Photoelectrocatalytic degradation of reactive red 141 using FeTiO$_3$ composite doped TiO$_2$/Ti electrodes

M Z Muzakkar$^1$, M Natsir$^1$, A Alisa$^1$, M Maulidiyah$^1$, L O A Salim$^1$, I Sulistiyan$^1$, F Mustapa$^2$, Ratna$^3$ and M Nuradin$^{1*}$

$^1$ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Halu Oleo, Kendari 93232, Southeast Sulawesi, Indonesia
$^2$ Department of Aquaculture, Faculty of Sciences and Technology, Institut Teknologi dan Kesehatan Avicenna, Kendari 93116, Southeast Sulawesi, Indonesia
$^3$ Chemistry Education Department FKIP Universitas Halu Oleo, Southeast Sulawesi, Indonesia

mnurordin06@yahoo.com (corresponding author)

Abstract. Fabrication of FeTiO$_3$-TiO$_2$/Ti composite electrodes has been successfully carried out by the hydrothermal method and dip coating. The purpose of this study was to determine the effect of the addition of Ilmenite (FeTiO$_3$) on TiO$_2$/Ti plates which will be applied to degrade Reactive Red 141 by photoelectrocatalytic. The characterization results using XRD showed the success of FeTiO$_3$ support on TiO$_2$/Ti produced in the form of anatase crystals with peaks of $2\theta = 39.88^\circ$, $52.71^\circ$, $62.71^\circ$, $64.51^\circ$ and $67.54^\circ$. The SEM results show that the thin films are 10 μm, 5 μm and 2 μm while the EDX results show that the FeTiO$_3$ dopant on the TiO$_2$/Ti plate is marked by marked peaks of Fe, Ti and O each with an elemental composition of 0.17%, 74.73%, and 25.10%. Characterization using FTIR showed the emergence of O-H, Ti-O, and Fe-O groups respectively with wave number absorption 3383 cm$^{-1}$, 1132 cm$^{-1}$, and 474 cm$^{-1}$. Characterization using LSV showed that the TiO$_2$/Ti electrode was active in UV light, while the FeTiO$_3$-TiO$_2$/Ti electrode was active in visible light. The degradation test against Reactive Red 141 using TiO$_2$/Ti electrodes under UV light showed maximum performance at a concentration of 0.5 ppm with a percent degradation of 89.21% while using FeTiO$_3$-TiO$_2$/Ti electrodes under visible light showed maximum performance at a concentration of 0.5 ppm with 96.65% degradation.

1. Introduction

Indonesia is a country that has various types of industries, one of which is the textile industry. One of the harmful substances in textile liquid waste is coloring. Textile industry wastewater is generally difficult to degrade and can cause problems in human life because of its aromatic structure and most dyes are made to have resistance to environmental influences such as the influence of pH, temperature, and microbes[1,2]. Dyes that are often used in the textile industry include Red HE 7B (Reactive Red 141), which is classified as one of the reactive dyes. Therefore, the results of reactive coloring have excellent washing resistance and are shinier than ordinary dyes[3-5].

Reactive Red 141 is one of the dyes commonly used by the textile industry which produces yarn, acrylic fabric and cotton[6,7]. Reactive Red 141 is an azo (aromatic amine) compound, which is very toxic and can cause cancer[8,9]. The method commonly used to treat Reactive Red 141 dyes is the Adsorption method from natural clay. However, this method still uses isotherm models, kinetics and thermodynamic parameters[10], electrocoagulation methods[11], photocatalytic methods using SDS and PVA which are covered with ZnO nanostructures[12].
Considering the danger posed by Reactive Red 141 liquid waste to the environment, the researchers intend to overcome the danger of environmental pollution, so that it can be broken down into compounds that are simpler and safer for the environment. One way to overcome this is by developing a method of photodegradation using TiO$_2$-photocatalysts and ultraviolet (UV) radiation whose energies correspond to or are greater than the photocatalyst bandgap energy [13-16]. Semiconductor material which has the photocatalytic ability when exposed to light with the appropriate wavelength ($\lambda$), will produce oxidizing agents to degrade organic compounds [17-19]. The advantage of this method is that it can break down dyes into CO$_2$ and H$_2$O molecules so that it will not endanger the aquatic environment [20-23].

