

A New Method for Water Desalination Using Microbial Desalination Cells

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Current water desalination techniques are energy intensive and some use membranes operated at high pressures. It is shown here that water desalination can be accomplished without electrical energy input or high water pressure by using a source of organic matter as the fuel to desalinate water. A microbial fuel cell was modified by placing two membranes between the anode and cathode, creating a middle chamber for water desalination between the membranes. An anion exchange membrane was placed adjacent to the anode, and a cation exchange membrane was positioned next to the cathode. When current was produced by bacteria on the anode, ionic species in the middle chamber were transferred into the two electrode chambers, desalinating the water in the middle chamber. Proof-of-concept experiments for this approach, using what we call a microbial desalination cell (MDC), was demonstrated using water at different initial salt concentrations (5, 20, and 35 g/L) with acetate used as the substrate for the bacteria. The MDC produced a maximum of 2 W/m² (31 W/m³) while at the same time removing about 90% of the salt in a single desalination cycle. As the salt was removed from the middle chamber the ohmic resistance of the MDC (measured using electrochemical impedance spectroscopy) increased from 25 Ω to 970 Ω at the end of the cycle. This increased resistance was reflected by a continuous decrease in the voltage produced over the cycle. These results demonstrate for the first time the possibility for a new method for water desalination and power production that uses only a source of biodegradable organic matter and bacteria.

Introduction

It is estimated that in the next 20 years the average per capita supply of clean water will decrease by one-third (1). Desalination is one option for producing potable water from brackish water and seawater in many parts of the world, but most water desalination technologies are energy and capital intensive (2). The main desalination technologies currently used are reverse osmosis, electrodialysis, and distillation. Continual improvements in desalination processes, par-

ticularly in the past decade, have made these systems more reliable and have reduced capital costs, but high energy requirements remain a concern in many parts of the world (3). Increasing attention is being placed on developing desalination processes powered by renewable energy, such as solar and wind driven electricity (4). New membrane systems are also being developed that reduce the need for high water pressure through the use of forward osmosis (5). All of these systems, however, require heat sources or electrical energy input. For example, reverse osmosis units require 3–5 kWh/m³ for water desalination (2).

In recent years there has been development of new bioelectrochemical systems (BES) that use bacteria to create renewable energy in the form of electricity, hydrogen, and methane (6–9). For example, a microbial fuel cell (MFC) generates electricity using bacteria to degrade organic matter and produce a current. MFCs are being developed that can treat domestic and industrial wastewaters by removing the organic matter from the water, while at the same time producing electrical power (10, 11). MFCs consist of an anode and a cathode, sometimes separated using a membrane. Various membranes including cation exchange membranes (CEMs), anion exchange membrane (AEMs), bipolar membranes, and ultrafiltration membranes have been used in MFCs (12–14). When bacteria in the anode chamber oxidize substrate and transfer electrons to the anode, an equal number of protons are released into the water. Due to the low concentration of protons at neutral pH, the primary cationic species transported through the CEM are Na⁺ and K⁺, leading to H⁺ accumulation in the anode chamber of two-chambered MFCs (15). When AEMs are used charge is balanced by transport of negatively charged species. MFCs with AEMs often show better performance than those with CEMs (16–18). The primary species transferred across the membrane with an AEM are Cl⁻, HCO₃⁻, and HPO₄²⁻, along with OH⁻ ions. While ionic imbalances are detrimental to the general operation of MFCs, the movement of ions across membranes during current generation provides a method for altering water chemistry in a manner that can be useful for achieving water desalination.

