

Photocurrent Responses of Metanil Yellow and Remazol Red B Organic Dyes by Using TiO₂/Ti Electrode

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Abstract. Studies on organic dyes profile were performed by using TiO₂/Ti electrode photoelectrochemical system. The TiO₂/Ti electrode was prepared by an anodizing technique. These photoelectrochemical profiles of metanil yellow and remazol red B organic dyes were investigated by Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Chronoamperometry (CA), and Potentiometric (V-t) methods. The profile tests of these organic dyes in concentrations of 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm, and 10 ppm were applied by Multi Pulse Amperometry (MPA). The highest of photocurrent responses of metanil yellow and remazol red B with the addition of electrolyte solution of 0.1 M NaNO₃ were 0.827 μ A and 0.475 μ A, respectively, meanwhile in non-electrolyte solution were 0.56 μ A and 0.213 μ A, respectively. The electrolyte solution influenced pH of the metanil yellow and remazol red B dyes in which their pH values were 6.31, 6.26, 6.18, 6.10, 6.07, 6.27, 6.25, 6.22, 6.20, and 6.15, for the concentrations of 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm, and 10 ppm, respectively.

Keywords. Electrode, organic compounds, pH, photoelectrochemical, and TiO₂/Ti.

1. Introduction

The textile industry is one of the fastest growing industries in Indonesia. The increasing number of the textile industry has a negative impact on the environment, especially dyestuff wastewater [1], [2]. Dyestuff waste resulting from textile dyeing processes, are usually difficult to decompose, causing environmental pollution, especially for aquatic environment [1], [3]. Organic dyes are widely used in the textile industry namely metanil yellow and remazol Red B. The existence of textile dyestuff waste has an effect on aquatic organisms due to the decrease of water quality so as it interferes with human health which can cause skin irritation, eye irritation and cancer [4].

Various methods have been done to overcome the dyestuff waste, including the adsorption method using activated carbon, filtration, coagulation and ozonation [2]. However, each of these methods has limited use and is less efficient. Coagulation method has excellent efficiency in waste treatment but generates new waste namely coagulant that cannot be reused. The purpose of activated carbon for dye degradation also requires high cost because the price of activated carbon is relatively high. One way to deal with dye waste more efficiently is to employ photocatalysis using semiconductors [5], [6].



Titanium dioxide (TiO_2) is one of the most widely used semiconductors for photocatalysis to treat organic wastes because they are inert, stable and strong oxidizers [2], [7]. The utilization of TiO_2 as a photocatalyst to degrade organic compounds is converting them into inorganic products that are environment-friendly in the form of CO_2 and H_2O [8]. Through the mechanism of photocatalysis the recombination occurs between electron and hole, so this process does not optimize 95 % of absorbed light energy. Improvement of semiconductor photocatalysis performance can be made through the photoelectrochemical process using semiconductor coating on conductor substrate as photoelectrode. This process is called photoelectrocatalysis, i.e the process of merging photocatalysis with the provision of potential [3].

Several previous studies on photoelectrocatalysis, for example Maulidiyah *et al* (2015), have performed photoelectrocatalytic response test using SnO-F as the conductor substrate on Inert Wall Conductive Glass Tube (IWCGT) against glucose, potassium hydrogen phthalate (PHP) and benzoic acid compounds [1]. Nurdin *et al* (2017) have also degraded the organic compounds using TiO_2/Ti electrodes [7]. However, these studies still use simple compounds, so it is necessary to develop an electrochemical profile system of TiO_2/Ti electrodes using more complex compounds [3], [9].

Based on literature search, no one has reviewed the electrochemical profile system of the TiO_2/Ti electrode in organic dyes (metanil yellow and remazol Red B) as organic wastes that can pollute the environment. In this research there will be tests of electrode activity of TiO_2/Ti that have been prepared by an anodizing method using Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Chronoamperometry (CA) and Potentiometry methods. Subsequently, the photocurrent response profile test was performed by Multi Pulse Amperference (MPA) from organic compounds. These studies are expected to be used as a model for the development of TiO_2 sensors electrochemically from various organic compounds.

2. Materials and methods

2.1. Fabrication of TiO_2/Ti electrode

Preparation of Ti plate was carried out by cutting Ti plate with a purity of 99.7 % and thickness of 0.5 mm with the size of 4 cm $\times$ 1 cm. Further furnished using sandpaper with size of 1200 cm³ until the surface was clean and shiny. The Ti plate was then washed using detergent, water, and aquadest. Then, the Ti plate was etched using a mixture of HF, HNO_3 , and aquadest with a ratio of 1:3:6 for 2 min.

