Desalination 325 (2013) 48–55

Contents lists available at SciVerse ScienceDirect

Desalination

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

Long-term investigation of fouling of cation and anion exchange membranes in microbial desalination cells

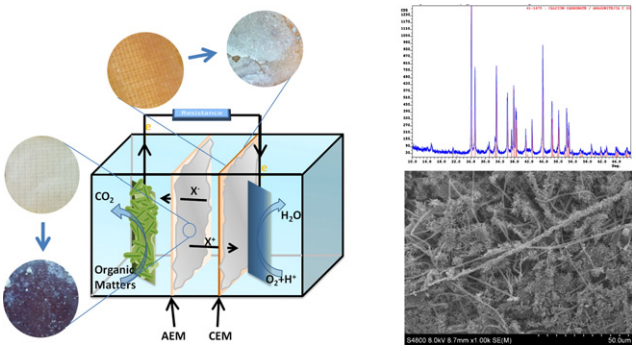
Qingyun Ping [a], Barak Cohen [b], Carlos Dosoretz [b], Zhen He [a,*]

[a] Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
[b] Faculty of Civil and Environmental Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

HIGHLIGHTS

- Operation of microbial desalination cell (MDC) results in membrane fouling.
- Biofouling dominates anion exchange membrane (AEM).
- Inorganic scaling appears on cation exchange membrane (CEM).
- The membrane resistance of CEM increases more significantly than AEM.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 May 2013
Received in revised form 27 June 2013
Accepted 30 June 2013
Available online 26 July 2013

Keywords:
Microbial desalination cell
Ion exchange membrane
Biofouling
Scaling
Wastewater

ABSTRACT

The fouling of ion exchange membranes in microbial desalination cells (MDCs) was investigated through an eight-month operation. Multiple MDCs were set up by using cation (CEM), anion (AEM), and/or proton (Nafion) membranes. The MDCs exhibited relatively constant reduction of conductivity of artificial seawater during the testing period (46.3 ± 6.3% in the CEM-MDC and 78.7 ± 0.8% in the Nafion-MDC in an operating cycle). However, the current generation decreased from 99 to 56 A/m^3 in the CEM-MDC after 250 days, and from 97 to 46 A/m^3 in the Nafion-MDC after 130 days, indicating the presence of membrane fouling. Theoretically the MDCs removed 6.7–12.1 kg TDS/m^3/d with a high charge transfer efficiency of 230–440%, suggesting that electric current was not the only factor to drive desalination; water dilution played an important role in conductivity reduction as well. It was observed that the AEM contained significant biofouling, resulting from wastewater and microbial growth on organic compounds migrating across the membrane, while the CEM had substantial inorganic scaling, mainly consisting of calcium and magnesium. The membrane resistance of the CEM increased more significantly than that of the AEM, indicating that CEM needs more maintenance during MDC operation.

1. Introduction

A microbial desalination cell (MDC) is proposed as an alternative approach for energy-efficient desalination integrated with simultaneous wastewater treatment [1]. A typical MDC consists of three chambers, an anode, middle (salt), and a cathode, separated by an anion exchange membrane (AEM, between the anode and the middle chambers) and a cation exchange membrane (CEM, between the cathode and the middle chambers), respectively (Fig. 1). Bacteria growing on the carbon-based anode electrode break down organic matters while releasing electrons and protons in the anode chamber. Terminal electron acceptors

* Corresponding author. Tel.: +1 414 229 5846; fax: +1 414 229 6958.
E-mail address: zhenhe@uwm.edu (Z. He).

0011-9164/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.desal.2013.06.025

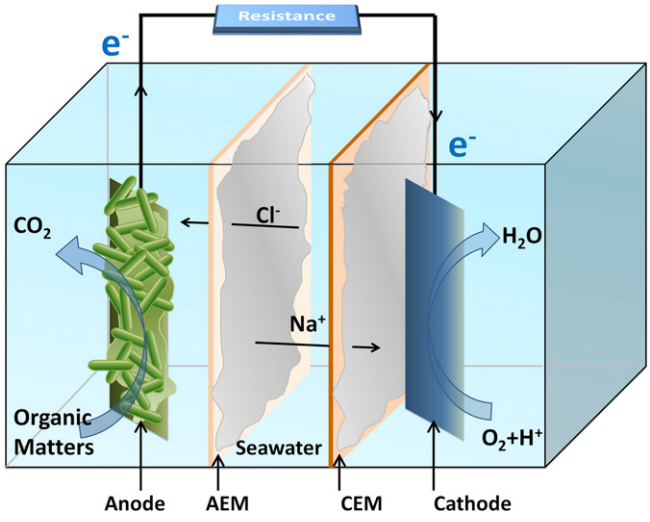


Fig. 1. The schematic of a microbial desalination cell (MDC). AEM: anion exchange membrane; CEM: cation exchange membrane.

(e.g., ferricyanide or oxygen) in the cathode chamber are reduced by accepting those electrons through an external circuit. Anions and cations are driven to migrate through AEM and CEM to balance the electric charge in the anode and the cathode chambers. Consequently, the salinity of the water in the middle chamber is greatly reduced [2].

