International Biodeterioration & Biodegradation 130 (2018) 91–97

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

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

A microbial desalination process with microalgae biocathode using sodium bicarbonate as an inorganic carbon source

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ARTICLE INFO

Keywords:
Microalgae
Wastewater
Microbial desalination
Sodium bicarbonate
Bioelectricity
Renewable energy

ABSTRACT

This research investigates a novel platform for an energy-yielding wastewater treatment and desalination scheme in which the organic matter present in wastewater is purposely fed to the exoelectrogenic bacteria to produce bioelectricity in a three-compartment bioelectrochemical system called photosynthetic microbial desalination cell (PMDC). The role of an inorganic carbon source in the microalgae biocathode was studied. Addition of sodium bicarbonate ($NaHCO_3$) increased power production, microalgae growth and desalination rate. A power density of 660 mW/m^3 was measured which is about 7.5 times higher than the PMDCs without $NaHCO_3$. Desalination rate was more than 40% after 72 h. Overall, the process could be energy-positive while producing 4.21 kWh per m^3 of wastewater treated including desalination energy savings and microalgae biomass energy potential.

1. Introduction

Urban water scarcity is increasing across the world which has created the necessity for water reuse and desalination in many regions (Gude, 2017, 2018). For example, population growth and industrialization in certain parts of the United States has caused the country to be the highest ranked country for water reuse followed by other countries in arid regions such as Saudi Arabia, Qatar, Israel, and Kuwait with high per capita wastewater reuse. Both wastewater treatment and reclamation technologies are energy- and cost-intensive. Most commonly used wastewater treatment process (activated sludge process) consumes large amounts of energy with high capital and maintenance costs (Gude, 2015a). Nutrient removal processes are even more burdensome in terms of costs and implementation (Gude, 2015b). There is a critical need for developing advanced and more affordable water purification technologies for both desalination and water reuse purposes to increase freshwater supplies (Gude, 2017, 2018).

Considering the issues at the water-energy-resource nexus, bioelectrochemical systems (BES) have shown promise for energy-positive and resource-efficient wastewater treatment. As a result, there is a growing interest in this technological area over the recent years. Microbial fuel cells (MFC), one of the BES have received much attention in recent years (Friman et al., 2013; Gude, 2016). MFCs produce bioelectricity directly from the biological oxidation of organic matter in wastewater mediated by exoelectrogenic bacteria (Mathuriya, 2016). This technology is suitable for treating low to high strength wastewaters with high conversion efficiencies at much less biosolids generation (Gude, 2015b, 2016). This technology provides a very convenient mechanism for integrated applications in centralized, decentralized and remote wastewater treatment applications including septic tanks, activated sludge processes, anaerobic lagoons and wetlands and other industrial wastewater treatment processes (Gude, 2016).

A microbial desalination cell (MDC) is a modification of MFC which allows for simultaneous wastewater treatment and desalination with bioelectricity production (Cao et al., 2009). Similar to MFCs, MDCs also suffer from low power densities due to losses in electron transfer and release mechanisms. To improve the performance of BES, cathodes are often coated with noble catalysts such as platinum and others or external aeration or chemical agents such as ferricyanide are provided (Kalleary et al., 2014; Debuy et al., 2015; Yang et al., 2018; Fang et al., 2018). To eliminate the cost and toxicity issues related to the utilization of noble catalysts and chemical electrolytes, biocathodes have been proposed as an alternative to abiotic cathodes (Kokabian and Gude, 2013, 2015; Kokabian et al., 2018a, 2018b; 2018c). The active microbial metabolism in various biological cathodes can be utilized to produce useful products (Mohanakrishna et al., 2015) or remove contaminants from wastewaters, such as nitrate and heavy metals (Jiang et al., 2017; Shen et al., 2017). Different microbial consortia were used as biocatalysts in biocathodes such as nitrifying and denitrifying bacteria and microalgae to produce electron acceptors required for reduction reaction at the cathode (He and Angenent, 2006; Clauwaert

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https://doi.org/10.1016/j.ibiod.2018.04.003
Received 8 February 2018; Received in revised form 27 March 2018; Accepted 4 April 2018
Available online 13 April 2018
0964-8305/

et al., 2007). Among these, microalgae biocathodes provide unique advantages that enhance the benefits of microbial desalination process. Microalgae biocathodes can be used to sequester the remaining dissolved organic matter and nutrients for microalgae biomass production which could be further processed for bioenergy production while providing superior treatment (Gude, 2016). Due to their superior characteristics to their counterparts such as terrestrial plants and crops for biofuel production, microalgae have been extensively studied for various forms of biofuels such as bioelectricity, biogas and biodiesel and other crude oils including high value health, medical, plastic and pigment products (Blair et al., 2014). Microalgae essentially depend on carbon dioxide and light to meet their carbon and energy needs through a photosynthetic process which produces carbohydrates and lipids. Different sources of carbon dioxide were considered as potential carbon sources for microalgae. Among these industrial flue gases and other power plant emissions have been encouraged for microalgae growth in integrated systems with relevant carbon credits and tax reliefs. Microalgae can be grown using inorganic carbon sources such as HCO_3^- and CO_3^{2-} provided by either sodium bicarbonate or sodium carbonate (Hsueh et al., 2007; Yeh and Chang, 2010). Among them, sodium bicarbonate is available at low cost and has higher solubility. Moreover, it was shown that microalgae grow better with sodium bicarbonate as an inorganic carbon source (Chi et al., 2013; Gardner et al., 2013). It should be noted that the metabolic efficiency and resulting microalgae composition of using CO_2 or carbonate/bicarbonate as carbon source varies from species to species (Giordano et al., 2005; Hsueh et al., 2007; Yeh and Chang, 2010).

