Effects of External Resistance on Microbial Fuel Cell's Performance

A. González del Campo, P. Cañizares, J. Lobato, M. Rodrigo, and F.J. Fernandez Morales

Abstract Microbial fuel cells (MFCs) are bioelectrochemical devices able to convert chemical energy into electricity. This chapter describes the effect of the external resistance on the performance of a MFC. Firstly, the state of the art of this topic has been comprehensively revised, and the effect of external resistance on cell voltage, anode potential, current and power generated, microbial diversity, structure and morphology of the biofilm, microbial metabolism and organic matter removal, coulombic efficiency, and time of stability is reported. Also, different methods to the control of external resistance as a function of internal resistance changing are explained. After that, the effect of changes in the external resistance on power generated and COD removal in a microscale MFC, used to treat wastewater, was studied. The obtained results indicated that when external resistance was increased, the power decreased. However, hysteresis was observed due to change in microbial diversity in the anode. During the first phase of increment of external resistance, the maximum power exerted, 1.69×10^{-3} mW, was obtained with a 2,700 Ω load. However, when decreasing the external resistance, the maximum power, 1.27×10^{-3} mW, was obtained with a 2,200 Ω load. Regarding COD removal, the effluent COD decreased when external resistance was increased, that is, the wastewater treatment was enhanced when external resistance was higher.

Keywords Electricity, External resistance, Microbial fuel cell, Microscale

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1 Introduction

Microbial fuel cells (MFCs) are electrochemical devices that exploit the metabolic abilities of electrogenic microorganisms to facilitate the generation of electricity from chemical energy, mainly from organic matter. In a MFC, organic matter is oxidized at an anode by biological process where microorganisms deliver the electrons to the anodic electrode. These electrons flow through an external load and are released at the cathode where they are consumed to reduce an oxidant agent, usually oxygen. This biological system has the potential to oxidize a large variety of organic compounds producing at the same time electricity [1, 2]. In literature the electricity generation using MFCs has been studied using pure organic compounds, such as acetate, butyrate, and glucose, and also with waste streams [3–5]. Anyway, the main advantage of electrogenic microorganisms is their ability to oxidize wastes with simultaneous energy generation [6].

In this way, one of the most attractive energy sources for MFCs is wastewater, because electricity production is combined with the wastewater treatment [7]. The use of MFCs for wastewater treatment presents several advantages, such as economical savings in aeration and solid handling. Aeration alone can account for half of the operation costs at a typical treatment plant [8] and in MFC aeration is not necessary. The MFC process is inherently an anaerobic process; moreover, the sludge yields for an anaerobic process are approximately one-fifth of that for an aerobic process. Thus, the use of MFCs could drastically reduce solid production at a wastewater treatment plant, reducing also the operating costs for solid handling [1].

The major bottleneck of MFC application is its relatively low power density; nowadays, the actual power density exerted by MFC is not high enough for industrial applications. In order to solve this drawback, research on MFC has been focused on power density improvement by optimizing operating conditions such as COD loads [9], operational pH [10, 11], flow rate [12], and temperature [8]. Additionally, one of the main factors to enhance the power output is by means of an integral component of the MFCs, the external resistance [13, 14]. The external resistance is used to dissipate the electrical energy when MFCs are operated independently of an electrical device and as an integrated part of an electrical grid that controls the output of fuel cells [15]. The external resistance controls the ratio between the current generation and the cell voltage [16]. A high external resistance results in a high cell voltage and low current, and a low external resistance results in a low cell voltage and high current. One way to minimize losses is to operate the MFC under optimal conditions for power production at an optimal external resistance [17]. Because of that, the effect of the external resistance on the activity of the biocatalyst and on the electricity production in MFCs is a key point that must be taken into account [18].

In this context, the aim of this chapter is to study the effect of change of external resistance on operation of MFCs and to indicate how to select the most appropriate external resistance.

1.1 Effect of External Resistance on Performance of MFC

The external resistance controls the ratio between the cell voltage, determined by the difference between the cathode potential and the anode potential, and the current (amount of electrons per unit of time which flow through the circuit). The Gibbs free energy which is available for the microorganisms during substrate oxidation is proportional to the number of electrons transferred to the electrode and the potential difference between the anode potential and the redox potential of the substrate [19]. In this way, the higher the anode potential and the higher the current, the more energy the microorganisms theoretically gain per unit of time [20, 21]. This would result in an increase of the current generation and a lowering of the cell voltage by the microorganisms, both influencing the power generation [13]. Taking into account these statements, it is clear that the external resistance has significant impact on MFC performance, including electricity production, COD removal and microorganism population evolution. In the literature the effect of external resistance on MFC performance has been addressed. In the following sections, the effect of external resistance on the main variables of the MFC operation will be revised and studied.

