Salt removal using multiple microbial desalination cells under continuous flow conditions

Youpeng Qu a, b, Yujie Feng a,⁎, Jia Liu a, Weihua He a, Xinxin Shi a, Qiao Yang a, Jiangwei Lv a, Bruce E. Logan a,c,⁎⁎

a State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, No. 73 Huanghe Road, Nangang District, Harbin 150090, China
b School of Life Science and Technology, Harbin Institute of Technology, No. 2 Yikuang Street, Nangang District, Harbin 150080, China
c Department of Civil and Environmental Engineering, 212 Sackett Building, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

• Microbial desalination cells were hydraulically connected in series.
• Cells were operated with anode to cathode flow to remove pH imbalances.
• Series operation of four cells increased the extent of desalination.
• There was both effective desalination and high power production.

ABSTRACT

Four microbial desalination cells (MDCs) were hydraulically connected and operated under continuous flow conditions. The anode solution from the first MDC flowed into the cathode, and then on to the anode of the next reactor, which avoided pH imbalances that inhibit bacterial metabolism. The salt solution also moved through each desalination chamber in series. Increasing the hydraulic retention times (HRTs) of the salt solution from 1 to 2 days increased total NaCl removal from 76 ± 1% to 97 ± 1%, but coulombic efficiencies decreased from 49 ± 4% to 35 ± 1%. Total COD removals were similar at both HRTs (60 ± 2%, 2 days; 59 ± 2%, 1 day). Community analysis of the anode biofilms showed that bacteria most similar to the xylose fermenting bacterium Klebsiella ornithinolytica predominated in the anode communities, and sequences most similar to Geobacter metallireducens were identified in all MDCs except the first one. These results demonstrated successful operation of a series of hydraulically connected MDCs and good desalination rates.

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1. Introduction

Brackish and seawater desalination is becoming more common around the world to increase production of potable water [1]. Due to the high energy demands of traditional desalination techniques, alternatives are needed to decrease the salinity of these water sources [1–3]. A microbial desalination cell (MDC) is a new type of bioelectrochemical system that can simultaneously desalinate water, produce electrical current, and treat wastewater [4–9]. Under certain operating conditions the MDCs can produce net energy in the form of electricity or hydrogen gas, from many different sources of renewable organic matter [7,8]. This process has great potential as a green method for water desalination, compared to more traditional methods of desalination such as reverse osmosis (RO) that require electrical grid energy (~3.7 kWh/m³) [8,10].

The most basic type of MDC consists of three chambers: the anode chamber, a desalinating middle chamber, and the cathode chamber. Exoelectrogenic bacteria grow on the anode and oxidize organic or inorganic matter, and release electrons to the anode and protons into the anolyte [4–9,11,12]. At the cathode, protons are consumed, releasing hydroxyl anions into the catholyte [13]. The ions of the salty water in the middle chamber are driven to the adjacent chambers, with anions such as Cl− moving through the anion exchange membrane into the anode chamber, and cations such as Na+ moving into the cathode chamber, balancing charge [4]. Overall desalination performance can be increased by using stacks of ion exchange membranes between the electrodes (versus a single middle chamber) to enhance the transfer of charge per electron released to the circuit, and by flowing the salt water solutions through several MDCs in series in order to increase the extent of desalination [5,14]. When one or more chambers are used between the electrodes, there can be pH

⁎ Corresponding author. Tel.: +86 451 86283068; fax: +86 451 82373516.
⁎⁎ Correspondence to: B.E. Logan, Department of Civil and Environmental Engineering, 212 Sackett Building, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 814 863 7908; fax: +1 814 863 7304.
E-mail addresses: yujief@hit.edu.cn (Y. Feng), blogan@psu.edu (B.E. Logan).
imbalance between the anode and cathode chambers. A large decrease in pH of the anode (pH < 6) will inhibit microbial activity, and a high pH in the cathode chamber can result in potential losses of 0.095 V per unit of pH, significantly reducing reactor performance [7, 11, 12, 15, 16].

