Electrochemical Characterization of Iron Oxide Composite Electrode for Degradation of Oxytetracycline Compounds

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Abstract—**Oxytetracycline is one of the antibiotic compounds which consumed by livestock including human and animal. The compounds causing a rise issues towards the environment where living organism will suffer from diseases that cannot be treated with pharmacotherapy. Thus, cyclic voltammetry test was carried out to characterize iron oxide composite as electrode for electrochemical degradation of oxytetracycline (OTC) compounds in 0.5M hydrochloride acid (HCl), 0.5M sodium hydroxide (NaOH) and 0.5M sodium chloride (NaCl). Comparison degradation of oxytetracycline compounds were investigated to select the optimum operating condition. As results, the best electrochemical degradation of OTC by using iron oxide composite electrode was observed in 0.5M HCl without the presence of carbon black.**

I. INTRODUCTION

Pharmaceutical compounds are bioactive substances with different structure, function and behavior. It has been used in the veterinary and hospitality as drugs. The compounds was used as therapeutic drugs in the hospitality to treat human disease [1]. Moreover, it was also used as feed additives to control and promote the growth of animal in farming. According to Yingying, et al. [2], the dosage of compounds that used in veterinary is higher than hospitality. It is stated that the compounds were not fully absorb into body and only some of the compounds were absorbed while the excess will emit as manure [3]. Hence, livestock producer industry maybe the biggest contribution for the environmental problem of pharmaceutical compound contaminant in the aquatic system.

There were a great number of pharmaceutical compounds had found in the aquatic system including antibiotics, analgesic, hormones and corticosteroid. According to Afonso-Olivares, et al. [4], antibiotics were the most compounds that contaminated in the seawater of Gran Canaria Island, Canada, due to the anthropogenic. The compounds are also reported to be found in the treated water even in low concentration of water sample due to the high resistance in biodegradation [5]. The impact of synthesized, used and disposed of antibiotics in modern society had given a rise issue towards the environment. Therefore, the compound had been declared as environmental contaminants due to the potential toxicological effect on living organism.

Oxytetracycline is the common types of antibiotic that may contribute to the adverse effect of aquatic life and they cannot be removed by biological method. According to Awartani [6], oxytetracycline is the major impact on health issues since the compound can lead us to allergic and hive.

Recently, several methods have been explored to degrade the pharmaceutical compounds namely, photocatalytic [7], chemical oxidation [7], electrochemical [8]. Among these methods, electrochemical degradation received a lot attention since it is a simple technology that required direct current and applied voltage to degrade the pharmaceutical compounds.

In this electrochemical degradation, three-dimensional electrode was used to characterize iron oxide composite as electrode. The capability of iron oxide electrode as electrode for degradation of pharmaceutical compounds was conducted with variable the supporting electrolyte and applied potential to evaluate the optimum operating condition.

Iron oxide was utilized as an adsorbent for removal for heavy metal such as copper and cadmium. It also has been discovered to perform well as detector to detect the presence of paracetamol [9]. However, there is limited number of works that explore the effectiveness of iron oxide composite as electrode for degradation of pharmaceutical compounds.

II. METHODOLOGY

A. Materials

The chemical formula of oxytetracycline hydrochloride (OTC) is $C_{22}H_{24}N_2O_9$.HCl and chemical structure is shown in Figure 1. The compound was supplied by Sigma-Aldrich (99%). The supporting electrolytes were 0.5M NaOH (alkaline), 0.5M NaCl (neutral) and 0.5M HCl (acidic). Iron oxide was mixed with carbon black (Alfa Aesar, 99%) to produce the electrode and defined as working electrode.

