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COBEM2021-1591 - THE EFFECT OF THE EXTERNAL LOAD ON THE PERFORMANCE OF MICROBIOLOGICAL FUEL CELLS FOR ACID MINE DRAINAGE REMEDIATION AND ENERGY GENERATION

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Abstract. *Microbial fuel cells (MFCs) are a new sustainable alternative for electric power generation and treatment of effluents. Such devices can convert several types of organic substrates directly into electricity. Acid mine drainage (AMD) is one of them. AMD is an environmental problem since it has bad effects on surface and subterranean waters due its low pH, high concentration of sulfates, toxic metals and dissolved salts. MFCs systems are complex and demand profound studies to determine the behavior and repeatability of their beneficial effects. The herein research presents experimental results of an external load connected to an MFC system for treatment of a synthetic AMD aiming to reduce the concentration of sulfates and to generate electric power. Eight MFCs of the type H were built using a proton exchange membrane (Nafion 117). The anodic chamber was inoculated with domestic wastewater sludge, the cathodic chamber was inoculated with sulfate-reducing bacteria (SRB) and the electrodes were made of Graphite cylinders. The influence of the external electric resistance on the reduction of sulfate and on the electric power generation was investigated. The experimental results show that there is an optimum value for the external resistance. There is a trade-off between the reaction rate and the overpotential losses; these parameters have influence on the microorganisms acclimation time and electric power. The maximum electric power generated was 5.47 W/m^2 and it was related to a relatively low external electric resistance (61.7 Ω) when compared to values documented in the literature. Also, the sulfate concentration at the cathode was reduced 99% (270 Ω). These preliminary results support the use of MFCs for AMD remediation and cost reduction to the available conventional technologies.*

Keywords*: Microbial fuel cells, acid mine drainage, energy generation, sulfates.*

1. INTRODUCTION

Microbial fuel cells (MFCs) are a new sustainable alternative for energy generation and treatment of effluents. MFCs are able to convert organic compounds, as for example, industrial effluents into electricity.

MFCs operate with a bioanode where microorganisms act like "living catalysts". The cathode can be either abiotic, using the same conventional catalysts used in other types of fuel cells (FCs), or biological (microorganisms) promoting the reduction reaction of the MFC.

The power generated by the MFCs is still low. The ratio of power generated to area (power density) is very low when compared to the power density generated by other types of fuel cells (Kong *et al.*, 2018). However, MFCs have become an option for supplying the energy needed in sewage treatment processes, since the sewage sludge has the necessary organic substrates for the bacteria's metabolism. Almost all the substrates that can be metabolized by micro-organisms can be used in MFCs, as for example, simple organic compounds, sewage sludge, agricultural waste, brewery wastewater, food industry waste, dairy farms and other effluents from industries.

AMD is the term used for the acid aqueous solution with high content of sulfates from wastewater of coal mining. Those metal sulfates are chemically and biologically oxidized generating a large amount of dissolved metals and acidity. AMD is harmful to the environment since it contaminates brooks and rivers close to the mines. The conventional AMD treatment is chemical neutralization process, but such process is expensive and generate a huge amount of sludge. Therefore, the biological reduction of sulfate (by sulfate reduction bacteria - SRB) is an alternative for the treatment of

AMD and mitigation of its negative environmental impacts. Under anaerobic conditions, metals can be removed from the solution promoting their precipitation in form of sulfates (Hedin *et al.*, 1994).

Some recent studies have evaluated the treatment of ADM combined with power generation by MFCS. In the study by Vélez-Pérez *et al*. (2020) two experiments were carried out over a short period (120h), evaluating the efficiency of removal of chemical oxygen demand (COD) (15%), alkalinity, pH, sulfate (20%) and nitrate (> 90%) removal, heavy metals and generated volumetric power (14 W / m^3). The open-circuit voltage (OCV) and the power generated with a load of 100 Ω were also evaluated. Peng *et. al*. (2017) achieved a removal of 1.2% of sulfate, 99.7% of heavy metals and 51.6% of the total chemical oxygen demand after 10 days of treatment and a maximum power density of 51.3 mW/m^2 was gotten.

