

Organic Compound Rhodamine B Degradation by TiO₂/Ti Electrode in a New Portable Reactor

Maulidiyah, Halimahtussaddiyah Ritonga, Richard Salamba,
Dwipayogo Wibowo, Muhammad Nurdin*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas
Halu Oleo, Kendari 93232 – Southeast Sulawesi, Indonesia

Abstract: The aim of this research was to design reactors of Ultra Violet Black Light Blue (UV-BLB) and Ultra Violet Light Emitting diode (UV-LED)-based portable photoelectrocatalytic. This reactor was used to test the performance of the TiO₂/Ti electrode in degrading organic compound of rhodamine B (RhB). Synthesis of TiO₂/Ti was conducted by anodizing. Furthermore, the degradation test of compound of RhB photoelectrocatalytic was done using reactors of UV-BLB and UV-LED. Characterization results of TiO₂/Ti using X-Ray Diffraction (XRD) showed the formation of anatase TiO₂ crystals. While the characterization results of surface morphology of TiO₂/Ti using Scanning Electron Microscopy (SEM) showed nano tube structures. Performance test of the reactor by measuring the photocurrent response showed TiO₂/Ti electrode were more active when using light irradiation of UV-BLB compared to UV-LED. Degradation of RhB using TiO₂/Ti electrodes by light irradiation of UV- BLB had better activity than UV-LED.

Keywords: Portable Reactor, TiO₂/Ti, Photoelectrocatalytic, UV-BLB, UV-LED, Rhodamine B.

1. Introduction

The rapid development of technology is faced by the problem of environmental pollution such as water pollution that will affect the life of living creatures. Wastewater produced has potential harmful to people and the environment such as wastewater of textile industry will destroy aquatic environment due to the dyes used that is discharged into the aquatic environment^{1,2}. The impact of dyes presence with high concentrations in aquatic environments can hinder the irradiation of sunlight into the water so that interfere activity of algae photosynthesis and the availability of oxygen in the water is decreased³. This problem cause the water to be contaminated, result in reduced oxygen levels in the water and the impact on the death of biota in aquatic environments⁴. Some characteristics of polluted water can be seen qualitatively from its color, viscosity and odor⁵.

The way to overcome pollution problem, among others, are by conventional way through a biological process using microorganisms or other approaches such as using activated carbon. However, conventional sewage treatment is less effective, because the structure of organic compounds contained in waste consist one or more benzene rings which are relatively stable⁶⁻⁸. Utilization of photocatalyst is one of the technologies that are effective in degrading organic pollutants to carbon dioxide completely, so it can be used in overcoming water pollution^{9,10}.

The use of photocatalytic technology using TiO₂ semiconductor catalyst is one way that can be used to overcome the problem of liquid waste pollution¹¹. Utilization of photocatalytic TiO₂ begins with photon energy

absorption by the semiconductor, which causes charge separation or photoexcitation in semiconductors. Electrons (e^-) will be excited into the conduction band by leaving a hole/positive hole (h^+) in the valence band. This positive hole is a very powerful oxidizing agent if there are organic compounds adsorbed on the surface of TiO_2 ¹². Efficiency of oxidation can be improved with the application of potential bias to transfer the electrons through the external circuit, thus preventing recombination of positive holes and electrons is known as photoelectrocatalytic method^{13,14}.

In order to use the photoelectrocatalytic process in improving the performance of TiO_2 semiconductor for wastewater treatment process, it is needed an electrode films TiO_2/Ti reactor the method of photoelectrocatalytic making which is cheap and easy to operate, thus allowing it to be applied on a large scale¹⁵. According to Izadifard, the fabrication of suitable reactor needs to consider constraints such as transfer electron, surfaces, and light reactive¹⁶. Currently some photoelectrocatalytic reactor designs are still limited to a simple test, while the reactivity of TiO_2 in terms of the amount of energy photon received to optimize the performance of TiO_2 semiconductor is very high^{17,18}. In this study, photoelectrocatalytic reactor has been designed, namely UV-BLB and UV-LED which aims to test the performance of TiO_2/Ti electrodes made by anodizing method of the photocurrent response in order to improve the performance of TiO_2 in degrading RhB organic pollutants.

