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Impact of volatile fatty acids on microbial electrolysis cell performance

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HIGHLIGHTS

- Acetate can be readily oxidized by ARB.
- Propionate is a less favorable substrate than acetate and butyrate in MEC.
- Butyrate and propionate are not consumed directly by ARB.
- The ratio of suspended biomass to attached biomass in MEC is approximately 1:4.

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ABSTRACT

This study investigated the performance of microbial electrolysis cells (MECs) fed with three common fermentation products: acetate, butyrate, and propionate. Each substrate was fed to the reactor for three consecutive-batch cycles. The results showed high current densities for acetate, but low current densities for butyrate and propionate (maximum values were 6.0 ± 0.28, 2.5 ± 0.06, 1.6 ± 0.14 A/m^2, respectively). Acetate also showed a higher coulombic efficiency of 87 ± 5.7% compared to 72 ± 2.0 and 51 ± 6.4% for butyrate and propionate, respectively. This paper also revealed that acetate could be easily oxidized by anode respiring bacteria in MEC, while butyrate and propionate could not be oxidized to the same degree. The utilization rate of the substrates in MEC followed the order: acetate > butyrate > propionate. The ratio of suspended biomass to attached biomass was approximately 1:4 for all the three substrates.

1. Introduction

Hydrogen plays a key role in sustainable energy production. Although hydrogen can be recovered by fermentation of organic material rich in carbohydrates, the majority of organic matter remains in the form of volatile fatty acids (VFAs). The primary fermentation end products during biohydrogen production are acetic, butyric, and propionic acids (Liu et al., 2005a). To achieve a higher conversion of a substrate to hydrogen, an alternative to fermentation for hydrogen production is the process of electrohydrogenesis using microbial electrolysis cells (MECs). Anode-respiring bacteria (ARB), such as *Geobacter Shewanella*, *Clostridium*, *Pseudomonas*, *Desulfuromonas*, *Esehertichia*, and *Klebisella*, are able to transmit their electrons to a solid electron acceptor as part of their energy-generating respiration (Lee et al., 2010; Torres et al., 2007, 2010). Three mechanisms of extracellular electron transfer have been proposed, i.e., direct electron transfer, electron shuttle, and via a solid conductive matrix (Torres et al., 2010). The energy in the electrons can be utilized for electricity generation in a microbial fuel cell (MFC) (Logan et al., 2006) or for hydrogen gas production in a microbial electrolysis cell (MEC) (Liu et al., 2005b). In MECs, ARB are of special interest for oxidizing biodegradable organic compounds present in wastes and other forms of biomass into protons, electrons, and bicarbonate (Lee et al., 2010; Torres et al., 2007). The electrons reach the cathode and react with water to produce hydrogen. Hydrogen production using MECs has been studied using simple organic compounds, such as acetate, propionate, glucose, glycerol (Cheng and Logan, 2007; Lu et al., 2012; Selembo et al., 2009; Sun et al., 2010); complex organic matter, such as starch, protein (Montpart et al., 2015; Nam et al., 2014); and real wastewater, for example, domestic wastewater, winery wastewater, and industrial wastewater (Cusick et al., 2011; Ditzig et al., 2007; Tenca et al., 2013).

Recently, combining dark fermentation with MECs seems to be very promising. Anode respiration process and fermentation can be combined in two different ways. One is adding the fermentative

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microorganisms and anode respiring bacteria in the same reactor to create a mixture of these two cultures in the MEC anode chamber. Montpart et al. (2015) obtained a group of microorganisms able to degrade a specific complex substrate (glycerol, milk and starch) by separately growing fermentative and ARB microbial communities in culture flasks and in an MFC respectively before combining both communities in a single chamber MEC. In this approach, they demonstrated that the growth of an anodic syntrophic consortium between fermentative bacteria and ARB was operationally enhanced and increased the potential of these complex substrates to be treated (Montpart et al., 2015). On the other hand, fermentation and hydrolysis could be separated into an independent reactor, with the MFC/MEC receiving simpler organic compounds typical of fermentation effluent, which are further consumed by ARB (Torres et al., 2007). For example, a two-stage dark-fermentation and electrohydrogenesis process was used to produce hydrogen gas by converting organic compounds such as cellulose (Lalaurette et al., 2009) and crude glycerol (Chookaew et al., 2014) to smaller compounds.

As the main end products from dark fermentation, VFAs have a vital impact on the performance of MECs. Escapa et al. (2013) found that acetate and butyrate were easily degradable, whereas propionate exhibited pseudo-recalcitrant behavior in a continuous two-chamber MEC fed with synthetic dark fermentation wastewater. However, this was contradictory to the findings of other groups. Li et al. (2014) indicated that the propionate had a higher priority sequence for hydrogen production than butyrate in a single-chamber MEC fed with corn stalk fermentation effluent. In their work, the removal efficiency of acetate, propionate and butyrate were reported as of 81–91%, 11–16% and 4%, respectively (Li et al., 2014). Torres et al. (2007) also demonstrated that acetate and propionate were consumed more effectively than the butyrate in the continuous-flow *H*-type MEC fed with a mixture of fermentation products. They reported a maximum current density for acetate of 9.0 A/m^2, 1.6 A/m^2 for propionate, and only 0.16 A/m^2 for butyrate. The detailed comparisons among the above studies are listed in Table 1. In order to clear this contradiction and figure out the impact of different VFAs on the MEC performance, this study compared MEC operational parameters by feeding the MEC with different VFAs, namely acetate, butyrate and propionate.

