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Generation of **Bioelectricity from Organic Fruit Waste**

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This research proposes an alternative for companies and farmers through the production of electricity using microbial fuel cells (MFCs) using waste from export products. Nine MFCs were manufactured with zinc and copper electrodes; and as substrates, pineapple, potato and tomato pulp wastes were used in the anode chamber, and residual sludge in the cathode chamber. It was observed that the MFCs with pineapple substrate generated higher values of the electrical parameters, resulting in voltage and current values of 0.3484 ± 0.003 V and 27.88 ± 0.23 mA, respectively. It was also observed that the maximum power density was 0.967 ± 0.059 W/cm² at a current density of 0.04777 A/cm² for the same substrate. Acid pH values were observed in the three samples, while the conductivity reached its maximum value on day 23 (69.47 ± 0.91 mS/cm) which declined until the last day of monitoring; the turbidity values increased abruptly after day 22 until the last day where a value of 200.3 ± 2.52 UNT was observed for the pineapple substrate. The scanning electron microscopy for the pineapple substrate MFC electrodes shows the formation of a porous biofilm on the zinc and copper electrodes. These results show that a new form of electricity production has been achieved by generating high voltage and current values, using low-cost materials.

Keywords: microbial fuel cells, bioelectricity, organic waste, current.

Introduction

The life on the planet has been made easier by electricity, which is generated in large quantities and its access represents a high cost for the most remote and poorer communities. More than 85 % of the world's energy is obtained from the combustion of oil, coal and natural gas (Khan et al., 2018; Rajaeifar et al., 2017). However, the great global demand for electricity has generated a demographic explosion that, together with industrialization, has entailed to an imminent depletion of the planet's fossil sources, generating a severe impact on the environment, as a result of which the scientific community has been forced to look for other unconventional energy sources such as renewable resources (Taparia et al., 2016). The renewable resources are those resources that can generate energy over and over again without being exhausted in the short or medium term, for example, solar energy, wind, biomass, geothermal, hydroelectric energy, etc. (Owusu et al., 2016). Among renewable energy sources, the hydroelectric energy is currently the most important source for the generation of electrical energy (Ferraço et al., 2018). This type of energy represents approximately 87 % of the renewable energy worldwide (Serrano Guzmán et al., 2017). On the other hand, bioenergy appears as a substitute for energy produced from non-renewable resources. This energy is produced from non-fossil organic material of biological origin (Kluts et al., 2017). Bioenergy can be used to produce electricity, and it is expected that in the future it will become the main source of energy generated by biomass with residues from forestry and agriculture, together with the organic waste the main source of fuel. By 2050, the contribution of bioenergy is expected to be approximately 20 % of supply of the global energy and 10 % of the global electricity production (Elum et al., 2017).

Currently, the generation of electricity is being studied through biolectrochemical systems, also called biolectrochemical fuel cells, which can be enzymatic fuel cells (EFCs) and microbial fuel cells (MFCs) (Ivars-Barceló et al., 2018). This technology is an emerging area for the alternative generation of renewable energy, which has a valuable potential in environmental bioremediation such as wastewater treatment (Ray and Ghangrekar, 2015; Hu et al., 2018; Javed et al., 2018). The design of the cell used in these systems has been the focus of attention by the scientific community in order to increase the production of energy (Mora and Bravo, 2017). Likewise, MFCs convert the available chemical energy in organic or inorganic substrates into electricity through the metabolic activity of microorganisms, which can function with a pure or mixed culture (Ucar et al., 2017). The MFCs with pure cultures are important to determine the capacity of the strains to produce current and to study the mechanisms of transfer of electrons from the anode to the cathode, using redox mediators (Liu et al., 2018). The redox mediators are soluble compounds that act by transporting the electrons from the cathode, where the bacteria are found, to the cathode, reoxidizing and becoming available again to be reduced by the microorganisms (Hauser et al., 2015).

