Bioresource Technology 147 (2013) 228–233

Contents lists available at ScienceDirect

Bioresource Technology

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

Enhanced performance of bio-cathode microbial fuel cells with the applying of transient-state operation modes

Peng Liang [a], Lulu Yuan [a], Wenlong Wu [a], Xufei Yang [b], Xia Huang [a,*]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, PR China
[b] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV 89512, USA

HIGHLIGHTS

- The ACD and IC modes enhanced the MFC's power generation and denitrification.
- The ACD and IC modes were better adapted to treat low-concentration wastewater.
- The MFC's power generation was limited by COD rather than nitrate concentration.
- The ACD and IC modes might enhance substrate transfer within and/or near biofilms.

ARTICLE INFO

Article history:
Received 9 June 2013
Received in revised form 29 July 2013
Accepted 2 August 2013
Available online 9 August 2013

Keywords:
Transient state
Denitrification
Microbial fuel cell
Bio-cathode

ABSTRACT

To enhance the MFC's denitrification performance, this study investigated three different external circuits/operation modes of the MFC: alternative charging and discharging (ACD), intermittent charging (IC) and constant external resistance (R). Results showed that the ACD and IC modes offered larger output currents as well as higher nitrate and COD removal rates than the steady R mode. The best performance was achieved with the ACD mode. At the initial [COD] = ~1200 mg/L and $[NO_3^-]$ =~ 140 mg/L, the ACD mode delivered an average power density of 0.91 W/m^3, an average nitrate removal rate of 15.5 mg/(L d) and an average COD removal rate of 137 mg/(L d), 268%, 207% and 168% respectively greater than those by the R mode. The enhancement by the ACD and IC modes was more pronounced at lower nitrate and COD concentrations and/or with the lack of stirring of electrolyte solutions.

1. Introduction

Biological denitrification is one of the most important nutrient removal processes and it requires electron donors, usually in the forms of chemicals (e.g., organic matter (OM), iron and sulfur), to reduce nitrate (NO_3^-) to N_2 and N_2O (Cai et al., 2008; Luna et al., 2010; Peng et al., 2012; Wen et al., 2012). Electrons for nitrate reduction can also be supplied by a cathode when cathodic nitrate reduction couples bacteria-catalyzed OM degradation/oxidation on an anode to form a microbial fuel cell (MFC) (Liu et al., 2012). This new denitrification technique shows great promise for wastewater treatment (Clauwaert et al., 2007) because it enables simultaneous removal of organic waste and nitrate while generates electricity that may further be utilized by other treatment processes, e.g., capacitive desalination (Yuan et al., 2012).

Assuming side electrochemical reactions are negligible on the cathode, the nitrate removal, i.e., denitrification performance is, in principle, positively related with an MFC's output current. As a supporting example, Virdis et al. recently reported that the MFC with larger output currents also delivered higher nitrate removal rates (Virdis et al., 2010). An easy way to increase an MFC's output current is to lower its external resistance, which has been affirmed to successfully improve the MFC's denitrification performance (Xie et al., 2011). Another feasible way is to lower the MFC's internal resistance by, e.g., optimizing the configuration of MFC reactors, exploring novel electrode and separating materials, and inoculating electrodes with highly active exoelectrogenic bacteria (Bond and Lovley, 2003; Logan et al., 2007; Rabaey et al., 2005; Wang et al., 2012; Zhang et al., 2009). More recently it was demonstrated that an MFC's output current can be increased by applying a "transient state" to the MFC. Rather than maintaining a constant external resistance, this approach incorporates electrical components, such as capacitors, diodes and switches, to the MFC's external circuits, thus allowing the MFC to run at a variety of transient states depending on the design and operation of the circuits (Dewan et al., 2009, 2010; Donovan et al., 2008, 2011; Gardel et al., 2009; Grondin et al., 2012; Kim et al., 2011). For example, by connecting a capacitor in parallel or in series with the external resistor, an MFC can be discharged and/or charged periodically with its current and

* Corresponding author. Tel.: +86 10 62772324.
E-mail address: xhuang@tsinghua.edu.cn (X. Huang).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.08.007

voltage varying over time (Dewan et al., 2009, 2010; Donovan et al., 2008, 2011); the switching of an MFC between different operating status can also be achieved by linking the MFC to a switch control or a power management system (e.g., capacitor-converter or charge pump converter) (Gardel et al., 2009; Grondin et al., 2012; Yang et al., 2012). Most reported transient-state experiments successfully improved the electricity generation (i.e., output current and voltage) of the MFCs (Kim et al., 2011). The enhancement of the MFC's performance may possibly be explained by that a varying electrode potential can improve the electron transfer from the anode-biofilm microbes to the anode (Liang et al., 2011). The varying electrode potential may additionally facilitate the substrate/ion transfer from the electrolyte to the anode-biofilm microbes as it weakens the built-up of the electric double layer that limits the mass transfer rate. However, the latter explanation yet lacks experimental evidence.

Previously we proposed two transient-state external circuits/operation modes (i.e., alternative charging and discharging (ACD) and intermittent charging (IC)) for regular MFCs and revealed that they substantially increased the MFC's output currents (Liang et al., 2011). In the current study, bio-cathode MFCs were constructed with aims to simultaneously degrade OM and nitrate in artificial wastewater. In addition to running with a constant external resistance (designated as the R mode), the bio-cathode MFCs were operated in the ACD and IC modes to examine their possible enhancement of the MFC's denitrification performance. We demonstrated that both the ACD and IC modes significantly increased the current generation and denitrification rates of the bio-cathode MFCs, and explored the possible mechanism of their positive effects.

