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## Resources recovery in the dairy industry: bioelectricity production using a continuous microbial fuel cell

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#### ABSTRACT

The increasing food demand and the exhaustion of non-renewable fuels provide new market opportunities in the agro-farming sector. Biological systems designed to add value to useless organic subproducts and to generate off-grid electricity may be one of the most interesting outcomes. Therefore, the capacity of some microorganisms to transfer electrons generated during organic carbon oxidation directly to an anode in a so-called microbial fuel cell (MFC) might be an asset in a sustainable management context. In this regard, the main goal of the present work was to evaluate the performance of a continuous MFC applied in a dairy industry. A maximum voltage of 576 mV was produced during continuous operation, corresponding to a power density of 92.2 mW m<sup>-2</sup> or 1.9 W m<sup>-3</sup>. MFC was able to remove 1298  $\pm$  617 mg L<sup>-1</sup> of chemical oxygen demand (COD) at a hydraulic retention time of 8.4 h, and the maximum COD removal (63  $\pm$  5%) was achieved after 20 days of continuous operation. In addition, the coulombic efficiency average was around 10.5  $\pm$  10% with a maximum of 24.2  $\pm$  1.5%. In average, the MFC was able to extract a specific energy of 8.95  $\times$  10<sup>-2</sup> kW h kg<sup>-1</sup> COD with a maximum output of 20.53  $\times$  10<sup>-2</sup> kW h kg<sup>-1</sup> COD. In conclusion, the MFC technology is a valuable option for simultaneous wastewater treatment and energy recovery and deserves to be tested and scaled-up in the dairy industry.

#### 1. Introduction

The access to food in quantity and quality is one of the key issues affecting human development and is a main driver for the circular economy growth and human equity. The increasing shortage of resources, namely water and energy, is highly challenging for science and technology. Nowadays, research on innovative, costeffective and competitive industrial processes are necessary to boost food production and the quest for sustainable technologies to process agro-industrial wastewaters is a step forward (Aydiner et al., 2016; Almuktar et al., 2015).

In response to this ambition, several efforts are being pursued trying to explore decentralized and clean energy sources. One of those possibilities is the use of microbial fuel cells (MFCs) (Logan et al., 2006; Martins et al., 2010). The MFC technology is based on the ability of some carbon-oxidizing microorganisms to transfer

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http://dx.doi.org/10.1016/j.jclepro.2016.04.027 0959-6526/© 2016 Elsevier Ltd. All rights reserved. electrons directly to an anode in anaerobic conditions (Peixoto et al., 2013; Logan et al., 2006). The standard design consists of an electrochemical cell with anodic and cathodic compartments separated by a proton exchange membrane. In the anode compartment, the conversion of different carbon sources is carried out through catalytic reactions, which involve anaerobic electroactive microorganisms (Franks and Nevin, 2010). Several environmental factors influence MFC performance, namely, inoculum type, carbon source, concentration, feed rate, pH, temperature and reactor configuration (Ren et al., 2014a; Cheng et al., 2006). Therefore, for full scale applications in wastewater treatment, continuous flow MFC could be more suitable than batch or fedbatch for a higher COD removal and power generation (Sevda et al., 2015; Zhuang et al., 2012; Rahimnejad et al., 2011). In continuous MFC operation, the maximum chemical oxygen demand (COD) removal is in the range of 70% and 99% (Pasupuleti et al., 2015; Rahimnejad et al., 2011). However, the hydraulic retention time (HRT) was higher (up to 48 h) than those adopted in conventional wastewater treatment systems (4-12 h) (Sevda et al., 2015; Ahn and Logan, 2013; Aelterman et al., 2006; Min et al.,

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2005). In conclusion, there have been few studies on wastewater treatment using MFC in a HRT range of ~10 h or less (Kim et al., 2015).

A cleaner and more competitive agro-industrial management is essential in order to face energy and water scarcity (Almuktar et al., 2015). In particular, dairy industry is one of the most significant examples of biodegradable organic based wastewaters that endanger surface waters quality. Therefore, a technology that achieves wastewater treatment with simultaneous bioenergy recovery will represent an asset towards an eco-efficient industry (Aydiner et al., 2016; Pant et al., 2010; Oh et al., 2010). Dairy wastewater is a complex organic mixture rich in carbohydrates, proteins and fats, presenting a significant biological oxygen demand (BOD) and COD (Karadag et al., 2015; Elakkiya and Matheswaran, 2013; Demirel et al., 2005). Biological processes are the standard in dairy wastewater treatment plant designs, often complemented by physico-chemical processes for fat and grease abatement or nutrient removal (Karadag et al., 2015; Martín-Rilo et al., 2015; Demirel et al., 2005). Lagoon systems are the preferred low-cost approach, but the performance is rather low and odour problems may occur (Bhatia and Goyal, 2014). On the contrary, activated sludge processes present a good performance but the energy consumption and sludge production are significant drawbacks (Demirel et al., 2005), Anaerobic filters (Lim and Fox, 2011) and upflow anaerobic sludge blanket reactors or related concepts (Ramasamy et al., 2004; Demirel et al., 2005) are used also. These reactors may have some performance limitations and being driven by biogas production requires further conversion processes to produce electricity (Passeggi et al., 2012). Therefore, there is a substantial gap that requires innovative designs towards a circular economy and clean production in the dairy industry (Kubota and da Rosa, 2013).

