A hybrid photocatalytic fuel cell integrated electro-Fenton system for Amaranth dye degradation and electricity generation

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Abstract. A dual-chambered hybrid system of photocatalytic fuel cell (PFC) and electro-Fenton (EF) process has become an emerging sustainable green approach for organic pollutant degradation and electricity generation. This hybrid system of PFC and EF (PFC-EF hybrid system) is an integration of two popular organic pollutants treatment methods, PFC and EF process. The double-cathodes configuration of PFC-EF hybrid system enhanced the oxygen reduction reaction reactivity in both PFC and EF. PFC-EF hybrid system with double cathodes achieved colour removal efficiencies of 86.2% and 84.7% in PFC and EF. Power density of 1.2211 μW cm⁻² was obtained in this PFC-EF hybrid system. Results revealed that this PFC-EF hybrid system was effective in the Amaranth dye degradation and power production simultaneously.

1. Introduction
Azo dye is used extensively in the industrial production, such as textile, food, paper to increase the aesthetic of products [1]. Azo dyes are the most common used commercial synthetic dye with a wide variety of colour and structure [2]. The dyeing water is discharged directly as effluent into the environment or indirectly due to the loss of dyes occurred during the dyeing process [3]. The release of dyeing water into the water bodies has caused the water pollution. The breakdown products of dyeing water such as aromatic amines are carcinogenic, toxic and mutagenic to living organisms. Besides, the consumption of dyeing water through the food chain of aquatic organisms has caused the physiological disorder in the aquatic organisms. Hence, seeking efficient method for dye degradation has become the main concern.

Recently, advanced oxidation processes (AOPs) become popular methods for degradation of azo dye [4]. AOP enables to degrade and mineralize the organic pollutants into recovered water and carbon dioxide. The high efficiency of AOP in oxidizing a wide of organic pollutants is attributed to the in-situ
generation of strong oxidizing species, mainly hydroxyl radicals (●OH) [5]. AOPs such as heterogeneous photocatalysis and Fenton process have been used for degradation of azo dye.

Photocatalytic fuel cell (PFC) is an integration of heterogeneous photocatalysis and fuel cell technology. PFC has drawn enormous attentions as it can degrade the organic pollutants and generate electricity simultaneously. PFC has been used widely in dye degradation and electricity generation simultaneously [6]. However, the recombination rate of electron-hole in PFC is high and deteriorates the dye degradation efficiency [7].

Electro-Fenton process is the combination of the classical Fenton’s chemistry and the electrochemistry [8]. In EF, the reaction between Fe^{2+} and H_{2}O_{2} yields ●OH radicals in the solution for degradation of organic pollutants [9]. EF process offers numerous advantages, include electro-generation and regeneration of Fe^{2+} ions [10], reduction of the cost by in-situ generation of H_{2}O_{2} and the risk in shipping and storage of H_{2}O_{2} [9]. However, the expenses related to the electrical supply in the EF operation is the main drawback of EF process [11].

Nordin et al. 2016 had developed a dual-chambered hybrid system of PFC and EF based on the working principles of PFC and EF to reduce the limitations and simultaneously improve the efficiencies of both PFC and EF [12]. PFC works as a power supply for the operation of EF, and thus the high recombination of electron-hole in PFC can be reduced and the power supply required in EF can be eliminated. Meanwhile, the electrons produced in EF are transferred from EF to PFC to promote the movement of electrons in this hybrid system. The aim of this study is to evaluate the performance of the dual-chambered PFC-EF hybrid system in double-cathodes configuration in term of colour removal efficiency of Amaranth dye and electricity generation.