2. Methods

2.1. Reactor set-up

The MEC was fabricated from plexiglass with anode and cathode volumes of 550 mL and 225 mL, respectively. The liquid volume in the anode varied from 500 mL to 530 mL since some of the liquid was washed out with the purge of nitrogen. One bundle of high density carbon fibers (2293-B, 24 K Carbon Tow, Fibre Glast Developments Corp., OH, USA) that was intertwined through holes drilled on a stainless steel frame was used as the anode module. The specific surface area of the fibers was 571,429 m^2/m^3 (fiber's diameter, 7 μm; length, 150 cm). The bundle contained 24,000 individual carbon filaments with a geometric surface area of 7913 cm^2. The geometric surface area of the anodes per MEC anode volume was 1583 m^2/m^3. The carbon fibers were pretreated with nitric acid (1 N), acetone (1 N) and ethanol (1 N) for 1 day each, and then washed with MilliQ water (18.2 MΩ-cm) (Dhar et al., 2013). The cathode electrode was made of a stainless steel mesh (Type 304, McMaster Carr, OH, USA). An anion exchange membrane (AMI-7001, Membrane International Inc., NJ, USA) was placed between the anode and the cathode as a separator, and the geometric surface area of the membrane was 18 cm^2. The membrane was pretreated at 40 °C in 5% NaCl solution for 24 h as per the manufacturer recommendations. To avoid possible short-circuiting and liquid leakage, non-conductive polyethylene mats were used between the electrodes and membrane (Dhar et al., 2013). The distance between the anode and cathode electrodes was less than 1 cm. A schematic and picture of the sandwich type anode-membrane-cathode are shown in Fig. 1.

A voltage of 1.0 V was applied across the electrodes using a power supply (B&K Precision Corp., California, USA). The positive lead of the power supply was connected to the anode, and the negative lead was serially connected to a 10 Ω resistor and the cathode. The temperature was maintained at room temperature (25 °C) during the whole experiment.

2.2. MEC inoculation and operation

The MEC was inoculated with 50 mL of effluent from a working MEC, which was selectively enriched from an activated sludge microbial consortium (Dhar et al., 2013). The anode chamber was fed with a medium containing 2.3 g/L KH_2PO_4, 4.66 g/L Na_2HPO_4, 0.038 g/L NH_4Cl and 0.84 g/L $NaHCO_3$ and 1 mL/L of a trace element mixture with the following composition: 25 mg/L $MgCl_2{\cdot}6H_2O$; 6 mg/L $MnCl_2{\cdot}4H_2O$; 1.2 mg/L $CaCl_2{\cdot}2H_2O$; 0.5 mg/L $ZnCl_2$; 0.11 mg/L $NiCl_2$; 0.1 mg/L $CuSO_4{\cdot}5H_2O$; 0.1 mg/L $AlK(SO_4)_2{\cdot}12H_2O$; 1 mg/L $Co(NO_3)_2{\cdot}6H_2O$; 0.1 mg/L H_3BO_3; 5 mg/L EDTA; 0.1 mg/L $Na_2WO_4{\cdot}2H_2O$; 0.1 mg/L $NaHSeO_3$; 0.2 mg/L $Na_2MoO_4{\cdot}2H_2O$. 20 mM $FeCl_2{\cdot}4H_2O$ and 77 mM $Na_2S{\cdot}9H_2O$ were also added to the medium (1 mL/L) (Dhar et al., 2013; Torres et al., 2007). The substrate concentrations (added as sodium acetate, sodium propionate, sodium butyrate) are noted below. Medium pH was constant at 7.2 ± 0.2. The cathode chamber was filled with distilled water.

Table 1
Summary of current densities and removal efficiencies by different authors using acetate, butyrate and propionate.

Substrate	Running mode	MEC type	Applied voltage (V) (unless otherwise stated)	T^a (°C)	pH	Influent component	Influent COD (mg/L)	Removal efficiency (%)	CD^d (A/m^3)	HPR^c (m^3/m^3/d)	Source
CSFE*	batch	Single chamber	0.8	36	7	acetate	1490^e	91	340	3.43	Li et al. (2014)
						butyrate	1967^e	4			
						propionate	45^e	14^d			
SDFE§	continuous	Two chamber (gas cathode)	1	25	7	acetate	1302^e	100	206	1.42	Escapa et al. (2013)
						butyrate	736^e	100			
						propionate	1227^e	<100			
SDFE§	continuous	*H*-type dual-compartment	Anode potential (+0.1 V vs Ag/AgCl)	30	7.4	acetate	2560^e		281^e		Torres et al. (2007)
						butyrate	6400^e		5^e		
						propionate	4480^e		50^e		

Note: T^a: temperature; CD^b current density; HPR^c: hydrogen production rate; ^{d}: the data was gotten from the figure in the reference; ^{e}: the data was calculated based on the information in the literature; CSFE *: corn stalk fermentation effluent; SDFE §: synthetic dark fermentation effluent.