

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

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Abstract: The purpose of this study was to develop a photocatalyst TiO₂ as a probe of Chemical Oxygen Demand (COD) determination method. This photocatalyst coated onto a glass slide SnO-F layer. Measurements were performed in an electrochemical cell with TiO₂ as a working electrode, platinum wire as an auxiliary electrode, and Ag/AgCl as a reference electrode. COD measurements was performed by using Multi Pulse Amperometry method. Regarding to the method, the sample was degraded by the photocatalyst by UV light. Photocurrent measured was plotted against time to be converted into the value of the charge (Q). Then, Q value was converted into the value of COD. Further, it was tested the response of this electrode system in a variety of organic compounds to investigate the nature of the probes designed. The research showed that the photocurrent of potassium hydrogen phthalate (KHP), benzoic acid, and 4-chlorophenol organic samples were observed in the range of concentration (1 – 80 ppm), with a linear response between the concentrations and the charge. COD sensor developed could be applied on several organic substances as model to detect the level of water pollution.

Keywords: Photocatalyst, photoelectrocatalytic, COD sensor.

1. Introduction

The use of a semiconductor as a photocatalyst for various processes, which include the mineralization of organic pollutants in the liquid phase or in the gas phase and the reduction of inorganic pollutants has been widely developed by researchers since the 1970s¹. Titanium dioxide (TiO₂) is one of semiconductors used as a photocatalyst because it is chemically inert, nontoxic, and not expensive. In the method development, TiO₂ is used as a photocatalyst in the suspension system and expand in the form of a thin layer immobilized on various support materials, such as fiber, glass, silica, and titanium plates².

Illuminated TiO₂ is one of the most powerful oxidant because of the high oxidation potential of the hole in the photoexcitation valence band, photocatalytic activity, chemical properties, photochemical stability, and very high oxidation ability. TiO₂ is selected by researchers to develop a method based on photocatalytic disinfection of bacteria, such as drinking water and waste water degradation³.

In this study, the value of COD of the sample was measured directly on a semiconductor electrode coated by TiO₂ nanoparticles through oxidative degradation photoelectrochemically process⁴. The advantages of the photoelectrocatalytic method are: (i) this method is a directly and absolutely measurement; (ii) measurement

does not require a standard for calibration; (iii) this method accurately measures the theoretical COD value due to the high efficiency of oxidation; (iv) it can overcome matrices effects by treating the photoelectrocatalytic system with the high effectiveness and perfectly oxidize organic compounds in water samples in a wide range of spectrum ^{5,6}.

This research developed the preparation method of TiO₂ coated on a glass slide conductor as COD sensor sandwich models. It was expected to overcome the limitations of photon penetration ability on the catalyst surface and the limitations of mass transfer.

2. Materials and Methods:

2.1 Materials

Materials used in this research were 97% titanium tetraisopropoxide (TTIP); HNO₃; 31% HCl; 40% HF; SnCl₂.2H₂O; 99.8% methanol; 98% acetone; NaNO₃; potassium hydrogen phthalate (KHP); benzoic acid; 4-chlorophenol, and distilled water.

2.2 Synthesis of Titanium Dioxide (TiO₂)

Sol-gel TiO₂ system was prepared by mixing TTIP, HNO₃ and distilled water. TTIP was very susceptible to hydrolysis when added to water and formed a Ti(OH)₄. The mixing was performed as follows: 150 ml of distilled water was filled in the round-bottom flask. The mixture then was added with 1 ml of HNO₃ and 15 ml of TTIP. This solution was refluxed at a temperature of 90°C for 3 days with agitation in order to obtain a sol-gel TiO₂^{7,8}.

2.3 Immobilization of TiO₂

Glass slide was immobilized by dip coating into the TiO₂ sol, and calcined at a temperature of 400°C⁹.

2.4 Probe Chemical Oxygen Demand

COD probe was made by using a glass cuvet and composed of three electrodes, namely: TiO₂ working electrode, Pt counter electrode, and Ag/AgCl reference.

2.5 Reactors and Electrodes

The measurements were applied by a light source of 1 × 6 Watts UV black light. The electrodes used were a SnO-F/TiO₂ working electrode, a platinum-wire counter electrode, and a Ag/AgCl reference electrode. Measurements were performed by using 0.1M NaNO₃ electrolyte solution¹⁰.

