Anal. Bioanal. Electrochem., Vol. 8, No. 6, 2016, 761-776

Analytical & Bioanalytical Electrochemistry

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Full Paper

Electrochemical Profile Degradation of Amino Acid by Flow System using TiO_2/Ti Nanotubes Electrode

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Received: 16 August 2016 / Received in revised form: 15 September 2016 / Accepted: 19 September 2016 / Published online: 30 September 2016

Abstract- The new method of electrochemical degradation of Amino Acid by flow system using TiO_2/Ti electrode had been carried out. The electrode was synthesized by anodic oxidation processes and analyzed its electrochemical profile degradation. The development of the flow system for determining the profile and photocurrent response of amino acid, i.e phenylalanine, glycine, and glutamine were performed by using Linear Sweep Voltammetry (LSV), Multi-Pulse Amperometry (MPA) and Cyclic Voltammetry (CV) techniques. The optimum pH measurement of phenylalanine, glycine, and glutamine were 8.54, 7.80 and 8.53, respectively. Data on photocurrent response showed the phenylalanine, glycine and glutamine were proportional to the increasing concentration. The photocurrent response with the addition of electrolyte on the analyte showed that the photocurrent response was higher than the $\overline{Ceq}$ value of each amino acid (196.9825 µA phenylalanine; 130.3333 µA glycine; 194.0193 µA glutamine) whereas without using electrolyte of each amino acid: 84.56667 µA phenylalanine; 60.55863 µA glycine; 91.79087 µA glutamine. This system design is potentially developed for chemical oxygen demand (COD) sensor.

Keywords- Electrochemical, Amino acid, Photoelectrocatalytic, pH, TiO_2/Ti

1. INTRODUCTION

The amino acid is the main component of protein that contributes the largest amount of nitrogen in nature [1,2]. The food that contains many proteins such as meat and milk are from the industrial manufacture so that they can produce amino acid waste [3-5]. The amino acid contains carboxylic acid (-COOH) and an amine group ($-NH_2$). Therefore the amino acid waste can easily dissolve in the water and difficult to dissolve in an organic (non-polar) solvent [6,7]. If this liquid waste pollutes the environment, it will cause the problem with the water quality such as eutrophication so that the growth of algae and bacteria in the environment keep increasing, the emergence of various diseases such as itch and respiratory disorder because of the smell from the putrefaction process [8,9]. The bad smell of the amino acid waste is caused by the degradation of the amino acid compound by the natural microbes [10,11].

The various ways had been done to solve the waste of the amino acid compound, such as the using of microorganism and adsorbent [12,13]. That way was less effective in solving the problem because it is affected by some factors on the environment and it needs a quite long time. During the last decades, the use of titanium dioxide (TiO_2) in solving the environmental pollution provides a good direction and it has been studied intensively [14,15]. The TiO_2 compound can be formed by electrochemistry method which is popular as anodic oxidation method [16,17]. This method can form the nanotube structure of the metal thin film of titanium [18].

The TiO_2 can be used in the photocatalyst process, sensing, photoelectrolysis, photovoltaic, solar cell, filtration and biomedical [19]. The utilization of TiO_2 compound in the photocatalyst field is for degrading the organic pollutant perfectly to be carbon dioxide in the aquatic environment [20]. However, along with its development, the photocatalyst method in the wastewater treatment still has some problems such as lower efficiency because it can cause the combination of electron hole. Therefore, to improve the performance of photocatalyst, the process of photocatalyst is combined with the electrochemistry process that they were called the photoelectrocatalyst. The photoelectrocatalyst had been proven as one of the most effective processes to degrade the organic pollutant in the water [21].

Maulidiyah et al. had conducted the test of the photoelectrocatalyst response by using SnO-F as the conductive substrate on Inner Wall Conductive Glass Tube (IWCGT) [22] against the amino acid compound (alanine) with the batch system. With the same system (batch) Li et al. had done the degradation of photocatalyst and photoelectrocatalyst of the sample of phenylalanine, tyrosine, and tryptophan amino acid using Indium Tin Oxide (ITO) that showed the efficiency of degradation to be better by the photoelectrocatalyst [7]. However, the batch system has the weakness such as the uneven organic compounds degraded.

According to the study of the literature, there was not any report about the development of the photoelectrocatalyst method of the flow system in determining the degradation profile of amino acid by using the TiO_2/Ti electrode. In this research, the test of TiO_2/Ti electrode's ability and the test of photocurrent response by phenylalanine, glycine, and glutamine acid will be done based on the flow system. In this research, the probe design of the flow system for the photoelectrocatalyst that has a role in the test of LSV, MPA and CV activity from TiO_2/Ti electrode. The electrode had been prepared by using anodic oxidation method and profile test of photocurrent response from the amino acid compound [23]. The result of this research was expected to determine the electrochemical profile of the various organic compounds of amino acid electrochemically.

