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Performance of a continuous flow microbial reverse-electrodialysis electrolysis cell using a non-buffered substrate and catholyte effluent addition

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HIGHLIGHTS

- The catholyte effluent used instead of buffer saline in MREC reactor.
- Maintain anolyte in neutral pH more necessary rather than increasing conductivity.
- Yield of hydrogen gas was 1.49 ± 0.15 mol-H_2/mole-COD.
- Hydrogen gas production rate was 0.91 ± 0.03 m^3-H_2/m^3-V_{an}/day.
- The addition of catholyte effluent into anode chamber improved MREC performance.

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ABSTRACT

A continuous flow microbial reverse-electrodialysis electrolysis cell (MREC) was operated under non-buffered substrate with various flow rates of catholyte effluent into anode chamber to investigate the effects on the hydrogen gas production. Adding the catholyte effluent to the anolyte influent resulted in increased salt concentration in the anolyte influent. The increasing anolyte influent salt concentration to 0.23 M resulted in improved hydrogen gas production, Coulombic recovery, yield, and hydrogen production rate to 25 ± 1.4 mL, 83 ± 5%, 1.49 ± 0.15 mol-H_2/mole-COD, 0.91 ± 0.03 m^3-H_2/m^3-V_{an}/day, respectively. These improvements were attributed to the neutral pH rather than increase in anolyte conductivity as there was no significant improvement in the reactor performance when the NaCl was directly added to the reactor. These results show that addition of catholyte effluent into the anode chamber improved the MREC performance.

1. Introduction

Bioelectrochemical systems (BES) and salinity gradient power (SGP) are well known emerging technologies that can provide energy from renewable materials. A microbial electrolysis cell (MEC) is a bioelectrochemical systems that can be used for hydrogen gas production while simultaneously treating wastewater (Liu et al., 2005). In an MEC, a high yield hydrogen gas production (88–93%) can be achieved as a result of the thermodynamic oxidation of organic matter on the anode coupled with oxygen reduction at the cathode and supplied with an additional external energy (0.6–0.8 V) as the potential energy generated by the oxidation of substrate (−0.30 V; 1.0 g/L acetate; pH 7) is not sufficient to split water for hydrogen gas generation (>1.2 V) (Cheng and Logan, 2007 and Logan et al., 2008). However, in practical application, the amount of energy used in an MEC (0.5–1.74 kWh/kg COD) (Call and Logan, 2008) is similar to those needed for aerators in activated sludge (0.7–2 kWh/kg COD) (Tchobanoglous et al., 2004), indicating that the additional external electrical energy in MEC is not cost-effective. Reverse electrodialysis (RED) systems, as a representation of SGP, are the membrane-based technologies that can convert potential energy from river and seawater into electrical energy (Post et al., 2007). RED systems consist of several pairs of anion- and cation-exchange membranes (AEMs and CEMs) that are situated between anode and cathode chambers. In RED, the electrical energy is produced as a result of the conversion ionic current that is generated by diffusion of ions through the AEMs and CEMs when seawater and river water are supplied to the systems. The RED system can generate as much as 0.10–0.20 V of energy per membrane pairs such that, for water electrolysis (1.2 V) at least 7–13 pairs of a membrane are required (Dlugolecki et al., 2009;

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Veerman et al., 2010). However, due to the internal and external resistance, the voltage generated from RED systems is always lower than theoretical. Thus, to achieve the expected energy, the number of membrane pairs must be increased, which leads to an increases in capital cost and reduction in energy recovery.

Recent research has demonstrated that the small pairs (5–10 pairs) of the RED system shows outstanding performance as an alternative to external electrical energy when coupled with MEC for hydrogen gas production (Kim and Logan, 2011; Nam et al., 2012; Watson et al., 2015). This combines the MEC and RED system into a module called a microbial reverse-electrodialysis electrolysis cell (MREC), which can yield approximately 1.4–1.7 mol-H_2/mole-COD at a hydrogen production rate of 0.80–1.60 m^3-H_2/m^3-V_{an}/day (Kim and Logan, 2011), which is consistent with the performance of an MEC with a 0.50–0.60 V of external power supply (Cheng and Logan, 2007; Call and Logan, 2008). Great results were also shown by Watson et al. (2015) using relatively large reactor (anode chamber: 150 mL; cathode chamber: 165 mL; 10 pairs of membrane) and actual wastewater, which produced 90–280 mL of hydrogen gas, indicating that the energy generated from small numbers of RED is sufficient to drive H_2 evolution in the MREC systems.

One of the critical problems with MREC experiments is the pH change in the anode chamber due to the accumulation of free protons during the oxidation of organic matter. Significant pH changes in the anode chamber would have an impact on the microorganism activity in the anode electrode as it requires a relatively neutral pH for optimal growth (Gil et al., 2003 and He et al., 2008). In terms of BES research, the addition of a chemical-based buffer saline such as phosphate and bicarbonate is the most common practice to prevent the pH change in the anode chamber (Fan et al., 2007; Nam et al., 2010). However, utilization of a high buffer concentration could be expensive, especially for wastewater treatment, and can also contribute to the eutrophication if there is effluent discharge into water bodies without phosphate treatment. The catholyte effluent from MREC reactor shows possibility for use as an alternative to buffered saline as it has high pH (pH > 11) and conductivity (~50 mS/cm). The addition of catholyte effluent into anode chamber increases the conductivity and buffering capacity of the anolyte, which may lead to improved reactor performance.

