrodes were produced in the form of anatase crystals. SEM results show that nanotubes formed on the surface of the thin layer of TiO$_2$/Ti. EDX results show the presence of manganese metal on the surface of TiO$_2$/Ti of 6.58%. The characterization results using LSV showed that the TiO$_2$/Ti electrode was active in UV light at a concentration of 1 ppm with 51.23% degradation and the Mn-TiO$_2$/Ti electrode was active at Visible light at a concentration of 1 ppm with 75.48% degradation.

1. Introduction

The textile industry is one of the fastest growing industries in various parts of the world, including Indonesia [1,2]. On the other hand, the textile industry provides many benefits for humans, on the other hand, the development of the textile industry also has a negative impact on the environment. This is because in the production of textiles always produces waste, one of which is the waste of dyes [3]. In general, dyes from textile industry liquid waste is an organic compound that has an aromatic structure, making it difficult to degrade naturally, not environmentally friendly, difficult to decompose, are resistant and toxic [4–6]. One of the dyes commonly used in the textile industry is congo red [7–9]. The existence of congo red dyes in aquatic environments can damage various species of living things because of the nature of congo red dyes which have quite high toxicity. Congo red which accumulates in the body can cause impaired liver, kidney and nerve function [10].

Several attempts have been made to overcome the problem of pollution, including conventional methods such as biological processes using microorganisms or other approaches such as activated carbon adsorption. In the use of microorganisms only describe biodegradable compounds while nonbiodegradable compounds will remain in the waters, whereas in the use of activated carbon only absorb non-polar organic pollutants with low molecular weight while non-polar compounds with high molecular weight are not eliminated. Conventional waste treatment is less effective because the structure of organic compounds contained in waste contains one or several benzene rings which are relatively stable [2,11].
One alternative method of handling waste pollution that is being developed to degrade various organic matter wastes and industrial processing is photocatalytic [9,12]. This method plays an important role in reducing toxic organic matter by utilizing UV light to produce oxidizing and reducing species on the catalyst surface. Photocatalytic method is a method that utilizes energy derived from light to activate the catalytic process on a semiconductor surface [13].

Titanium dioxide (TiO$_2$) is a semiconductor oxide that has been extensively studied as a photocatalyst since the light sensation effect was discovered by Honda and Fujishima in 1971 [14]. TiO$_2$ semiconductor is widely used as a photocatalyst because it is chemically and biologically inert, non-toxic and cheap [15–17]. In this technique, the TiO$_2$ semiconductor is irradiated with UV light and produces a pair of hole electrons, which can then form hydroxyl radicals. The hydroxyl radical formed can degrade organic pollutants [18]. However, the wide band gap of anatase TiO$_2$ (around 3.2 eV) which is equivalent to UV light (388 nm wavelength) limits its photocatalytic application, so its use is only limited to the UV region and not to the visible light region [19,20]. Whereas it is known that visible light is very abundant as sunlight reaches the Earth and will be very beneficial if there are photocatalysts that can be activated by visible light which is very abundant [21].

Doping technique is one technique that is considered effective to reduce the band gap of TiO$_2$, the principle is to insert dopants in the TiO$_2$ matrix where the dopant element makes the new catalyst matrix have a smaller gap energy equivalent to visible light energy [22]. Paul and Choudhury [23] have tested photocatalyst activity under Visible light by doping Mn metal on TiO$_2$ which shows better results than not doping. Hua Chen et al. [24] doped Mn metal on TiO$_2$ with photocatalyst to degrade Rhodamin B compound. Combining Mn metal doping with photocatalysis is expected to accelerate the process of degradation of congo red organic compounds under Visible light.

2. Experimental Methods

2.1. Tools and materials
The tools used in this research are measuring flask of 25 mL, 50 mL, 100 mL and 1000 mL (Iwaky Pyrex), beaker measuring 50 mL and 100 mL (Iwaky Pyrex), measuring pipette 10 mL and 5 mL (Iwaky Pyrex), filler, stem stirrers, spatulas, porcelain cups, tweezers, dropper pipettes, spray bottles, scissors, stamps and clamps, aquarium pumps, stopwatches, UV and Visible reactors, Bossecom Money Detector UV lamps, Philips Balloon Halogen 150W Visible lamps, Analytical scales, Power Supply, portable potentiostat (e-DY2100PN), furnace thermolyne, XRD, UV-Vis spectrophotometer and SEM-EDX.

