Bioresource Technology 143 (2013) 76–82

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

A decentralized wastewater treatment system using microbial fuel cell techniques and its response to a copper shock load

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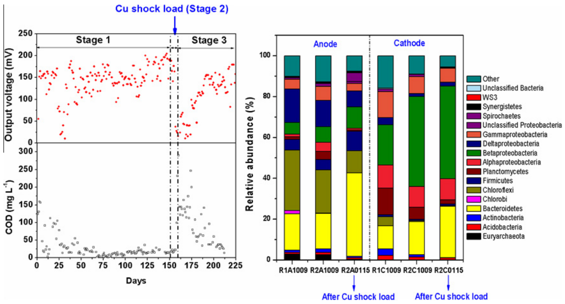
HIGHLIGHTS

- A bench-scale decentralized wastewater treatment system using MFC techniques was developed.
- Immobilized *P. pantotrophus* cells enhanced denitrification in the cathodic chamber.
- The developed MFC system could recover from a copper shock load.
- The copper shock load significantly changed the microbial composition in the MFC.

GRAPHICAL ABSTRACT

COD concentration and output voltage change of NDMFC without and with the Cu shock load (left panel); anode and cathode microbial community composition obtained from pryosequencing (right panel).



ARTICLE INFO

Article history:
Received 9 March 2013
Received in revised form 7 May 2013
Accepted 9 May 2013
Available online 17 May 2013

Keywords:
Microbial fuel cells
Nutrient removal
454 Pyrosequencing technique
Microbial community
Cu shock load

ABSTRACT

Bench-scale decentralized wastewater treatment systems using microbial fuel cell (MFC) techniques were constructed for simultaneous removal of carbonaceous and nitrogenous pollutants and electricity production from wastewater. The MFC was operated in continuous mode and immobilized *Paracoccus pantotrophus* cells were added in the cathodic compartment to achieve simultaneous nitrification–denitrification. After 150-day operation, the MFC system could effectively remove >96% COD and 100% ammonium, with 60–80% total nitrogen removal and around 0.2 V voltage production. The results of copper (Cu) shock load showed that although 125 mg L^{-1} Cu (II) would deteriorate the effluent quality and completely inhibit the electricity production, the microbial populations restored their ability to treat wastewater and produce electricity after a period around 30 days. Community analysis by the 454 pyrosequencing technique showed that the microbial compositions were significantly different and decreased in diversity after the Cu shock load.

1. Introduction

Microbial fuel cells (MFCs) have attracted increasing attention as an emerging technology which converts energy contained in organic matter to useful electrical power directly (Logan et al., 2006). Simultaneous removal of organic matter and nitrogenous compounds has been demonstrated in different MFC-based bioreactors. In the cathodic chamber, biological denitrification can be accomplished through a bio-cathode with electrons supplied by microorganisms oxidizing organic substrates at the anode (Clauwaert et al., 2007). Virdis et al. (2008) improved the design to achieve nitrification and denitrification by a “loop configuration”, which used an external aerobic nitrification bioreactor for oxidizing ammonium to nitrate before nitrate solution flowed into the cathodic chamber for denitrification. Virdis et al. (2010) further developed another more complex MFCs that allowed simultaneous nitrification and denitrification at the cathodic chamber through one loop

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http://dx.doi.org/10.1016/j.biortech.2013.05.038

connecting the anode and cathode, two recirculation, and some external control equipments which were used to vary dissolved oxygen (DO) and C/N ratios. These studies have shown that biological denitrification could be achieved in MFCs through bio-cathode. However, according to the redox potential between $NO_3^-/0.5\ N_2$ (+0.74 V) and O_2/H_2O (+0.82 V), it seems that the denitrification process could be limited by the competition between oxygen and nitrate as the electron acceptor (Jia et al., 2008), and this will bring challenges to the systems. Therefore, studies have developed different ways instead of using bio-cathode to achieve simultaneous removal of organic matter and nitrogenous compounds in MFCs. For example, Yu et al. (2011) developed a continuous flow membrane aerated MFC (MAMFC) which can control the DO concentration at low level (<0.5 mg L^{-1}) in the cathodic chamber to achieve simultaneous nitrification and denitrification. However, the nitrogen removal of MAMFC was only 52% and the control of membrane aeration was laborious. Considering that both the external set-up and external control equipments may raise the cost and need more power consumption, development of new MFCs which are easily to operate, low-cost and higher nitrogen removal efficiencies is still necessary.

Meanwhile, it is noticeable that wastewater composition could contain potential toxicants such as heavy metals. Heavy metals have been reported in significant concentrations in various wastewater streams (Hu et al., 2004; Liang et al., 2010). Although a low level exposure does not affect microbial activity and viability remarkably, sudden surges of high concentration metals could deteriorate the performance of the biological treatment process and disturb microbial population. The MFC is a new technique which uses microorganisms on the anode to catalyze the conversion of organic matters into electricity. If high concentration toxic metals occur in the influent, metabolic activity of anaerobic bacteria at the anode will be inhibited, and the effects can be reflected by the variation of voltage data. Therefore, it has the potential to be used as a quick-responding indicator for toxic substances in the influent. Up to now, most effort has been focused on the development of MFCs for wastewater treatment, whereas only a limited number of studies focused on MFC response to shock load of toxicants (Kim et al., 2007; Dávila et al., 2011). In addition, sudden shock load of toxicants may lead to the changes of microbial population in MFCs and these changes are still unclear.