Many approaches have been used to reduce the adverse effects of pH on electrode performance, such as increasing the anolyte volume [4] or adding acids or bases [4–6]. Another approach was recirculation of the solutions between the anode and cathode chambers [11]. This recirculation was shown to effectively eliminate large changes in pH, but the extent of desalination was limited by operation of the MDC in fed-batch mode, and by the use of only a single MDC. Continuous flow operation has been used to improve performance in MDCs, but in previous tests the anolyte or catholyte was only recirculated through the same electrode chamber [6, 7].

In this study, the performance of three-chambered MDCs hydraulically connected in series was examined in terms of power density, effluent pH, and anode microbial community. The organic medium flowed through the anode and into the cathode chamber of the first MDC, and then on to the next MDC, eliminating large changes in pH. Changes in chemical oxygen demand (COD), coulombic efficiencies, NaCl removal (percent) and removal rates were examined at two different HRTs (1 day and 2 days). Xylose was used as a fermentable substrate as it is a waste product produced in the hydrolysis step in biofuel production using corn stover, and the microbial communities that developed using these substrates were examined. This is the first time microbial communities have been examined for multiple MDCs fed a fermentable substrate.

2. Materials and methods

2.1. Reactor construction

Four MDCs were constructed as previously described [9]. The anode chamber (4 cm long, 3 cm diameter; 28 mL liquid volume), middle chamber (2 cm long, 3 cm diameter; 14 mL liquid volume) and cathode chamber (2 cm long, 3 cm diameter; 14 mL liquid volume) were cylindrical with a cross-sectional area of 7 cm². The desalination chamber was formed by using an anion exchange membrane (AEM, DF120, Tianwei) next to the anode, and a cation exchange membrane (CEM, Ultrex CM70000, Membrane International) adjacent to the cathode. The anodes were carbon graphite fiber brushes 26 mm in diameter and 3 cm long that were heat treated (450 °C, 30 min) [17]. The air cathodes were carbon cloth (30% wet proofed, BASF, USA) that contained platinum catalyst on the water-facing side (3.5 mg Pt over 7 cm²) [18], and four PTFE diffusion layers on the air side [18].

2.2. Operating conditions

The reactors were inoculated (50%, v/v) with the effluent of an existing microbial fuel cell (MFC) operated at ambient temperature (25 °C). The external resistance of 1000 Ω was used during the start-up phase, and 10 Ω was used in the subsequent experiments to maximize power generation. The medium contained xylose (1 g L⁻¹) in a 50 mM phosphate buffer solution (PBS) containing trace minerals and vitamins as previously described [19]. The middle desalination chamber was filled with 20 g L⁻¹ NaCl in distilled water. The cathode chambers were initially filled with 50 mM PBS buffer.

MDCs were initially operated as fed-batch reactors over the three first cycles (start-up). After stable voltages were generated, a series of hydraulically connected MDCs were assembled using four MDCs and operated in continuous flow mode (Fig. 1). Two pumps (BT100-2 J, Lange, China) were used to maintain constant medium and salt solution flow into the MDCs. The medium was first pumped into the anode chamber of MDC-1 and then it flowed from the anode chamber through a thin tube (connecting the anode chamber and cathode chamber) into the cathode chamber of the same MDC, and from there it flowed on to the next MDC and then through the other two reactors. The salt water was pumped into the middle chamber of the first MDC, and then on through MDCs two through four (Fig. 1A). The HRTs of the salt solution were 1 day (0.04 mL min⁻¹) or 2 days (0.02 mL min⁻¹). The 1 day HRT was chosen to allow comparison to a previous study [6] and the longer HRT was used to increase desalination. For polarization tests, the flow rate of the salt solution in the desalination was increased to 1 mL min⁻¹ (HRT = 1 h) to obtain the maximum power (i.e. to reduce the ohmic losses produced by desalinated water). The flow rate of the medium was 0.25 mL min⁻¹ in all tests, as this condition resulted in optimum NaCl removal. Tests to determine this optimal flowrate are given in the supplementary data (Fig. S1).

