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Short communication

A novel bioelectro-Fenton system for coupling anodic COD removal with cathodic dye degradation

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ABSTRACT

The typical electro-Fenton process requires electricity to produce H_2O_2 electrochemically on the cathode for generating powerful oxidants (e.g., hydroxyl radical) to degrade persistent organic pollutants. A new bioelectro-Fenton system in a two-chamber microbial fuel cell (MFC) was proposed using a Fe@Fe_2O_3/carbon felt composite cathode for simultaneous oxidation of wastewater at the anode and cathodic degradation of biorefractory pollutant by Fenton's reaction. Under the short-circuit conditions, it was found that the rate of Rhodamine B (RhB) decolorization, TOC removal and stoichiometric efficiency was significantly improved as compared with that found under close-circuit conditions (1000 Ω). The enhancement was determined to be caused by an increase in cathodic current density that was favorable for H_2O_2 production.

1. Introduction

The use of advanced oxidation processes (AOPs) based on Fenton's reaction is a favorable technique for the treatment of recalcitrant organic contaminants due to the generation of hydroxyl radicals ($^\bullet$OH) from Fenton's reagents (Fe^{2+} and H_2O_2). The electro-Fenton system replaces the use of expensive H_2O_2 by generating H_2O_2 electrochemically at cathode [1–6]. Though the addition of H_2O_2 is avoided in the electro-Fenton system, the system suffers from high operating costs due to the need for high-energy input in real time applications.

Microbial fuel cells (MFCs) are a newly developed bioelectrochemical system (BES) that employs microorganisms as catalysts to oxidize organic and inorganic matters for electricity generation [7]. The electrons released by bacteria are transferred to the cathode where they are consumed to reduce electron acceptor, commonly oxygen. For an MFC using oxygen, the reduction of oxygen to water requires a four-electron transfer, but it is also possible that oxygen reduction results in H_2O_2 production by a two-electron transfer reaction as shown in Eq. (1) [8,9].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (1)$$

The cathodic production of H_2O_2 is generally seen as an unwanted reaction that diminishes power generation in MFCs, however, recent researches have discovered an optimistic use for the undesired H_2O_2 production in MFCs. Rozendal et al. [8] reported that using an applied voltage of 0.5 V, the MFC was capable of producing about 1.9 kg H_2O_2/m^3/day at a concentration of 0.13 wt%, which represents a novel alternative to the industrial production of H_2O_2. In addition, a concept of using the biological electrons produced from an MFC to power an electro-Fenton system to treat wastewater containing biorefractory pollutants was proposed [9,10]. Zhu and Ni [9] demonstrated the reaction of *in situ* generated H_2O_2 at a carbon felt cathode and Fe^{2+} released from adscititious scrap iron resulted in the formation of $^\bullet$OH for degrading *p*-nitrophenol. Feng et al. [10] reported the complete decolorization and mineralization of Orange II by Fenton process in an MFC equipped with a carbon nanotube (CNT)/γ-FeOOH composite cathode. In their experiments, the efficiency of organic degradation in the electron-Fenton reaction may have been limited by the low cathodic current density caused by resistance load in the MFCs [11].

In this study, we built a two-chamber MFC equipped with a newly developed Fe@Fe_2O_3/carbon felt (CF) composite cathode that allows for a relatively sustainable release of Fenton's reagents (Fe^{2+}) [12]. Simultaneous treatment of different wastewaters in one MFC unit was attempted by stimulating an electron-Fenton process (Eq. (2)) for cathodic degradation of refractory pollutants (using Rhodamine B (RhB) as a model compound) (Eq. (3)) coupled with anodic COD removal of real wastewater (Eq. (4)). To exploit the degradation efficiency in the electron-Fenton system, the degradation kinetics and stoichiometric efficiency of RhB were further investigated under different electric circuit conditions (with and without resistor load).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \qquad (2)$$

