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Generation of Electricity Through Papaya Waste at Different pH

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A large amount of fruit waste is being a great environmental and social problem due to a lack of adequate storage. Among the most abundant waste is papaya, due to its high consumption in various varieties. These wastes can generate bioelectricity through organic waste, being an important parameter the pH. In this research, low-cost laboratory-scale microbial fuel cells were fabricated, using papaya waste as fuel at different pH (4, 5.73, 7, and 9) to obtain the optimum operating pH. It was possible to observe the maximum values of electric current and voltage of 17.97 mA and 1.02 V on days 16 and 14, in the cell with pH 7; while the cell with pH was the one that showed the lowest values. The electrical conductivity values increased from the first day, observing a maximum peak of 172.50 mS/cm for the cell with pH 7. However, the internal resistance values were low, the maximum value being for the cell with pH 4 (234.61 ± 34 Ω) and the minimum for the cell with pH 7 (46.543 ± 3.6 Ω). In the same way, the maximum power density was for the cell with pH 7 of approximately 645.74 ± 33.64 mW/cm^2 and a current density of 5.42 A/cm^2.

Keywords: pH, papaya waste, bioelectricity, microbial fuel cells, generation.

Introduction

The great environmental problems generated by the excessive use of fossil fuels have led research centers to look for new ways to generate electricity in a clean way (Gupta et al., 2020; Procha et al., 2019). One of the most outstanding ways is biodiesel, which is already being applied mainly in China and India (Yang et al., 2021). This is mainly due to the fact that it is obtained from vegetable and animal derived feedstocks, with vegetable derivatives being the most widely used (Fattah et al., 2014). In this sense, the large agricultural productions of different fruits and vegetables have increased exponentially due to the high demand that exists on the part of society, since the population currently continues to expand, which demands greater consumption of these products because they are an elemental part of the diet of people (Parajuli et al., 2019; Calderón and López, 2020). The US Department of Agriculture and Health and Human Services has recommended consuming 5 to 9 servings of fruits and vegetables per day (Tait et al., 2015). Due to this, the amount of food waste generated both in the sales process and in consumption has increased. It has been estimated that almost 2 billion organic wastes are generated per year and a large part of these wastes are not organized in a coordinated way that is correct and safe for the environment, generating contamination mainly in the surroundings of the supply centers where food is distributed (Thygesen et al., 2021; Grilli and Curtis, 2021). The need to be able to count on solid government policies to practice a mechanism for a good organization of waste for the second use in favor of the community must be a priority (Alibardi et al., 2020). One of the most consumed fruits is papaya (*Carica papaya*). In 2017 alone, approximately 13 million metric tons were harvested, with India and Brazil being the countries with the largest agricultural participation; this fruit is consumed in various ways (raw, jam, jelly sweets, pickles, etc.), and the entire plant itself (peels, seeds, flowers, etc.) is used, due to its nutritional content and medicinal effects (Khee et al., 2022; Rojas-Flores et al., 2020). However, it has been reported, for example, on Hawaii Island that 35–50% of the total production is of poor quality and cannot be sold and is wasted, a factor that is repeated in other countries, although not with such high figures (Heller et al., 2015). Due to this, research has been carried out for the use of this type of waste for its application mainly as compost such as fertilizers, biogas, obtaining ethanol, etc., although its application as a chemical precursor for the synthesis of nanoparticles is also currently being studied (Castro et al., 2011). One of the most interesting and promising applications is the use of papaya waste for the generation of bioelectricity through microbial fuel cells (MFCs) (Rojas-Flores et al., 202; Segundo et al., 2022).

