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

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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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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 $NaMo.O_4•2H_2O$ (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), $Na_2MoO_4•2H_2O$ (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,