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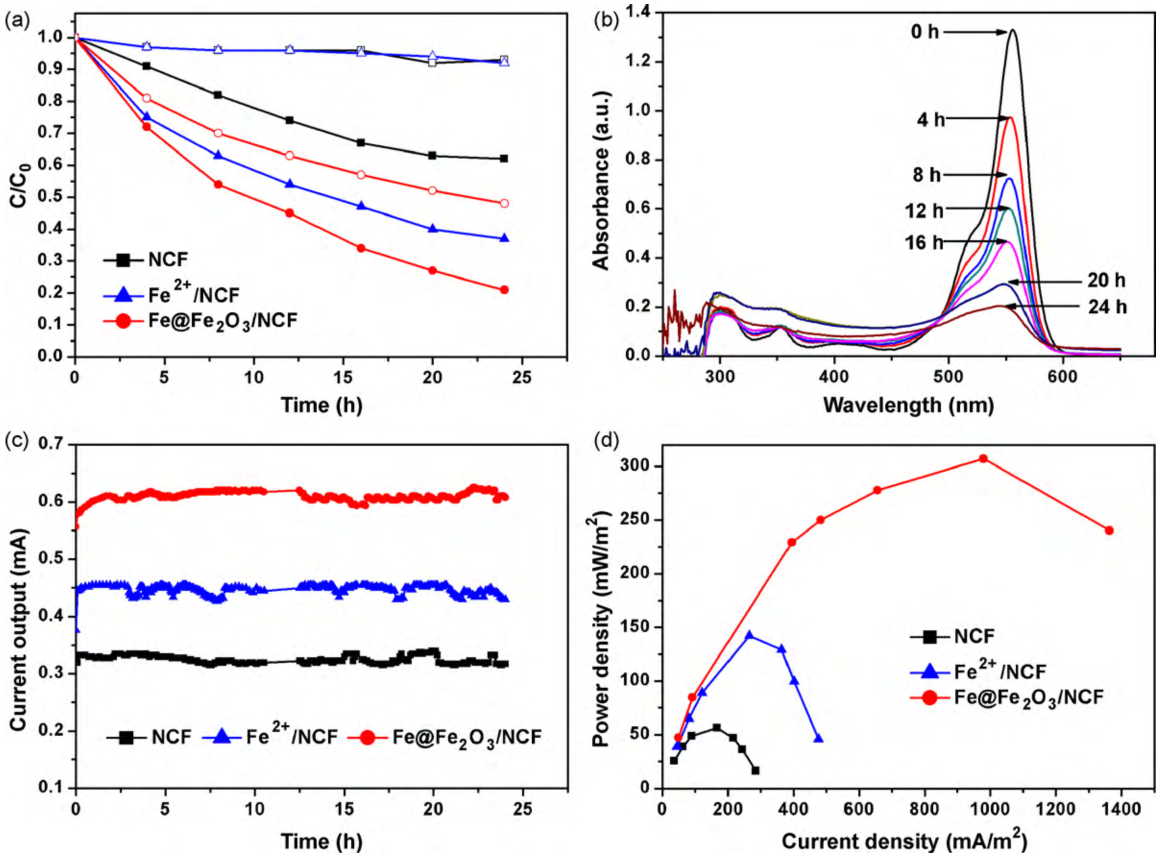

Fig. 1. (a) Decolorization of RhB for the NCF, Fe^{2+}/NCF and Fe@Fe_2O_3/NCF cells (open symbols: under open-circuit condition; solid symbols: close-circuit conditions with an external resistor of 1000 Ω); (b) UV–vis spectra changes of RhB in the Fe@Fe_2O_3/NCF cell; (c) Current output curves as a function of incubation time for the three cells; and (d) Power density curves as a function of current density for the three cells.

$$C_{28}H_{31}ClN_2O_3 + 146 \cdot OH \rightarrow 28CO_2 + 87H_2O + 3H^+ + 2NO_3{}^- + Cl^- \quad (3)$$