Therefore, the technology of microbial fuel cells (MFCs) is presented as a promising technology to provide an excellent alternative to society by generating electricity, using its organic waste as fuel. These cells consist of two chambers (anodic and cathodic) which are almost always linked by a proton exchange membrane and contain electrodes inside, which are linked by an external circuit (Ramya and Kumar, 2022; Erensoy et al., 2022; De La Cruz et al., 2021). This technology is based on the conversion of the chemical energy present in the organic waste into electrical energy, where the oxidation occurs in the anodic chamber and the reduction in the cathodic chamber, the electrons produced in the oxidation are captured by the anodic electron, and travel by the external circuit to the cathodic electrode, which generates a flow of electrons producing the electric current (Sravan et al., 2021; Tan et al., 2021; Jatoi et al.,2011). One of the most influential parameters is the pH of the substrate because the growth of electricity-generating microorganisms depends on the ideal environmental conditions for their proliferation (Andriukonis et al., 2021). Some research has been reported in this regard, for example, Margaria et al. (2017) used marine consortiums as fuel with pH values established at 3, 7, and 11, obtaining maximum voltage peaks of 0.75 V for cells with basic pH. In the same way, wastewater has been used adjusting the pH to the values of 5.5, 6, 6.5, 7, and 7.5 with KH_2PO_4 and K_2HPO_4, managing to generate electric current peaks of 0.7 mA for the cells with a pH of 7 (Jadhav and Ghangrekar, 2009).

Due to this, the main objective of the research is to generate energy by varying the pH values of the substrate (papaya waste) to observe the optimal operating pH of single-chamber microbial fuel cells at a laboratory scale, to which the values of current, voltage and electrical conductivity were monitored for 30 days. Thus, the values of power density, current density, internal resistance and FTIR spectrum of the substrate were also observed. In this way, a novel method of generating bioelectricity will be provided, optimizing the pH parameters in papaya waste to improve the performance of microbial fuel cells. This research will give important advances in the area of renewable energy, because it will demonstrate the importance of pH in the performance of MFCs with papaya wastes, so that exporting and importing companies and farmers dedicated to the planting and harvesting of this fruit can obtain a more productive generation of bioelectricity using their own wastes as fuel.

Materials and Methods

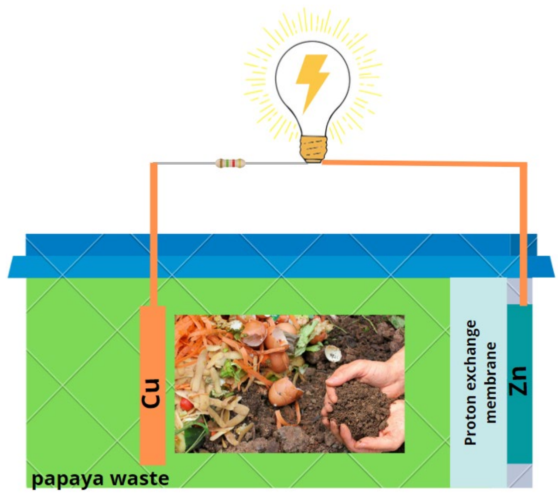
Construction of single-chamber microbial fuel cells

Four single microbial fuel cells were manufactured for which 200 mL polyethylene terephthalate (PET) was used, and an 18 cm^2 hole was made in one of the faces in which the cathodic electrode was placed (Zinc-Zn), the anodic electrode (Copper-Cu) was placed inside the MFC; both electrodes were joined through an external circuit with a resistance of 100 Ω. The PEM (proton exchange membrane) was obtained with 10 mL of the concentration of 6 g of KCl plus 14 g of agar and 400 mL of H_2O (see *Fig. 1*).

A. Collection of papaya waste and its pH variation

Papaya waste was obtained from La Hermelinda market, Trujillo, Peru, from where 5 kg were collected and then taken to the laboratory and washed several times to eliminate any type of contaminant attached to the environment. The waste was crushed in an extractor (Labtron, LDO-B10-USA) obtaining approximately 3 liters of waste. The pH values were 4, 7, and 9, and the blank to adjust the pH to 4 used 15 mL of hydrochloric acid at 0.1N, while to adjust the pH to 7, 9, 12 and 17 mL of sodium hydroxide were used. sodium at 0.1 N respectively. Finally, the pH of the white (natural papaya waste) was 5.73.

Fig. 1. *Schematization of the prototype of the microbial fuel cell*



B. Characterization of microbial fuel cells

The electrical parameters of current, voltage, power density, and current density were measured using a multimeter (Prasek Premium PR-85, USA) following the method described by Rojas-Flores et. al (2021) whose external resistances were 10 ± 0.2, 40 ± 2.3, 50 ± 2.7, 100 ± 3.2, 300 ± 6.2, 390 ± 7.2, 560 ± 10, 680 ± 12.3, 820 ± 14.5, 1000 ± 20.5 Ω (Rojas et al., 2022). The internal resistance was found using the energy sensor (Vernier ± 30 V and ± 1000 mA, USA). Likewise, the pH and electrical conductivity values were monitored with a pH meter (110 Series Oakton, USA) and a conductivity meter (CD-4301, USA), during the 30 days of operation. The initial and final transmittance values were measured by FTIR (Thermo Scientific IS50, USA).