2. EXPERIMENTAL

2.1. Preparation of Titanium (Ti) Plate

The preparation of Ti plate was done by cutting the Ti plate (99% purity) and the thickness of 0.5 mm with the size of 4 cm×1 cm then it was sanded by using 1200 CC sandpaper until the surface was clean and shiny. Then it was washed by using detergent liquid, water, and distilled water. After the Ti plate was dried in the air, it was then immersed in the mixed solution of HF, HNO_3, and distilled water with the ratio of 1:3:6 for 2 minutes. The last stage of this preparation was rinsing the Ti plate with distilled water to eliminate the remaining etching solution on the surface of the Ti plate, then it was dried in the air [16,17].

2.2. Synthesis of TiO_2/Ti Electrode by Anodic Oxidation Method

The prepared was put into a probe containing NH_4F 0.27 M electrolyte solution and distilled water in the 98% glycerol. Preparation of the electrolyte solution was weighed to be 0.99 gram of NH_4F dissolved by using 4 mL of distilled water and 96 mL of 98% glycerol. The process of anodic oxidation was done by positioning the Ti plate as the anode and Cu plate as the cathode and gave 25-volt potential bias that was connected to the Power Supply. This anodic oxidation process was done during 4 h. The last stage was calcined the Ti plate in an oven for 1.5 h with the temperature of 500 °C in order to get the TiO_2 anatase crystal [16,17].

2.3. Design of Flow System Probe

The Probe of the flow system was made by using cylinder glass with the diameter of 1.8 cm and 4 cm high and the probe volume was 7.5 mL. The probe has consisted of three electrodes, i.e: TiO_2 working electrode, Pt counter electrode, and Ag/AgCl reference electrode.

2.4. Electrolyte Solution

The preparation of the 0.1 M $NaNO_3$ electrolyte solution was carried out by weighing 0.85 gram of $NaNO_3$ (MW=84.99 g/mol) and it was dissolved by using distilled water in a 100 mL flask.

2.5. pH Determination of the Amino Acid Compounds

The pH determination of amino acid (glutamine, glycine, and phenylalanine) used a pH meter. The measurement was done from the concentration of 1; 3; 5; 7 and 10 ppm with and without $NaNO_3$. Then, the relationship line between pH and the analyte concentration was presented.

2.6. Activity of TiO_2/Ti Electrode by LSV and CV Methods

The measurement was performed by LSV and CV method using $NaNO_3$ 0.1 M solution. The LSV was done from the potential of -1.0 Volt to 1.0 volt with the scan rate 1×10^{-4}V/s, whereas on CV it was done from the potential of -1.5 Volt to 1 Volt. The TiO_2 electrode was applied by varying the intensity of UV lamp bias. The result of LSV and CV was to observe the photoelectrocatalyst activity during the process of the test by using the flow system.

2.7. Photocurrent Response of TiO_2/Ti Electrode by MPA Method

The photocurrent response measurement of amino acids (glutamine, glycine, and phenylalanine) using TiO_2/Ti electrode by MPA technique with the potential bias of 0.5 Volt was done for 10 minutes with the variation of concentration 1; 3; 5; 7 and 10 ppm (+$NaNO_3$). This process was done by using the reactor of photoelectrocatalyst based on the flow system. After the measurement of photocurrent response, it was continued to count the amount of the water discharge from the flow system used.

3. RESULTS AND DISCUSSION

3.1. Preparation of Thin-film TiO_2/Ti

The preparation of thin-film TiO_2 on the surface of Ti plate has been carried out by anodic oxidation method for 4 h with the potential of 25.0 Volt. The structure was formed nanotubes of TiO_2 film. Generally, the anodizing process would form nanomaterial having the size of 1–100 nm; this forming of nanotubes with anodizing could produce nanotube arrays [18,24].

Anodizing was an oxidation process of electrochemical that would produce the addition of the film on a metal surface. The plate was then calcinated on the temperature of 500 °C for 1.5 h [16]. This calcination process aimed to evaporate the organic solvents trapped on the

titanium plate. The calcination was needed to oxidize chelate ligands bonded on the titanium plate so that the result of calcinating was expected only the metal oxide [18]. Besides, this calcination process aimed to get the TiO_2 anatase crystal that had the better photocatalyst activities than the other kinds of crystal with the temperature range from 500 °C to 800 °C. This was because the anatase crystal had the larger surface area and active side so it could absorb the light better than the rutile crystal. The bandgap energy of the anatase structure was 3.2 eV which was equivalent to the wavelength of 388 nm UV. This bandgap energy stated how much energy needed for the electron transition from the valence band to the conduction band [25].

The mechanism happened in the process of TiO_2 forming on the Ti plate by anodizing method was as follows [26].

