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A dual-chamber microbial fuel cell with conductive film-modified anode and cathode and its application for the neutral electro-Fenton process

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ABSTRACT

This study reports on the modification of the anode and the cathode in a dual-chamber microbial fuel cell (MFC) with a polypyrrole (PPy)/anthraquinone-2,6-disulfonate (AQDS) conductive film to boost its performance and the application of the MFC to drive neutral electron-Fenton reactions occurring in the cathode chamber. The MFC equipped with the conductive film-coated anode and cathode delivered the maximum power density of 823 mW cm^{-2} that was one order of magnitude larger than that obtained in the MFC with the unmodified electrodes. This was resulted from the enhanced activities of microbial metabolism in the anode and oxygen reduction in the cathode owing to the decoration of both electrodes with the PPy/AQDS composite. The MFC with the modified electrodes resulted in the largest rate of H_2O_2 generation in the cathode chamber by the two-electron reduction of O_2. The increase in the concentration of H_2O_2 was beneficial for the enhancement in the amount of hydroxyl radicals produced by the reaction of H_2O_2 with Fe^{2+}, thus allowing an increased oxidative ability of the electro-Fenton process towards the decolorization and mineralization of an azo dye (i.e., Orange II) at pH 7.0.

1. Introduction

A microbial fuel cell (MFC) is a renewable energy device that converts energy available in organic compounds to electricity via the catalyzation of microorganisms. Its power output has been greatly improved in recent years, but the maximum power (200–250 W m^{-3}) is still several orders of magnitudes lower than that of chemical fuel cells (CFCs) [1]. A recent report, for example, showed that the dual-chamber MFC with non-precious metal catalysts cathode and aerated catholyte produced the maximum power density of 22.9 W m^{-3} [2]. The anode associated with microbial metabolism and the cathode related to oxygen reduction reaction are often the limiting factors that affect power performance. A conductive film-modified anode material demonstrated to have a beneficial impact on enhancing the power density of a MFC by increasing the surface area and the biocompatibility of the carbon substrate [3–6]. It is of great interest to us to further improve the anode performance by immobilization of an electron mediator like anthraquinone-2,6-disulfonate (AQDS) coupled with the deposition of a conductive film on the anode surface [7]. This was achieved by electropolymerizing the pyrrole monomer in the presence of AQDS counter-ions to form a conductive polypyrrole (PPy)/AQDS film. Because AQDS on the anode surface facilitated the electron transfer from the cell to the anode [7,8], the resulting PPy/AQDS film could not only multiply the number of active sites for microbial metabolism, but also substantially improve the efficiency of the anode process. In addition, the PPy/AQDS-modified carbon-based material can be applied to enhance the performance of an aerated cathode in a dual-chamber MFC, because it showed superior electrocatalytic activity toward oxygen reduction reaction when compared to the bare carbon electrode [9,10].

To stimulate future development of the MFC technology, efforts should not be restricted to raise power performance. Indeed, in addition to its application as an alternative power source, the MFC has found additional uses such as wastewater treatment [11,12], biosensors [13,14] and hydrogen production [14]. This creates extra value purposes for MFCs. Very recently, Zhu and Ni [15] have proposed an idea of using electrons produced from a microbial reaction to drive electro-Fenton reactions for pollutant degradation in the MFC cathode. This would save energy cost when compared to the traditional electro-Fenton system and at the same time broaden the application fields of MFCs. In such a system, H_2O_2 is continuously generated in the cathode chamber by two-electron reduction of oxygen (Reaction 1) and then reacts with Fe^{2+} to produce hydroxyl radicals (Reaction 2). Due to its strong oxidizing power, the hydroxyl radical can react with organic compounds and

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results in an oxidative breakdown of organic pollutants. The performance of the electro-Fenton process is highly dependent on the production rate of H_2O_2 [9,10,16,17].

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

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\bullet + OH^- \quad (2)$$

The preliminary work [15] conducted at the acid catholyte solution (pH 3.0), however, might not be preferable from a practical perspective. This study reported electron-Fenton reactions occurring in the MFC cathode chamber under circumneutral conditions. Instead of directly using Fe^{2+} as the iron source, we used a mineral iron oxide (i.e., γ-FeOOH) for the neutral electron-Fenton process, because this allowed a facile recovery and recycling of the iron regent [18,19], and more importantly, a total mineralization of an organic pollutant can be achieved at a neutral pH value [20]. Furthermore, the MFC equipped with the PPy/AQDS-modified anode and cathode was used to drive the electro-Fenton reactions, because it allowed the generation of increasing amount of H_2O_2 in the cathode chamber.

