

HYBRID WASTEWATER TREATMENT SYSTEM OF PHOTOCATALYTIC FUEL CELL AND ELECTRO-FENTON PROCESS

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ABSTRACT

A new sustainable and green system was developed for electricity generation and wastewater treatment. This hybrid system composed of a photocatalytic fuel cell (PFC) and electro-Fenton process. The electron generated from PFC is used to generate the hydrogen peroxide at the electro-Fenton reactor for dye degradation through accelerating in-situ generation of Fe^{2+} from sacrificial iron. The process involves the generation of hydroxyl radical which is a very powerful oxidizing agent ZnO/Zn photoanode was prepared by using anodizing method. The anodized ZnO films photoanode was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The removal efficiency of RB5 at PFC and electro-Fenton reactor was 6.90 % and 77.8 %. Results indicated that the dye removal efficiency at electro-Fenton reactor occurred faster than the PFC reactor. The maximum power density in this hybrid system was 13.98 mW/cm². This study demonstrated that the hybrid system of PFC and electro-Fenton process is an effective and environmentally friendly technology for wastewater treatment.

Keywords: Dye degradation; electricity generation; electro-Fenton process; photocatalytic fuel cell; wastewater treatment.

INTRODUCTION

In recent years, a single photocatalytic fuel cell (PFC) has been previously investigated method to degrade various organic pollutants along with generating electricity simultaneously [1–4]. Upon UV illumination, the photogenerated electrons are excited from the valence band to the conduction band of the photoanode, generating electron-hole pairs. The organic compound is degraded into CO₂ and H₂O by the positive holes as are powerful oxidants while the negative electrons act as are powerful reductants. The photogenerated electron that produced in the PFC system is passed through the conductive substrate to the cathode. In this process, the chemical energy is transformed to the electrical energy [2,5]. However, the single PFC systems had low performance which it is need a longer time to complete the degradation of the organic pollutant due to the low amount of hydroxyl radical is produced in this system. Besides, PFC system was also totally depends on the photoanode material and UV illumination to oxidize any organic pollutant and produce usable energy through the generation of electron hole-pairs in the system [3,6].

To improve the performance of the PFC system, a modified type of electro-Fenton process is presented here by using PFC to drive the production of H₂O₂ and Fe²⁺ in a second electrochemical reactor. Electro-Fenton process involves the reaction of hydrogen peroxide (H₂O₂) and Ferrous ion (Fe²⁺) to generate hydroxyl radical have attracted great attention for industrial wastewater treatment due to the production of hydroxyl radicals as a strong oxidation potential [7–9]. This process is effective in degrading many organic pollutants such as phenols, anilines, dyes, pesticides and heteroaromatic derivatives [8]. However, electro-Fenton process requires the use of electrical power [7]. Thus, the hybrid system of PFC and electro-Fenton process is developed to eliminate the electrical grid energy usage and chemical addition.

The hybrid system of PFC and electro-Fenton process is created as an effort to develop the technologies of H₂O₂ production which are cost-effective, efficient and sustainable for wastewater treatment. Furthermore, there is very limited report available about the hybrid system of PFC and electro-Fenton process on electricity generation and degradation of Reactive Black 5 (RB5) so far. Therefore, the aim of this study is to develop and evaluate the performance on electricity generation and dye degradation in the hybrid system of PFC and Fenton process.

METHODOLOGY

Preparation and Characterization of the Photoanode ZnO/Zn

The photoanode ZnO/Zn was prepared through an anodizing method by using a piece of Zn foil with thickness 0.5 mm, purity 99.9 % and dimensions 5.0 cm x 3.0 cm. The surface of the Zn foil was polished by using silicon carbide paper up to a mirror finish. Then, the Zn foil was cleaned by 0.5 M sodium hydroxide and ethanol followed by distilled water. The same dimension of stainless steel plate was used as a cathode. The anodizing process was conducted in 500 mL of 0.5 M phosphoric acid solution at 30 V using a laboratory DC power supply (GW Instek GPR-25H30D) for 2 h reaction time. The anodized ZnO/Zn was rinsed by deionized water and dried at room temperature. The anodized ZnO/Zn photoanode was characterized by using X-ray diffraction (XRD) from Shimadzu (Model: XRD-6000) and scanning electron microscopy (SEM) from JEOL (Model: JSM 6460 LA).

Reactors Configuration and Operation

The schematic diagram of hybrid system of PFC and Fenton system is shown in Figure 1. The reactors were constructed by using two beakers of 500 mL. Two pieces of carbon plates (thickness 3.0 mm) with dimensions 5.0 cm x 3.0 cm were used as cathode in the PFC and Fenton reactor, respectively. ZnO/Zn photoanode was connected to the Fenton cathode using a copper wire. A commercial iron plate (thickness 1.2 mm, purity 99 %) with dimension 5.0 cm x 3.0 cm was used as the anode at Fenton reactor and was connected to the PFC cathode using a copper wire. The distance between anode and cathode in each reactor was set at 7 cm.