There was Ti oxidation reaction forming the TiO_2 film on the anode.

$$Ti \rightarrow Ti^{4+} + 4e^- \text{ or}$$

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+$$

$$Ti + O_2 \rightarrow TiO_2$$

The entire reaction became,

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$

The Ti metal had the high reactivity to the O_2 so the stable oxide film could be produced. An the Cu cathode, the reduction reaction happened so it produced H_2 gas in the reaction,

$$4H^+ + 4e^- \rightarrow 2H_2$$

On the early anodizing, the dissolution of TiO_2 film in the electrolyte solution containing F^- ion from NH_4F dominated so it caused the forming of small holes as pores. This form of small holes based on the reaction,

$$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + 2H_2O$$

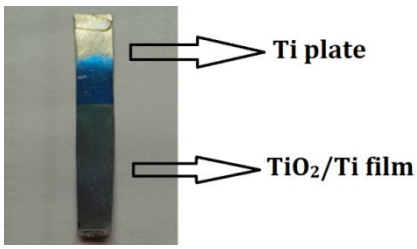

Fig. 1. The result of anodizing process of Ti plate forming TiO_2

The small pores in a short distance area would integrate to be a big pore. The presence of pores and the empty room (void) on the surface of TiO_2 film was the beginning step of the nanotube forming and the high level of acidity at the bottom of the tube helped the pores form the structure of the tube. The result of this technique was the TiO_2/Ti formed on the surface of Ti plate. The Figure 1 showed visually that the TiO_2 film produced by anodizing method.

3.2. Process of Photoelectrocatalyst on the electrode surface

The working electrode of TiO_2 film would cause electron and hole pairs if it was exposed to UV, but some of the electron and hole pairs could be recombined; however, the positive bias potential given to the photoelectrocatalysis caused the forming of electric field near the interface, so the combination of electron and hole pairs could be prevented [21].

The hole would initiate the oxidation reaction on the surface of TiO_2, whereas the electrons were streamed to the counter electrode and transferred to the electron catcher in the solution. The flow of electrons could be observed as the photocurrent that figured out a number of organic compounds oxidized on the surface of TiO_2/Ti electrode. The photodegradation on the surface of TiO_2 catalyst was begun with the solution absorption to the active surface of TiO_2 so the concentration on the surface of the catalyst would be higher than the concentration of a solution in bulk. At the time of illumination, the surface of catalyst would actively do photodegradation on the surface of a catalyst. The presence of •OH caused the forming of electron-hole pairs when the TiO_2 was illuminated. The organic compounds were then degraded either by direct oxidation by the hole or by the attack of •OH formed when the hole reached the surface of TiO_2, so the response on the potentiostat would appear, which was called initial photocurrent.

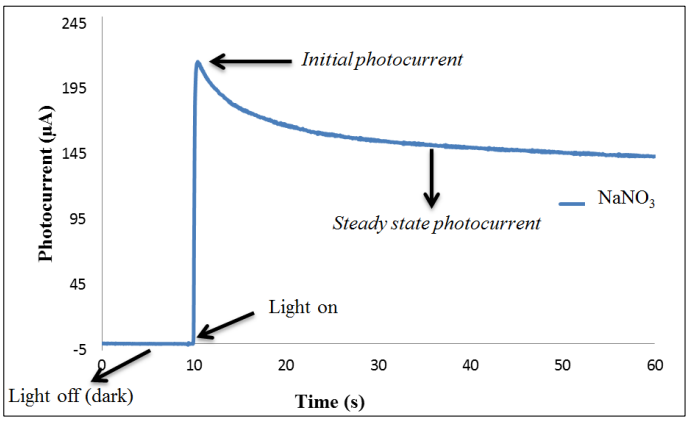

Fig. 2. The response of photoelectrocatalysis

After that, the photocurrent would decrease when the organic compounds on the surface of catalyst were fully oxidized; therefore the process of photodegradation on the surface of

catalyst would cause the concentration difference in the bulk solution to the solutions around the surface of catalyst [27,28].

On this system, at certain time, the steady state mass transfer would happen, in which the speed rate of hole was proportional to the rate of mass transfer / the diffusion of organic compounds in the bulk solution to the solutions on the surface of catalyst so it produced steady state photocurrent.

Steady state photocurrent (i_{st}) showed the oxidation of the organic compounds on the surface that were proportional to the concentration of the bulk solution. This is the profile of initial photocurrent and the steady state photocurrent [22].

There was a balance between the solution and the surface of photocatalyst on the photoelectrochemistry at the blackout. Then, there would be absorption of organic compounds on the surface of photocatalysis. After the lamp was switched on, the electrode and hole pairs would be formed. After that, the organic compounds on the surface were oxidized well by the •OH [21].

The formed electrons would flow from the photocatalyst and would be taken by the potentiostat system. Then they would flow back to the counter electrode, at the same time there was also oxidation reaction around the electrode surface because of the forming of a hole and •OH. This entire process would be measured by potentiostat. The response appeared to be the increasing of current. When the lamp was switched off, the photocurrent was measured the background current from the initial condition of the solution [27].

