Photocatalytic sensor for chemical oxygen demand flow system using N-TiO$_2$/Ti electrode: determination of glucose and potassium hydrogen phthalate

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Abstract. The design of the Chemical Oxygen Demand (COD) flow system using TiO$_2$/Ti and N-TiO$_2$/Ti electrodes has been carried out. TiO$_2$/Ti electrodes were synthesized from the anodizing process followed by the sol-gel method as nitrogen doping (N) to obtain N-TiO$_2$/Ti electrodes. The test results obtained that TiO$_2$/Ti electrodes are only active in UV light and N-TiO$_2$/Ti electrodes can be active in visible light. Determination of the COD value of the flow system for glucose and potassium hydrogen phthalate at various concentrations respectively of 5, 10, 20, and 30 ppm was carried out using the Multi Pulse Amperometry (MPA) technique. The results of the COD sensor measurement of the flow system on the potassium hydrogen phthalate and glucose obtained light currents increase in proportion to the increase in concentration, which is also significantly proportional to the increase in COD value. The highest COD values for glucose and potassium hydrogen phthalate were at concentrations of 30 ppm respectively of 29.73 and 31.34 mg/L O$_2$ using TiO$_2$/Ti electrodes and for N-TiO$_2$/Ti electrodes respectively 30.91 and 29.20 mg/L O$_2$.

1. Introduction

Water is a basic need for life on earth, is no exception for humans. For every need for water use, water quality requirements are required according to their designation. One important requirement is a measure of the amount of organic matter present in water[1–3]. Even at low concentrations, organic compounds can cause interference with the reduction of oxygen in the water. Therefore, the determination of organic substances in water is one of the important parameters in determining water quality[4–6].

At present, there are two standard analytic methods that are widely used to determine oxygen demand in water, namely Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)[7–9]. Determination of photocatalytic COD value using TiO$_2$ as a photocatalyst replacing the conventional Cr (VI) oxidizer has been carried out [10]. The use of a flow system is a new method in designing COD sensors based on photoelectrocatalysis to determine the value of dissolved oxygen and detect the contamination of organic compounds in water. The flow system is more effective for detecting organic waste due to the movement of the solution through the TiO$_2$/Ti catalyst so that organic compounds will be degraded evenly or thoroughly[11–13]. The application of the flow system reactor can be used in sewers, rivers, and dams that have been contaminated.

To improve the performance of photocatalyst TiO$_2$ can be done electrochemically by combining the process of photocatalysis with the electrochemical process, known as photoelectrocatalysis[14–17]. The addition of metal dopants can increase photocatalyst activity on visible light exposure. COD sensors developed using titanium plates have advantages such as environmentally friendly, economical, non-toxic and faster degradation power, but TiO$_2$ is only active on UV light with a wavelength of 388 nm[18–23], so that TiO$_2$ modification is done by coating the N-TiO$_2$ sol-gel to increase the performance of TiO$_2$ which can work by utilizing solar energy.
Organic compounds such as glucose and potassium hydrogen phthalate have been widely used as test compounds in photoelectrochemical studies[24–26]. Glucose is used as a model compound to test the response to weak adsorbate compounds, this is because the glucose structure is relatively simple and is a good hole catcher (hole scavenger) [27], while potassium hydrogen phthalate is one examples of acidic compounds, which have strong interactions with the TiO$_2$ layer[28].

Based on the literature review above, this research developed N-TiO$_2$/Ti-based photoelectrocatalyzed COD value using a flow system, which will be tested on glucose and potassium hydrogen phthalate test compounds.

2. Experimental Methods

2.1. Preparation of Ti Plate
Ti plates were cut 4 cm x 1 cm and then cleaned. Ti plate was etched in a mixture of fluoride acid, nitric acid and distilled water in a ratio of 1: 3: 6 for 2 minutes. Furthermore, the Ti plate was rinsed with distilled water to remove the remaining solution on the surface of the Ti plate and then dried[23].

2.2. Anodizing
Ammonium fluoride electrolyte solution in glycerol 98%. Anodizing the Ti plate is done by giving a potential bias of 25 volts which is connected to the power supply for 4 hours[29].