We propose here a new type of water desalination method, called a microbial desalination cell (MDC), which is based on transfer of ionic species out of water in proportion to current generated by bacteria. The device consists of three chambers, with an AEM next to the anode and a CEM by the cathode, and a middle chamber between the membranes filled with water that is being desalinated. When current is generated by bacteria on the anode, and protons are released into solution, positively charged species are prevented from leaving the anode by the AEM and therefore negatively charged species move from the middle chamber to the anode. In the cathode chamber protons are consumed, resulting in positively charged species moving from the middle chamber to the cathode chamber. This loss of ionic species from the middle chamber results in water desalination without any water pressurization or use of draw solutions (5), and no electrical energy or water pressure is required. Instead, electricity is generated while the water is desalinated. This process is somewhat similar to electrodialysis, but in that case an external electrical energy source is used to provide the energy for separating the ionic species.

We demonstrate proof-of-concept of the MDC process by modifying a small scale laboratory reactor that was originally developed to function as an MFC. Using this MDC, it is demonstrated that it is possible to achieve about 90%

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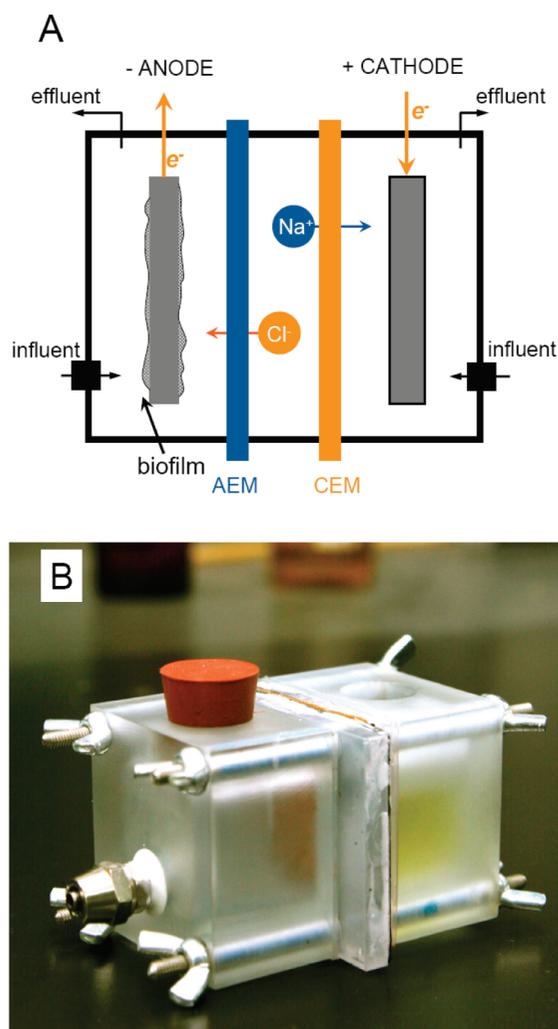


FIGURE 1. Three-chamber MDC used for desalination tests: (a) schematic, and (b) photograph.

salt removal during a single batch desalination cycle, while at the same time producing useful amounts of electricity.

Materials and Methods

MDC Construction. The design of the MDC was based on a cubic-shaped MFC, where the electrode chamber is produced by drilling a hole in a solid block of polycarbonate (13). The MDC consisted of three chambers (anode, middle desalination, and cathode), separated using AEM and CEM membranes, clamped together with gaskets that provide a water seal between the chambers (Figure 1). An AEM (DF120, Tianwei Membrane) was used to separate the anode and middle chambers, and a CEM (Ultrex CMI7000, Membranes International) was used to separate the middle and cathode chambers. The cross section of the working area of these two chambers was 9 cm². The inside volumes of the anode, middle desalination, and cathode chamber were 27, 3, and 27 mL, respectively. When the anode and cathode chambers were filled with electrode material, which consisted of carbon felt (19), the liquid chamber volume decreased to 11 mL. External electrical contact to the electrodes was produced by pushing a graphite rod (5 mm diameter) into the felt. Prior to use, the carbon felt and rod were washed for 48 h in 1 M HCl and rinsed with water to remove trace metals.