In this study, a membrane-less MFC combining autotrophic nitrification and aerobic denitrification was developed as a new decentralized wastewater treatment system. The electricity production as well as the nitrogen removal efficiency was examined under closed circuit. A copper (Cu) shock load which is high enough to completely inhibit the electricity production was applied to test the ability of the system to recover from the shock load. The microbial community changes before the shock load and after the regained electricity production were analyzed using 454 pyrosequencing. The results of this study suggested that the newly designed MFC system not only had the potential for wastewater treatment with electricity production and total nitrogen removal but also had the ability to recover from a shock load.

2. Methods

2.1. Chemicals and reagents

Polytetrafluoroethylene (PTFE) (60% dispersion in water), Tetrahydrofuran (THF) (⩾96.5% pure), Iron (II) phthalocyanine (FePc) (⩾96% pure) were purchased from the J&K Scientific Ltd. Carbon nanoparticles (Vulcan XC-72) with 254 $m^2\ g^{-1}$ in surface area and 30 nm in particle size were obtained from the Cabot Corporation in U.S.

2.2. MFC configuration and operation

Two three-rectangular-chamber MFC bioreactors (anode chamber, cathode chamber and clarifier) were constructed according to the previous study (Yu et al., 2011) with slight modification. The three compartments were separated by Plexiglas baffle without conventional PEM. The effective volumes of each chamber were 1.1, 1.6 and 0.9 L. Two holes with a diameter of 5 mm were made on the baffle between the anodic and cathodic compartments to allow wastewater to flow though the system. Carbon cloth with a size of 10 × 10 cm was used as the electrode in both the anodic and cathodic compartments. The cathode was a composite electrode of carbon cloth loaded with 2 mg cm^{-2} FePc and carbon nanoparticles mixture using PTFE as a binder, which was prepared according to (Zhao et al., 2005). Inexpensive non-noble metal FePc was used as the cathode catalyst based on oxygen reduction as an alternative to Pt for MFCs. A layer of micro-fibrous non-woven fabric cloth (with a surface are of 100 cm^2) was on both sides of the cathode to support nitrifying biofilm formation. The cathodic chamber was sparged with air to provide enough DO (around 2.0 mg L^{-1}) for the reactions of electrons, protons and oxygen at the cathode. The anode and cathode electrodes were connected with Ti wire (0.5 mm in diameter) through a fixed external resistance of 1 kΩ. Sludge which was collected from a municipal wastewater treatment plant in Xiamen was cultured for almost one month under anaerobic and nitrifying conditions respectively as inocula to accumulate electrochemically active microorganisms at the anode and nitrifying bacteria at the cathode.

Aerobic denitrifying bacterium *Paracoccus pantotrophus* ATCC 35512, obtained from the Bioresource Collection and Research Center, Food Industry Research and Development Institute, Hsinchu, Taiwan, were immobilized with cellulose triacetate as mono-carrier using the method described in the previous study (Yang et al., 1988). The immobilized *P. pantotrophus* cells were added to the cathodic chamber of one MFC to achieve simultaneous nitrification and denitrification (hereinafter, refer to as NDMFC) while the other MFC without the immobilized *P. pantotrophus* was operated as control (hereinafter, refer to as NMFC). The two MFCs were continuously fed with a synthetic wastewater as previously described (Yu et al., 2011). Sodium acetate was used as the sole carbon source in the influent. Both the MFCs were developed for decentralized wastewater treatment and operated for 212 days (from June 2011 to January 2012) at room temperature under identical hydraulic retention time (HRT = 3 d or at a flow rate of 1.2 L d^{-1}).

A seven-day Cu (II) shock load intended to completely inhibit the electricity production of NDMFC was applied after 5 months of operation. The first concentration of Cu (II) in the influent (day 152–155) was 25 mg L^{-1} but it showed no significant effect on the performance of the NDMFC. The influent Cu (II) concentration was further increased to 125 mg L^{-1} (day 155–159) and it effectively inhibited the electricity production and deteriorated the effluent water quality of the NDMFC. The NDMFC was further operated for close to two months until it regained its electricity production and water quality.

2.3. Analytical methods

All procedures for pre-treatment of samples were done in accordance with standard methods (American Public Health Association, 2005). The chemical oxygen demand (COD) was quantified using the COD measurement system and kit (Lianhua Technology, Beijing, China). The mixed liquid samples were immediately filtered through Millipore filter units (0.45 μm pore size) for the analysis of ammonium (NH_4^+–N), nitrate (NO_3^-–N), and nitrite (NO_2^-–N). NH_4^+ concentration was analyzed with a Lachat QC8500 flow