Bahareh Kokabian and Veera Gnaneswar Gude
Photosynthetic microbial desalination cells (PMDCs) for clean energy, water and biomass production
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Current microbial desalination cell (MDC) performances are evaluated with chemical catalysts such as ferricyanide, platinum catalyzed air-cathodes or aerated cathodes. All of these methods improve power generation potential in MDCs, however, they are not preferable for large scale applications due to cost, energy and environmental toxicity issues. In this study, performance of microbial desalination cells with an air cathode and an algae biocathode (Photosynthetic MDC – PMDC) were evaluated, both under passive conditions (no mechanical aeration or mixing). The results indicate that passive algae biocathodes perform better than air cathodes and enhance COD removal and utilize treated wastewater as the growth medium to obtain valuable biomass for high value bioproducts. Maximum power densities of 84 mW m\(^{-3}\) (anode volume) or 151 mW m\(^{-3}\) (biocathode volume) and a desalination rate of 40% were measured with 0.9 : 1 : 0.5 volumetric ratios of anode, desalination and algae biocathode chambers respectively. This first proof-of-concept study proves that the passive mechanisms can be beneficial in enhancing the sustainability of microbial desalination cells.

Environmental impact

Existing engineered environmental processes for wastewater treatment and desalination are energy intensive and not sustainable. For instance, wastewater treatment in the United States requires an estimated 21 billion kW h of prime energy per year with concomitant carbon dioxide emissions of nearly 20.2 billion kg per year. If sustainable environmental processes are to be developed, external energy consumption has to be minimized and the energy recovery/saving schemes need to be optimized. Microbial desalination cells (MDCs) integrate wastewater treatment with desalination of salt water while simultaneously producing electricity. Current MDC technologies are based on expensive chemical catalyst utilization and intensive aeration in the cathode chambers. If passive biocathodes can be developed to minimize the energy and chemical consumption, and to maximize the operational benefits of MDCs, this technology can provide a sustainable approach to desalination and wastewater treatment in an integrated configuration.

Introduction

Provision of clean water and wastewater treatment have become major issues with increasing population and dwindling water resources in many parts of the world. Wastewater treatment through conventional processes like activated sludge and freshwater production through desalination are both energy- and cost-intensive and contribute to greenhouse gas emissions. For instance, in the U.S., wastewater treatment consumes an estimated 21 billion kilowatt hours (kW h) per year of prime energy with concomitant carbon dioxide emissions of nearly 20.2 billion kg per year.¹ Energy requirements for water and wastewater treatment processes, energy generation potential and their environmental impacts are shown in Table 1.²⁻⁴ It is almost impossible to provide clean water without energy investment and the same is true for wastewater treatment.⁵ Freshwater drawn from the groundwater source requires 0.14–0.24 kW h m\(^{-3}\) for a pumping head of 120–200 ft and treatment of surface waters to potable quality requires 0.36 kW h m\(^{-3}\).² Similarly, including pretreatment, the state of the art reverse osmosis process has a specific energy consumption of 2.5 kW h m\(^{-3}\).³⁻⁴

Microbial desalination cells (MDCs), a recent technological discovery, allow for simultaneous wastewater treatment and desalination of saline water with concurrent electricity production.³ The premise for MDC performance is based on the principles that bioelectrochemical systems (BESs) convert wastewaters into treated effluents accompanied by electricity production and the ionic species migration (i.e. protons) within the system facilitates desalination. This integrated process appears to be particularly attractive for areas with severe water issues (high saline groundwater or seawater) since the two different processes can be combined to result in an energy-gaining process.⁵ The recent versions of MDCs include three chamber MDCs, microbial desalination-electrolysis cells
(MECs), bipolar MDCs, osmotic MDCs (OMDCs), stacked MDCs and upflow MDCs (UMDCs). All these MDC process configurations have demonstrated the technical feasibility of this novel technology.