2. Materials and methods

2.1. Fabrication of immobilized ZnO/C photoanode
The immobilized ZnO/C photoanode was fabricated by using immobilization method [13]. First, the cleaning of a commercial carbon plate (7.5 × 3.0 cm) in deionized water followed by ethanol was carried out by using ultrasonic bath. ZnO suspension was prepared by dispersing 2.0 g of commercial ZnO powder into 30.0 mL of deionized water. The cleaned carbon plate was dipped into the prepared ZnO suspension and ultrasonicated for 30 min. Then, the immobilized ZnO/C photoanode was dried in an oven at 60 °C for 24 h, followed by heat treatment process in a furnace at 300°C for 2 h. Finally, the immobilized ZnO/C photoanode was rinsed with deionized water to eliminate any loosely adhered residual photocatalyst powder.

2.2. Setup and operation of PFC-EF hybrid system
The PFC-EF hybrid system was set up as shown in figure 1. All electrodes (carbon plates and iron plate) were prepared in the same dimension with immobilized ZnO/C photoanode (7.5 × 3.0 cm). The anode was put in between of two cathodes in both PFC and EF reactors with electrode distance of 2 cm, respectively. The immobilized ZnO/C photoanode in PFC was connected to the two carbon plates as the cathodes in EF through an external load of 1 kΩ, meanwhile the iron plate as anode in EF was connected to the two carbon plates as the cathodes in PFC. Concealed copper wires were used for the connection of the electrodes in this setup. The immobilized ZnO/C photoanode was illuminated to the light by an ultraviolet A (UVA) lamp (36 W/78, 2G11, Osram Dulux) at distance of 7.0 cm from the surface of photoanode. 500 mL of 10 mg L^{-1} of Amaranth dye solution in both reactors was stirred by magnetic stirrer and supplied with air bubbles at a flow rate of 1 L min^{-1} by aeration pumps and aeration stones over the reaction time.

The experiment was conducted at ambient temperature over 8 h reaction time. A pH meter (PHS-3DW) was used to measure the pH of Amaranth dye solution. The pH solution for PFC was remained at natural pH (pH 5.7) while 0.5 M of sulfuric acid solution was used to adjust the pH solution for EF to pH 3. The experiments were carried out in duplicate for accuracy.
2.3. Measurement and analysis
The concentration of the collected Amaranth dye solution samples was measured by an ultraviolet-visible (UV-Vis) spectrophotometer (Me-UV1300, Mesu Lab Instruments) at \( \lambda_{\text{max}} = 530 \text{ nm} \). The colour removal efficiency of Amaranth was calculated by using formula (1):

\[
\text{Colour removal efficiency (\%)} = \frac{C_t - C_0}{C_0} \times 100\%
\]  

where \( C_0 \) is initial dye concentration and \( C_t \) is the dye concentration at certain reaction time, \( t(\text{h}) \). The voltage output across 1 k\( \Omega \) of external load was measured by a digital multimeter from Sanwa Electric Instrument (CD 800a). The resistance variation from 1000 k\( \Omega \) to 10 \( \Omega \) during the polarization study was performed by a resistor box. The power density (\( P, \mu\text{W cm}^{-2} \)) of the hybrid system was determined by using formula (2):

\[
P = \frac{VI}{A}
\]

where \( V \) is the voltage output of PFC (mV), \( I \) is the current (mA) and \( A \) is the area of the double cathodes in EF (30 cm\(^2\)).

3. Results and discussion
Figure 2 shows the colour removal efficiency of 10 mg L\(^{-1}\) Amaranth dye in PFC and EF. PFC and EF respectively achieved colour removal efficiency of 86.2\% and 84.7\%. Results revealed that the PFC-EF hybrid system was an effective system for degradation of Amaranth dye.
In PFC, the photoexcitation of ZnO photocatalyst occurred when the immobilized ZnO/C photoanode was illuminated by UV light. The electrons were photo-excited from the valence band to the conduction band and transferred externally to the double cathodes in EF for oxygen reduction reaction (ORR). The external transfer of photo-excited electrons from photoanode in PFC to the cathodes in EF could promote the separation of electron-hole and restrict the recombination problem. The accumulated photo-generated holes reacted with H$_2$O to generate ⋅OH radicals for degradation of dye [14]. Besides, the photo-generated holes could directly oxidize the dye and mineralize the intermediate products [14]. The reactive species, such as ⋅OH radicals and photo-generated holes degraded the dye efficiently [15], and thus contributed to the effective decolourization of Amaranth dye in PFC.

