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Review article

Performance and recent improvement in microbial fuel cells for simultaneous carbon and nitrogen removal: A review

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ABSTRACT

Microbial fuel cells (MFCs) have become a promising technology for wastewater treatment accompanying electricity generation. Carbon and nitrogen removal can be achieved by utilizing the electron transfer between the anode and cathode in an MFC. However, large-scale power production and high removal efficiency must be achieved at a low cost to make MFCs practical and economically competitive in the future. This article reviews the principles, feasibility and bottlenecks of MFCs for simultaneous carbon and nitrogen removal, the recent advances and prospective strategies for performance improvement, as well as the involved microbes and electron transfer mechanisms.

Introduction

Carbon and nitrogen contamination in wastewater is a worldwide environmental problem. Conventional biological treatment of wastewater requires an additional carbon source and power input to maintain high removal efficiency, which increases the treatment cost (Pous et al., 2015; Puig et al., 2012). In addition, a large amount of sludge is generated during the denitrification process. Wastewaters are increasingly recognized as renewable resources in addition to wastes. The conflict between the existing wastewater treatment technologies and the struggle for conservation of energy has driven the development of sustainable processes (Virdis et al., 2010).

Recently, MFCs have been widely used as an alternative technology due to the advantages of higher contaminant removal efficiency than the conventional biological treatment techniques, bioelectricity generation, no need for energy and carbon addition, and less excess sludge generation (Jia et al., 2008; Kim et al., 2007; Kondaveeti and Min, 2013; Rahimnejad et al., 2015; Wang et al., 2015; Wu et al., 2015). MFCs have the potential of being applied in bioenergy generation, wastewater treatment, and synthesis of valuable added materials (ElMekawy et al., 2015; Ryu et al., 2013; Zhang et al., 2014a). Great efforts have been made toward producing energy from wastewater using MFCs in the past years. Nitrate is deemed to be removed at the cathode during the process of denitrification (Huang et al., 2013c; Puig et al., 2011). In comparison to the traditional biological treatment, this new approach reduces the carbon requirements per nitrogen denitrified by minimizing the competition between aerobic and anaerobic microorganisms for carbon oxidation (Virdis et al., 2011).

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In this article, we review the electron transfer mechanisms, together with the feasibility, performance, and bottlenecks of carbon and nitrogen removal in MFCs. Furthermore, recent advances and prospective strategies that can improve the performance of MFCs are discussed. This review is expected to give an informative overview of the current development, and to encourage more thinking and investigation toward further sustainable development of efficient technologies for contaminant removal and electricity generation in a MFC.

1. Principle of microbial fuel cells (MFCs) for simultaneous carbon and nitrogen removal

1.1. MFCs

A microbial fuel cell (MFC) is a bio-catalyzed electrochemical system which can directly convert chemical energy to electrical energy through a series of redox reactions (Rahimnejad et al., 2015; Venkata Mohan et al., 2014). The half-cell reactions of the anode and cathode in MFCs are listed (Table 1). During the carbon and nitrogen removal process in an MFC, the principle relies on the fact that organic substrates are oxidized by electroactive bacteria in the anode chamber and produce electrons. The produced electrons are then transferred from anode to cathode through an external circuit. Microorganisms in the cathode chamber subsequently denitrify the nitrate by taking up the electrons (Fig. 1).

1.2. Electron transfer mechanisms

Electron transfer between microbes and electrodes determines the energy conversion and efficiency of wastewater treatment. The electron transfer mechanisms at the anode have been widely investigated, however, the transfer mechanisms from the cathode to microorganisms are poorly understood (Kracke et al., 2015; Rosenbaum et al., 2011).

Electrons produced from the oxidation of carbon are transferred to the anode by means of several mechanisms: direct as well as mediated electron transfer mechanisms (Kracke et al., 2015; Mook et al., 2013b; Rahimnejad et al., 2015; Schroder, 2007). Direct electron transfer (DET) refers to electrons transferred by c-type cytochromes (CTCs), flavin bound to c-type cytochromes and conductive pili, which may serve as biological nanowires (Fig. 2) (Debabov, 2008; Yang et al., 2012; Reguera et al., 2005; Okamoto et al., 2014a; Okamoto et al., 2014b). Mediated electron transfer (MET) means the addition of external electron mediators to shuttle electrons between electrodes and microorganisms that are unable to carry electrons directly to the electrodes (Lovley, 2006; Mook et al., 2013b).