2 Experimental

2.1 Preparation of Ti (titanium) Plate

Preparation of Ti (titanium) plate was done by cutting Ti plate with purity of 99.7% (thickness of 0.5 mm, Shanxi Yuanlian Rare Metal, Ltd.) with a size of 4 cm x 2 cm and then sanded using fine sandpaper with the size of 1200CC until the surface was clean and shiny then washed with a solution of detergent, water, and distilled water. After drying in the air, Ti plate then soaked (etched) using a mixed solution of HF, HNO_3 , and distilled water in the ratio of 1: 3: 6 for 1 minute. The final stage in the preparation of Ti plate was rinsed it with distilled water and then dried it in the air^{8,19}.

2.2 The Preparation of TiO_2 Coating using Anodizing Method

Titanium plate was soaked in the probe that has been filled with the electrolyte solution in the form of 0.27 M NH_4F and 4 mL Aqua bidestilata in 99.5% glycerol (p.a.). Anodizing process was carried out for 4 hours by giving potential bias of 25 Volts and putting it in furnace for 1.5 hours at a temperature of 500°C to obtain crystalline anatase of TiO_2 which have photodegradation activity better than other crystal types^{8,19}.

2.3 The Fabrication of Photoelectrocatalytic Reactor

2.3.1 The fabrication of UV-BLB Reactor

The design of photoelectrocatalytic system reactor assembled based on simple electronic compartment with good intensity. The reactor was designed with 4 watt of 8 unit UV-BLB bulbs with a total power of 32 watts. Lights installed around the box were made with size of 20 cm x 10 cm, each bulb was arranged using 10 watt transformer with a 5 Watt capacity adjusted to UV -BLB bulbs.

2.3.2 The fabrication of UV-LED Reactor

The reactor was in the form of a cylindrical tube of the Polyvinyl Chloride (PVC) pipe with a diameter of 6-inch and a length of 7 cm and then coated with wood and white plastic paper to increase UV-LED bulbs light intensity. UV-LED bulbs used were 2.1 volt with diameter of 5 mm by 32 units lights mounted on the inner surface of the photoelectrochemical cell tube wall. UV-LED light reactor source used voltage of 12 volts, and was equipped with a switch to turn off and turn on the lights.

2.4 Performance Test of TiO_2/Ti Electrode using UV-BLB and UV-LED Reactors

2.4.1 Performance Test of Photocurrent Response with Linear Sweep Voltammetry (LSV) Method

Measurements were made with the LSV method using solution of 0.1 M $NaNO_3$, LSV was conducted

from the potential of -1 volt, up to 1 volt, with a scan rate of 1×10^{-4} V/s. Where each TiO_2 electrodes were tested by illuminating bias light on UV-BLB reactor and UV-LED reactor. Results of LSV intended to see photoelectrocatalytic activity during the testing process.

2.4.2 Degradation Test of Dye with Photoelectrocatalytic System using UV-BLB dan UV-LED Reactors

Degradation test of RhB dye of 0.5; 1.0; 2.0 and 3.0 ppm (+0.1 M NaNO_3) was conducted using Multi Pulse Amperometry (MPA) with a duration of 10 minutes and a bias potential of 0.5 volts using UV-BLB and UV-LED reactors. Each span of 10 minutes in 1 hour was measured 6 times. Absorbance using UV-Vis spectrophotometer, was determined the decrease in dye concentration.

3 Results and Discussion

3.1 The Preparation of TiO_2/Ti Electrodes

The preparation of TiO_2 thin film on the Ti plate surface using anodizing method which was carried out for 4 hours. Anodizing process is a process of anodic oxidation from Ti thin plate in the electrolyte solution NH_4F and glycerol with a predetermined bias potential. Ti plate acts as the anode, while acting as the cathode was woven Pt wire. Anodizing is an electrochemical oxidation process that fosters a layer/film on top of a metal surface. The anodizing plate was then calcined at a temperature of 500°C for 1.5 hours. The aim was to evaporate the organic solvents trapped in the titanium plate and to obtain crystalline anatase TiO_2 (Fig. 1). According to Nurdin and Maulidiyah, anodizing method on Ti plate which was calcined at a temperature of 500°C will form a structure of nano-sized crystalline anatase TiO_2 ¹⁹. Anatase crystal have a larger surface area and greater active side so that it can absorb light better than any kind of rutile crystals. For anatase structure, it has an energy gap of 3.2 eV ($\lambda = 388$ nm) while rutile of 3.0 eV ($\lambda = 405$ eV)^{20,21}, the value of E_g was higher which yielded greater active surface area and generate more effective photoactivities the differences of anatase and rutile crystal structures result was differences in density, surface area and its active side. The band gap energy states is required for the transition of electrons from the valence band to conduction band.

