Using single-chamber microbial fuel cells as renewable power sources of electro-Fenton reactors for organic pollutant treatment

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HIGHLIGHTS

► A new type of electro-Fenton system was developed for wastewater treatment.
► Degradation efficiency of organic pollutants was substantially improved.
► Operation cost was greatly reduced compared to other microbial fuel cell designs.

ARTICLE INFO

Article history:
Received 9 January 2013
Received in revised form 23 February 2013
Accepted 25 February 2013
Available online 5 March 2013

Keywords:
Fenton
Pollutant
Microbial fuel cell
Bioelectrochemical

ABSTRACT

Electro-Fenton reactions can be very effective for organic pollutant degradation, but they typically require non-sustainable electrical power to produce hydrogen peroxide. Two-chamber microbial fuel cells (MFCs) have been proposed for pollutant treatment using Fenton-based reactions, but these types of MFCs have low power densities and require expensive membranes. Here, more efficient dual reactor systems were developed using a single-chamber MFC as a low-voltage power source to simultaneously accomplish \( \text{H}_2\text{O}_2 \) generation and \( \text{Fe}^{2+} \) release for the Fenton reaction. In tests using phenol, 75 ± 2% of the total organic carbon (TOC) was removed in the electro-Fenton reactor in one cycle (22 h), and phenol was completely degraded to simple and readily biodegradable organic acids. Compared to previously developed systems based on two-chamber MFCs, the degradation efficiency of organic pollutants was substantially improved. These results demonstrate that this system is an energy-efficient and cost-effective approach for industrial wastewater treatment of certain pollutants.

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1. Introduction

Fenton reactions, based on the reaction of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) with ferrous ion (\( \text{Fe}^{2+} \)) to generate hydroxyl radicals, have attracted great attention for industrial wastewater treatment due to the strong oxidation potential of hydroxyl radicals. Previous studies [1–4] have demonstrated that Fenton reactions are effective in degrading many organic pollutants, including phenols, anilines, dyes, pesticides, and heteroaromatic derivatives. However, conventional chemical Fenton processes require chemical storage and transport of unstable \( \text{H}_2\text{O}_2 \) and \( \text{Fe}^{2+} \), which have higher reaction efficiencies and therefore are of great interest [7–10]. However, the process requires the use of electrical power, and thus the process could be more useful and sustainable by developing Fenton-based systems that do not require either chemical addition or electrical grid energy.

Microbial fuel cells (MFCs) are bioelectrochemical systems that use bacteria to oxidize organic wastes and generate electricity [11–13]. Microorganisms on the anode oxidize organic substrates and simultaneously generate electrons and protons. The electrons are transferred to the cathode through external circuit, and protons are released into solution. At the cathode, oxygen react with electrons and protons to form water. In the past decade, MFCs have been extensively investigated due to the advantage of recovering green energy (electricity) from wastewaters and waste biomass sources. The power output of MFCs has increased from only a few milliwatts per square meter of electrode to 4.3 W/m\(^2\) [14–16]. These higher power densities could therefore make it practical to use MFCs as power sources for electro-Fenton systems.

Two-chamber MFCs have been previously investigated as a method to degrade pollutants using electro-Fenton reactions, but these systems have had very poor performance due to the intrinsic setup of the system [17–19]. In two-chamber MFCs, the electrons generated by bacteria on the anode are used to reduce oxygen to \( \text{H}_2\text{O}_2 \) on the cathode, but a membrane must be used to prevent oxygen and \( \text{H}_2\text{O}_2 \) from reaching the anode. At the cathode, the \( \text{H}_2\text{O}_2 \) reacts with \( \text{Fe}^{2+} \) (added or released from certain types of cathodes).
to form hydroxyl radicals that can then be used to degrade pollutants such as p-nitrophenol and various dyes (Rhodamine B and Orange II). Two-chamber MFCs have lower power output (relative to single-chamber, air-cathode designs), due to the high internal resistance produced by the membrane, and the low pH produced in the anode chamber (which reduces current production by bacteria) due to the inefficient transport of protons across the membrane. Also, H₂O₂ will damage the membrane, ferrous salts or specific cathodes (such as carbon nanotube/γ-Fe₂O₃ and carbon felt/Fe@Fe₂O₃) are needed to provide Fe²⁺, and membranes can become fouled by iron [20,21]. Recently, a different type of electro-Fenton process was proposed where a two-chamber MFC was used to accelerate in situ generation of Fe²⁺ from sacrificial iron. However, this system required the addition of H₂O₂ because it could not be generated in situ in this system [22]. For these reasons, two-chambered MFCs do not appear to be a feasible approach for pollutant degradation using Fenton reactors.