Current wastewater treatment schemes are merely targeted towards environmental protection through energy-intensive processes (Gude, 2015a, 2015b). This research develops a three-compartment bio-electrochemical system called a photosynthetic microbial desalination cell (PMDC, Kokabian and Gude, 2013, 2015 and Kokabian et al., 2018a, 2018b; 2018c). The three compartments hold wastewater (anolyte), saline water and a microalgae suspension (catholyte) respectively. The electron generating process in the anode compartment is augmented by the electron accepting mechanism provided by the photosynthetic microalgae species, *Chlorella vulgaris,* in biocathode compartment while ionic imbalance in the anode and cathode chambers facilitates desalination by migration of counter ions. We studied the role of sodium bicarbonate as an inorganic source for microalgae biocathode in PMDCs. This approach has two purposes: 1) to increase the microalgae biomass growth by utilization of dissolved sodium bicarbonate which would produce dissolved oxygen under in-situ conditions as an electron acceptor required for completing the redox reaction in the MDC and 2) use of sodium bicarbonate may enhance the chemistry related to desalination in the MDC by providing ionic concentration difference and species migration among the desalination and biocathode chamber. We evaluated the effect of sodium bicarbonate on the PMDC performance in terms of COD removal rate, desalination rate, microalgae growth and electricity production. The power density, maximum and cumulative voltage profiles, and desalination rates are derived from the experimental results. This is the first study attempting to understand the effect of an inorganic carbon source on microalgae biocathode and its impact on the performance of a PMDC in terms of wastewater treatment, desalination and bioelectricity and microalgae biomass production.

2. Materials and methods

2.1. Microbial consortia and nutrient media

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 acclimatize to anaerobic conditions in synthetic wastewater containing 300 mg/L 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 mg/L, KH_2PO_4 (4.4 g/L), K_2HPO_4 (3.4 g/L), NH_4Cl (1.5 g/L), $MgCl_2$ (0.1 g/L), $CaCl_2$ (0.1 g/L), KCl (0.1 g/L), $MnCl_2.4H_2O$ (0.005 g/L), and $NaMo.O_4{\bullet}2H_2O$ (0.001 g/L) (Kokabian and Gude, 2013, 2015; Kokabian et al., 2018a, 2018b; 2018c). The COD concentration used in the MDC anode chamber was 500 mg/L. The microalgae *Chlorella vulgaris* used in the cathode compartment was grown in the following mineral solution: $CaCl_2$ (25 mg/L), NaCl (25 mg/L), $NaNO_3$ (250 mg/L), $MgSO_4$ (75 mg/L), KH_2PO_4 (105 mg/L), K_2HPO_4 (75 mg/L), and 3 mL of trace metal solution with the following concentration was added to 1000 mL of the above solution: $FeCl_3$ (0.194 g/L), $MnCl_2$ (0.082 g/L), $CoCl_2$ (0.16 g/L), $Na_2MoO_4{\bullet}2H_2O$ (0.008 g/L), and $ZnCl_2$ (0.005 g/L). *Chlorella vulgaris* was chosen due to its tolerance for high levels of CO_2 and high efficiency in utilizing CO_2 through photosynthesis. A known volume of this algal consortium with a known cell density was transferred into the cathode chamber.

2.2. MDC experimental setup

The MDC reactors were prepared by inserting a desalination chamber between anode and cathode chambers of a microbial fuel cell reactor. Cation exchange membrane (CEM, CMI 7000, Membranes international) separated the cathode and desalination chambers while an anion exchange membrane (AEM, AMI 7001, Membranes international) separated the anode and desalination chambers. The anode, desalination and cathode chambers contained 60, 30, 60 mL of wastewater, saline water and microalgae suspension respectively. Thus, the volume ratios in the photosynthetic MDC system were 1: 0.5: 1 for anode, desalination and cathode chambers respectively.

The cylindrical-shaped MFC chambers were made of plexiglass with a diameter of 7.2 cm. Carbon cloth was used as anode and cathode electrodes. The area of the anode electrode and that of the cathode electrode were 16 cm^2.

