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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.

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

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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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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 $N\text{-}NO_3\text{-}$ or $N\text{-}NO_2\text{-}$ 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.

Fresh swine manure from a nearby facility is fed as anode fuel. Its pH and conductivity are maintained constant at 8.0 ± 0.1 and 2.7 ± 0.3 mS/cm, respectively, throughout the study period. The substrate is continuously fed to the anode at the rate of 1.5 L/d, while the cathode is fed an oxygen-saturated mineral solution. Internal recirculation (170 L/d) in each compartment maintains well-mixed conditions, and minimizes concentration gradients. A methacrylate cylinder at the anode effluent serves as a gas trap. Operating temperature of the system is controlled at 21 ± 1 °C. Anode potential is monitored with an Ag/AgCl reference electrode (+197 mV vs. Standard Hydrogen Electrode, SHE), and recorded, with cell voltage, at 5-min. intervals by means of two online multimeters with data acquisition system.

Anode and cathode chambers are inoculated with a mixture of : aerobic activated sludge from the Girona municipal wastewater treatment plant (20%), anode effluent from a parent MFC (10%), swine wastewater (10%), and tap water (60%). The anode inoculum contains also 9.5 mM 2-bromoethanesulfonate (BES), in order to initially inhibit methanogenics growth [17]. Inoculation occurs in closed electric loop mode, with R_{ext}=30 Ω, maintaining a low recirculation rate of 86 L/d to promote bacterial fixation on the electrodes' surface. This approach is meant to provide a growth advantage to exoelectrogenic bacteria, against the proliferation of methanogenics [9, 13]. While in operation, the MFC is connected to a MPPT system for automatic control of external resistance. This system automatically adjust the value of R_{ext}, to match that of R_{int}, by a Perturbation-and-Observation (P/O) method [11,14].

After 4 days from inoculation, the MFC is switched to continuous-feed mode, and MPPT control turned on. The cell is fed initially at high (anode) OLR of 11.2 ± 3.0 kg COD/m^{3}d for the first 7 weeks (1st period). On day 53, the OLR is decreased by 50% to reach the lower value of 5.3 ± 1.4 kg COD/m^{3}d. This is maintained for another 5 weeks (2nd period). On day 88, OLR is decreased again by 90% at a final value of 0.7 ± 0.1 kg COD/m^{3}d. This latter condition is then maintained for 2 weeks, until the end of the study.

Samples for the determination of total and soluble COD (COD_t , COD_s) and 5-day BOD (BOD_5) are taken regularly from the anode influent ($_{IN}$) and effluent ($_{EFF}$) streams, and analyzed according to Standard Methods [18]. Anode OLR is calculated as the daily influent organic matter concentration (COD_t) divided by the hydraulic retention time. Organic Removal Rate (ORR) is calculated as the difference between influent and effluent OLRs. pH and conductivity are measured twice weekly for both anode and cathode influents. Current intensity (I) and cell voltage (V) are continuously recorded. Applied external resistance (R_{ext}) is calculated by means of Ohm's law, and polarization curves are obtained periodically, imposing linear potential decrease and increase of 0.5 mV/s from the Open Circuit Voltage (OCV) to a cell voltage of 0 mV, and vice-versa to the cell. Internal resistance is calculated from polarization curves, by means of the power density peak method [4]. Anode Coulombic Efficiency (CE) is calculated according to Logan et al. [19] using daily average data.

Anode off-gas is trapped in an external chamber, sampled and analysed to determine CO_2, CH_4, O_2, and N_2 with a GC System. Gas production rates are calculated to take into account their dissolved fractions released with the effluent. Anode off-gas production is measured and analyzed also in open (electric) circuit condition, to (temporarily) halt the exoelectrogens' metabolic pathway and thus quantify the activity of methanogens alone.