1.1.1 Influence of External Resistance on Anode and Cathode Potentials and Cell Voltage

The maximum cell voltage in a MFC is obtained at open circuit, that is, when external resistance is infinite. When the external resistance decreases, the voltage exerted by the MFC also decreases. According with Menicucci et al. [22], this is because of the limitations imposed on the electrode reaction kinetics, on mass transfer, and on charge-transfer processes at the current-limiting electrode (one of

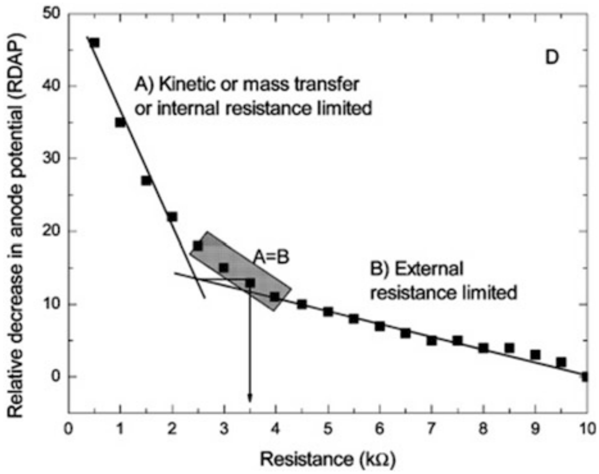


Fig. 1 Relative decrease in anode potential in a MFC as a function of external resistance (extracted from Menicucci et al. [22])

the two electrodes that exhibits the slower charge-transfer kinetics). In this research Menicucci et al. [22] evaluated the performance of MFC with different external resistances from 6 to 0.125 kΩ. The cell voltage decreased when external resistance decreased. The decrease was more significant when they applied an external resistance less than 3 kΩ. They used the relative decrease in anodic potential (RDAP) to select the external resistance to measure the maximum sustainable power of their MFC. In Fig. 1, the variation of percent deviation of anodic potential with respect to the applied external resistance in that work is shown.

When external resistance was high, the RDAP increased linearly with decreasing external resistance because external resistance limited the electron delivery to the cathode. When a low external resistance is applied, the electron delivery to the cathode is limited by kinetic and/or mass transfer (or internal resistance), and the RDAP increased linearly with decreasing external resistance. However, the RDAP also increased linearly with decreased external resistance, with different slopes, for external resistance-limited or internal resistance-limited conditions. When both lines intersected, they draw a horizontal line from the intersection to estimate the external resistance that allows them to measure sustainable power. Thus, in the study of Menicucci et al. [22] external resistance between 2.5 and 4 kΩ provided very close power values.

Ghangrekar and Shinde [23] also studied the effect of external resistance on MFC, and they observed that cell voltage increased with the increase in external resistance from 0 to 4,000 Ω; the maximum voltage of 358 mV was observed at an external resistance of 4,000 Ω.

Later on, Rismani-Yazdi et al. [15] obtained similar cathode potentials at different external resistances. However, anode potential varied under different external resistance employed. MFCs with lower external resistances resulted in higher anode potentials. This was also observed in the study of Song et al. [24] carried out using a sediment microbial fuel cell (SMFC). In that study, an increase in external resistance was accompanied with a significant decrease in anode potential. The anode potential for SMFCs with an external resistance of 10 Ω was much higher than those with other external resistances, around 30 and 80 mV higher than those with external resistance of 100 and 1,000 Ω, respectively. However, the cathode potential for the SMFC with 10 Ω external resistance was only 2–8 mV lower than those for SMFCs with 100 Ω and higher external resistances, which were found to be quite similar.

Similar results were found in other studies. In the study of Chae et al. [25], the anode potential became more negative with the increased external resistance. Zhang et al. [26] used the same MFC configuration but with different external resistance, and they concluded that MFC with a lower external resistance showed a higher steady anode potential after start-up.

These results indicate that the external resistance in MFCs regulates anode potentials. In order to maximize electrical energy output of a MFC, the anode potential should be as low and the cathode potential as high as possible [16]. However, the anode potential controls the theoretical energy gain for microorganism [27]. At low anode potential, the redox potential at the anode was probably too low to make it a favorable electron acceptor for the microorganisms [28], that is, there is low energy per electron transferred available for growth and cell maintenance. In this way, the differences in MFC performance with different external resistances may be associated with variations in activation losses at the anode, which is a function of electrochemical activity of anode-reducing microorganisms [15]. Therefore, there existed an optimum anode potential enabling the microbial consortia to balance electrode reduction kinetics with potential energy gain, which could be easily achieved through selection of the desired external resistance [24]. The activation losses have little influence on the MFC operation under optimal or close to optimal external resistance, which occurs when external resistance is close to the internal one [7]. Schroder [21] suggested that the differences observed in the anode potential under various external resistances can select for different electrochemically active microorganisms.

1.1.2 Influence of External Resistance on Electric Current of MFC

When MFC is operated with a low external resistance, the MFC generated higher current [15, 24, 25, 29, 30] due to the highest electron transfer to the cathode supporting faster cathode reaction and high electrogenic activity.

In this way, various studies have observed that stepwise decreases in the external resistance of an MFC improved the current generation over time [13, 15, 31, 32]. In the study of Aelterman et al. [13], the descent of external resistance from 50 to 25 Ω and finally to 10.5 Ω resulted in a significant increase in the continuous current generation. Moreover, Aeltermant et al. [13] observed that when the MFCs were operated at lower resistances, the mass transfer or kinetic limitations observed during polarization lowered, resulting in a less steep descent of the current density.

In a SMFC, Song et al. [24] observed that while there was not much difference among the currents produced at five different external resistances during the initial 10 days of operation, currents produced by the SMFCs were different after that. The highest average current of 0.22 mA was produced from SMFCs with an external resistance of 100 Ω, followed by those at 10 Ω and then 400 Ω. This can be explained because when working at low external resistance, a slight increase in internal resistance can dramatically decrease a fuel cell's performance [33] which reduces the current production mainly because of the internal resistance but not due to the external one. The SMFCs with an external resistance of 1,000 Ω produced the lowest current [24]. Similar to previous studies, Zhang et al. [26] observed that a conventional MFC with a lower external resistance showed a higher current generation after start-up.