2.3. Experimental studies

Experimental studies were conducted in the following manner. First, a set of experiments were conducted to verify the reliability of the process. Three MDCs were operated in parallel to study the variations in wastewater treatment potential, desalination rates and bioelectricity production in MDCs. A calibration curve was developed correlating the absorbance (−) of microalgae suspension and the biomass concentration (mg/L) with microalgae grown in our laboratories. As shown in Fig. S1, a good correlation was observed. Microalgae dry biomass concentration was calculated using the following equation.

$$microalgae\ concentration = \frac{\text{absorbance at OD 620 nm}}{0.8702}$$

All experiments were conducted with a pre-measured microalgae absorbance of 0.2. First, the effect of sodium bicarbonate was studied with concentrations at 0 mg/L, 0.25 mg/L, 0.5 mg/L, 0.75 mg/L, and 1 mg/L respectively. Next the effect of desalination chamber was evaluated at 15, 35 and 55 g/L and a desalination compartment volume of 10, 20 and 30 mL, respectively. This volume variation refers to 1:6; 1:3; and 1:2 with respect to wastewater and microalgae suspension volumes.

2.4. Analytical procedures

The voltage was recorded using a digital multimeter (Fluke, 287/FVF) and a 1 kΩ resistor was used in closed circuit tests. Current was calculated using the Ohm's law while power density was calculated as per the anode/cathode chamber volume or the electrode surface. COD tests were carried out according to the standard methods. 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 an YSI 5100 system. Microalgae growth was monitored by measuring the optical density of the microalgae suspension with a Spectronic20 Genesys spectrophotometer at a wavelength of 620 nm. Measurements were taken at regular intervals and three replicates were tested for each experimental condition. Based on the measurements, desalination rates, power production and microalgae growth were calculated. The desalination rate (Q_d, mg/h) was calculated by

$$Q_d = \frac{C_o - C_t}{t}$$

Where, C_o and C_t are the initial and the final TDS of saltwater in the middle chamber over a batch cycle of time t.

3. Results and discussion

3.1. Preliminary experiments for reproducibility

Following anaerobic culture enrichment and biofilm formation on the electrodes through a set of preliminary studies, an evaluation of reproducibility and performance variation was conducted by running three MDCs in parallel and simultaneously for two runs. The voltage generation (Fig. 1a, Fig. 1b and 1c) and cumulative voltage (Fig. 1d, e, and Fig. 1f) profiles at 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance for microalgae suspension are shown in Fig. 1. It was observed that the maximum voltage potential varied between 206 mV and 256 mV (Cell 1: 249 mV, 256 mV for cycles 1 and 2 respectively; Cell 2: 206 mV, 221 mV; Cell 3: 232 mV, 246 mV) among the three cells during the first 1000 min. The cumulative voltage production at 4000 min of operation time varied between 19,881 mV and 29,818 mV (Cell 1: 19851 mV, 22,866 mV for cycles 1 and 2 respectively; Cell 2: 19,880 mV, 23,308 mV; Cell 3: 25,880 mV, 29,818 mV) among the three cells. It should be noted that the electricity generation activity has sped up in the second run as evidenced by the shortened time for peak voltage as shown in Fig. 1a, b, and Fig. 1c. In addition, the productivity increased as shown by cumulative voltage values for run 1 and run 2. These results have shown that the PMDCs can be operated with results that are reproducible with consistent output across different reactors for a given set of physiological conditions.

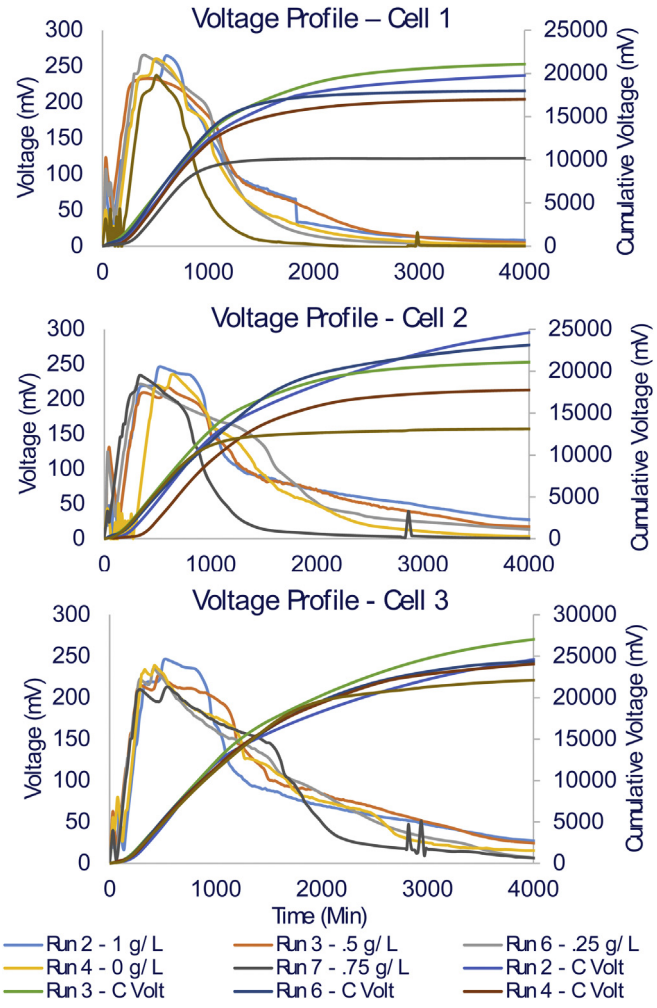

Fig. 2. Voltage generation and cumulative voltage profiles for three cells under five experimental runs with various concentrations (0–1 g/L at 0.25 g/L intervals) of sodium bicarbonate and 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance for microalgae suspension.