Consequently, the aim of this study was two-fold: first, to increase the performance of a dual-chamber MFC by modifying its anode and cathode with the PPy/AQDS conductive film; second, to apply this improved MFC which showed high ability of H_2O_2 electrogeneration to drive the neutral electro-Fenton reactions. We chose an azo dye (i.e., Orange II) as the model pollutant which was subjected to degradation and mineralization in the cathode chamber of MFCs.

2. Experimental

2.1. Preparation of PPy/AQDS-modified electrode by electropolymerization

The electropolymerization of PPy was conducted in a three-electrode electrochemical cell containing 0.1 M pyrrole (Aldrich) and 20 mM AQDS (Aldrich). Prior to use, the pyrrole monomer was purified by distilling in twice. The working electrode was a piece of carbon felt (5.0 cm × 5.0 cm × 0.6 cm) which was purchased from Liaoyang Jingu Carbon Fiber Sci-Tech Co., Ltd. (China). A saturated calomel electrode (SCE) and a Pt mesh (4 cm × 4 cm) were used as the reference electrode and the counter electrode, respectively. All the potentials reported throughout this paper were referred to SCE. By applying a constant potential of 0.8 V modulated by an Autolab potentiostat (PGSTAT30, Eco Chemie), the PPy/AQDS conductive film was formed on the carbon felt surface and its thickness was controlled by the charge passed to the working electrode. The charge applied was 0.3 C cm^{-2} (per geometric electrode area). A thorough rinse of them with 0.1 M phosphate buffered solution (PBS, pH 7.0) was performed to remove the aqueous pyrrole and AQDS before further use.

The surface morphology of the PPy/AQDS-modified electrode was examined by using a LEO 1530 VP scanning electron microscope. To identify the incorporation of PPy/AQDS composite on the electrode surface, cyclic voltammetry (CV) tests were performed in 0.1 M PBS solution (pH, 7.0) by using the modified electrode as the working electrode, a SCE as the reference electrode and a Pt mesh as the counter electrode. The scan range was between −1 V and +0.6 V and the scan rate was 50 mV s^{-1}.

2.2. Construction and operation of MFCs with PPy/AQDS-modified electrodes

The dual-chamber MFC was constructed by using the PPy/AQDS-modified carbon felt both as the anode and as the cathode. A cation exchange membrane (Zhejiang Qianqiu Group Co., Ltd. China) was used to separate two electrodes. The effective volume of each cell chamber was 75 mL. For MFC inoculation, one mL of the activated *Shewanella decolorationis* S12 [21] was added to the sterilized anode chamber containing the lactate-based growth medium that was composed of 20 mM lactate, 0.1 M PBS (pH 7.0), 5.84 g L^{-1} NaCl, 0.10 g L^{-1} KCl, 0.25 g L^{-1} NH_4Cl, 10 mL of vitamin solution [22] and 10 mL of mineral solution [22]. The cathode solution was 0.1 M PBS (pH 7.0) and bubbled with air at a rate of 100 mL min^{-1}. For comparisons, four MFCs (MFC-A, MFC-B, MFC-C, MFC-D equipped with unmodified anode and unmodified cathode, unmodified anode and modified cathode, modified anode and unmodified cathode, and modified anode and modified cathode, respectively) were operated at a controlled temperature of 30 °C. An external resistance of 1000 Ω was used to connect both electrodes and cell voltages were recorded by using a 16-channel voltage collection instrument (AD8223, China).

The cell performance was evaluated in terms of the polarization and power density curves. They were obtained by measuring the cell voltage with the external resistor over the range from 10 to 5000 Ω. At each fixed resistance, voltage was collected when a relatively constant value was reached. Current density (I) was calculated as $I = V$ (cell voltage)/R (external resistance), and power density (P) was calculated as $P = V \times I$. Both I and P were normalized to the geometric anode surface area. The anode potentials were also recorded as a function of the external resistor by placing a sterilized SCE electrode into the anode chamber. The cathode potentials were calculated as the sum of the anode potential and the cell voltage.

