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Microbial electrolysis cell scale-up for combined wastewater treatment and hydrogen production

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HIGHLIGHTS

- We demonstrate microbial electrolysis cell scale-up from a 50 mL to a 10 L cell.
- MEC operation on domestic wastewater showed an energy consumption of 0.9 Wh/g-COD removed.
- Low wastewater strength led to low volumetric rate of hydrogen production.
- High rate of hydrogen production can be only achieved at high organic loads.

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ABSTRACT

This study demonstrates microbial electrolysis cell (MEC) scale-up from a 50 mL to a 10 L cell. Initially, a 50 mL membraneless MEC with a gas diffusion cathode was operated on synthetic wastewater at different organic loads. It was concluded that process scale-up might be best accomplished using a "reactor-in-series" concept. Consequently, 855 mL and 10 L MECs were built and operated. By optimizing the hydraulic retention time (HRT) of the 855 mL MEC and individually controlling the applied voltages of three anodic compartments with a real-time optimization algorithm, a COD removal of 5.7 g $L_R^{-1}d^{-1}$ and a hydrogen production of 1.0–2.6 L $L_R^{-1}d^{-1}$ was achieved. Furthermore, a two MECs in series 10 L setup was constructed and operated on municipal wastewater. This test showed a COD removal rate of 0.5 g $L_R^{-1}d^{-1}$, a removal efficiency of 60–76%, and an energy consumption of 0.9 Wh per g of COD removed.

1. Introduction

Microbial Electrolysis Cells (MECs) are bioelectrochemical devices that produce hydrogen by combining the hydrogen evolution reaction at the cathode with the ability of anodophilic bacteria to oxidize organic matter and transfer electrons to the anode. Although this process requires electricity to be supplied, the specific energy consumption is much lower than that consumed by water electrolysis for hydrogen production (Logan, 2004; Rozendal and Buisman, 2005; Rozendal et al., 2006, 2008). Furthermore, MECs can operate on a variety of carbon sources, including wastewaters, thus combining the chemical oxygen demand (COD) removal with the production of a valuable energy carrier (Cusick et al., 2011; Ditzig et al., 2007; Wagner et al., 2009).

Several laboratory studies evaluated the degradation of complex organic materials in a MEC. It was demonstrated that the mixed microbial consortium of the anodic compartment hydrolyzes and ferments the organic feed to volatile fatty acids and acetate, while the anodophilic bacteria predominantly utilize acetate as a source of carbon (Escapa et al., 2012; Wagner et al., 2009; Wang et al., 2011). Nevertheless, pure anodophilic strains were demonstrated to grow on other carbon sources (Chaudhuri and Lovley 2003).

Owing to the process novelty, MEC experiments are typically conducted in laboratory setups with an anodic compartment volume of several mL. Very few attempts at process scale-up have been reported so far. A pilot-scale 1000 L MEC operated on winery wastewater (Cusick et al., 2011) highlighted several difficulties of MEC scale-up, including low volumetric rates of H_2 production, H_2 losses to hydrogenotrophic methanogenesis, and a relatively low efficiency of chemical oxygen demand (COD) removal. A study of electricity production from brewery wastewater in a pilot-scale 1000 L microbial fuel cell (MFC) led to similar conclusions, as this test showed limited current generation and a low biochemical oxygen demand removal (Keller and Rabaey, 2008).

The study presented below was aimed at identifying main bottlenecks in MEC scale-up and demonstrating approaches for

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resolving these issues. Initially, process performance was evaluated in a laboratory-scale MEC with an anodic compartment volume of 50 mL. Process scale-up was demonstrated by increasing the anodic compartment first to 855 mL and then to 10 L, with the latter setup operated on raw municipal WW.

2. Methods

2.1. Analytical methods and media composition

Acetate was analyzed in an Agilent 6890 gas chromatograph (Agilent Technologies Inc, Santa Clara, CA, USA) equipped with a flame ionization detector. The gas composition was measured using a gas chromatograph (6890 Series, Agilent Technologies, Wilmington, DE) equipped with a 11 × 3.2 mm 60/80 mesh Chromosorb 102 column (Supelco, Bellefonte, PA, USA) and a thermo conductivity detector. The carrier gas was argon. The pH and conductivity of the effluent were measured using PHCN-37 pH meter (Omega Canada, Laval, QC, Canada) and XL-30 conductivity meter (Fisher Scientific, Ottawa, On, Canada), respectively. The concentration of COD was determined according to the Standard Methods (APHA, 1995). Additional details are provided in Tartakovsky et al. (2009).

The protein content of carbon felt anodes was measured following the Bio-Rad protein assay protocol (Bio-Rad Laboratories Ltd., Mississauga, ON, Canada). For the analysis, carbon felt samples were taken from the middle of each anode at the end of MEC operation. More details of the analytical procedure are provided in Gil-Carrera et al. (2011).

Several synthetic carbon source solutions, including acetate-based, sucrose-based, and synthetic wastewater (sWW) were used. Details are provided in Table 1. Also, the pilot-scale MEC were fed with raw municipal wastewater (rWW), which had a total COD content of 250–300 mg L^{-1} (first batch) and 100–180 mg L^{-1} (second and third batches).