Ferrous ion (Fe$^{2+}$) and hydrogen peroxide (H$_2$O$_2$) are Fenton’s reagents required for in-situ generation of ⋅OH radicals [16]. The oxidation of iron plate in EF could supply Fe$^{2+}$ ions continuously in EF process [17], meanwhile the electrons produced were transferred externally to the double cathodes in PFC for ORR reactivity. Besides, the Fe$^{2+}$ can be regenerated at the double cathodes through the reduction of Fe$^{3+}$ [17]. This could ensure the enough supply of Fe$^{2+}$ ions in EF process. The continuous transferred photo-excited electrons from PFC to the double cathodes in EF were consumed for ORR. Thus, H$_2$O$_2$ was continuously electro-generated at the double cathodes through the two-electrons ORR pathway [18]. Fe$^{2+}$ ions catalysed H$_2$O$_2$ to generate ⋅OH radicals continuously in degradation and mineralization of Amaranth dye.

PFC showed higher colour removal efficiency of Amaranth dye compared to EF. Although ⋅OH radicals were the main oxidizing agents in degradation of Amaranth dye in both PFC and EF processes, but the photo-generated holes were also reactive species in degradation and mineralization of Amaranth dye in PFC [19]. Thus, ⋅OH radicals and photo-generated holes could work together in the dye degradation and contributed to higher colour removal efficiency in PFC.

The voltage output and polarization and power density curve of the hybrid system are displayed in figure 3 and figure 4, respectively. Based on figure 3, the voltage output at initial reaction time was 113.4 mV, increased to 156.1 mV at the 5th reaction hour and slowed down thenceforth. At the final reaction hour, voltage output of 157.2 mV was achieved in the hybrid system. The increasing trend for the voltage output was attributed to the high consumption of electrons for ORR reactivity at the double cathodes in EF. The in-situ generation of H$_2$O$_2$ through two-electron reduction of dissolved oxygen under aerated and acidic required large number of electrons and this promoted continuous transfer of the photo-excited electrons from the photoanode in PFC to the double cathodes in EF. The higher number of transferred electrons contributed the higher voltage output at the final reaction hour.
The open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$) and maximum power density ($P_{max}$) of this hybrid system were 869 mV, 0.0061 mA cm$^{-2}$ and 1.2211 μW cm$^{-2}$, respectively. In this hybrid system, the corrosion of iron plate contributed to a large number of electrons [20] and these electrons were drawn to the double cathodes in PFC for ORR reactivity. The permeation flow of electrons from the cathode to the anode in PFC could lead to the elevated number of migrated electrons through external circuit and high-power production. Results revealed that the inter-connection between the electrodes in the hybrid system could promote the electrons flow and movement in this hybrid system, and thus contributed to considerably high electricity generation in this hybrid system.

4. Conclusion
In conclusion, the dual-chambered hybrid system of PFC and EF in double-cathode configuration was effective in the colour removal of Amaranth dye and electricity generation simultaneously. The reactive species, •OH radicals generated in the hybrid system contributed to excellent degradation of Amaranth in both PFC and EF. Colour removal efficiencies of 86.2% and 84.7% were achieved in PFC and EF, respectively. Considerably high voltage output of 157.2 mV was produced in the hybrid system simultaneously. The hybrid system could achieve $V_{oc}$, $J_{sc}$, $P_{max}$ of 869 mV, 0.0061 mA cm$^{-2}$ and 1.2211 μW cm$^{-2}$. 

![Figure 3](image1.png)

**Figure 3:** Voltage output profile of PFC-EF hybrid system over 8 h reaction time.

![Figure 4](image2.png)

**Figure 4:** Polarization and power density curve of PFC-EF hybrid system.
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