$$(CH_2O)_n + nH_2O \rightarrow nCO_2 + 4nH^+ + 4ne^- \quad (4)$$

2. Experimental

2.1. MFC construction and operation

This study used the similar two-chamber MFCs as previously described [12]. The two identical chambers were made of plexiglass and separated by GORE-TEX® cloth (an expanded polytetrafluoroethylene (e-PTFE) laminated cloth). Each cell chamber has an effective volume of 75 mL. The carbon felt (4.5 cm × 9.0 cm) functioned as the anodic electrode and three different kinds of cathode electrodes were used: (1) non-catalyzed carbon felt (NCF); (2) NCF in the presence of Fe^{2+} solution (Fe^{2+}/NCF); and (3) Fe@Fe_2O_3/NCF composite cathode. The Fe@Fe_2O_3/NCF composite cathode was constructed following the method described elsewhere [12]. Similar to our previous work [13], the anode chamber was inoculated with pre-acclimated microbial community from another MFC that had been running with brewery wastewater under fed-batch mode over 12 months. The anode chamber was continuously fed with brewery wastewater (pH = 7.5, conductivity = 6.9 ms/cm) at a volumetric loading rate of 2.13 g COD L^{-1} d^{-1}. The cathodic solution was the synthetic dye wastewater containing RhB at an initial concentration of 15 mg L^{-1}, and the cathodic pH was maintained around 3.0 by the addition of diluted HCl.

2.2. Power measurements and chemical analyses

The cell voltage outputs were continuously monitored using a 16-channel voltage collection instrument (AD8223, China). The power density curves as a function of current density were obtained by varying the external resistance from 5 to 5000 Ω when the voltage output approached steady state. The power densities were normalized to the projected surface area of the cathode (20.25 cm^2).

The concentration of RhB was determined using a UV–vis spectrophotometer (TU1800-PC, Beijing China) at 555 nm at an interval of 4 h. The mineralization of RhB was determined by measuring total organic carbon (TOC) loss of the cathodic solution. TOC was analyzed with a Shimadzu TOC-VCPH analyzer (U.S.A.). The chemical oxygen demand (COD) was measured using the standard closed reflux method [14]. The concentrations of H_2O_2 in the cathode chamber were determined by spectrophotometric analysis using the iodide method [15,16]. Stoichiometric efficiency (η), defined as the Coulombs ratio of the cathodic RhB mineralization and the anodic COD consumption, was calculated as $\eta = C_{cathode}/C_{anode} \times 100\%$, where $C_{cathode}$ (C) is the cumulative RhB mineralization expressed as charge, C_{anode} (C) is the theoretical amount of Coulombs that can be calculated based on COD removal.

3. Results and discussion

3.1. Bioelectro-Fenton process with simultaneous electricity output

Fig. 1a shows the decolorization efficiency of RhB in the cathode chamber of three MFCs equipped with different cathode electrodes over 24-h period under both open- and close-circuit conditions. Under open-circuit conditions, the red color remained unchanged in both the NCF and Fe^{2+}/NCF cells, while 52% of the RhB was decolorized in the Fe@Fe_2O_3/NCF cell. This was likely attributed to the reaction of zero-valent iron with dissolved O_2 to form the reactive intermediates (e.g., $HO_2/{}^{\bullet}O_2{}^{-}$, H_2O_2, $^{\bullet}OH$) [12,17] that are effective oxidizers for RhB decolorization. Under close-circuit conditions with an external resistor of 1000 Ω, the decolorization efficiency of RhB was enhanced for all cells. As previously demonstrated, under close-circuit conditions, H_2O_2 production in the NCF would reach 0.02 mM after 24 h [12], which responded for 38% of RhB decolorization in the NCF cell in this study. In the Fe^{2+}/NCF cell, *in situ* produced H_2O_2 reacted with Fe^{2+} in the solution, leading to the formation of reactive •OH radicals for decolorizing RhB (63%). The Fe@Fe_2O_3/NCF cell achieved the highest color removal of 79% and its UV–vis spectrum (Fig. 1b) showed the gradual diminishing absorption peak at $\lambda = 555$ nm within 24 h, suggesting the decomposition of the conjugated xanthene ring in RhB [18]. The increased RhB color removal in the Fe@Fe_2O_3/NCF cell was a consequence of the Fenton's reaction between *in situ* generated H_2O_2 and the iron reagents (Fe^{2+}) leached from Fe@Fe_2O_3, resulting in a greater amount of reactive oxidants [12]. Fitting the first-order kinetic model to the data gave a R^2 value (correlation coefficient of a least-squares fit) of 0.991, 0.967 and 0.989 for the NCF, Fe^{2+}/NCF and Fe@Fe_2O_3/NCF cells, respectively, indicating that RhB decolorization follows a pseudo-first-order kinetics.