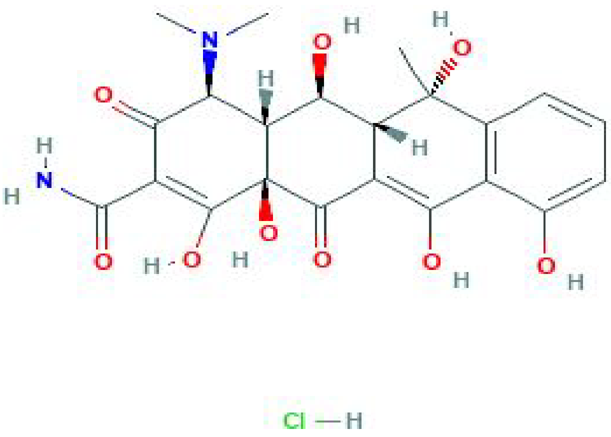

Figure 1: The chemical structure of OTC

B. Electrode preparation

The electrode preparation were adopted from Hawaiah Imam

Maarof [10]. Iron oxide was weighed by mass ratio of iron oxide (Fe_2O_3), carbon black (CB) and polytetrafluoroethylene (PTFE) with ratio of 4:1:1 and 1:0:1. The mass ratio of Fe_2O_3, CB and PTFE are varied to determine the optimum value of electrode preparation for degradation of OTC. Then, 1,3-propanediol was added as solvent to produce an electrode paste. The paste was kneaded and squeezed by using stainless steel. The paste was drying at 80 ˚C ˚C for 2 hours, 125 ˚C for 1 hour and 220 ˚C for 1 hour in the oven. The dried electrode is packed into 5 mm electrode tip and readied for electrochemical characterization to study effect of difference ratio in electrode preparation.

Another method for electrode preparation is introduced by mixing Fe_2O_3 with Nafion (5 wt%, Aldrich) as binder at mass ratio 1:4 in the microcentrifuge tube. The mixture is thoroughly mixed by using vortex mixer. Take about 15 micro liter and drop it on the screen-printed carbon electrode (SPCE) (Metrohm, DRP-C110). The prepared electrode will be dried at room temperature for 2 hours. The SPCE is constituted by a layer of iron oxide-binder ink, a counter electrode of carbon and a reference electrode of silver (Ag).

C. *Cyclic Voltammetry*

To study the effect of difference ratio in electrode preparation, a glass compartment of potentiostat was set up at room temperature. The electrodes consist of Ag/AgCl, platinum and prepared electrode were placed in the glass cell. Ag/AgCl is acted as reference electrode, platinum as counter electrode while iron oxide as working electrode. All the electrodes were rinsed with distilled water before running the experiment. The electrolyte is not being stirred during experiment to prevent formation of bubble at the surface of electrode tips.

For another method, A screen-printed carbon electrode (SPCE) was set up at room temperature. The electrode is a disposable device which consist of working electrode, reference electrode and counter electrode. The device is attached to computer to observed cyclic voltammogram. The electrode was rinsed with distilled water and dried before running the experiment. While, the supporting electrolyte was placed on top of the carbon surface by using micropipette. The drops of supporting electrolyte need to cover all surface area of working electrode, reference electrode and counter electrode.

D. *Electrochemical Characterization*

Voltammetric studies have been carried by using a manual three-dimensional electrode and SPCE. The effect of three difference factors that may be influenced the optimum operating electrochemical has been determined; (A) ratio of electrode preparation, (B) method of electrode preparation, (C) pH supporting electrolyte and (D) applied potential. These factors could give a significant effect on the operating condition of the electrochemical system where the capability and the performance of the electrode was observed by cyclic voltammetry.

To evaluate the degradation of OTC by iron oxide composite electrode, the electrochemical characterization by cyclic voltammetry was carried by using a potentiostat (Metrohm, Autolab PGSTAT204). The instrument was equipped with NOVA 1.11, used for data presentation and analysis.

E. *Effect of Supporting Electrolyte*

Three supporting electrolytes were used in the experiment namely, NaOH, NaCl and HCl at similar concentration 0.5M. Each of solution is represented as alkaline, neutral and acidic pH value, respectively. The effect of supporting electrolyte was studied without the presence of the oxytetracycline compounds.

F. *Effect of Applied Potential with The Best Supporting Electrolyte*

OTC was characterized by using the applied potential of -0.1 V to 0.1 V, -0.5 V to 0.5 V, -0.5 V to 1.0 V, -0.5 V to 1.5 V and -0.5 V to 2.0 V. The solution of supporting electrolyte with and without OTC was prepared with distilled water to achieve the desired concentration.

III. RESULTS AND DISCUSSION

A. *Effect of Carbon Black in the Electrode Composite*

The carbon black was added in the electrode to improve the conductivity of the electrode while polytetrafluoroethylene (PTFE) was used as binder. Effect of carbon black in the electrode was observed by removing the composition of carbon black in the electrode preparation. According to J. L. Boudenne [11], a sufficient amount of CB could mineralize chlorine ions but not for chlorophenol ions in water. Hence, the ratio in mixing the iron oxide, carbon black and PTFE was varied with 4:1:1 and 1:0:1. Figure 2 shows that the cyclic voltammogram when excluding carbon black in the electrode preparation while Figure 3 shows the presence of carbon black in the electrode preparation.