As previously discussed, the studies presented indicate the possibility of using MFCs to treat effluents (wastewater and ADM) and, therefore, in this study, we sought to evaluate the performance of a MFC in two chambers to simultaneously generate electric power and treat ADM as a function of the external load, to know the influence of this parameter on the period of acclimation of the bacteria, reaction rates and its consequences on energy production and effluent treatment (reduction of sulfates and consumption of COD) .

2. METHODOLOGY

The MFCs used in the experimentation were of the type "H". They were built with an anodic and a cathodic chamber with diameters of 8cm, height of 11.5 cm and were hermetically sealed to promote an anoxic environment. Anode and cathode were made of graphite rods 0,8 cm diameter and 5 cm high. Nafion® 117 (5 cm of diameter) was used as a proton exchange membrane (PEM). The membrane was pre-treated with H_2O_2 and H_2SO_4 before its use following the recommendations of as described by CAPPADONIA (1995).

In total eight MFCs were assembled with identical anodic and cathodic chambers. The external load (electric resistance) was varied according as shown in the Tab. 1. The MFC 1 was chosen to be the one where with OCV and the external load varied from 1000 to 24 Ω for the others MFCs. The magnitude of the external loads was chosen according to those presented by Serra *et al.* (2020) who obtained a numerical and experimental polarization curve in steady state for an MFC.

Table 1 – MFCs and their external load, respectively

MFC	External Load (Ω)
1	0 (OCV)
2	1000
3	470
4	270
5	100
6	61.7
7	50
8	24

The anodic chambers were filled with 350 mL mineral medium as described by FENG et al, 2008, pH 7.0 containing 1g/L of acetate, and inoculated with 50mL of anaerobic domestic wastewater sludge from Santa Luiza Water Treatment Station– Criciúma –Santa Catarina-Brazil. The cathode chambers were filled with 350 mL of the medium Postegate C as described by CHEUNG GU, 2003, pH 4.0, and inoculated with 50 mL of a supernatant liquid already enriched with sulfate-reducing bacteria from a previous experiment.

The Figure 1 shows the eight MFCs in the first day of the experiment, when the circuit was closed with the respective external loads (Tab. 1)

Figure 1. Eight MFCs connected to the external load at the beginning of the first experiment. The MFC 1 is on the bottom left-hand side and the MFC 4 on the top left-hand side. The MFC 5 is on the bottom right-hand side and the MFC 8 is on the top right-hand side.

The experiment was performed for 91 days. The MFCs were monitored for the energy production, change in pH, COD consumption and sulfate reduction. Each one of these procedures will be explained in the next sessions.

A multimeter was used to measure the OCV or the electric potential generated by the MFCs connected to their external loads. On the day 13th, after noticing that the power generation and the COD was low, 15 mL of cultivation medium was added to all anodes.

The COD analysis was performed following the methodology presented by APHA (2005). Sulfate concentrations were determined through the method of precipitation of sulfate ions with barium chloride forming barium sulfate which due to its low solubility, caused turbidity. The turbidity was measured photometrically at 450nm. Sulfate removal was defined as the ratio between total sulfate left in the chamber in a determined time and the sulfate given to the reactor. For COD removal is computed as the ratio between the total COD consumed in the process and the COD at the beginning of the experiments.

3. RESULTS AND DISCUSSION

The designed MFC system was evaluated according to its capacity to produce electric power and to treat effluents (wastewater and AMD).

3.1 Energy Generation

It was observed that in the first 13 days for most of the evaluated MFCs there was no energy generation, which is believed to be due, as several studies report, a period of adaptation for the consortium of microorganisms at the anode and cathode. In this adaptation period most of the substrate is consumed and destined for the growth and maintenance of metabolic activities and the formation of biofilm that allows the effective delivery of electrons to the circuit. And thus, after the first 13 days, the effective production of electrical potential begins. After that a plateau is reached and eventually the energy generation starts to decline.