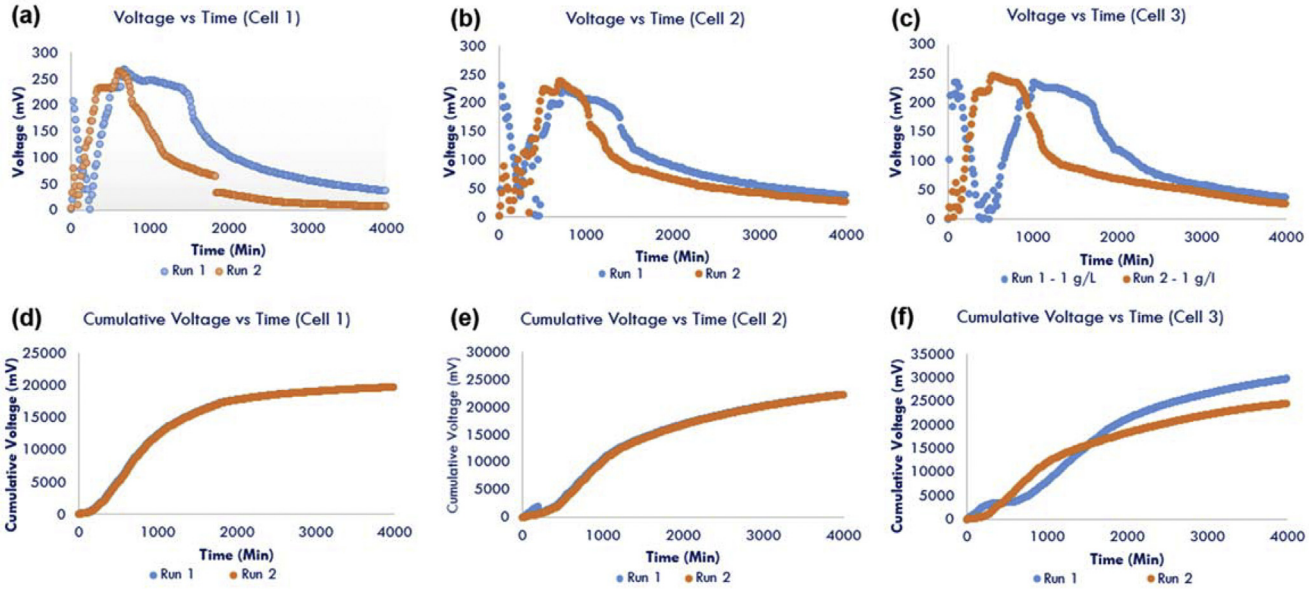

Fig. 1. Voltage generation (a,b,c) and cumulative voltage (d,e,f) profiles for three cells under two experimental runs with 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance for microalgae suspension.

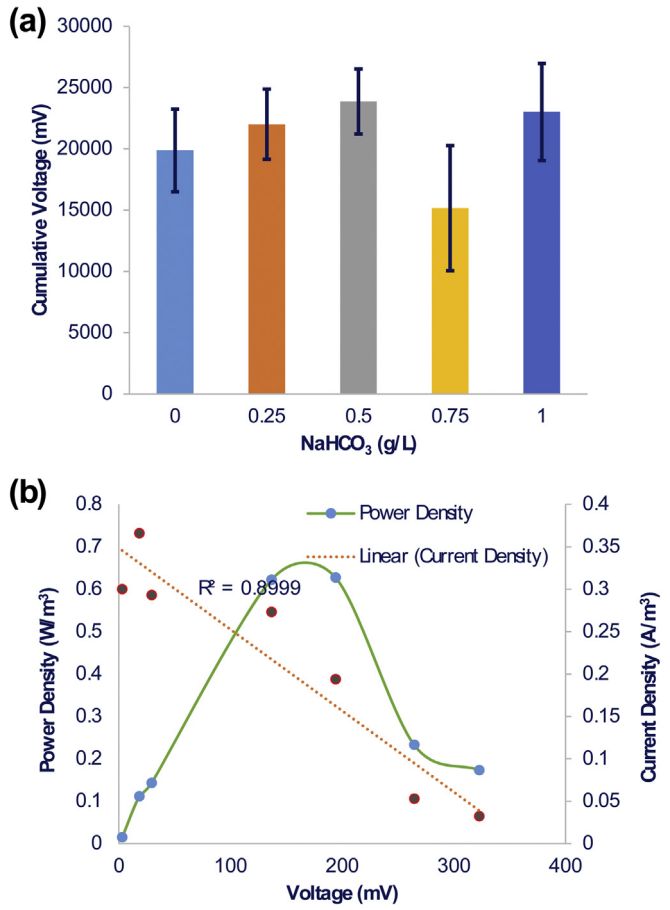

Fig. 3. (a) Comparison of cumulative voltage at different sodium bicarbonate concentrations and 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance of microalgae; (b) polarization curve for PMDC with 0.5 mg/L of sodium bicarbonate in microalgae biocathode and 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance of microalgae.