Results and Discussion

Fig. 2 (a) shows the voltage values generated during the monitoring period, observing that the MFC with pH 7 is the one that generated the highest voltage values (1.02 V) on day 14. Meanwhile, the other cells showed lower values: the MFC with pH 4 generated the lowest value (0.72 V), approximately 41.67% less than the MFC with pH 7; on the other hand, all MFCs showed voltage drops in the last days of monitoring. The increases in the voltage values are due to the carbonaceous compounds present in the waste used, but the variations in the values in the different cells observed are mainly due to the adjusted pH for each MFC since the microorganisms depend on the pH present in their environment (Halim et al., 2021; De La Cruz Noriega et al., 2021; Rojas-Flores et al., 2021). In *Fig. 2 (b)*, the values of electric current generated by the MFCs are shown, where the cell with pH 7 is the one that generated a greater electric current on day 16 of approximately 17.97 mA, followed by the one with pH 9 with a peak value of 12.70 mA on day 17, and the lowest value was for the cell with pH 4 with a maximum current of 5.22 mA on day 17, being 226.92% less than the cell with pH 7 on the same day. The increase in electric current values is due to the formation of biofilm on the electrode by microorganisms over time (Flores et al., 2021). In a series of works, it has been reported that the optimum operating pH for different substrates is around 5 to 7 (Parkash A., 2018; Do et al., 2020; Nguyen et al., 2021), which depends on the type of substrate and the conditions to which the cells are subjected. For this investigation, the optimum operating pH was found to be 7 to 22 ± 1.5°C. *Fig. 2 (c)* shows the monitoring values of the electrical conductivity of the substrate. In all the cells, an increase in the values is observed from day 1, observing the peak values of 70.33, 111.87, 172.50 and 125.18 mS/cm for pH of 4, target, 7 and 9; respectively. According to Santiago et al. (2020), the increases and decreases in electrical conductivity are due to fermentation (release of electrons) and sedimentation (absence of electron releasers) of papaya waste (Santiago et al., 2020).

Fig. 2. *Values of (a) voltage, (b) electrical current, and (c) electrical conductivity obtained from the microbial fuel cells during monitoring*