The prepared Ti plate was inserted in the probe which has been filled with an electrolyte solution of 0.27 M NH_4F and aquadest in 98 % glycerol. The anodic oxidation process was carried out by placing the Ti plate as anode and Cu as a cathode, and providing a potential bias of 25 V from the power supply. This anodic oxidation process was applied for 4 h. The final step was to calcine the Ti plate for 1.5 h with a temperature of 500 °C to evaporate the remaining electrolyte solution on the surface of Ti plate.

2.2. Photoelectrochemical activity test

The activity test of TiO_2/Ti electrode was performed by Linear Sweep Voltammetry (LSV), Cyclic Voltammetry (CV), Chronoamperometry (CA) and Potentiometric (V-t) methods using 0.1 M NaNO_3 solution. The LSV test was conducted from potentials of -1 V to 1 V with a scan rate of (1.0×10^{-4}) V/s. The CV was performed from potentials of -1.5 V to 1.0 V with a scan rate of 0.05 V/s. The CA was conducted from potentials of -1 to 1 V with a scan rate of (1.0×10^{-3}) V/s, and the potentiometric test was done from potentials of -2 V to 2 V. Testing of the TiO_2/Ti electrode in each method was carried out by giving a variation of UV light intensity.

2.3. Photoelectrochemical test based on organic compounds

Measurements of dyes (metanil yellow and remazol Red B) photocurrent responses were performed using the TiO_2/Ti catalyst with Multi Pulse Ampermmetry (MPA) technique at a potential bias of 0.5

V for 60 s. The concentration variations used were 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm with the addition of 0.1 M NaNO₃.

2.4. Determining pH of organic compounds

A pH meter was used to measure pH of the dyes. Measurements were made for the concentrations of 2 ppm, 4 ppm, 6 ppm, 8 ppm and 10 ppm with NaNO₃ and without NaNO₃. Then, the relationship chart between pH and analytical concentration was made.

3. Results and discussion

3.1. Photoelectrochemical activity test

Measurement of photocurrent activity as a potential function was derived from electron transfer during the analyte oxidation-reduction process of 0.1 M NaNO₃ using Pt counter electrode, TiO₂/Ti working electrode and Ag/AgCl comparison electrode. This measurement was performed using a potentiostat with LSV, CV, CA, and V-t methods (Figure 1).

The LSV technique was used for qualitative test of TiO₂ crystal photoactivity. Using this method, we can know TiO₂ activity could be observed by the increase of photocurrent on the LSV curve after the electrode is irradiated with UV lamps. The LSV activity test of TiO₂/Ti electrode showed the highest activity during UV lamp irradiation (Figure 1.a). This indicates the presence of photons absorbed by TiO₂ so that the electrons are excited from valence band to conduction band. TiO₂ has photoelectrocatalysis activity on UV irradiation because of the TiO₂ is only active at a wavelength less than 388 nm related to the bandgap energy of 3.2 eV. While in the dark condition, there is no current increase (zero-generated current) so that no electron from the conduction band to the valence band.

Measurement of CV aims to determine the activity of anodizing TiO₂/Ti plate. In this method, current and potential changes were observed. Figure 1.b shows that in the dark condition, the current is generated at the zero region, while during UV lamp was illuminated the current increases. This indicates that without lamp illumination, the TiO₂/Ti electrode does not exhibit photoelectrochemical activity because there is no generation of electron-hole pairs on the electrode surface.

The measurement of CA is an electrochemical method that uses a potential bias. Figure 1.c shows differences in current generated. The current increases when the electrode is subjected to UV light, while in the dark condition the obtained current value is lower. According to Adan *et al* (2016), when the electrode is subjected to UV light the increase in anodic spike occurs due to the separation of the electron-hole pairs, then a decrease in current due to the recombination of electron-hole pairs [10], [11].

The method of potentiometric analysis is based on the measurement of electric photocurrent as the function of potential electrical bias. Figure 1.d shows that the potential produced by the UV illuminated TiO₂/Ti electrode is lower than potential in the dark. According to Cheshideh *et al* (2017), when the TiO₂ electrode in the electrolyte solution is irradiated, the electrons and holes are formed. Furthermore their potential will switch to a negative value because the holes are trapped on the surface and switches to the solution, therefore the electrons are accumulated in the electrode.