Fig. 1c and d compared the current output and power density curves for the three MFCs with an external resistor of 1000 Ω. Data showed that the NCF, Fe^{2+}/NCF and Fe@Fe_2O_3/NCF were capable of producing steady currents of 0.32, 0.44 and 0.61 mA, and achieved maximum power densities of 56, 142 and 307 mW/m^2, respectively. The electricity generation of the MFCs was similar to previous studies [9,10,12].

3.2. Bioelectro-Fenton process for RhB degradation under short-circuit conditions

As an attempt to attain high degradation efficiency, RhB degradation by bioelectro-Fenton process was investigated under short-circuit conditions (i.e. at an external resistor of 0 Ω). Within 12 h, RhB color removals in the NCF, Fe^{2+}/NCF and Fe@Fe_2O_3/NCF cells approached 49%, 64% and 95%, respectively (Fig. 2a), which was approximately twice as many as the color removals obtained under close-circuit conditions (Fig. 1a). Fig. 2b shows gradually increasing TOC removal with time, with about 90% of TOC removed after 12 h in the Fe@Fe_2O_3/NCF cell, which was 78% and 40% higher than the NCF and Fe^{2+}/NCF cells, respectively.

Table 1 compared the performance of anodic COD removal and cathodic RhB degradation under both close- and short-circuit conditions. Regardless of the circuit conditions, the Fe@Fe_2O_3/NCF system consistently performed better than the Fe^{2+}/NCF and NCF systems. Data suggested that the anodic COD removal of wastewater was not evidently affected by the circuit conditions. However, the cathodic RhB degradation was highly enhanced under short-circuit conditions, especially for the Fe@Fe_2O_3/NCF cell. With an external resistance of 0 Ω vs. 1000 Ω, the pseudo-first-order rate constant of RhB decolorization ($K_{\text{decolorization}}$), TOC removal and stoichiometric efficiency for the Fe@Fe_2O_3/NCF system were 0.0675 h^{-1} vs. 0.257 h^{-1}, 34.7% vs. 89.9% and 3.2% vs. 8.2%, respectively. Previous study had demonstrated that the cathodic current density was a key factor affecting H_2O_2 generation and consequently the $^{\bullet}OH$ formation for pollutant degradation [11]. Results showed that the steady current densities under short-circuit conditions were 2.1–2.6 times higher than those under close-circuit conditions (Table 1). In a supplemental experiment, the concentrations of H_2O_2 in the NCF cell were measured to be 0.01 and 0.02 mM under close- and short-circuit conditions, respectively, which provided direct evidence for greater H_2O_2 production at higher cathodic current density. Under close-circuit conditions, the cumulative energy output across the 1000 Ω resistor, expressed as charges, was 13.8–25.9 kC. Relatively, the energy was reserved for increasing the cathodic current density and more H_2O_2 generation under short-circuit conditions, which was associated with the faster RhB decomposition, more effective mineralization and higher stoichiometric efficiency.