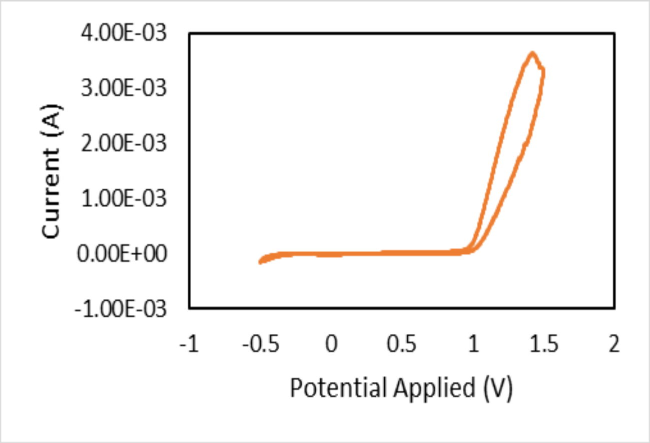

Figure 2: Cyclic voltammogram for iron oxide composite electrode in 0.5M NaCl solution at scan rate of 50 mV/s without CB in the electrode preparation.

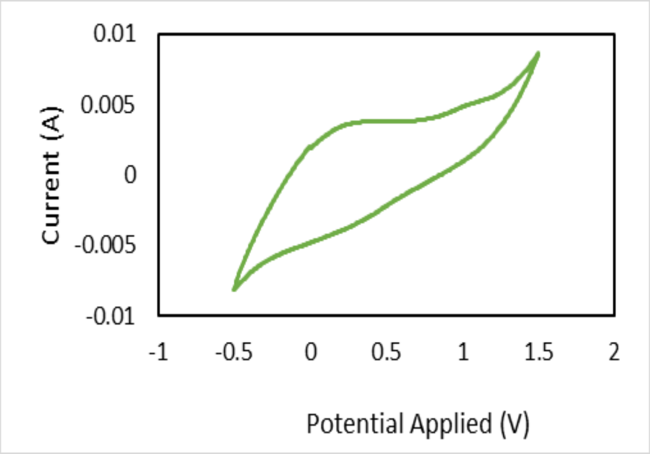

Figure 3: Cyclic voltammogram for iron oxide composite electrode in 0.5M NaCl solution at scan rate of 50 mV/s, with the presence of CB in the electrode preparation.

Based on cyclic voltammogram, the anodic peak is appeared between applied potential from 1.0 V to 1.5 V when using iron oxide composite electrode without CB in the iron composite electrode as shown in figure 2. The peak shows that oxidation process is occurred during the operation. Meanwhile, there is no significant peak appeared at the same applied potential, scan rate, concentration of supporting electrolyte with presence of CB in the iron oxide composite electrode as shown in figure 3. According to Jiazhi Hu [12], the stronger binder interface could give a better conductivity. Thus, CB cannot give sufficient adhesive strength to act as conductor in iron oxide composite.

B. *Effect of Different Electrode Preparation Method*

There are two methods are introduced for electrode preparation. Manual three-dimensional method consists of Ag/AgCl as reference electrode, platinum (Pt) as counter electrode and a prepared electrode as working electrode. The ratio in the working electrode is modified with mass ratio of 4:1:1 and 1:0:1 to observe the effect of ratio in electrode preparation. Meanwhile, SPCE is introduced as another method for electrode preparation to observe the effect of supporting electrolyte and applied potential. SPCE is a disposable device consists of counter electrode, reference electrode and working electrode. The electrode is prepared by dropping iron oxide-binder at SPCE.

In manual three-dimensional method, the working electrode can modify according the desired modification meanwhile the ratio of working electrode in SPCE is fixed. The effect of carbon black in the electrode cannot be observed by using SPCE. It also shows that SPCE had a simple techniques of electrode preparation compared to the manual three-dimensional method. The error in SPCE is easy to identify and control rather than the manual three-dimensional method. Thus, the most preferable technique for preparing electrode in electrochemical is using SPCE as it more compatible regardless the fixed ratio.

