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Enhanced bio-decolorization of acid orange 7 and electricity generation in microbial fuel cells with superabsorbent-containing membrane and laccase-based bio-cathode

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ABSTRACT

This study investigates the decolorization of the azo dye Acid Orange 7 (AO7) and the simultaneous generation of electricity in air-cathode microbial fuel cells (AC-MFCs) with a fungal bio-cathode. The laccase-producing white-rot fungus *Ganoderma lucidum* BCRC 36123 that was seeded on wood-chips around the cathode of the AC-MFCs functioned synergistically with an anaerobic microbial consortium in the anode chamber to degrade AO7. Superabsorbent polymer (SAP) was mixed with polyvinyl alcohol (PVA) to form a polymer electrolyte membrane (PEM) that separated the cathode from the anolyte of the AC-MFC to provide high proton transfer rate and water retention capacity, promoting the decolorization of AO7 and electricity generation. The solid-state cultivation of *Ganoderma lucidum* yielded 17.3 times more laccase than did the liquid-state cultivation of the same fungus. A maximal open-circuit voltage of 699 mV and a 96.7% decolorization of AO7 at 500 mg/L were achieved in AC-MFCs that were equipped with a PEM with an optimal PVA/SAP ratio of 1:2. A maximal power density of 207.74 mW/m^2, which was 10–15 times those obtained in similar studies in the literature, was obtained at an AO7 concentration of 500 mg/L. Over 84% of the by-products of AO7 decolorization were further degraded in the AC-MFC during a 30 day test period. This study reveals the feasibility of using both the improved PEM and a white-rot fungus in a solid-state culture on the cathode to increase considerably the pollutant removal efficiency of MFCs and the amount of electricity they generate.

1. Introduction

Azo dyes are a large group of synthetic colorants that are extensively used in the leather, textile, paper, and printing industries. These dyes are recalcitrant compounds that frequently accumulate in highly turbid and colored industrial wastewater. Many of these compounds are also toxic or carcinogenic (Chen, 2006; Saratale et al., 2011). Therefore, the efficient treatment of azo dye-containing wastewater has become a critical issue. Adsorption is the conventional method of choice by which activated carbon is often used as the adsorbent for decolorization, but high prices have prevented its large-scale use in wastewater treatment (Saleh et al., 2017; Yang et al., 2011). In recent years, the environmentally friendly method of biodegradation by microorganisms or enzymes has been increasingly regarded as a potential alternative to conventional methods (Kanagaraj et al., 2015; Sen et al., 2016).

Acid Orange 7 (AO7) is a typical azo dye that is used in the textile industry. Many technologies including adsorption and the use of microbial fuel cells (MFC) have been used to remove AO7 from wastewater. However, most of these methods only decolorize AO7-containing wastewater by breaking the azo bond (–N=N–) of AO7 without completely mineralizing the pollutant. Breaking the azo bond of AO7 yields the toxic products sulfanilic acid and 1-amino-2-naphthol (Fernando et al., 2012; Mani et al., 2017), both of which can only be degraded completely by a prolonged aerobic process (Fernando et al., 2014).

The MFC is a green energy device that uses bacteria in its anode

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chamber to degrade oxidatively organic compounds with a concomitant reduction of atmospheric oxygen at the cathode to produce electricity (Gude, 2016). MFC technology has been developed rapidly and the areas in which it can be used have expanded in recent years (Zhang et al., 2016). For example, the MFC has been used successfully to decolorize in the decolorization of azo dye-containing wastewater (Xu et al., 2017). However, the high cost of the platinum catalyst that is used in this process limits its further development. The MFC will become a practical device for azo-dye removal only when a low-cost and sustainable catalyst can be used.

Many white-rot fungi produce and excrete laccase, a copper-containing oxidative enzyme that extracts a single electron from phenolic or aromatic amine molecules and transfers it to atmospheric oxygen. Accordingly, laccase has the potential both to act as a cathode catalyst that transfers electron from the cathode to oxygen molecules and to participate directly in the degradation of recalcitrant aromatic compounds (Lee et al., 2014; Pozdnyakova et al., 2006). Although commercially available from many sources, purified laccase is expensive and requires repetitive replenishment during continuous MFC operation because enzyme activity can drop rapidly under harsh environmental conditions (Mani et al., 2017). An alternative is the use of solid-state cultivation of live fungal mycelium that continuously generates laccase.

In this work, solid-state cultivation (Rodríguez-Couto, 2012) or solid-state fermentation (Pandey et al., 2000) refers to the attachment and growth of white-rot fungi on solid substrates that simulate the natural habits of the fungi. Agricultural wastes, such as barley bran, wheat straw, barley straw, and wood shavings, are the preferred materials for use in solid substrates as they provide essential nutrients in support of fungal growth and stimulate the steady production of excreted enzymes including laccase. In MFCs, these fungi facilitate dye decolorization by generating laccase, catalyzing the reduction of oxygen at the cathode (Couto et al., 2002).