3.2. Effect of sodium bicarbonate in microalgae biocathode

Following the reproducibility tests, the effect of sodium bicarbonate on the biocathode performance was evaluated. The sodium bicarbonate concentrations were varied between 0 g/L and 1 g/L at 0.25 g/L intervals across five different tests and reactors. The voltage generation profiles and cumulative voltage are shown in Fig. 2. The average values and the standard deviations for different $NaHCO_3$ concentrations are shown in Fig. 3a. Aeration was provided in the cathode chamber at 0 g/L $NaHCO_3$ concentration. It was noted that the average cumulative voltage was higher at 0.5 g/L $NaHCO_3$ concentration. However, higher $NaHCO_3$ concentrations did not necessarily increase the cumulative voltage. The continuous voltage production was on par or higher when compared with other $NaHCO_3$ concentrations. Further tests were conducted at 0.5 g/L of $NaHCO_3$ concentration in the microalgae biocathode.

A polarization curve was developed by applying a range of resistances across the electric circuit at the highest voltage generation point. The resistance was varied between 4 Ω and 40,000 Ω. The power density and current density are shown with respect to voltage in Fig. 3b. A maximum power density of 660 mW/m^3 (or current density of 325 mW/m^3) was observed in this study which is about 7.5 times higher than it was previously reported for PMDCs (Kokabian and Gude, 2013). These densities are expressed in terms of working anolyte volumes in the anode chamber. The addition of sodium bicarbonate has enhanced the microalgae activity which improved the availability of dissolved oxygen.

3.3. Microalgae growth in the biocathode compartment

Microalgae growth was monitored by measuring the absorbance of the catholyte suspension. Again varying but consistent observations were made at different concentrations of $NaHCO_3$. As shown in Fig. 4a, the biomass growth rate was higher at both low concentrations of $NaHCO_3$ and microalgae as evidenced at 0.25 g/L. The average biomass growth rates were 25%, 72.6%, 40.0%, 28.2% and 5.5% respectively (see Fig. 4b). Many factors including physiological conditions affect the growth of microalgae. The biomass produced in this process can be beneficial in many ways (Blair et al., 2014). It is estimated that about 1.8 kW h of bioelectricity can be generated in microbial desalination cells by treating 1 m^3 of wastewater while a reverse osmosis technology requires 2.2 kWh of electricity for the same amount of water desalination (Jacobson et al., 2011). 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 kWh/m^3 of energy savings can be achieved (Kokabian and Gude, 2013). In this system, assuming an algal lipid production of 0.04 kg/m^3-d from the algal biomass (with a specific energy value of 48 MJ/kg and an electric conversion efficiency of 40%), a maximum electrical energy of 0.21 kWh/m^3 of treated wastewater can be obtained which further increases the net energy benefit of the PMDC system to 4.21 kWh/m^3 or 2.01 kWh/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) (Kokabian and Gude, 2013). In systems integrated with microalgae harvesting, the energy recovery benefits could be even higher since microalgae have an energy content of 5–8 kWh/kg-dry weight. This energy can be recovered in the form of biofuels such as biogas, biohydrogen, and biodiesel (Martinez-Guerra and Gude, 2016).

3.4. TDS removal and water recovery rates

Total dissolved solids removal and water recovery (as g/L) are shown in Fig. 4c and d respectively. The initial TDS concentration was 35 g/L for all sodium bicarbonate concentrations. The final TDS concentrations (as g/L) were 21.6, 18.5, 23.3, 20.9 and 21.7 respectively which translates to 39.3%, 47.1%, 33.4%, 40.3%, and 38% TDS removal rates respectively. The corresponding water recovery rates were 34.4%, 45%, 33.9%, 48.3% and 31.1% respectively.

The TDS removal and water recovery rates were lower at 0.5 g/L of sodium bicarbonate concentration. The ionic species migration between the anode, desalination and biocathode compartment is strongly influenced by the bicarbonate chemistry and the pH in the biocathode. In addition, the anionic and cationic exchange membranes at anode and cathode compartments allow for migration of chloride and sodium ions from the desalination compartment respectively. On the other hand, the chemistry of the biocathode compartment can be explained as follows. According to the equilibrium $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$, H^+ is consumed during the conversion of HCO_3^- to CO_2, and this CO_2 is ultimately fixed during photosynthesis by microalgae. The steady-state use of HCO_3^- as the original carbon source for photosynthesis leaves OH^- in the cell, and this has to be neutralized by H^+ uptake from the extracellular environment. The reduction of H^+ in the culture medium unavoidably leads to an increased pH, which subsequently changes the equilibrium between different carbonate species. The pK_a of HCO_3^- in fresh water at 25 °C and 1 atm is 10.33; therefore, the acid/base bicarbonate/carbonate pair can act as a strong buffer around this pH. The increased pH will ultimately result in higher CO_3^{2-}: HCO_3^- ratio. Thus, the microalgae biocathode regenerates carbonate by means of the light energy provided (Chi et al., 2011). The migration of Na^+ ions to the biocathode chamber also facilitates high alkaline conditions. The pH values in the anode and biocathode chambers varied between 5 and 7 and between 8 and 10 respectively.