When the lamp was starting to switch on, the reaction happened on the surface of the electrode and the electrode started to flow, on the Figure 2 there were surges on the current that was called as the initial photocurrent. Then, the compound concentration decreased on the surface of the photocatalyst that was indicated by the decreasing photocurrent to the phase of steady state. On the phase of steady state, the balance could be obtained in the compound degradation on the surface and in the diffusion of the solution.

3.3. Determination of the TiO_2/Ti Electrode Activity

The photocurrent was the current observed when the electrode was radiated by UV light in the measurement for the rate of the interfacial charge transfer rate of the semiconductor/electrolyte, so that it could be used as the measurement for •OH forming rate on the surface of the catalyst [29]. In this research, the measurement of the photocurrent as the potential function was performed by LSV and CV technique to produce the current response coming from the electron transfer during the oxidation and reduction process of the analyte. Thermodynamically, the electrode potential could be used for qualitative and quantitative analysis.

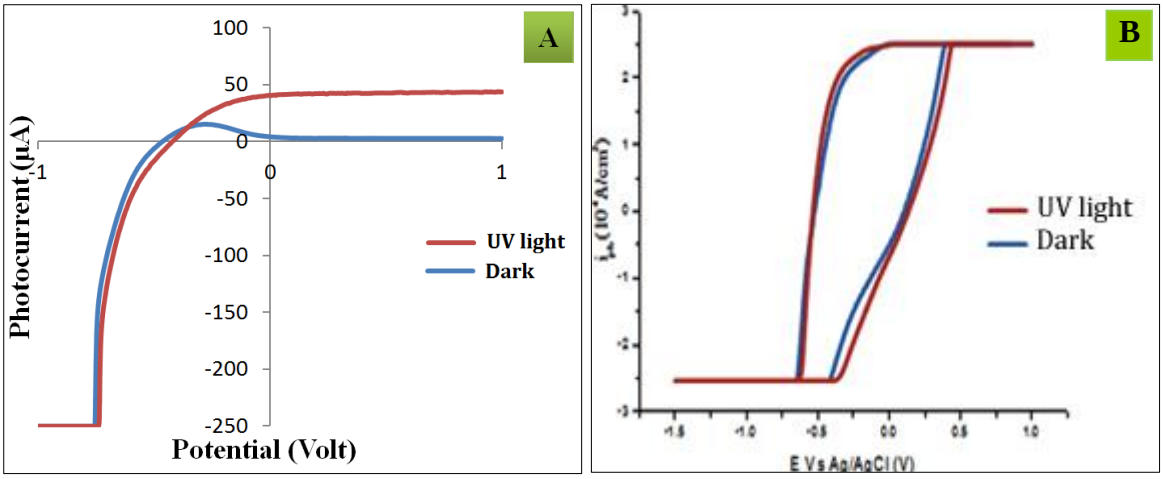

Fig. 3. The result of voltammogram; (A) Linear Sweep Voltammetry (LSV); (B) Cyclic Voltammetry (CV)

Figure 3 (A) LSV from the TiO_2/Ti electrode was produced the highest activities when it was radiated by the UV light, this was appropriate to the theory that TiO_2 had the photoelectrocatalysis activity when it was radiated by UV light, because it was active on the wavelength ≤388 nm, with Eg 3.2 eV [16]. When it was dark, the photocurrent response observed was almost zero, which was the sign that the electrode activity was not active in the darkness.

Based on the Figure 3 (B) that the result of the voltammogram showed the signal of excitation on the first potential for sweeping from 1.0 V to 1.5 V versus Ag/AgCl, whereas the switching potential produced the sweeping of positive back to the early potential 1.0 V. The cathodic and anodic current could be shown, the cathodic current was the current used at the time the sweeping from the biggest potential to the smallest potential and the anodic current was the sweeping from the smallest to the biggest potential.

The UV light showed a greater dilution than the dark, this proved that the working electrode of TiO_2/Ti showed the reduction – oxidation activities in the UV light whereas in the dark, the working electrode of TiO_2/Ti was not effective in $NaNO_3$ 0.1 M.

3.4. PH Determination of Amino Acid Compounds

The pH of Amino Acid could be determined from some groups of amino acids [30]. The aromatic amino acid group included phenylalanine, whereas glycine and glutamine amino acid belonged to the uncharged R polar group. The amino acid in the form of the solution had the characteristic of amphoteric, which tended to be acid in the base solution and tended to be base in the acid solution. This behavior occurred because the amino acid was able to be zwitterion. Besides, the zwitterion on the amino acid was in the condition of neutral (isoelectric pH that was between 4.8–6.3) and was in the form of dipolar ion [31]. To know

the effect of $NaNO_3$ electrolyte solution to the pH of amino acid, a graphic of the relationship between the analyte concentration and the pH to phenylalanine, glycine, and glutamine synthetic was needed to be presented.

