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Enhancement of azo dye decolourization in a MFC–MEC coupled system

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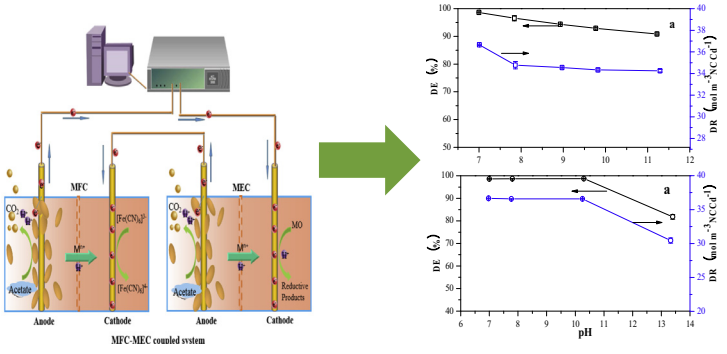
HIGHLIGHTS

- Azo dye removal was significantly enhanced in a MEC assisted by a MFC.
- Substance concentration positively affected system performance.
- Cathodic pH in both MFC and MEC had a slight influence.
- Higher short-circuit current of MFC than MEC is essential for developing coupled system.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) have shown the potential for azo dye decolourization. In this study, a MFC–MEC (microbial electrolysis cell) coupled system was established in order to enhance azo dye decolourization, and the influence of several key factors on reactor performance was evaluated. Moreover, a theoretical analysis was conducted to find the essential preconditions for successfully develop this MFC–MEC coupled system. The results indicate that the decolourization rate in the coupled system had a 36.52–75.28% improvement compared to the single MFC. Anodic acetate concentration of both the MFC and the MEC showed a positive effect on azo dye decolourization, while the cathodic pH of both MEC and MFC in the range of 7.0–10.3 had an insignificant impact on reactor performance in the coupled system. The theoretical analysis reveals that the MFC should have higher short-circuit electricity generation than the MEC before connecting together for a successful coupled system.

1. Introduction

Azo dyes, the most commonly used synthetic dyes in commercial applications, are aromatic compounds with one or more azo double bound groups (Rajaguru et al., 2000). Large quantities of azo dyes can be found in textile industries wastewater, which are toxic and highly persistent to biodegradation, raising attention for environmental concerns. The developed technologies for azo dye treatment involve adsorption by inorganic or organic materials, decolourization or mineralization by photocatalysis and oxidation processes, microbiological or enzymatic decomposition, etc. (Hao et al., 2000).

Microbial fuel cell (MFC), which uses microorganisms as catalysts for oxidation and/or reduction reactions at the electrodes,

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has shown the potential applications for wastewater treatment and energy recovery (Pant et al., 2010; Pant et al., 2012; He et al., 2015). Recently, MFC has also received much attention for its advantage in the decolourization of azo dye from wastewater (Mu et al., 2009; Feng et al., 2010; Sun et al., 2011; Liu et al., 2012). In order to enhance azo dye decolourization in the MFC, previous studies have developed different approaches, such as through optimization of reactor configuration and operation (Solanki et al., 2013), and electrode modification (Li et al., 2006; Liu et al., 2011; Kong et al., 2014). Among all the methods, the most simple way is to provide an external power source, i.e., with a microbial electrolysis cell (MEC) in operational mode, which has been widely adopted to improve azo dye removal in many previous investigations (Wang et al., 2013; Cardenas-Robles et al., 2013; Cui et al., 2014; Shen et al., 2014). However, the energy consumption was considerably high in these researches, therefore reducing electricity supply is one of the key issues for azo dye decolourization in the MEC (Kalathil et al., 2013; Kong et al., 2015).

A MFC–MEC coupled system has been successfully developed for hydrogen generation (Sun et al., 2008) and CO_2 reduction (Zhao et al., 2012) without the need for external energy input. In this coupled system, the electric energy generated from the MFC is provided to the MEC for in situ utilization and thus external power supply is omitted, which is able to save equipment for electricity storage and diminish the power loss. Moreover, the required energy for hydrogen production and CO_2 conversion could be completely harvested from wastes. To the best of our knowledge, so far there are no published reports on the MFC–MEC coupled system for azo dye decolourization.

Therefore, the present study was aimed at investigating the feasibility of the MFC–MEC coupled system for enhancement of azo dye decolourization from wastewater. Methyl orange (MO) was chosen as a model azo dye in this study. A comparison between the MFC–MEC coupled system and the single MFC was initially conducted for MO decolourization, and then the influence of several key factors on the performance of the coupled system was investigated. Moreover, a theoretical analysis was conducted to evaluate the relationship between the MFC and the MEC in successfully developing a coupled system to improve azo dye decolourization.