A modified type of electro-Fenton system is presented here that overcomes the limitations of previous systems by using a single-chamber MFC to drive H₂O₂ and Fe²⁺ production in a second electrochemical reactor. H₂O₂ is produced on a cathode made of carbon felt, while Fe²⁺ is released from a sacrificial iron anode in an undivided electrochemical reactor that is separate from the MFC. The feasibility of this system was examined using phenol as the model pollutant, because phenol is a typical pollutant in many industrial wastewaters [23,24]. This modified type of treatment system may provide a more energy-efficiency and cost-effective approach for industrial wastewater treatment.

2. Materials and methods

2.1. Reactors construction and operation

The schematic diagram of our modified electro-Fenton system powered by a single-chamber MFC is shown in Fig. 1. MFCs were constructed from a solid cube of Lexan with a cylindrical chamber 4 cm long by 3 cm in diameter (empty bed volume of 28 mL).

Fig. 1. Schematic diagram of the electro-Fenton system powered by a single-chamber MFC.

A carbon fiber brush (2.5 cm diameter, 2.5 cm length, 0.22 m² total fiber area) was used as the anode, which had been heat treated at 450 °C for 30 min [25]. A piece of carbon cloth with a 0.5 mg-Pt cm⁻² catalyst layer on the water side was used as the air cathode (projected surface area of 7 cm²). No membrane was used between the anode and the cathode. To reduce oxygen diffusion to the anode, four polytetrafluoroethylene layers were coated on the air side of the cathode [26]. The brush anode was placed horizontally in the center of the cylindrical chamber and the air cathode was vertically placed on the other end of the same chamber, with the tip of the brush anode 1.25 cm from the air cathode. MFCs were inoculated using the effluent of other MFCs, and operated with an external resistance of 1000 Ω at room temperature (about 25 °C). The medium contained (per L): 1 g sodium acetate, 4.28 g Na₂HPO₄, 2.45 g NaH₂PO₄, H₂O, 0.31 g NH₄Cl, 0.13 g KCl, 12.5 mL minerals, and 5 mL vitamins [27]. The voltages across the external resistors were recorded every 20 min using a multimeter data acquisition system (model 2700 Keithley Instruments). When reproducible cycles were obtained, these MFCs were then tested as the power source for the electro-Fenton reactors.

Electro-Fenton reactors were constructed using a 100 mL bottle. An iron plate (2 cm × 2 cm) used as the anode was connected to the MFC cathode using a copper wire. A piece of carbon felt the same size as the cathode was connected to the MFC anode also using a copper wire. Carbon felt cathodes were used in this study because previous studies [17,28] have demonstrated oxygen can be effectively reduced to H₂O₂ using this material, and they are relatively inexpensive. The distance between the anode and the cathode was about 2 cm, which is common in electro-Fenton systems [9,29]. For every experiment, 80 mL of phenol wastewater (1 mM phenol + 50 mM KH₂PO₄) was added to the medium bottle and pH was adjusted to 3.5, or 7 using 85% H₃PO₄ and 0.2 M NaOH. Phosphate buffer was used here to avoid significant changes in pH during the experiments. The reactor solution was bubbled using a porous diffuser. Samples were withdrawn from the bottle and filtered through 0.22 μm-porosity polytetrafluoroethylene (PTFE) membranes prior to chemical analysis. Experiments were carried out under normal lab daylight and room temperatures (25–30 °C). Every experiment was repeated at least two times.