3.4.1. Determination of pH on Phenylalanine

The relationship between concentration, pH and the response of photocurrent showed that the higher concentration of phenylalanine the higher photocurrent response would be shown by the amperogram. Based on Figure 4, the relationship between pH and the photocurrent was not proportional because the pH on each concentration showed the maximum level of the concentration of 7 ppm, in which the phenylalanine compound was in base pH: 8.54. This was because the amino acid had the characteristic of amphoteric, which tended to be acid in the base solution and tended to be base in the acid solution. However, that test compound could be concluded in the base condition with pH 8 on average, because the movement of electrons in the structure of phenylalanine tended to lead to the nitrogen basic groups, so it became a base.

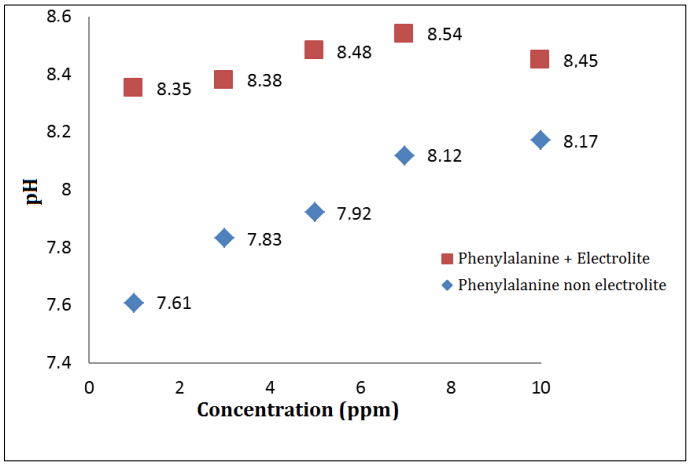

Fig. 4. The pH of phenylalanine with electrolyte and non-electrolyte

From the result of the experiment done (Figure 4), the phenylalanine with the addition of $NaNO_3$ 0.1 M electrolyte solution and without electrolyte showed the base pH, about pH 8 on the concentration of 7 ppm. This was because of the structure of phenylalanine that tended to show the direction of electrons pulled to the nitrogen (amino) basic groups so that it dominantly had the characteristics of a base, and without electrolyte on the concentration of 7 ppm had reached the optimum pH on 8.12.

The pH of phenylalanine amino acid with the electrolyte that had been produced had a high pH after being measured by using pH meter, but the acid pH with non-electrolyte that

had been produced had a low pH because of the effect of the electrolyte solution to the compound.

3.4.2. pH Determination on Glycine

Based on Figure 5, the relationship between concentration and pH of the compound was not significant because there was decreasing pH on the high concentration, so there was an optimum pH level of the compound. According to the result of observation, the optimum level was at the concentration of 5 ppm in the base condition that was pH 7.8. This was because of nitrogen basic groups which tended to be dominant in the compound, so it became a base.

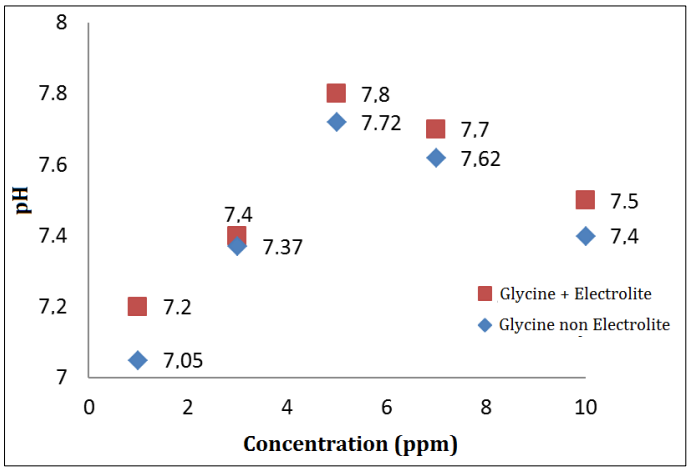

Fig. 5. The pH of glycine with electrolyte and non-electrolyte

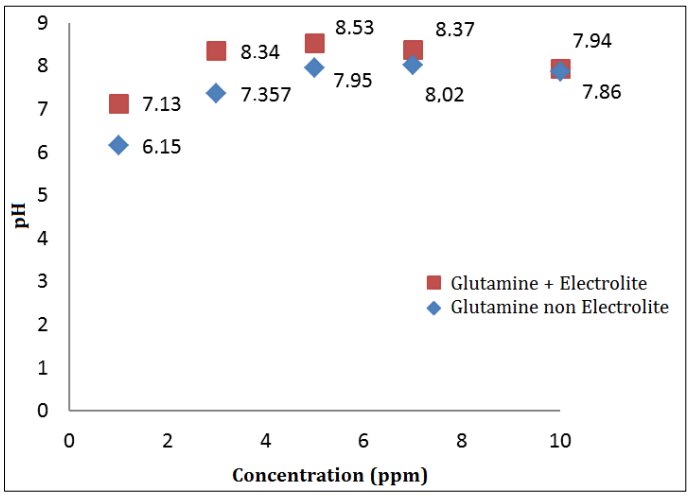

Fig. 6. The pH of glutamine with electrolyte and non-electrolyte

3.4.3. pH Determination on Glutamine

Figure 6 showed that there was not any effect on the degradation (photocurrent response) of amino acid to the pH of and the concentration because; the relationship between amino acid pH and concentration was not directly proportional.