While anaerobic conditions in the anode chamber are ideal for degradation of a variety of environmental pollutants (by oxidation of organic compounds), provision of clean electron acceptors in the cathode chamber is an existing issue in bioelectrochemical systems. Chemical compounds such as ferri-cyanide were used as catholytes which are sacrificial in nature requiring replacement. Additionally, these chemicals are expensive and toxic to the environment. This suggests that their use as electron acceptors in large scale applications is not sustainable. Among the many electron acceptors, oxygen has been recognized as a practical terminal electron acceptor (TEA) due to its high reduction potential and its availability. The cathodes using oxygen as the TEA are known as air cathodes. The major limitation to the air cathodes is that they suffer with a disadvantage of slower redox kinetics under ambient conditions; these cathodes therefore require expensive catalyst materials (e.g. platinum) for minimizing activation overpotential associated with oxygen reduction. Another disadvantage is related to the high energy requirements associated with mechanical equipment used to maintain optimal dissolved oxygen concentrations in the air cathodes. The previous MDC designs have required aeration of the cathode chamber, offsetting the benefits of power generation by power consumption for aeration. Therefore, passive methods of oxygen production by using biocathodes can be a sustainable solution to address this issue. Biocathodes (biological cathodes) use microorganisms as biocatalysts to accept electrons and provide a different path that avoids the use of noble or non-noble catalysts for oxygen reduction, thereby enhancing the economic viability and environmental sustainability of bioelectrochemical systems, and offer flexibility in producing valuable commodities.

In this paper, we present the preliminary proof-of-concept study on the performance of photosynthetic microbial desalination cells (PMDCs) or microbial solar desalination cells supported by a photosynthetic microorganism, i.e., microalgae (Chlorella vulgaris sp.), as a biocatalyst in the biocathode. We report the beneficial use of algae as a passive biocathode by in situ oxygen generation and COD removal and compare its performance with a passive air cathode MDC. To the best of our knowledge, this paper reports the first study on photosynthetic microbial desalination cells (PMDCs) incorporating algae as a sustainable biocathode.

**Methods**

**Microbial consortium and algae preparation**

Microbial consortium in the anode compartment was collected from the aerobic sludge of the wastewater treatment plant in Starkville, Mississippi. The sludge was allowed to acclimate to anaerobic conditions in synthetic wastewater containing 300 mg L⁻¹ of COD for over 150 days. The microbial consortium was grown in air and algal cathode MFCs prior to its transfer into the air and algal MDCs respectively. The synthetic wastewater in the anode chamber has the following composition: glucose 468.7 g L⁻¹, KH₂PO₄ (4.4 g L⁻¹), K₂HPO₄ (3.4 g L⁻¹), NH₄Cl (1.5 g L⁻¹), MgCl₂ (0.1 g L⁻¹), CaCl₂ (0.1 g L⁻¹), KCl (0.1 g L⁻¹), MnCl₂·H₂O (0.005 g L⁻¹), and NaNO₃ (250 mg L⁻¹). The COD concentration used in the MDC anode chamber was 500 mg L⁻¹. The microalgae Chlorella vulgaris used in the cathode compartment was grown in the following mineral solution: CaCl₂ (25 mg L⁻¹), NaCl (25 mg L⁻¹), NaNO₃ (250 mg L⁻¹), MgSO₄ (75 mg L⁻¹), KH₂PO₄ (105 mg L⁻¹), K₂HPO₄ (75 mg L⁻¹), and 3 ml of trace metal solution with the following concentration was added to 1000 ml of the above solution: FeCl₂ (0.194 g L⁻¹), MnCl₂ (0.082 g L⁻¹), CoCl₂ (0.16 g L⁻¹), Na₂MoO₄·2H₂O (0.008 g L⁻¹), and ZnCl₂ (0.005 g L⁻¹). Chlorella vulgaris sp. was chosen due to its tolerance for high levels of CO₂ and high efficiency in utilizing CO₂ through photosynthesis. A known volume of this algal consortium with a known cell density was transferred into the cathode chamber.