In this work, we demonstrated the use of a catholyte effluent to mitigate the pH change in anolyte of MREC with a non-buffered substrate for the hydrogen gas production. The experiments were conducted under continuous flow for both the anode and cathode chamber. The catholyte effluent was supplied continuously along with anolyte influent into anode chamber with the various flow rate and normalized into the anolyte influent salt concentration. The anolyte was maintained at 1.0 g/L acetate to avoid differences in the initial concentration due to the addition of catholyte effluent. Additional experiments were conducted by using only the substrate with or without buffered saline in order to evaluate the effect of catholyte effluent on hydrogen gas production. The performance of the MREC reactor was evaluated by hydrogen gas production, COD removal, COD removal rate, Coulombic recovery, yield, and hydrogen gas production rate.

2. Methods

2.1. Reactor setup

The MREC reactor consisted of anode and cathode chambers, which were made of acrylic and possessed the same working volume of 28 mL (3.0 cm diameter, 4 cm width) (Hidayat et al., 2016) (Fig. 1). The Tedlar bag (EvergreenTop Co., Ltd., South Korea) was connected to the top of the cathode chamber to collect the hydrogen gas. A graphite fiber brush pretreated in a furnace at 450 °C for 30 min was used as the anode electrode (2.5 cm diameter, 3.0 cm length, T700 SC-12000, Toray, Japan). Titanium mesh coated with platinum catalyst (2.8 cm diameter, 2.0 μm of thickness) was used as a cathode electrode. The Ag/AgCl reference electrode was assembled on each of the chambers to measure the electrode potentials.

The RED stack, which was situated between the anode and cathode chambers, was comprised of 10 pairs of anion- and cation-exchange membranes (AEMs and CEMs) (3.5 cm length, 2.5 cm height, Selemion CMV and AMV, Asahi Glass, Japan). These membranes were separated by silicon gaskets (3.5 cm length, 2.5 cm height) and a nylon mesh spacer (3.25 cm length, 2.25 cm height), forming flow channels for alternating high concentration (HC) and low concentration (LC).

2.2. Reactor operation

The anode electrode was inoculated with sludge and biofilm from an existing microbial fuel cell (MFC) and enriched with sodium acetate in the single chamber of the MFC. In order to avoid the inhibition effect from chloride ions, the anode was adapted to gradually increase the concentration of NaCl (0.10–0.35 M) and transferred to the MREC when the reactor produced stable voltages for two cycles.

The anolyte was prepared using sodium acetate (1.0 g/L) as the substrate along with trace vitamins and minerals without buffered saline (an additional experimental 100 mM phosphate buffered saline (PBS) was added to the substrate) (Cheng et al., 2009). Acetate was used as a substrate because of having inaction characteristics to biological conversions such as fermentation and methanogenesis in the room temperature. Further, acetate is the end of a product of several metabolic pathways for carbon sources which contained in the wastewater, so that it is one of the compounds that potential to be used as carbon source in the real application. The catholyte solution was synthetic seawater consisting of 35 g/L sodium chloride (NaCl) prepared in deionized water without buffered saline. The feed solution for the RED stack was prepared using 35 g/L and 0.7 g/L of NaCl for HC and LC, respectively, and created a salinity ratio of 50. The total volume of the MREC was 28 (anode) + 28 (cathode) + 4.3 (RED stack) = 60.3 mL. The feed stack solution was operated at a flow rate of 1.2 mL/min.

The MREC reactor was operated under continuous mode both in the anode and cathode chambers. The catholyte was continuously fed into the cathode chamber at various flow rates (0.6, 1.2, and 1.8 mL/h). Furthermore, the catholyte effluent was supplied along with the influent of anolyte to the anode chamber which resulted in increments of 0.10, 0.17, and 0.23 M anolyte influent salt concentration (namely with 0.10, 0.17 and 0.23 M reactors). To avoid the effects of the different initial substrate due to the dilution effects from recirculation of catholyte effluent, the amount of acetate for each experimental adjusted to 1.0 g/L with mass balance calculation and fed into the anode chamber at an organic loading rate of 2.0 g/L/d. A separate experiment was conducted with only the substrate with or without buffered saline and no catholyte effluent addition (namely with PBS and N-PBS reactors) in order to evaluate the effect of catholyte effluent on MREC performance.

2.3. Experimental analysis and calculations

The electrode potentials and cell voltages across a 10 Ω resistor were monitored and measured every 5.0 min using a voltage recorder (VR-71, T&D Corporation) connected to a computer. The current was calculated based on the cell potential across the 10 Ω resistor using Ohm's law.