On the other hand, when operating at high external resistance that almost mimics an open circuit, microorganisms were unable to transfer their electrons to such an unfavorable electron acceptor. In this situation, the high external resistance restricts the current that is able to flow from anode to cathode, and this may affect which microorganisms are able to colonize the anode [28, 34]. In the study of Ghangrekar and Shinde [23], it was demonstrated that when external resistance is very high, the current was brought to minimum and nearly constant value. Moreover, in this case, the limiting factor is the external resistance, and the current production is almost independent of another factor, such as the distance between the electrodes and surface of the anode.

1.1.3 Influence of External Resistance on Electric Power of MFC

According to the information presented above, when external resistance is low, the cell voltage is low and current is high. Taking into account that the power is the product of current and cell voltage, a question arises: Which value of external resistance makes that power maximum?

In order to determine that, it is necessary to take into account the following argument: If external resistance is low, then the equilibrium potential of the cell initially generates a high instantaneous electric current, higher than the maximum sustainable rate of charge transfer to/from the current-limiting electrode. As a result, the potential across the cell decreases quickly and adjusts to the rate of charge transfer to the current-limiting electrode, effectively decreasing the current in the external circuit. However, if the external circuit has a relatively high electrical resistance, then the equilibrium potential of the cell generates an electric current lower than the maximum sustainable rate of charge transfer to/from the current-limiting electrode. The potential of the cell adjusts to the external resistance. In the latter case, the power generation is sustainable but lower than it could be if the resistance of the external circuit were lower [22].

In this way, the maximum power transfer theorem states that maximum power is drawn when the external resistance (R_{ext}) of electric power source equals the internal resistance of power sources. Moritz von Jacobi published the maximum power (transfer) theorem around 1840, and it is also referred to as "Jacobi's law."

Then, the mathematical demonstration of maximum power transfer theorem for a DC circuit can be demonstrated as follows [35]:

Considering the MFC as a DC circuit, a voltage drop (V) drives an electric current (I) through internal (R_{int}) and external (R_{ext}) resistances. By Ohm's law,

$$I = \frac{V}{R_{\text{ext}} + R_{\text{int}}}$$

And the power (P) is

$$P = I^2 \cdot R_{\text{ext}} = \frac{V^2}{(R_{\text{ext}} + R_{\text{int}})^2} \cdot R_{\text{ext}} = \frac{V^2}{R_{\text{int}}^2/R_{\text{ext}} + 2R_{\text{int}} + R_{\text{ext}}} \cdot R_{\text{ext}}$$

P is maximum when the denominator is minimum. Differentiating the denominator with respect to R_{ext},

$$\frac{d\left(R_{\text{int}}^2/R_{\text{ext}} + 2R_{\text{int}} + R_{\text{ext}}\right)}{dR_{\text{ext}}} = -\frac{R_{\text{int}}^2}{R_{\text{ext}}^2} + 1$$

For maximum or minimum, the first derivative is zero, so

$$R_{\text{int}}^2/R_{\text{ext}}^2 = 1$$

Therefore, the power is maximum when $R_{\text{ext}} = R_{\text{int}}$.

If external resistance is higher or lower than internal resistance, generated power will decrease.

Because of its importance, multiple studies have been checking this theorem in MFC [13, 28, 34, 36–39].

Katuri et al. [36] observed that when external resistance was increased from 0.1 to 1 kΩ, the power density increased, reaching a maximum power density of 10.1 mW m^{-2}. A fall in power generation was observed at external resistance values from 10 to 50 kΩ. In the Fig. 2, the power generation in that work under different external resistances is shown. It is important to mention that internal resistance of the MFC used in that study was around 1 kΩ.

In the study of Lyon et al. [28], the internal resistance was 300 Ω, and the highest power production was obtained with an external resistance of 470 Ω, followed by 1,000 Ω, 100 Ω, 10 kΩ, and finally 10 Ω. The external resistance of 10 Ω produced the weakest power production as the resistance was too low compared to the internal resistance (300 Ω).

In the work of Ren et al. [34], the internal resistance of the MFCs was around 190 Ω, which explains why the peak power from MFCs was achieved at the 265 Ω external resistance. On the other hand, in that work the influence of increasing and

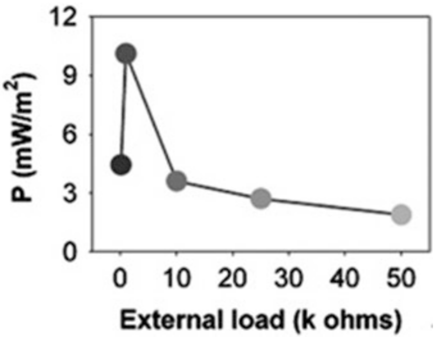


Fig. 2 Relationship between peak power generation and external resistance (extracted from Katuri et al. [36])

decreasing of external resistance at 25 min intervals on power density was studied. Higher power density values were observed when external resistances were changed from high to low (from 5,000 to 10 Ω) compared to low to high (from 10 to 5,000 Ω).

