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Application of a weak magnetic field to improve microbial fuel cell performance

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Abstract Microbial fuel cells (MFCs) have emerged as a promising technology for wastewater treatment with concomitant energy production but the performance is usually limited by low microbial activities. This has spurred intensive research interest for microbial enhancement. This study demonstrated an interesting stimulation effect of a static magnetic field (MF) on sludge-inoculated MFCs and explored into the mechanisms. The implementation of a 100-mT MF accelerated the reactor startup and led to increased electricity generation. Under the MF exposure, the activation loss of the MFC was decreased, but there was no increased secretion of redox mediators. Thus, the MF effect was mainly due to enhanced bioelectrochemical activities of anodic microorganisms, which are likely attributed to the oxidative stress and magnetohydrodynamic effects under an MF exposure. This work implies that weak MF may be applied as a simple and effective approach to stimulate microbial activities for various bioelectrochemical energy production and decontamination applications.

Keywords Electrochemical activity · Electricity production · Magnetic field (MF) · Microbial fuel cells (MFCs) · Mixed culture

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Introduction

The merit of microbial fuel cells (MFCs) for simultaneous electricity generation and wastewater treatment has been widely recognized (Lovley 2008; Pant et al. 2012; Li et al. 2014). Application of MFCs for wastewater treatment offers great advantages because the small-amount of in situ generated electricity can be effectively utilized to enhance biodegradation and biotransformation of toxic chemicals (Luo et al. 2009; Mathuriya 2014). MFC performance can be affected by many factors, such as cell configuration (Di Lorenzo et al. 2010; Li et al. 2011a), microbial community (Borole et al. 2009, 2011), electrode materials (Zhou et al. 2011; Mohanakrishna et al. 2012), and substrate types (Pant et al. 2010). Especially, the electrochemical activity of anodic microorganisms is usually limiting in practical application (Pham et al. 2009; Lovley 2011).

Various physical, chemical and biological approaches have been explored to "activate" the anodic microorganisms in MFCs and improve electricity generation (Sun et al. 2011; Wang et al. 2013; Xiang et al. 2009; Zhang et al. 2015). Especially, magnetic fields (MFs) stimulation offers a potentially low-cost and convenient approach to enhance microbial activity, since a static MF can be continuously and conveniently applied to any biosystem without need for extra energy input (Ji et al. 2010; Filipic et al. 2012). Previous studies have demonstrated that implementation of an appropriate MF could raise microbial activity and accelerate contaminant degradation in wastewater treatment systems (Liu et al. 2008; Kriklavova et al. 2014; Zaidi et al. 2014). MFs have also been found to promote bioelectrocatalytic activities of several enzyme assemblies linked to electrodes through accelerating electron transfer at electrode-solution interfaces (Katz et al. 2005). Our previous study showed that MF could enhance

the power generation of *Shewanella*-inoculated single-chamber MFCs (Li et al. 2011b). However, such pure-culture system has poor robustness and need sterilization of wastewater. For practical application, MFCs with mixed-culture inoculums would be essential (Wang et al. 2012; Solanki et al. 2013). A recent study showed that MF could also exert positive impacts on two-chamber MFCs with activated sludge (Tao and Zhou 2014), but the application range and stimulation mechanisms of such approaches remain unclear. In this study, we provide further evidences to show that such an MF stimulation technology is also applicable for single-chamber MFCs and shed light into the underlying stimulation mechanism. A weak static MF (100-mT) was applied at the anode proximity. Electrochemical and fluorescence spectroscopic analyses were performed to explore the mechanisms of the MF enhancement effects. This work suggests a high potential of applying a weak MF as a cost-effective and convenient strategy to enhance MFC performance.

Materials and methods

MFC assembly and operation

The single-chamber air–cathode MFC had a working volume of 125 mL and was composed of a carbon-paper bioanode and a Pt-coated carbon-cloth cathode separated by a proton exchange membrane (PEM, GEFC-10 N, GEFC Co., China). The effective surface areas of the anode and cathode were 16 and 25 cm^2, respectively. The PEM separator was attached to the cathode surface. A 100-mT static MF was applied by binding a magnet onto the external chamber wall near the anode side to constitute an MF-coupled MFC (hereafter denoted as MF system). The schematic and photograph of the MF system are shown in Fig. 1. Another identical MFC without applying MF was run as the control.