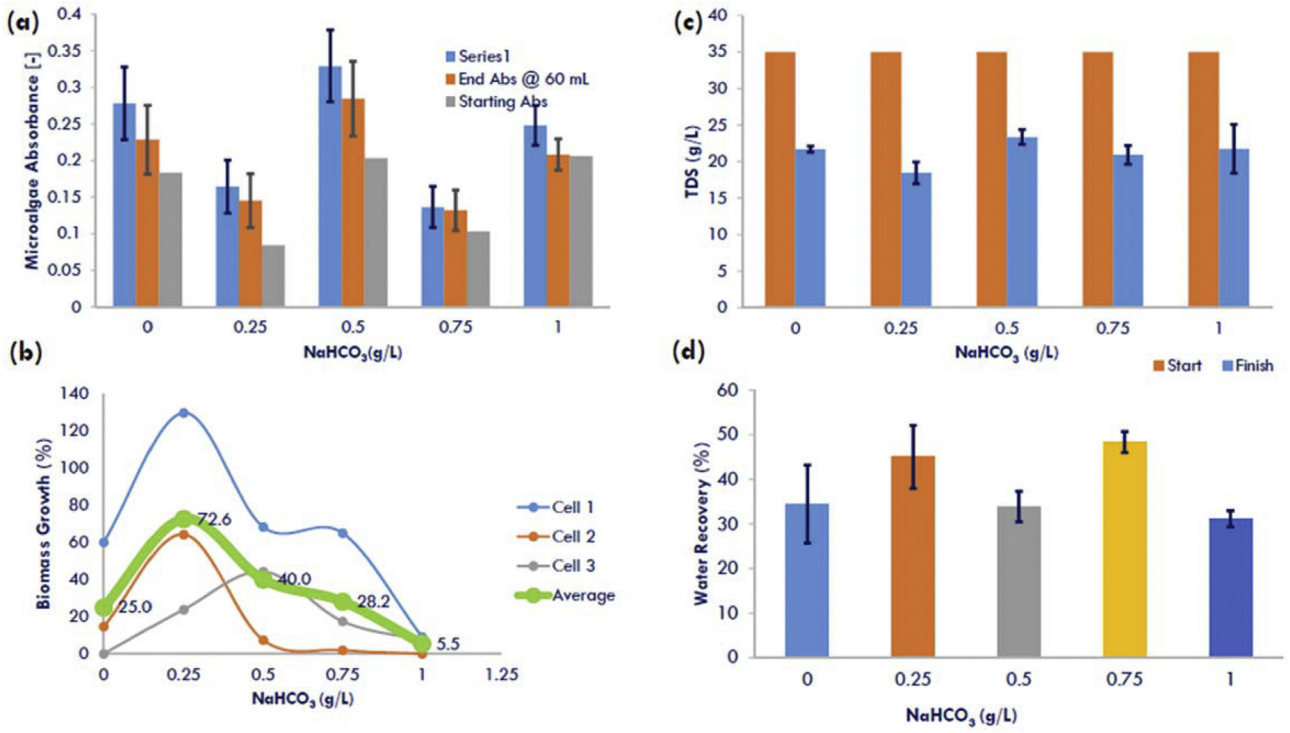

Fig. 4. (a) Comparison of microalgae absorbance before and end of experiments at different sodium bicarbonate concentrations and 500 mg/L of COD, 35 g/L of TDS, and with varying absorbance of microalgae suspension; (b) comparison of biomass growth (%) at different sodium bicarbonate concentrations and 500 mg/L of COD, 35 g/L of TDS, and with varying absorbance of microalgae suspension; (c) comparison of TDS removal at different sodium bicarbonate concentrations and 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance of microalgae suspension; (d) comparison of water recovery (%) at different sodium bicarbonate concentrations and 500 mg/L of COD, 35 g/L of TDS, 0.2 absorbance of microalgae suspension.