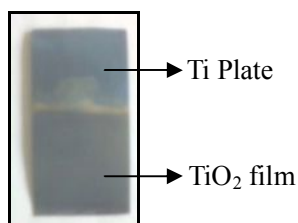


Fig. 1. Results of anodizing process on Ti plate forming a layer TiO_2 film

3.2 UV-BLB Reactor

The reactor system of photoelectrocatalytic design was made by simple electronic arrangement with a certain intensity variation. The reactor is designed by UV-BLB lamp with type of fluorescent linear with 4 Watt power that assembled using 8 pieces bulbs with total power of 32 watt bulbs, bulbs installed around the box were made with a size of 20 cm x 10 cm, each one was arranged using a 1 piece of phillips bulb ballast (transformer) with a capacity of 5 watts. The function of the ballast was to limit the amount of current in operating bulb in electrical characteristics accordingly so that this tool was a supplier of electrical current in the bulb. The reactor was equipped with a switch to turn off and turn on the bulbs. Photoelectrocatalytic reactor which had been made is shown in Fig. 2.



Fig. 2. The schemes and figure of photoelectrocatalysis reactor; (A) The scheme of UV Reactor (UV-BLB); (1) the probe tube-shaped, (2) counter electrode (Pt) (3) electrode work TiO_2/Ti , (4) Ag/AgCl electrode reference, (5) the UV-BLB lamp; (B) the picture of UV-BLB reactor design.

3.3 UV-LED Reactor

UV-LED reactor was designed with simple electronics system, namely by a series circuit method, a series circuit is one electrical circuit arranged in parallel which components are installed sequentially. UV-LED light were arranged on the surface of the cylindrical tube wall of polyvinyl chloride (PVC) pipe with a diameter of 6 inches and a length of 7 cm and then coated with a cube-shaped timber and inside the pipe was coated with a silver-colored plastic paper to increase the light intensity of lights. UV-LED light that used was 5 mm in size with 2.1 volt power lights which were arranged together as many as 32 bulbs, each 3 bulbs were arranged using 1 resistor of 2 ohm. Resistor is one of the electronic components that function as retaining the current flowing in a circuit and in form of terminal which manage and lower the voltage, as well as limit the current flowing in a string of lights to suit the needs and dividing the power supply voltage to each UV-LED lamp. The reactor was equipped with a switch to turn off and on the lights, UV-LED lamps reactor used 12 volt voltage source. UV-LED lamps-based photoelectrocatalytic reactor which had been made is shown in Fig. 3.

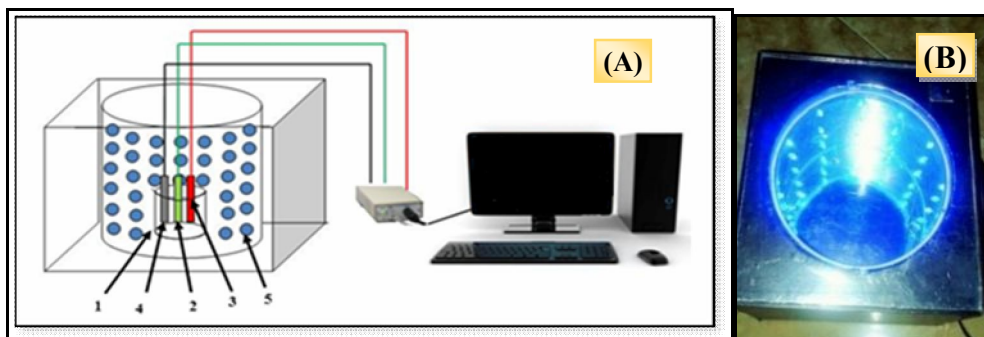


Fig. 3. The schemes and figure of photoelectrocatalysis reactor; (A) The scheme of UV Reactor (UV-LED); (1) the probe tube-shaped, (2) counter electrode (Pt) (3) electrode work TiO_2/Ti , (4) Ag/AgCl electrode reference, (5) the UV-LED lamp; (B) the picture of UV-LED reactor design