Medium. The anode chamber of the MFC was fed a solution of sodium acetate (1.6 g/L) in a nutrient buffer solution containing (per liter in deionized water): 4.4 g KH₂PO₄, 3.4 g K₂HPO₄•3H₂O, 1.5 g NH₄Cl, 0.1 g MgCl₂•6H₂O,

0.1 g CaCl₂•2H₂O, 0.1 g KCl, and 10 mL of trace mineral metals solution (20). The cathode chamber was fed a ferricyanide catholyte, containing (per liter in deionized water): 16.5 g K₃Fe(CN)₆, 9.0 g KH₂PO₄, 8.0 g K₂HPO₄•3H₂O. The middle chamber was filled with the water to be desalinated, at NaCl concentrations of 5, 20, or 35 g/L. These concentrations represent a reasonable range of salinities for brackish water and seawater (4).

MDC Operation and Experimental Procedures. Three-chamber MDCs were inoculated with a mixed bacterial culture from the anode of an active acetate-fed laboratory MFC. Before conducting desalination experiments, the anodes were acclimated by running the reactors in MFC mode using only a single CEM, until peak voltage was stable at about 600 mV and reproducible over 10 cycles. When operated in MDC mode (Supporting Information), solutions from individual feed reservoirs (100 mL each) were continuously recirculated through the anode and cathode chambers at a rate of 5 mL/min using a peristaltic pump (BT00–300T, Lange, China). The anolyte in the feed bottle was replaced every 12 h to ensure a sufficient supply of substrate for the bacteria, and avoid a drop in pH (Supporting Information). Due to the large difference in the anode and feed reservoir volume (100 mL) compared to that of the desalination chamber (3 mL), the total change in conductivity of the feed solutions, if not changed, would have been <5%. Thus, changing these solutions did not substantially affect the osmotic pressure in the electrode chambers over a single cycle. Salt solution in the middle chamber was replaced when the voltage was <50 mV, forming a single desalination cycle even though there were multiple replacements of the anode solution.

Identical reactors were operated in open circuit mode as controls for charge transfer in the absence of current generation. The external resistance (R_e) was fixed at 200 Ω , except as noted, using a resistance box (ZX21, Tianshui, China; range of 0.1 Ω to 99,999 Ω). All MDCs were operated in duplicate at ambient temperature (25 ± 1 °C).

Analyses and Calculations. The voltage across the external resistor (R_e) in the circuit of the MFC was recorded using a data acquisition system (DAQ2213). The current (I) through the electrical circuit was determined from the measured voltage (E) according to $I = E/R_e$.

Salt concentrations were evaluated by conductivity measurements using a conductivity meter (SG3-ELK, Mettler Toledo). In some tests cation concentrations (Na^+ , K^+) were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Intrepid II XSP, Thermal).

Electrons harvested through the electrical circuit (Q), expressed in coulombs (C), was determined by integrating current over time ($Q = \int I dt$). The theoretical amount of coulombs (Q_{th}) that can be produced from the movement of the NaCl was calculated by $Q_{th} = 2(m_0 - m_t)F$, where F is Faraday's constant (96 485 C/mol), and m_0 the initial and m_t the final molar NaCl over a batch cycle of time of t . The charge transfer efficiency was calculated as the ratio Q_{th}/Q .

Change in ohmic resistance was monitored by electrochemical impedance spectroscopy (EIS, CHI660A, U.S.). EIS measurements were conducted at open circuit voltage (OCV) over a frequency range of 10⁵ to 10⁻² Hz, with a sinusoidal perturbation of 5 mV amplitude. The anode was used as the working electrode and the cathode was used as the counter and reference electrode. The internal resistances of the cell were obtained from Nyquist plots, where the intercept of the curve with the Z_{re} axis is defined as the ohmic resistance (21).