In a hydrogen fuel cell, the cathode and anode are always separated by a proton exchange membrane, which prevents the mixing of gaseous hydrogen and oxygen while allowing the passage of protons. In many microbial fuel cells, a Nafion® membrane (Dupont) is used in place of a salt bridge to shorten the inter-electrode distance and to separate the anolyte from the catholyte as their mixing can theoretically reduce the voltage and the columbic efficiency of the cell. However, an MFC does not have to have a separating membrane, and its presence sometimes worsens electrochemical performance by increasing internal resistance and permitting the passage of both dissolved oxygen and substrate molecules (Kim et al., 2007; Leong et al., 2013). These shortcomings of the Nafion membrane and its high cost have prompted researchers to find and test alternatives such as cation exchange membrane, anion exchange membrane, ultra-filtration membrane, and ionic liquid immobilized polymer membrane (Hernández-Fernández et al., 2016; Kim et al., 2007; Koók et al., 2017; Leong et al., 2013). Additionally, hydrogel has been introduced to improve electrode-membrane contact and to increase the water content of an air cathode-membrane assembly (Kim et al., 2009).

In this investigation, superabsorbent polymers (SAP) were tested as materials for making the polymer electrolyte membrane (PEM). SAP is a polymer with a high molecular weight that contains many hydrophilic carboxyl (−COOH) and hydroxyl (−OH) substituents and swells in water (Essawy et al., 2016). Although not water-soluble, SAP can absorb hundreds to thousands of times its own mass of water, and is characterized by its high water absorbency and retentive capacity (Chang et al., 2010). Therefore, SAP is extensively used in horticulture, agriculture, and construction (Cuadri et al., 2017), and is present in many house-hold items, including dehydrating agents, thickeners, soil amendments, flocculants, dispersants, and water absorbents in napkins and diapers (Ambrosio et al., 2011).

In this study, SAP-containing PVA gel was used to improve the proton transfer efficiency of the PEM, and to increase its water absorbency and water retention to enable water easily to reach the cathode to establish moist conditions that favor fungal proliferation and pollutant degradation.

2. Material and methods

2.1. Screening and cultivation of white-rot fungi

Four species of white-rot fungi, *Trametes polyzona*, *Trametes hirsute*, *Ganoderma lucidum*, and *Simplicillium obclavatum* were tested to measure their laccase production using solid-state cultivation. The mycelia of these fungi were inoculated on potato dextrose agar (PDA) plates to form sclerotia. One 1 cm × 1 cm square of a sclerotium was cut from a PDA plate using a sterile knife and (1) dropped into 200 mL of potato dextrose broth (PDB) in an Erlenmeyer flask for liquid-state cultivation for 1 week at 25 °C or (2) mixed with 10 g of wood chips and 1 g of rice grains that were wetted with 10 mL of PDB for solid-state cultivation for 1 week at 25 °C.

2.2. Configuration and operation of air-cathode microbial fuel cell

An air-cathode microbial fuel cell (AC-MFC), presented in Fig. 1, which was composed of a fungal chamber (0.5 L) and an anode chamber (1 L) that were made from cylindrical polypropylene bottles, was constructed. The centers of the two chambers were connected by a perforated plastic pipe that was filled with a mixture of SAP and PVA to form the PEM. Both electrodes were carbide porous ceramic (CPC) rings (with an inside diameter of 0.6 cm, an outside diameter and height of 1.3 cm, and surface area of 10.83 cm^2) (Menchavez et al., 2014; Valdés-Solís et al., 2001). The anolyte comprised 450 mL of sludge from a wastewater treatment plant for the dyeing industry, 0.5 L of a phosphate buffer solution, and 50 mL of an AO7 solution with a concentration of 30–1000 mg/L. One hundred microliters of ethyl acetate was added daily as a co-substrate.

2.3. PEM characteristics

To evaluate the proton transfer of the PEM, PVA and SAP were mixed in various ratios to form PEM hydrogel, which was sandwiched between two 0.6 L H-type Pyrex glass bottles. One of the bottles was filled with 0.5 L of 0.1 M HCl solution, and the other was filled with 0.5 L of de-ionized water. The concentration of hydrogen ion was measured using a pH meter (SX751, Major science).

The water absorbency of PEMs was determined using an experimental setup similar to that shown in Fig. 1 by firstly placing the PEM on the water surface and dry wood chips on the surface of the PEM, and then measuring the weight of wood chips after one day. The water absorbency (WA) was calculated from the dry weight (DW) and the wet weight (WW) of wood chips using the equation WA = (WW - DW)/DW.

2.4. Electrochemical analyses

MFC was continuously monitored using a data collection system that was connected to a digital electronic multimeter (Model 2700, Keithley Instrument, USA). Polarization and power curves were plotted using the single-cycle method (Noori and Darzi, 2016) by varying the external resistances from 510 kΩ to 30 Ω.