Energy loss factors are calculated, in relation to the three experimental periods, from the energy balance [20]:

$$E_{cell} = E_{emf} - \eta_{An} - \eta_{Cat} - E_{ionic} - E_{\Delta pH} - E_T \quad (1)$$

where the parameters represent: E_{cell} (cell voltage), E_{emf} (overall cell electromotive force), η_{An} (anode overpotential), η_{Cat} (cathode overpotential), E_{ionic} (ionic loss), $E_{\Delta pH}$ (pH gradient loss) and E_T (transport loss).
E_{emf} represents the maximum voltage that can be extracted from the MFC. E_{ionic} is related to the electrolyte resistance of anolyte and catholyte. $E_{\Delta pH}$ represents the potential loss related to the pH gradient developing over the membrane during MFC operation. E_T is related to the ionic transport resistance of the membrane. Insights related with the calculation of each specific overpotential can be found in a previous works [21]. Following the methodology of Sleutels et al. [20], ohmic losses other than ionic losses of the electrolytes are not measured, and included in the overpotentials of anode and cathode.

3. Results

The MFC operated according to the above specifications for 14 weeks. Figure 1 illustrates power generated together with punctual values of OLR. The figure also reports applied external resistance (R_{ext}) and values of internal resistance (R_{int}), calculated from polarization curve analysis.

Inoculation procedure started on day 1 under closed electric loop conditions. After 3 days, continuous-mode feed at high OLR started, and the MPPT control system was activated. In 14 days, due to MPPT control [14], start-up was completed, and semi-stable trends of power and external resistance could be identified. Subsequent highs and lows of power production can be related to punctual OLR peaks due to the variable nature of the feed. Power production reached an average value of 2.1 ± 0.3 mW between days 14th and 49th, meanwhile R_{ext} oscillated in the range 6.5 – 25.5 Ω. From day 38th to day 49th the MFC a showed stable R_{ext} of 8 ± 2 Ω and power production of 2.3 ± 0.2 mW. After this first period the MFC was run in open circuit for 3 days, in order to quantify the activity of methanogenic microorganisms alone, under these conditions. On day 53rd, the electric circuit was closed again and OLR was decreased from 11 to 5 kg COD/m^{3}d. This perturbation induced the increase of R_{int} from 8 to 18 Ω and, accordingly, the MPPT control increased the R_{ext} value to maximize again MFC power output. By adopting this system, the MFC took only 5 days to restore steady-state working conditions, and power output remained at the high value of 2.0 ± 0.2 mW, but at a lower OLR. After day 64th, R_{ext} remained stable at 15 ± 3 Ω. The MFC was left to operate at this steady-state condition for a further 3 weeks, then the electrical circuit was opened on day 79th, for 3 days. On day 88 the OLR was decreased for the second time, to reach a final value of 0.7 kg COD/m^{3}d. The MPPT control system took less than one day to adjust to the OLR decrease; a 90% OLR variation from 5 to 0.7 kg COD/m^{3}d was strong enough to double R_{int} in just 16 hours. In this case, power production dropped down to 0.3 mW in less than 3 days. Applied R_{ext} stabilized on values near 17 Ω and did not vary significantly until the end of the study, power generation oscillated around 0.7 ± 0.5 mW. On day 101st the electrical circuit was opened for the last time, until day 103rd.

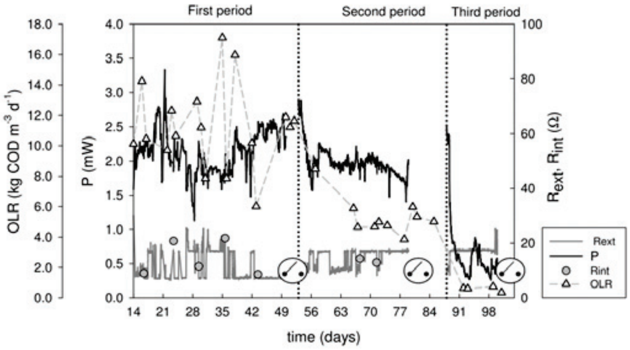

Figure 1 – Power production (P), applied external resistance (R_{ext}), calculated internal resistance (R_{int}) and applied Organic Loading Rate (OLR) over studied time. Vertical bars represent OLR variations. Electrical switch symbol represents periods where the MFC operates in open circuit condition