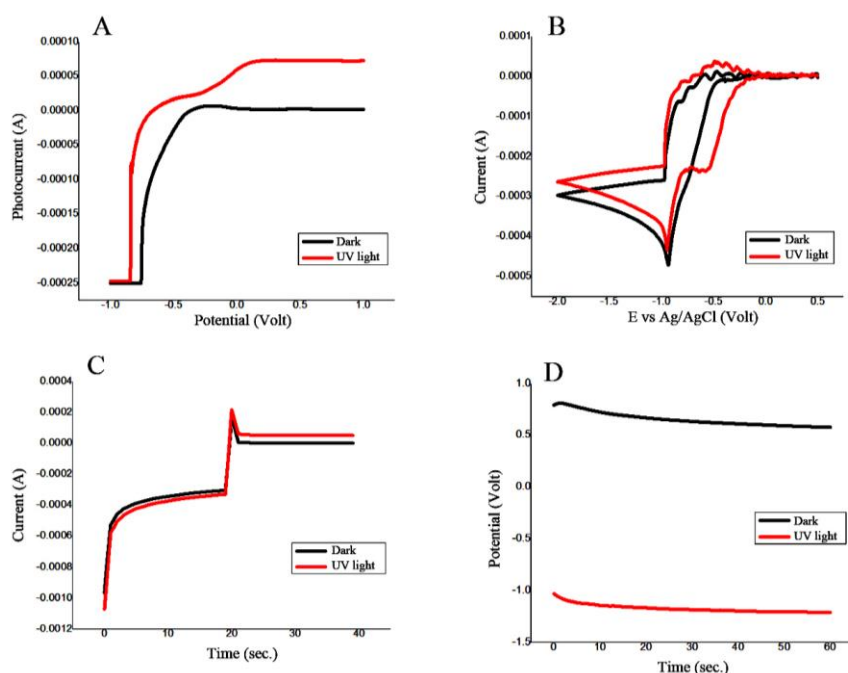


Figure 1. Voltammogram Graph. (a) Linear Sweep Voltammetry (LSV), (b) Cyclic Voltammetry (CV), (c) Chronoamperometry (CA), and (d) Potentiometric (V-t)

3.2. Photoelectrochemical test based on organic compounds

The measurement of photocurrent response generated from the photoelectrocatalytic system was developed from a test solution containing several organic compounds. Photocurrent measurements were made using a potentiostat under the MPA technique. The potential bias used was 200 mV, carried out based on the previous optimization results at a potential bias of 200 mV to 500 mV in capturing light and preventing the direct electrochemical process.

Metanil yellow is azo aromatic group dye with a molecular formula of $C_{18}H_{14}N_3O_3SNa$. Measurement of photocurrent response with a variation of metanil yellow concentration of 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm, and 10 ppm was carried out using TiO_2/Ti electrode with UV light.

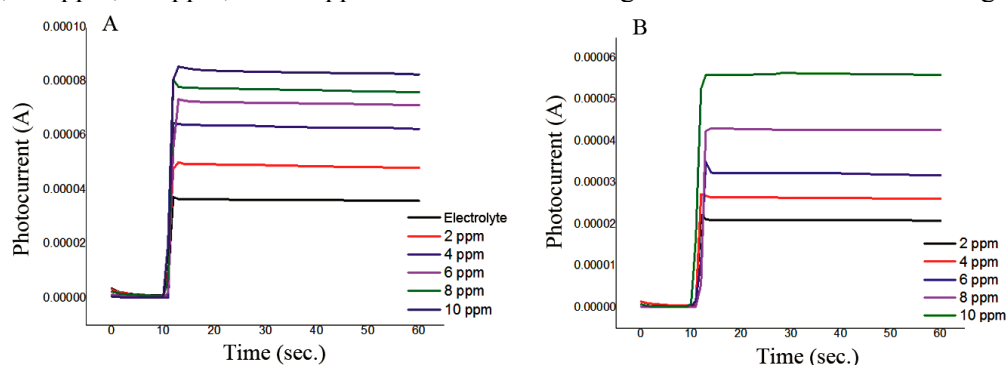


Figure 2. Photocurrent response based on metanil yellow, (a) by adding the electrolyte solution 0.1M $NaNO_3$ (b) without the electrolyte solution

Figure 2.a shows that the higher the concentration of a compound the higher the resulting photocurrent value. The photocurrent response was measured horizontally, the possibility of this compound difficult to degrade by TiO_2 photocatalyst so that the photocurrent decrease is not

significant [10]. In Figure 2.a it is also seen that the current does not coincide with current blank of NaNO_3 electrolyte which indicates that metanil yellow was not degraded perfectly. This may be due to metanil yellow having aromatic groups with strong aromatic bonding which is difficult to degrade. The photocurrent response without the electrolyte was lower when compared to the photocurrent response in metanil yellow due to the electrolyte solution affecting photocurrent as can be seen in Figure 2.b.