C. *Effect of Supporting Electrolyte*

Supporting electrolyte are generally used to improve their conductivity and thus the reduce the energy consumption [13]. Three different supporting electrolytes was employed to determine the effect of pH value in the electrochemical degradation. The right pH of supporting electrolyte can influence the chemical structure and reactivity of the process [14]. According to Sarah Belkacem [15], pH 4.3 at the natural pH value of Na_2SO_4 is the most effective degradation of oxytetracycline compounds in anodic oxidation methods. Introduction of tetracycline compounds can cause dehydration to yield anhydrotetracycline and will increase the formation of yellow color solution [16, 17].

Figure 4 shows the cyclic voltammetry applied potential of -0.5V to 1.5V while Figure 5 shows the cyclic voltammetry at applied potential of -0.5V to 2.0V. Both applied potentials are investigated in different pH value; acidic medium, neutral medium and alkaline medium.

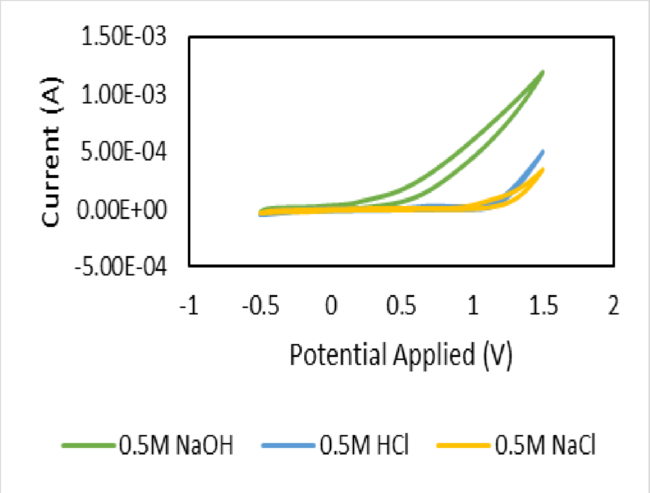

Figure 4: Cyclic voltammogram for iron oxide composite electrode in 10 mM in 0.5M HCl, 0.5M NaCl and 0.5M NaOH of supporting electrolyte at applied potential of -0.5V to 1.5V.

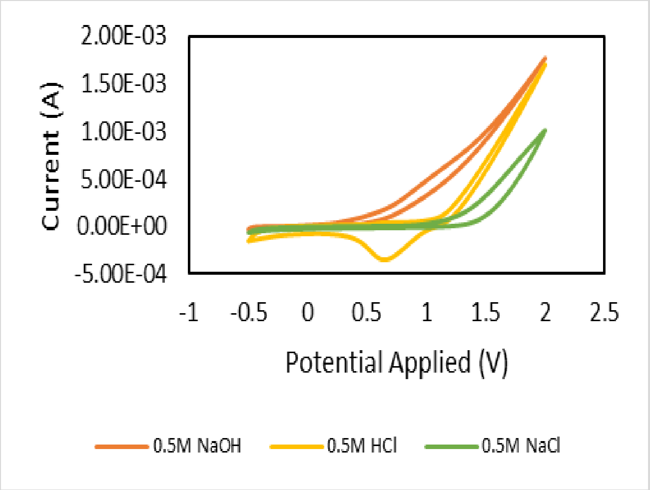

Figure 5: Cyclic voltammogram for iron oxide composite electrode in 10 mM OTC in 0.5M HCl, 0.5 M NaCl and 0.5 M NaOH of supporting electrolyte at scan rate 50 mV/s and applied potential from -0.5 V to 2.0 V.

Based on Figure 4 and Figure 5, there is no process of oxidation and reduction happen in neutral medium as it does not show any significant peaks. Meanwhile, there is a significant peak in acidic medium where it shows an anodic peak and a cathodic peak respectively in both figures. The acidic medium shows that the degradation of OTC can happen at this condition as both figures are showing an electron exchange at the same applied potential. It was also observed that only oxidation is appeared in alkaline medium from applied potential of 0.5 V to 1.5 V as shown in Figure 5. Thus, the optimum operating condition for supporting electrolyte is acidic medium as it shows the process of giving and receiving electron either in both figures.

D. *Effect of Applied Potential Range*

Cyclic voltammetry without the presence of OTC in 0.5–M supporting electrolyte were operated to determine the effect of applied potential in electrochemical. The applied potential were varied at -0.5V to 0.5V, -0.5V to 1.0V, -0.5V to 1.5V, -0.5V to 2.0V and -0.1V to 0.1V. Figure 6 shows the cyclic voltammogram at applied potential of -0.5 V to 1.0 V while Figure 7 shows the cyclic voltammogram at applied potential -0.5 V to 2.0 V to differentiate the operating condition.