2.6 Measurement of the Photocurrent Response

The photocurrent response was obtained from the measurement of the current by using a Linear Sweep Voltametry (LSV) method in the potential range of -0.4 – 0.4 V with a scan rate of 0.01 V/s. Measurement of charge for each substance tested was conducted by using a Multi Pulse Amperometry (MPA) with a span of 0 – 75 seconds and the potential bias of 100 mV. Linear response was investigated with all kinds of compounds with various concentrations. Measurement of photoelectrocatalytic was performed by applying a portable e-DAQ.

3. Results and Discussion:

3.1 Conceptual Approach

TiO₂ photocatalytic semiconductor properties is widely used compare with other conductor materials, because the value of the band gap of semiconductor material (0.5–5 eV) allows electrons in the valence and conduction bands moved to form electron pairs and holes. The conductor materials, the valence band and the conduction band coincide so that the age of the holes is shorter. The existence hole can form hydroxyl radicals with water, while the electrons flow to the external circuit formed as a photocurrent¹¹.

In a photoelectrochemical system when the lights illuminated, equilibrium system of photocatalyst was formed in the solution. After the lamp was turned on, electron pairs and holes were formed. Furthermore, organic compounds on the surface was oxidized by hydroxyl radicals.

Electrons would flow from the coat of photocatalyst leading to conductive layer (SnO-F) and carried by the circuit to the potentiostat system¹². Furthermore, it would flow back to the auxiliary electrode. While the oxidation reaction was occurred around the electrode surface due to the formation of holes and hydroxyl radical¹³. This entire process would be measured through a potentiostat. When the lights off, the background of the current measured was the initial photocurrent of solution.

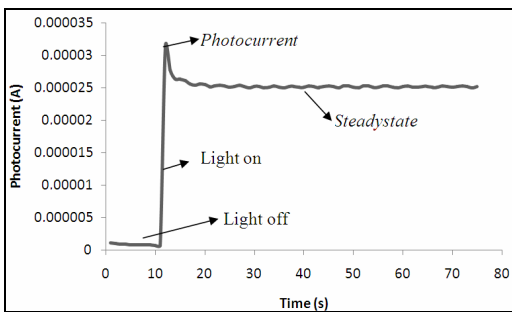


Figure 1. Response of Photoelectrocatalytic

When the lights began to illuminate (Figure 1) there was appeared to be a surge in current known as initial photocurrent. The decrease of concentration of the photocatalyst surface compound was characterized by declining photocurrent. Finally, photocurrent would horizontally flow when it reached steady state. At equilibrium phase, steady state was occurred on the surface of the compound degradation and diffusion solution¹⁴.

The response curve can be determined by using the following equation:

$$dQ/dt = I \dots \dots \dots (1)$$

The charge (*Q*) was calculated as the surface area under the curve, as can be seen in Figure 2.

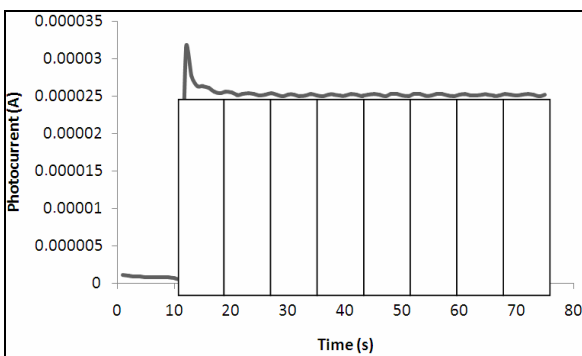


Figure 2. Determination broad curve

Wide curve was calculated from the total amount of each of the square. Therefore, broad curve can be determined by the equation below.

$$Q = \Sigma [width \times (photocurrent_1 + photocurrent_2)] : 2 \dots \dots \dots (2)$$

3.2 Photoelectrochemical Response

In this study, the photocurrent was measured from solution tested containing organic compound in the photoelectrochemical system. It was different with previous systems that used ITO glass. The system applied was used a sandwich-TiO₂. The advantage of this system was the ability of TiO₂ layer to directly absorb the UV light, so it was expected to have a better response.

Current changes were measured using a potentiostat in Multi Pulse Amperometry (MPA) mode, which was given a potential bias of 100 mV at the working electrode. The initial measurement of the UV lamp was turned off position, and switched on after running for 10 seconds.

