Determination of COD based on Photoelectrocatalysis of FeTiO3.TiO2/Ti Electrode

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Abstract. Iron infrastructure technology of (Fe)-doped TiO2 nanotubes arrays (NTAs) was prepared for COD photoelectrocatalysis sensor. Fe-TiO2 NTAs was prepared using sol-gel method and coated with TiO2/Ti electrode by immersion technique. The optimization of COD photoelectrocatalytic sensor against Rhodamine B, Methyl Orange, and Methylene Blue organic dyes using photoelectrochemical system in a batch reactor. The high ordered FeTiO3.TiO2/Ti NTAs to determine COD value showed the high photocurrent response linearity and sensitivity to MO organic dye from the concentration of 5 ppm to 75 ppm with an average RSD value of 3.35. The development in this research is to utilize ilmenite mineral as model applied to COD sensor.

1. Introduction
The aquatic environment has become a phenomenal issue in recent years because wastewater generated from human activities caused environmental pollution [1,2]. The high content of harmful chemical compounds such as dissolved organic substances in water bodies causes various diseases [3,4]. The needed techniques to quickly detect the water pollution level in aquatic environment is a determinant factor of wastewater quality [5,6]. According to Zhang et al. one of the indicators of water quality as a polluted water control index is by determining Chemical Oxygen Demand (COD) [7]. The determination of COD values is a national standard requirements for determining the pollution content of organic waste in water bodies as applied in developed countries such as Japan and China [8].

The technique of determining COD values is still experiencing problems such as potassium dichromate (K2Cr2O7) usage as a strong oxidizing agent. It has an effect on dangerous experimental conditions such as high temperature and H2SO4, high-toxicity exposure (Hg(II) and Cr(VI)), expensive reagent (Ag2SO4), and automation difficulty [9]. In last years the determination of COD values has been developed and studied intensively by Zhang et al. using the electrocatalytic oxidation technique electrochemically by utilizing an environmental-friendly titanium dioxide (TiO2) semiconductor material [10]. Determination of COD value based on photoelectrocatalytic is an infrastructure

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technology that will be developed, which is more likely to be considered than conventional methods which can be harmful for humans.

The determination of COD photoelectrocatalytic is considered a strong oxidizing agent characterized by the number of electrons transferred when induced in photon energy [11,12]. This phenomenon excite the electron-hole on TiO$_2$ semiconductor which initiated a reduction-oxidation (redox) reaction [13,14]. This is evidenced by Nurdin et al. in utilization of TiO$_2$ semiconductor as degradation of organic compounds in water sample [15].

A COD photoelectrocatalytic system using TiO$_2$ semiconductors was measured by correlating the measured analytical signal PEC as electro catalytic and photocatalytic approach to overcome the oxygen demand problems in organic wastewater [16,17]. Based on Gracia-Munoz et al. the development of TiO$_2$ semiconductor from ilmenite (FeTiO$_3$) compound has a strong oxidation agent [18]. It can be developed as an electrode for determining COD value by PEC system.

FeTiO$_3$ is a semiconductor belonging to iron-titanium oxide mineral that can be obtained naturally with extraction method. It was obtained through two distinct ways: iron sand extraction [13,14] and sol-gel synthesis [19]. The extraction method has constraint, i.e. the high solubility properties in acid solvent makes it hard to obtain high-purity yields, hence it is necessary to develop the synthesis method as a model of natural FeTiO$_3$ immobilized in the working electrode. According to Wilson et al. (2005) the substitution of Fe$^{3+}$ ions in TiO$_2$ crystal can occur because the radius of Fe$^{3+}$ ion is smaller than the radius of Ti$^{4+}$ (Fe 0.64 Å; Ti 0.68 Å) ions which allows FeTiO$_3$ to form [20,21].

In this research, FeTiO$_3$ has been synthesized using the sol-gel method then immobilized on TiO$_2$-NTAs to determine COD value based on PEC of RhB, MO, and MB organic dyes. The organic dyes are often used in the coloring process within textile industry and easy to accumulate aquatically. The pollution resultant of organic substances can cause unpleasant odors because it contains several elements of Nitrogen (N) and high-stability elements due to some delocalization of electron in benzene rings which are difficult to degrade so that good oxidation agent is needed by using FeTiO$_3$ electrode.