**MDC construction**

The cylindrical-shaped MFC chambers were made of plexiglass with a diameter of 7.2 cm. The anode and cathode chambers were separated by an ion exchange membrane. Graphite papers were used as anode and cathode electrodes. The area of the anode electrode and that of the cathode electrode were 28.27 cm². The volume of the anode and cathode chambers was 180 ml after inserting the electrodes. The MDC reactors were prepared by inserting a desalination chamber between anode and cathode chambers in MFC reactors. Cation exchange

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**Table 1 Environmental processes, energy requirements, energy gain potentials and environmental impacts**

<table>
<thead>
<tr>
<th>Process</th>
<th>Science: principle of operation</th>
<th>Energy consumption (kW h m⁻³)</th>
<th>Environmental impact (kg CO₂ m⁻³)</th>
<th>Energy gain potential (kW h m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water treatment</td>
<td>Chemical addition and physical separation</td>
<td>0.14–0.36</td>
<td>0.13–0.35</td>
<td>0</td>
</tr>
<tr>
<td>Wastewater treatment</td>
<td>Biochemical reactions and physical separation</td>
<td>0.5–1</td>
<td>0.48–0.96</td>
<td>0.09–0.14</td>
</tr>
<tr>
<td>Desalination</td>
<td>Thermal evaporation or membrane separation</td>
<td>2.5–15</td>
<td>2.4–14.4</td>
<td>0</td>
</tr>
<tr>
<td>PMDCs</td>
<td>Bio-electrochemical reactions with ionic transport</td>
<td>~0</td>
<td>~0</td>
<td>1.8 + 2.2 + 0.21 = 4.21</td>
</tr>
</tbody>
</table>
membrane (CEM, CMI 7000, Membranes international) separated the cathode and desalination part while an anion exchange membrane (AEM, AMI 7001, Membranes international) separated the anode and desalination chambers. The volume of the desalination chamber was about 200 ml with a salt concentration of 10 g L\(^{-1}\) NaCl. The volume of the algae chamber was maintained at 100 ml to represent a passive algae biocathode. No external mechanical aeration was provided. Thus, the volume ratios in the photosynthetic MDC system were 0.9 : 1.0 : 0.55 for anode, desalination and cathode chambers respectively.

The voltage was recorded using a digital multimeter (Fluke, 287/FVF) and a 10 kohm resistor was used in closed circuit tests. The current was calculated using the Ohm’s law, \(I = \frac{V}{R}\). The power density was calculated (using \(P = V \times I\)) as per the anode/cathode chamber volume or the electrode surface. COD tests were carried out according to the standard methods.\(^{21}\) Electrical conductivity, TDS removal and salinity removal were recorded using a conductivity meter (Extech EC400 ExStik Waterproof Conductivity, TDS, Salinity, and Temperature Meter). The pH of the samples was measured using a pH meter (Orion 720A+ advanced ISE/pH/mV/ORP). Dissolved oxygen was measured using a YSI 5100 system. Algae growth was monitored by measuring the optical density of the algal medium with a Spectronic\(^{\circ}\)20 Genesys spectrophotometer at a wavelength of 620 nm. Measurements were taken at regular intervals and three replicates were measured per sample. The desalination rate (\(Q_D, \text{mg h}^{-1}\)) was calculated by \(Q_D = (C_0 - C_t)/t\), where \(C_0\) and \(C_t\) are the initial and the final TDS of saltwater in the middle chamber over a batch cycle of time \(t\). Illumination on the algae cathode chamber was provided by CFL white light at 60 W (276 \(\mu\)mol m\(^{-2}\) s\(^{-1}\)).

**Results and discussion**

**MDC operation**

Fig. 1 shows the schematic of the microbial desalination cell with algae as the bioacthode, similar to the experimental set-up shown in Fig. S1.† Two microbial desalination cells were tested, one with air cathode and the other with algal biocathode. The air cathode MDC served as the control MDC. The microbial consortium was grown in air and algal biocathode MFCs prior to its transfer into the air and algae biocathode MDCs respectively.

**Power production in MDCs**

Fig. 2 shows the voltage generation profiles for the air cathode (control) and algal biocathode MDCs. The operation time was considered when the voltage was stable. The voltage for the air cathode MDC increased slowly for the first 50 hours of operation which can be related to the lag phase for microorganisms to establish their mechanisms for extracellular electron transfer and form a biofilm on the electrodes.\(^{23,24}\) This lag phase was shorter for the algal biocathode showing the influence of in situ oxygen generation by algae in the cathode side which increases the electron mobility. In situ produced oxygen via algal
photosynthesis can be seen in Fig. 1. Algae may produce oxygen according to the following reaction:

\[ n\text{CO}_2 + n\text{H}_2\text{O} \xrightarrow{\text{algae, } \text{hv}} (\text{CH}_2\text{O})_n + n\text{O}_2 \]