Each MFC was considered productive when presented potentials above 100 mV. The experiment lasted 91 days and the average potential was calculated during this period. It was also computed in how many of the measurements, in a total of 18, each MFC was the one with the greatest potential within the set. Those results can be seen in the Tab. 2 and also in the Fig. 2.

Table 2 – Experimental results of electric potential generated by the eight MFCs

MFC	External load (Ω)	Maximum electric potential (mV) / day	Average electric potential (mV)	Time (days)	Number of days generating maximum electric potential (days)
C1	OCV	260.0 / 24	172.15	69	0
C2	1000	386.0 / 5	143.00	21	1
C3	470	345.9 / 11	215.69	30	0
C4	270	277.5 / 70	188.78	91	4

C5	100	440.3 / 14	198.36	19	1
C6	61,7	617.7 / 11	308.44	91	13
C7	50	226.0 / 8	185.43	13	0
C8	24	321.0 / 2	200.00	30	1

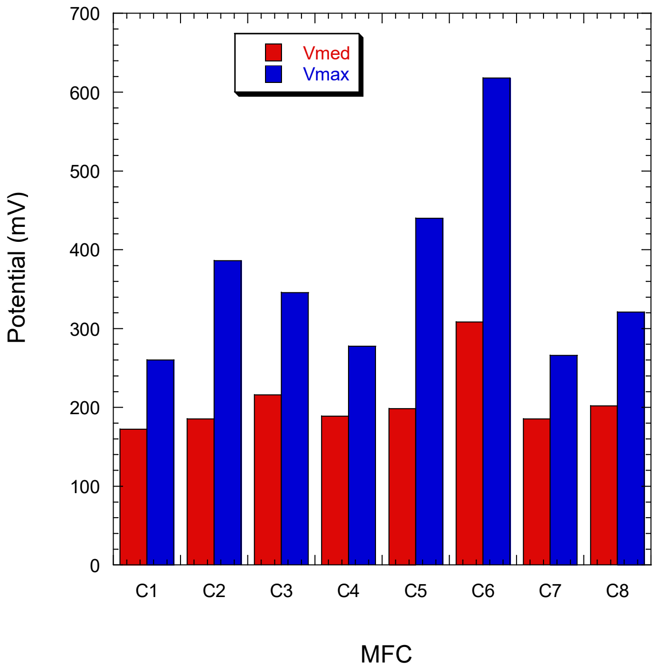

Figure 2. Average and maximum electric potential for each MFC

The results presented above demonstrate that there is an optimum external load for this system that can maximize its performance. On the one hand, it is expected that reducing the electrical resistance of the external load would tend to facilitate the transfer of electrons, but it is believed that there other factors also have a significant impact on the balance between reaction rate and overpotential losses, which affect time adaptation of microorganisms and their energy production. Not only a high value of an electrical potential is relevant but also how long the system is able to maintain this energy production.

The output of the MFC 6 as a function of time is presented in the Fig. 3. The MFC 6, connected to the 61.7 Ω external resistor, presented the best results throughout the experiment and did not have fungus at the cathode at any moment during the experiment. The electrical potential output increased relatively fast in the beginning of the experiment and the MFC was productive until the end of the experiment with average electrical potential of 308.44 mV. After the addition of growth medium on the 13th day, the output electrical potential was kept above 100 mV. On the 24th day, the MFC 6 reached its maximum electrical potential (617.7 mV). It was the MFC that presented the highest electrical potential values in 13 measurements, out of the 18 carried out. We believe that the electrical potential could be kept around 600mV if more culture medium were added. The MFCs that were connected to the external load immediately above (100 Ω) and below (50 Ω) delivered lower values of electric potential, 440mV and 226mV, respectively.

