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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.

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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

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

	Half-cell reactions	Reference
Anode	$\text{CH}_3\text{COO}^- + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^-$	Cheng et al. (2012)
	$\text{C}_2\text{H}_{12}\text{O}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 9\text{H}^+ + 8\text{e}^-$	Mook et al. (2013b)
	$\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$	Mook et al. (2013b)
Cathode	$2\text{NO}_3^- + 10\text{e}^- + 12\text{H}^+ \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$	Cheng et al. (2012)
	$\text{NO}_3^- + 2\text{e}^- + 2\text{H}^+ \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$	Nguyen et al. (2015)
	$\text{NO}_2^- + \text{e}^- + 2\text{H}^+ \rightarrow \text{NO} + \text{H}_2\text{O}$	Nguyen et al. (2015)
	$\text{NO} + \text{e}^- + \text{H}^+ \rightarrow 0.5\text{N}_2\text{O} + 0.5\text{H}_2\text{O}$	Nguyen et al. (2015)
	$0.5\text{N}_2\text{O} + \text{e}^- + \text{H}^+ \rightarrow 0.5\text{N}_2 + 0.5\text{H}_2\text{O}$	Nguyen et al. (2015)
	$\text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O}$	Du et al. (2007)

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).

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 $\text{NO}_3^-/0.5\text{N}_2$ (+0.74 V at pH 7) has similarity to that of $\text{O}_2/\text{H}_2\text{O}$ (+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.

Fig. 2 – Direct electron transfer mechanisms via (a) outer membrane cytochrome, (b) conductive nanowire, and (c) flavin bound to c-type cytochrome.

demonstrated that nitrate is competitive with oxygen as an electron acceptor (Fang et al., 2011). It was recently shown that nitrate and also nitrite could effectively be used to drive current generation and simultaneous carbon and nitrogen removal. Intensive studies have been carried out to determine the feasibility of carbon and nitrogen removal using MFCs (Feng et al., 2015; Mook et al., 2012; Ryu et al., 2013; Sayess et al., 2013; Viridis et al., 2010; Xie et al., 2011; Zhang et al., 2013). Removal of carbon and nitrogen from food, swine, and aquaculture wastewater using MFCs has been increasingly reported (Blanchet et al., 2015; ElMekawy et al., 2015; Lim et al., 2012; Ryu et al., 2013; Vilajeliu Pons et al., 2015). Kuroda et al. (1996) reported that COD and nitrates could be removed simultaneously when the C/N ratio was less than 2.8. Lefebvre et al. (2008) designed a two-chambered MFC with a denitrifying biofilm in the cathode, and this system generated up to 9.4 mW/m² power density at the anode surface for more than 1.5 month, while removing over 65% of COD, 84% of TN, and 30% of suspended solids, with domestic wastewater as a substrate. Yan and Regan (2013) doubled the gas diffusion area by adding an additional air cathode or a diffusion cloth, and this procedure was found to significantly increase the ammonia and COD removal rates. Viridis et al. (2010) found carbon and nitrogen removal were 100% and 94.1 ± 0.9 under the COD/N ratio of 4.49 ± 0.01 and DO of 4.35 ± 0.08 mg/L at the cathode, produced through specific aeration. Zhang et al. (2013) developed a single chamber MFC with a rotating biocathode, and they found that the removal efficiencies of TOC and TN were 85.7 ± 7.4% and 91.5 ± 7.2% with a maximum power output of 585 mW/m³ with a COD/N ratio of 5:1. These proved that MFCs had great potential to be applied in removing carbon and nitrogen from wastewater.

