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Continuous mode operation of microbial fuel cell (MFC) stack with dual gas diffusion cathode design for the treatment of dark fermentation effluent

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ABSTRACT

Three microbial fuel cells (MFC) with dual gas diffusion cathode design were operated individually in different operation modes, viz., batch (MFC-BM), semi-continuous (MFC-SCM) and continuous (MFC-CM), using dark fermentation effluent (DFE). MFC-BM depicted lower power density (PD, 1.31 \pm 1.75 mW/m²) due to the electron losses and mass transfer limitations, while, MFC-SCM (19.06 \pm 2.01 mW/m²) and MFC-CM (15.53 \pm 2.51 mW/m²) depicted higher PD. Though MFC-SCM showed higher power output, the energy conversion efficiency (ECE) was higher during MFC-CM (9.85 \pm 1.02%) operation over MFC-BM and MFC-SCM operations. Henceforth, the stacking approach was carried out in continuous mode operation using DFE which showed a very good power output along with treatment efficiency. Stack mode operation was carried out at decreasing external loads to increase the overall power output as well as the electron delivering ability of the biocatalyst. Stack MFC depicted its maximum PD (3163 mW/m 3 ; 19.79 mW/m 2), across 2 k Ω of external resistance (R_{ex}) along with the treatment efficiency of 80 \pm 2%. Further decrement in R_{ex} to 1 kΩ has resulted in lower and unstable PD, due to the inability of the biocatalyst to meet the electron requirement by the circuit. A detailed understanding of the stack MFC was made in terms of electrogenesis, electron discharge, coulombic and energy conversion efficiencies as well as the bioprocess parameters.

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Introduction

Microbial fuel cell (MFC) technology involves chemical energy conversion into electrical energy by the interactions between electrochemically active bacteria (EAB) and solid electrodes $[1-5]$ $[1-5]$. The MFC technology is continuously undergoing significant advancements in key factors that improve its efficiency in power generation and/or wastewater treatment. Upscaling of MFC technology is a critical matter and it still needs to overcome several bottlenecks in industrially-relevant dimensions $[6-14]$ $[6-14]$. Among various MFC designs available, air-cathode MFCs hold a greater potential for upscaling due to their simple configuration and relatively high power densities $[15-19]$ $[15-19]$.

The maximum theoretical voltage from a single air cathode MFC is 1.14 V only, when oxygen is used as an electron acceptor [from the redox potentials of microbial $\,$ metabolism by considering NADH (-0.32 V) and pure oxygen $\,$ $(+0.82 \text{ V})$ redox potentials vs standard hydrogen electrode (SHE) at neutral pH $[1,17]$. Moreover, the practical values were much lower than the theoretical values, due to ohmic over potentials and mass transfer limitations [\[20\]](#page--1-0). This illustrates the limitations of MFC upscaling by volume alone. Thus, a stacked approach for upscaling of the MFC technology is a promising strategy to achieve higher power output for practical applications. In fact, only upscaling by stacking approach makes sense, as current is an extensive variable with respect to the surface area of the electrodes. There are few studies that specifically focused on MFC upscaling by stacking approach using laboratory prototypes $[8,11,14,19,21-26]$ $[8,11,14,19,21-26]$ $[8,11,14,19,21-26]$.

Series connection in the MFC stack allows similar current flow through each of the cell but the voltage across the circuit will be cumulated from all the cells. Contrary to that, parallel circuit keeps the same voltage across each cell and the current will be cumulated from all the cells. Power production in MFC is a microbially-resolved process and yields were not only effected by the electrical connection but also by its mode of operating conditions [\[5,27\].](#page--1-0) Based on the premises of bioreactor design and engineering, an important question to be raised is how the mode of operation impacts on MFC performance. MFCs can be operated in three different modes; batch, semi-continuous and continuous mode. In an anaerobic fermentation process, each of these modes of operation has a direct impact on the microbial specific growth rate, product and substrate dilution, accumulation of inhibitors, and waste removal [\[5\]](#page--1-0). In classical electrochemical systems, the ratios between the electrode active surface area, electrolyte volume and molar amount of substrate defines the available charges to be transformed. Whereas in this case of microbialelectrochemical systems, it can be anticipated that the mode of operation plays a direct role on the amount of charges available for electron-transfer reactions as well as on wash-out of microbes from the electrode surface [\[17\]](#page--1-0).

Along with the mode of operation the selection of an appropriate substrate to operate a stacked MFC is regarded as one of the most important factors affecting overall energy efficiency [\[4\].](#page--1-0) A wide variety of substrates were already used in MFC for electricity generation [\[27,28\].](#page--1-0) However, integration of multiple bioenergy systems for various forms of energy generation is considered more viable than individuals in terms of environmental and economic concerns [\[4\].](#page--1-0) In this context, secondary integration of MFCs to acidogenic dark fermentation process by utilizing the dark fermentation effluent (DFE) as substrate gained more interest due to the possibility of energy recovery from the residual carbon source. MFC is of particular interest in DFE treatment, which increases the process efficiency through the integration by utilisation of residual carbon source along with volatile fatty acids (VFAs) of each individual processing system [\[4,29\].](#page--1-0) In this direction, present study investigated the upscaling of MFC technology through stacking approach of three identical and individual cells using real field DFE as substrate. Prior to stacking, influence of operating modes (batch, semi-continuous and continuous) were investigated individually. A detailed evaluation in terms of power generation, substrate utilization, energy conversion efficiency and bio-electrochemical parameters were carried out in both individual and stacked configurations.

Material and methods

MFC construction

The construction of MFC was described in detail in the previous work and operation of MFC was done in similar way [\[17\]](#page--1-0). Three identical MFCs were designed and fabricated, using polyvinylchloride (PVC), to have a two-compartment system (total/working volume, 550/100 mL). VITO-CoRE™ cold-rolled gas diffusion electrodes (GDEs) were used as cathodes [\[30\]](#page--1-0) on both sides of MFC and carbon cloth (Mast Carbon™, Basingstoke, UK) was used as anode in between them. Projected surface area of the each electrode was 110 cm^2 . Ion permeable separators (Zirfon®) were placed on both sides of anode to prevent the exchange of gases coming from the cathode (O_2 or H_2) which can be produced during potentiodynamic electrochemical measurements [\[10\].](#page--1-0) All the electrodes and membrane were pre-treated in phosphate buffer solution (PBS) as described earlier [\[31\].](#page--1-0) Both anode and cathode included a stainless-steel mesh current collector, which has been previously described [\[4\]](#page--1-0). Ag/AgCl-3.5 M KCl (+197 mV vs. SHE) was used as reference electrode (Radiometer Analytical, France) to measure anode and cathode potentials, respectively. Electrodes were connected externally through concealed copper wire through an external resistance (R_{ex}) , except when stated otherwise. Ambient air was fed at the catholyte via the GDE at an overpressure of 5 mbar. All MFCs were operated at room temperature (17 \pm 1 °C). A feed bottle (250 mL) was connected to the anode chamber of each MFC by using silicone tubing to recirculate the electrolyte containing the substrate through the reactor. The feed bottle was placed on magnetic stirrer (300 rpm) and nitrogen was flushed continuously to remove dissolved oxygen (DO).

Biocatalyst

Farm manure was collected from a livestock Cattle farm in Boeretang area in Mol, Belgium, and was used as the raw

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