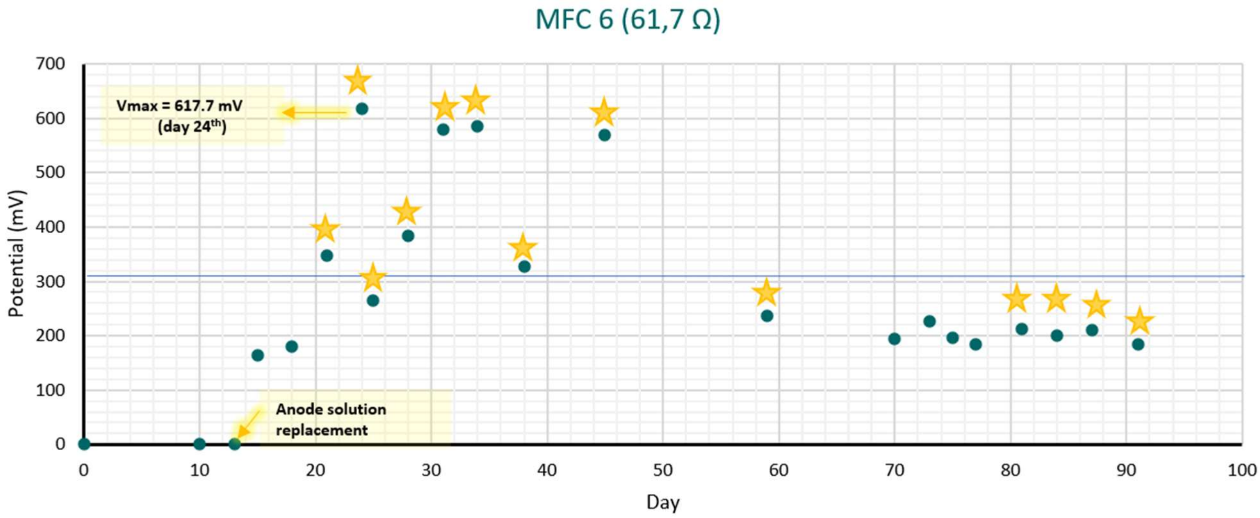

Figure 3. Electrical potential output of the MFC 6. External load 61.7Ω

Figure 4 shows the behavior of the MFC 6 in several days of the experiment. It is noticed that since the first picture (day 25) there is a lot of sediment in the two chambers, which indicates bacterial growth or the deposition of metallic salts. The anode presented a large amount of black sediments up to the day 66. The sediments precipitated in the cathode were brown. A change in the color of the cathode was expected, but as it is believed that the inoculum was initially very diluted, the change did not happen.

