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Hydrogen production in single chamber microbial electrolysis cells with different complex substrates

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ABSTRACT

The use of synthetic wastewater containing carbon sources of different complexity (glycerol, milk and starch) was evaluated in single chamber microbial electrolysis cell (MEC) for hydrogen production. The growth of an anodic syntrophic consortium between fermentative and anode respiring bacteria was operationally enhanced and increased the opportunities of these complex substrates to be treated with this technology. During inoculation, current intensities achieved in single chamber microbial fuel cells were 50, 62.5, and 9 A m^{-3} for glycerol, milk and starch respectively. Both current intensities and coulombic efficiencies were higher than other values reported in previous works. The simultaneous degradation of the three complex substrates favored power production and COD removal. After three months in MEC operation, hydrogen production was only sustained with milk as a single substrate and with the simultaneous degradation of the three substrates. The later had the best results in terms of current intensity (150 A m^{-3}), hydrogen production (0.94 m^3 m^{-3} d^{-1}) and cathodic gas recovery (91%) at an applied voltage of 0.8 V. Glycerol and starch as substrates in MEC could not avoid the complete proliferation of hydrogen scavengers, even under low hydrogen retention time conditions induced by continuous nitrogen sparging.

1. Introduction

Bioelectrochemical systems (BES) are a recently developed technology that allows current generation or production of value added compounds, such as hydrogen, from wastewater (Liu et al., 2005). These systems are known as microbial fuel cells (MFC) and microbial electrolysis cells (MEC), respectively. MEC are interesting in view of hydrogen production when compared to alternative technologies such as dark fermentation and photosynthesis because i) they require much lower energy input when compared to hydrogen obtainment from water electrolysis and ii) they have higher hydrogen yield (Lee and Rittmann, 2010).

BES operation relies on the presence of a group of microorganisms that have the ability to use an external insoluble electrode as electron acceptor and are therefore known as exoelectrogens or anode respiring bacteria (ARB). ARB consume organic matter anaerobically, donating the last electron involved in their metabolic pathway to the electrode. The flow of electrons generated because of the organic matter consumption can be used as electricity or to drive specific reduction reactions, such as the reduction of protons to hydrogen, on the cathode. Whereas electricity production in

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MFC is a thermodynamically favored process, hydrogen production in MEC requires some energy input. As a consequence, to consider the process economically interesting (i) the energy recovered as hydrogen gas should be higher than the energy input or (ii) the energy input should be lower than energy requirements for treating wastewater in conventional wastewater treatment systems.

Lab scale studies have broadly investigated BES fed with synthetic wastewater containing easily biodegradable substrates, mainly acetic acid. However, real wastewaters contain a wide range of substrates with different biodegradability. In order to reach a real application of this technology, it is fundamental to study the potential of current intensity and hydrogen production simultaneously to the degradation of the organic matter present in real wastewater.

In systems where a complex substrate is used, an initial hydrolysis and fermentation step is necessary to break macromolecules to simpler ones and to convert them to acetate and other readily biodegradable substrates, which will be further degraded by ARB. Hence, a syntrophic consortium between fermentative bacteria and ARB needs to be developed. Syntrophic interactions between fermenters and ARB have been reported to allow the utilization of complex organic matter in BES, where different substrates entail the development of different microbial communities (Kiely et al., 2011; Lu et al., 2012).

BES studies fed with complex substrates as sole carbon source show the necessity to develop such syntrophy in the system (Cheng et al., 2011; Gómez et al., 2011; Lalaurette et al., 2009; Sun et al., 2012; Velasquez-Orta et al., 2011) and present the hydrolysis and fermentation step as the limiting one (Velasquez-Orta et al., 2011). They also show that a pre-acclimation to single products improves later degradation in a complex mixture and increases hydrogen yield (Lalaurette et al., 2009). In general, the substrates that have been tested so far in BES include synthetic wastewater containing starch (Ghosh et al., 2012; Herrero-Hernandez et al., 2013; Lu et al., 2009; Velasquez-Orta et al., 2011), cellulose (Cheng et al., 2011; Lalaurette et al., 2009), glycerol (Chignell and Liu, 2011; Escapa et al., 2009; Nimje et al., 2011; Reiche and Kirkwood, 2012), methanol (Montpart et al., 2014), phenol (Song et al., 2014), landfill leachates (Mahmoud et al., 2014), municipal wastewater (Escapa et al., 2012; Heidrich et al., 2013) and industrial wastewater like dairy (Elakkiya and Matheswaran, 2013; Mardanpour et al., 2012), brewery (Cusick et al., 2011) and biodiesel wastewater (Feng et al., 2011).

Practical implementation of MEC will mainly require operation at low cost. From all the various configurations that have been discussed in the literature, a single chamber membrane-less MEC would offer the lowest installation and operation costs because of being a single unit without membrane. In addition, avoiding the use of an ionic membrane decreases the internal resistance of the system, which represents one of the voltage losses appearing in MECs. In addition, the possibility to immobilize the syntrophic consortia in the anode introduces an improvement in the system, since a pre-treatment tank would not be required. Nevertheless, MEC operation in membrane-less single chamber is not straightforward, since it faces some bottlenecks.

One of the major problems that single chamber MEC still deals with is the growth of methanogens (Zhang and Angelidaki, 2014), as the anaerobic environment of a MEC favors their growth. Methanogens compete with exoelectrogens for both substrate and product. Acetoclastic methanogens convert acetate to methane and hydrogenotrophic methanogens consume hydrogen to produce methane. Because of their growth and activity, hydrogen production decreases and the gas obtained is less rich in hydrogen. This represents a loss in terms of energy obtained from MEC, since hydrogen possesses higher combustion energy than methane. It also introduces extra costs when the goal is using hydrogen as a feedstock, since a previous separation process would be necessary. Some long-term and pilot scale studies have shown that once methanogenic *archaea* takes over it is very complicated to get rid of them (Cusick et al., 2011; Rader and Logan, 2010).

Research on how to limit methanogenic growth and activity includes operational strategies such as temperature, pH, oxygen exposure and periodic aeration (Ajayi et al., 2010; Chae et al., 2010; Wang et al., 2009), loading rate (Lalaurette et al., 2009), applied voltage (Hu et al., 2008; Torres et al., 2009) and dosage of chemical inhibitors like 2-bromoethanesulfonate (Chae et al., 2010; Wang et al., 2009; Zhuang et al., 2010). The later is an efficient chemical inhibitor of methanogenesis, but its cost limits its usage in MEC. Other strategies like working at low retention time to reduce the interval that hydrogen is available in the system have been suggested (Lalaurette et al., 2009).

The aim of this work was studying the long-term opportunities of various complex substrates for net hydrogen production in single chamber MEC without addition of chemical inhibitors of methanogenesis. Milk, starch and glycerol were chosen as carbon sources in view of their differences in composition and therefore biodegradability. In this sense, glycerol was chosen for being a short chain fermentable substrate, starch a large polysaccharide and milk a mixture of sugars, fats and proteins. These substrates were representative of different industrial wastewater (biodiesel industry wastewater, potato industry and dairy industry), with wastewater treatment systems that could be upgraded by producing hydrogen with MEC. In addition, the advantages of codigesting the three substrates at the same time were explored, a situation that could be extrapolated to an urban wastewater, where a variety of compounds is typically available.

2. Materials and methods

2.1. *Experimental setup*

A consortium able to degrade a specific complex substrate was obtained by separately growing fermentative and ARB microbial communities in culture flasks and in MFC respectively. Next, both communities were joined in MFC. Once it was ensured that a syntrophic consortium had developed in MFC, the biologically enriched anodes were moved to MEC.