2. Methods

2.1. Reactor construction and operation

As shown in Fig. 1(a), the coupled system consisted of a MFC and a MEC with the same configuration by assembling two equal rectangular Perspex frames with internal dimensions of $14 \times 12 \times 2$ cm. For each reactor, the chamber volume of the anode and the cathode was 0.336 L, both filled with graphite granules (average diameter 0.20–0.60 cm), making both the volume of net anode compartment (NAC) and net cathode compartment (NCC) 0.12 L. Graphite granules were washed in 32% HCl for 24 h to exclude microorganisms and possible biocatalyst effects (Freguia et al., 2008). The anode and the cathode were separated by a cation exchange membrane (CMI7000, Membranes International Inc., US), and graphite rods with 0.5 cm diameter were used to connect the external circuit. An Ag/AgCl reference electrode was placed close to anode electrode for potential measurement. During our experiments, the closed circulation was connected in series with an electrochemical workstation (VMP3, Bio-Logic Science Instruments, France) for online current measurement during the experiments and the potential was measured by a multimeter (Fluke 15B, Fluke, US).

The bioanodes were developed in two reactors with anaerobic sludge as inoculum and acetate as substrate, as described by Mu et al. (2009). The growth medium (1 L solution contained: KCl, 52 mg; $CaCl_2$, 10 mg; $MgCl_2{\cdot}6H_2O$, 72 mg; $FeSO_4{\cdot}7H_2O$, 3.2 mg; $CoCl_2{\cdot}2H_2O$, 1 mg; $MnCl_2{\cdot}4H_2O$, 0.8 mg; $Na_2Mo_7O_4{\cdot}2H_2O$, 3 mg; H_3BO_3, 0.2 mg; $NiCl_2{\cdot}6H_2O$, 0.5 mg; $CuCl_2{\cdot}2H_2O$, 1.1 mg; $ZnSO_4{\cdot}7H_2O$, 3.2 mg; EDTA, 1 mg; NH_4Cl, 0.31 g) was fed continuously at the flow rate of 540×10^{-6} m^3 NAC d^{-1}. The growth medium contained 50 mM phosphate buffer (17.2 mM KH_2PO_4 and 32.8 mM Na_2HPO_4) to control anodic pH at 7.0. The open circuit potential of the anode was decreased to around −500 mV vs Ag/AgCl after several months, indicating that stable biofilm had formed on the anode electrode in each reactor. The cathode chamber of the MFC was connected with a 1-L bottle containing $K_3Fe(CN)_6$ with phosphate buffer, while the cathode of the MEC was continuously fed with 0.92 mM MO. Both anolyte and catholyte were sparged with nitrogen gas for at least 30 min to remove dissolved oxygen before experiments. Besides, in order to maintain well-mixed conditions and avoid concentration gradients and clogging of the granular matric during continuous feed, both the anolyte and the catholyte were recirculated at an approximate rate of 3 L h^{-1}.

2.2. Experiments

A comparison study was initially carried out between the coupled system and the single MFC at various hydraulic retention times (HRTs) for MO decolourization, and the operational conditions are summarized in Table 1. After that, a series of experiments were conducted to investigate several key factors including anodic substrate concentration and cathodic pH on the performance of the coupled system, as summarized in Table 1. Both anolyte and catholyte contained 50 mM phosphate buffer to maintain pH at 7.0 during experiments, except for cathodic pH investigations. Different cathodic pHs of the MEC were controlled by adjusting phosphate buffer concentration in the feeding of catholyte, while at the cathode of the MFC the pH was changed to various tested values using NaOH solution. Moreover, NaCl was dosed into the cathodic feeding to keep a constant ionic strength (Cheng et al., 2006). Additionally, the reactor was continuously running at an open circuit for 1 week before each experiment in order to exclude the effect of possible MO adoption onto the cathode material.

Each experiment lasted at least 4 days to ensure that the reactor reached to a steady state, judging from the slight variation of azo dye decolourization efficiency and rate as well as anodic and cathodic potentials. The temperature of the MFC–MEC coupled system was maintained at around 25 °C throughout experimental period.

2.3. Analysis and calculation

Samples taken from the reactors were filtered immediately through a 0.22 μm membrane before analysis. For acetate measurement, 2 mL sample was added to 2 mL 10% formic acid solution and then analyzed by a gas chromatography (model 7890A, Agilent Inc., USA), using a polar capillary column (DB-FFAP) at 140 °C and a flame ionization detector at 250 °C. MO and its reductive products were identified and quantified using the high performance liquid chromatography (HPLC, Model 1260, Agilent Co., US) with HC-C18 column (reversed phase column, particle size 5 μm, 4.6×250 mm) and UV-detector (detection wavelength of 245 nm). Ammonium acetate (10 mM, pH 4.0) and methanol were used as the eluent with a volume ratio 1:1 at the flow rate of 0.03 L h^{-1}.

To evaluate the performance of the coupled system, both decolourization efficiency (DE: %) and rate (DR: mol m^{-3} NCC d^{-1})