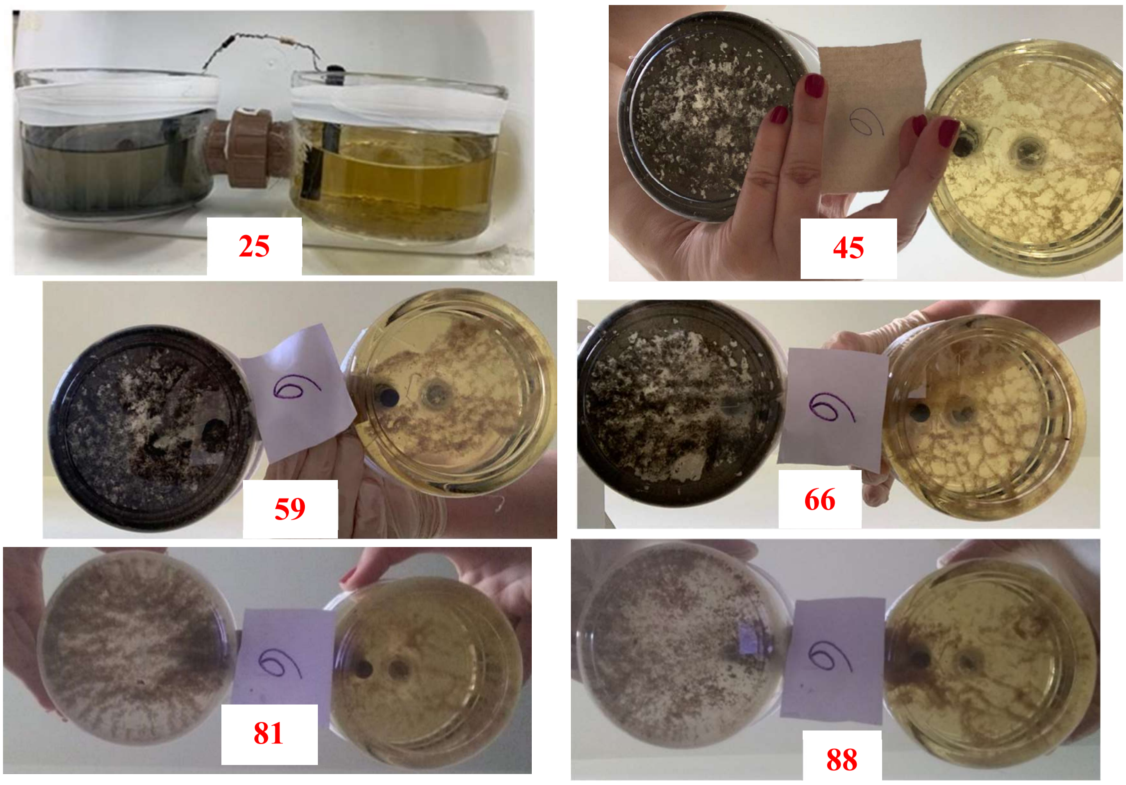

Figure 4. 1Pictures of the MFC 6 in several days of the experiment

It would have been beneficial to use a strategy of "re-feeding" the MFC with growth media when a specific value of minimal electrical potential was reached (100mV, for example). It is possible that the re-feeds would keep the MFCs generating power for longer.

The energy generation was monitored for 91 days, measured once a day. The duration of the experiment was longer than many that we found in the literature, but improvement must be made on the data acquisition system. We plan on using a continuous data acquisition system for the next experiment when we can monitor the transient behavior of the MFCs after an alteration (external load, for example). The data can be collected at every hour or every 30 minutes.

Even though we sealed the MFCs, it is possible that oxygen might have entered the chambers and caused the slow growth of the bacteria at the cathode. Reducing the ratio superficial area to height of the chamber is a possible solution since a smaller area would be in contact with the oxygen minimizing its negative impact.

3.1.1 Power Generated

As discussed in the previous section, the maximum power output of all the MFCs was achieved by the MFC 6 (61.7 Ω) on the 24th day, 5.468 mW/m^2. The Fig. 5 shows the maximum power output, power output on the days 15 (two days after the addition of new growth medium), 24 (best average values) and 45 (32 days after the addition of new growth medium). It can be seen that the MFC 6 reached the best power output in those days. The MFC 4 also showed good results, despite a different behavior. Its electrical potential took a while to rise, but kept good values until the end. It is noteworthy that the 24th was the best energy production day for most CCMs.

The energy production in this study showed a good value when compared to similar experiments in the literature, such as Serra *et al.* (2020), for example, that even with the system with a better behavior (polarization curve in the expected format and that reached Steady State) obtained the maximum power of 895 mW/m^2.