2.3. Dip-coating
N doping is carried out by dip-coating using the sol gel to make the N precursor. Sol is made from a TiO$_2$ colloid solution and acetylacetonate is dissolved in 99% ethanol. The second solution is made ethanol, distilled water and acetic acid. Both solution mixes are refluxed for 3 hours at 50°C. NH$_4$Cl was added to produce TiO$_2$ soles containing nitrogen. The sol is evaporated for 48 hours to form a gel. Then the resulting gel is heated to a temperature of 80°C in the oven for 30 minutes. The dyeing process is carried out in an area that has been overgrown with TiO$_2$ on a titanium plate for 10 minutes.

2.4. Characterization of N-TiO$_2$ thin films
N-TiO$_2$ thin films were characterized using a Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX).

2.5. Measurement of Photocurrent Response
Measurement of glucose and potassium hydrogen phthalate photocurrent response using TiO$_2$/Ti and N-TiO$_2$/Ti electrodes was carried out using the Multi Pulse Amperometry (MPA) technique with a potential bias of 0.5 Volts, 60 seconds degradation time in the light is on. Measurement using Linear Sweep Voltammetry (LSV) using 0.1 M sodium nitrate solution, where 0.85 grams of sodium nitrate are dissolved in a 100 mL measuring flask. LSV testing is done from potential -1 Volt to 1 Volt. With a scan rate of 1x10$^{-4}$ V/s[30].

3. Results and Discussion

3.1. N-TiO$_2$/Ti Electrode
Thin layer of TiO$_2$ was made on the surface of the Ti plate by anodizing method which was carried out for 4 hours with a potential difference of 25 Volt. Calcination carried out at 500°C for 1.5 hours produce anatase crystal structures that have better photocatalytic activity. This is caused by anatase crystals that have a larger surface area and larger active side so that are able to absorb light better. The making of Nitrogen (N) used the sol-gel method. Anions such as N on TiO$_2$ able to increase absorption up to ~500 nm. Nitrogen is found to be the most effective dopant because the size of the atom is similar to the ionization of oxygen from good, weak and good energy. Electrodes that have been successfully made are displayed on Figure 1.
3.2. SEM-EDX Characterization

SEM measurement results provide information about the surface topography of a crystal. Figure 2A and 2B shows the surface shape of the N-TiO$_2$/Ti electrode, rough surface, forming chunks like a rock. The calcination process causes the atoms making up N-TiO$_2$/Ti to move together and arrange each other to form the agglomeration of particles of crystal growth and phase transformation[31–33]. The composition contained on the surface of the electrode is known by EDX (Energy Dispersive X-ray) There of N peaks as an indication of the presence of nitrogen elements in N-TiO2 indicates the success of doping the nitrogen element into the TiO$_2$ matrix (Figure 3) The composition data of the elements making up the N-TiO$_2$/Ti electrodes can be seen in Table 1.

| Element | Position peak (KeV) | Composition (%) |
|---------|---------------------|-----------------|
| N       | 0.392               | 2.5             |
| O       | 0.525               | 52.3            |
| Ti      | 4.511               | 45.2            |

3.3. Conductive electrochemical tests and working electrodes

In Figure 4A, the LSV of the TiO$_2$/Ti electrodes produced has the highest activity during UV irradiation, this is in accordance with the theory of TiO$_2$ which has photoelectrocatalysis when the UV light is irradiated, which is active when the wave increases $\leq$ 388 nm, with an Energy gap $\geq$ 3.2 eV. With the TiO$_2$/Ti matrix without dopants not responding to light currents, compiling, and responding to irradiated light currents, visible light is because the energy obtained from the source of visible light is smaller to activate TiO$_2$, Figure 4B, LSV N-TiO$_2$/Ti electrodes resulting from photoelectrocatalysis activity. Visible in the dark and when illuminated by UV light,
the observed light response current is close to zero whereas when the electrode is exposed to visible light it has good intensity. N-TiO$_2$/Ti electrode activity shown by visible light irradiation proves that doping N on TiO$_2$ has good activity and is capable of photoelectrocatalysis with visible light irradiation.

Figure 4. LSV graph (a) TiO$_2$/Ti Electrodes (b) N-TiO$_2$/Ti Electrodes

3.4. Photoelectro catalysis process on electrode surface
At 0 seconds, illumination has not yet occurred so the adsorption process only occurs. Illumination occurs at the 4th second, where both the flow of electrolyte light and organic compounds give rise to a high initial light current surge due to oxidation on the catalyst surface. Over time, the concentration in the catalyst surface area decreases so that mass transfer occurs from the bulk solution to the solution around the catalyst surface (Figure 5). In electrolyte samples in the form of NaNO$_3$, the light current will decrease until it reaches a steady state mass transfer where the rate of hole capture is in line with the mass transfer rate of the organic compound[34–37].