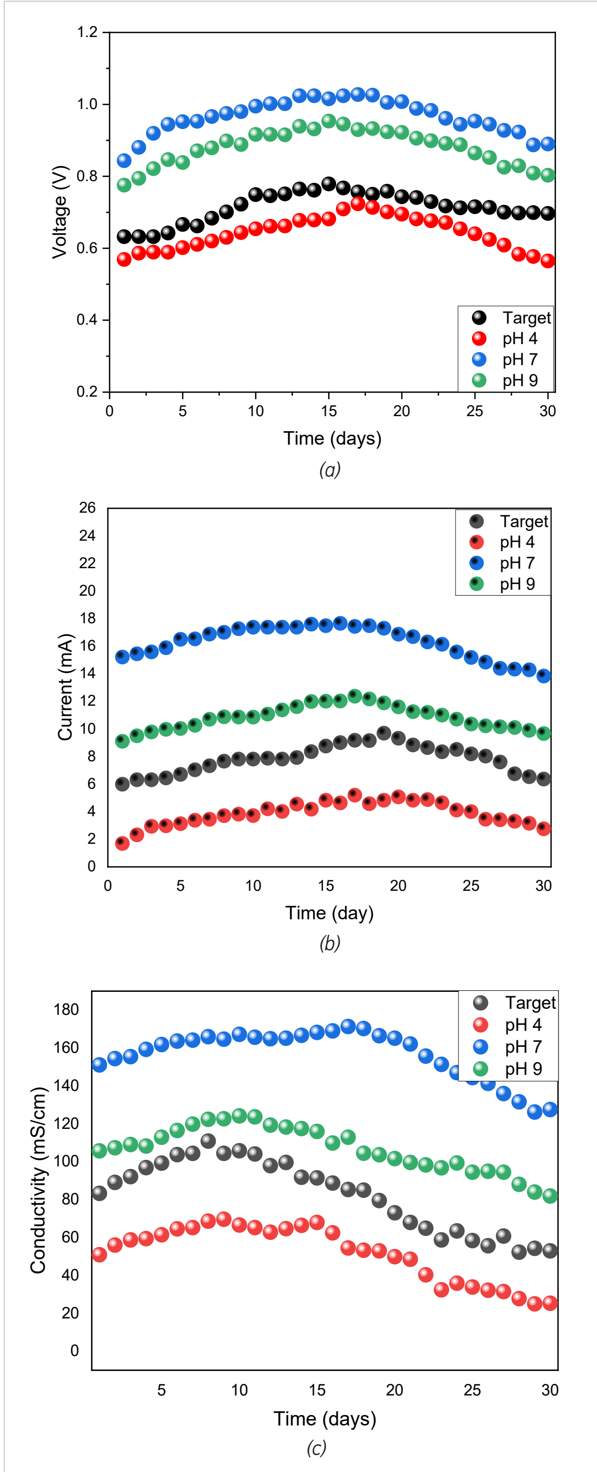


Fig. 3 shows the graphs of the voltage as a function of the electric current for obtaining the internal resistance of the microbial fuel cells using Ohm's law, where the electric current (I) is in X and the voltage (V) in Y. The slope of the linear adjustment is the internal resistance ($R_{int.}$) of the electronic device. The internal resistance values of the MFCs found were 0.23461 ± 0.034, 0.133452 ± 0.0251, 0.046543 ± 0.0036 and 0.089312 ± 0.00214 KΩ for the MFCs at pH 4, target, 7 and 9; respectively. The R_{int} of MFC at pH 7 is considerably low compared with other investigations; for example, Liu et al. (2020) in their MFCs operated at a pH of 7 with a $R_{int.}$ minimum of 162.9 ± 3.5 Ω using granulated carbon felt as electrodes; meanwhile, Rossi and Logan (2021) in their MFCs operated on R_{int} of 62 ± 6 Ω with a neutral pH and graphite electrodes. The low resistance values are mainly due to the electrodes used (metallic nature) and the good electrical conductivity properties of the papaya waste with pH 7 (Liu et al., 2020; Segundo et al., 2022).

Fig. 3. *Internal resistance values of microbial fuel cells at pH (a) 4, (b) target, (c) 7 and (d) 9*