However, there are also several drawbacks that block the application of MFCs: (1) the anaerobic conditions in the anode chamber inhibit the contaminant removal, which prefers aerobic conditions (Kelly and He, 2014); (2) significant pH drift occurs in the electrode-biofilm, due to the generation and consumption of protons by the oxidation of carbon and the denitrification of nitrate, respectively (Cheng et al., 2012); (3) poor efficiency of electron transfer, at both the anode and

cathode (Pham et al., 2009); (4) high overpotential loss and poor electricity productivity (Clauwaert et al., 2008; Hamelers et al., 2010); (5) the volume of MFC reactors in most studies is limited to a small scale due to the poor electricity generation (Cheng et al., 2012; Kondaveeti and Min, 2013; Liu et al., 2005; Puig et al., 2011; Van Doan et al., 2013), so that it is crucial to solve the problem of reactor scale-up for further application of the technology.

2. Recent advances in improving the performance of MFCs

2.1. Improvement of the electrode materials and reactor configurations

Electrode and reactor configurations can affect the power output, microbial growth community and removal efficiency. A summary of results obtained in carbon and nitrogen removal by using a variety of electrode materials and different reactor configurations of MFCs are listed in Table 2.

Electrodes act as the electron acceptor or donor as well as the carrier for the microorganisms. Carbon-based materials, such as granular activated carbon, fiber, and graphite, are widely used as electrodes because of their mechanical strength, biocompatibility, and rough surface (Guo et al., 2015b; Mook et al., 2013b). However, their application is limited by low electrical conductivity and high cost (Guo et al., 2015a). It was found that a rough surface and larger electrode surface area promoted bacterial adhesion and colonization and that high-energy surfaces collected more bacteria, and selected for specific bacteria, which could improve the efficiency of simultaneous carbon and nitrogen removal (Huang et al., 2011). Thus, the modification and pretreatment of electrodes and utilization of more efficient materials have been suggested by many researchers. A number of studies have been focused on changing materials to increase electroactive bacteria and denitrifying bacteria attachment area and amount. In the case of biocathode MFCs, the increase of cathode surface area could increase the quantity of catalyst bacteria on the cathode (Logan, 2009) and thereby improve the performance of the MFC by decreasing the activation overpotential in the biocathode.

Optimal configuration of MFCs can increase the efficiency of electricity generation by minimizing the internal resistance. The performance can be improved by shortening the electrode distance and enlarging the membrane surface area. Liu and Logan (2004) developed an air-cathode in an MFC, which could increase the oxygen reduction and power output and reduce the cost because of the passive diffusion of oxygen. Ryu et al. (2013) reported a loop configuration MFC which was used to eliminate the pH gradient, and COD and nitrogen removal rates of 0.523 and 0.194 kg/m³/day were achieved, while generating a stable power density of 1081.6 mW/m³. A three-stage rotating bioelectrochemical contactor, integrating an MFC with rotating biological contactor (RBC) technology, was constructed for the removal of carbon and nitrogen, and it was found that the RBC-MFC unit presented better nitrogen removal compared to the RBC unit (Sayess et al., 2013). An MFC system coupled with an

Table 2 – A summary of results obtained in simultaneous carbon and nitrogen removal by reforming the electrode materials and reactors configuration of MFCs.

Configuration	Electrode material		Results	Reference
	Anode	Cathode		
MFCs and nitrification reactor	Granular graphite	Granular graphite	COD: 2 kg/(m ³ NCC·day) NO ₃ -N: 0.41 kg/(m ³ NCC·day) Current density: 133.3 ± 1.0 A/m ³ NCC	Virdis et al. (2008)
Oxic/anoxic-biocathode MFC	Graphite felt	Graphite felt	COD: 98.8% NH ₄ ⁺ -N: 97.4% TN: 97.3% Power density: 14 W/m ³ NCC	Xie et al. (2011)
Cylindrical MFC	Carbon brush	Carbon filtration	TOC: 93.6% NH ₄ ⁺ -N: 97.2% TN: 91.6% Power density: 581.5 mW/m ² Current density: 1671.4 mA/m ²	Pandit et al. (2012)
A tubular dual-cathode MFC	Carbon cloth	Outer: Pt-coated carbon cloth Inner: Carbon brush	Organic: 85%–99% TN: 66.7%–89.6%	Zhang and He (2012)
A single chamber MFC with a rotating biocathode	Carbon felt	Carbon felt	TOC: 85.7% ± 7.4% TN: 91.5% ± 7.2% Power density: 585 mW/m ³	Zhang et al. (2013)
Membrane-less MFC	Carbon cloth	Carbon cloth	COD: 100% Nitrate: 36.7% Power density: 0.0712 W/m ³ Current density: 0.844 A/m ³	Zhu et al. (2013)
Up-flow undivided reactor	Nano-crystalline PbO ₂ coated carbon	Granular activated carbon	Organic matter removal: 83% Nitrate: 99%	Mook et al. (2013a)