In other studies, although internal resistance was not measured, an increase in power was observed when external resistance was increased until a value, and then, when external resistance continued to increase, the power decreased [25, 26]. In the study of Zhang et al. [26], the power obtained after start-up increased from 1.96 to 6.05 mW when external resistance increased from 10 to 50 Ω. Then, when external resistance increased from 50 to 1,000 Ω, the power decreased to 0.64 mW. The best power of MFC with an external resistance of 50 Ω may come from the highest active biomass production on the surface of electrode. The lower performance with 10 Ω, despite the higher active biomass, might be due to the significant ohmic loss resulting from the existence of void spaces in the interior of the biofilm.

In the study of Chae et al. [25], the power density increased when external resistance increased from 10 to 100 Ω and showed a maximum value of 124 mW cm^{-2} at 100 Ω. When external resistance was increased from 100 to 2,500 Ω, the power density decreased.

It is important to remark that the theorem is not satisfied in several MFC studies [24, 40]. Song et al. [24] observed that power density increased with the increase in external resistance and the highest power density of 3.15 mW m^{-2} was obtained at an external resistance of 1,000 Ω. However, the internal resistance varied between 132 and 214 Ω. This fluctuation could be explained because internal resistance is not a system constant and depends on the external resistance applied to the MFC. In the study of Lee et al. [40], MFC with highest external resistance had better power densities.

1.1.4 Influence of External Resistance on Microbial Diversity

For practical purposes and in large-scale applications, mixed cultures are generally preferred over pure cultures because they are more readily obtainable in large quantities, more tolerant to environmental fluctuations, and more accommodating to a variety of substrates [41]. But other microorganisms such as methanogens are ubiquitous in sludge used as inoculum in MFC. Because of that, it is important to control and inhibit the competing microorganisms in a MFC.

In literature the influence of external resistance on microorganism diversity has been studied. In all studies, a change in microorganism diversity was observed when external resistance was changed [15, 28, 34, 36, 39], and new knowledge has been generated.

In this way, the external resistance in an MFC directly influences the anode potential, which is equivalent to the anode availability as an electron acceptor; therefore, it influences on anode biofilm development and performance [42]. Low resistance leads to more positive potentials, which provide more free energy to the microorganisms and enable a higher flux of electrons through electrogenic metabolisms [26], imparting a selective advantage to electrogenic over competing microorganisms [15, 39]. Thus, several studies have demonstrated that low external resistance enhances the presence of electrogenic microorganisms in the MFC anode chamber [40, 43–46] and that high external resistance reduces the anode potential enhancing the presence of strictly anaerobic microorganisms [18, 40, 45, 46]. In this way, independent of the microbial composition of the inoculum, proliferation of the electrogenic microorganisms could only be achieved at external resistance values that are equal to or less than the MFC internal resistance [18].

In addition to influencing this competition with other groups, the external resistance (anode potential) also exerts a selective pressure on the electrogenic community composition due to their different attributes related to anode affinity and maximum substrate utilization rate [42, 47]. This presents an opportunity to tailor the anode biofilm structure and composition and potentially MFC performance with respect to power output and substrate utilization, through the adjustment of external resistance [34].

Lyon et al. [28] demonstrated that the microbial community structure in MFC's biofilm operated at external resistance appreciably above internal resistance (1 to 10 kΩ) was significantly different from that observed in the MFC operated at low external resistance (10, 100 and 470 Ω) [28]. As mentioned above, a low external resistance promotes growth and metabolic activity of the electrogenic microorganisms since electron transport to the cathode is facilitated [18].

Rismani-Yazdi et al. [15] proved that within the anode-attached microorganisms, samples from MFCs with lower external resistance (higher anode potential), 20 and 249 Ω, had more similarity (75%) than those with higher external resistances (65% similarity between 480 and 1,000 Ω). It is because, as has been explained, operating the MFCs at low external resistance selects for microorganisms that have higher activity of electron transfer to the anode [48–50]. This interpretation is supported by Liu et al. [51] and Torres et al. [42], who suggest that a more positive anode potential is associated with greater colonization of anode-reducing microorganisms on the electrode.

Katuri et al. [36] also observed that different communities were selected at different external resistance which may represent selection of electrogenic organisms at lower external resistance. In the study of Jung and Regan [39], increasing external resistance to 9,800 Ω, the anode microorganism communities changed significantly, while continued operation at 970 Ω and a reduction to 150 Ω had little effect on them, although, in general, the modification of the external resistance load did not consistently affect the abundance of these functional groups.

In the study of Lyon et al. [28], with high external resistance, different electrode-reducing microorganisms colonized the anode that when external resistance was low. Regardless of the high external resistance, some microorganism species were still able to use the anode as an electron transfer intermediate. When external resistance is increased from 470 to 10 kΩ, the maximum power was slightly increased. However, during the initial period of higher maximum power output, there were two peaks that appear on the polarization curve. This could indicate two separate populations of microorganisms that were capable of producing electricity. Therefore, community structure changed with external resistance; however, different communities were capable of producing the same level of power production.

In the work of Ren et al. [34], bacteria with a filamentous structure dominated and formed relatively thin and patchy biofilm (0–30 μm) on the anodes under high external resistances (1,000 and 5,000 Ω), while rod-shaped cells accumulated and formed dense biofilms (more than 50 μm) that covered the anodes under lower resistances (10, 50 and 265 Ω). As the external resistance decreased, the biofilm cells tended to aggregate and finally covered the whole anode with thick biofilm.

1.1.5 Influence of External Resistance on Structure and Morphology Biofilm

Previously, the relationships between the microorganism diversity and the external resistance in a MFC have been studied. Moreover, the external resistance may also affect the structure and morphology of the biofilm in the anode. Therefore, in some research, the influence of external resistance on structure and morphology of the biofilm has been studied.