3.5. Possible carbon concentrating mechanisms in biocathode chamber

Current atmospheric carbon dioxide concentration available for microalgae utilization or absorption is around 404 ppm of CO_2 (NOAA, 2017). Partial pressures of 0.04 Kpa and a minimum of 0.15 Kpa of CO_2 are required to overcome the kinetic uptake limitations by microalgae. Based on the stoichiometric relationship, 1.7–1.8 g of CO_2 per g of microalgae biomass is required for cell production. About 3 g CO_2 per gram of microalgae biomass is required for lipid-rich microalgae production (Morweiser et al., 2010). The possible mechanisms for CO_2 uptake and the use of sodium bicarbonate can be explained as follow. Similar to other photosynthetic organisms, microalgae concentrate or store CO_2 through a Calvin-Benson cycle and a redox reaction which involves the conversion of CO_2 into carbohydrates with an energy source. When sodium bicarbonate is dissolved in the microalgae growth medium, dissolved inorganic carbon (DIC) exists in water in the form of CO_2, HCO_3^-, CO_3^{2-} and H_2CO_3 when the dynamic ionization equilibrium is reached, but only CO_2 and HCO_3^- are the main DIC forms which can be used by microalgae cells in different ways. For instance, both HCO_3^- and CO_2 can be simultaneously used by most of microalgae. HCO_3^- has been demonstrated to be used not only via a direct way, e.g., active transport (Sültemeyer et al., 1991) and cation exchange (Amoroso et al., 1998), but also via an indirect way which catalyzes HCO_3^- as CO_2 and OH^- by periplasmic carbonicanhydrase (pCA). However, there is an exception that only CO_2 can be used by some microalgae (Zhao and Su, 2014).

Lower levels of CO_2 in the atmospheric air is not adequate to promote a higher biomass production because the major carbon-fixing enzyme, RuBisCo, has a very low affinity for CO_2 under these conditions. Low CO_2 concentrations in natural surface water bodies force the microalgae to overcome this insufficiency by adopting carbon-concentrating mechanisms (CCMs). With CCMs, microalgae increase the intracellular CO_2 concentration by active transport of inorganic carbon into the cells and the release of CO_2 near RuBisCo by the activity of the carbonic anhydrase enzyme (Spalding, 2007; Eaton-Rye et al., 2012). The inorganic carbon source provided in this study more than doubles the required concentrations for microalgae biomass production and photosynthetic synthesis and survival. As noted here, higher concentrations over 2:1 (g CO_2: g microalgae biomass) which is over 0.5 g/L did not result in favorable conditions for this application. However, in commercial applications, CO_2 is supplied to the culture in gaseous form mixed with air, or as soluble inorganic carbonates such as Na_2CO_3 and $NaHCO_3$. CO_2 concentrations of about 1%–5% can often support a maximal microalgal growth, but generally laboratory microalgal cultures are aerated with 5%–15% CO_2 routinely to overcome carbon limitation in fast-growing cultures (Kunjapur and Eldridge, 2010). CO_2 reduction to methane by microorganisms (microbial methanogenesis) is another application which could occur naturally in many industrial and oil producing wastewaters (Yang et al., 2016). CO_2/$NaHCO_3$ enrichment can have a significant impact on the mehtanogenesis process with minimal impact on the microbial biodiversity (Ma et al., 2018) which needs to be monitored in this system.

3.6. Effect of desalination feed concentration and volume

The effect of desalination in MDCs may potentially be caused by two major phenomena, the ionic concentration difference and the osmotic pressure difference across the compartments. The wastewater used as anolyte also contained high total dissolved solids due to the use of high buffer concentrations. Microalgae growth medium consisted of sodium bicarbonate and the trace elements in a nutrient solution with moderate TDS concentration. The desalination compartment was fed with TDS at 15 g/L, 35 g/L and 55 g/L which is considerably higher than the TDS concentrations in other compartments (Fig. 5a and Fig. 5b). This creates