2.2. Electrical power analysis

The cell voltages and electrode potentials of the MFCs and the electro-Fenton reactors were recorded using a multimeter data acquisition system (model 2700 Keithley Instruments). To measure the potentials of the electrodes in the MFCs and electro-Fenton reactors, Ag/AgCl reference electrodes were inserted into the reactors. All potentials were reported here versus Ag/AgCl, which was +210 mV vs. a standard hydrogen electrode.

To perform polarization tests, a resistor box was connected between the MFC anodes and the electro-Fenton cathodes (Fig. 1). The resistances were manually varied from open circuit to 5000 Ω, 1000 Ω, 500 Ω, 100 Ω and 0 Ω, and the cell voltages and electrode potentials of the MFCs and the electro-Fenton reactors were recorded. The power output of the MFCs connected to the electro-Fenton reactors (P, mW/m²) was calculated using P = UI/A, where U is the cell voltage of MFCs (V), I is the current (A), and A is the cathode area of the electro-Fenton reactors (4 cm²).

2.3. Chemical analysis

Phenol and degradation intermediates were measured using a high-performance liquid chromatography (Shimadzu LC-20AT) equipped with an Allure® Organic Acids 5 μm column and a diode array detector set at a wavelength of 210 nm. The mobile phase was
50 mM KH₂PO₄ buffer (pH 2.31 adjusted by H₃PO₄) at a flow rate of 1.0 mL min⁻¹. Total organic carbon (TOC) analysis was performed with a Shimadzu TOC-VCSN Total Organic Carbon analyzer.

Hydroxyl radicals were detected through a spin trap by N,N-dimethyl-p-nitrosoaniline (RNO) [30,31]. For every test, 80 mL of 50 mM KH₂PO₄ buffer (pH 3, pH 5, or pH 7) containing 200 μM RNO was added to the electro-Fenton reactor, and the bleaching of the yellow color (RNO) was monitored at 440 nm using a spectrophotometer (DR2700, HACH).

3. Results

3.1. Electrical performance and electron-transfer mechanisms of this system

Single-chamber MFCs were incubated for about one month at an external resistance of 1000 Ω, until reproducible cycles of voltage production were obtained (Fig. 2). These MFCs were then used as power sources for the electro-Fenton reactors to degrade phenol in solutions at three different initial pHs of 3, 5, and 7. The voltages produced by the MFCs in the system were 0.2–0.3 V at pH 3 and pH 5, and 0.5–0.6 V at pH 7 (Fig. 2). Good repeatability was exhibited for consecutive multiple cycles. The higher voltage at pH 7 was due to the larger resistance of the electro-Fenton reactors (about 750 Ω) compared to those at pH 3 and pH 5 (50–100 Ω) since the Fenton reaction and iron corrosion are slower at neutral pH.

In order to examine the electrical performance of this system, we conducted polarization tests at three different pHs (Fig. 3). When the external resistance was zero (no resistor in the circuit between the MFCs and the electro-Fenton reactors), the power densities were 1746 ± 100 mW/m² (pH 3), 1964 ± 150 mW/m² (pH 5), and 630 ± 100 mW/m² (pH 7). These results show that the power densities that can be produced here are much higher than those achieved in two-chamber electro-Fenton systems (300–500 mW/m²) [17–19].