At low external resistance (higher anode potential and current), more electrogenic microorganisms should be able to transfer electrons to the anode and gain more energy; it leads to a more diverse and denser anode biofilm [26, 34]. Following this argument, Ren et al. [34] obtained different biofilm morphologies and densities in the MFCs under different external resistances (10–1,000 Ω).

Mclean et al. [32] described how the differences in external resistances affect cellular electron transfer rates on a per cell basis and overall biofilm development in *Shewanella oneidensis* strain MR-1 by monitoring the real-time microscopic imaging of anode population. They found that the anode of a MFC started up at a low external resistance (100 Ω) had a thinner biofilm and higher current per cell, compared with that at a high external resistance (1 MΩ).

Another effect of external resistance on morphology and structure of the biofilm was discovered by Zhang et al. [26]. They observed that although the biofilm formed at 10 Ω contained less active biomass than that at 50 Ω, both biofilms were of similar thickness. This is because the microorganisms were more loosely packed in the biofilm developed and the extensive voids were found to be distributed within biofilm at 10 Ω (the less external resistance). These voids were beneficial for mass transport within the biofilm by forming water channels that facilitate the substrate and buffer supply, as well as product removal. However, void spaces also lead to imperfect contact between the electrogenic microorganisms and the anodes, causing a decrease in the electrical conductivity of the biofilm matrix and consequently reduced the performance of the MFCs. By contrast, the biofilm formed at 50, 250, and 1,000 Ω appeared quite homogeneous and showed a compact structure, in which cells were tightly linked together by visible polymeric viscous materials.

1.1.6 Influence of External Resistance on Microbial Metabolism and Organic Matter Removal

The external resistance also influences on the microbial metabolism. The differences in MFC performance with different external resistances result mainly from the differences in the catalytic activity at the anodes [24] affecting therefore the microbial metabolisms and organic matter removal.

In this way, Aelterman et al. [13] observed that at the highest external resistance (50 Ω), feeding the biomass with an increased loading rate did not result in a rise of the continuous current generation. The amount of energy which was available for growth and maintenance, as determined by the external resistance, was probably too low to sustain a higher metabolic activity of the microorganisms. Therefore, no increase of the current generation at higher loading rates could be noted. Only during polarization or at lower external resistances, when higher electron fluxes and lower anode potentials were allowed, enabling a higher energy gain for the microorganisms, significant increases of the current generation and power outputs were observed.

At lower external resistance, the COD removal was higher, and with the increase in external resistance, a decrease in COD removal occurs [5, 29, 30, 36, 39, 40]. This is because, at higher external resistances, there is a lower anode potential, which may alter the metabolic activities of the anodic microbial community, and the presence of different microbial species could provide different mechanisms for efficient utilization of organic matter [36]. MFCs operated at higher anode potential (low external resistance) may lead to enhanced wastewater treatment since drawing a greater current from the MFC accelerates the COD removal [36]. In the work of Sajana et al. [52] carried out in a SMFCs, better COD and TN removal were observed when the system operated with lower external resistance than when operated with higher ones.

According to this argument, the total SCFA concentration of the anolyte increases with external resistance [36], and it can affect pH in the anode biofilm [53, 54]. The increased production of SCFAs with high external resistance may result from a high competition for organic matter in the anode and/or reduced consumption of metabolites with higher external resistance because of lower rates of respiration and anodic electron transfer activity. Also, Pinto et al. [7] observed that methane production was higher when MFC was operated at higher external resistance.

On the other hand, in various studies [26, 36, 45], a lower biomass yield at low external resistances has been obtained. Microorganisms may also produce extracellular polymeric substance (EPS) during growth on the anode surface, consuming energy which is available for microorganism growth [55]. Therefore, a higher portion of energy is consumed for the synthesis of EPS rather than for microorganism growth in the case of MFC with lower external resistance. In the study of Zhang et al. [26], EPS content of biofilm decreased from 296.8 to 51.9 mg g^{-1} as the external resistance increased from 10 to 1,000 Ω. Considering that the active biomass of the biofilm developed at 10 Ω was lower than that of 50 Ω, whereas the energy gain was higher, this result suggested that a greater portion of energy was consumed for EPS synthesis in the case of the biofilm developed at 10 Ω. Low sludge yield was reported to be advantageous in the water industry as it accounts for around 25–65% of total plant operating costs [56].

1.1.7 Influence of External Resistance on Coulombic Efficiency

Coulombic efficiency is the ratio of total recovered coulombs by integrating the current over time to the theoretical amount of coulombs that can be produced from organic matter removal. Therefore, taking into account that current and organic matter removal is influenced by external resistance, coulombic efficiency is also influenced by external resistance.

Generally, coulombic efficiency increases when external resistance is decreased. It is because current is increased [15, 40], anode potential is increased [39], and the share of fermentative and anaerobically respiring microorganisms is reduced [25, 34, 36, 57].

In this way, in the study of Rismani-Yazdi et al. [15], a maximum coulombic efficiency of 19% was obtained in MFCs with 20 Ω external resistance, and with 1,000 Ω the coulombic efficiency was 12%. It was due to changes in microbial diversity and the differences in current flow induced at various external resistances and other factors: accumulation of metabolites, biomass growth, substrate crossover, and competing reactions for electrons or reduction of O_2 diffusion through the membrane.