oxic-biocathode MFC and an anoxic-biocathode MFC could provide maximum COD, NH₄⁺-N and TN removal rates of 98.8%, 97.4%, and 97.3% (Xie et al., 2011).

2.2. Optimization of operational conditions

Operational parameters such as, C/N ratio, potential, external resistance, concentration level of electron acceptors, and pH, greatly influence the performance of MFCs.

C/N ratio can affect contaminant removal and by-product formation. Huang et al. (2013b) found that increasing the C/N ratio benefited the nitrate removal of the MFC and inhibited nitrite accumulation. Zhou et al. (2007) developed a three-dimensional biofilm electrode reactor to remove nitrate and organic pollutants, and they found that nitrite accumulation increased significantly when the C/N ratio decreased from 2.5 to 0.97.

The anode potential regulates the growth and electrochemical activity of the microorganisms in an MFC (Aelterman et al., 2008; Busalmen et al., 2008; Kokko et al., 2015). The cathode potential affects the treatment efficiency and intermediate products during nitrate reduction. Different bacterial communities were enriched in a biofilm developed with the cathode biased at different potentials (Kim et al., 2015). The nitrate removal rate increased from 1.05 to 5.44 mg NO₃-N L/NCC/hr when the cathode potential decreased from +597 to 403 mV vs SHE. The highest rate of nitrate conversion to N₂ (93.9%) occurred at −123 mV using water as anode electron donor (Pous et al., 2015). The cathode potentials also could regulate the transformation of nitrate to N₂ or ammonium in nitrate removal (Zhang et al., 2014b).

The external resistance may also influence the MFC performance by affecting the structure of the biofilm in the anode and

current generation of the MFCs. Zhang et al. (2011) found biofilm with a higher external resistance tended to form a compact structure with less active biomass. This led to an increase of the maximum power density with the decrease of external resistance. However, when the external resistance was lower than the optimum value, a loose biofilm structure with a less active biomass would be developed, resulting in more void spaces, which would benefit proton and buffer transport and reduction of the electrical conductivity within the biofilm.

The concentration of electron acceptors determines power generation in MFCs, because electron acceptors can reduce the potential losses on the cathode (Du et al., 2007; He et al., 2015). Oxygen is the most commonly used electron acceptor in MFCs for the cathodic reaction. A low DO would cause ammonia accumulation in the final effluent, while a high DO would inhibit denitrification, resulting in nitrate accumulation (Kelly and He, 2014). Therefore, it is important to determine the optimal DO value. Yu et al. (2011) suggested that at 0.5 mg/L DO, a membrane-aerated MFC had the highest COD (>97%) and nitrogen removal (52%).