The electrochemical impedance spectra (EIS) measurements were performed for the anode and cathode separately with a potentiostat in a three-electrode mode [23]. Anode impedance spectra were obtained using the anode as the working electrode and the cathode as the counter electrode; cathode impedance spectra were obtained using the cathode as the working electrode and the anode as the counter electrode. In both cases, the SCE in the anode chamber was used as the reference electrode. The MFC was connected to a potentiostat in a two-electrode mode with one electrode serving as the working electrode and the other functioning as both the reference and counter electrodes. Experiments were conducted at an open-circuit condition using an Autolab Frequency Response Analyzer System (FRA, Eco Chemie, The Netherlands). The impedance spectra were recorded in the frequency range from 10000 to 0.01 Hz with a sinusoidal excitation signal of 10 mV. The data were fitted to an equivalent electrical circuit using the Autolab impedance analysis software. The concentration of H_2O_2 generated from the cathode chamber was determined by spectrophotometric (TU1800-PC, Beijing China) analysis using the iodide method [16,24]. Liquid samples (500 μL) in the cathode chamber were transferred to a vial using a microsyringe and immediately mixed with 0.75 mL of potassium biphthalate and 0.75 mL of iodide reagent (0.4 M potassium iodide, 0.06 M NaOH and 0.1 mM ammonium molybdate). Then, the mixture was added to a 10 mm quartz cuvette for the spectrophotometrical determination at 351 nm.

2.3. Degradation and mineralization of Orange II in the cathode chamber of MFCs

When MFCs were operated in a steady state, the γ-FeOOH powders (homemade according to the procedures described in our previous work [25]) were added to the cathode chamber, serving as the iron source [18,19] for the electro-Fenton process. Except as otherwise noted, the initial concentration of γ-FeOOH in the cathode chamber was controlled at 1 g L^{-1}. In some experiments, 2 or 4 g L^{-1} iron oxide was also used. Fe^{2+} was generated [18,19] by the reduction of Fe^{3+} originated from the dissolution of the iron oxide and its concentration was determined by the light absorption of its complex with 1,10-phenantoline at 508 nm. After 20-h reaction, a model organic pollutant, Orange II dye, was injected to the cath-

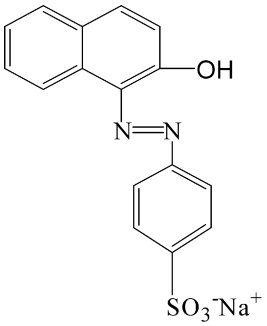

Fig. 1. Chemical structure of Orange II.

ode chamber with an initial concentration of 0.20 mM. The cathode pH was maintained at 7.0. As a result, the neutral electro-Fenton system was constructed for the degradation and mineralization of Orange II. Fig. 1 shows the structure of Orange II. The concentration of Orange II was determined by a UV–vis spectrophotometry (TU1800-PC, Beijing China) at 484 nm. The mineralization of Orange II was verified by measuring Total organic carbon (TOC) loss of the solution. The TOC analyses were carried out with a Shimadzu TOC-VSCN analyzer.

3. Results and discussion

3.1. Modification of anode and cathode with PPy/AQDS conductive film

The modification of MFC electrode materials was completed by electropolymerization of pyrrole in the presence of AQDS counterions. Scanning electron microscopy (SEM) tests were performed to examine the morphology of PPy/AQDS-modified carbon felt electrode. The as-received carbon felt was composed of a number of carbon wires with diameter of 10–20 μm (Fig. 2a). In comparison to the unmodified carbon felt (Fig. 2b), the conductive film-coated carbon felt possessed much rougher surfaces (Fig. 2c). The uniform and porous layer prepared by electropolymerization caused a significant increase in the electrode surface area [26]. This implies that the incorporation of conductive PPy on the anode and the cathode surfaces would supply increased amounts of active centers for the bio-electrocatalytic and electrocatalytic reactions happened in the anode and the cathode, respectively, thus leading to an enhancement in performances of both electrodes.

CV results further confirmed the successful binding of the PPy/AQDS film with the carbon felt surface. As shown in Fig. 3, the modified electrode resulted in larger current responses when compared to the unmodified electrode in the scan range between -1 V to 0.6 V. This was a result of the enhanced surface area of the PPy/AQDS-modified electrode. In addition, a pair of redox peaks attributed to the electrochemically active AQDS mediator [10] was clearly visible at −0.36 V (oxidation) and −0.56 V (reduction), demonstrating the successful doping of AQDS in the conductive film.