At present, the generation of energy through the use of organic matter (OM) as fuel has taken a greater interest; for example, wastewater contains OM with existing chemical compounds as electron carriers (Kim et al., 2010). Likewise, pineapple waste after its processing or use is thrown to download sites without any subsequent use (Buliah et al., 2019), according to Ayeni et al. In 2019, pineapple production ranked 12 with more than 18 million tons of production; by-products (pineapple waste) such as skin contain 16.7 % of crude fiber (Adrizal et al., 2017). Many residues of different organic matter still contain monosaccharides derived from sugars, polyalcohols, amino acids, organic acids, alcohols and heterocyclic nitrogen compounds, which are beneficial for electricity generation (Khandelwal et al., 2018). Due to this, food waste represents a source of organic matter that has potential for its use in the generation of electrical energy (Girotto et al., 2015). However, most studies for the generation of electrical energy from organic compounds using MFCs have been carried out on sewage waste and very few studies have focused on food waste such as fruits (Yoshimura et al., 2018).

This research proposes the generation of electrical energy from a pineapple pulp in a state of decomposition in the anode chamber, and residual sludge in the cathode chamber with the help of a microbial fuel cell. Parameters of interest such as generated voltage, current, pH, conductivity and turbidity were monitored. In addition, the power and current density of the cells of each substrate and the micrographs of the biofilms which are adhered to the anodes results are shown, demonstrating the potential use of the pineapple's waste for its reuse as a method to generate electrical current in a friendly way for the environment.

Materials and methods

The materials for the manufacture of the microbial fuel cells and the substrates used were duly sterilized before the use.

Manufacture of double chamber microbial fuel cells

Two hermetic plastic polyethylene chambers of 1.5 L were used for each cell (9 MFCs in total, 3 for each substrate) as anode and cathode chambers. Some holes were made in the center of them, with the holes of 2.5 cm in diameter on one of the sides of each chamber for the passage of the proton exchange membrane (esparto rope 10 and 2.5 cm long and in diameter, respectively). The PEM was wrapped with an insulating tape inside a polyvinyl chloride tube. In each anode and cathode chamber, a hole was made in the center for the passage of the conductive wire (copper of 1.5 mm in diameter) that joined the electrode inside the chambers with the external resistance. The electrodes used were 10 x 10 cm² and 3.5 mm thick zinc and copper.



Fig. 1. Diagram of the double chamber microbial fuel cell prototype

Collection and preparation of the pineapple waste and residual sludge

The organic waste of potato, pineapple and tomato was collected from La Hermelinda Market, Trujillo, Peru. It

was washed 3 times with distilled water to eliminate any type of impurity (dust, insects or others), allowing them to dry in an oven (Labtron, LDO-B10) for 24 h at 25 ± 0.5 °C. Then the fruits were stripped of their peel leaving only the pulp of each fruit, and with an extractor (Maqorito, 400 rpm) 3 L were obtained (1 L for each MFC). On the other hand, the residual sludge was collected from the Wastewater Treatment Plant, Covicorti, Trujillo, Peru. Each cell contained 1 L of the juices from each fruit and residual sludge in the anode and cathode chamber, respectively.

Fig. 2. Collection of (a) pineapple, (b) residual sludge, and (c) both substrates in the MFCs



Characterization of Microbial Fuel Cells

The voltage and current generated values were monitored using a multimeter (Prasek Premium PR-85), continuously for a period of 30 days, 30 minutes daily. For the values of current density (DC) and power density (PD), the procedure performed by Zhuang et al. (2012) was used, with external resistances of 0.3 (\pm 0.1), 0.6 (\pm 0.18), 1 (± 0.3), 1.5 (± 0.31), 3 (± 0.6), 10 (± 1.3), 20 (± 6.5), 50 (± 8.7), 60 (± 8.2), 100 (± 9.3), 120 (± 9.8), 220 (± 13), 240 (± 15.6), 330 (± 20.3), 390 (± 24.5), 460 (± 23.1), 531 (± 26.8) , 700 (± 40.5) , 1000 (± 50.6) Ω . The monitoring of changes in conductivity (conductivity meter CD-4301), pH (pH meter 110 Series Oakton) and turbidity (Harch 2100 Q) were also measured. TECSAN VEGA 3 LM scanning electron microscope (SEM) equipped with a SPI 11430-AB gold coating system (TESCAN USA, USA) was used for the micrographs. The data points in Figs 3, 4, and 5 are the average values of 3 replicates, and the error bars represent the standard deviations.