The materials used in this study are titanium plates (Ti) with a purity of 99% with a thickness of 0.5 mm, fine sandpaper size of 1200 CC and 220 CC, aquades, fluoride acid (HF), copper plate (Cu), nitric acid (HNO$_3$) (pa), ammonium fluoride (NH$_4$F) (pa), sodium nitrate (NaNO$_3$), Glycerol 98% (pa), manganese dioxide (MnO$_2$) and congo red dyes.

2.2. Manganese doping process on TiO$_2$/Ti electrodes by electrodeposition
The electrodeposition process of Mn-TiO$_2$/Ti electrodes was carried out using MnO$_2$ as a source of Mn metal dopants with a concentration of 0.4 M electrolyte solution. The electrodeposition method was carried out for 3 seconds with a potential bias of 1 volt, where titanium plates that had been overgrown with TiO$_2$ were placed at the cathode poles and copper plate at the anode pole. The formed Mn-TiO$_2$/Ti electrodes were dried in a desiccator for 24 h.

2.3. Degradation test with Multi Pulse Amperometry (MPA) on congo red dyes
Degradation test of congo red dyes 1 ppm, 2 ppm, and 3 ppm were performed with Multi Pulse Amperometry (MPA) with a duration of 10 minutes and a potential bias of 0.5 volts in the light of the UV light, each span of 10 minutes for 1 hour as well as the visible light test. The absorbance measurements were then performed using a UV-Vis spectrophotometer to determine the decrease in the concentration of the dye. Measurements were made on TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes.
3. Results and Discussion

3.1. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

The characterization morphology and composition of Mn-TiO$_2$/Ti electrode was carried out by using SEM/EDX. Figure 1 shows the results of SEM-EDX characterization on the Mn-TiO$_2$/Ti electrodes using the electrodeposition method. Figure 1 (a,b) shows the presence of particles and crystals that are on the surface of the TiO$_2$/Ti electrode. The red color indicates the presence of O$_2$ elements, the yellow color indicates the presence of Ti elements and the green color indicates the spread of the Mn element [22]. Figure 1 (c) EDX data shows the presence of Mn metal present on the surface of TiO$_2$/Ti electrodes. The spectra found on EDX showed the peak of Mn at 0.792 keV, O$_2$ at 0.525 KeV and Ti at 0.452 keV. The formed Mn peak indicates the presence of Mn metal on TiO$_2$/Ti electrode which shows the success of manganese metal doping using the electrodeposition method.

![Figure 1. Morphology and elements characterization of Mn-TiO$_2$/Ti electrode; (A,B) SEM Mn-TiO$_2$/Ti with a magnification of 5000 times; (C) EDX of Mn-TiO$_2$/Ti](image)

3.2. Effect Determination of Electrode Activities using Linear Sweep Voltametry (LSV) Method

Test using the LSV method purpose to determine the activity of TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes based on current and potential measurements. TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes are dipped in 0.1 M sodium nitrate solution which functions as an electrolyte solution that can conduct electric current so that contact with the electrodes occurs [25–27]. Measurement using LSV involves three electrodes, namely TiO$_2$/Ti and Mn-TiO$_2$/Ti as working electrodes, platinum (Pt) as counter electrodes and Ag/AgCl as comparison electrodes [26,27].
Figure 2. Graph Linear Sweep Voltammetry (LSV) (A) TiO$_2$/Ti electrode; (B) Mn-TiO$_2$/Ti electrodes

Figure 2 shows the LSV graph of the TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes. Figure 2 (a) shows the LSV of the TiO$_2$/Ti electrodes produced having the highest activity when irradiated by UV light irradiation. This is corresponding with the theory that TiO$_2$ has photocatalytic activity when it is irradiated by UV lamps because it is active at wavelengths $\leq$388 nm with an energy gap ($E_g$) 3.2 eV [28]. TiO$_2$/Ti electrodes provide a low light current response when irradiated by Visible light [29]. This is because visible light has a greater wavelength so that the energy obtained from a visible light source is smaller to activate TiO$_2$/Ti [30].