Figure 5. Results of potassium hydrogen phthalate and NaNO$_3$amperograms

Light flow that is horizontal (steady-state photocurrent) is the flow of light that results from the photodegradation process, where the change in the value of the light current does not change significantly over
time. In this case, the horizontal flow of light shows the balance of the oxidation rate which is in line with the rate of mass transfer that occurs in the photoelectrocatalysis system.

### 3.5. Measurement of photocurrent response

In this study, 100 ppm glucose which has been diluted previously is made into 5, 10, 20 and 30 ppm which will be tested on TiO$_2$/Ti electrodes using UV light and N-TiO$_2$/Ti electrodes using visible light. Photocurrent responses generated from glucose using TiO$_2$/Ti electrodes and UV light can be seen in Figure 6.

**Figure 6.** (A) Photocurrent response using TiO$_2$/Ti electrodes and UV light on glucose, (B) Clean current ($i_{net}$) to glucose concentration using TiO$_2$/Ti electrodes and UV light.

In theory, it is known that the greater the concentration of a compound, the greater the value of the current produced, this corresponds to the current produced from glucose. The visible photo flow resulting from glucose increases with increasing concentration. Light current generated from glucose will be calculated as a net current value ($i_{net}$). The net current ($i_{net}$) is the difference from the total steady-state oxidation lamp ($i_{tot}$) to 0.1 M blank-state steady-state NaNO$_3$ ($i_{blank}$) which will be used in determining the COD value. The following is a graph of the relationship of concentration with net current ($i_{net}$) in glucose figure 6A. In Figure 6B it appears that the net flow ($i_{net}$) of glucose will increase with increasing glucose concentration. This situation is in accordance with Faraday's equation where the current produced is proportional to the concentration of the compound. Photocurrent responses are generated from glucose using N-TiO$_2$/Ti electrodes and visible light can be seen in Figure 7.

**Figure 7.** (A) Current photo responses use N-TiO$_2$/Ti electrodes and visible light in light, (B) Net current ($i_{net}$) to glucose concentration using N-TiO$_2$/Ti electrodes and visible light.

Figure 7A shows the same thing using TiO$_2$/Ti electrodes and UV light, from which it can be seen that the electric current will increase with increasing glucose concentration. The difference in the current response of glucose light using N-TiO$_2$/Ti electrodes and visible light using TiO$_2$/Ti electrodes and UV rays is a stable non-linear curve that shows the flow of light produced up and down. This event is caused by a clot on the surface of the TiO$_2$/Ti electrode which is treated with nitrogen so that the surface of the electrode is not flat so that the resulting light current also fluctuates.
In this study, the previously diluted 100 ppm potassium hydrogen phthalate was made into 5, 10, 20 and 30 ppm which will be tested on TiO₂/Ti electrodes using UV light and N-TiO₂/Ti electrodes using visible light. The response of photographs produced from potassium hydrogen phthalate by using TiO₂/Ti electrodes and UV light can be seen in Figure 8.

![Figure 8](image1)

**Figure 8.** (A) Photocurrent response using TiO₂/Ti, (B) Net current (i_{net}) to potassium hydrogen phthalate concentration

Based on Figure 8, information is obtained that the light current increases with increasing potassium hydrogen phthalate concentration. This is in line with the increasing rate of potassium hydrogen phthalate degradation. The initial cash flow characteristics produced by the potassium hydrogen phthalate are very different from glucose. This difference is caused by differences in interactions on the surface of TiO₂, where potassium hydrogen phthalate has a stronger interaction compared to glucose interactions. The strong interaction with the surface of the catalyst causes an increase in the rate of degradation of organic compounds so that the value of the resulting light current is also higher and sharper than glucose. The following is a graph of the relationship of concentration with net current (i_{net}) on the potassium hydrogen phthalate. Photocurrent responses generated from potassium hydrogen phthalate using TiO₂/Ti electrodes and visible light can be seen in Figure 9.