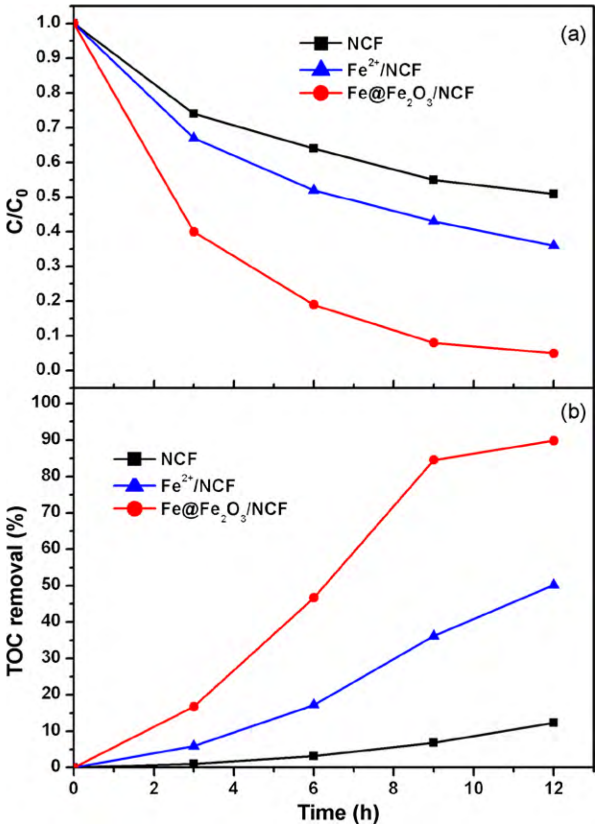

Fig. 2. Decolorization of RhB (a) and TOC removal (b) for the NCF, Fe^{2+}/NCF and Fe@Fe_2O_3/NCF cells under short-circuit conditions (at an external resistor of 0 Ω).

3.3. Environmental implications

By applying a Fe@Fe_2O_3/NCF composite electrode, the two-chamber MFC was endowed with the oxidative ability of the electro-Fenton system towards destruction of biorefractory organic contaminants in the cathode compartment. Compared with previous studies [9,10], our MFC has certain advantages: (1) GORE-TEX® cloth was adopted as an economical separator material that has an additional attribute for preventing membrane degradation caused by H_2O_2; (2) the preparation of Fe@Fe_2O_3/NCF composite cathode was simple and avoided the complicated synthesis of nanostructured materials; (3) the Fe@Fe_2O_3/NCF composite cathode can provide a controllably releasing Fenton iron reagent and an air-fed cathode to electro-generate H_2O_2 [19]. Such an MFC-driven bioelectro-Fenton system could have important environmental applications for wastewater treatment. Due to the powerful oxidative ability of Fenton's system, the MFC is expected to be capable of treating various non-biodegradable pollutants. For practical implementation, the scale-up of MFC capability and low stoichiometric efficiency need to be addressed. The improvement of H_2O_2 production may be achieved by applying an external voltage for increasing the cathodic current density [8] or by optimizing the cathode com-

Table 1
Comparison of MFC performance under close- and short-circuit conditions.

Treatments		Anodic COD removal (kg/m^3 day)	Cathodic RhB degradation				Overall Cell	
Cathode electrode	External resistor		$K_{decolorization}$ (h^{-1})[a]	Residual RhB after 12 h (%)	Residual TOC after 12 h (%)	Current density[b] (uA/cm^2)	Cumulative energy output[c] (kC)	Stoichiometric efficiency[d] (%)
Fe@Fe_2O_3/NCF	1000 Ω	0.815	0.0675	53.5	65.3	30.1	25.9	3.19
Fe^{2+}/NCF		0.633	0.0484	63.2	77.6	20.7	18.9	2.65
NCF		0.602	0.0241	82.4	92.4	15.3	13.8	0.09
Fe@Fe_2O_3/NCF	0 Ω	0.821	0.2572	5.4	10.1	65.2	0	8.21
Fe^{2+}/NCF		0.585	0.0922	36.3	49.8	43.7	0	6.44
NCF		0.574	0.0634	51.0	86.7	39.8	0	1.79

[a] The pseudo-first-order rate constant of RhB decolorization.
[b] The steady current density on the cathode electrode (normalized to projected surface area of the cathode, 20.25 cm^2).
[c] The cumulative energy output within 12 h, expressed as charges (kC, kilocoulomb).
[d] Stoichiometric efficiency is defined as the Coulombs ratio of the cathodic RhB mineralization and the anodic COD consumption.

position [10]. In future study, we will explore the system under neutral pH and application for other organic pollutants such as nitro aromatic and chlorinated organic compounds.

4. Conclusions

The use of a bioelectro-Fenton MFC system without energy input showed that anodic COD removal and cathodic dye mineralization could be achieved successfully at the same time. The RhB decolorization and mineralization at the cathode showed a high dependence on the cathodic current density. Attributed to the increased current density under short-circuit conditions, approximately 95% RhB and 90% TOC were removed in the Fe@Fe_2O_3/NCF system within 12 h, giving a $K_{decolorization}$ of 0.26 h^{-1} and a stoichiometric efficiency of 8.2%.

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