The MDC concept has been advanced from several aspects, including reactor architecture, operation, and functions, through various studies [3]. In most bench-scale MDCs, a synthetic solution (e.g., containing acetate) and a NaCl solution were used as the anolyte and the salt solution, respectively. While a ferricyanide catholyte remains more efficient, dissolved oxygen as a terminal electron acceptor has proved to be more applicable [4]. MDC configurations have been optimized through upflow tubular reactors for possible scaling up [5,6], or by using stacked reactors to improve the charge transfer efficiency [7,8]. To reduce the operating cost due to the use of a buffer solution in the cathode chamber, the researchers applied recirculation to the electrolyte between the anode and the cathode to buffer the pH [9,10]. New features have been introduced to MDCs by inserting a bipolar membrane to produce acid and alkali [11], or applying an external voltage to produce hydrogen gas in the cathode [12,13]. An MDC could also be modified to act as a microbial salinity-reduction electrolysis cell for saline wastewater treatment [14]. Accelerated desalination was achieved by replacing the AEM with a forward osmosis membrane to accomplish both water dilution due to water extraction from wastewater and salt removal driven by electric potential [15]. Ion-exchange resins were added into an MDC for treating low-salinity solution [16]. MDCs were also studied to soften hard water by removing calcium and magnesium ions [17].

As ion exchange membranes serve a key role in creating different chambers (environments) and transporting the targeting ions, they are the critical components of an MDC system. The performance of those membranes will largely affect the performance of an MDC (both desalination and wastewater treatment). However, a major concern of applying membranes to a bioelectrochemical treatment system is fouling, especially with actual wastewater and seawater that are much more complex than the lab-prepared solutions. Biofouling occurs because of the presence of organics and microorganisms in wastewater [18] and transparent exopolymer particles in marine water that play an important role in the initiation and development of biofilm [19]. Abiotic fouling such as deposition of inorganic compounds also can form scaling.

Membrane fouling has not been well addressed in bioelectrochemical systems, and there is a lack of studies to examine fouling issues in microbial fuel cells (MFCs [20]) or MDCs. In an early study of a two-chamber MFC operated for 400 days, it was found that cation precipitation exhibited more influence on the performance of a Nafion membrane than biofouling, and periodic chemical cleaning was recommended for stable performance [21]. In an MFC equipped with a proton exchange membrane (Nafion 117), physical blockage caused by cations was found to decrease the current and intensify the pH-gradient after running for 90 days [22]. Thus far, the only study of membrane fouling in MDCs was conducted with domestic wastewater and salt solution (NaCl and $NaHCO_3$) in an MDC that was operated for eight months [23]. Their results showed only minor scaling on the CEM; however, biofouling on the AEM was found to distinctly increase the MDC resistance, resulting in a decrease in both current density and desalination efficiency.

To further understand membrane behavior in MDCs, we have conducted a long-term study (over eight months) and investigated how ion-exchange membranes were deteriorated by fouling/scaling with actual wastewater and synthetic seawater (prepared with sea salts). We examined the conductivity and turbidity of treated seawater and recorded the electricity generated by the MDC during the operation. We analyzed the contribution of electric current and water osmosis to conductivity reduction, and measured the membrane resistance using electrochemical impedance spectroscopy (EIS). Using scanning electron microscopy (SEM) and X-ray diffraction (XRD), we also studied the fouling and scaling on the membrane surface.

2. Materials and methods

2.1. MDC setup

Multiple MDCs were established by using plate-shaped reactors, each consisting of three chambers, the anode, the middle (salt), and the cathode (Fig. 1). An anion exchange membrane (AEM, AMI-7001, Membrane International, Inc., Glen Rock, NJ, USA) was used to separate the anode and the middle chambers, while a cation exchange membrane (CEM, CMI-7000, Membrane International, Inc.), or Nafion Membrane 117 (Fuel Cell Earth, LLC, Stoneham, MA, USA) was installed between the middle and the cathode chambers, resulting in a liquid volume of 24 mL in the anode or the cathode chamber. Several layers of rubber gaskets were installed between the AEM and the CEM with a distance of 1 cm, creating a middle chamber with a liquid volume of 24 mL. The anode and cathode electrodes were made of carbon cloth (3.0 × 7.5 cm, Zoltek Companies, Inc., St. Louis, MO, USA) attached to a piece of stainless mesh (3.0 × 2.5 cm) that acted as both a supporting structure and a current collector. The cathode electrode contained the catalyst prepared by applying a mixture of Pt/C powder with Nafion solution to the surface of the carbon cloth with a final Pt loading rate of 0.3 mg Pt/cm^2, as described in our previous work [24]. A separate MDC with membrane surface area of 110 cm^2 was built to investigate the substrate diffusion through AEM, with each chamber volume of 60 mL.

2.2. MDC operating conditions

The MDCs were operated at a room temperature of ~22 °C. The anodes were inoculated with a mixture of aerobic and anaerobic sludges, and the feeding solution was the primary effluent of a domestic wastewater treatment plant (Jones Island and South Shore Water Reclamation Facilities, Milwaukee, WI, USA). The primary effluent contained 225.8 ± 115.0 mg TCOD/L (TCOD: total chemical oxygen demand), 99.4 ± 68.1 mg SCOD/L (SCOD: soluble COD), 22.2 ± 7.1 mg NH_4^+-N/L, 7.8 ± 4.6 mg PO_4^{3-}/L, and an average pH of 7.0. Sodium acetate (5 g/L) was added to ensure an adequate electron supply to drive the desalination. The catholyte was tap water at pH 6.8. All the anode chambers were linked to a shared 3-L reservoir, and the cathode chambers were linked to a shared 1-L reservoir, respectively, which provided the anolyte or the catholyte that were recirculated between the anode or the cathode chambers and the reservoirs at a rate of 24 mL/min. The large-size reservoirs were used to ensure a sufficient supply of the anolyte and the