2.3. Community analysis

Biofilm samples were taken at the end of the continuous desalination experiments from each of the four MDC anodes by removing a piece of the carbon graphite fiber brush with sterile scissors. Total
DNA was extracted using a MiniBEST Bacterial Genomic DNA Extraction Kit (TaKaRa Biotechnology, Japan) according to the instructions of manufacturer. PCR amplification of 16S rRNA gene fragments were performed using the universal bacterial primer pairs of 518 F (CCAGCAGCCGCGGTAAT) and 1401R (GGCTGTTGACAAGACCC). PCR products were purified and cloned using a pMD18-T Vector cloning kit (TaKaRa Biotechnology, Japan), and were used to construct 16S rRNA gene clone library. 16S rRNA gene sequences were analyzed in the National Center for Biotechnology Information (http://blast.ncbi.nlm.nih.gov/blast.cgi). A sequence similarity >97% was defined as an operational taxonomic unit. The coverage of the clone libraries was calculated as previously described [20].

2.4. Analyses and calculations

Cell voltages (E) were recorded every 10 min across a fixed external resistance (R, 10 Ω) [5,14] using a data acquisition system (PISO-813, ICP DAS Co., Ltd) [21]. Current was calculated according to Ohm’s law (I = E/R). Power density was calculated as P = E/A (mW m⁻²), where A (m²) is the projected surface area of the cathode. COD measurements were made using standard methods [22]. Xylose was measured using a high performance liquid chromatograph (LC-10A, Shimadzu, Japan) equipped with a refractive index detector. Samples (20 μL) were analyzed using an Aminex HPX-87P column (Bio-Rad, USA) at 50 °C, with 5 mM H₂SO₄ as eluent at a flow rate of 0.6 mL min⁻¹. Volatile fatty acids were measured using gas chromatograph (7890A GC, Agilent, USA) with a 2-m Ample-Wax column (Restek, USA) at 280 °C in split mode. Methanoic acid (99.5% pure, 100 μL) was added to 1 mL of effluent sample, and then 1 μL of the acidified sample was injected and analyzed. Reaction temperature was maintained at 240 °C during analysis, with 170 °C injector and 240 °C detector temperatures. COD removals were calculated for each MDC, and coulombic efficiency (CE) was calculated based on measured COD removal [23]. The pH was measured using a pH meter and probe (PB-10, Sartorius Ltd, Germany). The desalination chamber effluent was analyzed for conductivity (DDS-307, SPSCI-Rex Instrument Factory, China) and NaCl removal as previously described [5]. The organic removal rates (ORRs, kg COD m⁻³ day⁻¹) were calculated based on the COD removal per day and the volume of the medium. The NaCl removal rate (g L⁻¹ day⁻¹) was calculated by the NaCl removal per day (g day⁻¹) based on the reactor volume of the medium. The operational parameters (COD removal, pH, CE, NaCl removal and removal rates, and ORRs) of the multiple MDCs were measured more than three times, with the results given based on ± S.D. for each result.

3. Results and discussion

3.1. Desalination performance

The MDCs were operated in series for more than one month prior to analysis of system performance at HRTs of 1 day or 2 days. The NaCl removal by a single MDC (MDC-1) was 42 ± 3% at an HRT of 1 day, and it decreased to 25 ± 2% when the HRT was decreased to 1 day. When four MDCs were linked in series, the total NaCl removal increased to 97 ± 1% at an HRT = 2 days, with a lower removal of 76 ± 1% at an HRT = 1 day (Fig. 2A). These results show that increasing the HRT enhanced NaCl removal as a result of the longer period of time for desalination.