3.2. Enhancement of cell performance with PPy/AQDS-modified electrodes

The dual-chamber MFC operated with the PPy/AQDS-modified anode and cathode generated substantially larger power densities versus the unmodified counterparts. Anode and cathode polarization curves of the four MFCs were separately obtained, as shown in Fig. 4a, There were insignificant differences in the open circuit potential (OCP) and working potentials of the anodes for different MFCs with the same anode material. Similar observations can

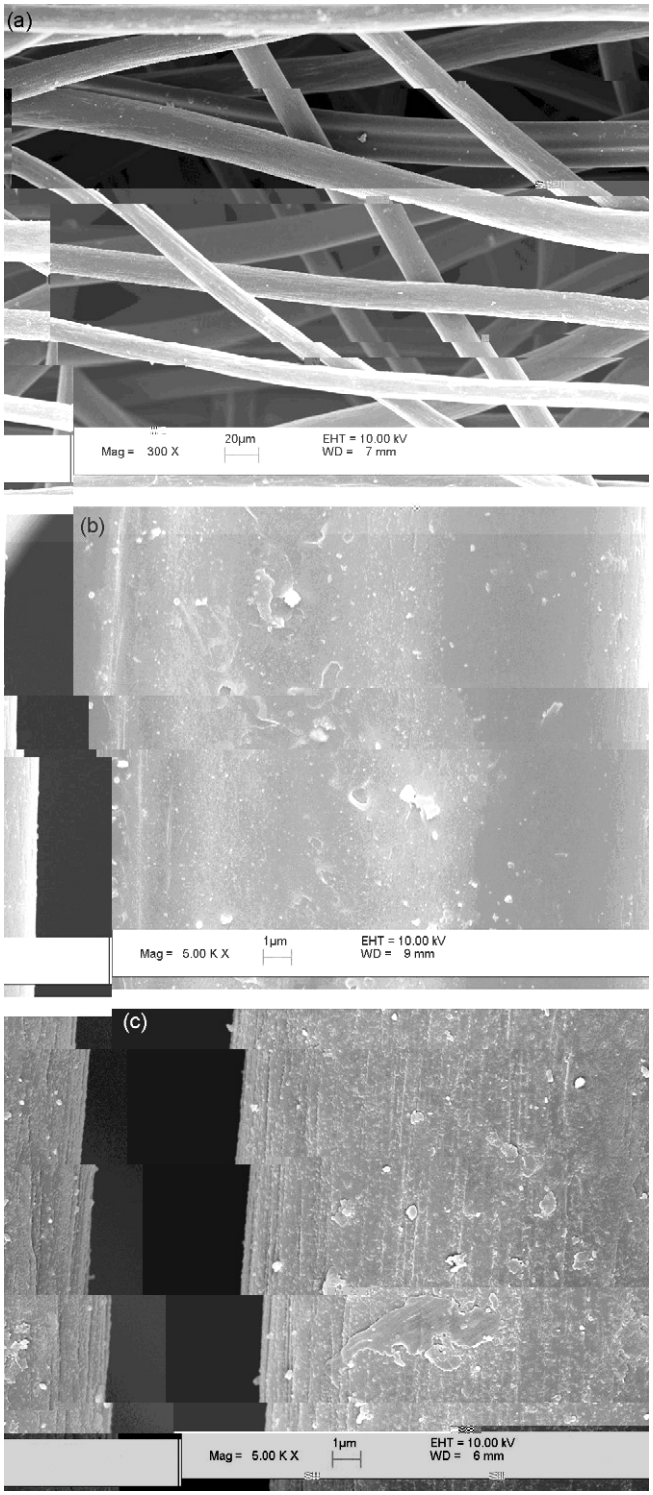

Fig. 2. SEM images of (a and b) as-received carbon felt and (c) PPy/AQDS-modified carbon felt with magnifications of (a) 300×, (b) 5000× and (c) 5000×.

also be made for the cathode polarization behavior when the same cathode was used. However, the OCP and polarization curves varied when the PPy/AQDS-modified electrode was present. It was found that the anode OCP moved toward more negative values from −0.31 V (MFC-A and MFC-B) to −0.52 V (MFC-C and MFC-D). Also, a sharp decrease in the slope of the anode polarization curve was observed in MFCs using the PPy/AQDS-modified anode versus those using the unmodified anode. From zero current to