![Figure 9](image2)

**Figure 9.** (A) Photograph responses used N-TiO₂/Ti electrodes and visible light at potassium hydrogen phthalate, (B) Net current (i_{net}) to potassium hydrogen phthalate concentration using N-TiO₂/Ti electrodes and visible light

Based on Figure 9A, photos can be obtained from the potassium hydrogen phthalate using the same N-TiO₂/Ti electrodes produced from the TiO₂/Ti electrodes, where the light current increases with increasing potassium hydrogen phthalate concentration, but the photo current is produced using the N-TiO₂/Ti electrode and visible light is lower than using N-TiO₂/Ti electrodes and UV light. The graph of the relationship between net current (i_{net}) and increasing concentration on potassium hydrogen phthalate can be seen in Figure 9B.

3.6. Determination of the value of COD by photoelectrocatalysis method

COD measurements using the photoelectrocatalyst method are based on the photocatalysis reaction that occurs
on the surface of TiO$_2$. TiO$_2$-photocatalyst functions as a substitute for chemical oxidizing agents in the dichromate method. Degradation is carried out at the reactor by using an electrochemical system so that it is expected to reduce the degradation time and maximize the degradation efficiency.

Glucose and potassium hydrogen phthalate COD values can be seen in Tables 2 and 3.

**Table 2. Glucose values and potassium hydrogen phthalate COD using TiO$_2$/Ti electrode**

| Concentration (ppm) | COD (mg/L O$_2$) | Glucose | Potassium hydrogen phthalate |
|---------------------|------------------|---------|-----------------------------|
| 5                   | 2.88             | 4.42    |
| 10                  | 12.89            | 10.56   |
| 20                  | 19.54            | 17.95   |
| 30                  | 29.73            | 31.34   |

**Table 3. Glucose and potassium hydrogen phthalate COD values using N-TiO$_2$/Ti electrodes**

| Concentration (ppm) | COD (mg/L O$_2$) | Glucose | Potassium hydrogen phthalate |
|---------------------|------------------|---------|-----------------------------|
| 5                   | 4.101            | 2.32    |
| 10                  | 12.26            | 13.12   |
| 20                  | 17.72            | 20.28   |
| 30                  | 30.91            | 29.20   |

**Table 4. The theoretical values of glucose and potassium hydrogen phthalate COD**

| Concentration (ppm) | COD (mg/L O$_2$) | Glucose | Potassium hydrogen phthalate |
|---------------------|------------------|---------|-----------------------------|
| 5                   | 5.33             | 5.68    |
| 10                  | 10.66            | 11.37   |
| 20                  | 21.31            | 22.73   |
| 30                  | 31.92            | 34.08   |

The COD value was obtained by the photoelectrocatalysis method using TiO$_2$/Ti and N-TiO$_2$/Ti electrodes, the value of glucose and potassium hydrogen phthalate COD obtained increased with increasing concentrations of the two organic compounds[38,39]. This is in accordance with Faraday's
law where the electric current will increase along with an increase in concentration which means the value of COD will also increase. The COD value obtained using the photoelectrocatalysis method differs from the theoretical determination of the COD value. This possibility is also caused by the growth of TiO$_2$ on the working electrode which is not perfect, but there may also be an error when diluting.

4. Conclusion
The CODflow sensor system is made of wood and aluminum-coated plywood inside, consisting of 24 UV lamps with 4 Watts of power, each mounted on four sides of the reactor’s wood wall, and a probe consisting of three electrodes, namely TiO$_2$/Ti or N-TiO$_2$/Ti working electrodes, Pt counter electrodes, and Ag/AgCl reference electrodes. Then it is equipped with inlet water hose, outlet water hose, water pump, test solution container. The performance of TiO$_2$/Ti thin film electrodes when illuminated by UV lamps results in net current values ($i_{\text{net}}$) at concentrations of 5, 10, 20 and 30 ppm, respectively in glucose 4.9, 12.08, 16.85, and 24.15 $\mu$A, and for potassium hydrogen phthalate respectively 24.43, 33.23, 43.83, and 63.07 $\mu$A. Using N-TiO$_2$/Ti electrodes when illuminated by visible lights, the net current value ($i_{\text{net}}$) at concentrations of 5, 10, 20 and 30 ppm in glucose respectively 3.14, 5.8, 7.58, and 11.88 $\mu$A, and for potassium hydrogen phthalate respectively 15.03, 25.03, 31.53, and 39.73 $\mu$A. The data obtained regarding the correlation of the measured current value in the photoelectrocatalysis system to determine the COD value is that the current formed increases with increasing concentration and the net current ($i_{\text{net}}$) increases with increasing concentration of the test compound. This is in accordance with Faraday’s Law which explains that the current will be proportional to the concentration of the solution.

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