2. Experimental Method

2.1. Fabrication TiO$_2$/Ti by anodizing

The preparation of Ti (titanium) plate was performed by cutting Ti plate with 99.7% purity with thickness of 1 mm with a size of 4 cm × 0.5 cm then sanded using fine sandpaper of 1200CC until the surface was clean and shiny. Then, it was washed using a detergent solution, water and distilled water (D.I. H$_2$O). Ti plate was etched using a mixture of HF, HNO$_3$ and D.I. H$_2$O with ratio of 1: 3: 6 for 30 seconds. The final step, Ti plate was rinsed with D.I. H$_2$O to remove the residual etching solution [22].

The Ti plate was put into probe which had been filled with electrolyte solution of NH$_4$F 0.27 M and D.I. H$_2$O in 98% glycerol. The anodizing process was carried out by placing Ti plate as anode and Cu plate as cathode using magnetic stirrer, and provided a potential bias of 25 Volts connected to the power supply for 4 hours. The final stage, Ti plate was calcined for 1.5 hours at a temperature of 500°C to evaporate the residual electrolyte solution and to obtain TiO$_2$ anatase crystal that has high-photodegradation activity [23].

2.2. Synthesis of FeTiO$_3$ using sol-gel

The synthesis of FeTiO$_3$ by modifying Raghavender et al. by using sol-gel method [19]. Solution 1: colloidal solution of FeTiO$_3$ was prepared by hydrolyzing in controlled using 4 mL of TTIP compound in 0.5 mL of acetyl acetone and 15 mL of 99% ethanol. Solution 2: 15 mL of 99% ethanol and 2 mL of D.I. H$_2$O with addition of 1 mL of 0.1 M acetic acid. The solution mixture was refluxed for 3 hours at 50°C using a magnetic stirrer followed by adding 1 mL of 0.5 M Fe(NO$_3$)$_3$ to produce FeTiO$_3$ sol. The resulting solvent was evaporated at temperature room for 48 hours to form gel, then heated at a temperature of 80°C in oven for 30 minutes. The coating process of FeTiO$_3$ sol-gel used immersion technique on TiO$_2$-NTAs surface. The immersion technique was performed in 1 day which aim to evaporate the solvent agent and form FeTiO$_3$ crystal on TiO$_2$-NTAs electrode. Finally, it was heated for 15 minutes at a temperature of 80°C to form FeTiO$_3$.TiO$_2$/Ti.
2.3. Determination of COD value using photoelectrocatalytic system

The concentration of RhB, MO, and MB organic dyes were 5, 10, 20, 30, 40, 50, 60, 75 and 100 ppm (+0.1M NaNO$_3$) then it was taken 15 mL of the volume into glass probe in the PEC batch system. Subsequently, the working electrode was assembled using a three-electrode system (working electrode, Ag/AgCl electrode, and Pt electrode). The measured process used a portable potentiostat DY2100B in Multi-Pulse Amperometry (MPA) with a time duration of 60s, scan rate 1×10$^{-4}$ V/s and bias potential of 0.5 Volt. The first 10s in dark condition obtained the stability of current in dark condition and the same condition, then turned on a UV light to obtain the initial photocurrent and stadystate condition. The data were interpreted by determining the linearity graph of net charge ($I_{net}$) to each concentration.

$$I_{net} = I_{sample} - I_{blank}$$

(1)

The linear graph was made in the concentration to obtain slope, $y = ax + b$, where $y$ is the value of $I_{net}$, $a$ and $b$ are constants and $x$ is the COD value of photoelectrocatalytic.

3. Results and Discussion

3.1. Determination of COD value by photocatalytic system

The organic dyes used RhB, MO, and MB organic dyes because it has used and easily found on dyeing process. The impact of organic dyes had potential as an aquatic pollutant in the environment due to easy accumulation in water and difficult to degrade naturally. Maulidiyah et al have reported that the organic dyes could degrade using undoped and doped of (M (Metal) – N (Nitrogen)) into TiO$_2$/Ti electrode [16]. In this research, the determination of COD values based on photoelectrocatalytic was done by using FeTiO$_3$.TiO$_2$/Ti electrode as material for photooxidation of compound test.