Lee et al. [40] observed that the coulombic efficiency values appeared to be decreased with increasing external resistance. High external resistance would bring high ohmic losses for electron transfer, thus probably resulting in a lower coulomb efficiency.

In the study of Jung and Regan [39], the high availability of the anode with low external resistance resulted in high coulombic efficiency.

Katuri et al. [36] obtained a maximum coulombic efficiency of 6.15% for MFC operated under the lowest external resistance (0.1 kΩ), and it decreased until 0.44% when external resistance increased until 50 kΩ. This behavior was perhaps due to competition for electron donor between electrogenic microorganisms and fermentative and anaerobically respiring microorganisms when external resistance was increased.

In the study of Juang et al. [57], it was observed that when external resistance ranged from 10 to 1,000 Ω, a lower resistance corresponded to a higher coulombic efficiency. It means that some electrons were consumed by some mechanisms other than the cathode reaction [58].

Chae et al. [25] determined that lowering the resistance from 600 to 50 Ω reduced the methanogenic electron loss by 24%. When the external resistance was lowered to 50 Ω after a run at 600 Ω for a period of 5 months, the level of methanogenic electron loss reduced from 53.2 to 40.6%, indicating its potential for controlling the methanogens. This resulted in a corresponding increase in coulombic efficiency from 32 to 42.8%, similar to the amount of saved electrons calculated by reducing methanogenesis. The undefined electron losses, including electron sink for microorganism growth, were about 4–10%.

In the work of Ren et al. [34], the average coulombic efficiency for the 10 Ω external resistance MFCs was 45%, while the average value for 5,000 Ω external resistance MFCs was only 6%. The low electron recovery at high external resistances was mainly due to the long batch duration, which resulted in more electron loss to non-electricity-related reactions such as aerobic respiration and perhaps methanogenesis, though the latter was not measured.

1.1.8 Influence of External Resistance on Time of Stability

When the external resistance is changed, the electrochemical response of the biofilm established at the antecedent quickly stabilizes. However, the biofilm takes much longer to stabilize, with changes in biofilm structure and community composition potentially leading to a long-term stable performance that differs from the short-term electrochemical response [34].

In the study of Jadhav and Ghangrekar [29], when the resistance was increased from 50 to 100 Ω, with initial sudden drop, the produced current increased with time and got stabilized within 20 min. However, when resistance was increased from 500 to 1,000 Ω, after initial sudden drop, the current slowly increased and got stabilized after 2 h. At lower resistance change, from 50 to 100 Ω, the current reached the stable value with less time after changing the resistance, but at higher resistance changes, it took long time for the current to reach the stable value.

Katuri et al. [36] also observed that the time taken to attain the peak current density decreased with decreasing external resistance. These observations may be due to different electron transfer rates under different external resistances and/or variations in microbial metabolic activities and kinetic differences in substrate utilization [46].

However, in the work of Menicucci et al. [22] only when the external resistance was large enough did the power generation reached a sustainable level quickly. The lower the external resistance, the longer the time needed for the cell to equilibrate and produce the sustainable power. In another study, He et al. [33] measured the power of their MFC and reported the maximum power that occurred when a 66 Ω resistor was applied. However, when they applied a larger external resistance, 100 Ω, the current decreased in time. When they applied a 470 Ω external resistance, the current did not change, showing the sustainable conditions.

In the work of Ren et al. [34], where the long-term operation of MFCs at different fixed resistances and the performances, architectures, and compositions of these different steady-state biofilms were studied, it was also observed that MFC under higher resistance showed reduced periods before reaching steady-state voltage. The lag time for 5,000, 1,000, 265, 50, and 10 Ω MFC to reach 80% of their maximum voltage was 91, 104, 106, 108, and 120 h, respectively. Higher external resistance could accelerate the biofilm acclimation process by providing a lower anode potential for a faster MFC start-up.

1.2 Control of External Resistance as a Function of Internal Resistance Changing

As it has been previously stated, the MFC power output is maximized when the external resistance connected to the cell is equal to the total internal resistance. An incorrect selection of external resistance, either larger or smaller than the internal resistance, may lead to large losses in power output. Meanwhile, variations in operating conditions (temperature, pH, influent strength, influent composition, and other factors) and the processes of biofilm growth and decay lead to significant changes of the internal resistance over time [22]. This inevitably results in a mismatch between the internal and the external resistances and, therefore, may lead to large losses in power output. For it, the external resistance control is an important requirement for industrial application of MFCs.

Premier et al. [59] demonstrated that the power production and coulombic efficiency of MFCs can be substantially improved using an automatic control strategy of external resistance.

The problem of optimizing the external load for power sources has been addressed before by online control, and it is often referred to as maximum power point tracking (MPPT). Thus, when internal resistance is increased or decreased due to the change in operation conditions, the MPPT algorithm decreases the external resistance value [18].

Woodward et al. [60] studied a method for external resistance control, which uses an online perturbation/observation (P/O) algorithm for maximizing the power output.

The P/O algorithm demonstrated excellent stability and fast convergence so that external resistance always remained close to internal resistance. This strategy might prevent MFC operation at external resistance values below its internal resistance, thus helping to avoid voltage reversal [61] after a feed disruption or another operating problem.

In this way, in the study of Pinto et al. [18], MFC-1, which was operated at a high external resistance, always had a low current density and a low coulombic efficiency, while MFC-2, which was operated at the lowest external resistance, and MFC-3, which was operated at an optimal external resistance by the P/O algorithm, showed larger values.