According to the result obtained, the relationship between amino acid and the concentration of the compound showed the increasing pH on the low concentration but it was decreasing on the high concentration. Therefore, it could show the optimum pH of phenylalanine, glycine, and glutamine were 8.54; 7.8 and 8.53, respectively. It was caused by the structure of the compounds of amino acid that could show the characteristic of base and acid of the carboxyl groups. The low concentration of the test compound showed the characteristics of acid but the high concentration showed the characteristics of base.

3.5. Photocurrent Response of the Compounds

The profile of amino acid degradation in this research was the profile produced from the development of the flow system on photoelectrocatalysis. The measurement of the photocurrent was done using a potentiostat by MPA method [22]. The constant potential bias used was 200 mV based on the result of the previous optimization that on the bias of 200 mV to 500 mV was good at taking the photocurrent and prevented the direct electrochemistry process. In this research, the measurement of photocurrent was obtained from the photoelectrocatalysis that was developed when the test solution contains some organic compounds by using the flow system to know the response photocurrent to the phenylalanine, glycine, and glutamine amino acid compounds.

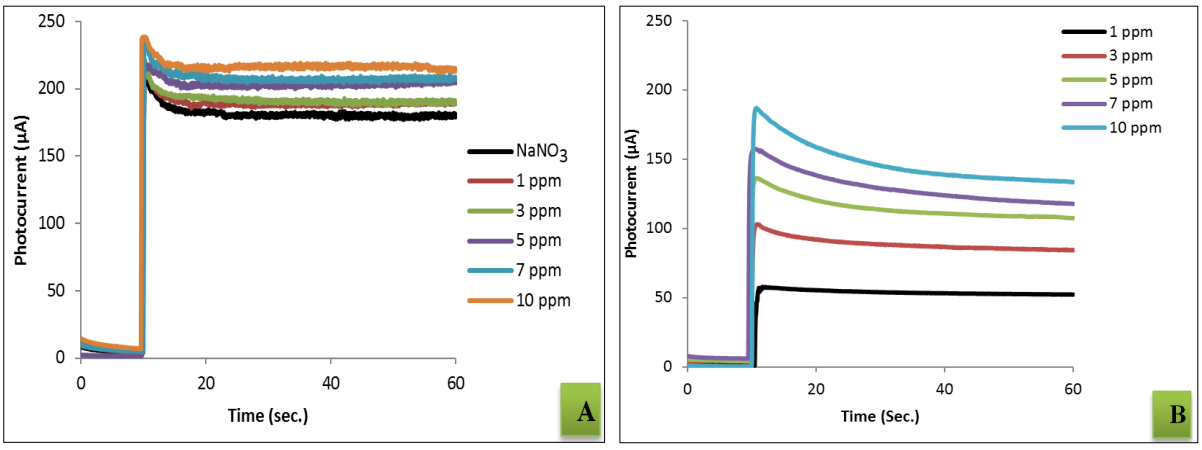

Fig. 7. The Response of Phenylalanine; A) The photocurrent response with $NaNO_3$ 0.1 M electrolyte; B) The photocurrent response without $NaNO_3$ 0.1 M electrolyte

3.5.1. Photocurrent Response of Phenylalanine

The electrode prepared was tested on the sample of phenylalanine. The phenylalanine was the comparing compound or the reference used in the determination of the compound degradation profile.

According to the Figure 7A, the increasing of Initial Photocurrent appeared on the increasing concentration of phenylalanine along with the increasing concentration of the sample, the MPA response showed that this compound was degraded well by photoelectrocatalyst. This could be explained because the phenylalanine had the aromatic component of the structure bonded amine and carboxyl groups so that it was easily adsorbed and degraded on the surface of photocatalyst [32].

According to Figure 7B, the response appeared was the lower current intensity of surges compared to those produced by phenylalanine using $NaNO_3$ 0.1 M electrolyte (Figure 7A). This was because the photocurrent of phenylalanine was not as good as the photocurrent of phenylalanine with the $NaNO_3$ 0.1 M electrolyte solutions.

3.5.2. Photocurrent Response of Glycine

Glycine was included with the uncharged R component if it was seen from its structure so that it was an amino acid group without asymmetric carbon. Glycine has been frequently non-polar. However, from the Figure 8, the R group (a hydrogen atom) did not have an effect to the hydrophilicity of the molecules. The test compound of glycine could be said as the amino acid without asymmetric carbon.

