Desalination 351 (2014) 77–81

Contents lists available at ScienceDirect

Desalination

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

Effects of salinity anions on the anode performance in bioelectrochemical systems

Guangli Liu *, Shuxian Yu, Haiping Luo *, Renduo Zhang, Shiyu Fu, Xiaonan Luo

School of Environmental Science and Engineering, Sun Yat-Sen University, Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology, Guangzhou 510275, China

HIGHLIGHTS

- With HCO_3^- from 0 to 100 mM, the coulombic efficiencies increased from 29% to 44%.
- The power density increased from 465 to 676 mW/m^2 by adding Cl^- from 0 to 50 mM.
- With the presence of 100 mM SO_4^{2-}, the power density decreased to 56 mW/cm^2.
- At the same conductivity, the best performance was obtained with HCO_3^- supplement.

ARTICLE INFO

Article history:
Received 7 May 2014
Received in revised form 12 July 2014
Accepted 22 July 2014
Available online 10 August 2014

Keywords:
Bioelectrochemical systems
Anion composition
Electricity generation performance
Microbial community structure

ABSTRACT

To study the feasibility to utilize the microbial desalination cell (MDC) to desalinate complex saltwater, the objective of this study was to investigate the effects of different salinity anions on anode performance. Experiments were conducted using three different salinity anions (Cl^-, SO_4^{2-}, and HCO_3^-) with different concentrations in the anode of two-chamber microbial fuel cell (MFC). Results showed that the supplement of anions, with concentration ranges of 25–50 mM for Cl^-, 25 mM for SO_4^{2-}, and 25–100 mM for HCO_3^-, into the substrate increased the voltage output of the MFC. With the HCO_3^- concentrations from 0 to 100 mM, the coulombic efficiencies increased from 29% to 44%, and the power densities increased from 465 to 1064 mW/m^2. At the same conductivity, the electron production in the MFC with the anions was in the order: $HCO_3^- > Cl^- > SO_4^{2-}$. The presence of HCO_3^- enhanced the buffer capacity of the anolyte and maintained the activity of the anode biofilm, in which the dominant species included *Geobacter uraniireducens*, *Desulfofaba fastidiosa*, and *Mycobacterium fortuitum*. This study suggests that the MDC can be used to desalinate complex saltwater to improve wastewater treatment in the anode chamber.

1. Introduction

Microbial desalination cell (MDC) is a new device that can be used to treat saltwater and brackish water using electrical power generated from organic substrates by exoelectrogenic bacteria [7,14,15,24,25]. With the MDC, the desalination rate of seawater can reach 60%–95% [4,11,18,19]. The stacked structure, forward osmosis, or bipolar membrane can be utilized in MDCs to achieve higher salt removal efficiency (95%) [5,11]. Brastad and He [3] used the MDC to soften hard water and removed more than 90% of hardness from several tested water samples. The MDC can serve as a pretreatment for subsequent reverse osmosis (RO) process and significantly reduce the desalination energy costs and membrane fouling potential. Therefore, the MDC is with great potential in desalination systems [10,20,22].

The MDC is developed on the basis of the two-chamber microbial fuel cell (MFC) by adding a desalination chamber between the anode and cathode chambers. Under the force of electrical field, anions and cations in saltwater filled in the desalination chamber move to the anode and cathode chambers, respectively. With movement of the salinity ions, the conditions of both anode and cathode chambers should change during operation of the MDC. The effect of the condition change can be significant in the anode chamber because of the existence of exoelectrogenic bacteria. Luo et al. [18,19] reported that desalination of saltwater containing NaCl and $NaHCO_3$ in the MDC improved wastewater treatment in the anode chamber, by increasing the conductivity by 2.5 times and stabilizing anolyte pH. Ieropoulos et al. [8] found that adding 150 mM Na_2SO_4 to the anode chamber led to 100% increase of power output and 32%–86% improvement of current output in an activated sludge MFC. Morris and Jin [23] noted that voltage output of the MFC was not affected when 790 mg/L of NaCl was introduced into the anode substrate. However, Lefebvre et al. [12] reported that coulombic efficiency (*CE*) of the MFC decreased when NaCl

* Corresponding authors. Tel.: +86 20 84110052; fax: +86 20 84110267.
E-mail addresses: liugl@mail.sysu.edu.cn (G. Liu), luohp5@mail.sysu.edu.cn (H. Luo).

http://dx.doi.org/10.1016/j.desal.2014.07.026
0011-9164/

concentrations in the anode substrate were over 500 mg/L. Therefore, both the concentration and composition of anions in the substrate can affect the performance of exoelectrogenic bacteria significantly. In the MDC, the anion concentrations in the anolyte increase gradually. Nonetheless, the effect of the increasing anion concentrations on anode microorganisms is still poorly understood.

The aim of this study was to investigate the performance and microbial community structure of the anode with addition of three different salinity anions (Cl^-, SO_4^{2-} and HCO_3^-) into the substrates. The effects of different concentrations of the anions on the system performance were also studied in terms of internal resistance, power density and coulombic efficiency.

2. Materials and methods

2.1. MFC set-up and operation

Two-chamber MFC reactors were constructed using plexiglass plastic cylinder (Fig. 1). Each chamber was formed by drilling a hole (3-cm diameter) in the cylinder, and the anode and cathode chambers were separated by a cation exchange membrane (CMI-7000, ULTREX™, China). Carbon cloth, with an effective area of 7 cm^2, was selected as the anode and cathode material. After inserting the electrodes, net volumes of the anode and cathode chambers were about 28 mL, respectively. Titanium wires were used to connect the circuit with an external resistance of 1000 Ω. The MFCs were operated with the fed-batch mode at room temperature.