Each MFC was inoculated with 10 mL of mixed sludge, collected from a lab-scale upflow anaerobic sludge blanket reactor and an activated sludge reactor. The anodic chamber was filled with 100 mL synthetic wastewater (culture medium) containing 1000 mg L^{-1} acetate as the substrate. The wastewater composition was as described by Sun et al. (2008). During the experiment, the culture medium was replaced by fresh one once the voltage declined to below 50 mV. All the MFCs were operated in an incubator at 25 ± 0.5 °C. The voltage across a 1000-Ω resistor was measured every 12 h by using a multimeter and the average value of two measurements was used.

Analysis

Polarization curves were recorded by varying the external resistance from 10,000 to 10 Ω at the relatively steady stage of electricity generation. In order to detect the possible redox mediators secreted by the microbes, the culture medium was subjected to electrochemical fluorescence spectral analysis at the end of the experiment. Cyclic voltammetry of the medium was measured using an electrochemical workstation (CHI660C, Shanghai Chenghua Instruments Co., China) at a scan rate of 5 mV s^{-1} in a beaker. A graphite rod, a Ag/AgCl electrode and a platinum wire were used as the working, reference and counter electrodes, respectively.

The culture medium, after centrifugation (10 min at 5000×*g*) and filtration through a 0.45-μm acetate cellulose membrane, was analyzed by three-dimensional emission-excision matrix (EEM) fluorescence spectrometry. EEM spectra are a collection of a series of emission spectra over

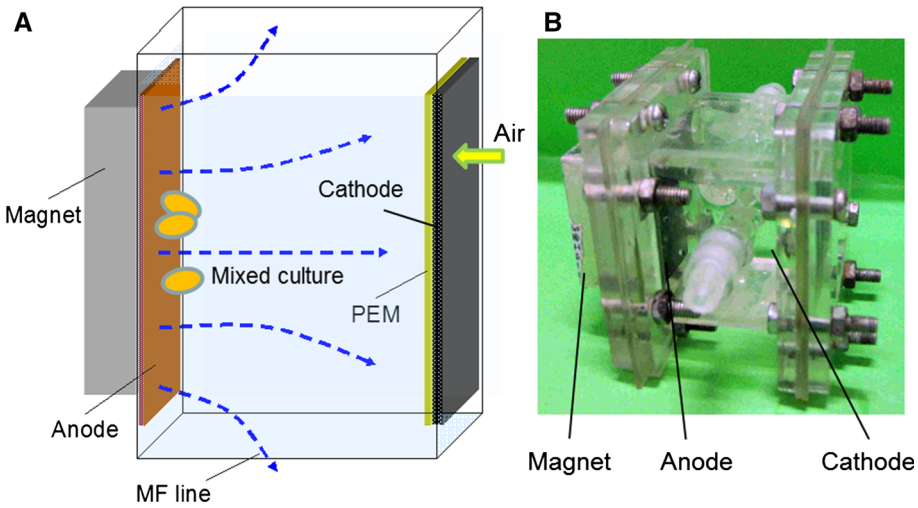

Fig. 1 **a** Schematic and **b** image of the magnetic MFC

a range of excitation wavelengths, which can be used to identify the fluorescent compounds present in solution (Wang et al. 2009). In this study, the EEM analysis was performed using a luminescence spectrometer (LS-55, Perkin-Elmer Co., USA), following the procedures proposed by Sheng and Yu (2006). The EEM spectra were collected with subsequent scanning emission spectra from 300 to 550 nm at 0.5 nm increments by varying the excitation wavelength from 200 to 400 nm at 10 nm increments. Excitation and emission slits were maintained at 10 nm and the scanning speed was 1200 nm min^{-1}. The EEM data were processed by MatLab 2007b software (MathWorks Inc., USA).

Results and discussion

Electricity generation

The output voltages of the MFCs in four consecutive operating cycles were illustrated in Figure 2. The start-up of the control MFC took 6 days, while the voltage in the MF system increased rapidly to a high level within just 2 days, suggesting that the MFC start up was accelerated by the MF, which was consistent with a previous report (Tao and Zhou 2014). It is suggested that such an acceleration was due to the creation of a more favorable environmental for growth and enrichment of electro-active microorganisms under the MF exposure. Notably, the maximum voltages of both systems were comparable in the first three running cycles, but a much higher voltage of the MF system was observed in Cycle 4. This results indicates that the MF application also led to increased electricity generation, but a relatively long influential time was needed. Considering that an immediate stimulation effect was observed in our previous study with pure culture inoculum (Li et al. 2011a), this result suggests that a longer period of adaptation is required for the mixed culture to establish a high electrochemical activity at the anode. Such an MF effect on other biochemical processes has also been reported previously. For example, an MF with moderate magnetic density was found to promote the bio-removal of toxic Cr(VI) in anaerobic sequencing batch reactor systems (Sun and Xu 2010). Increased biodegradation of formaldehyde by activated sludge was achieved under a static MF exposure (Łebkowska et al. 2011). In addition, an MF was also found to alleviate the toxicological effect induced by cadmium in mungbean seedlings (Chen et al. 2011).