The hybrid system of PFC and Fenton was operated with an external resistance of 1 kΩ at room temperature. RB5 was used as a synthetic wastewater in this study. RB5 was prepared at 10 mg/L of initial concentration in 500 mL beaker as a medium of the hybrid system. The pH of the RB5 solution at the Fenton reactor was adjusted to pH 3 using 0.5 M of H₂SO₄ and 0.5 M of NaOH for every experiment. An aeration stone and magnetic stirrer was used to bubble and stir the both reactor, respectively. The PFC reactor was irradiated using an ultraviolet A (UVA) lamp (Osram Dulux ®, 36 W/78. 2G11). Experiments were carried out under normal room temperature. Every experiment was repeated 2 times [10].

Evaluation of PFC-Fenton System

A digital multimeter (Model CD 800a from Sanwa Electric Instrument, Japan) was used to record the cell voltage across the 1 kΩ external resistors for every 1 hour. To conduct the polarization tests, a resistor box was connected between the PFC anodes and the Fenton cathodes as shown in Figure 1. The cell voltages of PFC and Fenton reactors were recorded and the resistances were varied from 1000 kΩ - 0.010 kΩ. The power density of this hybrid system (P, mW/cm²) was calculated using:

$$P = \frac{UI}{A} \quad (1)$$

where, U is the cell voltage of PFC (V), I is the current (A), and A is the cathode area of the Fenton reactors (15 cm²).

UV-Vis Analysis

The concentration of RB5 was determined by using a UV-Vis spectrophotometer (ME-UV1300 PC Mesulab, China) at $\lambda_{\max} = 607$ nm where the water sample was measured at an interval of 1 h over 8 hours reaction time.

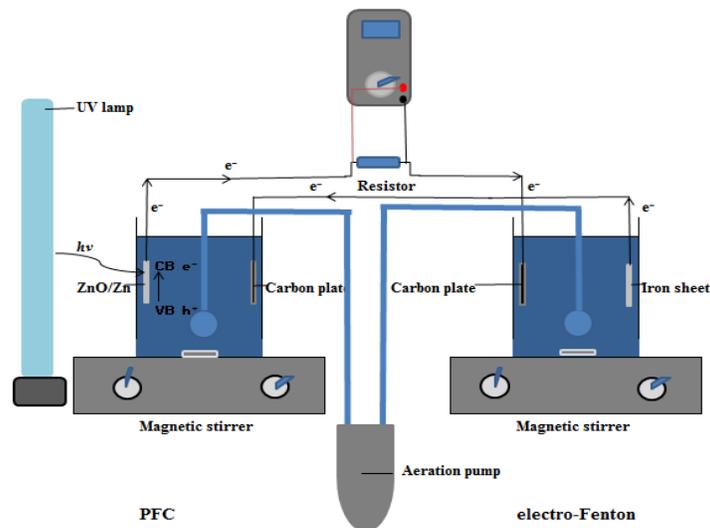


Figure 1. Schematic diagram of hybrid system of PFC and Fenton process

RESULT AND DISCUSSIONS

Characterization of the Photoanode ZnO/Zn

Figure 2 shows the morphology of anodized ZnO on Zn foil in 0.5 M phosphoric acid for 2 hours with magnification of x3000 and x10 000 respectively. From the results, it can be observed that the phosphoric acid as electrolyte in the anodizing of ZnO on zinc foil has become the acid etching condition when are pores were formed on the rough surface of zinc foil. The porous structure formation on the surface of Zn foil can be seen clearly by increasing the magnification of the SEM images.