However, the existence of electron-hole recombination can cause a decrease in TiO$_2$ activity which is characterized by changes in energy in the form of heat. The addition of dopants (both metal and non-metal) can increase photocatalyst activity on visible light exposure [24-26]. TiO$_2$ was developed using titanium plate that are environmentally friendly, economical, non-toxic and faster degradation power, but TiO$_2$ is only active on UV light with a wavelength of 388 nm, so it is necessary to modify TiO$_2$ with the addition of FeTiO$_3$ metal dopants to increase the performance of TiO$_2$ which can work by utilizing solar energy. Based on the above literature, the focus of the study in this study is to examine the ilmenite metal dopants (FeTiO$_3$) on the TiO$_2$/Ti electrodes with the hydrothermal method to degrade Reactive Red 141 dyes by photo electrocatalysis.

2. Apparatus and Methods

2.1. Tools and materials

The tools used in this study were analytical scales, spatulas, scissors, stirring rods, a set of reflux apparatus (three neck flasks, condensers, connecting hoses), spray bottles, beaker, tweezers, drop pipettes, measuring pipettes (2 mL and 5 mL), filler, porcelain cup, petri dish, measuring cup, 50 mL measuring flask, stirring rod, UV reactor, Visible Lamp, magnetic stirrer, hot plate stirrer, furnace, Power Supply, portable potentiostat (e-DY2100PN), X-Ray Diffraction (XRD) (Inspect F50), UV-Visible spectrophotometer, Fourier Transform Infrared (FTIR), Linear Sweep Voltammetry (LSV) and Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX).

The materials used in this study are Ti (Titanium) plate, 1200 CC fine sandpaper, distilled water, detergent, HF (pa), HNO$_3$ (pa) (nitric acid), NaNO$_3$ (sodium nitrate) 0.1 M, TTIP (titanium tetra isopropoxide), Acetyl Acetone, C$_2$H$_5$OH (ethanol), CH$_3$COOH (acetic acid) 1 M, Fe(NO$_3$)$_3$ (iron III nitrate) 0.1 M and Reactive red 141 dyes.

2.2. Preparation sample dan substrate

The implementation of this research was carried out in several stages, namely:

- Ti plate preparation (titanium) by growing the TiO$_2$ thin layer on the Ti plate by the anodizing method [27].
- The second step is making the TiO$_2$ layer by the hydrothermal method by preparing prepared Ti plates and then putting them into a porcelain cup then calcining at 500°C using a furnace for 90 minutes and making FeTiO$_3$Dopan by the sol-gel method. The next steps of TiO$_2$/Ti Plate Coating with FeTiO$_3$ Sol-gel using the Dip-coating Method [27, 28].
- The Characterization of FeTiO$_3$-TiO$_2$/Ti Electrodes with instruments such as X-Ray Diffractometer (XRD), Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX), Fourier Transform Infrared Spectrophotometer (FTIR), Linear Sweep Voltammetry (LSV) and UV-Vis Spectrophotometer.
- Photoelectrolysis activity test in the form of making a standard solution, determining the standard curve, electrode activity test, and dye degradation test.

3. Results and Discussion

3.1. Titanium Plate (Ti) Preparation

Titanium Plate preparation is done by cutting the Ti plate with a size of 4 cm x 0.5 cm, then both sides of the surface of the Ti plate are sanded using fine sandpaper measuring 1200 CC until the surface becomes clean and shiny. Ti plates that have been washed clean using a mixture of detergent solution and distilled water and then rinsed with distilled water which aims to clean the Ti plates of impurities to obtain pure Ti plates, then the Ti plates are dried in the air freely. Titanium metal is very easy to react with oxides so it needs to be done etching (immersion) using a mixture of distilled water: HNO$_3$: HF in a ratio of 6: 3: 1 for 2 minutes. After that, it is then
rinsed with distilled water which aims to remove the remnants of etching solution on the surface of Plate Ti [26,29].

3.2. Manufacture of thin layer TiO$_2$/Ti by hydrothermal method

The production of Thin Layer TiO$_2$/Ti by the Hydrothermal method is carried out by inserting the Ti plate into a porcelain cup and calcined at a temperature of 500°C for 90 minutes in order to oxidize the Ti plate to TiO$_2$. Hydrothermal titanium plates can be seen in (Figure 1).