2. Methods

2.1. Reactors and operation

Three identical two-bottle H-type MFCs were constructed for the current study. In each MFC, the two bottles were separated by a cation membrane (CMI7000, Membranes International Inc., USA) and sealed air-tightly with rubber stoppers. Both the anode and cathode were made of a graphite rod stacked in-between a pair pieces of graphite felt (size of each piece: 2 × 2 × 0.5 cm; Sanye, China). A saturated calomel electrode (SCE; 0.242 V vs. a standard hydrogen electrode, Leici, China) placed in the anode chamber was employed as the reference electrode. The substrate solution in the anode chamber contained 1.64 g/L NaAc, 1.5 g/L NH_4Cl, 0.6 g/L KH_2PO_4, 0.1 g/L $MgCl_2{\cdot}6H_2O$, 0.1 g/L $CaCl_2{\cdot}2H_2O$ and 0.1 g/L KCl (Note: acetate, i.e., NaAc, was selected as a surrogate for OM). The electrolyte solution in the cathode chamber was comprised of 50 mM phosphate buffer (4.4 g/L $KH_2PO_4{\cdot}3H_2O$ and 3.4 g/L K_2HPO_4), 1.92 g/L $NaHCO_3$, 0.15 g/L NH_4Cl, 0.1 g/L $MgCl_2{\cdot}6H_2O$, 0.1 g/L $CaCl_2{\cdot}2H_2O$ and 0.85 g/L $NaNO_3$. Both the anode and cathode electrolytes were continuously stirred at 60 rpm using magnetic stir bars unless otherwise specified.

The MFCs were inoculated with mixed bacterial cultures collected from a bio-cathode MFC that had been operated for >6 months in our laboratory. Prior to switched to the ACD and IC modes, the MFCs were first operated in the R mode with external resistance of 500 Ω until a peak voltage of ~530 mV was achieved and reproducible over five consecutive cycles (Note: each cycle lasted for 3 days and the MFC's internal resistance remained at 200–220 Ω).

Three operation modes were examined: R, IC and ACD (Fig. 1), with one MFC running in each mode. A detailed description of the ACD and IC modes can be found from Liang et al. (2011). To make experimental results comparable, an external resistor (R_e) of 102 Ω were selected in each of the three circuits (Fig. 1) and the supercapacitors in the IC and ACD modes were of the same capacitance (3.3 F).

The COD and nitrate concentrations were determined following the Standard Methods of the American Public Health Association (APHA, 1998): the COD concentration was measured using a HACH DRB-200 COD reactor (HACH Co., USA) and the NO_3^-—N concentration was determined using a HACH DR 5000 UV–Vis spectrophotometer (HACH Co., USA).

2.2. Calculation

The voltage drop (U_R, V) across the external resistor (R_e, Ω) was recorded using a data acquisition system (DAQ2213, ADLINK, China) and the current (I, A) in the circuit was calculated as: $I = U_R/R_e$. The quantity of electric charge (Q, C) harvested from the MFC is determined as: $Q = CU_C$, where C (F) refers to the capacitance of the supercapacitor and U_C (V) the voltage drop across the capacitor.

In the ACD and IC modes, the average current (I', mA) over a charging–discharging cycle is calculated as: $I' = Q'/T$, where Q' (C) refers to the total (net) quantity of electric charge and T the duration of the entire cycle. In the R mode, since the direction of the current remained unchanged, the average current was determined as: $I' = U'/R_e$, where U' (V) is the average voltage drop over the whole experiment.

In the R mode, the MFC's output power density (PR, W) was calculated as:

$$P_R = \frac{\int_0^{T_R} I^2 R_e \, dt}{T_R} \quad (1)$$

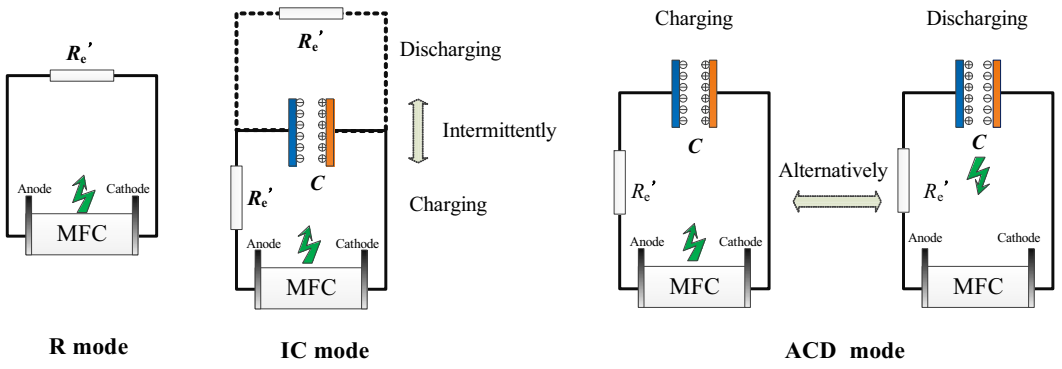

Fig. 1. Simplified schematic diagrams of the three operation modes: R – constant external resistance; IC – intermittent charging; and ACD – alternative charging and discharging. The resistor and the supercapacitor were rated at 102 Ω and 3.3 F, respectively. Note for the IC mode, only half of the external circuit was shown: when one supercapacitor was charged by the microbial fuel cell (MFC), the other supercapacitor was discharged to a second resistor ($R_e' = 102$ Ω; thus a RC discharging circuit was formed). A detailed description of the IC and ACD modes can be found from Liang et al. (2011).