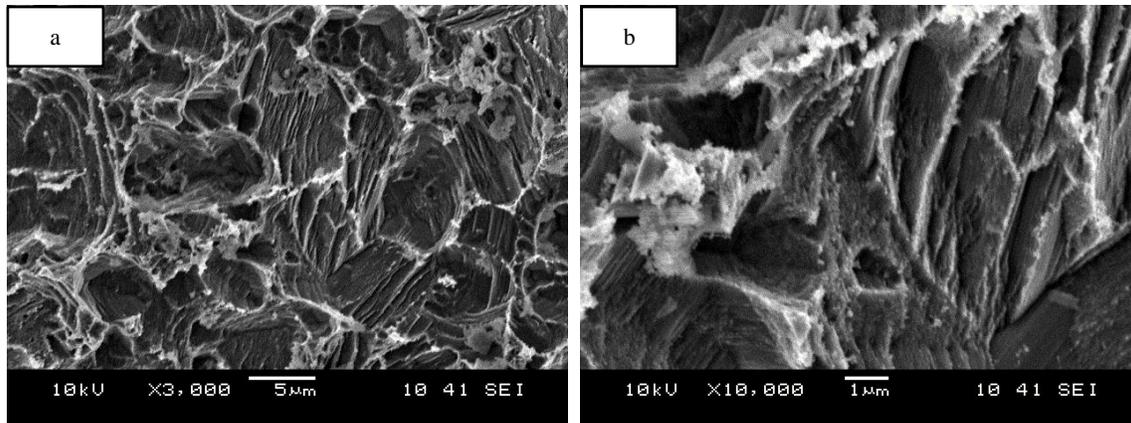


Figure 2. SEM images of (a) ZnO anodized on Zn foil photoanode under 0.5M phosphoric acid with x3 000 magnification, (b) ZnO anodized on Zn foil photoanode under 0.5M phosphoric acid with x10 000 magnification for 2 hours

To confirm the formation of ZnO on the Zn foil, the anodized samples were examined by XRD technique as seen in Figure 3. From the results, it can be observed that all the XRD patterns can be clearly indexed to a hexagonal structure of zinc (JCPDS card No. 04-0831) except the peak intensity of 2θ at 32.3° , 35.6° , 36.8° , 49.2° and 62.9° which it was indicated a fine preferential growth of the ZnO in the (100), (002), (101), (102) and (103) orientations, respectively (JCPDS card No. 36-1451). The peaks showed that the ZnO was synthesized with low crystallinity nature. The Zn peaks that were observed correspond accordingly to the Zn substrate [11,12].

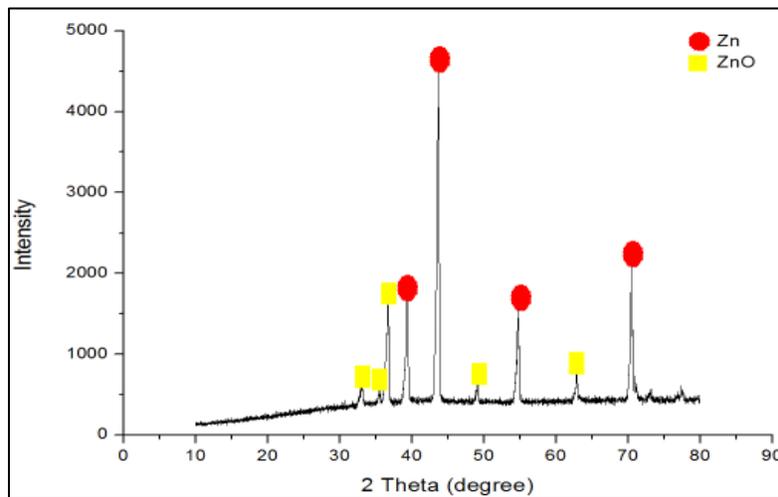


Figure 3. XRD pattern of anodized ZnO/Zn photoanode

Electricity Generation of Hybrid System PFC and Electro-Fenton Process

The voltages produced by this hybrid system of PFC and electro-Fenton process at an external resistance of $1\text{ k}\Omega$ are shown in Figure 4. The voltage output decreased rapidly from 641.0 mV to 434.0 mV and decreased continuously until 331.6 mV at the end of the processes. At the initial hour, the voltage output was dropped due to the degradation of dye which are actively occurs in the system and the gradual formation of intermediates which were more difficult to be degrade. Besides, the degradation of dye also would lead to voltage decline at the end of the reaction [10,13]. Maximum power density of 13.98 mW/cm^2 respectively at $2\text{ k}\Omega$ internal resistance was observed from the polarization test as shown in Figure 5.