![Figure 1. Surface appearance (A) Pure titanium plate and (B) TiO$_2$/Ti plate](image)

3.3. TiO$_2$/Ti doping process with FeTiO$_3$ sol-gel using the dip-coating method

The coating of TiO$_2$/Ti films with ilmenite (FeTiO$_3$) was carried out by the sol-gel method. The sol-gel is synthesized from the basic material titanium tetra isopropoxide (TTIP) which functions as a dopant ion distribution medium to form FeTiO$_3$-TiO$_2$/Ti. Acetyl acetate is used as a stabilizer and inhibitor of hydrolyzed TTIP compounds when reacted with distilled water and ethanol. TTIP, acetyl acetate, ethanol, acetic acid, and distilled water are refluxed for three hours at 50°C to increase interactions between compounds. The addition of acetic acid is done to control the rate of hydrolysis and help the process of pore formation so that it can lead to the formation of anatase phase TiO$_2$ mesostructures[28,30]. Dip-coating or coating by immersion is one method of growing nanoparticles. Subsequently, the dip-coating process is carried out by immersing the TiO$_2$/Ti plate in the core solution (sol-gel FeTiO$_3$) for 5 minutes and proceed with the calcination process at 70°C for 10 minutes with the aim that the thin layer of FeTiO$_3$ adheres to the surface of TiO$_2$. The attachment of FeTiO$_3$ to the surface of TiO$_2$ that has been formed through the dip-coating process can be seen in Figure 2.

![Figure 2. The surface of TiO$_2$/Ti which has been immobilized by FeTiO$_3$-TiO$_2$/Ti](image)

3.4. Characterization of FeTiO$_3$-TiO$_2$/Ti Electrodes

3.4.1. SEM-EDX

Figure 4 The SEM results showed the shape of white lumps on the surface of the electrode which indicates the attachment of FeTiO$_3$ sol-gel to the surface of the TiO$_2$/Ti electrode. The size used in the measurement process is very large so the image that appears is only a small lump. According to Chang [31], Huang [32], Chappanda[33],...
and [34] that their research found the tube size of TiO$_2$ reached 10-60 nm. Therefore from the TiO$_2$ image, the results of the synthesis did not show the formation of the tube.

![Figure 3. Surface of FeTiO$_3$-TiO$_2$/Ti with 3000x magnification](image1)

![Figure 4. Characterization of FeTiO$_3$-TiO$_2$/Ti electrode by using EDX](image2)

The composition of elements present on the surface of the FeTiO$_3$-TiO$_2$/Ti electrode can be determined by analysis using EDX (Figure 4). The peak discussing titanium depends on energy levels of 0.4 and 4.5 keV, the peak discussing oxygen at an energy level of 0.5 keV while the existence of non-iron is at peaks of 0.6 and 6.5 keV. The peak of Fe which discusses Fe which proved successful metal doping by dip-coating technique. The peak position obtained in the EDX spectra corresponds to the peak position obtained by [35].

3.4.2. Fourier Transform Infrared (FTIR)

![Figure 5. FTIR spectrum of FeTiO$_3$](image3)

Figure 6 shows some bonds that are formed namely O-H, Ti-O, and Fe-O. The appearance of absorption at the 3383 cm$^{-1}$ wave number was indicated by the presence of OH stretching with a strong signal. The presence of O-H groups is thought to originate from the titania group as the terminal Ti-OH from the crystalline phase of TiO$_2$ or from water absorbed on the surface[36-38]. Wavenumber 1250 cm$^{-1}$ forms a Ti-O bond with an absorption peak of 1132 cm$^{-1}$. Whereas at wave number 580 cm$^{-1}$ a Fe-O bond was formed at the peak of absorption of 474 cm$^{-1}$[39].
3.4.3. Electrochemical Characterization using LSV technique

Figure 6A shows the activity of the effects of UV and visible and non-irradiating (dark) irradiation on the TiO$_2$/Ti working electrodes. Figure 7B shows the activity of the influence of UV light irradiation, visible and non-irradiating (dark) light on the working electrodes of FeTiO$_3$-TiO$_2$/Ti. Electrodes illuminated with visible light have better activity than UV irradiation and without irradiation (dark), this occurs due to the addition of Ilmenite (FeTiO$_3$) on the surface of TiO$_2$/Ti which can shift the electrode absorption area from the valence band to the conduction band, thus the FeTiO$_3$-TiO$_2$/Ti electrode can absorb light with a greater wavelength with smaller energy.

![Figure 6. LSV graph(A) TiO$_2$/Ti electrodes, (B) FeTiO$_3$-TiO$_2$/Ti electrode](image)

3.5. Degradation Test

3.5.1. Determination of Maximum Wavelength ($\lambda_{\text{max}}$) using UV-Vis Spectrophotometer

Figure 7 provides information that an electron transition has occurred involving electron conjugated electrons along with the chromophore group of Reactive Red 141 compounds by absorbing energy and is evidence why Reactive Red 141 shows red color due to transitions in the visible area.