Table 1 presents average cell operating data. Data during the start-up period (first 14 days) and open circuit conditions (3 days before each OLR variation) were not taken into account to describe the steady-state behaviour of the MFC. The use of actual swine manure as a substrate implied small OLRs oscillations during the experimental period. This, in turn, slightly affected the determination of organic matter removal and Coulombic Efficiency, while electrical performances seemed to be less affected. MFC instantaneous performance is strongly dependent on punctually applied OLR. The Organic Removal Rate decreased almost linearly while decreasing OLR from 11 to 5 to 0.7 kg COD/m^{3}d; the gradient of the function ORR = f(OLR) represents the organic matter removal efficiency. This slightly increased (from 39% to 52%) while decreasing OLR, meaning that bacterial consortia were more efficient in removing carbon, when subjected to substrate limiting conditions. Current production improved at high OLRs, and reached almost 15 mA (on average) during the 1st period. Although η_{CODt} was higher at lower OLRs, current intensity decreased since less electrons were available from the substrate. Similar conclusions were also obtained by Sleutels et al. [22] on acetate-fed MFCs. Power measurements were coherent with current intensity values and decreased with decreasing OLR. However, the relationships I = *f* (OLR) or P = *f* (OLR) were not linear. In both cases the gradient was more pronounced at lower loading condition, suggesting the idea of a saturation-type relationship between I (or P) and OLR values. This is consistent with other studies performed on MFCs treating swine manure [6].

Table 1 – Comparison of Organic Loading Rate (OLR), Organic Removal Rate (ORR), organic matter removal efficiency (η_{CODt}), power production (P_{mean}), current production (I_{mean}) and Coulombic efficiency, for the three experimental periods performed (within the days reported in parenthesis). CE values are calculated based on soluble COD removal (CE_{CODs}) and total BOD_5 removal (CE_{BODt}). Error values represent standard deviations of replicate samples.

Experimental period	OLR (kg COD m^{-3} d^{-1})	ORR (kg COD m^{-3} d^{-1})	η_{CODt} (%)	P_{mean} (mW)	I_{mean} (mA)	CE_{CODs} (%)	CE_{BODt} (%)
First (14-49)	11.2 ± 3.0	4.6 ± 2.7	39 ± 16	2.1 ± 0.3	14.9 ± 3.6	16 ± 9	19 ± 10
Second (53-78)	5.3 ± 1.4	2.4 ± 0.3	47 ± 10	2.0 ± 0.2	12.0 ± 2.1	15 ± 5	15 ± 1
Third (88-100)	0.7 ± 0.1	0.4 ± 0.2	52 ± 22	0.7 ± 0.5	6.2 ± 2.7	68 ± 33	77 ± 10

4. Discussion

In the perspective of MFC optimization, the "best" balance should be sought between organic matter removal efficiency, and electric power production. A parameter that could be useful in searching the best operational condition is the Coulombic Efficiency. CE is calculated, in this case, based on soluble COD removal, to take into account the filtration effect of the granular matrix filling the anode chamber, that could act as a trap for the particulate organic matter still present in the feed. CE remained around values between 15% – 19% during the first two experimental periods, but sharply increased to more than 70% when the lower OLR value (0.7 kg COD/m^3d) was applied. While current production decreased (as well as ORR) at this lower value, CE increased (as η_{CODt}), because the exoelectrogenic bacterial fraction resulted more efficient than other species in transferring electrons to the anode while oxidizing carbon. Low CEs during the first two experimental periods can be explained by the likely possibility of side-reactions occurring when high OLRs are fed to the cell (including methanogenesis and bacterial growth). It was in fact demonstrated that is almost impossible to prevent methanogens growth in MFCs at substrate concentrations higher than 1 g acetate/L [22]. Electrons used for methane production (and/or biomass growth) diminish the total electron quantity available for current generation, and, as a result, CE decreases. When adopting a low OLR, the kinetics of exoelectrogens is faster, and they may outcompete methanogenic microorganisms (i.e. CE increases): Pinto et al. [9] in fact report a half-saturation constant for exoelectrogenic bacteria growth equal to 20 mg acetate/L, compared to a value of 80 mg acetate/L for methanogens, confirming this hypothesis. MPPT control also contributes to enhance exoelectrogenic activity against methanogens, as it was observed in a previous work [14]. Indeed, continual electric optimization of the MFC can generate a selective pressure that favors exoelectrogenic bacteria metabolism, despite the electrically unproductive methanogenesis reaction.