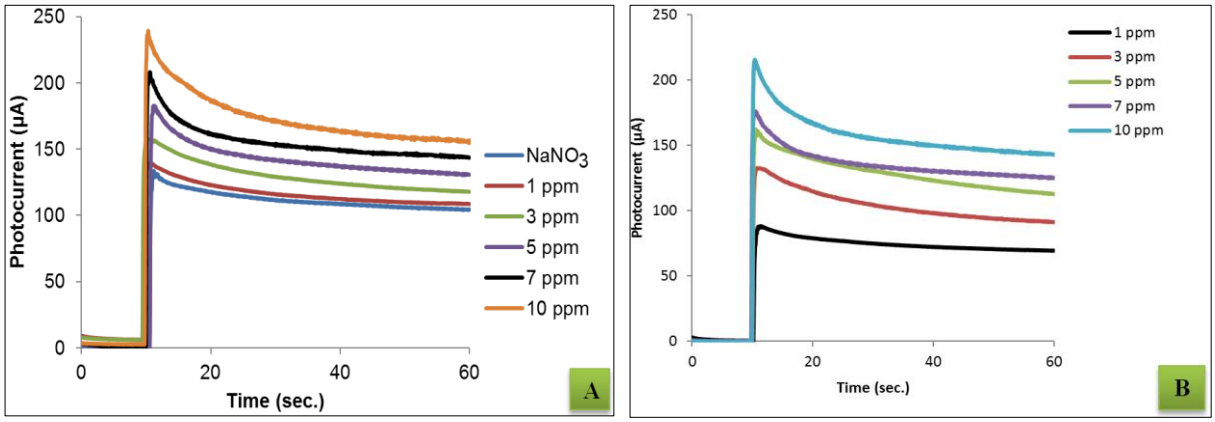

Fig. 8. The response graphic of glycine; A) The photocurrent response with $NaNO_3$ 0.1 M electrolyte; B) The photocurrent response without $NaNO_3$ 0.1 M electrolyte

Figure 8 showed there were photocurrent response differences between the test compound using $NaNO_3$ 0.1 M electrolyte and without using electrolyte. On the Figure 8A, the photocurrent response was higher than that on Figure 8B. This could be explained because

there was electrolyte solution that had the function as a conductor so that it would increase the photocurrent in the test compound.

3.5.3. Photocurrent Response of Glutamine

Glutamine (abbreviated as Gln or Q, and frequently called as L-glutamine) with the concentration about 500–900 µmol/L. The side chain amide was formed by changing the side chain of glutamic acid hydroxyl with an amine functional groups, turning it to be amide from glutamic acid [33]. This research used 100 ppm glutamine amino acid that had been diluted to be 1, 3, 5, 7 and 10 ppm examined on the TiO_2/Ti electrode by using UV light. The photocurrent response from glutamine by using TiO_2/Ti electrode and UV light could be seen in Figure 9.

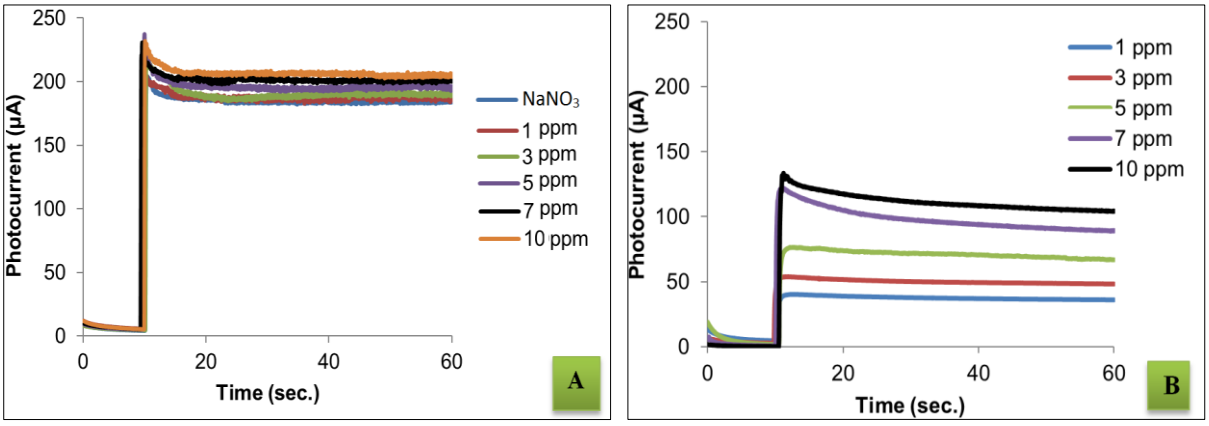

Fig. 9. The response of glutamine; A) The photocurrent response with $NaNO_3$ 0.1 M electrolyte; B) The photocurrent response without $NaNO_3$ 0.1 M electrolyte

According to Figure 9, the photocurrent was increasing along with the increasing concentration of glutamine. This was in line with the increasing degradation rate of glutamine. The characteristics of photocurrent responses of glutamine with and without electrolyte were very different because of the interaction differences on the surface of TiO_2, in which the glutamine amino acid with electrolyte had a higher interaction than the non–electrolyte glutamine. The stronger interaction to the surface of catalyst caused the increasing degradation rate of the organic compounds so that the value of photocurrent obtained was also higher and sharper than that of non-electrolyte glutamine.

