Enhanced Electricity Generation and H$_2$O$_2$ Production in a Photocatalytic Fuel Cell and Fenton Hybrid System Assisted with Reverse Electrodialysis

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ABSTRACT: A novel integrating system coupled with photocatalytic fuel cell and Fenton system assisted by reverse electrodialysis (PREC) is proposed. The results demonstrate that H$_2$O$_2$ concentration increased continuously in the reaction process to finally reach 960 mg/L and the current became stable at around 5.2 mA. The salinity-driven potential derived from the high concentration and low concentration cells in the hybrid system was 0.72 and 0.90 V respectively, at the salinity ratio of 50 and 100. The hybrid system has an energy recovery of 16%, a cathodic efficiency of 51%, and the maximum power of 76 W/m$^2$ at a salinity ratio of 50, with a 100 Ω external resistance. It is proved that PREC-Fenton possessed great potential in industrial wastewater treatment.

1. INTRODUCTION

Electro-Fenton as one of advanced oxidation processes has been attracting extensive interests with significant advantages such as easy operation and environmental compatibility. It is regarded to be a promising technology for treating refractory-containing industrial wastewater, which is attributed to the production of powerful oxidizing species. However, external electricity supply severely impedes its large-scale applications.$^{1}$ To overcome the above shortcomings, increasing attention is paid to bioelectro-Fenton system in which the microbial fuel cell (MFC) is combined with electro-Fenton. In this system, bacteria in the anode chamber could oxidize the substrates to generate electrons, which are transported through an external resistor to the cathode chamber, thereby forming H$_2$O$_2$ via the reduction of dissolved oxygen.$^{2,3}$ Nevertheless, MFC still faces many challenges including complex operation, low potential, long start-up time, and stringent working conditions. Moreover, the potential generated by MFC is very low.$^{4−6}$ Comparably, photocatalytic fuel cell (PFC), which can decompose organics pollutants by radical reactions and simultaneously generate electricity by the self-bias between photoanode and cathode, may be an useful alternative. In this system, electricity is generated by the flow of photogenerated electrons from photoanode to cathode.$^{7,8}$ Compared to MFC in which much attention should be paid to maintaining and monitoring the microbial activity, PFC system could be much more easy to develop and operate.$^9$

Additionally, another interesting water treatment technology is reverse electrodialysis (RED), which is built as alternately stacked cation membranes and anion-exchange membranes.$^{10}$ It is reported that RED is a valid process to generate electricity directly based on the salinity gradient between water and seawater river.$^{11}$ Consequently, integration of PFC and RED would be an ideal technology to obtain higher electrical energy and contaminant-degrading ability. However, up to date, no reports of combination of PFC and RED have been published.

In this study, an integrating system coupled with photocatalytic fuel cell and Fenton system assisted by reverse electrodialysis (PREC) is proposed. The H$_2$O$_2$ production, salinity-driven energy, energy recovery, and energy efficiency were investigated. The integrated system possessed great potential in industrial wastewater treatment.

2. RESULTS AND DISCUSSION

2.1. Enhanced H$_2$O$_2$ Production in PREC. The formation of H$_2$O$_2$ plays an important role in Fenton reactions, since it controls the evolution of *OH. The H$_2$O$_2$ concentration change in different systems is shown in Figure 1. Clearly, the H$_2$O$_2$ concentration increased with reaction time, reaching approximately 960 mg/L at 24 h (Figure 1a) without further increase under an extended operation time, indicating that the accumulated H$_2$O$_2$ reached a steady state, where its production rate was the same as the decomposition rate. The similar phenomenon has been founded in PFC systems. The possible reason is the generation of H$_2$O$_2$ in the process of electrical reaction, the decrease of H$_2$O$_2$ on cathode, and the self-decomposition of H$_2$O$_2$, which may occur at the same time. Comparatively, the H$_2$O$_2$ yield in the control reactors was very
low during the same operation time (Figure 1a). The respective H$_2$O$_2$ concentration were 110, 4.8, and 10.9 mg/L in the absence of salinity gradient in the RED (Control 1), applied current (Control 2), and ultraviolet irradiation on the anode (Control 3).

Along with H$_2$O$_2$ production, the current was investigated. As displayed in Figure 1b, no current could be detected in Control 2 and Control 3. Although current in Control 1 reached 2.8 mA, it was much lower than 5.2 mA in normal condition. These results demonstrated the RED stack and ultraviolet irradiation have significant influence on the increase in current and H$_2$O$_2$ generation in PREC.12 In PREC, the H$_2$O$_2$ generation could be driven and enhanced with the help of an external power derived from salinity gradient energy. Moreover, H$_2$O$_2$ generated in the cathode could be further reduced to *OH for destroyed pollutants in the wastewater, which is important for further applications.

2.2. Salinity-Driven Energy and Electrochemical Analysis. The performance of RED stack has very significant influence on the production of H$_2$O$_2$ in PREC. Under the driving effect of concentration gradient, cations and anions in high concentration solution would penetrate through the membranes and migrate into low-concentration solution, resulting in potential difference. In this study, 5 cell membrane pairs were used to investigate the effect of the salinity gradient. Results show that the salinity-driven potential ($\Delta \phi_{jct}$) created in RED was contrary to the salt concentration of the LC solution. Under the salinity ratios (SR) of 50 and 100, $\Delta \phi_{jct}$ was 0.72 and 0.90 V, respectively. This is consistent with the cell potentials achieved in PREC. When the current densities were lower that 0.5 mA/cm$^2$, the system achieved a smaller maximum cell potential with SR = 50 compared with SR = 100 (Figure 2a). However, the power density at SR = 50 was 76 W/m$^2$, which is much higher than that of 41 W/m$^2$ for SR = 100 (Figure 2b). The reasons for poor performance under larger SR are higher internal resistance and minimal increase in current. There are two key factors associated with internal resistance in RED: solution conductivity in LC compartment and mass transfer limitations at the membrane interface, which significantly increased at bigger SR.13