2.2. MEC design and operation

A continuous flow MEC-1x was equipped with a gas diffusion cathode and had a 50 mL anodic compartment and a gas collection compartment of the same volume. The anodic compartment contained one layer of 5 mm thick carbon felt measuring 10 × 5 cm (SGL Group, Kitchener, On, Canada). A 50 cm^2 gas diffusion cathode (Sigracet GDL 25 BC carbon paper, SGL Group) containing electrodeposited Ni particles at a load of 0.25 mg-Ni/cm^2 and 0.5–0.7 mm thick pieces of polyester cloth were sandwiched between the anode and hydrogen collection compartment plates. The electrodeposition procedure and a detailed diagram of this MEC can be found elsewhere (Hrapovic et al., 2010). In all MEC-1x tests a HRT of 20 h was maintained.

A 855 mL MEC-17x also was equipped with a gas diffusion cathode. MEC-17x consisted of three anodic compartments connected in series (Fig. 1A) and a shared gas collection (cathodic) compartment. Each anodic compartment had a volume of 285 mL and contained four layers of the carbon felt. Similar to the 50 mL setup, the cathode was made of Sigracet GDL 25 BC carbon paper with electrodeposited Ni (0.28 mg-Ni cm^{-2}). The cathode had a total surface area of 315 cm^2. The cathode and the non-conductive separator cloth were sandwiched between the plates. Each anodic compartment had an external recirculation loop equipped with a Masterflex peristaltic pump (Cole-Parmer Canada, Montreal, Canada). A shared cathode condensate collector was used to collect the condensate and the anodic liquid percolated through the cathode. This liquid was returned to the influent stream as shown in Fig. 1A.

MEC-17x was continuously fed using a 4 L bottle containing the feed solution. The flow rate was controlled to obtain the desired HRT. The feed bottle was maintained at a room temperature. The WW volume in the bottle was allowed to fluctuate between 1–4 L and the bottle was replenished every 2–3 days with a fresh solution to maintain an average HRT of 4 days. This resulted in partial hydrolysis of the WW in the feed bottle. VFA and total COD content, pH, and conductivity of the feed solution was measured twice a week.

A 10 L MEC-200x consisted of two 5 L MECs in series (Fig. 1B). Each 5 L MEC contained seven layers of the 5 mm thick carbon felt used as an anode. The gas diffusion cathode of the MEC-200x was made of the carbon paper with electrodeposited Ni (0.25–0.30 mg-Ni cm^{-2}). The cathode had a total surface area of 3024 cm^2. Each gas collection compartment had a volume of 1.5 L. As in the MECs described above, a polyester cloth was used to separate the electrodes and the cathode was sandwiched between the plates forming the anodic and the gas collection compartments. Each anodic compartment of MEC-200x had an external recirculation loop. Similar to MEC-17x, there was a cathode condensate collector and the collected liquid was returned to the influent stream (Fig 1B).

MEC-1x and MEC-17x were inoculated with a homogenized anaerobic mesophilic sludge (A. Lassonde Inc., Rougemont, QC, Canada). MEC-200x was inoculated with the effluent of MEC-17x. With the exception of acetate and sucrose stock solutions, all MECs were fed using Masterflex peristaltic pumps (Cole-Parmer Canada, Montreal, Canada). In MEC-1x tests concentrated stock solutions of acetate and sucrose were fed with an infusion pump (model PHD 2000, Harvard Apparatus, Holliston, MA, USA) at a rate of 5.0 mL d^{-1}. To maintain the desired hydraulic retention time, dilution water containing trace metals (1 mL per L) and 17 g L^{-1} of NH_4HCO_3 was simultaneously fed by a peristaltic pump. The carbon source solutions used in the tests are described in Table 1.

All MECs were equipped with temperature and pH control loops. Anodic compartment mixing was provided by external recirculation loops (0.57, 1.7, and 4 L h^{-1}, for MEC-1x, MEC-17x, and MEC-200x, respectively). MEC-1x was operated at 30 °C, while

Table 1
Composition of synthetic wastewater used in MEC tests. Notations: HS-high strength, LS-low strength. HC-high conductivity, LC-low conductivity, Ac-acetate, Su-sucrose, MS-medium strength, TM-trace metal solution.

Feeding solution	Sodium acetate g L^{-1}	Sucrose g L^{-1}	Pepticase g L^{-1}	Beef Extract g L^{-1}	Yeast extract g L^{-1}	NH_4HCO_3 g L^{-1}	K_2HPO_4 g L^{-1}	KH_2PO_4 g L^{-1}	Na Cl g L^{-1}	TM g L^{-1}
HS/HC	–	–	2.5	2.5	1.5	0.85	0.087	0.075	2.81	1
LS/HC	–	–	0.179	0.179	0.107	0.85	0.087	0.075	2.81	1
HS/LC	–	–	2.5	2.5	1.5	0.0607	0.00625	0.00537	0.2	1
Ac/HC[a]	8.37	–	–			–	0.49	0.42	–	–
Su/HC[a]	–	6.8	–			–	0.49	0.42	–	–
MS/HC[b]	–	0.22	0.046	–	–	0.52	1.38	0.69	0.83	1

[a] Influent stream concentration after mixing with dilution water.
[b] Also contained (in g/L): $MgSO_47H_2O$ 0.26 and $MnSO_47H_2O$ 0.26.