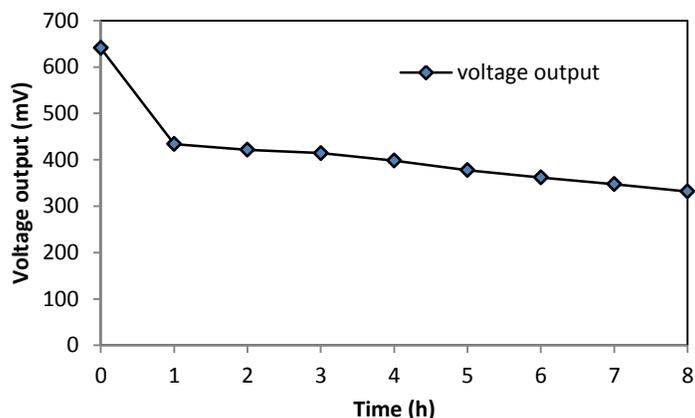


Figure 4. Voltage output of hybrid system of PFC and electro-Fenton process

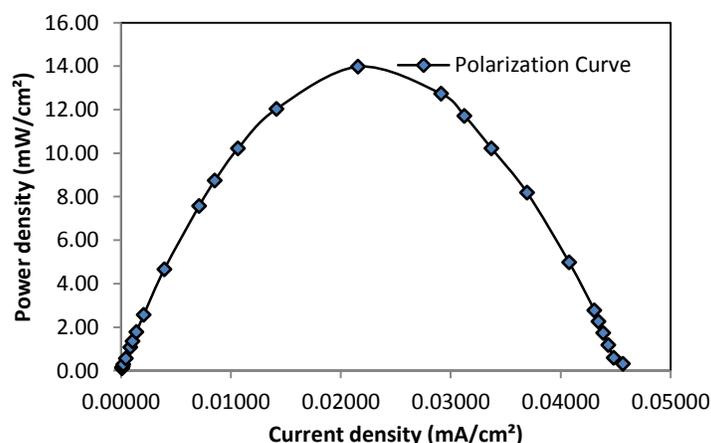


Figure 5. Power density curves of hybrid system of PFC and Fenton process

RB5 Degradation in Hybrid System of PFC and Electro-Fenton Process

The results of RB5 degradation at PFC reactor and electro-Fenton reactor are shown in Figure 6. At PFC reactor, RB5 was gradually degraded approximately 6.90 % within 8 h. The removal efficiency of RB5 at electro-Fenton reactor was 77.8 % which was appreciably higher than that of PFC reactor. The results imply that Fenton process was occurred faster than PFC due to the different reaction involved in the both system [10]. Besides, this could lead to the different amount of hydroxyl radical formation at PFC and electro-Fenton reactor.

At the PFC reactor, the Zn/ZnO photoanode yields electrons and holes pairs in the present of UV irradiation (equation 2). These photogenerated electrons are transferred to the cathode of the electro-Fenton reactor via copper wires. The oxygen in the electro-Fenton reactor will undergo reduction process to produce H₂O₂ (equation 4). The holes oxidize the RB5 to further degrade and produced the oxidized product (equation 3). At the anode of the electro-Fenton reactors, Fe²⁺ and electrons are generated through the iron oxidation process (equation 5). These electrons are moved to the cathode of the PFC where oxygen is reduced to water (Equation 6). Overall, peroxi-coagulation (PC) process was involved in the electro-Fenton reactor where H₂O₂ generated at the cathode was reacted with Fe²⁺ generated from sacrificial iron anode to produce hydroxyl radicals (equation 7). These hydroxyl radicals play an important role to oxidize organic pollutant [7,8,14]. This process reasonably caused the RB5 removal efficiency at Fenton reactor occurs faster than the PFC reactor.

At PFC anode



At Fenton cathode



At Fenton anode



At PFC cathode



Overall Fenton process



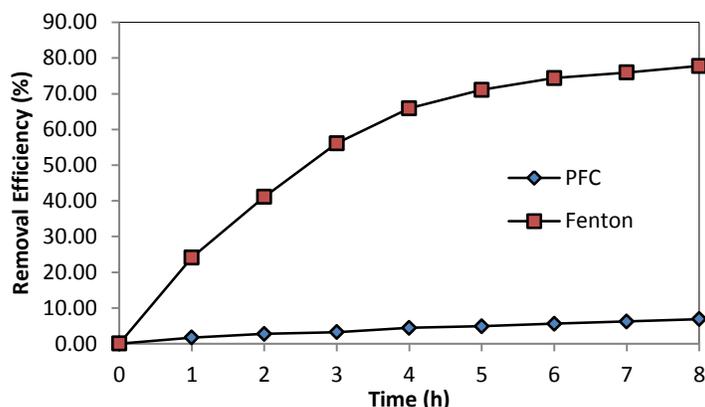


Figure 6. RB5 removal efficiency of PFC and electro-Fenton reactor

CONCLUSION

In conclusion, a hybrid system of PFC and electro-Fenton process was developed for electricity generation and wastewater treatment. Results revealed that the removal efficiency at Fenton reactor was higher than at PFC reactor. The removal efficiency of RB5 at PFC and electro-Fenton reactor was 6.90 % and 77.8 %. The maximum power density of hybrid system PFC and electro-Fenton process was 13.98 mW/cm² respectively at 2 kΩ internal resistance. In this hybrid system, PFC plays an important role to generate the H₂O₂ at electro-Fenton reactor and produced hydroxyl radical when react with Fe²⁺ ions. Besides, PFC reactor could be considered as the power source for the Fenton reactor in this hybrid system. It could be considered that the proposed hybrid system is a promising and sustainable method for wastewater treatment and electricity generation.

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