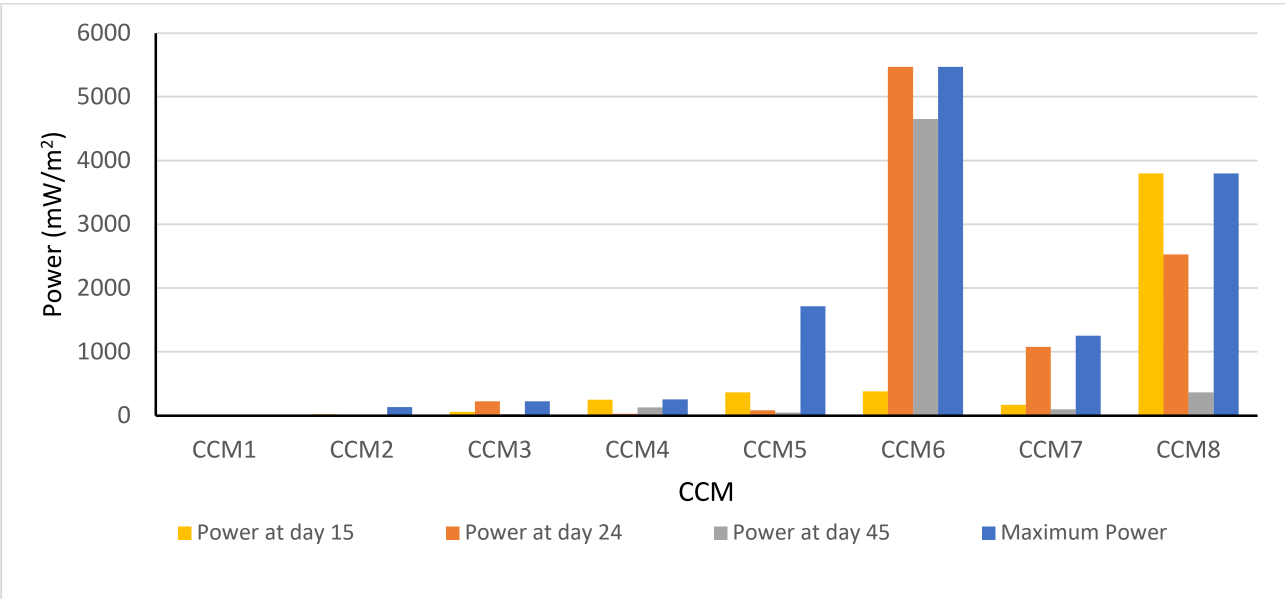

Figure 5. Maximum power output and power output on the days 15, 24 and 45.

4. WASTEWATER AND SYNTHETIC AMD TRATAMENT

4.1 Effect of the external load on the sulfate reduction

Samples of the cathode of the MFC 6 were studied to evaluate the activity of the SRBs and the adequate treatment of the AMD. All the MFC had a similar outcome when comparing the sulfate concentration, they all showed a decreased on the day 13. That can be related to the addition of the new cultivation medium which increased the reaction rate at the anode improving the electron transfer rate to the cathode. The MFC 6 has another decrease on the day 28, two days after the maximum power output (day 24), keeping the high level of power output until the end of the experiment. The same trend is followed by the MFCs 4 and 5. The Fig, 6 shows the percentage of sulfate removal of all the MFCs. MFC 4 showed the best performance in terms of sulfate removal (99,2%).

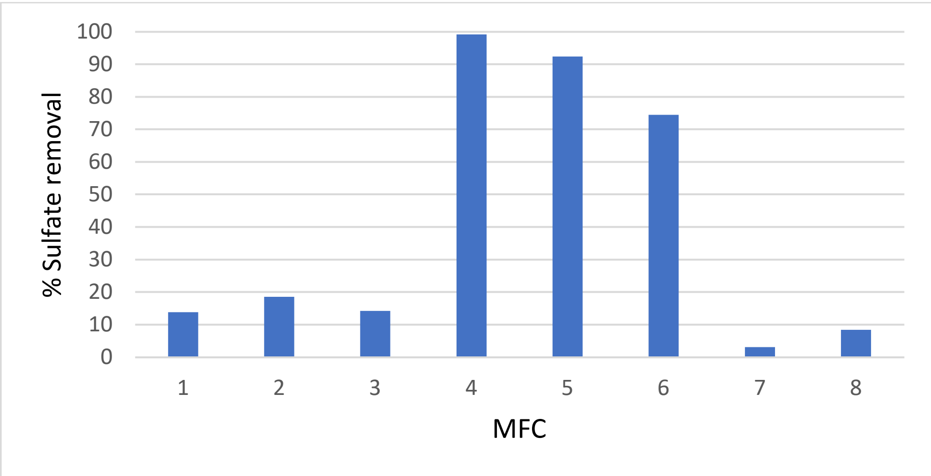

Figure 6. Sulfate removal of each MFC

4.2 Effect of the external load on pH

pH levels were evaluated up to the day 66. On the day 13 the pH of the anode and cathode was 7.5 and 4, respectively. There was no significant variation of the pH during that period in any of the chambers. This can be attributed to the effects of anode medium buffering and the low concentration of BRS at the cathodes as discussed above. An increase in the pH of the cathodes was expected as a consequence of the activity of the BRSs, as they would consume the sulfate and there would be an increase in pH, due to the precipitation of sulfide and evolution of H_2S.