A mixture of anaerobic and aerobic sludge (from Liede wastewater treatment plant of Guangzhou, China) was used as the inoculum in the MFCs. The anodic medium contained (in 1 L deionized water): 1.0 g CH_3COONa, 4.0896 g Na_2HPO_4, 2.544 g NaH_2PO_4, 0.31 g NH_4Cl, 0.13 g KCl, and 12.5 mL trace metal solution and 12.5 mL vitamin solution [17], except mentioned otherwise. Ferricyanide solution of 50 mM with phosphate buffer (pH = 7) was used as the electron acceptor in the cathode chamber.

Before data collection, all MFCs were operated with acetate medium as the sole substrate until reaching stable voltage outputs. After all MFCs were started up, three types of anions (Cl^-, SO_4^{2-}, and HCO_3^-) were added into the anode medium, respectively. For each type of anion, two MFCs were used as a parallel group, in which four concentrations (25, 50, 75 and 100 mM) were applied sequentially. For each concentration, the MECs operated for two cycles (about 240 h). The MFC without anion addition was used as the control.

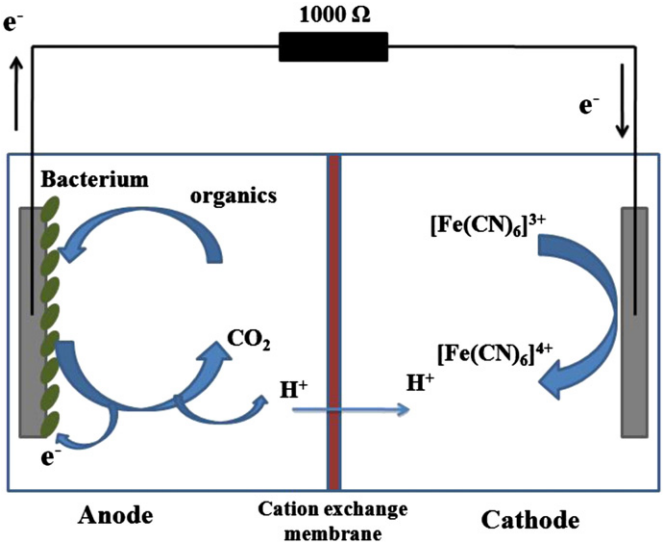

Fig. 1. The schematic diagram of the microbial fuel cell reactor.

2.2. Analyses and calculations

At the end of each cycle, samples from the anode solutions in the MFCs were treated by filtration through a membrane (with a pore diameter of 0.22 μm) to remove cells. Values of chemical oxygen demand (COD) of the samples were measured using the potassium dichromate method [2]. During the operation, voltages across the external resistance (1000 Ω) of the MFCs were measured using a data acquisition system at a time interval of 15 min. The current was calculated based on the voltage and the external resistance. The maximum power density was obtained from polarization curves using different resistances (100 to 10,000 Ω). The area power density (P_A, W/m^2) was calculated as follows:

$$P_A = \frac{IU}{A} \tag{1}$$

where I is the current (A), U is the voltage (V), and A is the area of the anode (m^2). The electron production (Q) was calculated by

$$Q = \sum_{i=1}^{n} I_i t_i \tag{2}$$

where I_i is the current (A) at time t_i. The coulombic efficiency, CE, is defined as the ratio of total coulombs actually transferred to the anode, to the coulombs if all substrate removal produced current [13]. The CE (%) was calculated by

$$CE = 100\% \frac{M\sum_{i=1}^{n} U_i t_i}{RFb\Delta SV} \tag{3}$$

Here U_i is the output voltage of MFC at time t_i, R is the external resistance (1000 Ω), F is Faraday's constant (96,485 C/mole electron), b is the number of moles of electrons produced per mol of the COD (4 mol e^-/mol COD), ΔS is the removal of COD concentration (g/L), V is the liquid volume (L), and M is the molecular weight of oxygen (32 g/mol).

2.3. Microbial community analysis

Biofilm samples were scratched from the anode electrode of MFC with two different concentrations (0 and 100 mM). DNAs were isolated from the bacteria in the biofilm samples using the soil DNA kit (Omega Bio-Tek) according to the manufacturer's instructions. The universal primer sets 518R (5′-ATTACGCGGCTGCTGG-3′) and GC-357F (5′-CGCC CGCCGCGCGGCGGGCGGGGCGGGGGCACGGGGGGCCTACGGGAGGCAG CAG-3′) (Invitrogen Biotechnology Co., Ltd) were used to amplify the V3 region of 16S ribosomal DNA (rDNA) from the extracted genomic DNA. The PCR amplification was performed using the following procedure: initial denaturation at 95 °C for 2 min; 30 standard cycles of denaturation at 94 °C for 30 s, annealing at 53 °C for 30 s, and extension at 72 °C for 30 s; and a final extension at 72 °C for 7 min.

The DGGE analysis of the PCR products was carried out in a denaturing gradient gel electrophoresis system (C.B.S. SCIENTIFIC, Del Mar, CA, USA) as previously described [21]. 16S rDNA gene fragments cut out from the DGGE gel were used for PCR amplification, and the PCR procedure was the same as that mentioned above, but using the universal primer sets of 357F (5′-CCTACGGGAGGCAGCAG-3′) and 518R (5′-ATTACGCGGCTG CTGG-3′). The PCR products were used for sequencing, and then the sequences were compared to the known sequences deposited in the GenBank database.

3. Results

3.1. Effects of salinity anions on performance of the MFCs

Representative voltage curves of the MFC affected by different anions are shown in Fig. 2. With the Cl^- concentrations from 0 to