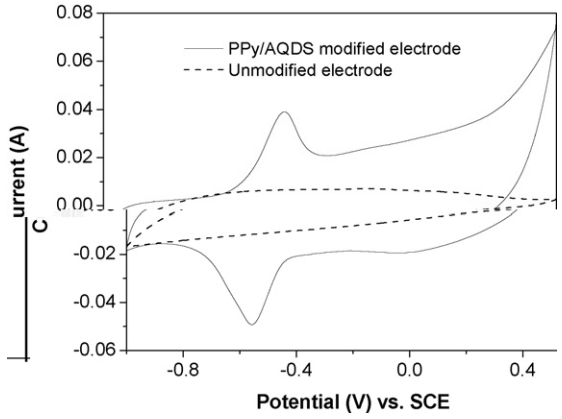

Fig. 3. Cyclic voltammograms of the PPy/AQDS-modified and unmodified carbon felt electrodes in PBS solution (0.1 M, pH 7.0). All the voltammograms were recorded at a scan rate of 10 mV s^{-1}.

1.26 A cm^{-2}, for example, the anode working potential in the MFC-B decreased by 94% from −0.31 (OCP) to −0.02 V; whereas, that in the MFC-D decreased only by 10% from −0.52 V (OCP) to −0.47 V. These results suggest that using the PPy/AQDS-modified anode material can markedly decrease the potential loss of bacterial metabolism. Moreover, a comparison of the cathode polarization curves among different MFCs indicated that the PPy/AQDS-modified material led to an enhanced performance of the cathodes. It was noted that the cathode OCP moved to a higher value, from 0.24 (MFC-A) to 0.28 V (MFC-B) and the curve slope of the MFC-B was slightly lower than that of the MFC-A. These observations indicate that the PPy/AQDS

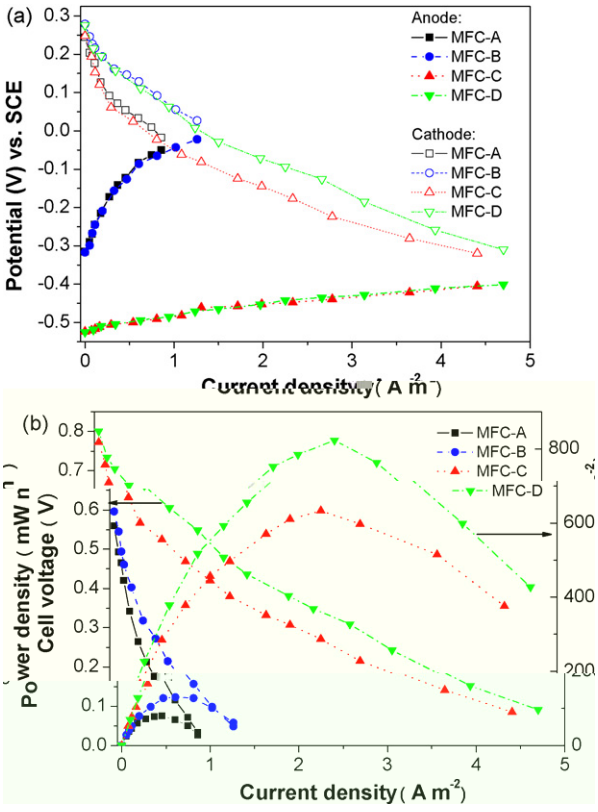

Fig. 4. (a) Anode and cathode polarization curves, and (b) cell polarization and power density curves of four MFCs equipped with different anode and cathode materials. Anode: *Shewanella decolorationis* S12 with the lactate-based growth medium; cathode: 0.1 M PBS solution (pH 7.0) bubbled with air at a rate of 100 mL min^{-1}. The operation temperature was 30 °C.

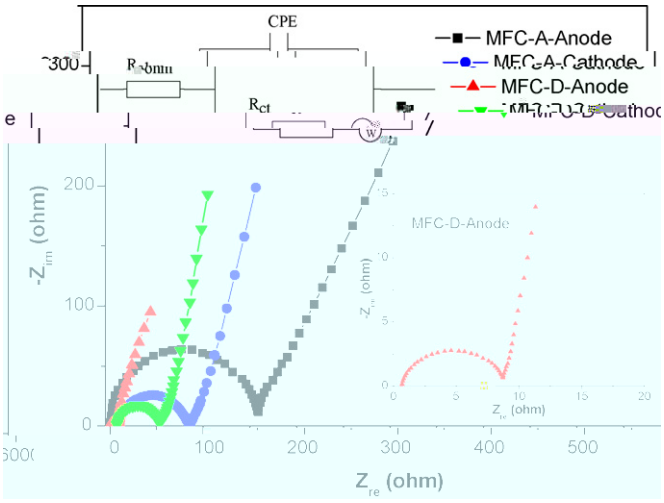

Fig. 5. Nyquist plots recorded for the anode and cathode separately at their open circuit potentials (OCPs) in the MFC-A and MFC-D. The inset shows the equivalent circuit of the one-time constant model.

composite has a beneficial effect in lowering the potential loss for oxygen reduction.