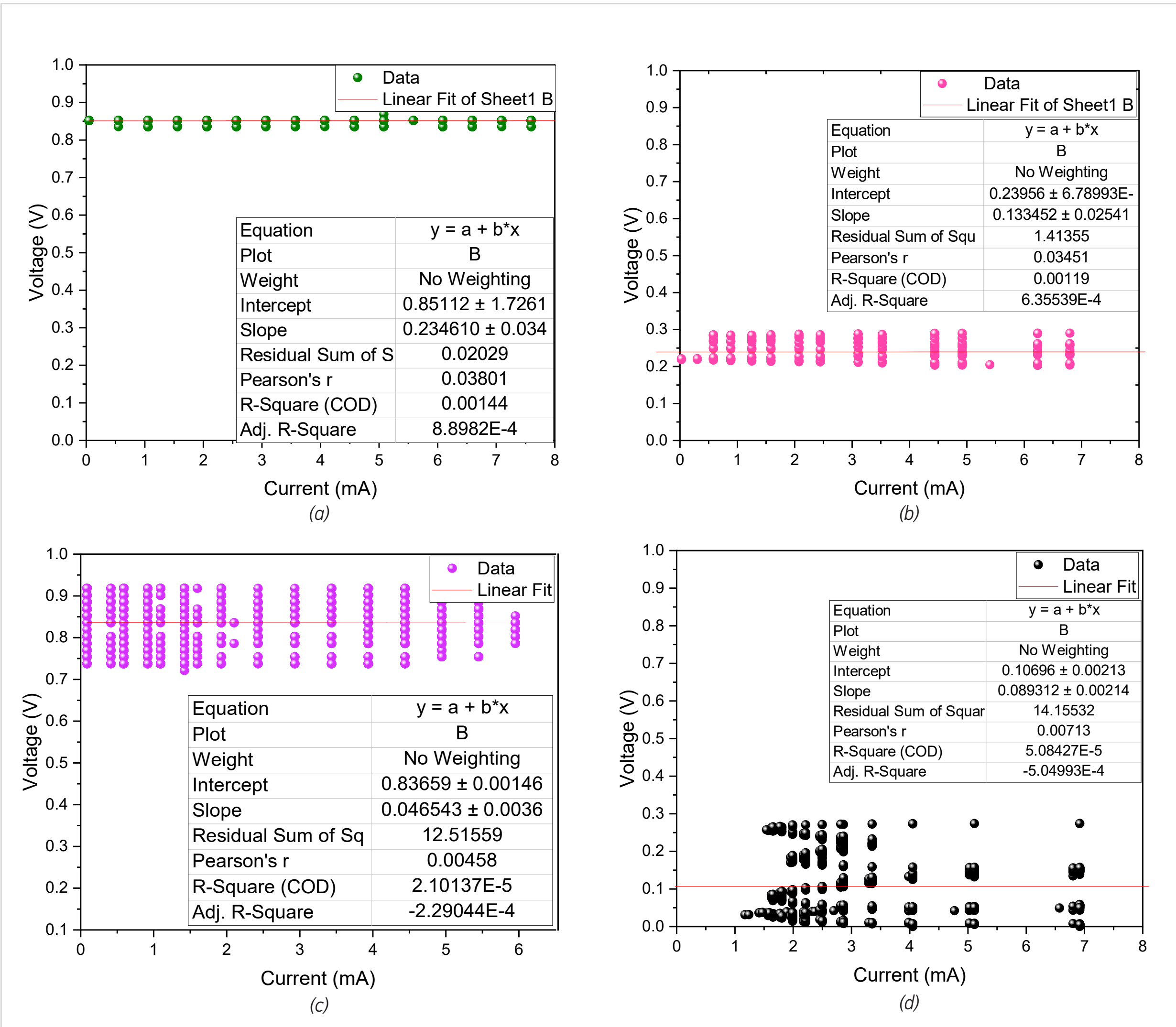
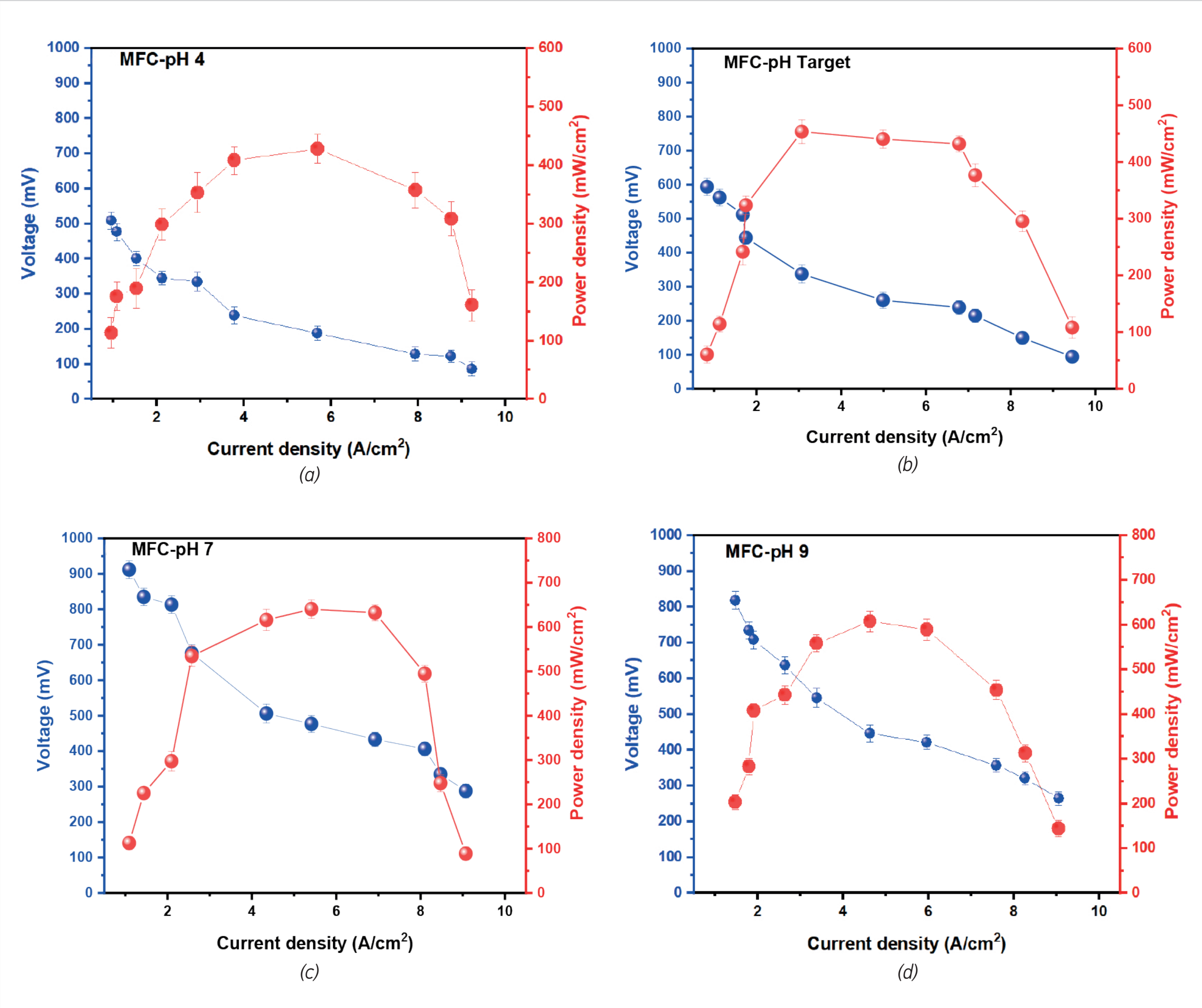