3.6. Linearity of the Compounds

To determine the linear boundary on this system, the curve of Ceq values of the three test compounds, i.e phenylalanine, glycine, and glutamine was made to know the value of linearity.

Figure 10 showed that on the low equivalent concentration, all the test compounds had almost the same slope. However, on the high equivalent concentration, the changes of slopes on each of the test compounds appeared. This showed an effect of the photodegradation to each of the test compounds. According to Zhao et al. on the low concentration, the process of photodegradation was only affected by the process of capturing the photo hole on the surface of the catalyst, whereas on the high concentration the compound structure affected the photodegradation of the test compounds [34].

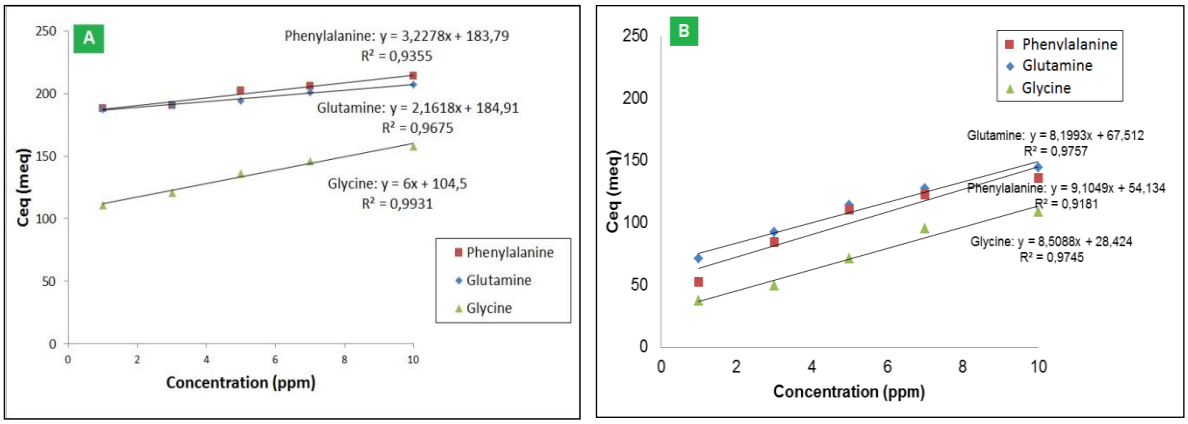

Fig. 10. The linearity of the test compound; A) By using electrolyte; B) Without using electrolyte

The high concentration caused the slope of glycine tended to be at the bottom of the other organic compounds. This was probably because the glycine had a more complex structure than the other organic compounds so that it was more difficult to be degraded. Whereas the Figure 10A, the linearity of glutamine tended to lead to the linearity of phenylalanine showed that the TiO_2/Ti electrode performance was active and strong in degrading both compounds of amino acid because the higher $\overline{Ceq}$ value was directly proportional to the electron transfer charge in the system. The $\overline{Ceq}$ value of each amino acid, i.e 196.9825 µA phenylalanine; 130.3333 µA glycine; 194.0193 µA.

The Figure 10B was the linearity obtained from the test compound without using electrolyte in which the equivalent concentration was increasing along with the increasing concentration of the test compound, but the value of $\overline{Ceq}$ obtained by without electrolyte was lower than using an electrolyte. The $\overline{Ceq}$ value of each amino acid, i.e 84.56667 µA phenylalanine; 60.55863 µA glycine; 91.79087 µA glutamine. This was because the using of electrolyte solution as the electron conductor was flowing in a system so that the photocurrent profile was increasing on the test compound.

4. CONCLUSION

The measurement result of the optimum pH of phenylalanine, glycine, and glutamine were 8.54, 7.80 and 8.53, respectively. The photocurrent response with the addition of electrolyte on the analyte showed that the $\overline{Ceq}$ value of each amino acid, i.e 196.9825 μA phenylalanine; 130.3333 μA glycine; 194.0193 μA glutamine, whereas without using electrolyte the $\overline{Ceq}$ value of each amino acid, i.e 84.56667 μA phenylalanine; 60.55863 μA glycine; 91.79087 μA glutamine. The result of the test compound profile of phenylalanine, glycine, and glutamine showed the different level on the photocurrent response that the phenylalanine had the higher photocurrent than glycine and glutamine.

Acknowledgement

We acknowledge the financial support of the DRPM – Ministry of Research, Technology and Higher Education, the Republic of Indonesia.

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