While Figure 2 (b) shows the LSV of the Mn-TiO$_2$/Ti electrodes produced has the highest activity when irradiated by visible light irradiation. This corresponds with the theory that the addition of Mn metal on TiO$_2$ can improve the performance of electrodes in the visible area and have good photocatalytic activity because when electrons move from the valence band to the conduction band the electrons are trapped by Mn metals which can reduce [31–33].

3.3. Determination of maximum wavelength on RB 160 using UV-Vis spectrophotometer

The maximum absorption area of congo red can be determined by measurements using a UV-Vis spectrophotometer. Figure 3a shows the maximum wavelength of the congo red of 486 nm and absorbance of 0.902. This provides information that an electron transition has occurred involving electron conjugated electrons along with the chromophore group of heterocyclic congo red compounds by absorbing energy and is evidence of why these compounds show red color due to transitions in the visible area.

Figure 3. (A) Maximum length curve CR, (B) calibration curve of CR
Figure 3b shows that between absorbance and concentration are very linear with \( R^2 = 0.9952 \). The calibration curve is obtained by plotting the concentration with absorbance to produce a straight line equation: \( y = 0.1924x + 0.0495 \). The purpose is made congo red calibration curve is to determine the concentration level of congo red in an environment with different conditions.

3.4. CR Degradation test of CR using TiO₂/Ti and Mn-TiO₂/Ti electrodes

CR degradation test using the Multi-Pulse Amperometry (MPA) method. The degradation process was carried out by using the photocatalysis process.

Figure 4 shows the maximum degradation value using Mn-TiO₂/Ti electrodes obtained at visible irradiation with a concentration of 1 ppm of 75.48%. Mn-TiO₂/Ti electrodes have a more active ability to degrade congo red during UV irradiation than when Visible ray irradiation [34]. This shows that the performance of TiO₂/Ti electrodes formed through the anodic oxidation process has photodegradation activity and is active in UV light irradiation which has \( \lambda \leq 388 \text{ nm} \) [35].
to degrade of congo red when visible beam irradiation compared to UV light irradiation. This shows that the performance of the Mn-TiO$_2$/Ti electrodes formed through the electrodeposition process has photodegradation activity and is active in visible light irradiation. The graph of decrease concentration for photocatalysis in the presence of Mn doping shows better results than the process of photocatalysis without using doping. Cause this process is less likely to occur electron-hole recombination due to the presence of Mn attached to the surface of the TiO$_2$/Ti electrodes so that active species that will cause degradation activity will increase [36,37].

![Graph of decreasing concentration of CR using TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes with photocatalysis process; (a) 1 ppm, (b) 2 ppm and (c) 3 ppm](image)

Figure 6. Graph of decreasing concentration of CR using TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes with photocatalysis process; (a) 1 ppm, (b) 2 ppm and (c) 3 ppm

Figure 6 shows the decrease concentration of CR using Mn-TiO$_2$/Ti electrodes is more active compared to TiO$_2$/Ti electrodes in degrading CR when visible beam irradiation. This is because the Mn-TiO$_2$/Ti electrodes are able to work well in the visible region and resist the recombination of electrons while TiO$_2$/Ti can only work well in the UV region.

4. Conclusion
In this research, we successfully synthesized of Mn-TiO$_2$/Ti electrode by the electrodeposition method. The activity of TiO$_2$/Ti electrodes made through anodic oxidation process has good activity on UV light and Mn-TiO$_2$/Ti electrodes made through the electrodeposition process have good activity on Visible light. The influence of TiO$_2$/Ti and Mn-TiO$_2$/Ti electrodes on congo red degradation through UV and Visible light irradiation using photocatalysis method obtained maximum results at 1 ppm of 51.23% with TiO$_2$/Ti electrodes using UV light. While the performance of Mn-TiO$_2$/Ti electrodes in degrading congo red at a maximum of 1 ppm was 75.48% using Visible light.

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