Bioresource Technology 148 (2013) 39–46

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Bacterial–fungal interactions enhance power generation in microbial fuel cells and drive dye decolourisation by an *ex situ* and *in situ* electro-Fenton process

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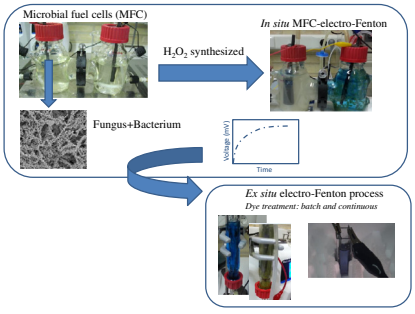
HIGHLIGHTS

- Bacteria are capable of use the infrastructure of the fungi to transport electrons.
- The power density was increased by 40% when *in situ* MFC electro-Fenton was developed.
- Dual benefits of MFC electro-Fenton: dye decolourisation and electricity generation.
- MFC can be used to drive *ex situ* electro-Fenton process in batch and continuous mode.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 June 2013
Received in revised form 10 August 2013
Accepted 14 August 2013
Available online 22 August 2013

Keywords:
Advanced oxidation technology
Electro-Fenton
Decolourisation
Dye
MFC

ABSTRACT

In this work, the potential for sustainable energy production from wastes has been exploited using a combination fungus–bacterium in microbial fuel cell (MFC) and electro-Fenton technology. The fungus *Trametes versicolor* was grown with *Shewanella oneidensis* so that the bacterium would use the networks of the fungus to transport the electrons to the anode. This system generated stable electricity that was enhanced when the electro-Fenton reactions occurred in the cathode chamber. This configuration reached a stable voltage of approximately 1000 mV. Thus, the dual benefits of the *in situ*-designed MFC electro-Fenton, the simultaneous dye decolourisation and the electricity generation, were demonstrated. Moreover, the generated power was effectively used to drive an *ex situ* electro-Fenton process in batch and continuous mode. This newly developed MFC fungus–bacterium with an *in situ* electro-Fenton system can ensure a high power output and a continuous degradation of organic pollutants.

1. Introduction

Microbial fuel cells (MFCs) offer the possibility to efficiently convert organic compounds into electricity (Logan et al., 2006). Similar to the conventional fuel cell, the MFC consists of an anode, a cathode and an ion-exchange membrane. The main difference is that the anode in MFCs uses microorganisms rather than noble metals as catalysts to convert chemical energy into electricity. The microorganisms combine multiple enzymes to catalyse the oxidation of the substrate, such as glucose or acetate in the anode, and pass electrons through an external circuit to the cathode, where electron acceptors accept electrons and protons are consumed. The microorganisms can self-regenerate, and thus the cost of this type of catalyst is much lower than that of a conventional chemical catalyst. Furthermore, no pollutants, such as metal ions, toxic gases or organic wastes, are generated during the operation of MFCs, thus rendering them environmentally friendly energy systems (Gong et al., 2011).

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http://dx.doi.org/10.1016/j.biortech.2013.08.084

MFC anode biofilms often contain diverse populations when enriched under different conditions. The electrogenic microorganisms in MFCs play a vital role in power generation (Lovley, 2008). MFCs can be operated using pure cultures, and typical electrochemical active bacteria are *Geobacteraceae* and *Shewanella* (Bond and Lovley, 2003). *Geobacteraceae* is an obligate anaerobe that is highly sensitive to the presence of oxygen. However, *Shewanella* is a facultative exoelectrogen, which can produce power under both anaerobic and aerobic conditions. More than thirty pure isolates have been reported in the literature as exoelectrogens, such as *Pseudomonas* sp., *Burkholderia* sp., *Escherichia coli*, *Rhodoferax ferrireducens*, *Tolumonas osonensis*, *Geopsychrobacter electrodiphilus*, *Clostridium sticklandii*, *Leucobacter komagatae*, *Microbacterium laevaniformans*, etc. (Zhang et al., 2006; Luo et al., 2013; Holmes et al., 2004; Chung and Okabe, 2009; Quan et al., 2013). However, mixed cultures are more suitable for the use of complex substrates, such as wastewater, as pure cultures generally metabolise quite a limited range of organic compounds and require sterile conditions (Kim et al., 2007). Therefore, it is possible to produce the energy in MFCs with different types of microorganisms as bio-catalysts from an extensive variety of carbon sources operating under different conditions.

Recently, the simultaneous degradation of pollutants in both anode and cathode chambers has been investigated (Luo et al., 2011; Xu et al., 2013). Advanced oxidation processes (AOPs) is a highly cost-effective process that has emerged as an important alternative for the elimination of several hazardous organic compounds from contaminated soil, sludge, and wastewater. In these processes, hydroxide radicals are produced to oxidise organic pollutants either completely into carbon dioxide, water and inorganic salts or incompletely into less hazardous intermediates (Rosales et al., 2012b). The traditional Fenton process, one of the AOPs, is widely used as a suitable treatment method for highly concentrated wastewaters. The reagents (Fe^{2+} and H_2O_2) are relatively inexpensive and environmentally benign; however, H_2O_2 could be readily decomposed to water and oxygen. Thus, new Fenton technologies, such as electro-Fenton, in which the *in situ* formation of H_2O_2 is possible, have attracted considerable attention (Rosales et al., 2012b).

