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ScienceDirect

Energy Procedia 74 (2015) 728 – 735

Energy Procedia

International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES15

Role of operating conditions on energetic pathways in a Microbial Fuel Cell

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Abstract

The electric performance of a Microbial Fuel Cell (MFC) fed with swine manure, and specifically the interactions between different coexisting bacterial populations are examined in relationship to the Organic Loading Rate (OLR) and External Resistance applied to the cell. Feasibility of swine manure treatment using MFCs was already demonstrated by previous studies, however low Coulombic efficiencies were attained due to a competing methanogenic degradation occurring in the same cells. External resistance (Rext) and Organic Loading Rate have been identified as two of the key parameters affecting the balance between exoelectrogenic and methanogenic bacterial populations in a MFC system; despite this, virtually no attention had been paid to the study of OLR influence on MFCs performance. This study evaluates the performance of a MFC, treating swine manure, in this perspective, demonstrating that high OLRs (up to 11.2 kg COD m^3/d) have a limiting effect on MFCs electrochemical losses, and increase absolute values of ORR (4.6 kg COD m^3/d) and current production (14.9 mA). On the other hand, adoption of low OLR (as low as 0.7 kg COD m^3/d) translates in an increase of both organic matter removal efficiency (52%) and Coulombic efficiency (higher than 70%). These improvements can be directly connected with the shifting balance between exoelectrogenic and methanogenic biomass populations, as confirmed by the cell's anode off-gas analysis. Hence, by adopting the appropriate design value of ORL and operating conditions, the MFC's biofilm exoelectrogenic population fraction, and thus its overall activity, can be improved considerably.

Peer-review under responsibility of the Euro-Mediterranean Institute for Sustainable Development (EUMISD)

Keywords: Bioelectrochemical System; Microbial Fuel Cells; Coulombic Efficiency; Energy recovery; Swine manure

1. Introduction

Microbial Fuel Cells (MFCs) are bioelectrochemical systems that directly convert chemical energy contained in organic matter bioconvertible substrate into electrical energy [1]. Exoelectrogenic bacteria catalyze one, or both, the

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doi:10.1016/j.egypro.2015.07.808

reactions occurring at the electrodes, that is substrate oxidation at the anode and oxidant reduction at the cathode. When wastewater containing organic matter is used as anode fuel, the MFC effectively performs wastewater treatment while recovering energy, thus leading to the future possibility of designing energy-producing wastewater treatment plants [2]. Among the practical issues to be solved, is the reduction of the systems' internal resistance, that would allow higher substrate-electricity conversion rates: Sleutels et al. [3] estimated that cost-effectiveness of MFCs would require values of internal resistance lower than 40 $m\Omega/m^2$, and current densities around 25 A/m^2. Considerable technological improvements are needed before MFCs can reach these targets, mainly because of cathode technology limitations. Efficient MFCs design must focus on reducing electrochemical losses as much as possible, in order to become competitive with other technologies (i.e. anaerobic digestion) of energy recovery from wastewater treatment.

To date, maximum volumetric treatment capacities up to 7 kg COD/m^3d have been estimated for full-scale MFCs [2], an indication that the technology could be well suited to treat high-strength wastewaters, such as feedstock wastewater, with direct bioenergy production [5,6,7]. Min et al. [6] report of obtaining a maximum power density of 261 mW/m^2 from a single-chamber MFC fed with swine manure. This was accompanied, however, by a low 8% Coulombic Efficiency (CE). The main problem interfering with microbial bioelectricity generation is linked to the anode's anaerobic condition, often leading to the appearance of unwanted side-reactions, such as methanogenesis or heterotrophic denitrification, if suitable amounts of $N\text{-}NO_3$- or $N\text{-}NO_2$- are contained in the substrate. Methanogens, in fact, compete against exoelectrogenic bacteria for the organic matter content of substrate, reducing electron recovery in the form of electricity. Coulombic Efficiency is a measure of this competition, and increases when higher MFC current densities are achieved [3]. Species balance can be dependent on anode potential and/or substrate concentration: a higher anode potential increases the energy available to exoelectrogens, giving them the possibility of outcompeting methanogens by means of their faster metabolism [8, 3]; Pinto et al. [9] show that high substrate concentrations favour in turn methanogenic activity. The combined effect of external resistance and Organic Loading Rate (OLR) on the bioelectrochemical performance of a dual-chamber MFC fed with sodium acetate was investigated by Aelterman et al. [10]: they observed that maximum current generation, shown by polarization curves, increased significantly when OLR increased, but only at external resistances values equal or lower than the system's internal resistance. They also showed that, at high OLRs, it was very difficult to prevent methane production.

Another strategy to enhance MFCs' power output by controlling the value of their external resistance has been proposed as Maximum Power Point Tracking (MPPT) [11]: in MFCs, maximum power is drawn when R_{ext} equals R_{int} [4]. Different authors demonstrated that MPPT control applied to an MFC decreases start-up time and increases current generation [12, 13, 14]. Moreover, R_{ext} optimization can generate a selective pressure inside the anode compartment, favouring exoelectrogenic bacteria with respect to methanogens, thus increasing the Coulombic Efficiency of MFCs [15]. Despite the potential importance of combining control of MFCs' external resistance and applied OLR, shown by Aelterman et al. [10], and the proven advantages arising from MPPT control, very little attention has been given so far to the study of OLR influence on MFCs working at the MPP ($R_{ext} = R_{int}$). This study evaluates the performance of a swine-manure fed MFC under different OLRs and operating at optimal electrical conditions, thus always satisfying the condition $R_{ext}=R_{int}$. Three OLR levels were tested, in steady-state conditions, while carrying out an assessment of the MFC in terms of observed power production, current intensity, internal resistance, energy losses distribution, organic matter removal and Coulombic Efficiency. Off-gas production was also measured and analysed, to determine the relative importance of exoelectrogenic and methanogenic activity.

2. Materials and Methods

The MFC consists of an anode and a cathode chambers placed on the opposite sides of a single rectangular methacrylate structure. Both chambers are filled with granular graphite (diameter 1.5-5 mm), with net volumes of 380 mL for the anodic compartment (NAC) and 350 mL for the cathodic compartment (NCC), respectively [16]. Two thin graphite rod electrodes (250 x 4 mm), are fitted in the chambers to allow external electrical connection. An Anion Exchange Membrane (AMI-7001) separates the anode and cathode compartments.