![Figure 7. Wavelength curve of Reactive Red 141](image)

3.6. Photoelectrocatalysis degradation test

Data from photoelektrocalatalysis research with TiO$_2$/Ti electrodes can be seen in Figure 8. Figure 8B shows that the percent degradation of Reactive Red 141 compounds using TiO$_2$/Ti electrodes in the photo electrocatalysis process showed maximum performance at a concentration of 0.5 ppm when irradiated by both UV and Visible light, which was 89.21%.
Figure 8. Graphs of Electrolyzed Catalytic Degradation of TiO$_2$/Ti Electrodes with UV and Visible light irradiation on Reactive Red 141 (A) Concentration Reduction Curve and (B) % Reactive Red 141 Degradation

Figure 9. Graphical Degradation of Electro-catalyzed FeTiO$_3$-TiO$_2$/Ti Electrodes with UV and Visible light irradiation on Reactive Red 141 (A) Concentration Reduction Curve and (B) % Reactive Red 141 Degradation

Data from the photo electrocatalysis research with FeTiO$_3$-TiO$_2$/Ti electrodes can be seen in Figure 9. Figure 9A shows that the activity of FeTiO$_3$-TiO$_2$/Ti electrodes looks very good in areas that are exposed to Visible rays. This can be seen from the decrease in the concentration of Reactive Red 141 at each concentration of 0.5 ppm, 1 ppm, 2 ppm, and 3 ppm and can also be active in UV light irradiation. Figure 9B shows that the percent degradation data provide information on the percent degradation of Reactive Red 141 compounds using FeTiO$_3$-TiO$_2$/Ti electrodes by photoelectrolysis working at a maximum of 0.5 ppm concentration under Visible light radiation with a percent degradation value of 96.65%.

4. Conclusion
From the results of the research that has been done, it can be concluded that TiO$_2$/Ti Electrodes are made by the hydrothermal method while the FeTiO$_3$-TiO$_2$/Ti Electrodes are made by the sol-gel method then proceed with the dip-coating method. TiO$_2$/Ti electrodes in the photo electrocatalysis process were very good in reducing the concentration of Reactive Red 141 in an area exposed to UV light with the highest degradation percentage of 89.21% at a concentration of 0.5 ppm. While the photoelectrolysis FeTiO$_3$-TiO$_2$/Ti electrodes were very good in reducing the concentration of Reactive Red 141 in areas that were exposed to Visible light with the highest percent degradation of 96.65% at a concentration of 0.5 ppm.

Acknowledgment
We acknowledge the financial support from the DRPM-Ministry of Research, Technology and Higher Education of the Republic of Indonesia under No. 171/SP2H/LT/DRPM/2019.

Reference
[1] Özdemir C, Öden M K, Şahinkaya S, and Kalipçi E2011 Clean–Soil, Air, Water39 60-7
[2] Ayangbenro A S and Babalola O O 2017 *International journal of environmental research and public health* **14** 94

[3] Karim M E, Dhar K, and Hossain M T 2018 *Journal of Genetic Engineering and Biotechnology* **16** 375-80

[4] Yaseen D and Scholz M 2019 *International journal of environmental science and technology* **16** 1193-226

[5] Borges G A, Silva L P, Penido J A, De Lemos L R, Mageste A B, and Rodrigues G D 2016 *Journal of environmental management* **183** 196-203

[6] Dolphen R, Sakkayawong N, Thiravetyan P, and Nakbanpote W 2007 *Journal of Hazardous Materials* **145** 250-5

[7] Aquino J M, Rocha-Filho R C, Rodrigo M A, Sáez C, and Cañizares P 2013 *Water, Air, & Soil Pollution* **224**

[8] Telke A, Kalyani D, Jadhav J, and Govindwar S 2008 *Acta Chimica Slovenica*

[9] Zazycki M A, Godinho M, Perondi D, Foletto E L, Collazzo G C, and Dotto G L 2018 *Journal of Cleaner Production* **171** 57-65

[10] Vanaamudan A and Sudhakar P 2015 *Journal of the Taiwan Institute of Chemical Engineers* **55** 145-51

[11] Salmani E R, Ghorbanian A, Ahmadzadeh S, Dolatabadi M, and Nemanifar N 2016 *Iranian Journal of Health, Safety and Environment* **3** 403-11

[12] Kakarndee S and Nanan S 2018 *Journal of environmental chemical engineering* **6** 74-94

[13] Liu J and Chen F 2012 *Int. J. Electrochem. Sci* **7** e9572

[14] Mursalim L, Ruslan A, Safitri R, Azis T, Wibowo D, and Nurdin M. Synthesis and Photoelectrocatalytic Performance of Mn-N-TiO$_2$/Ti Electrode for Electrochemical Sensor. in *IOP Conference Series: Materials Science and Engineering*. 2017. IOP Publishing.