The maximum produced voltage in the closed circuit for the algal cathode MDC (0.236 V) was also higher than the air cathode MDC (0.219 V) for similar experimental conditions at 10 kΩ. This process is limited by the electron receiving mechanism that is to be developed in the algae cathode chamber or it can be called a cathode-driven process. The voltage generation follows a sigmoidal increase which could be explained as the lag phase required for both the biofilms to form in the anode and cathode chambers especially in this process, until a suitable electron acceptance mechanism is established by algae. This type of sigmoidal pattern was also observed in previous biocathode based microbial fuel studies. In photosynthetically driven systems, the role of algae in the electron transfer is not clear. They may contribute to indirect electron transfer as shown in Fig. 1. For passive air cathode MDCs, the lag phase can be very significant since the electron transfer is not catalyzed by an external chemical catalyst. A 50 hour lag phase was observed in a modified air cathode (platinum applied carbon cloth) study by Mehanna et al. also.

Our results are similar in nature to those observed by Wen et al. They used an aerobic consortium as a bacterial catalyst in the cathode chamber, which produced maximum voltage higher than that of an air cathode MDC operated under similar conditions. Wen et al. used an aerator to supply an air flow rate of 200–300 ml min⁻¹ without platinum catalyst. The higher maximum voltage in the algae biocathode MDC compared with that in the air cathode MDC in our study indicated that reduction of protons and electrons at the cathode will be higher by microbially catalyzed aerobic biocathodes. Microbially catalyzed biocathodes produce a stable voltage for longer periods unlike the potential reduction which occurs when a chemical catalyst like ferricyanide was used as the catholyte. Although it appears that the air and algae biocathodes have performed at comparable levels, it should be noted that only about 55% of the cathode volume was used for algae biocathodes in this study which indicates that the power production as well as desalination rates could be further improved with algae biocathodes. Illumination was provided by an external source in this study, but for large scale applications, the light requirements can be replaced by natural sun light or aerobic microbial consortium can be used as the biocathode.

**COD removal in MDCs**

The COD removal in the anode chambers in algae and air cathode MDCs over a fed-batch cycle was about 65.6% and 56.6% respectively. Fig. 3 shows the COD concentration of influent and final effluent for both MDCs. The higher produced voltage in the algal MDC means more electrons were released from organic matter degradation by biofilm in the anode. As a result the organic removal which is reported as COD removal will be higher for the algal cathode MDC compared to the air cathode MDC. On the other hand, higher removal of COD will induce higher carbon dioxide generation to be transferred to the cathode chamber. Higher CO₂ would improve the photosynthesis activity of algae and thus oxygen generation as electron acceptors. However, in this study, the algae biocathode was not supplied with air or CO₂ after its transfer from a pre-aerated bioreactor.

**Desalination rates in MDCs**

Fig. 4 shows desalination profiles for both MDCs. The initial electrical conductivity for 10 g L⁻¹ of NaCl was 17.78 mS cm⁻¹. The percentage salinity removal in air cathode and algae biocathode MDCs was 24.2 and 40.1% respectively. The desalination rate (Qᵅ) of the algal MDC was 0.161 g L⁻¹ d⁻¹ (6.71 mg h⁻¹), about 2.1 times higher than the air cathode MDC with Qᵅ equal to 0.076 g L⁻¹ d⁻¹ (3.2 mg h⁻¹). The higher

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**Fig. 3** COD removal in air (control) and algae biocathode MDCs.