Remazol Red B is one of mono-azo synthetic dye because it has one double bond of $\text{N}=\text{N}$ [11]. Measurement of photocurrent response was performed using the TiO_2/Ti electrode under UV light with a variation of Remazol Red B concentration of 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm, and 10 ppm.

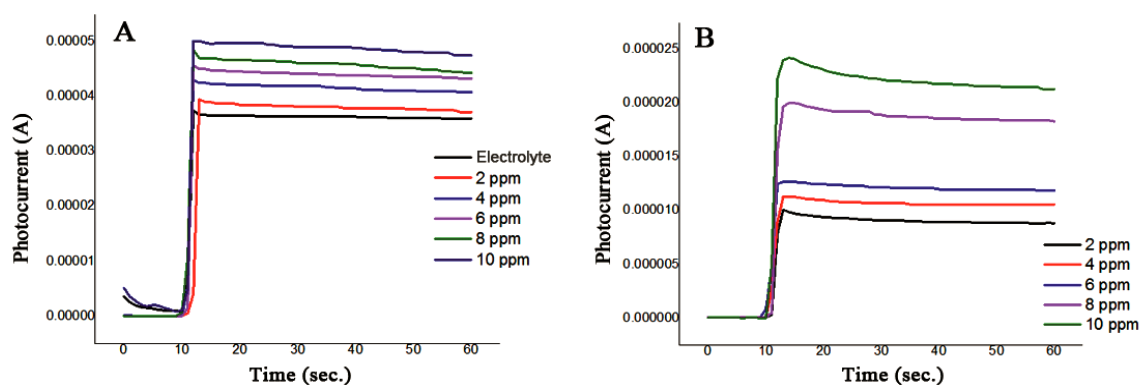


Figure 3. Photocurrent response based on remazol red B, (A) by adding the electrolyte solution 0.1M NaNO_3 (B) without the electrolyte solution

Figure 3.a shows the increase of photocurrent response as the concentration of the test solution increases. The photocurrent response indicates that this compound was not degraded well enough by photoelectrocatalysis. The photocurrent of remazol red B does not coincide with a blank current of the electrolyte at a concentration more than 4 ppm. This observation indicates that remazol red B cannot be degraded perfectly within the observed time range. It is also possible that the electrode has been saturated by continuous measurements on the same electrode. However, the initial photocurrent values tend to increase in proportion to concentrations.

Figure 3.b shows differences in photocurrent responses of electrolyte and non-electrolyte test compounds. The photocurrent response to the electrolyte test compound is higher than that of the non-electrolyte test compound. This is because of the electrolyte solution which acts as a current conductor can increase the photocurrent in the test compound.

The linear regression equation applied to the results must have intercept values not significantly different from zero. If the non-zero significant intercept is obtained, it must be proved that this has no effect on the accuracy of the method [12].

Figure 4.a shows the linearity of test compounds by electrolytes. Metanil yellow and remazol red B have increased photocurrent along with increasing concentrations. However, there is a change of slope value on each test compound. It can be seen that the increased linearity of the current due to the increase of metanil yellow and remazol red B concentrations have $R^2 = 0.9539$ and $R^2 = 0.9714$, respectively. This shows the effect of the photodegradation process of each test compound. According to Nurdin *et al* (2009), at low concentration the photodegradation process is only influenced by photo hole capture process on catalyst surface while at high concentration compound structures affect the photodegradation process of the compounds [5], [13].

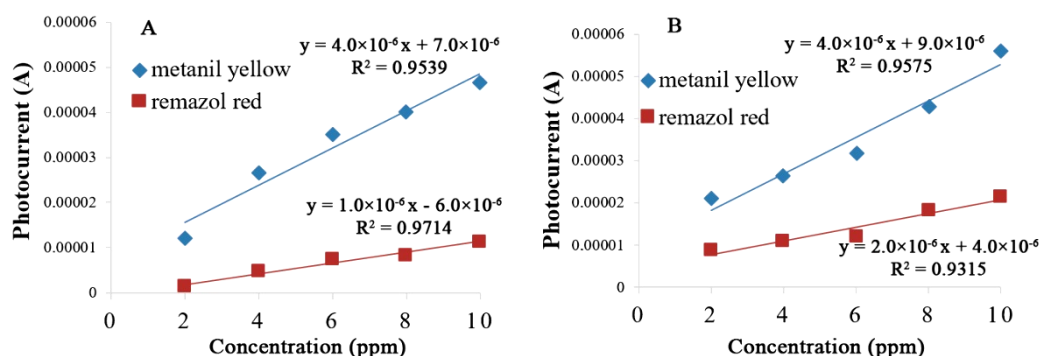


Figure 4. Linear graph, (a) by using electrolyte 0.1M NaNO₃ solution, (b) without the electrolyte solution