Results

In Fig. 3 (a), the voltage monitoring of the MFCs is shown, where it was observed that the minimum average voltage

(VP) was on the first day (0.249 \pm 0.008 V) after which it increased to a maximum Vp of 0.3484 ± 0.003 V on day 21. In the following days, the values decreased to $0.318 \pm$ 0.013V on the last day for the tomato waste. On the other hand, the pineapple waste generated higher Vp from day 12, reaching a maximum Vp on day 22 of 0.432 ± 0.013 V. These values are governed by the microbiota present on the surface of the anode which influence the voltage differences (Khan et al., 2017). Miran et al. (2016) showed that the size of the particles is important because it slows down hydrolysis, limiting the generation of maximum voltage (V_{max}). Priya and Setty (2019) manufactured an MFC using apple juice in the anode chamber, managing to generate a Vp of 0.400 V on day 7. Although the cell manufactured by them is not larger than those found in this research, they show that the juices of different fruits or vegetables have great power to generate bioelectricity, generating added value to the production of methanol, wines and others from these wastes.





Fig. 3 (b) shows the monitoring of current values, where it is observed that the pineapple wastes were those that generated the highest average current (Cp) from day 14 (~ 27.88 ± 0.23 mA). In contrast, the cells with the tomato waste generated a Cp of 18.1 ± 0.19 mA on the last day of monitoring. The current is generated due to the fermentation microorganisms that convert the substrate (fermented fuel) like glucose into small chain organic acids, hydrogen and carbon dioxide, managing to generate electricity and at the same time forming an interaction of the reduced compounds that are produced under redox conditions which are produced during fermentation or possibly in some direct transfer of electrons between the microorganisms and the surface of the anode (Takahashi et al., 2016). Although Cu is a highly conductive and versatile material, it should be useful for the transfer of electrons to the cathode (Zn). It can be observed that the current values for the substrates decrease in the last days of monitoring; it would indicate that it is a toxic material for the microorganisms in charge of transferring electron. This is based on what was found by Richter et al. (2008) when they used a gold (Au) anode in their microbial fuel cells, concluding that redox active proteins (for example, cytochromes) can be attracted to the anode (Au), resulting in denaturation and loss of its electron transfer.

In Fig. 4, the power density (PD) values dependent on the current density (DC) values are shown. The maximum average DP was 782 \pm 12.9 mW/cm² in a DC of 6.02 A/ cm^2 with a peak voltage of 363.94 \pm 7.2 mV, belonging to the MCC with pineapple substrate. The PD values of the pineapple substrate in a state of decomposition were higher compared with the data obtained in other works where different substrates are used. Zhang et al. (2016) used residual sludge as substrate and carbon felt as anode, managing to obtain DP_{max} and DC values of 20.4 mW/cm² and 25.86 mA/cm², respectively, which may be due to adjusting the substrate to pH > 8. Yoshimura et al. (2018) also used a carbon anode from rice bran and pond mud as substrate in the MFCs, managing to obtain a peak voltage of 400 mV, which is lower than the values obtained by the fruit in a state of decomposition in our work. Cattle manure has also been reported for its use as a substrate, managing to generate 16.3 mW/m² of DP and a V_{max} of approximately 0.7 V on the first day, which is a much lower value compared with our results (Inoue et al., 2013). Also, studies show that PD values can be

influenced by pH values; for example, Jiang et al. (2016) showed that the DP increased by 80%, that is, from 0.36 W/m² at a pH 6 to 0.66 W/m² for a pH 9.5; however, when the pH reached a value of 10, it generated a DP of 0.5 W/m², i.e., decreased. In this research, we worked with the pH values naturally generated by the same fruits.