pH is another important factor affecting the performance because of its effects on microbial metabolism and overpotential. Clauwaert et al. (2009) found that nitrogen removal was increased from 0.22 to 0.50 kg NO₃-N m^{−3} NCC day^{−1} by maintaining the pH in the cathode chamber at 7.2. During the carbon and nitrogen removal process, production of protons at the anode and consumption of protons at the cathode may cause a pH drift, and this is expected to inhibit the biofilm activity. Several researchers attempted to minimize the pH drift. Kelly and He (2014) suggested that protons generated from the anode could buffer the high pH in the catholyte due to oxygen reduction. Cord Ruwisch et al. (2011) demonstrated that the ammonium/

ammonia couple can be used to control electrolyte pH by shuttling protons from the anolyte to the catholyte in a two-chamber bioelectrochemical cell equipped with a cation exchange membrane. To control the pH drift without adding external chemicals, Cheng et al. (2012) developed a single electroactive biofilm operated as both a bioanode and a biocathode, and it was found the alkalinity produced from cathodic denitrification partially (19%) neutralized the acidity of the anodic reaction. This system, to some degree, avoids the pH drift, which can severely inhibit biofilm activity and eventually stall the entire process and lower the removal efficiency.

3. Microbiological approaches

The microbial community and biofilm formation on the electrode surface significantly influence a system's performance (Huang et al., 2013a). Electroactive bacteria (EAB) grown and enriched at the anode offer an opportunity for the development of an efficient and sustainable technique for production of energy. The EAB biofilm formation is influenced by anode materials, temperature, pH, and external resistance (Liu et al., 2010; Patil et al., 2010, 2011; Zhang et al., 2011). Thus, one strategy for high power output is to enrich the EAB on the anode surface and optimize the bacteria-electrode electron transfer (Carmona Martinez et al., 2013; Venkata Mohan et al., 2014). Zhao et al. (2015) fabricated hybrid electroactive biofilms by inserting bacteria into graphene-carbon-nanotube networks as an anode for MFCs. This novel strategy greatly enhanced direct extracellular electron transfer between *Shewanella oneidensis* and the electrode. A cathode biofilm served as a barrier for ions migrating to the cathode-electrolyte interface (Ahmed and Kim, 2011). The biocathode can be enriched with amphiphilic microorganisms that can accept electrons by reducing oxygen, nitrate and metal ions. Kim et al. (2015) found the performance of an MFC can be improved through the use of electrochemically-active oxygen-reducing bacteria, which act as the cathode biocatalyst.

Another approach to improve the performance of MFCs is to refine the structure of the biofilm. Biofilm formation is critical for electron transfer and bioelectrogenic activity. However, thick biofilm deposition hampers the electron flow. Hence, the selection of biofilm thickness is important for achieving significant power output (Venkata Mohan et al., 2014). Reguera et al. (2006) found that a biofilm of *Geobacter sulfurreducens* with 50 μm thickness could produce conductive pili without decreasing the current production. Clauwaert et al. (2008) suggested that an open, 'coral-like' biofilm structure with a high specific surface area was likely to supply more electroactive species. In addition, a compact and dense biofilm could shorten the electron transfer distances to improve the electron transfer efficiency, but might increase concentration gradients between the substrate and product.

4. Conclusions and future prospects

The available literature has demonstrated the feasibility and performance of simultaneous carbon and nitrogen removal using MFCs. Recent advances that improve the performance

of MFCs mainly focus on the electrode materials and surface area, reactor configurations, and optimization of operational conditions, while novel and integrative strategies of microbiology involved in the carbon and nitrogen removal process need to be clarified for practical application.

MFCs are currently limited to laboratory studies due to their poor power output. Future studies are needed to improve the electron transfer rate and minimize the voltage losses in MFCs. Thus, from the viewpoint of engineering, intensive research should focus on the development of inexpensive and efficient electrodes, and especially reducing the cost of the cathode. Priority should be given to electrode designs that ensure an active surface and materials that have excellent electrical conductivity and biocompatibility. Another direction worthy of investigation is combining MFCs with aerobic and anaerobic biological technology. From the point of view of microbiology, it is vital to explore the relevant principles of microbiological ecology, including electroactive bacteria metabolism, the development of efficient electroactive bacteria, the interactions between microbial community with themselves and electrodes, and the role of biofilm and strategies to optimize the biomass density and biofilm structure.

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