Fig. 4b shows the polarization and power density curves of the four MFCs investigated. The PPy/AQDS-modified anode (MFC-C and MFC-D) significantly improved performance of MFCs, as evidenced from the increased open circuit voltage (OCV), the decreased slope of cell polarization curves, and the increased in the maximum power density as compared to the unmodified anode (MFC-A and MFC-B). These results are the consequence of an enhanced anode performance by increasing the anode surface area and the biocompatibility of the substrate [3–6]. The carbon felt electrode modified with the conductive PPy layer has increased number of sites for microbial colonization; and hence boosts electricity generation. Similar results were obtained in the literature using the polyaniline (PANi)-modified anode [4–6] which showed superior power performance to the unmodified anode. Treatment of the anode material with the conductive polymer can also add more quinone groups which are suggested to facilitate bacterial adhesion and increase electron transfer [27]. Moreover, surface functionalization with AQDS is another crucial factor to promote the electron transfer efficiency because this mediator is able to shuttle electrons transferred from the microbial cell to the anode [7,8]. A further comparison of cell performance between the MFC-C and MFC-D indicates that there was an increase in the maximum power density from 633 to 823 mW cm^{-2} when the PPy/AQDS-modified carbon felt was also applied to the cathode. This can be understood that the immobilization of quinone groups on the electrode surface catalyzes the oxygen reduction reaction, as also suggested by the increased OCV of the MFC-D against the MFC-C. Previous studies [9,10] have shown that the oxygen reduction potential shifted to more positive value on the electrode containing PPy/AQDS composite when compared to that with less quinone compounds.

The variation in performance of different MFCs can be reflected by the different resistances contained in the anode, cathode, electrolyte and membrane. Fig. 5 shows the representative impedance spectra (Nyquist plots) of both the anode and cathode at their open circuit potential (OCP) for the MFC-A and MFC-D. A semicircle was observed in each curve, suggesting that the impedance spectra of both the anode and cathode follow the one-time constant model. The relevant equivalent circuit [28] (shown in the inset of Fig. 5) consists of an ohmic resistance (R_{ohm}), connected in series with a parallel combination of an electrochemical charge transfer resistance (R_{ct}) and a Warbug's diffusion element (W) with a double

Table 1
Dependences of ohm resistance, charge transfer resistance, concentration of H_2O_2, concentration of Fe^{2+}, and k_{TOC} on MFCs equipped with different anode and cathode materials.

Sample	Anode material[a]	Cathode material[a]	Resistance (Ω)				Concentration of H_2O_2 ($mg\,L^{-1}$)[b]	Concentration of initial γ-FeOOH ($g\,L^{-1}$)	Concentration of Fe^{2+} ($mg\,L^{-1}$)[c]	k_{TOC} (h^{-1})
			R_{ohm}-a	R_{ohm}-c	R_{ct}-a	R_{ct}-c				
MFC-A	Unmodified CF	Unmodified CF	0.81	7.52	170.4	77.5	0.63	1	1.05	0.063
MFC-B	Unmodified CF	Modified CF	0.79	7.49	168.1	60.2	1.25	1	1.07	0.075
MFC-C	Modified CF	Unmodified CF	0.78	7.44	8.9	75.1	2.29	1	1.12	0.123
MFC-D	Modified CF	Modified CF	0.76	7.36	7.9	54.2	2.79	1	1.14	0.145
MFC-D	Modified CF	Modified CF	0.78	7.24	7.4	55.5	2.72	2	1.81	0.179
MFC-D	Modified CF	Modified CF	0.75	7.45	8.1	57.8	2.86	4	3.43	0.256

