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Sustainable processing of dairy wastewater: Long-term pilot application of a bio-electrochemical system

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ABSTRACT

Demographic growth, increasing food demand and non-renewable fuels depletion require new sustainable industrial approaches in all areas of the agro-farming sector. Microbial fuel cells (MFCs) could represent an eco-innovative technology for energy and resources recovery from agrofood processes wastewaters. This study was conducted to: (i) assess the bioelectrochemical treatability of dairy wastewater by means of MFCs; (ii) determine the effects of the organic loading rate (OLR) on MFCs performance; (iii) evaluate the reactors' overpotentials, and identify possible strategies oriented to their reduction. For this purpose, two replicate MFCs were built and continuously operated for 65 days. The anode chamber was fed with undiluted dairy wastewater at 1 L d^{-1}. An aerated mineral medium was fed to the cathode chamber with the same flow-rate. The study demonstrated that these types of industrial effluents can be treated by MFCs with 82% (average) organic matter removal, recovering a maximum power density of 26.5 W m^{-3}. Coulombic efficiency (CE) of the lab-scale reactors decreased by increasing the OLR (organic loading rate). The highest CE was found to be 24% at a OLR of 3.7 kg COD m^{-3} d^{-1}. MFCs energy losses were mainly due to cathode reaction (34–39% of total loss) and ionic transport through the membrane (27–33%). Achieved results were better than previously reported MFC-experiences dealing with dairy (or similar) wastewater treatment.

1. Introduction

Research pursuing green and renewable energy sources, efficiency of buildings and industrial processes, energy and chemicals recovery from wastewater is quite diffuse at present. Applications in decentralized and clean energy sources are being investigated and tested in many civil and industrial sectors (Capodaglio et al., 2017a, 2016a), as well as possibilities to reduce energy consumption from traditional processes and activities (Capodaglio et al., 2015b). It should be considered that, on average, the energetic consumption of wastewater treatment with conventional processes is about 0.2–0.8 kWh m^{-3}, depending on various factors, including process type. In the case of aerobic processes, the energy used for mixed liquor aeration (oxygenation) alone can be more than 50% of the total used by the treatment facility (Spellman, 2013).

Microbial fuel cells (MFCs), bioelectrochemical systems based on electro-active bacteria (EABs) catalysis, allowing the direct conversion of the chemical energy contained in an organic substrate, into electrical energy (Rabaey and Verstraete, 2005) appear to provide a potentially attractive alternative to traditional wastewater treatment processes. MFCs are extremely versatile in reference to treatable substrates. Experiences with simple substrates, such as glucose (Chaudhuri and Lovley, 2003), volatile fatty acids (Daghio et al., 2015) and alcohols (Kim et al., 2007) are reported, as well as with more complex mixtures, such as domestic wastewater (Capodaglio et al., 2013; Koók et al., 2016), pharmaceutical (Cecconet et al., 2017), brewery (Wang et al., 2008), dairy (Faria et al., 2017; Molognoni et al., 2018) and food-processing effluents (Abourached et al., 2016).

Notwithstanding their diverse and usually high treatment capacity, and non-negligible advantages over other biological processes (low biofilm yield, possibility to operate at low temperatures, lack of substantial aeration needs, direct electricity conversion), MFCs are still characterized by drawbacks, including low electric production (10–100 W m^{-3} of total reactor), compared to the theoretical one, that are still limiting the industrial "appeal" of the technology (Rozendal et al., 2008). Attempts of MFCs optimization include development of non-Platinum-group catalyzers for cathodes (Santoro et al., 2015), morphologic modification and

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combination of different electrode materials (Fiset and Puig, 2015), development of biocathodes (Xia et al., 2013), hydraulic and electric stacking of multiple units (Ieropoulos et al., 2008), tracking methods achieve optimal external resistance (Molognoni et al., 2014).

Agrofood substrates (swine manure, brewery, dairy and winery effluents) seem particularly promising for MFCs industrialization, given their high organic content (COD values up to 10 g L^{-1}) and biodegradability (generally BOD/COD ratio > 60%) (Cercado-Quezada et al., 2010; Capodaglio et al., 2016b). However, complex substrates increase bacterial community complexity, and can lead to interrelated connections between single microbial species (Vilajeliu-Pons et al., 2016). Anode chamber anaerobic condition may lead to the appearance of unwanted side-reactions such as methanogenesis or heterotrophic denitrification (Capodaglio et al., 2017b, 2015a). High fermented substrate concentrations favor methanogenic activity compared with exoelectrogenesis, reducing MFCs' Coulombic Efficiency (CE) (Pinto et al., 2010).

Bioelectrochemical recovery of electricity from dairy wastewater with MFCs has been investigated in recent years. Single chamber, dual-chamber, and tubular MFCs have been tested, with electrodes of different materials including carbon, graphite, stainless steel or composites. The highest reported power density (20.2 W m^{-3}) so far was achieved by Mardanpour et al. (2012), using a tubular MFC equipped with a 0.5 mg Pt cm^{-2} catalyst load on the cathode. Other studies demonstrated that cathode catalysts may be avoided, without negative effects on organic matter removal efficiency, but with considerable reduction of power density (90% lower) and CE (44% lower) (Elakkiya and Matheswaran, 2013; Venkata Mohan et al., 2010). Experiences of continuous-fed MFCs treating dairy wastewaters achieved generally worse results than batch-fed systems, in terms of both power density and COD removal, but achieved higher CEs (Faria et al., 2017). Venkata Mohan et al. (2010) observed increasing MFC electrical performance with increasing organic loading rates (OLRs) to the anode chamber. On the other hand, Elakkiya and Matheswaran (2013) noticed that high anolyte's COD concentration (up to 2800 mg L^{-1}) can cause membrane fouling, and gradual decrease of electric production. Also, development of unsustainably thick anodic biofilm, which will suffer from high concentration overpotentials could result from high loads of proteins and lipids (Cercado-Quezada et al., 2010).