Also, a logic-based control approach for adjusting the external resistance has recently been proposed in literature [59].

Both methods provide real-time optimization of the external resistance; however the practical implementation of these methods would require a device with a variable electrical load that can be fitted on demand. Meanwhile, the electrical loads are not always adjustable.

Another mode of operation is described by a duty cycle, which suggested that by operating an MFC with intermittent connection/disconnection of the external resistance, the MFC power output could be improved without significant losses in power output even at external resistance values below internal resistance [62].

Coronado et al. [63] elaborated on the approach of intermittent (periodic) connection of the electrical load by analyzing the MFC frequency response in a range of 0.1–1,000 Hz and operating the MFC at a sufficiently high switching frequency, equivalent to a pulse-width modulated connection for the external resistance (R-PWM mode of operation). In the study of Coronado et al. [63], external resistance was disconnected during a time in each duty cycle in the R-PWM mode of operation. In this way, by comparing power outputs of MFCs operated in the R-PWM mode and with a constant resistance equal to the estimated total internal resistance value, the R-PWM mode operation was demonstrated to improve MFC performance by up to 22–43%.

In a stack of MFCs, the initially small difference in potential between cells can eventually dominate and suppress the performance of neighboring cells [64]. This voltage reversal can detract from the expected total power output in serial connection and can also deleteriously affect the electrogenic biofilm on the electrode [61]. Grondin et al. [65] used intermittent and periodic connection of the load as an alternative to MPPT operation to match internal and external impedance in order to obtain maximum power transference. Several duty cycles of open and closed circuit operation in benthic MFCs increased power output; however little or no effect on the anode community development was seen [66].

2 Experimental Procedure

2.1 Experimental Setup

The setup used in this study (see Fig. 3) consisted of a two-chambered microscale MFC separated by a proton exchange membrane, PEM (Sterion®) [9, 67]. Both the anodic and cathodic chambers were built on a graphite plate; the anode chamber volume was 0.95 cm^3 and the cathode chamber volume with serpentine channels was 0.5 cm^3. Toray carbon papers TGPH-120 (E-TEK, USA) (3 × 3 cm) were used as electrodes in the anodic and the cathodic chambers. The anodic electrode contained 20% of Teflon, and the cathodic electrode contained 10% in order to improve the mechanical properties of the carbon support [68]. At the cathode, a catalytic layer with 0.5 mg Pt/cm^2 loading was deposited onto a microporous layer [69]. The membrane-electrode assembly was performed according to literature [8]. The active areas of the anodic and cathodic electrode were 4.65 and 2.85 cm^2, respectively. Both electrodes were connected by an external resistance of 120 Ω (initial conditions) [70]. A scheme of the setup used is shown in Fig. 3.

The anodic compartment was inoculated with activated sludge from Ciudad Real Wastewater Treatment Plant and operated in the fed-batch mode until steady state was reached [9]. After acclimatization, the MFC was operated in continuous mode. To do that, the anodic chamber was fed with a synthetic wastewater, which contained 9 g L^{-1} glucose and fructose as organic substrates and COD 343 mg L^{-1} and trace minerals, at a flow rate of 0.5 mL min^{-1}. In order to avoid the degradation of the wastewater during its storage, it was sterilized for 30 min at 105°C. The composition of the synthetic wastewater used in the experiments can be found elsewhere [71].

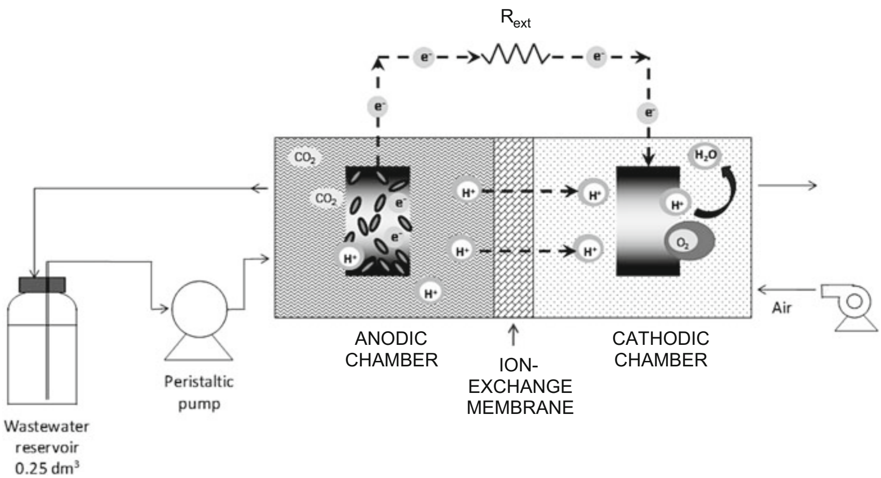


Fig. 3 Schematic view of the setup

An air-breathing cathode was used. Air-breathing systems use free convection airflow to supply oxygen to the cathode.

2.2 Characterization Techniques

A digital multimeter was connected to the system to monitor continuously the cell voltage at the value of the external load (R_{ext}). These cell voltages (V) are directly related to the current flowing between the electrodes (I) by the Ohms law. Power was calculated from current and voltage.

The effluent's COD from anodic compartment was determined by photometric methods with a MERCK COD cell test and Pharo 100 MERCK spectrophotometer.