4.3 Effect of the external load on COD removal

To further investigate the practicability of MFC in treatment of the sludge from water treatment and AMD, the consumption of the COD for the MFC 6 is discussed below. COD consumption at the anode was high on the first 17 days, with 78% of removal rate. After the day 17, the COD removal declined due to increase of the consumption of the substrate to generate power. Since the external load was the same for each MFC during the entire experiment, the day 24 was the day of maximum power and also the day of maximum electric potential (600 mV) up to the day 45. After that it was observed a decline in the potential (236 mV), which corroborates the low level of the substrate in the anode indicating the need of addition of growth medium to keep the power output at high levels. It was observed that the COD removal at the anode was 94.5% in 60 days, this can be supported by the experimental phenomena that the color of the anode chamber wastewater changed from black to light grey after treatment by MFC on Figure 4. These results support the hypothesis that the substrate consumption was high at the anode and higher values of electric potential were reached when the growth medium was added at second time.

The COD removal at the cathode was 28.14%. That low removal percentage is due to the low SRB activity at the cathode and the contamination by oxygen. Leiva-Aravena *et al.* (2019) showed an importance of type and origin of SRB inoculum on COD removal and energy production in MFC, when they used BRS inoculum from high sulfate concentration from synthetical AMD could be obtained more COD removal (88%) and energy production (LEIVA-ARAVENA *et al.* 2019).

Peng *et al.* (2017) performed a similar study where a MFC was used to remove metals and sulfates from AMD using organic sewage sludge to simultaneously generate electric power. They reached the 51.6% of COD removal at the anode chamber during the first 10 days. That shows that the technology is promising reducing the demand of oxygen (PENG *et al.*, 2017).

5. CONCLUSIONS

The influence of the external load was and important factor on MFC performance. In our study, the maximum power generation was associated to a low external load (61.7 Ω) following the trends presented in the literature, where low external loads deliver higher power output.

The MFC 6 delivered the most significant power output, 5468 mW/m^2 and percentage of sulfate removal at the cathode of 74.5%. Besides MFC 4 showed the best performance in terms of sulfate removal (99,2%). The pH was only evaluated and was not noted any change in any of the chambers during this period. We believe that this MFC 6 can generate electric potential values as high as 600 mV as long as more growth medium is added.

It was possible to assess visually and by measuring the power output generated and the constant pH that the concentration of SRB was low at the cathode. However, there are half-reduction reactions taking place as a potential difference was measured between the two chambers. It could be the activity of the BRSs (which would be confirmed by the increase in cathodic pH) or the reduction of some metal in the medium.

COD removal at MFC 6 anode was 94.5% in 60 days and on cathode was 28.14%. Additionally, as the experiment was batched, substrate depletion occurred in the anode chamber, as indicated by the consumption of COD and therefore, re-feeding strategies are necessary to keep the good power output generation. Improvements in the data acquisition system are also needed, for continuous measurement of potential, checking the transition of the system in the load change. In order to avoid contamination by oxygen and keep the chamber in an anaerobic environment, a smaller ratio diameter/height of the reactor will be used in future experiments.

These preliminary results support the use of MFCs for AMD remediation and cost reduction to the available conventional technologies.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

APHA. Standard methods for the examination of water and waste water. Washington, DC: American Public Health Association, 2005.

Cappadonia, M., 1995. "Conductance of Nafion 117 membranes as a function of temperature and water content". *Solid State Ionics*, [S. l.], vol. 77, p. 65–69.