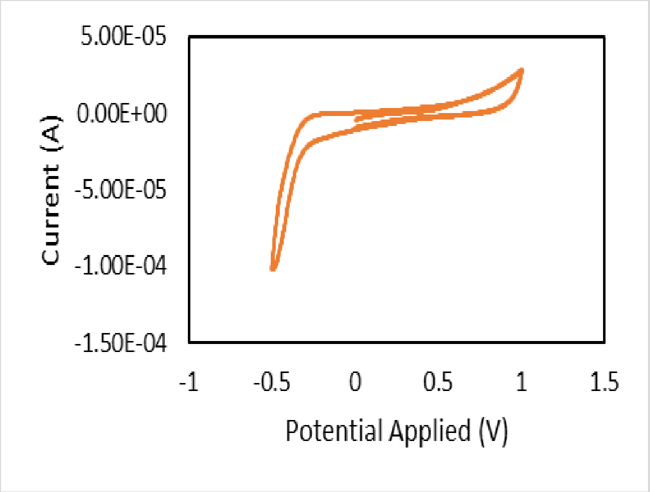

Figure 6: Cyclic voltammogram without the presence of OTC in 0.5 M NaCl of supporting electrolyte at scan rate 50 mV/s and applied potential -0.5 V to 1.0 V

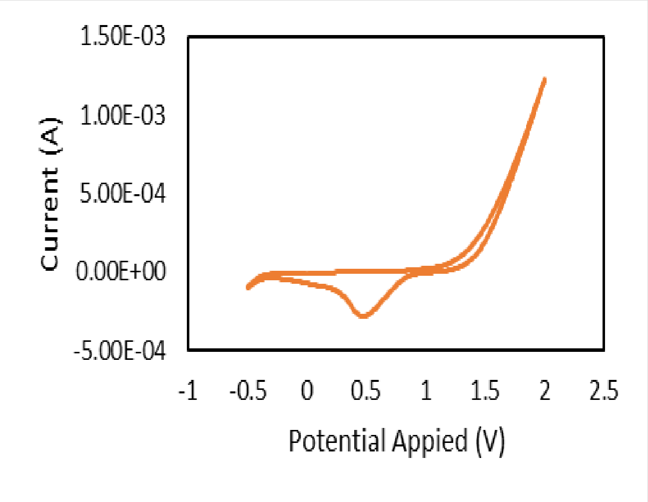

Figure 7: Cyclic voltammogram without the presence of OTC in 0.5 M NaCl of supporting electrolyte at scan rate 50 mV/s and applied potential -0.5 V to 2.0 V

It shows that the anodic or cathodic peak does not appear when applying applied potential range between -0.5 V to 1.0 V at scan rate 50 mV/s as shown in Figure 6. However, the cathodic peak is appeared between applied potential 0.0 V to 1.0 V when the potentiostat is set at applied potential range of -0.5 V to 2.0 V with the same scan rate as shown in Figure 7. The presence of bubble at the surface of screen-printed electrode during the experiment is showing that the reduction happens in higher applied potential. It shows that the ability for hydrogen interaction once the voltage is applied in the system could give gradual increase in surface area where larger surface area will give a better conduction for degradation happen [18]. According to Wenming Tian [19], the higher applied potential will lead to more open pits. Thus, the bubble is indicating the occurrence of corrosion where reduction happen at the surface of screen-printed. It shows that the higher applied potential is needed to perform the degradation.

IV. CONCLUSION

The formation of anodic or cathodic peak in both 0.5M NaOH and 0.5M HCl shows that the degradation of OTC was taking placed in alkaline and acidic conditions. However, acidic medium has better degradation than alkaline medium based on the cyclic voltammetry test since acidic medium is showing both peak of oxidation and reduction at 0.5 V to 1.0 V regardless variation of applied potential range. However, only a peak of oxidation is appeared in alkaline medium at 0.5 V to 1.5 V when applying potential range of -0.5 V to 2.0 V. Meanwhile, the electrode preparation without the presence of CB also showing an oxidation process was occurred at 1.0 V to 1.5 V when applying potential range of -0.5 V to 1.5 V. Since, CB is not showing any significant contribution of degradation, SPCE technique is the most preferable method for this test. Hence, the optimum operating condition for degradation of OTC was the best in 0.5 HCl solution without CB in the electrode composition.

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