**Fig. 4** Salinity removal and electrical conductivity.
Salinity removal rate for the algae biocathode MDC is due to its higher potential difference between the anode and cathode which stimulates the transfer of ions in the middle chamber to the anode and cathode chamber. Wen et al. (2012) also found higher salinity removal for the biocathode MDC compared to the air cathode MDC.\footnote{26}

Salinity removal in microbial desalination cells is dependent on many factors such as salt solution volume, wastewater volume, hydraulic retention times (HRTs) of wastewater and salt solution concentration, membrane surface area, microbial oxidation and oxygen reduction reactions.\footnote{13} It has been reported that the shorter the distance between electrodes, the lower the internal resistance will be in microbial fuel cells.\footnote{29} Also, the higher the volumetric ratio, the higher will be the desalination rates. In our study, the ratio of the anode compartment to the desalination compartment was 0.9 (v/v). In the study by Cao et al. (2009) who achieved about 90% salt removal in a MDC with ferricyanide as the cathode with initial NaCl concentrations of 5, 20 and 35 g L\(^{-1}\), this ratio was about 9 (v/v).\footnote{7} Mehanna et al. (2010) used equal chamber volumes for anode, cathode and desalination chambers and obtained 43–67% desalination rates with initial NaCl concentrations in the same range as Cao et al., in an air cathode with Pt.\footnote{26} Luo et al. (2012) observed 66% salinity removal in a MDC with the anode to desalination volume ratio of 2.33 (v/v).\footnote{7} Zhang and He (2012) designed an osmotic MDC with a ratio of 0.8 (v/v) and achieved 57.8% salinity removal.\footnote{11} These studies indicate that the MDC design and the volume of wastewater in the MDC have a significant effect on salinity removal and further optimization of microbial desalination cells in terms of reactor volumes is essential to improve the desalination rates.

Salinity removals in three-chamber MDCs can be above 90% from 30–35 g L\(^{-1}\) NaCl solutions that have conductivities similar to seawater. However, very high salinity removals have required a large volume of non-salty water, primarily the anolyte but also the catholyte, with 55 to 133 times the volumes of desalinated water (Table 2). Similarly, 86% removal from 10 g L\(^{-1}\) NaCl was reported at the volume ratio of 6. These results indicate that the required amount of wastewater is also dependent on the initial salinity of salt water in MDCs.\footnote{12} MDCs can be more effective for partial removal of salinity. For instance, the required wastewater was only two to three times the desalinated water when MDCs achieved 40 to 60% salinity removal. These results imply that, for practical applications, MDCs are more likely to be used for partial salt removal from seawater.\footnote{22}

### Extended power performance in MDCs

In order to investigate the current generation potentials of the algae biocathode MDC, different external resistances from 4 \(\Omega\) to 10 k\(\Omega\) were applied and the polarization curve was obtained. Fig. 5 shows the current profiles for different external resistances. The maximum current increased by decreasing the ohmic external resistance. The current goes up to a maximum level and then starts to decrease along the whole cycle. However, when the external resistance continued to reduce from 100 \(\Omega\) to 4 \(\Omega\), the maximum currents declined sharply. These observations are similar to those by Chen et al. in stacked MDC studies. At very low resistances, the exoelectrogenic bacteria could not produce enough electrons.\footnote{16}

Mitra and Hill observed similar phenomena in the algae based MFC in which at low external resistances, the produced voltage was low.\footnote{21} Based on the polarization curve for algae MDCs (Fig. 5), the maximum power density point (MPP) for the 200 \(\Omega\) external resistance was 84.02 mW m\(^{-2}\) with a current density of 1520 mA m\(^{-2}\) (anode volume). When considering the algae biocathode volume (100 ml), these were 151.25 mW m\(^{-2}\)