Corrêa, J. S., 2018. *Electricity generation from rice hull using microbiological fuel cell (in portuguese)*. Master's thesis, Graduate Program in Energy and Sustainability, Federal University of Santa Catarina, Araranguá, Brazil.

Feng, Y., Wang, X., Logan, B.E. and Lee, H., 2008 "Brewery wastewater treatment using air-cathode microbial fuel cells". *Applied Microbiology and Biotechnology,* vol. 78, pp. 873–880

Gude, V.G., 2016. "Wastewater treatment in microbial fuel cells – an overview". *Journal of Cleaner Production*, vol. 122, p. 287–307.

Hedin, R.S., Watzlaf, G.R. and Nairn, R.W., 1994. "Passive Treatment of Acid Mine Drainage with Limestone". *Journal of Environmental Quality* , vol. 23, pp. 1338-1345.

Kloch, M. and Toczylowska-maminska, R., 2020. "Toward optimization of wood industry wastewater treatment in microbial fuel cells-mixed wastewaters approach". *Energies*, vol. 13.

Kong, X., Yang, G. and Sun, Y., 2018. "Performance Investigation of Batch Mode Microbial Fuel Cells Fed With High Concentration of Glucose". *Biomedical Journal of Scientific & Technical Research*, vol. 3, n. 2, pp. 2–7.

Leiva-Aravena, E., Leiva, E., Zamorano, V., Rojas, C., Regan, M., Vargas, T. 2019. "Organotrophic acid-tolerant microorganisms enriched from an acid mine drainage affected environment as inoculum for microbial fuel cells", *Science of The Total Environment,* vol. 678, pp. 639–646.

Ma, F., Yin, Y. and Li, M., 2019. "Start-Up Process Modelling of Sediment Microbial Fuel Cells Based on Data Driven". *Mathematical Problems in Engineering*, vol. 2019, pp. 1–10.

Munoz-Cupa, C., Hu, L., Xu, C. and Bassi, A., 2021. "An overview of microbial fuel cell usage in wastewater treatment, resource recovery and energy production". *Science of The Total Environment*, vol. 754, pp. 1-21.

Peng, X., Tang, T., Zhu, X., Jia, G., Ding, Y., Chen, Y., Yang, Y. and Tang, w., 2017. "Remediation of acid mine drainage using microbial fuel cell based on sludge anaerobic fermentation". *Environmental Technology*, v. 38, n. 19, p. 2400–2409.

Radeef, A.Y. and Ismail, Z.Z., 2019. "Polarization model of microbial fuel cell for treatment of actual potato chips processing wastewater associated with power generation". *Journal of Electroanalytical Chemistry*, vol. 836, p. 176–181.

Serra, P. M. D., Espírito-Santo, A. and Magrinho, M., 2020. "A steady-state electrical model of a microbial fuel cell through multiple-cycle polarization curves". *Renewable and Sustainable Energy Reviews*, vol. 117, pp. 1-17.

Vélez-Pérez, L. S., Ramirez-Nava, J., Hernández-Flores, G., Talavera-Mendoza, O., Escamilla-Alvarado, C., H.M. Poggi-Varaldo, H.M., Solorza-Feria, O. and López-Díaz, J.A., 2020. "Industrial acid mine drainage and municipal wastewater co-treatment by dual-chamber microbial fuel cells". International Journal of Hydrogen Energy, vol. 45, n. 26, p. 13757–13766.

Xia, C., Zhang, D., Pedrycz, W., Zhu, Y. and Guo, Y., 2018. "Models for Microbial Fuel Cells: A critical review". Journal of Power Sources, vol. 373, pp. 119-131.

Zhao, L, Brouwer, J, Naviaux, J, & Hochbaum, A. "Modeling of Polarization Losses of a Microbial Fuel Cell." Proceedings of the ASME 2014 12th International Conference on Fuel Cell Science, Engineering and Technology collocated with the ASME 2014 8th International Conference on Energy Sustainability. Boston, Massachusetts, USA.

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