3.4 Determination of the Electrodes Activities using Potentiostat Portable with Linear Sweep Voltammetry (LSV) method

Photocurrent response is a response of electrode that is observed when irradiated by appropriate light and given the current in form of voltage, where the current is the size of electrons occurred on the surface of the electrode²¹. In this study, the measurement of optimum Ti plate layer was conducted, and comparing the photocurrent response of UV-BLB and UV-LED reactors as a potential function using LSV technique with the use of 0.1 M of NaNO_3 solution as an electrolyte solution. Measurements of bias potential performed on -1000 to 1000 eV potentiostat and scan rate of 10^{-4} mV/s. Measurement of TiO_2 current response to UV light is shown in Fig. 4.

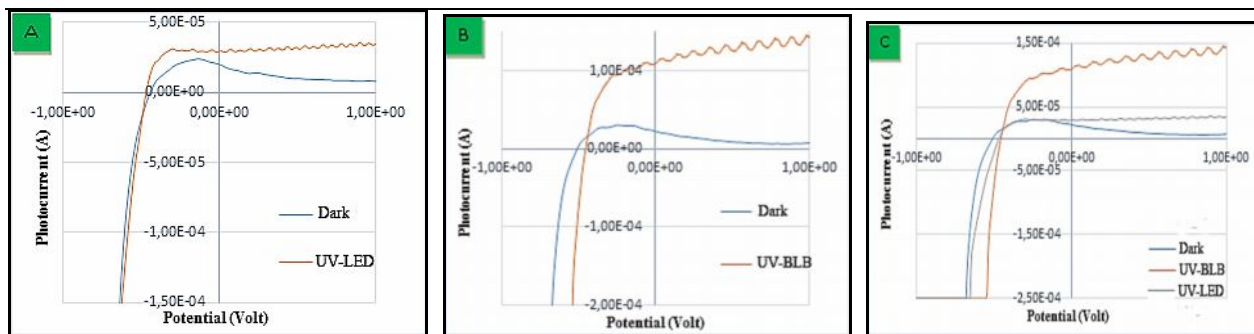


Fig. 4. Graphs of Linear Sweep Voltammetry (LSV); (A) TiO₂/Ti electrode using UV-LED reactor, (B) TiO₂/Ti electrode using UV-BLB reactor, (C) The comparative data of LSV uses UV-reactor BLB and UV-LED

Figs 4A and 4B are the results of LSV measurements using UV-LED reactor and UV-BLB reactor to observe the value of light photocurrent response of TiO₂/Ti electrode of each reactor, while Fig. 4C is a combination of the value of LSV photocurrent response using UV-BLB and UV-LED reactors which showed highly significant differences in the photocurrent response from the TiO₂/Ti electrodes. When TiO₂/Ti electrodes irradiated by light using UV-BLB reactor, they showed greater photocurrent response activities compared to UV-LED reactor. While in the dark condition when no photoelectrocatalytic activities occurred on the TiO₂/Ti electrode. This proved that Ti plate had been coated by conductive TiO₂ semiconductor as well as more active in using UV-BLB reactor characterized by the photoactive activity against UV light during irradiation using UV-BLB reactor. Meanwhile, when using UV-LED reactor, they showed photoactive activities but not as good as UV-BLB reactor.

From results of LSV measurements, it showed that the more layers, the photocurrent response was smaller. It was due to TiO₂ layer grown on Ti plate getting thicker so that generated electrons due to UV light irradiation was not transferred to semiconductor bulks, and only on the surface of the catalyst. As the result, semiconductors bulk can not transfer electrons toward the counter electrode as the cathode. Besides the thickness of TiO₂ thin layer grown on Ti plate resulted in the penetration of UV light was difficult to reach the inside layer of TiO₂ film.