### Table 2  A comparison of desalination and power density performances in MDC studies

<table>
<thead>
<tr>
<th>(V_a : V_d : V_c)</th>
<th>NaCl conc. (g L(^{-1}))</th>
<th>Removal rate (%)</th>
<th>Desalination rate (mg h(^{-1}))</th>
<th>Anode</th>
<th>Cathode</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3 : 1 : 9.2</td>
<td>35</td>
<td>92</td>
<td>2.8</td>
<td>1.6 g L(^{-1}) sodium acetate (1248 mg L(^{-1}) COD)</td>
<td>Biocathode</td>
<td>26</td>
</tr>
<tr>
<td>13 : 1 : 10</td>
<td>35</td>
<td>77</td>
<td>2.3</td>
<td>1 or 2 g L(^{-1}) sodium acetate (780–1560 mg L(^{-1}) COD)</td>
<td>Air cathode</td>
<td>26</td>
</tr>
<tr>
<td>1 : 1 : 1</td>
<td>20</td>
<td>37</td>
<td>1.7</td>
<td>1.6 g L(^{-1}) sodium acetate (1248 mg L(^{-1}) COD)</td>
<td>Air cathode/Pt</td>
<td>25</td>
</tr>
<tr>
<td>100 : 1 : 33</td>
<td>35</td>
<td>93</td>
<td>2.7</td>
<td>500 mg L(^{-1}) COD glucose</td>
<td>Ferricyanide</td>
<td>5</td>
</tr>
<tr>
<td>0.9 : 1 : 0.5</td>
<td>10</td>
<td>40</td>
<td>6.7</td>
<td>Chlorella vulgaris biocathode</td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type</th>
<th>COD removal (%)</th>
<th>Power density (mW m(^{-2}))</th>
<th>Power density (W m(^{-2}))</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC</td>
<td>NA</td>
<td>0.95</td>
<td>0.02 M potassium ferrocyanide</td>
<td>Chlorella vulgaris</td>
<td>22</td>
</tr>
<tr>
<td>MFC</td>
<td>89–92%</td>
<td>0.6</td>
<td>20 g L(^{-1}) glucose (21.33 g L(^{-1}) COD)</td>
<td>Chlorella and Phormidium</td>
<td>30</td>
</tr>
<tr>
<td>MDC</td>
<td>56.2 ± 6.0%</td>
<td>940</td>
<td>14.49</td>
<td>1.6 g L(^{-1}) sodium acetate (1248 mg L(^{-1}) COD)</td>
<td>Aerobic consortium</td>
</tr>
<tr>
<td>MDC</td>
<td>62.6 ± 4.4%</td>
<td>540</td>
<td>8.74</td>
<td>Air cathode</td>
<td>26</td>
</tr>
<tr>
<td>MDC</td>
<td>65.6%</td>
<td>5.35</td>
<td>0.151</td>
<td>Chlorella vulgaris</td>
<td>This study</td>
</tr>
<tr>
<td>MDC</td>
<td>56.6%</td>
<td>5.35</td>
<td>0.151</td>
<td>Air cathode</td>
<td>This study</td>
</tr>
</tbody>
</table>
and 2750 mA m$^{-3}$ respectively. Beyond this point, an increase in ohmic losses and electrode overpotentials resulted in the power drops to the point where no more power is produced. The current generation profiles for air and algae biocathode MDCs are shown in Fig. S2, and S3.$^\dagger$ Current and voltage responses to different external resistances are shown in Fig. S4.$^\dagger$ Table 2 compares the power densities reported in different algae or aerobic biocathode MFC/MDC studies and air/ferricyanide cathode MDC studies. The reasons for lower power productions in our study are explained in previous sections. However, the performance can be improved by process modification involving material/electrode configurations, reactor volumes and by increasing the algae concentrations.

Enhanced COD removal in algae biocathode MDCs

Further experiments were conducted to study the potential of advanced wastewater treatment by the algae biocathode in the MDCs. These tests were conducted in two stages: (1) synthetic wastewater treatment in the anode chamber followed by; (2) enhanced COD removal in the biocathode chamber. Treated effluent (anolyte) from the anode chamber was recycled through the biocathode chamber to enhance the COD removal and to supplement the growth medium requirements for algae. Fig. 6 shows the voltage profiles for the two stages: stage 1 representing the anaerobic treatment of synthetic wastewater and stage 2 enhanced treatment in the biocathode. At the end of stage 1, the anolyte was replaced with fresh solution and the anolyte from stage 1 was used as the algal growth medium. Stage 1 operated for 196 hours while stage 2 operated for 94 hours. A COD removal of 71.2% was achieved in the first stage with an additional COD removal of 9.1% in the second stage totalling 80.3% (Fig. 7). This shows that algae can enhance wastewater treatment by utilizing organic carbon. As seen in Fig. 6, the MDC had a significant lag phase (due to the fresh start-up), however, once the biofilm is established the voltage generation as well as COD removal evolved at a faster rate. For instance, in this study, the COD removal rate for stage 1 was 2.38 mg L$^{-1}$ h$^{-1}$ while the same was 4.01 mg L$^{-1}$ h$^{-1}$ in the second stage. The COD removal rate in the algal biocathode was 0.59 mg L$^{-1}$ h$^{-1}$ in stage 2. A cumulative desalination rate of 28% was observed over a 12 day period (Fig. 8). The desalination rate ($Q_D$) of algal MDCs was 0.199 g L$^{-1}$ d$^{-1}$ (8.333 mg h$^{-1}$) in the first stage, about 1.7 times higher than the second stage operation with $Q_D$ equal to 0.107 g L$^{-1}$ d$^{-1}$ (4.47 mg h$^{-1}$). It should be noted that these desalination rates are higher than those reported in similar studies (Table 2).