Fig. 4 shows the values of the power density (PD) as a function of the current density (CD) for the different MFCs, as the PD_{max} is observed. They were 430.19 ± 11.36, 451.74 ± 35.71, 645.74 ± 33.64 and 610.45 ± 31.15 mW/cm² in a CD of 5.687, 3.11, 5.42 and 4.60 A/cm² with a peak voltage of 509.47 ± 7.2, 599.61 ± 13.916, 912.2 ± 22.54, and 827.54 ± 29.87 V for the MFCs with pH of 4, target, 7 and 9; respectively. The PD values shown are high compared with those in the literature, for example, Choudhury et al. (2021) showed that the maximum PD of their cells was 50 mW/cm² at a CD of 141 mA/cm² using wastewater as substrates; but both investigations have the same behavior which is dependent on the external resistance values. In the same way, Prasidha et al. (2020) managed to observe a maximum PD of 27 mW/m² on day 3 in their single-chamber cells using fruit and vegetable waste as substrate (Prasidha, W., 2020).

Fig. 5 shows the transmittance spectrum of papaya waste at different pH (4, target, 7, and 9), with the peak 3308 cm⁻¹ belonging to the O-H groups, phenols, N-H stretching and carboxylate acids; similarly, the peaks 2928 and 2850 cm⁻¹ are associated with alkane and aldehyde C-H stretching; and in the same way, peak 1606 cm⁻¹ is associated with C=C stretching, N-H primary amine and C==N stretching. The 1408 cm⁻¹

Fig. 4. *Values of power densities as a function of the current density of the microbial fuel cells at (a) 4, (b) target, (c) 7, and (c) 9 of pH*



peak indicates the presence of alkane C-H stretching, alkene C=C stretching, C==N stretching, primary and secondary amine C-N stretching; and finally, the 1014 cm^{-1} peak indicates the presence of amide (Ashfaq et al., 2022; Jaihan et al., 2022). In the literature, it has been shown that the presence of phenols increases the release of electrons in different types of bioreactors, which would explain the high values of voltage and current in the MFC at pH 7 (Shen et al., 2021; Hassan et al., 2018).