The COD determination test was performed in a batch system with varied concentration in 5, 10, 20, 30, 40, 50, 60, 75 and 100 ppm (+0.1M NaNO$_3$). This system was chosen to obtain the ability of oxidation level and linearity limit of COD measurement using FeTiO$_3$.TiO$_2$/Ti electrode. The solution test took 15 mL to be put into glass probe in three electrode systems connected to the potentiostat. The dark condition in 10 s obtained the uniformity initial photocurrent and reduced measurement errors due to non-uniformity of the start time in amperomogram profile.

The oxidation current of the organic compound could be determined by reducing $I_{sample}$ to $I_{blank}$. The resulting current (Figure 1A) was very low ($<1.0 \times 10^{-5}$ A) indicating the difficulty to be degraded by photoelectrocatalytic because RhB compound belongs to cationic compounds which could affect hole formation and increase saturation on working electrode due to a similar charge in the system and it was affected by dyes that could absorb photon so the incoming intensity was not too large [9].
Figure 1. Photoelectrocatalytic profile of RhB; (A) Amperomogram of RhB, (B) Inet value of RhB (C) the linearity performance of RhB.

Figure 1B shows that at concentrations above 60 ppm there is a decrease in photocurrent response due to the difficulty of capturing photo-hole by RhB as characteristic of the cationic compounds and reducing the active side of a catalyst. Figure 1 shows that the optimal performance area of the working electrode to determine RhB COD value is <60 ppm, whereas for > 75 ppm the decrease in electrode activity occurred (Figure 1C).

The MO compound was organic dye anionic derived from a hydrophobic group of benzene ring and hydrophilic group derived from S atom binding to an O atom [24]. This group was rich in electrons (negatively charged groups) so it could form hydrogen bonds when dissolved in water. The photocurrent response of analyte (Figure 2A) at a concentration of 75 ppm has a low initial photocurrent compared to the others because the electron excitation ability was affected by the analyte concentration in system.

Figure 2. Photoelectrocatalytic profile of MO; (A) Amperomogram of MO, (B) Inet value of MO (C) the linearity performance of MO.
Figure 2 shows the reduced $I_{\text{net}}$ values between $I_{\text{sample}}$ and $I_{\text{blank}}$. The result showed that the increase of $I_{\text{net}}$ is very stable up to a concentration of 75 ppm (Figure 2C), but at concentration of 100 ppm there has been a decrease of $I_{\text{net}}$ caused by higher concentration of analyte which can affect the performance of active side of electrode surface with $I_{\text{net}}$ value of $7.02 \times 10^{-5}$ A.

The photocurrent response test in MB solution had a relatively low photocurrent response value compared to MO test compound. Amperomogram data shows that the concentration is increased and it is proportional to photocurrent response which increased as well. Amperomogram in Figure 3A has been lower because the photoelectrocatalytic oxidation process of MB solution resulting in ammonium ions ($\text{NH}_4^+$) caused to affect the performance of reference electrodes. The difficulty of being adsorbed on the electrode surface reduced the oxidation process of MB compounds by holes while on the other side the reduction process was at Pt electrode.

**Figure 3.** Photoelectrocatalytic profile of MB; (A) Amperomogram of MB, (B) $I_{\text{net}}$ value of MB (C) the linearity performance of MB.

Figure 3 shows $I_{\text{net}}$ values are the reduced results of $I_{\text{sample}}$ and $I_{\text{blank}}$ values. The results shows that the concentrations of 75 ppm and 100 ppm, there was a decrease of photocurrent responses. This is because the saturation on the electrode and intensity of UV light is difficult to penetrate to working electrode. These data show that electrode performance area of MB test compound is limited to 60 ppm.