Additionally, it could be calculated that at the SR = 50, the energy recovery of PREC was 16%. These results mean that 91.8% of the recovered energy in PREC was derived from the salinity difference. Moreover, a much higher cathodic efficiency ($R_{cat}$) of 51% in PREC was calculated compared with previous reported cathodic efficiency of 42%.14 Although H$_2$O$_2$ accumulation is still very low, but the small energy

Figure 1. H$_2$O$_2$ production (a) and current (b) in PREC-Fenton under normal and different control conditions (Control 1: both high concentration (HC) and low concentration (LC) solution are 500 mM NaCl solution; Control 2: open circuit; Control 3: no ultraviolet irradiation on photoanode).

Figure 2. Polarization (a) and power densities (b) at different SR in PREC-Fenton.
consumption of 0.85 kWh/kg H₂O₂ still makes the technology very promising.

2.3. Practical Significance and Perspectives. Results in this study demonstrated the PREC-Fenton shows great prospects in the fields of electricity production and wastewater treatment, as well as simultaneous H₂O₂ production. The integrated process has excellent advantages in following aspects: first, compared with single PFC system, the performance was greatly improved with the help of RED. Second, a stable and persistent electric potential difference could be obtained between the two electrodes due the sustainable photocatalytic reaction in the system. Third, the PREC-obtained between the two electrodes due the sustainable stable and persistent electric potential difference could be obtained between the two electrodes due the sustainable photocatalytic reaction in the system. The PREC process is energy efficient with a lower energy consumption of 0.85 kWh/kg H₂O₂, indicating its potential for further application in wastewater treatment.

3. CONCLUSIONS

Electrical power could be derived from salinity gradient in a RED system. In this study, a novel integration of PFC and Fenton process assisted with RED was designed for enhanced H₂O₂ production. Results demonstrated that H₂O₂ production increased by adding a 5-pair cells RED stack. The PREC-Fenton with an SR of 50 achieved a maximum power density of 76 W/m², an energy recovery of 16%, and a cathodic Fenton with an SR of 50 achieved a maximum power density of 47 W/m², indicating its potential for further application in industrial wastewater treatment.

4. MATERIALS AND METHODS

4.1. Reactor Setup and Operation. The schematic diagram of PREC-Fenton reactor is depicted in Figure 3. A novel dual-chamber PREC-Fenton system consisted of an anode and a cathode chamber, and a working volume of 50 mL (5 cm × 5 cm × 2 cm) each, all connected by a RED stack with five cell pairs. Every cell pair of RED stack has an anion-exchange membrane, a cation-exchange membrane, a high concentration (HC) cell, and a low concentration (LC) cell. Membrane spacing was 1.5 mm and was divided by silicon gasket. The HC solution flows from the HC cell beside the cathode to the HC cell beside the anode, whereas the LC solution flows in the opposite direction. A 5 mol/L NaCl was selected as the HC solution and deionized water containing NaCl for three different salinity ratios (SR) of 100 (0.05 M), 50 (0.1 M), and 1 (5 M) was the LC solution. They were continuously injected into the RED stack through a peristaltic pump. Prior to each experiment, the cathode chamber was washed with NaCl solution. Unless otherwise stated, the initial pH in the anode and cathode chambers was 7.0 and 5.0, respectively. Fresh air was bubbled into the catholyte continuously at 16 mL/min. An ultraviolet lamp was used as light source of the PFC. The prepared ZnO/Zn and FeVO₄/CF was used as a photoanode and a cathode, respectively. All these experiments were carried out in duplicate for accuracy.

4.2. Electrochemical Analysis and Calculations. The solution pH was determined by a pH meter (PH 210). The H₂O₂ concentration was determined with potassium titanium-(IV) oxide using UV–vis spectrophotometry (Spectronic 20D). A digital multimeter (PISO-813) was used to measure the voltages with a 100 Ω external resistors at an interval of 30 min. Current density was calculated normalized to the cathode area. The potentials were determined with the reference of saturated calomel electrode (+0.242 V vs SHE) under the resistances varied from 20 000 to 5 Ω. The junction potential (Δφu) across an ion-exchange membrane with different salinity could be calculated as follows:

\[ |Δφ_u| = \frac{RT}{2F} \ln \left( \frac{\text{HC}}{\text{LC}} \right) \]

In the equation, R, T, and F are the gas constant, the absolute temperature, and the Faraday constant, respectively. z, a, and t are the ionic charge, the activity, and the transport number, respectively. The superscripts “HC” and “LC” are the HC solution and the LC solution, whereas the subscripts “counter” and “co” indicate the countercations and co-ions, respectively.

The energy recovery (Rₑ) is a normalized value between the produced power and the provided power in PREC:

\[ R_e = \frac{P}{\Delta H_e n_e^a / t_b + X_c^b} \]

In the equation, P, ΔHₑ, and nₑ are the power produced (W), the substrate combustion heat (J/mol), and the supplied substrate (mol), respectively. However, tₑ and X_c are the time span and the theoretical energy (W), respectively. Cathodic H₂O₂ efficiency (RₑCO) was determined by the ratio of real cumulative H₂O₂ production and the theoretical amount, which could be calculated as follows:

\[ R_{\text{cat}} = \frac{2Fn}{\int_{t_0}^{t_b} \text{d}t} \]

In the equation, n is the mole of H₂O₂ generated during the time interval of t₋t₀.

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Notes
The authors declare no competing financial interest.

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