3.5 Performance Test of UV-BLB and UV-LED Reactors

Photoelectrocatalytic system is a combination of electrochemical processes with the photocatalyst, wherein the working electrode of TiO₂/Ti is subjected to UV light provides positive pairs of electrons and holes (h^+). Positive hole will initiate an oxidation reaction on the electrode surface, while the electrons flow through the back contact to the counter electrode and transferred to the electrons catcher present in the solution. The flow of electrons can be observed as light current and the amount is proportional with RhB organic substances in solution.

These electron-hole separation would increase with the provision of a positive bias potential on the working electrode which was immersed in solution, as a result the electric field near the interface was formed, so that the surface of the working electrode was anodic. In this situation the recombination of electrons and holes by transferring it to solution through the auxiliary electrode was cathodic¹³. In this way the bias potential will increase the charge separation so that the efficiency of OH radicals formation was higher so that accelerate the process of degradation of RhB organic compounds.

Degradation testing of RhB organic compound was performed using a concentration of 0.5 ppm, 1 ppm, 2 ppm and 3 ppm by irradiating UV-BLB and UV-LED light with treatment photolysis, photocatalytic and also photoelectrocatalytic. Photolysis method is a method used to degrade a compound by using radiation only, as shown in Fig. 5.

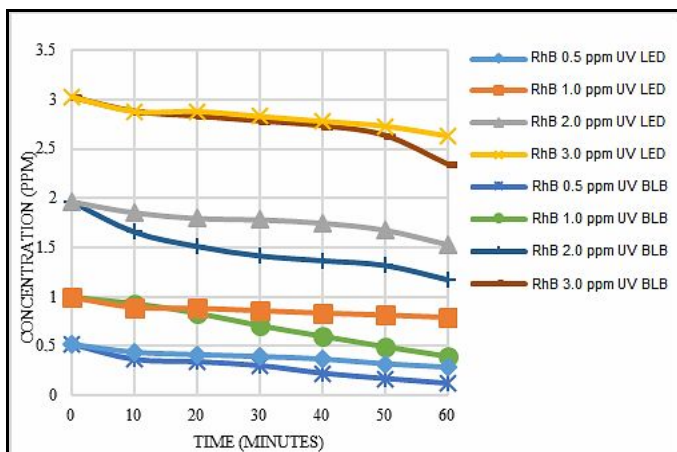


Fig. 5. Graph decrease concentration of RhB by photolysis method by using TiO₂/Ti catalyst with variable of UV-BLB and UV-LED reactors

Fig. 5 shows decrease in the concentration of RhB when irradiated with UV-BLB and UV-LED, photolysis there was slowly concentration decreasing, this was due to the oxidation reaction of RhB and bond breaking during UV-BLB or UV-LED irradiation. Photocatalytic reaction is a chemical transformation that are affected by light along with catalyst. The catalyst in this photocatalytic process has the ability to absorb photons, so that the photocatalyst can also be defined as a process that occurs based on the dual capability of a photocatalyst to absorb photons simultaneously¹⁵. With photocatalytic method during irradiation time ranging from 0-60 minutes, there were RhB concentrations decreased of each concentration of 0.5; 1.0; 2.0 and 3.0 ppm. In this case, TiO₂ is a semiconductor photocatalyst that absorbs the energy of photons in the UV region. Fujishima et al. reported the use of TiO₂ electrodes by energizing from light without the addition of an electric potential from the outside can solve the water/molecule²². In fact, in addition to generating hydrogen, it also was generating electrical energy. Fig. 6 shows a decrease RhB concentration for 60 minutes, respectively.

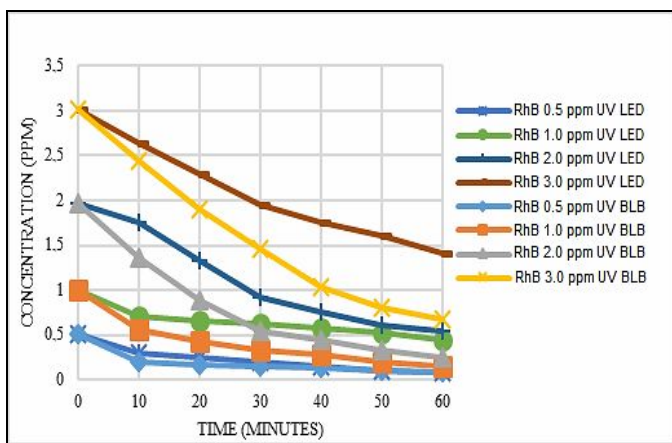


Fig. 6. Graph concentration declines of RhB in photocatalyst method by using catalyst TiO₂/Ti for irradiation of UV-BLB and UV-LED reactors