### 3.2. Parameters of working electrode

#### 3.2.1. Reproducibility.

Figure 4 is the results of 10 repetitions of a 5 ppm RhB analyte solution for 120 s. The results show that repeated photocurrent responses obtained a highly stable photoelectrochemical profile and met the reproducibility standard with an average photocurrent responses of $3.43 \times 10^{-5}$ A with a STD value of $6.2 \times 10^{-7}$. Figure 4 shows that FeTiO$_3$/TiO$_2$/Ti electrode has good precision capability against photocurrent response to compound test. The repeatability of measurement of photoelectrocatalytic system has decreased analytical concentration since this system was applied in the degradation process.
of organic compounds electrochemically [25]. In short, representation of proportional electrochemical measurement results is comparable to the analyte concentration in the system.

![Figure 4](image-url)

**Figure 4.** the reproducibility amperomogram of FeTiO$_3$.TiO$_2$/Ti electrode.

### 3.2.2. Sensitivity

Figure 5 shows the comparison of photocurrent responses to various compound tests. The working electrode has a sensitivity to MO compound characterized by the increased photocurrent response which is greater than test compounds of RhB and MB. This factor is due to the highly degradable photoelectrocatalytic presented to the emerging photocurrent charge [26]. MO test compound has good COD proximity from 5 ppm to 60 ppm compared to RhB and MB with average STD values of 3.35, 45.78, and 11.60, respectively.

![Figure 5](image-url)

**Figure 5.** The sensitivity graph of test compounds.

### 3.2.3. Linearity

Figure 6 represents the linearity of data of COD values measurement on each of the test compounds of RhB, MO, and MB using FeTiO$_3$.TiO$_2$/Ti electrode to see the theoretical COD value approach with photoelectrocatalytic. Figure 6A compares theoretical COD values and COD PEC values as the RhB concentration increases from 5 ppm to 100 ppm. The data shows that the increase in the concentration of RhB compound makes COD PEC values are away from linearity to the theoretical COD values, so probability of linearity was observed at RhB concentration from 5 ppm to 20 ppm (Figure 6B). Figure 6C shows FeTiO$_3$.TiO$_2$/Ti electrode can work well on MO test compound with concentration ranges from 5 ppm to 75 ppm. The linearity data shows the proximity of theoretical COD value of MO compound with photoelectrocatalytic system is not much different, so it can be assumed that FeTiO$_3$.TiO$_2$/Ti electrode worked very well on MO compound (Figure 6D).

Figure 6E shows photoelectrocatalytic COD values of MB test compound also experienced a change in linearity from theoretical COD measurement. This case is similar to RhB compound with linearity of MB compound from concentration 5 ppm to 30 ppm. Compared to test compounds of RhB
and MB. The effectiveness of linearity is still better in MB compound. This phenomenon suggests that the possible roles of the test compound properties are anionic and cationic, as well as the magnitude of the test compound so as to rapidly cover the active side of catalyst on electrode surface.

Figure 6. Determination of linearity values (A) COD values of RhB (B) proximity of RhB linearity (C) COD values of MO, (D) proximity of MO linearity (E) COD values of MB, (F) proximity of MB linearity.

4. Conclusion
The determination of COD values used FeTiO₃:TiO₂/Ti electrode on various compound tests of RhB, MO, and MB showed the performance linearity of each compound test i.e. RhB at concentration of 5 ppm, 10 ppm and 20 ppm with COD values of 7.00 mg/L, 13.29 mg/L, and 25.07 mg/L. MO compounds at concentrations of 5 ppm, 10 ppm, 20 ppm, 30 ppm, 40 ppm, 50 ppm, 60 ppm, and 75 ppm with COD values of 7.86 mg/L, 11.862 mg/L, 24.37 mg/L, 41.63 mg/L, 54.57 mg/L, 67.733 mg/L, and 77.00 mg/L, respectively. While MB compounds at concentrations of 5 ppm, 10 ppm, 20 ppm, 30 ppm with COD values of 5.91 mg/L, 11.66 mg/L, 25.04 mg/L, and 43.04 mg/L with average value of STD sensitivity of 45.78; 3.35; and 11.60, respectively.
5. References

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