Internal resistance

The MF stimulation effect was also evidenced by the power density and polarization curves of the MFCs. The MF system showed a maximum power density of around 25 mW m^{-2}, which was ~2.5 fold higher than the control (Fig. 3). It can be also seen from the power density curves that the ohm resistances of both MFCs were very close. However, the polarization curves reveal a much smoother initial voltage drop in the MF system over the control, implying a decreased activation loss under the MF (Logan et al. 2006), which agrees well with a previous report (Yin et al. 2013). Given that the influential area of the MF was limited to only the anode vicinity and all the other conditions are identical, here the decreased activation overpotential under MF should be ascribed to enhanced electrochemical activity of the anodic microorganisms (Logan et al. 2006).

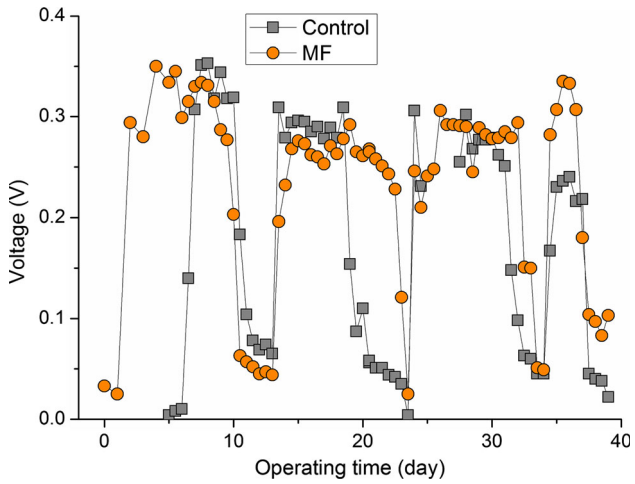

Fig. 2 Output voltages of MFCs during four consecutive operation cycles

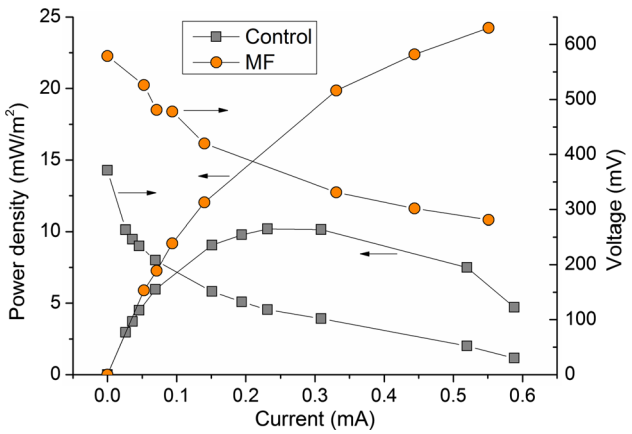

Fig. 3 Power density and polarization curves of MFCs

Soluble redox mediator secretion

Many bacteria can secrete redox compounds that act as electron mediators to assist electrochemical interaction with an electrode (Torres et al. 2010; Lovley 2008). To find out whether the MF effect work by such a mechanism, we characterized the culture medium at the end of the experiment by voltammetry and three-dimensional EEM spectroscopy.

The EEM spectra of both systems showed only one peak at the excitation/emission wavelength (Ex/Em) of 260/380 nm (Fig. 4), which could be ascribed to the protein-like substances in soluble microbial products (SMPs) (Sheng and Yu 2006). No peak of flavins (a common electron shuttle, typically occurring at Ex/Em of 450/525 nm), was observed in both MFCs, indicating that the improved power generation was not due to increased redox mediator secretion.