The electron transfer process of the cathode for nitrogen removal focuses on electron transfer from the biocathode to microorganisms. To date, two main mechanisms have been reported, namely direct and mediated electron transfer. The direct electron transfer mechanism was demonstrated with *Geobacter* species that were able to retrieve electrons directly from a graphite electrode, and used these electrons to reduce nitrate to nitrite (Gregory et al., 2004). Besides pure-culture systems, electron transfer has also been demonstrated to be involved in transformation of nitrate to N_2 in mixed-culture biocathodes (Chen et al., 2010; Zhu et al., 2013). While some bacteria perform direct electron transfer, some microorganisms can excrete redox-active compounds to carry out mediated electron transfer with electrodes. *Acinetobacter calcoaceticus* was prevalent in a mixed-culture microbial cathode (Rabaey et al., 2008). Besides the self-excreted redox-active compounds, microorganisms can also accept electrons from a solid-state electrode via the cathodic production of hydrogen or the reduction of various external added mediators (Huang et al., 2011).

Table 1 – Half-cell reactions of the anode and cathode.

	Half-cell reactions	Reference
Anode	$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9\ H^+ + 8e^-$	Cheng et al. (2012)
	$C_2H_{12}O_2^- + 4H_2O \rightarrow 2HCO_3^- + 9\ H^+ + 8e^-$	Mook et al. (2013b)
	$C + 2H_2O \rightarrow CO_2 + 4\ H^+ + 4e^-$	Mook et al. (2013b)
Cathode	$2NO_3^- + 10e^- + 12\ H^+ \rightarrow N_2 + 6H_2O$	Cheng et al. (2012)
	$NO_3^- + 2e^- + 2\ H^+ \rightarrow NO_2^- + H_2O$	Nguyen et al. (2015)
	$NO_2^- + e^- + 2\ H^+ \rightarrow NO + H_2O$	Nguyen et al. (2015)
	$NO + e^- + H^+ \rightarrow 0.5N_2O + 0.5H_2O$	Nguyen et al. (2015)
	$0.5N_2O + e^- + H^+ \rightarrow 0.5\ N_2 + 0.5H_2O$	Nguyen et al. (2015)
	$O_2 + 4e^- + 4\ H^+ \rightarrow 2H_2O$	Du et al. (2007)

1.3. Simultaneous carbon and nitrogen removal using MFCs

There has been research on organics removal and bioelectrochemical denitrification in microbial fuel cells. It has been shown that the redox potential of $NO_3^-/0.5N_2$ (+0.74 V at pH 7) has similarity to that of O_2/H_2O (+0.82 V at pH 7), and has been

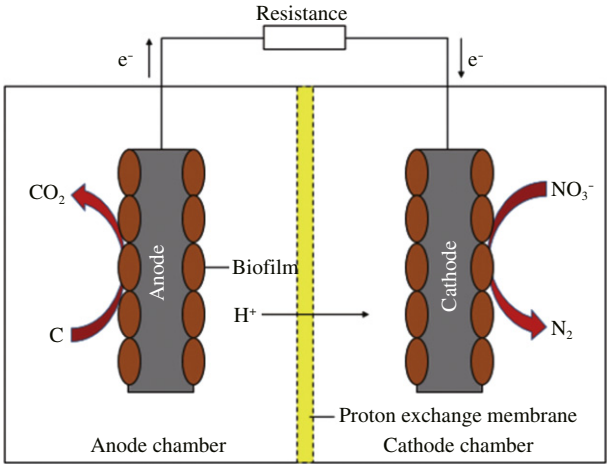

Fig. 1 – Schematic of simultaneous carbon and nitrogen removal in a typical two-chamber microbial fuel cell.