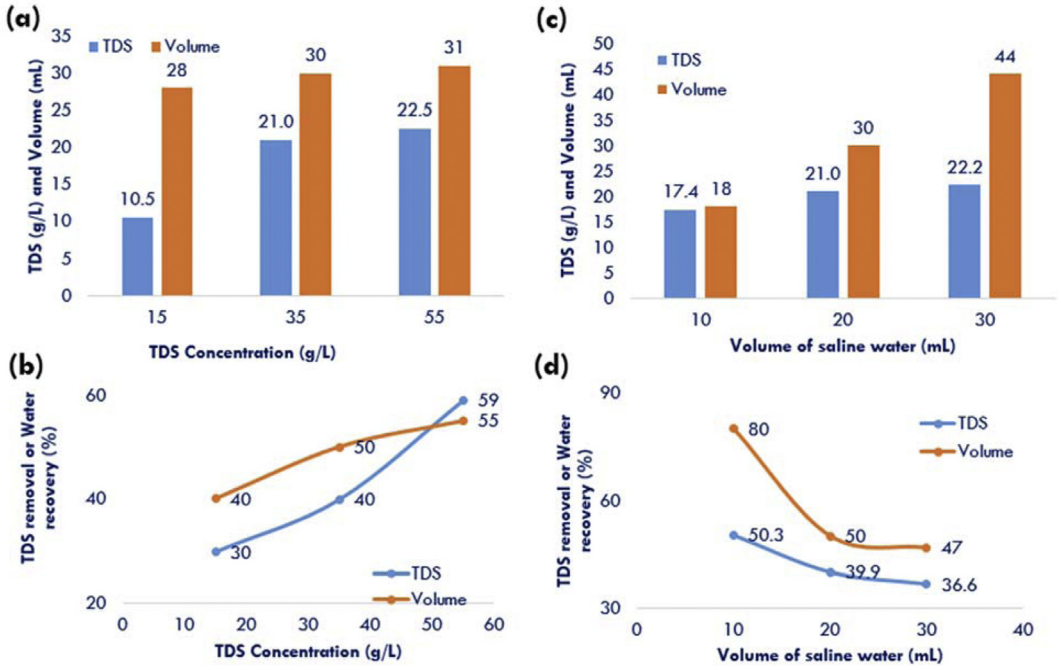

Fig. 5. Effect of TDS concentration in saline water on TDS removal and water recovery: (a) actual concentrations (g/L) and volumes (mL) after the tests; (b) removal of TDS and water recovery in percentages at 0.5 g/L sodium bicarbonate concentration, 500 mg/L of COD, 35 g/L of TDS, and 0.2 absorbance of microalgae suspension. Effect of saline water volume on TDS removal and water recovery: (c) actual concentrations (g/L) and volumes (mL) after the tests; (d) removal of TDS and water recovery in percentages at 0.5 g/L sodium bicarbonate concentration, 500 mg/L of COD, 35 g/L of TDS, and 0.2 absorbance of microalgae suspension.

an osmotic difference promoting natural osmosis process in which the fresh water from the low TDS water would diffuse through the membrane to reach the desalination chamber until an equilibrium can be established between the solvents in the two chambers. The high transfer or increase in water volumes in desalination chamber supports this fact. It should be noted that to reach an equilibrium state, a long residence time may be needed. Another major influential factor for the desalination effect in MDCs is the ionic migration caused between the MDC compartments. Biological degradation of organic compounds in the anode compartment results in release of protons accompanied by electron release to be transferred to or accepted by the anode (electrode). There is a possibility for the chlorides to migrate from the desalination chamber through the anion exchange membrane to the anode compartment to produce hydrochloric acid. High concentration of buffer maintained in the anode compartment would help control changes in pH. Similarly, the migration of Na^+ ions takes place between the desalination and biocathode chambers through the cation exchange membranes. On the other hand, the dissociation of sodium bicarbonate in the microalgae growth medium would release bicarbonates and the chemistry is similar to that was explained in section 3.4.

Our observations show that an increase in the TDS concentration of the desalination feed increased the desalination rate as well as the water recovery due to diffusion and osmotic process. The desalination rate increased from 40% to 55% with increase in feed water TDS concentrations between 15 g/L and 55 g/L. The TDS removal rate also increased from 30% to 59% in this range, almost doubling the rate. The higher concentration gradient with higher TDS feed water increased potential for both ionic transfer as well as water transfer within the compartments through anionic and cationic exchange membranes. The cumulative voltage for the TDS concentrations, 15 g/L, 35 g/L and 55 g/L were 25,080 mV, 16,575 mV and 18,062 mV respectively. Microalgae biomass growth rates were 67%, 229%, and 260% respectively.

In another set of experiments, the effect of desalination compartment volume was studied (Fig. 5c and d). The volume ratio of desalination feed water was changed between 1:2 and 1:6. It was noted that lower desalination volume advanced the water recovery rate as well as the TDS rate. For example, the TDS removal was about 50% at 1:6 (60 mL of anode and biocathode chamber volumes and 10 mL of desalination volume) with corresponding water recovery of 80%. When the anode: desalination and biocathode chamber volumes were 1:3 (60 mL of anode and biocathode chamber volumes and 20 mL of desalination volume) and 1:2 (60 mL of anode and biocathode chamber volumes and 30 mL of desalination volume); the TDS removal rates were 39.9% and 36.6% respectively and water recovery rates were 50% and 47% respectively. The water recovery rates were influenced by the hydraulic pressure between the compartments when the volumes were higher.

4. Conclusions

This study demonstrated the effect of sodium bicarbonate on the performance of photosynthetic microbial desalination cells. Cumulative voltage was higher at 0.5 g/L when compared to 1 g/L of sodium bicarbonate in the biocathode chamber. A maximum power density of 625 mW/m^3 was measured which is 7.5 times higher than studies without addition of sodium bicarbonate using PMDCs. Up to 40% of total dissolved solids were removed with over 50% increase in total water volume in the desalination chamber. Desalination rates increased when the saline water volume was kept at 20 mL. Microalgae growth was more than 50% in 72 h of cell operation. Higher sodium bicarbonate concentrations more than 0.5 g/L did not have a positive effect on the process performance. Experimental results suggest that a more detailed, mechanistic study is required to determine the effect of salt concentration, saline water volumes, reactor design and more importantly, wastewater and microalgae concentrations. In addition, electrochemical analysis of PMDCs is recommended to better understand the process and its optimization. When these challenges are addressed, this process could become a promising technology for providing sustainable wastewater treatment.

Acknowledgements

This research was supported by the United States National Science Foundation (NSF) under the grants REU-INFEWS 1659830 and EAGER 1632019.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ibiod.2018.04.003.

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