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Fig. 4. Values of the DC and DP of the MFCs with substrate of (a) pineapple, (b) tomato, and (c) potato



Fig. 5 (a) shows the increase of conductivity in the MFCs as time progresses. Particularly, the MFC with pineapple substrate had higher conductivity values, achieving its maximum on day 23 with an average value of 69.47 \pm 0.91 mS / cm. It should be noted that the values from





day 18 to 24 are very close. After day 25, the conductivity declines until the last day ($60.51 \pm 2.8 \text{ mS/cm}$). On the other hand, the MFC with tomato substrate showed lower conductivity values throughout the monitoring.

Fig. 5 (b) shows the pH values of the MFCs. It can be seen the MFC with pineapple substrate had a lower pH throughout the monitoring, in contrast with the rest of the MFCs. All cells were kept at the slightly acid limit. The changes in pH are due to the different components in the substrate in terms of the microbiota and structural components, such as glucose, which can be the producer of energy (Zhang et al., 2009). However, due to the different microbial groups that can grow the substrate, it is possible that the pH affects the ability of these microorganisms to produce bioelectricity, because there is an optimal pH in which the production performance is improved, which a variation above or below the optimum pH stopping the production (Puig et al., 2010). In Fig. 5 (c), you can see the turbidity values of the anode chambers of the MFCs, from an average value of 125 \pm 5.16 UNT (on the first day) to 200.3 \pm 2.52 UNT (on the last day), with day 22 where an abrupt change is observed from 161.8 ± 8.96 UNT to 182.8 ± 1.32 UNT,

for the pineapple substrate. On the other hand, the MFC with tomato substrate is the one that shows the lowest conductivity, which is less than 80 UNT.

Figs. 6 (a) and (b) show the micrographs of the Cu electrodes in their initial and final state, respectively. As it can be seen in Fig. 7 (a), the surface of the electrode is smooth and the EDS shows a large percentage of Cu in the sample. Fig. 7 (b) shows the adhesion and porosity of the biofilm. Meanwhile, in Fig. 7 (c), the Zn electrode is shown in its initial and final state. As it can be seen in its initial state, the electrode shows imperfections on its surface and the EDS shows a high percentage of Zn with other compounds (for example, C, Si, Cl, etc). In Fig. 7 (d), greater agglomeration of compounds is observed on the surface in the form of spheres. In all the anodes (of the MFCs with pineapple substrate), small layers of biofilms that had begun to detach from the metal surface were observed. According to previous works carried out on other metal surfaces, the authors observed the same phenomenon, attributing them to the absence of extracellular polysaccharides apparent cells that attached the cells to each other or to the electrode (Erable et al., 2017).

Fig. 6. Micrographs of the Zn and Cu electrodes in their initial and final state of the MFC with pineapple substrate





Conclusions

This work successfully demonstrates the generation of electricity using organic waste obtained from La Hermelinda Market, Trujillo, Peru, by manufacturing lowcost microbial fuel cells. In contrast with the potato and tomato, the pineapple substrate produced the highest generated voltage and current values during the entire monitoring, achieving peaks of 0.3484 \pm 0.003 V and 27.88 ± 0.23 mA, respectively. All substrates showed a slightly acidic pH. The maximum values of power and current densities were 782 \pm 12.9 mW/cm² and 6.02 A/ cm² belonging to the MFCs with pineapple substrate. These results are of vital importance because they show the use of Cu and Zn electrodes with a potential for use in MFCs. In addition, they give the possibility to exporting and importing companies and farmers of different fruits or vegetables to generate their property electricity using the decomposed fruits or vegetables that are discarded as fuel. For future work, the area of the electrodes

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(anodic and cathode) must be increased to increase the values of the electrical parameters, because, due to previous work, there are improvements in said parameters, up to a limit value.

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