3 Results and Discussion

In this study, the influence of the external resistance over the power and wastewater treatment capacity of a microscale MFC was evaluated. In this way, the first external resistance studied was 120 Ω, external load used for the normal operation of the cell. Gradually, the external resistance was stepwise increased from 120 to 3,300 Ω. The maximum resistance was selected in order to overcome the internal resistance of MFC, which was around 2,200 Ω. Afterward, the external resistance was decreased from 3,300 to 120 Ω, in order to evaluate the effect of the lowering of the external resistance on the MFC.

In this way, each external resistance was kept in the system of MFC until the steady state was reached.

3.1 External Resistance Effect on Power Production

The effect of the external resistance on power generation was studied. In Fig. 4 the generated power in the steady state for each evaluated resistance is shown.

The generated power by MFC increased with the increment of external resistance. When the external resistance increases from 120 to 560 Ω, a great increment in power from 3.76×10^{-4} to 1.57×10^{-3} mW was observed. From 1,000 Ω power stayed constant around 1.6×10^{-3} mW; this is because the increment of external resistance adversely affects the electricity production. In the phase of decrement of external resistance, a decrement of power from 1.6×10^{-3} to 4.8×10^{-5} mW was observed. It is important to highlight that this loop has hysteresis. In this way, the obtained power for each external resistance was always higher in the phase of increment of the external resistance than in the phase of decrement of the external resistance. Lyon et al. [28] noted changes in microbial community structure both at

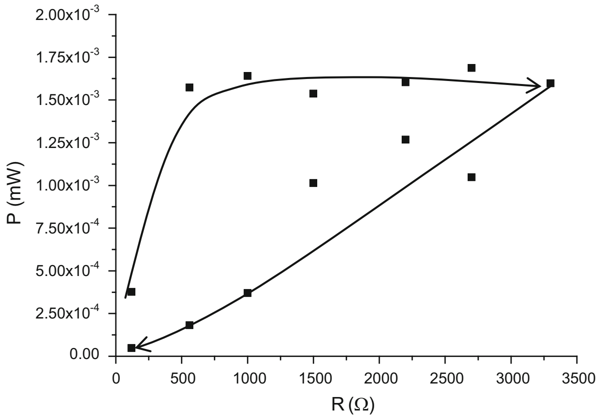


Fig. 4 Power in steady state at every external resistance

the highest external resistance and when the resistances were changed. It could be the reason for the reduction observed in the power exerted when the systems worked with high external resistance and also to the existence of a hysteresis loop. The difference in MFC performance with different external resistances may be associated with variations in activation losses at the anode, which is a function of electrochemical activity of anode-reducing microorganisms [15]. It has been suggested that differences observed in the anode potential under various external resistances can select for different electrochemically active microorganisms [21].

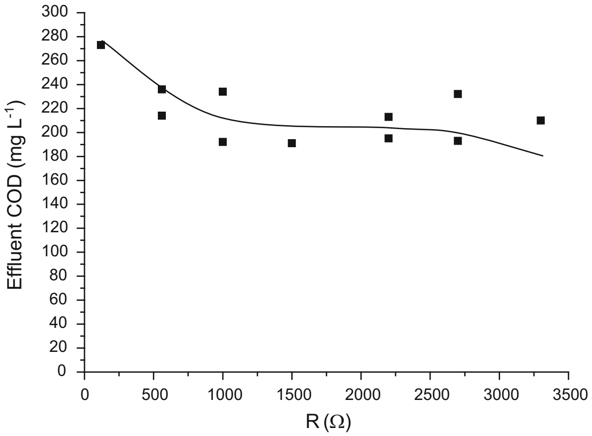
On the other hand, during the first phase of increment of external resistance, the maximum power, 1.69×10^{-3} mW, was obtained with 2,700 Ω. The reason for this is that the behavior of MFC changed during the phase of increment of external resistance, and it is possible that the internal resistance also changed. However, in the phase of lowering of the external resistance, the maximum power, 1.27×10^{-3} mW, was obtained with 2,200 Ω.

3.2 External Resistance Effect on Wastewater Treatment

In the MFC, the microorganisms of the anodic compartment oxidize the organic substrate to carry out its vital functions, thereby removing organic pollutants from wastewater. In this section, the effect of external resistance on the purifying capacity of MFC is studied.

In Fig. 5, the effluent COD as a function of external resistance is observed. As it can be seen, the COD of the effluent decreased when the external resistance was increased; therefore, the consumed substrate by microorganisms increased. In this way, the purifying capacity of the MFC enhanced when the external resistance was increased. However, taking into account that the electricity production decreased, it is clear that greater consumption of organic matter was not caused by the improvement in the behavior of electrogenic microorganisms. Thus, at the anodic compartment, there were other microorganisms (not electrogenics) that degraded organic matter of wastewater.

Fig. 5 Effluent COD in steady state at every external resistance



Concluding Remarks

The external resistance directly influences on anode potential and current, and they influence on other variables in a MFC, such as microbial diversity, biofilm morphology, power generated, coulombic efficiency, and MFC stability among other variables. In this way, the selection of the optimal external resistance in order to get the best performance in the MFC is very important. Moreover, it is necessary to take into account that modifications in the operational conditions could change the internal resistance and, therefore, the optimal performance of MFC. Therefore, it is necessary to control the external resistance as a function of internal resistance. Based on the observation made, it can be also concluded that the external resistance select the microbial population growing in the anodic chamber of the MFC. As a consequence of higher external resistance, microbial diversity changed and the lower power was obtained for the same external resistance. It was also observed that when working with high external resistance, the COD removal from the wastewater was higher.

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