4.1 Energetic aspects of MFC operation under different conditions

To complete the characterization of the MFC behaviour, energy loss factors were calculated for the different operating conditions. According to Lyon et al. [23], one way to minimize energy losses in MFCs, is to operate them under optimal external resistance for power generation. In our case, therefore, the MPPT control system should be able to guarantee such reduction. Figure 2 presents energy losses distribution for the three operational periods, excluding start-up and open circuit conditions: cathode overpotential (η_{Cat}) represents the main energy loss component, regardless of the applied ORL. This is a typical limitation associated with oxygen reduction on graphite, and it has been observed by several authors [17, 24]. Anode overpotential (η_{An}) and pH gradient loss ($E_{\Delta pH}$) are the other two major contributions, while energy losses related with electrolytes and membrane resistance are negligible. In relative terms, therefore, the cathode contributes for 73-80% to the total energy losses (depending on OLR) while the anode and pH-gradient are jointly responsible for the remaining 15-23%. In particular, η_{An} decreases passing from the 1st to the 2nd experimental period. This decrease is due to a lower electrode potential (from -250 to -266 mV vs. SHE), that approaches the thermodynamic value for acetate oxidation (-284 mV); at the same time, $E_{\Delta pH}$ also decreases, as the lower MFC current production reduces electrolytes polarization. At low OLR, overpotential distribution is different: the cathode shows a slightly lower energy loss, due to increase of the electrode potential (from -91 to -25 mV vs. SHE), while, η_{An} increases to threefold the 1st period value. The reason is an abrupt variation of the electrode potential (up to -155 mV vs. SHE), caused by mass transfer limitations linked to the lower substrate concentration (down to 169 ± 81 mg COD/L). $E_{\Delta pH}$ decreases during the 3rd period, due to lower (ionic) current production.

The Organic Loading Rate affected specific overpotential components: the low value (0.7 kg COD/m^{3}d) limited the pH-gradient between the two chambers while, as secondary effect, produced a decrease of η_{Cat}. On the other hand, substrate limiting conditions increased dramatically η_{An} resulting in a total energy loss higher than those at higher OLRs. Conversely, an OLR of 11 kg COD/m^{3}d decreased η_{An} but increased $E_{\Delta pH}$ and η_{Cat} , due to higher current production.

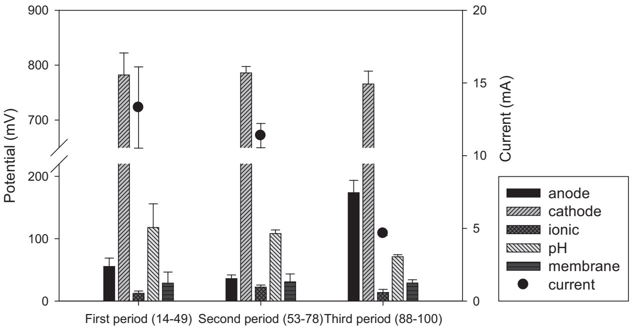

Figure 2 – Energy losses distribution, calculated for the three experimental periods performed. Circled points indicate the average current sourced by the MFC in each period. Error bars represent standard deviations of replicate samples.

To assess the effects of the competition occurring between exoelectrogenic and methanogenic microorganisms in the cell, both should be allowed sufficient time to grow and develop [22]. Higher OLRs were tested initially, exactly to give methanogens a chance to develop, at abundant levels of available substrate, until they could reach a stable population level. The subsequent decreases of applied OLR were designed to influence that initial balance, encouraging the development of the exoelectrogenic population [9]. Since Coulombic Efficiency is an indirect measure of that competition, from Table 1 it can be seen that the exoelectrogenic process is responsible for just 15-19% of the total organic matter removal during the first two test periods, while more than 80% of the available electrons end up in different, non-current producing, sinks (methane, bacterial maintenance, etc.). In order to better identify these internal electron fluxes, anode off-gas sampling and analysis were done for each OLR condition. Anode off-gas was also analysed under open (electric) circuit conditions, evaluating, therefore, the activity of methanogens alone, as the metabolic pathway of exoelectrogens is artificially stopped by opening the MFC's electric circuit [25].

4.2 Anode off-gas analysis

Figure 3 shows anode off-gas production rates for each experimental period, in closed and open circuit conditions. Carbon dioxide (CO_2) and methane (CH_4) are always detected, as they are the end products of exoelectrogenic respiration and methanogenesis. Nitrogen gas (N_2) production could be an index of heterotrophic denitrification in the anode chamber, but its presence was not further investigated in this study. Oxygen (O_2), on the other hand, was never detected in the anode off-gas: the low diffusivity of the anionic exchange membrane surely limits its transport from the cathode to the anode chamber, and heterotrophis may act than as oxygen scavengers at the anode [26].