Fig. 5. *Transmittance spectrum of organic waste at different pH*

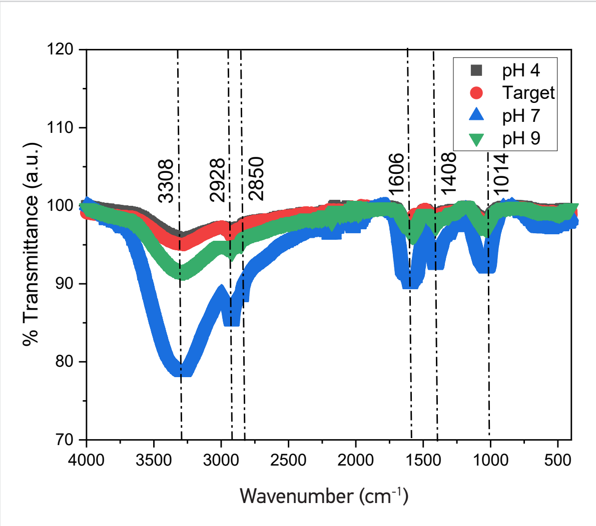


Table 1 shows the values of the electrical parameters obtained in other works. It can be clearly seen that the 1.02 V obtained in the MFC at pH 7 is higher than others observed in the literature. Although in the research conducted by Rojas et al. (2021), the values are very close, this may be due to the fact that the electrode sizes and the amount of papaya waste substrate used were larger than ours. On the other hand, Asefi et al. (2019) managed to generate 0.600 ± 0.025 V using food waste as substrate, which may be due to the fact that the pH used was not neutral but acidic. Also, the power density found in this research was 645.74 ± 33.64 mW/cm^2, while the highest found in the literature was 2.19 ± 0.06 W/cm^2. This value exceeds ours, but it may be because it connects several MFCs in series and does not record unit values of each cell in the publication.

Conclusions

Bioelectricity was successfully generated using laboratory-scale microbial fuel cells with zinc and copper electrodes, monitored for thirty days. It was observed that the MFC at pH 7 managed to generate higher voltage and electric current of approximately 1.02 V and 17.97 mA on days 14 and 16, respectively; on the other hand, the MFC at pH 4 was the one that generated the lowest values, with 41.67% less voltage than the

Table 1. *Electrical parameter values obtained in MFCs published in the literature*

Substrate type	MFC type	Maximum voltage (V)	Power density (PD) (W/m^2)	Current density (CD) (mA/cm^2)	Reference
Fruit leachate	Dual chamber	0.260	25	0.11	Kebaili et al. (2021)
Papaya waste	Single chamber	0.99 ± 0.131	0.878	7.245	Rojas et al. (2021)
Lime, orange and tangerine waste	Single chamber	0.99 ± 0.089	0.0625	0.049	Flores et al. (2020)
Blackberry, dragon fruit and noni	Single chamber	0.97 ± 0.12	0.0719 ± 0.0012	0.051	Rojas et al. (2020)
Human orine	Dual chamber	0.65	2.19 ± 0.06	----	Santoro et al. (2019)
Food waste	Dual chamber	0.600 ± 0.025	0.345	830	Asefi et al. (2019)

MFC at pH 7. The values of the electrical conductivity of the substrate in all the MFCs increased from the first day reaching peaks of 172.50, 125.18, 111.87, and 70.33 mS/cm and then descended to the last one; the MFC that showed the best conductivity was the one adjusted to pH 7. The values of the internal resistances of the MFCs found were low compared with other investigations, with the lowest resistance found being 0.046543 ± 0.0036 kΩ (46.543 ± 3.6 Ω) belonging to the MFC at pH 7 and the highest at pH 4 with a resistance of 0.23461 ± 0.034 kΩ (234.61 ± 34 Ω). The maximum power density found was 645.74 ± 33.64 mW/cm^2 at a current density of 5.42 A/cm^2 with a peak voltage of 919.42 ± 22.51 V for the MFC with pH 7; the high peak (3308 cm^{-1}) of the FTIR spectrum belonging to the phenolic compound of the MFC with pH 7 compared with the other MFCs would be the main reason for its high electrical values, because it has been proven in other investigations that phenol has a high degree of release of electrons. For future research, it would be necessary to cover the electrodes with some non-toxic chemical compounds for microorganisms to increase the durability of energy generation; along with the adhesion of porous nanomaterials to increase the area per unit volume and to be able to capture a greater number of electrons.

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