If compared, photoelectrocatalytic method of TiO₂/Ti, with the provision of a potential bias of 0.5 volts in various types of concentrations and variations of light using a portable potentiostat, it showed activities in degrading RhB organic compounds rapidly when compared to the use of photocatalysts. This proved that the presence of any potential bias that flows and UV light energy from the surface of the TiO₂/Ti catalysts can activate the TiO₂/Ti catalyst and prevent the occurrence of electrons and holes recombination so that excited electrons from the valence band to the conduction band leaving a hole in the valence band. Electrons in the conduction band reacted with molecular oxygen to form superoxide ions which in turn formed the hydroxyl radical (•OH) that will be very reactive to attack the RhB compound⁸. Fig. 7 shows the result of a decrease in the RhB compound concentration using TiO₂/Ti catalyst photoelectrocatalytic.

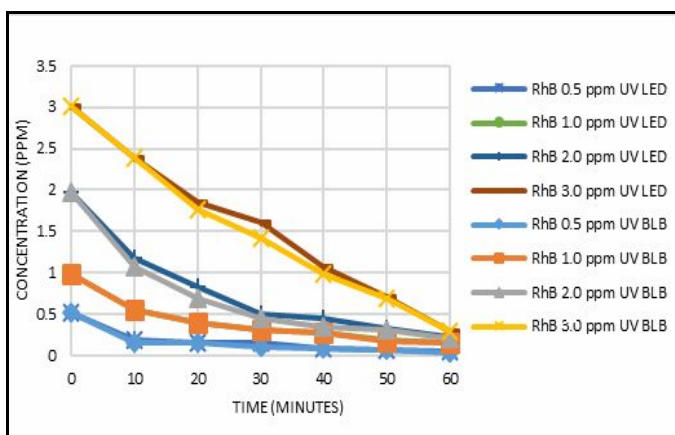


Fig. 7. Graph of the concentration decrease of RhB in photoelectrocatalysis system by using catalyst TiO_2/Ti with irradiation of UV-BLB and UV-LED reactors.

Based on Figs 5, 6 and 7 there are markedly differences in the level of degradation produced by photolysis, photocatalytic and photoelectrocatalytic processes. Fig. 5 is a photolysis process which showed the lowest degradation activity compared to both other processes during illumination with photons there was possibility of termination of the bonds on the RhB compound slowly. According to Wilhelm and Stephan, the reaction of N-deetilasi from RhB compound by irradiating UV light and oxygen formed Rhodamine (Rh) compound²³, as shown in Fig. 8.

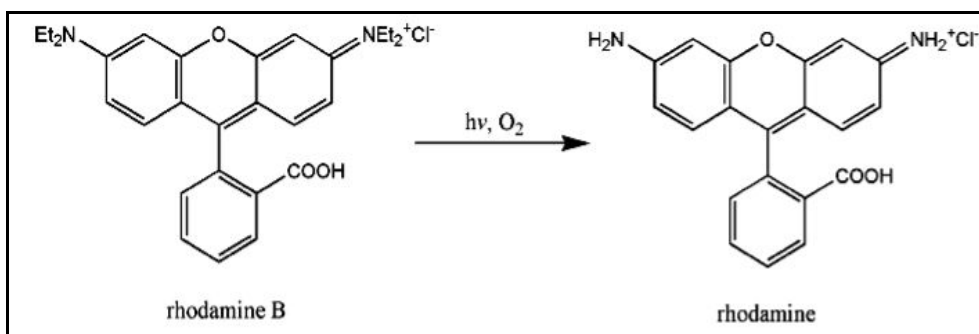


Fig. 8. RhB mechanism to Rh²³

In the process of photolysis and photocatalysis, it had shown good activity degradation although not as good as photoelectrocatalytic process. This was because the photoelectrocatalytic process basically not much different with the photocatalytic process, the addition of electrons (electric current) prevented the electron-hole recombination process when illumination was done. Results showed that the molecular degradation of RhB dye, this process sometimes also have some constraints from the electron-hole recombination so that active species will be reduced which will result in lower degradation activities²⁴.