Methanogenic activity was favoured by high OLRs applied during the 1st and 2nd experimental periods. Methane production rates of about 200 mL CH_4/L NAC d were calculated, a value similar to the results reported by Martin et al. [27] on a glucose-fed MFC. Pinto et al. [13] showed that an effect of MPPT control was to reduce anodic methane production by 70%, when treating synthetic wastewater; an observation corroborated by computer simulations using a two-population MFC model [9]. As it can be observed in Figure 3, CH_4 production in our MFC remained almost constant when decreasing the applied OLR from 11 to 5 kg COD/m^3d. The slight increase from 76 mL/d (1st period) to 83 mL /d (2nd period) corresponds to a 14% decrease of CE (Table 1), and confirms the strict relation existing between Coulombic Efficiency and exoelectrogens/methanogens competition [22]. Open (electric) circuit conditions enhance CH_4 production when high OLRs are applied. Stopping the exoelectrogenic pathway, by opening the circuit, had indeed the effect that all of the substrate becomes solely available to methanogens, thus increasing their activity. On the other hand, an OLR decrease to 0.7 kg COD/m^3d, causes an abrupt change in microbial population balance: methane production decreases to 3.8 mL CH_4/d, while CE increases by more than 70%. The low OLR of 3rd period was in fact so unfavourable to methanogenic microorganisms, that no gas production was detected still after 3 days of open circuit conditions.

CO_2 represents almost 60% of the total gas production during the first two periods. Its presence can be ascribes both to methanogenesis and exoelectrogenesis (and, possibly, to heterotrophic denitrification). In open circuit conditions, the ratio between CO_2 and CH_4 in the anode off-gas equals 50%. This can be directly related to methanogenic metabolism [25]. Subtracting it from the total gas production in closed circuit conditions (indicated by "MPPT ON" in Figure 3), the fraction of CO_2 related to exoelectrogenic bacteria respiration can be estimated. This CO_2 aliquot increased when decreasing OLR, to a maximum of 77% in correspondence with the lower ORL value. CE increased accordingly, demonstrating that methanogenesis was limited and exoelectrogenesis was indeed favoured.

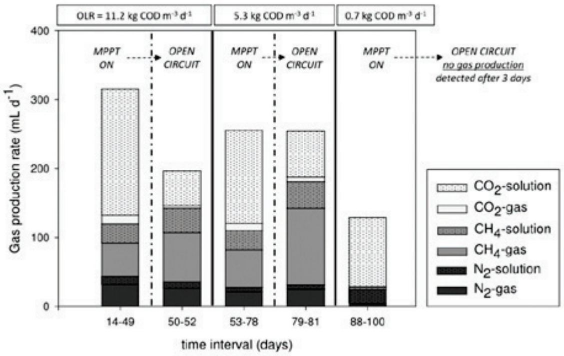

Figure 3 – Anode off-gas production rate and composition, as a function of applied OLR. Analyses were repeated in open and closed (electric) circuit condition, to distinguish contributions of exoelectrogens and methanogens.

5. Conclusions

This study evaluated OLR and R_{ext} influence on the performance of a MFC fed with swine manure. In a perspective of process optimization, the study aimed at identify key parameters to quickly evaluate the efficiency of both substrate removal and bioenergy production in MFCs: organic matter removal efficiency, Coulombic Efficiency and electrochemical losses were studied. MPPT control, to maintain optimal external resistance values in the cell, and sequential decreases of OLRs were applied to modify internal microbiological population balance, and encourage anode biofilm exoelectrogenic activity. The study demonstrated that a high OLR (11.2 kg COD/m^3d) limits electrochemical losses and increases absolute values of ORR (4.6 kg COD/m^3d) and current production (14.9 mA). On the other hand, adopting a low OLR (0.7 kg COD/m^3d) increases both organic matter removal efficiency (52%) and Coulombic Efficiency (higher than 70%) of the MFC. The observed effect of combined resistance control and OLR modification towards lower values favours exoelectrogenic bacteria growth and activity against methanogens proliferation. Such indications could be useful for future studies about MFCs applications, and in the selection of system operating parameters in order to achieve efficient start-up, operation, and improve electric current generation.

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