Results

Electricity Generation and Desalination Performance. The three-chamber MDC produced an OCV of ~700 mV, which

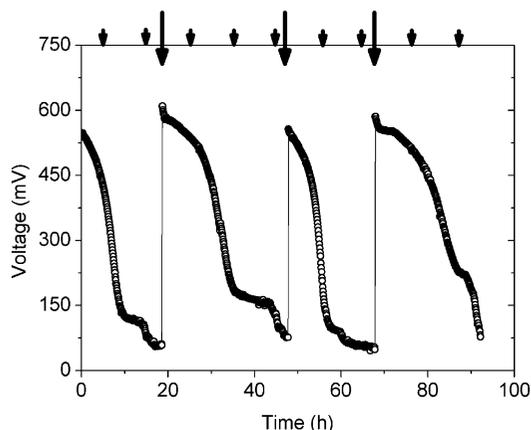


FIGURE 2. Voltages generated in tests using the three-chamber MDC with an initial salt concentration in the middle chamber of 20 g/L (Large arrows indicate salt solution replacement; small arrows indicate anolyte replacement).

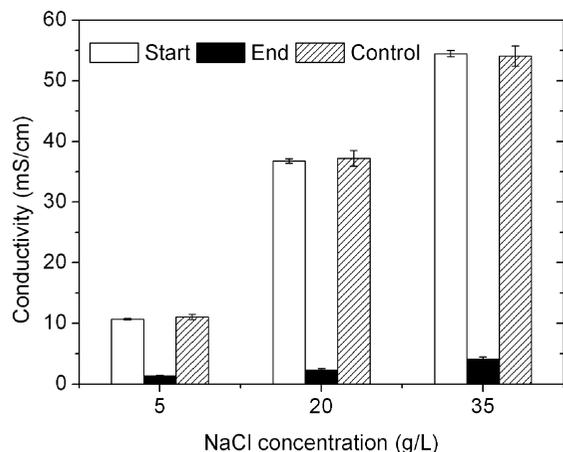


FIGURE 3. Change of solution conductivity in the middle desalination chamber over complete batch cycles with different initial salt concentrations (The control is the same system but operated with an open circuit).

is comparable to that obtained in previous tests using a similar MFC design (13). The maximum voltage produced during MDC operation with an initial salt concentration of 20 g/L (200 Ω external resistor) was \sim 600 mV, with a maximum current of 3 mA (Figure 2). Under this fixed resistance condition, this translates to a maximum power output of 2 W/m² (based on the cross section area of 9 cm²), and 31 W/m³ based on the total reactor volume (all three chambers, 57 mL). The anolyte solution was frequently replaced (every 12 h) to avoid substrate limitations for bacteria on the anode or changes in pH. When the anolyte was replaced there was little change in voltage, demonstrating the current generation was not affected by substrate levels. In a typical MFC, voltage production is usually constant over a cycle until the acetate concentration reaches a low level. However, here the voltage immediately and continuously decreased over the cycle. This shows that the main impact on the voltage produced in the MDC was the decrease in the conductivity of the solution in the desalination chamber over the full cycle, which changed the ohmic resistance (see below).

The water in the middle chamber was efficiently desalinated at all three initial salt concentrations. Based on the change in solution conductivity, the salt removals at each initial salt concentration were about $88 \pm 2\%$ (5 g/L), $94 \pm 3\%$ (20 g/L), and $93 \pm 3\%$ (35 g/L) (Figure 3). There was little change in solution conductivity in the open circuit control.

The total NaCl removal at different initial salt concentrations and two different external resistances (200 Ω and 800

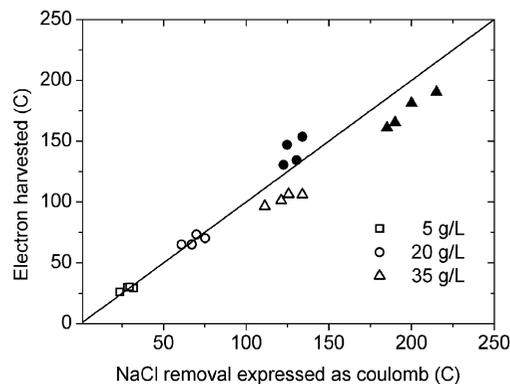


FIGURE 4. NaCl removal compared to total Coulombs transferred (electrons harvested) for different initial salt concentrations and external resistances (open symbols, 800 Ω ; filled symbols, 200 Ω).