Irradiation of UV-LED blue light can activate hole on TiO_2/Ti to form hydroxyl radicals which produce degradation reaction of organic species²⁵. From the comparison of degradation data it proved that the UV-LED light can work well to degrade RhB organic compounds, because of the data obtained resulted in decreasing concentration of the test compound with the TiO_2/Ti electrode photoelectrocatalytic, which indicated that photoelectrocatalytic process was faster. This was caused by using the same amount of catalyst, then the active surface will have the same amount. So the RhB dye solution with lower concentrations will be adsorbed entirely on the electrode surface resulting more efficient photoelectrocatalytic process. While high concentrations of RhB tendency of degradation constant value was getting decreased. According to Tian et al., the decreasing value is affected by the degradation of the active side of catalyst in generating O_2 radicals and OH radicals to degrade the test compound as well as the absorption of UV-BLB and UV-LED lights on the test compound so that accelerate the effectiveness in degrading RhB compound¹⁸.

4. Conclusions

1. By using simple electronics method, UV-BLB and UV-LED light-based photoelectrocatalytic reactor can be made by the application of photoelectrocatalytic system.
2. Measurement of photocurrent response of TiO₂/Ti electrodes by using UV-BLB and UV-LED light-based photoelectrocatalytic reactors. Results showed the photocurrent response from UV-LED light can activate the performance of TiO₂/Ti electrodes but not maximized them when compared to the use of UV-BLB reactor which had an excellent activity.
3. Test results of photoelectrocatalytic activities to degrade RhB organic compounds using TiO₂/Ti electrodes with bias of UV-LED light had good activities but not optimal when compared to UV-BLB light.

Acknowledgement

We acknowledged the financial support of the Ditlitabmas-Dikti Ministry of Research, Technology and Higher Education, the Republic of Indonesia.

References

1. Nurdin, M. Preparation, Characterization and Photoelectrocatalytic Activity of Cu@N-TiO₂/Ti Thin Film Electrode, *Int. J. Pharm. Bio. Sci.*, 2014, 5(3):360-369.
2. Sherine J, Gnaneshwar PV, Veluswamy P. Synthesis and Characterization of Fabric coated with Nano Titanium oxide prepared using sol-gel, hydrothermal & Sonochemical technique, *Int. J. ChemTech Res.*, 2015, 7(3):1125-1134.
3. Zainal Z, Hui LK, Hussein MZ, Taufiq-Yap, YH, Abdullah AH, and Ramli I. Removal of dyes using immobilized titanium dioxide illuminated by fluorescent lamps, *Journal of Hazardous Materials*, 2005, 125(1-3):113-120.
4. Wang C-C, Lee C-K, Lyu M-D and Juang L-C. Photocatalytic degradation of C.I. Basic Violet 10 using TiO₂ catalysts supported by Y zeolite: an investigation of the effects of operational parameters, *Dyes and Pigments*, 2008, 76(3):817-824.
5. Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium dioxide, *Progress in Solid State Chemistry*, 2004, 32:33-177.
6. Barka N, Assabbane A, Nounah A. and Ichou YA. Photocatalytic degradation of indigo carmine in aqueous solution by TiO₂-coated non-woven fibres, *Journal of Hazardous Materials*, 2008, 152(3):1054-1059.
7. Karthik V, Saravanan K, Bharathi P, Dharanya V, Meiaraj C. An overview of treatments for the removal of textile dyes, *Journal of Chemical and Pharmaceutical Sciences*, 2014, 7(4):301-307.
8. Maulidiyah, Nurdin M, Wibowo D, Sani A. Nano Tube TiO₂/Ti Electrode Fabrication With Nitrogen And Ag Metal Doped Anodizing Method: Performance Test of Organic Compound Rhodamine B Degradation, *Int. J. Pharm. Pharm. Sci.*, 2015, 7(6):141-146.
9. Rauterberg-Wulff A. and Lutz M. Impact Assessment of the Low Emission Zone Berlin, *UMID: Umwelt und Mensch Informationsdienst*, 2011, 4:11-18.
10. Lorenz J. Particulate Matter: Immission Control Concerns Us All – Experience with Low Emission Zones in Munich, *UMID: Umwelt und Mensch – Informationsdienst*, 2011, 4:19-26.
11. Ibhaddon AO and Fitzpatrick. Heterogeneous Photocatalysis: Recent Advances and Applications, *Catalysts*, 2013, 3:189-218.
12. Maulidiyah, Nurdin M, Erasmus, Wibowo D, Natsir M, Ritonga H, Watoni AH. Probe Design of Chemical Oxygen Demand (COD) Based on Photoelectrocatalytic and Study of Photocurrent Formation at SnO-F/TiO₂ Thin Layer by Using Amperometry Method, *Int. J. ChemTech Res.*, 2015, 8(1):416-423.
13. Nurdin M, Wibowo W, Supriyono, Febrian, MB, Surahman H, Krisnandi, YK and Gunlazuardi J. Pengembangan Metoda Baru untuk Penentuan COD (*Chemical Oxygen Demand*) Berbasis Fotoelektrokatalisis: Karakterisasi Elektroda Kerja Lapis Tipis TiO₂/ITO, *J. Makara Seri Sains*, 2009, 13(1):1-8.
14. Sahu O. and Karthikeyan MR. Reduction of textile dye by using heterogeneous photocatalysis, *American Journal of Environmental Protection*, 2013, 2(3):90-94.