Based on the potentials of MFC anodes, MFC cathodes, electro-Fenton anodes, and electro-Fenton cathodes during polarization tests (supporting information S1), the electron transfer processes in the proposed system should proceed as shown in Fig. 1. At the MFC anode, acetate is oxidized to CO₂ by bacteria, and electrons and protons are produced (Eq. 1). These electrons are transferred to the cathode of the electro-Fenton reactor through copper wires, where oxygen is reduced to H₂O₂ (Eq. 2). At the anode of the electro-Fenton reactors, iron is oxidized to Fe²⁺, and electrons are released (Eq. 3) to the cathode of the MFCs where oxygen is reduced to water (Eq. 4). In the electro-Fenton reactors, H₂O₂ reacts with Fe²⁺ to produce hydroxyl radicals to oxidize organic pollutants (Eq. 5). Only the primary reactions were considered here. Other reactions might also occur in the electro-Fenton reactors, such as the oxidation of Fe²⁺ to Fe³⁺ by oxygen (Eq. 6) and the reduction of Fe³⁺ to Fe²⁺ at the cathode (Eq. 7). At pH 3, the cathode potentials of electro-Fenton reactors were very low (−0.72 V) when MFC was directly connected, which would improve the efficiency of H₂O₂ generation. On the other hand, the anode potentials of electro-Fenton reactors increased from −0.6 V to −0.4 V with a decrease in the external resistance, which would enhance iron corrosion and performance.

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\begin{align*}
\text{CH}_3\text{COO}^- + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_2 + 7\text{H}^+ + 8e^- \\
\text{O}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{H}_2\text{O} \\
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \rightarrow \text{H}_2\text{O} \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{OH}^- + \text{OH}^- + \text{Fe}^{3+} \\
\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ & \rightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O} \\
\text{Fe}^{3+} + e^- & \rightarrow \text{Fe}^{2+}
\end{align*}
\]

In order to confirm the generation of hydroxyl radicals by a Fenton reaction, hydroxyl radical concentrations in the electro-Fenton reactors powered by the MFCs were measured after 4 h (Fig. 4). The measured concentrations were 166 ± 8 μM (pH 3), 107 ± 40 μM (pH 5), and 12 ± 10 μM (pH 7). The highest concentrations of hydroxyl radicals were generated at pH 3, in agreement with the power output of MFCs at different pHs and the expected optimum conditions for Fenton reactions [1,10,32].

3.2. Phenol degradation rate and pathway

The concentrations of phenol and TOC were monitored over time during a fed batch cycle (22 h) (Fig. 5). When MFCs were connected to power the electro-Fenton reactors, the removal rates of phenol and TOC were significantly enhanced for the pH 3 and pH 5 conditions, with little change at pH 7. The optimal pH condition was pH 3, consistent with the electric performance of this system and known ideal conditions for Fenton-based reactions. After 22 h, phenol was completely removed and TOC was reduced by 75 ± 2%. Controls (no power added) were also conducted under the same conditions to examine phenol losses due to adsorption, volatilization, and precipitation. For the control experiment at pH 3, there was appreciable removal of phenol and TOC, which was likely due...
to increased rates of iron corrosion and consequently more effective precipitation than at pH 5 and pH 7.

To investigate the stability of the electro-Fenton system for degradation, experiments were conducted at these different pHs over multiple cycles (5 times). Each time MFCs were replenished with fresh medium, the electro-Fenton reactors were rinsed using DI water and refilled with solutions containing phenol at the indicated pH. The extent of phenol removal showed good repeatability for each condition. After 6 h treatment, the phenol removals were maintained at 95% (pH 3), 80% (pH 5), and 35% (pH 7) (Fig. 6a). TOC removals during a cycle had larger variations, especially for pH 5 and pH 7 conditions (Fig. 6b). These variations could be partly a consequence of the measurement method. For TOC analyses, samples were highly diluted (10×) in order to measure TOC concentrations in the range of the instrument (0 to 10 mg L−1), making the low TOC of the dilution water (0.2–0.5 mg/L) and dissolved CO2 (especially at pH 5 and 7) a greater contributor to variations in the calculated TOC changes.

The intermediates formed during phenol degradation at different pHs were also monitored (Fig. 7). Five main intermediates were identified: hydroquinone, fumaric acid, maleic acid, oxalic acid, and formic acid. After 3 h, approximately 85% of removed phenol was degraded to intermediates based on carbon balance, consistent with Fenton reactions being important in this system. The remaining 15% of the phenol was likely lost to adsorption, volatilization, and precipitation.