The total rate of desalination decreased when the HRT was increased from 1 day to 2 days (5.21 ± 0.05 g L⁻¹ day⁻¹ at an HRT = 1 day, 3.36 ± 0.02 g L⁻¹ day⁻¹ at an HRT = 2 days). A similar decrease in the NaCl removal rate was observed on the basis of the analysis of a single MDC (from 6.72 ± 0.58 g L⁻¹ day⁻¹ to 5.69 ± 0.39 g L⁻¹ day⁻¹ for MDC-1) (Fig. 2B). The rate of NaCl removal occurring in each of the four MDCs decreased along the length of flow at both HRTs (Fig. 2B). The lower desalination rates in the downstream MDCs were due to the reduced concentration of salt in the middle chamber (Fig. 2A), which increased the internal resistances (Fig. S2) and produced greater potential losses (Fig. S3) [14].

3.2. Power generation and COD removal

The four MDCs were operated with the salt solution in the middle chambers flowing at a high rate (1 mL min⁻¹) in order to determine the power that could be produced by this system. The maximum power densities ranged from 712 ± 32 to 860 ± 11 mW m⁻² under this optimal flow condition (Fig. 3A). These power densities were much greater than those previously obtained using individual three-chamber MDCs when they were operated under fed batch conditions of 424 mW m⁻² (using 5 g L⁻¹ NaCl) and 198 mW m⁻² (20 g L⁻¹ NaCl) [9]. However, these power densities are similar to those obtained using a single MDC when there was continuous flow through the MDC (931 ± 29 mW m⁻² with a 50 mM phosphate, buffer solution (PBS) in the anode solution, and 776 ± 30 mW m⁻² with 25 mM PBS). Thus, continuous-flow operation prevented large pH differences between the solutions in the anode and cathode chambers. By operating several reactors in series, as done here, the overall desalination was improved compared to previous studies with a single MDC, and pH changes were similarly avoided. The effluents of the MDCs were all maintained here at slightly below neutral pH (6.7 ± 0.1, MDC-1; 6.7 ± 0.2, MDC-2; 6.5 ± 0.1, MDC-3; 6.5 ± 0.1, MDC-4) (Fig. 3B).

The first MDC (MDC-1) of the four MDCs operated in series had the best performance in terms of electricity generation, ORRs and COD removal, compared to the three downstream MDCs. The maximum
power density of the MDCs decreased from 860 ± 11 (MDC-1) to 712 ± 32 mW m\(^{-2}\) (MDC-4) along the direction of fluid flow (Fig. 3A). The decrease in power was likely a result of reduced COD concentrations in the solution (Fig. 4A), as substrate concentrations can affect reactor performance [24].

The COD removed by each MDC decreased from 21 ± 1% (MDC-1) to 11 ± 1% (MDC-4) at an HRT = 2 days, and from 21 ± 3% (MDC-1) to 12 ± 1% (MDC-4) at HRT = 1 day (Fig. 4A). All xylose was completely consumed in MDC-1. Therefore, the effluent of MDC-1 into the downstream MDCs contained fermentation end products such as volatile fatty acids, with the specific composition given in Table S1. Although the combined COD removal rates for all four reactors in series (ORRs of 1.18 ± 0.04 kg COD m\(^{-3}\) day\(^{-1}\), HRT = 2 days; and 1.15 ± 0.04 kg COD m\(^{-3}\) day\(^{-1}\), HRT = 1 day) were less than that of a single MDC (MDC-1) (Fig. 4A), the extent of COD removal was improved compared to a single MDC (MDC-1) by 60 ± 2% (HRT = 2 days) and 59 ± 2% (HRT = 1 day) (Fig. 4A).

The flowrate of the salt solution only slightly affected COD removal rates and ORRs, as these values were similar at HRTs of 1 day or 2 days. The overall CE varied inversely with HRT (from 35 ± 1%, HRT = 2 days; to 49 ± 4%, HRT = 1 day). The CEs were slightly higher in the second MDC than the first MDC, but then the CEs decreased in the third and fourth MDCs (Fig. 4C). The different trends in the first CE (a lower CE in the first MDC compared to the second one) was due to the different substrates available in the first reactor compared to downstream MDCs. As noted, xylose was the main substrate in the first MDC and it was fermented, which did not require current generation. Also, dissolved oxygen was not removed from the influent medium and so there was substrate removal in the first MDC by aerobic microorganisms, compared to anaerobic feeds for the downstream MDCs. In the second through the fourth MDCs, the CEs decreased in the direction of flow as the salt concentrations decreased in the middle chamber, which increased internal resistance (Fig. S3) and reduced current production (Fig. S4) [14].