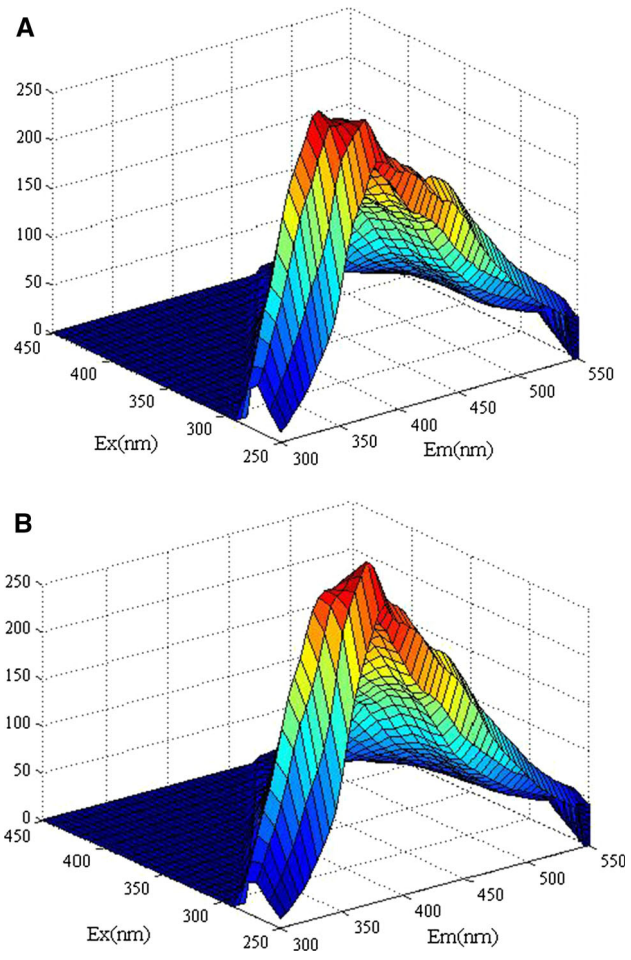

Fig. 4 EEM fluorescence spectra of the medium in: **a** the control; and **b** MF system

The irrelevance of mediator secretion with the MF effect was further proven by the cyclic voltammetry (CV) result (Fig. 5). The media from both MFCs showed a redox couple at the same position (i.e., an oxidation peak at approximately −200 mV and a reduction peak at −290 mV) with similar peak density. Thus, the possibility of MF-induced secretion of redox mediators under MF exposure can be ruled out, and the promotion effects of MF should be ascribed to other mechanisms that enhance the metabolism or extracellular electron transfer of anodic microorganisms.

Possible mechanisms of microbial electrochemical activity simulation by MFs

The MF effects here might be associated with an oxidative stress response of the anodic microorganisms. It has been previously reported that an MF exposure could increase the activity, concentration and lifetime of oxidative metabolites and free radicals (Jones et al. 2007), or improve the activity of some enzymes (Afanasyeva et al. 2006). In addition, a magnetohydrodynamic effect might have also contributed to the improved microbial electrochemical activity (Katz et al. 2005). Specifically, the MF may decrease the thickness of the diffusion double layer at the solution-biofilm interface (Katz et al. 2005), thereby promoting mass transfer and bioelectrocatalytic oxidation of substrate. In all, oxidative stress and magnetohydrodynamic effects could be important mechanisms accounting for the MF stimulation effects in this study, although the exact mechanisms are yet to be clarified.

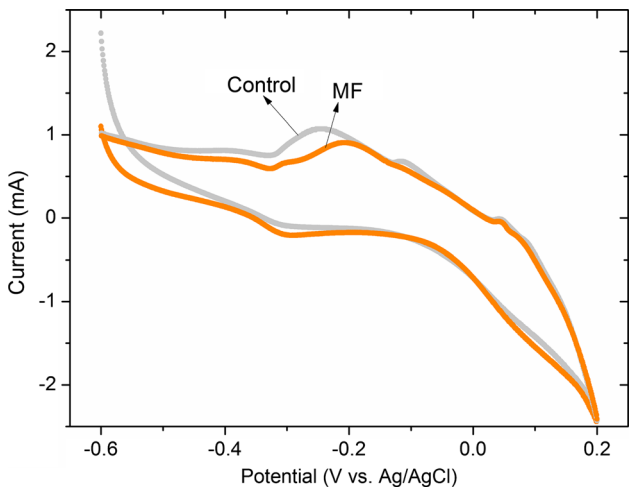

Fig. 5 Cyclic voltammetric curves of the culture media

Conclusions

The implementation of a 100-mT MF at the MFC anode distinctly accelerated the reactor startup and increased electricity generation via enhancing bioelectrochemical activities of the anodic microorganisms. The CV and EEM spectroscopy revealed no distinct differences in concentration of redox mediator in the culture medium, suggesting the MF did not induce redox mediator secretion. Oxidative stress and magnetohydrodynamic effects are likely the major reasons accounting for the elevated bioelectrochemical activity under MF exposure. This study suggests that MF stimulation may offer a simple and cost-efficient approach to stimulate the electrochemical-active microorganisms in various bioelectrochemical energy production and remediation applications.

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Compliance with Ethical Standards

Conflict of interest All authors declare that they have no conflict of interest.

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