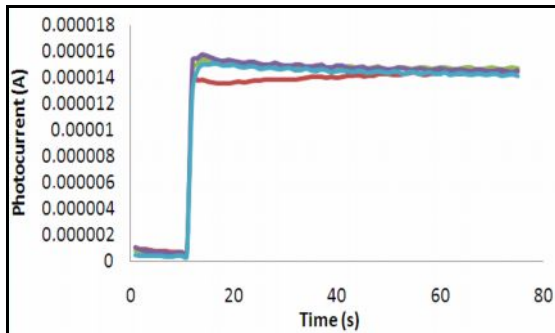


Figure 3. Photocurrent response with 0.1 M NaNO₃ sample after several measurements

From Figure 3, it can be seen a change of the photocurrent measurement repeatability of 0.1 M NaNO₃. The measured photocurrent of the system was very small (microampere scale). There was a slight change of the repeatability values of the measurement results. Photocurrent of the sample was measured by injecting a few milliliters of the sample into the blank solution of 0.1 M NaNO₃ to prevent the saturation of TiO₂ photocatalyst. Saturated photocatalyst can be seen from the Figure 4 that it was overlapped as the measurement result of KHP sample.

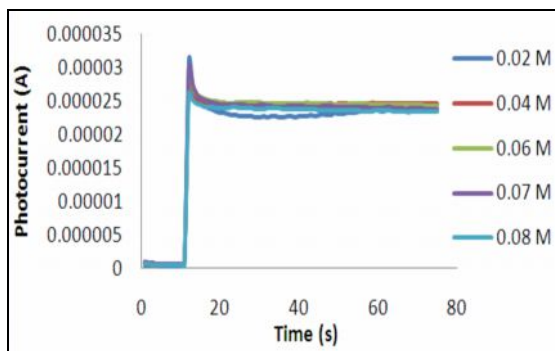
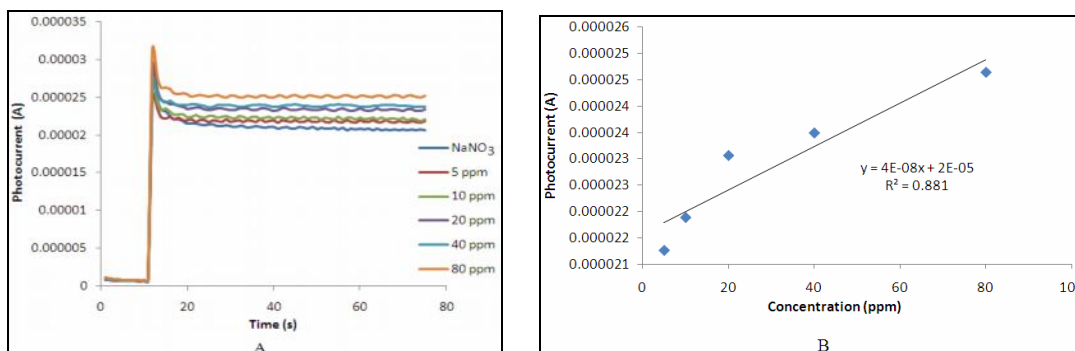


Figure 4. Accumulated response

Figure 4 is the photocurrent profile formed caused by the analyte or its intermediate compound on photocatalyst surface.

3.3 Response to KHP

Before measurement of the photocurrent in organic compounds, it has been prepared 419 pieces electrodes for testing on KHP. KHP was a standard compound used in the COD measurement.



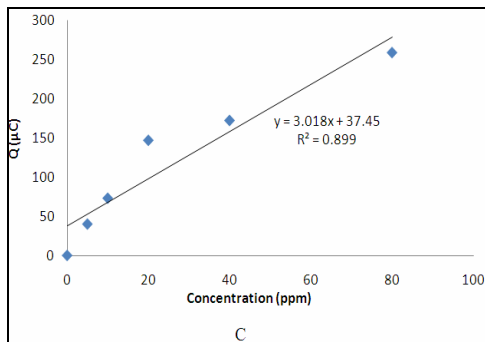


Figure 5. KHP response: A) The photocurrent response; B) Photocurrent vs. concentrations; C) The charge (Q) vs. concentrations

Figure 5 showed the increase of the initial photocurrent along with the increase of the sample concentration. MPA response showed a strong indication that this compound was degraded quite well by the photocatalyst. This can be reasonable because KHP was a strong adsorbate so that it can easily be adsorbed on the surface of the photocatalyst¹⁵.

3.4 Response to Benzoic Acid

Benzoic acid is an aromatic compound. This compound has carboxyl group (COOH) that was expected to have a good activity absorption on the surface of TiO₂.