15. Tseng TK, Lin YS, Chen YJ, and Chu H. A Review of Photocatalysts Prepared by Sol-Gel Method for VOCs Removal, *Int. J. Mol. Sci.*, 2010, 11:2336-2361.
16. Izadifard M, Achari G. and Langford CH. Application of photocatalysts and LED light sources in drinking water treatment, *Catalysts*, 2013, 3(3):726-743.
17. Chen X, and Mao SS. Titanium dioxide Nanomaterials: Synthesis, properties, modifications and applications, *Chem. Rev.*, 2007, 107:2891-2959.
18. Tian M, Wu G, Adams B, Wen J, Chen, A. Kinetics of photoelectrocatalytic degradation of nitrophenols on nanostructured TiO₂ electrodes, *J. Phys. Chem. C.*, 2008, 112:825–831.
19. Nurdin M. and Maulidiyah. Fabrication of TiO₂/Ti Nanotube Electrode by Anodizing Method and Its Application on Photoelectrocatalytic System, *Int. J. Sci. & Tech. Res.*, 2014, 3(2):122-126.
20. Isley SL, Jordan, D.S., and Penn, R.L. Titanium dioxide nanoparticles: Impact of increasing ionic strength during synthesis, reflux, and hydrothermal aging, *Mater. Res. Bull.*, 2009, 44:119-125.
21. Frites M. and Khan SUM. Effect of Cathodic Polarization of N-TiO₂ Thin Films on Their Photoresponse towards Water Splitting Reactions, *ESC Electrochemistry Letters*, 2014, 3(12):44-46.
22. Fujishima A. and Honda K. Electrochemical photolysis of water at a semiconductor electrode, *Nature*, 1972, 238:37–38.
23. Wilhelm P. and Stephan D. Photodegradation of rhodamine B in Aqueous solution via SiO₂@TiO₂ nano-spheres, *Journal of Photochemistry and Photobiology A: Chemistry*, 2007, 185:19-25.
24. Maulidiyah, Nurdin M, Widianingsih E, Azis T, Wibowo D. Preparation of Visible Photocatalyst N-TiO₂ and Its Activity on Congo Red Degradation, *ARPJ Journal of Engineering and Applied Sciences*, 2015. (*In press*)
25. Saravanan R, Karthikeyan N, Gupta VK, Thirumal E, Thangadurai P, Narayanan V, A. Stephen. ZnO/Ag Nanocomposite: An Efficient Catalyst for Degradation Studies of Textile Effluents under Visible Light. *Materials Science and Engineering*, 2013, 33(4):2235-2244.