Many more intermediates were produced at pH 3 than at the other two pH conditions, due to the faster phenol degradation rate (Fig. 7). Complex intermediates (hydroquinone, fumaric acid, and maleic acid) were gradually degraded to simple carboxylic acids, and finally mineralized to CO2. After one cycle (22 h), little simple carboxylic acids (oxalic acid and formic acid) remained in the system. These end products are similar to those formed from phenol by other advanced oxidation processes, such as ozonation, electrochemical oxidation, and photocatalysis [33–35].

In general, phenol degradation proceeded in three steps. First, aromatic intermediates (e.g., hydroquinone) were formed through a series of radical reactions initiated by hydroxyl radicals. Second, aromatic intermediates were degraded with ring breakage to various carboxylic acids (i.e., fumaric acid, maleic acid, oxalic acid, and formic acid). Finally, carboxylic acids were completely mineralized.
These results suggested that the electro-Fenton system will be useful to pretreat industrial wastewaters, and that the effluent of this treatment could be used as influent for power production in MFCs.

4. Discussion

The use of a single-chamber MFC for providing power to an electro-Fenton reactor can be an effective method for phenol degradation. The pollutant degradation rates were similar to previous electro-Fenton systems using two-chamber MFCs where H₂O₂ was generated at the cathodes (requiring Fe²⁺ addition or iron-amended cathodes) [17–19]. Phenol was 95% degraded within 6 h here, compared to 70–90% removals for p-nitrophenol, Rhodamine B, and Orange II in previous systems within the same time (6 h). TOC was removed by 70–80% after 22 h. The anode and cathode (electro-Fenton) chamber volumes in previous two-chamber MFC electro-Fenton systems were usually the same, but here the electro-Fenton reactor volume (80 mL) was about three times that of the MFC volume, allowing for a treatment of a larger volume of wastewater per volume of solution used in the MFC. This situation allows more efficient degradation of pollutants than previous systems, which was due to the improved power densities produced by using the single-chamber MFCs. Moreover, previous systems contained expensive membranes and chemically-amended cathodes (such as carbon nanotube/γ-FeOOH and carbon felt/Fe₂O₃), or required Fe²⁺ addition. The modified electro-Fenton system here has circumvented these disadvantages.

Compared to previous electro-Fenton systems that required addition of H₂O₂ and Fe²⁺ release from iron driven by a MFC [22], the operation costs of the electro-Fenton system here should be much less due to the lack of a need for H₂O₂ or expensive membranes. For example, in a previous test 0.63 kg of H₂O₂ solution was needed to treat 1000 kg of industrial wastewater [22], and the current price of industrial grade H₂O₂ is $390–500 per ton. Proton exchange membranes can cost about $100 per square meter or more.

One disadvantage of the proposed electro-Fenton system here is that it needs to be operated under acidic conditions, so it is best suited for treating acidic industrial wastewaters, or the wastewater pH would need to be adjusted. Additionally, acetate was used as the substrate in MFCs. If other biodegradable wastewaters were used, or the effluents of electro-Fenton reactors with simple organic acids were utilized to feed the MFCs, the overall process would become more energy-efficient and cost-effective.

5. Conclusions

A modified two-reactor electro-Fenton system based on using the power produced by a single-chamber MFC to drive a Fenton reactor was shown to be an effective method for phenol degradation under acidic conditions. After one cycle (22 h), phenol was completely degraded to simple organic acids (such as oxalic acid and formic acid) and 75% of the TOC was removed. Compared to previous electro-Fenton systems with two-chamber MFCs, the degradation efficiency of organic pollutants was substantially improved and the operation cost was greatly reduced. This process is therefore a very promising method for treating acidic industrial wastewaters containing organic pollutants that can be degraded using Fenton reactions.

Acknowledgement

The authors acknowledge support from the King Abdullah University of Science and Technology (KAUST) by Award KUS-I1-003-13.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.02.051.

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