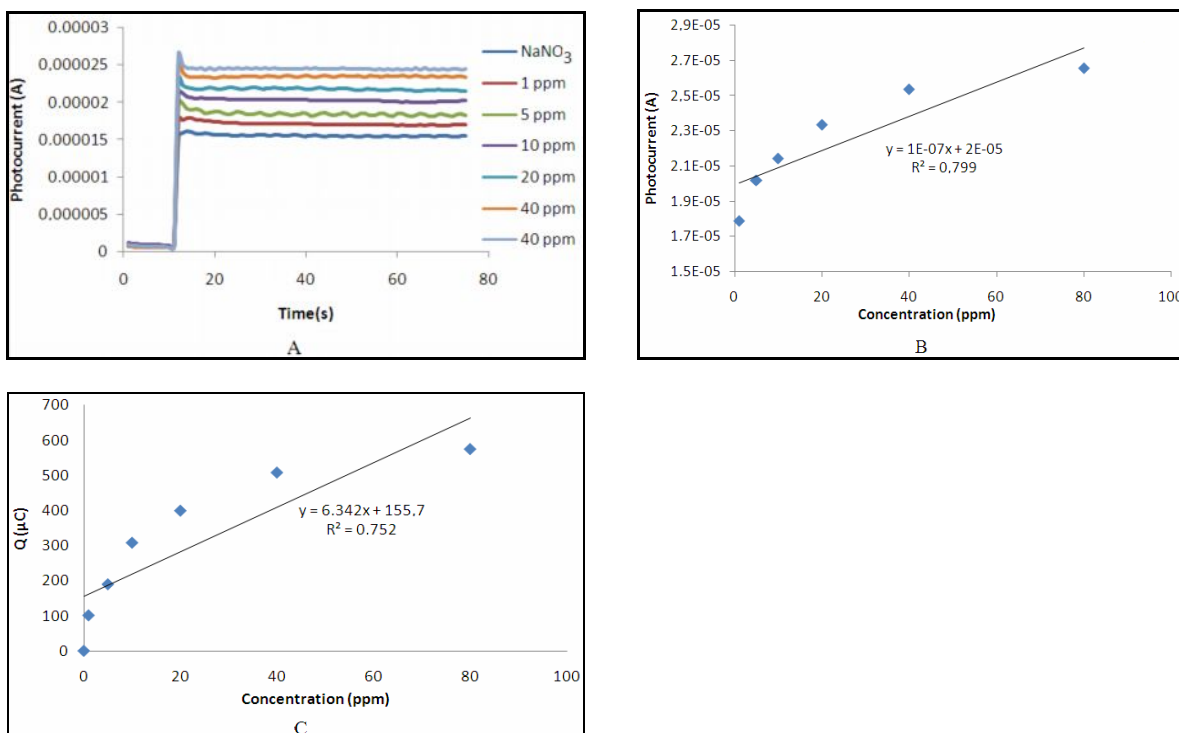


Figure 6. Benzoic acid response: A) Photocurrent response; B) Photocurrent vs. concentrations; C) The charge (Q) vs. concentrations

Based on Figure 6, it can be seen the rise of significant photocurrent of benzoic acid that is directly proportion with the increase of concentration, thus the initial photocurrent is still tend to rise proportionally to the concentration. Photocurrent measurements have not coincided with the end of the blank electrolyte for all concentrations, which indicated that the system was not perfectly degraded benzoic acid in the observed time span.

3.5 Response to 4-Chlorophenol

Phenol is an aromatic compound which has a hydroxyl group (OH). This compound was included in the class of acid compound because of the ability of the molecule to release H⁺ ions. Hydroxyl group on 4-chlorophenol was expected to have a good activity absorptive to the surface of TiO₂. In addition, the simple molecular structure of 4-chlorophenol was very likely be degraded completely.