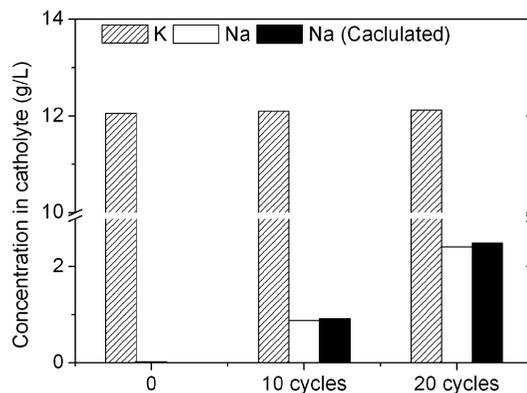


FIGURE 5. Initial and final concentrations of sodium in the cathode chamber after multiple batch cycles compared to that calculated based on total Coulombs of charge transferred.

Ω) was compared to the total amount of charge transferred (Figure 4). Overall, there was good agreement between electrons harvested and NaCl removal, and therefore the charge transfer efficiency was nearly 100%. This transfer of ionic species relative to charge is high in the MDC when compared to traditional electro dialysis. Lower efficiencies are observed in electro dialysis as a result of water splitting in the diluate, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the diluate due to high current densities. In the MDC, however, the current densities are relatively small and therefore there was negligible water splitting to compensate for the limiting current. Back-diffusion of ions from electrode chambers to the middle chamber was negligible. At salt concentration of 35 g/L, the theoretical charge transfer (Q_{th}) was slightly higher than Q . This likely indicates that there was some salt removal due to the large concentration gradient between the middle chamber and the anode (cathode) chamber.

The transfer of the ions out of the middle chamber was also examined on the basis of Na⁺ accumulation in the cathode chamber relative to that of K⁺. The solution in the cathode chamber contained only potassium and no sodium ions, making it possible to monitor chemical species responsible for charge transfer. When the system was operated, sodium ions accumulated in the cathode chamber up to levels of 0.9 g/L (10 batches) and 2.4 g/L (20 batches) (Figure 5). These values were within 96% of that calculated based on total Coulombs transferred over the multiple cycles of operation. Variations in the concentration of potassium in the cathode chamber during the experimental runs were negligible. This demonstrates that there was negligible potassium cross over from the cathode chamber to the middle chamber by back diffusion.

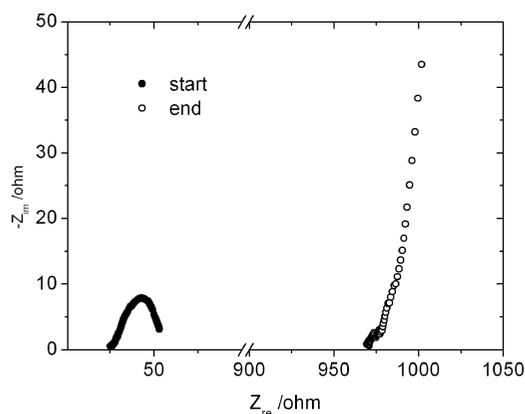


FIGURE 6. Nyquist plots used to determine ohmic resistance at the start and end of a batch cycle.

Changes in Ohmic Resistance Over a Desalination Cycle.