Fig. 9 shows the pH changes in the anode and cathode chambers for stages 0, 1 and 2. The anode pH at stages 0, 1 and 2 was 6.8, 6.4 and 6.7 respectively while the pH in the cathode
chamber was 8.7, 9.7 and 6.4 respectively. The resultant pH of the anolyte and catholyte mixture was 6.6 at stage 2. Although MDCs improve the conductivity of the anolyte, pH drop still occurs in the anode chamber because of the accumulation of protons. Similarly, the pH in the cathode chamber rises due to hydroxyl ions generated by cathodic reactions such as oxygen reduction. These pH imbalances may affect the MDC performance by inhibiting the activity of exoelectrogenic microorganisms. In our study, due to high buffer concentration in the anolyte, the pH drop was not significant, however the catholyte pH increased in stage 1. One of the benefits of recirculation of anolyte to the cathode chamber is that the pH of the catholyte solution can be brought down to neutral conditions by mixing with anolyte.

**Energy perspective of the proposed system**

As shown in Table 1, conventional water treatment and desalination technologies do not have the potential to produce electricity. Wastewater treatment by anaerobic digestion can generate an electrical energy equivalent of 0.09–0.14 kW h m⁻³ through biogas production. Contrary to conventional desalination methods, MDC is considered an energy gaining process. The microbial desalination cells produce bioelectricity while desalinating the saline water. It is estimated that about 1.8 kW h of bioelectricity can be generated in MDCs by treating 1 m³ of wastewater while a reverse osmosis technology requires 2.2 kW h of electricity for the same amount of water desalination. This suggests that desalination combined with MDCs has the potential to become a sole power generator along with wastewater treatment. Combining the energy produced by MDCs and the energy saved by desalination, a total 4 kW h m⁻³ of energy savings can be realized (Table 1). On a side note, in studies involving hydrogen production, it was determined that the MDC or MEC system has recovered 2.3 times more energy than that was invested originally.8

In the proposed system, assuming an algal lipid production of 0.04 kg m⁻³ d⁻¹ (ref. 33) from the algal biomass (with a specific energy value of 48 MJ kg⁻¹ and an electric conversion efficiency of 40%), a maximum electrical energy of 0.21 kW h m⁻³ of treated wastewater can be obtained which further increases the net energy benefit of the PMDC system to 4.21 kW h m⁻³ or 2.01 kW h m⁻³ respectively with and without the desalination energy credit (assuming that the electricity production and desalination rates in PMDCs are improved to the current performance levels of MDCs). In systems integrated with algal harvesting, the energy recovery benefits could be even higher since algae have an energy content of 5–8 kW h kg⁻¹ dry weight. This energy can be recovered in the form of biofuels such as biogas, biohydrogen, and biodiesel.4

**Conclusions**

This study demonstrated the performance of passive algae bioelectrodes for in situ oxygen generation. Although the produced current is not comparable to the MDC configurations with platinum catalyzed air-cathodes and chemical based cathodes, the current production is much higher than the MDCs with passive air cathodes and MFCs with algae bioelectrodes. The desalination rates are comparable to the other existing MDC configurations. This study provides an environmentally benign approach in which algae can serve as an in situ oxygen generator and help remove COD further in the cathode chamber. Further developments in the MDC reactor design and electrode/material configurations will definitely increase the power generation potential in the PMDCs. Since cathode driven processes carry many specific advantages such as continuous supply of electron acceptors which omits the need for additional chemical transport, storage, dosing and post-treatment, algae bioelectrodes in PMDCs can improve their performance via an environmentally sustainable manner. The tested configuration produced algal biomass which is another highly valued feedstock enhancing the sustainability of PMDCs.

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References