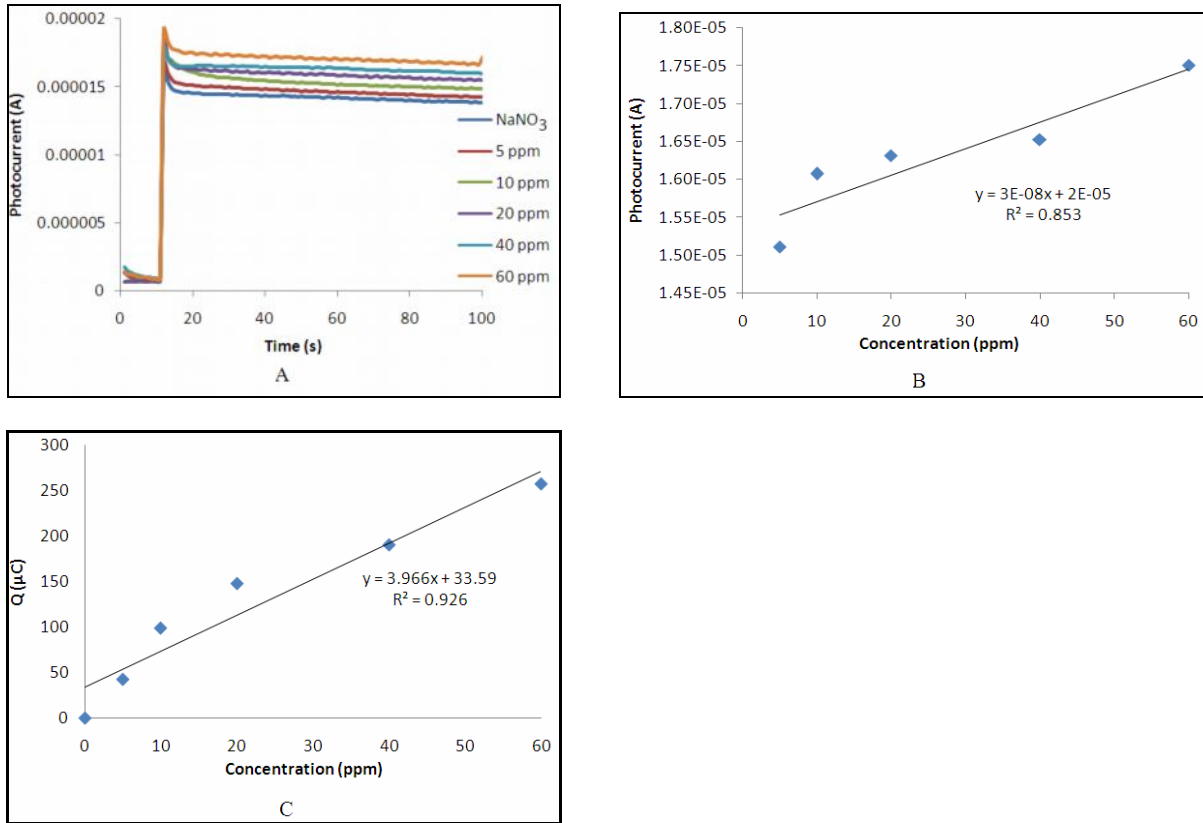
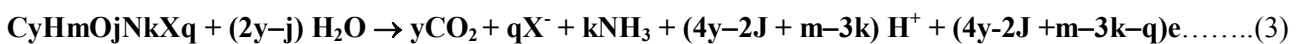


Figure 7. 4-Chlorophenol response: A) Photocurrent response; B) Photocurrent vs. concentrations; C) The charge (Q) vs. concentrations

Based on Figure 7, it can be seen significantly the increase of the photocurrent of 4-chlorophenol in accordance with the increase of concentration, thus the initial photocurrent is still tend to rise proportionally to the concentration.

3.6 Determination of COD

To investigate the response of COD of various test compounds, there were necessary equivalent concentration of each of test compounds that describes electrons involved in the degradation process perfectly on the test compound. The number of electrons involved depends on the structure of organic compounds degraded. Generally, organic compounds degraded would perfectly obey the following equation ²:



The number of electrons transferred in perfect degradation process were:

$$n = 4y - 2j + m - 3k - q \dots \dots (4)$$

Then the COD value obtained by the equation:

$$COD \left(\frac{mg}{L O_2} \right) = \frac{Q}{4FV} \times 32000 \dots \dots (5)$$

Table 1. COD values of each organic compound

Concentration (ppm)	COD (mg/L O ₂)		
	KHP	Benzoic Acid	4-klorophenol
0	0	0	0
1	-	21.06	-
5	8.36	39.51	8.70
10	15.26	64.18	20.63
20	30.69	83.17	30.88
40	35.98	105.83	39.70
60	-	-	53.73
80	54.10	119.77	-

Table 1 showed the increase of the COD value in line with the increase of concentration of the sample being tested. At a concentration of 10 ppm KHP required approximately 15.26 mg/L O₂ for perfectly degraded into simple molecules.

4. Conclusions:

The conclusions of this research are as follows:

1. The sensor probe of COD was made of glass cuvet which immobilized SnO-F/TiO₂ as the working electrode. The sensor was made in the sandwich model that could be applied to the measurement of the photocurrent.
2. In the photoelectrochemical system, when the lights illuminated, the system in equilibrium was between the solution and the surface of the photocatalyst. Photocurrent measured was plotted against time to be converted into the value of charge (Q), then Q was converted into the value of COD.
3. The range concentration of COD sensor based on photoelectrocatalytic system is 1-80 ppm.

5. Acknowledgement

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