There are numerous papers on the synthesis of H_2O_2 in chemical fuel cells (Lobyntseva et al., 2007; Otsuka and Yamanaka, 1990), and several studies have reported that it is possible to develop MFC for H_2O_2 production from wastewaters (Rozendal et al., 2009; Fu et al., 2010). H_2O_2 can be synthesised in an MFC by coupling anodic oxidation of organic compounds to cathodic production of H_2O_2. The electrons released by microorganism are transferred to the cathode where they are consumed to reduce an 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 might result in H_2O_2 production by a two-electron transfer reaction, as shown in Eq. (1).

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

Recently, Fu et al. (2010) and Rozendal et al. (2009) reported that H_2O_2 can be synthesised at the cathode of an MFC. Fu et al. (2010) determined the optimal condition for H_2O_2 production, and these authors reported that a concentration of 78.85 mg L^{-1} was reached after 12 h of operation with an external resistance of 20 Ω. Rozendal et al. (2009) reported that the MFC was capable of producing approximately 1.9 kg H_2O_2/m^3/day from acetate, which represents a novel alternative to the industrial production of H_2O_2. Based on these results, Zhuang et al. (2010) developed an integrated system coupling the cathodic electro-Fenton process with MFC.

The low-voltage electricity generated in an MFC could be used for other electrochemical processes (Rabaey and Rozendal, 2010). For this reason, it is expected that an MFC could be used to supply extra electricity to drive external electro-Fenton processes. Furthermore, the demonstrated synthesis of hydrogen peroxide in the MFC could be used for the degradation of organic pollutants in the cathode chamber. Therefore, the aim of this study is to apply the bacterial–fungal interactions to enhance power generation in the MFC. In addition, an MFC fungus–bacterium was employed to develop the continuous electro-Fenton process in the cathode chamber through the production of H_2O_2 in the presence of iron fixed in alginate beads. Finally, the energy supplied by the MFC was applied to an *ex situ* electro-Fenton process operating in batch and continuous mode.

2. Methods

2.1. Microorganisms

Trametes versicolor (CECT 20148) was maintained at 4 °C on malt agar plates and sub-cultured every month.

Shewanella oneidensis MR-1 (ATTCC 700550) was maintained at −20 °C on pellets and cultured on TSA agar plates.

2.2. Microbial fuel cell design and operation

An H-type reactor MFC with two-chambers of 250 mL separated by a Sterion® Cation Exchange Membrane was used (Fig. 1a). The electrodes were placed in each chamber in parallel with a gap between them of 12 cm. Graphite rod electrodes were used as the cathode and anode (Goodfellow Cambridge Limited, UK). The power energy evolution was recorded by AutoLab PGSTAT 302 N potentiostat. Prior to starting the MFC, the graphite anode of the MFC was inoculated with *T. versicolor* and *S. oneidensis* MR-1 in submerged cultures in a 1.8 L Fernbach flask containing 90 mL of growth medium composed of (g L^{-1}) glucose 10, yeast extract 15, NH_4Cl 0.75, KH_2PO_4 2, $MgSO_4{\cdot}7H_2O$ 0.5, $CaCl_2{\cdot}2H_2O$ 0.1 and KCl 0.5. This basal medium was sterilised at 121 °C for 20 min. After four days the anode was fixed in the anode chamber. The anode chamber was fed continuously with the defined medium composed of (g L^{-1}) $C_2H_3NaO_2$ 0.408, $NaH_2PO_4{\cdot}2H_2O$ 3.32, Na_2HPO_4 8.23, KCl 0.31 and NH_4Cl 0.31. The pH was initially adjusted to 7, and the solution was autoclaved at 121 °C for 20 min. Nitrogen and air was continuously pumped through the anode and cathode compartments to maintain anaerobic or aerobic conditions, respectively. Both chambers were mixed with magnetic stir bars to maintain homogeneous conditions.

2.3. MFC-electro-Fenton reactor

In the following experiments, the MFC fungus–bacterium described above was used (Fig. 1a). The H_2O_2 is produced via oxygen reduction in the MFC using a graphite bar as the cathodic electrode (Fu et al., 2010). To reach a high dissolved oxygen concentration, air at a controlled flow rate of 2 L min^{-1} was blown near the cathode. For the *in situ* electro-Fenton reactions to take place in the cathode chamber, the iron dosage was added as iron alginate beads (10 g) to a final iron concentration in the chamber of 150 mg L^{-1}. The fixation of iron onto a matrix permits the operation in continuous mode. The iron alginate beads were obtained by means of a solution of sodium alginate 2.0% (w/v), supplied by Sigma–Aldrich, which was dropped into the hardening solution composed of 0.05 mol L^{-1} $Fe_2(SO_4)_3$ by a peristaltic pump, and spherical alginate beads were formed (Rosales et al., 2012a). The beads formed were cured at 4 °C for 2 h in the gelling solution and then filtered off and washed repeatedly with distilled water and finally stored at 4 °C in distilled water.