In electricity driven world, MFCs are probably the comprehensive answer for such a demand in the agro-food industry, being a more efficient answer than biogas production, especially when we compare the net electrical efficiency of anaerobic digestion (10%– 15%) with the coulombic efficiency of MFCs (20%–80%) (Mardanpour et al., 2012; Pant et al., 2010; Oh et al., 2010). In addition, MFCs are not affected by high concentrations of volatile fatty acids that are known to inhibit conventional anaerobic digestion processes (Oh and Martin, 2009; Hawkes et al., 2007; Logan and Regan, 2006). However, to date only a few attempts tried to apply MFC technology in the framework of industrial dairy wastewaters, especially in a continuous flow mode. Therefore, the goal of the present work is to assess the performance of a continuous MFC for dairy wastewater treatment and energy valorisation.

#### 2. Material and methods

#### 2.1. MFC setup and operation

A dual chamber MFC was assembled by connecting two compartments of transparent poly methylmethacrylate, with equal dimensions (12 cm  $\times$  8 cm  $\times$  5 cm). The two compartments were physically separated by a proton exchange membrane (Nafion Membrane 117, DuPont Co., USA), sealed with a silicone rubbers, and to keep it tight, rubber gaskets and stainless steel screws were used. Total volume of each chamber was 480 mL with approximately 350 mL of liquid volume. The electrodes, both carbon Toray TP-090 (QUINTECH, USA) sheet (6 cm  $\times$  6 cm = 72 cm<sup>2</sup>), were connected to an external resistance using copper coated wires (2 mm diameter). The circuit was closed with a fixed resistance of 500  $\Omega$ , according to the results obtained by Elakkiya and Matheswaran (2013). In Fig. 1 it is depicted a schematic diagram of continuous MFC setup.

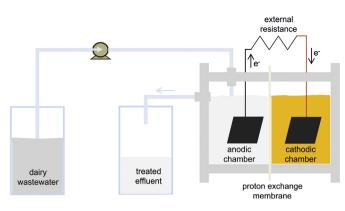


Fig. 1. Schematic diagram of continuous MFC setup.

In order to promote biofilm formation on anode surface and to produce power density, 350 mL of pre-screened municipal wastewater (with an average chemical oxygen demand (COD) concentration of  $500 \pm 100 \text{ mgL}^{-1}$ , conductivity of  $790 \pm 20 \ \mu\text{S cm}^{-1}$  and pH  $7 \pm 0.2$ ) was used as a batch stirred anolyte at room temperature ( $\approx 22 \ ^{\circ}\text{C}$ ). After sampling, the wastewater was deoxygenated with nitrogen gas and kept at 4  $^{\circ}\text{C}$  until use (Peixoto et al., 2013). When necessary, wastewater was replaced to avoid organic carbon limitations on bioelectricity production. In the cathode compartment and to avoid oxygen limitation, 50 mM of hexacyanoferrate in phosphate buffer (50 mM) at pH 7, was used as a catholyte solution.

After the steady state was reached (i.e: when similar values of power density were obtained along three consecutively cycles), the flow regime was changed from fed-batch to continuous and a dairy wastewater was used to feed the MFC at a flow rate of 1 L d<sup>-1</sup>. A synthetic feed was prepared in order to simulate the average composition of a dairy wastewater (1500–5000 mgCOD L<sup>-1</sup>; Elakkiya and Matheswaran, 2013; Mardanpour et al., 2012), and no precise mode was in place regarding synthetic effluent preparation because wastewater COD values in the dairy industry present significant variations due to process operations and due to discontinuity in the production cycles of different products (Farizoglu and Uzuner, 2011). Therefore, the synthetic effluent was prepared by adding ~100 mL of low fat pasteurized milk to ~5 L of tap water, without macro or micronutrient supplementation.

#### 2.2. Electrochemical and chemical analysis

Bioelectricity production was measured by recording every 30 min the voltage between anode and cathode. Data were collected automatically and stored in a computer by a USB-9215A BNC connector data logger (National Instruments) and a data acquisition software (Labview 6.0) (Martins et al., 2014). Electrochemical analysis was performed according to Martins et al. (2010). Briefly, the current intensity (I) was calculated according to the Ohm's law (Equation (1)), where V is the voltage and R the resistance. The current density (*j*) was calculated as depicted in Equation (2), where *A* is the projected surface area of the anode electrode. The power density (P) is calculated as the product of current intensity and voltage divided by the projected surface area of the anode (Equation (3)). The polarization curve, describing the voltage and the power density as a function of the current density (Peixoto et al., 2013) was recorded using a series of resistances in the range of 71.1 k $\Omega$  to 50  $\Omega$  during biofilm formation and the stable phase of bioelectricity production along the continuous operation (Peixoto et al., 2013). The internal resistance of the MFC (Rint) was calculated from the slope of the polarization curve in the region

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