These results show that hydraulic flow through the reactors can be used to avoid pH changes and achieve desalination to an extent dependent on the HRT of the salt solution. It is too early to estimate how these operational conditions and the cost of the MDC materials might compare to other, more developed methods of water desalination such as reverse osmosis (RO). There are many developments of MDCs underway, as described in a recent review [25]. The costs of the materials used in MDCs are also decreasing [26], but at this point in time the technology is not yet ready for commercial applications as that will require larger-scale studies than those conducted here.
3.3. Community analysis

Bacterial clone libraries were constructed from the anodes of the four MDCs at the end of the completion of the continuous flow experiments based on a total of 61–65 random clone sequences from each bacterial library, resulting in 15 operational taxonomic units (OTUs) enriched in MDC-1, 16 in MDC-2, 20 in MDC-3, and 18 in MDC-4. The coverage of the clone libraries was 87.1% (MDC-1), 86.9% (MDC-2), 80.6% (MDC-3), and 89.2% (MDC-4). The most abundant sequences were most similar to Klebsiella ornatihilinolytica (48.4% in MDC-1, 50.8% in MDC-2, 37.1% in MDC-3, and 44.6% in MDC-4) (Fig. 5), which is a facultative anaerobe [27] that can ferment D-xylene to mixed acids and butanediol [27,28]. This suggests that this microbe would have been able to consume dissolved oxygen and help maintain anaerobic conditions for exoelectrogenic bacteria in the air-cathode MDCs while degrading the xylene.

Other relatively abundant sequences in MDC-1 were most similar to a Propionibacterium sp. [29] (9.7%) and Bacteroides rodentium [30] (6.5%) (Fig. 5), both of which are known to ferment D-xylene to mixed acids. The percentage of sequences associated with bacteria able to ferment xylene was >64% in MDC-1, which was the highest among the four MDCs. All xylene was completely consumed in MDC-1, and thus it was not used as a substrate in downstream MDCs (Table S1). The relatively high abundance of bacteria capable of xylene fermentation in the first MDC was consistent with data showing that the CE was lower in the first MDC than the second MDC, despite the higher COD in the first reactor (Fig. 4).

Bacteria with sequences similar to the Fe(III)-reducing bacterium Geobacter metallireducens were detected in MDC-2 (4.5%), MDC-3 (12.7%), MDC-4 (6.2%), but no clones with sequences similar to known Geobacter species were found in MDC-1 (Fig. 5). The reason for the lack of sequences similar to known Geobacter species in MDC-1 is not known, although many factors could have contributed to this apparent absence. The concentration of oxygen was likely highest in MDC-1, and thus it was not used as a substrate in downstream MDCs determined from 16S rRNA gene libraries.

Fig. 5. Distribution of bacterial community of the series of hydraulically connected MDCs determined from 16S rRNA gene libraries.

4. Conclusions

Four MDCs were operated under continuous flow mode, eliminating large pH changes and increasing the extent of desalination as much as possible compared to a single reactor. By increasing the HRTs from 1 to 2 days, NaCl removals were increased, but NaCl removal rate and overall CE decreased. Overall COD removals and ORRs were only slightly affected by the different HRTs. The most abundant sequences suggested that the most abundant bacterium in the reactors was the xylene fermenting bacterium K. ornatihilinolytica. The only known exoelectrogen identified based on the sequences obtained from the anodes was G. metallireducens, which was identified in all MDCs except the first one. These results demonstrate effective desalination using four three-chambered MDCs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.desal.2013.02.016.

References