[15] Nurdin M, Maulidiyah M, Muzakkar M Z, and Umar A 2019 *Microchemical Journal* **145** 756-61

[16] Nurdin M, Azis T, Maulidiyah M, Aladin A, Hafid N, Salim L O A, and Wibowo D. Photocurrent Responses of Metanil Yellow and Remazol Red B Organic Dyes by Using TiO$_2$/Ti Electrode. in *IOP Conference Series: Materials Science and Engineering*. 2018. IOP Publishing.

[17] Watoni A, Wibowo D, and Nurdin M. Synthesis of Nano-Ilmenite (FeTiO$_3$) doped TiO$_2$/Ti Electrode for Photoelectrocatalytic System. in *IOP Conference Series: Materials Science and Engineering*. 2017. IOP Publishing.

[18] Maulidiyah M, Natsir M, Fitrianingsih F, Arham Z, Wibowo D, and Nurdin M 2017 *Oriental Journal of Chemistry* **33** 3101-6

[19] Hayakawa K, Yokobaba C, Ichiki N, Muzakkar M Z, Shinmura T, and Nagaoka S 2001 *Research journal of chemistry and environment* **5** 7-15

[20] Nurdin M, Zaeni A, Rammang E T, Maulidiyah M, and Wibowo D 2017 *Anal. Bioanal. Electrochem.* **9**

[21] Nurdin M, Darmanwati D, Maulidiyah M, and Wibowo D 2018 *Journal of Coatings Technology and Research* **15** 395-402

[22] Azis T, Nurwahidah A T, Wibowo D, and Nurdin M 2017 *Environmental nanotechnology, monitoring & management* **8** 103-11

[23] Nurdin M, Prabowo O A, Arham Z, Wibowo D, Maulidiyah M, Saad S K M, and Umar A 2019 *Surfaces and Interfaces* **16** 108-13

[24] Naraginti S, Thejaswini T, Prabhakaran D, Sivakumar A, Satyanarayana V, and Prasad A 2015 *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **149** 571-9

[25] Mathew S, Ganguly P, Rhatigan S, Kumaravel V, Byrne C, Hinder S J, Bartlett J, Nolan M, and Pillai S C 2018 *Applied Sciences* **8** 2067

[26] Nurdin M, Muzakkar M Z, Maulidiyah M, Maulidiyah N, and Wibowo D 2016 *J. Mater. Environ. Sci* **7** 3334-43
[27] Nurdin M and Maulidiyah 2014 *International Journal of Scientific & Technology Research* 3 122-4
[28] Mawarnis E R, Ali Umar A, Tomitori M, Balouch A, Nurdin M, Muzakkar M Z, and Oyama M 2018 *ACS Omega* 3 11526-36
[29] Muzakkar M Z, Nurdin M, Ismail I, Maulidiyah M, Wibowo D, Ratna R, Saad S K M, and Umar A A 2019 *Emission Control Science and Technology* 3 1-9
[30] Muzakkar M, Umar A, Ilham I, Saputra Z, Zulfikar L, Maulidiyah M, Wibowo D, Ruslan R, and Nurdin M 2019 *Journal of Physics: Conference Series* 1242
[31] Chang H-Y, Tzeng W-J, and Cheng S-Y 2009 *Solid state ionics* 180 817-21
[32] Huang L, Zhang S, Peng F, Wang H, Yu H, Yang J, and Zhao H 2010 *Scripta Materialia* 63 159-61
[33] Chappanda K N, Smith Y R, Misra M, and Mohanty S K 2012 *Nanotechnology* 23 385601
[34] Yin Y, Jin Z, and Hou F 2007 *Nanotechnology* 18 495608
[35] García-Muñoz P, Pliego G, Zazo J, Bahamonde A, and Casas J 2016 *Journal of environmental chemical engineering* 4 542-8
[36] Mehandjiev D, Naydenov A, and Ivanov G 2001 *Applied Catalysis A: General* 206 13-8
[37] Tian J, Xu L, Yang Y, Liu J, Zeng X, and Deng W 2017 *International Journal of Mineral Processing* 166 102-7
[38] Li F, Zhong H, Zhao G, Wang S, and Liu G 2016 *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 490 67-73
[39] Nurdin M, Maulidiyah A H W, Abdillah N, and Wibowo D 2016 *Int. J. ChemTech Res* 9 483-91