Despite all the promising results obtained so far, MFCs scientific literature is still lacking long-term studies in continuous working conditions. The aim of this study is precisely to evaluate the long-term performance of MFCs, continuously fed for 65 days with undiluted dairy wastewater. A complete assessment of two parallel systems is carried out, in terms of observed power production, current intensity, internal resistance, energy losses distribution, organic matter removal and CE.

2. Material and methods

2.1. Experimental setup

Two identical, dual-chamber MFCs were constructed using a previously described design (Molognoni et al., 2016), consisting each of an anode and a cathode chambers placed on the opposite sides of a single methacrylate rectangular cell, separated by a Cationic Exchange Membrane (CMI-7000, Membranes International Inc. USA) (Fig. 1). Both chambers are filled each with 800 g of granular graphite (model 00514, diameter 1.5–5 mm, EnViro-cell, Germany), reducing free volumes to 435 mL net anodic compartment (NAC) and 420 mL net cathodic compartment (NCC), respectively. A graphite rod electrode (250 × 4 mm, Sofacel, Spain), previously washed in 1 M HCl and 1 M NaOH solutions to remove possible metal and organic contamination, is introduced in each chamber to allow external electrical connection. Both electric circuits of the cells are equipped with an external 33 Ω resistance, chosen to be as close as possible to their assumed static internal resistance, based on previous experiences on similar working cells.

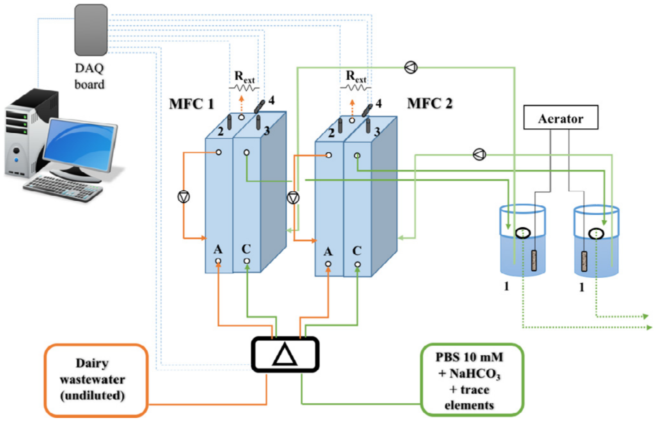

Fig. 1. Liquid, electric and monitoring circuits schemes: anodic and cathodic circuits - continuous lines; electric and monitoring circuits - dashed lines. Legend: (A) anode chamber; (C) cathode chamber; (R_{ext}) external resistance; (1) aeration tanks; (2) anode electrode; (3) cathode electrode; (4) Ag/AgCl reference electrode.

Wastewater collected from the flotation unit outlet of a large local cheese factory was used as anode fuel. The waste was collected periodically, stored at 4 °C to limit prior organics degradation, then transferred into collapsible 10 L collapsible jerry cans (light-shielded, at environmental temperature) for anodes' continuous feed. This consisted of a cyclic feed routine pumping a 3 L d^{-1} flow into each MFC for 20 min every hour, after which pumping stopped. This resulted in an average feed rate per MFC of 1 L d^{-1}, although it was clear from previous short-term tests that the cells had a much higher capacity than the one thus applied. Cathodes were fed with the same mode and flow-rates with oxygen-saturated phosphate buffer medium (10 mM, pH 7) containing: 819 mg L^{-1} Na_2HPO_4, 507 mg L^{-1} NaH_2PO_4, 1000 mg L^{-1} $NaHCO_3$, 130 mg L^{-1} KCl, 310 mg L^{-1} NH_4Cl and other trace elements. An internal recirculation loop (10 L d^{-1}) in each chamber was added to maintain well-mixed conditions, minimizing concentration gradients and the chance of clogging within the cells. Recirculation lines of both cathodic chambers were also saturated with oxygen, by means of two, 200 mL, external aeration chambers. Both MFCs operated at environmental temperature (23 ± 3 °C) for the entire time. Anode potential of each cell was monitored with an Ag/AgCl reference electrode (+197 mV vs Standard Hydrogen Electrode, Xi'an Yima Opto-electrical Technology Co. China). Anode potentials and overall cell potentials were recorded at 1-min interval by means of a multifunction acquisition board (NI USB-6008, National Instruments Italy, Milan) connected to a LabVIEW™ equipped computer.

2.2. Inoculation and operation

Anode and cathode chambers were each inoculated with 2.5 L of liquor composed by 30% (aerobic) activated sludge from the industrial plant treating the dairy waste samples; 10% dairy wastewater; and 60% distilled water. In the anode chamber inoculum solution, 2-bromoethanesulfonate (BES) was also added (at 10 mM concentration), to inhibit initial methanogen biomass growth (Chae et al., 2010). Inoculation was performed in closed electric loop mode, with 33 Ω resistance, maintaining a recirculation rate