Based on Figure 4.b it can be seen that the metanil yellow and remazol red B compounds have increased the current along with increasing concentrations. It can be seen that the increase linearity of the current due to the increase of metanil yellow and remazol red B concentrations that have values of $R^2 = 0.9575$ and $R^2 = 0.9315$, respectively. However, the resulting linearity values using non-electrolyte test solution are lower than using solution with electrolyte. This is because the electrolyte solution can increase the photocurrent to the test compound.

3.3. Determination of pH in organic compounds

The pH value has an important role in determining waste characteristics and the formation of hydroxyl radicals. Photocatalysis of dye may occur by reaction mechanism, i.e., hydroxyl radical attack and direct oxidation by holes, depending on conditions of substrate base and pH [8]. The effect of NaNO₃ electrolyte solution on pH can be determined by making the correlation between analyte concentration and pH on metanil yellow and remazol red B test compounds as shown in Figure 5.

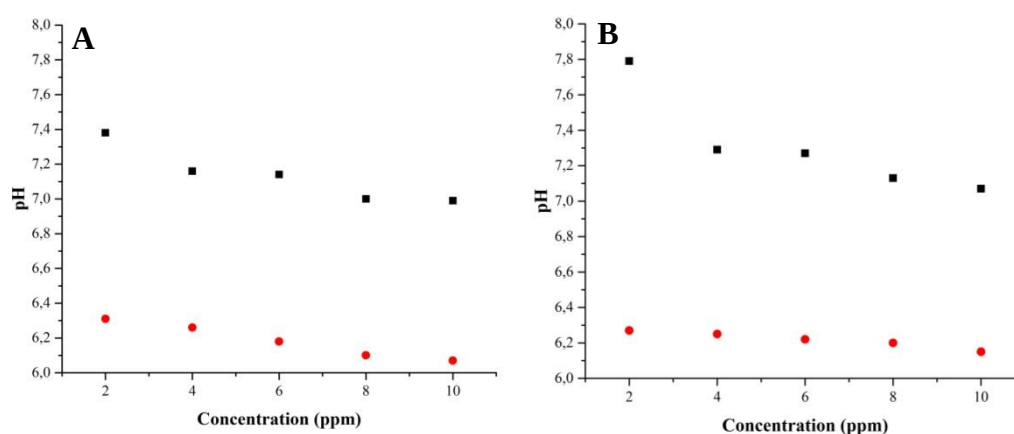


Figure 5. Correlation between concentration and pH, dot square: by adding electrolyte; dot cycle: without electrolyte (a) metanil yellow (b) remazol red B

The correlation between concentration and pH on electrolyte and a non-electrolyte metanil yellow test compound is the decrease in pH values at high concentrations (Figure 5.a). Each test compound has a maximum pH at a concentration of 2 ppm i.e. 6.31 and 7.38. Non-electrolyte metanil yellow exhibited alkaline properties, while electrolyte metanil yellow exhibited acid properties. This is due to the structure of the metanil yellow which shows the basic properties of the amine group and the acidic

properties of sulphonate group. Figure 5.b also shows the correlation between concentration and pH on test compound where there is a decrease in the pH value at high concentration. Each test compound has a maximum pH at concentration of 2 ppm i.e. 6.27 and 7.29. Non-electrolyte remazol red B exhibited alkaline properties, whereas electrolytes Remazol red B exhibited acid properties. This is due to the structure of remazol red B which can show the alkaline properties of a hydroxyl group and the acidic properties of the sulphonate group.

4. Conclusions

It can be concluded that the photocurrent responses produced by the metanil yellow and remazol red B test compounds are higher along with the increase of test solution concentrations. Metanil yellow and remazol red B compounds with the addition of electrolyte (NaNO_3) at 10 ppm concentration yielded photocurrent values of $0.827 \mu\text{A}$ and $0.475 \mu\text{A}$, respectively. For metanil yellow and remazol red B test compounds without electrolyte produced photocurrent values of $0.56 \mu\text{A}$ and $0.213 \mu\text{A}$, respectively. The results of metanil yellow and remazol red B test profile showed good photocurrent response. The photocurrent response of metanil yellow and remazol red B test compounds was influenced by pH, the more acidic pH of the test solution the higher the photocurrent response values.

Acknowledgments

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