[a] Unmodified CF: unmodified carbon felt; modified CF: PPy/AQDS-modified carbon felt.
[b] The concentration of H_2O_2 was measured during the 50th hour after the operation of MFC.
[c] The concentration of Fe^{2+} was measured during the 20th hour after the addition of γ-FeOOH.

layer constant phase element (CPE). On the Nyquist plot, the high frequency intercept with the *x*-axis.4 bilenotestheohR

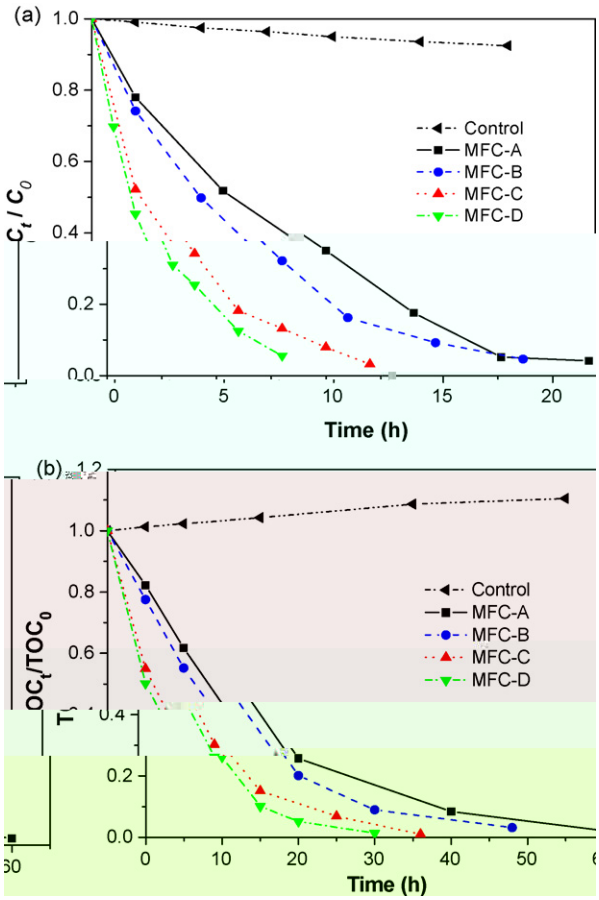

Fig. 7. Kinetics of Orange II decoloration (a) and mineralization (b) in the cathode chambers of four MFCs. The control experiments were conducted under the open-circuit condition in the MFC-D. Operation conditions: 0.2 mM Orange II, 1 g L^{-1} γ-FeOOH, pH 7.0, external load of 1000 Ω and air bubbled to the cathode at a rate of 100 mL min^{-1}.

3.4. Degradation and mineralization of Orange II by neutral electro-Fenton reactions

A neutral electro-Fenton system driven by the MFC was constructed when the iron source (i.e., γ-FeOOH) was added to the cathode solution (pH 7.0), followed by the addition of an organic pollutant (i.e., Orange II). Fig. 7a shows the decay in Orange II concentration (C_t, normalized to the initial concentration (C_0)) as a function of reaction time (t). A control experiment was also conducted under the open-circuit condition to investigate the adsorption of Orange II on the carbon felt. As shown in Fig. 7a, there was less than 8% loss of Orange II due to its adsorption at pH 7.0. An exponential relationship between C_t/C_0

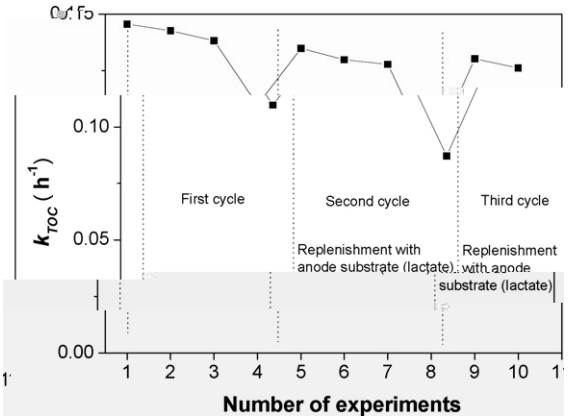

Fig. 8. Dependence of k_{TOC} on the increasing number of experiments for Orange II mineralization. The anode was replenished with the fresh lactate when k_{TOC} was significantly reduced by the depletion of substrate. Operation conditions: 0.2 mM Orange II, 1 g L^{-1} γ-FeOOH, pH 7.0, external load of 1000 Ω and air bubbled to the cathode at a rate of 100 mL min^{-1}.