As the water is desalinated over a cycle, the ohmic resistance should increase as the conductivity of the middle chamber decreases. To follow this process, the ohmic resistance of the MDC was evaluated over a cycle using EIS (Figure 6). The ohmic resistance increased from 25 Ω at the beginning of the desalination cycle to 970 Ω at the end of the cycle in tests with an initial salt concentration of 5 g/L. This shows an increase in resistance by a factor of 40. In contrast, the resistance of the electrolyte solutions increased only by a factor of 8 based on measured conductivity changes (Figure 3). This result means that under low electrolyte conditions, the resistance of the membrane solution interface or the ion exchange membrane resistance must have increased. It was reported previously that a higher electrolyte concentration decreased the membrane solution interface resistance due to the compression of electrical double layer (22). This increase in membrane resistance over a cycle is also consistent with previous results obtained in MFC tests with Nafion 117 at low electrolyte concentrations (17). The change in ohmic resistance explains the variation in voltage observed over a single desalination cycle. The voltage rapidly reached an initial peak, and then continuously decreased over the course of the cycle (Figure 2), consistent with the observed increase in ohmic resistance (Figure 6).

Discussion

The results obtained in this study show that in principle, an MDC can be used to desalinate water. About 90% of the salt was removed from the water over a single desalination cycle, and there was no need to pressurize the water or use an external source of electricity. The process was effective for desalinating water even at a salt concentration as high as 35 g/L. This can be compared to traditional electrodialysis which is recommended for use at salt concentrations up to 6 g/L of dissolved solids (23) due to the high energy demands of the process. It was found that the internal resistance of the MDC increased more rapidly than we expected based on changes in solution conductivity, likely as a result of the increased membrane/solution interface resistance due to the electrical double layer. This increase in internal resistance will limit the efficiency and performance of the system, and thus it needs to be further studied and minimized to increase MDC performance.

The experiments conducted here were designed to demonstrate the proof-of-concept of an MDC, but further work will be needed to make the MDC useful for practical applications. For example, the volume of water used in the electrode chambers to achieve desalination was large relative to the desalination chamber, and it was not optimized here. The anode and feed solution (100 mL)

was changed many times over a single desalination cycle in order to study the effects of the water desalination on current (and internal resistance), and to eliminate possible effects of substrate limitation on bacteria in the anode chamber. This resulted in the use of much more water than would be needed to minimize the volume of the anode solution. In addition, we used a ferricyanide catholyte because as it allowed us to control the cathode potential and to easily measure sodium ion transfer into the cathode chamber. While using ferricyanide allowed us to demonstrate the feasibility of the MDC process, its use would not be acceptable in practice. Further development of the MDC process using chemical air cathodes or biocathodes is needed (24–26).

While we used an acetate substrate here, the use of actual wastewaters should also be examined as low cost fuels in future studies. The low salinity of these wastewaters may benefit process efficiency due to passive ion transfer from the saline water into the wastewater, which could help to reduce ohmic losses and charge accumulation in the membranes. In addition it might solve a problem of extracting energy from wastewater using MFCs as the conductivity of most domestic wastewaters is low (~ 1 mS/cm), which limits achieving higher power densities (27).

Many wastewaters have a low alkalinity, and therefore a low buffering capacity. The extraction of ions into the cathode and cathode chambers increases the salinity of these solutions, and can also cause imbalances in pH. Changes in solution pH in electrode chambers in MFCs is common when membranes are placed between the electrodes (14, 15). These pH changes were avoided here by using a buffer and frequently changing the anode solution. Through adjustment of the flow rates into the electrode (anode and cathode) chambers, and the desalination chamber, it should be possible to limit pH changes to desired levels. The addition of inexpensive bicarbonate buffer (28) or the use of anode to cathode recirculation (29) are two possible approaches for addressing this problem.

Another challenge will be to develop stacked desalination systems. While only a single stack (three chambers) was used here, increasing the number of cells will increase the diluate production, although at a cost of producing higher internal resistances. We have examined only batch processing of the water for desalination, but future studies are needed with continuous flow systems. The MDC process can be looked at as a new type of BES, and its further development will benefit from advances being made in other electrochemical systems such as MFCs.

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Supporting Information Available

Additional information including one figure and three tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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