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Polarization and power density trends of a soil-based microbial fuel cell treated with human urine

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Summary

Microbial fuel cells (MFCs) are bio-electrochemical devices that use microbial metabolic processes to convert organic substances into electricity with high efficiency. In this study, the performance of a soil-based MFC using urine as a substrate was assessed using polarization and power density curves. A single-chamber, membrane-less MFC with a carbon-felt air cathode and a carbon-felt anode fully buried in biologically active soil was constructed to examine the impact of urine treatment on the performance of the MFC. The peak power of the urine-treated MFC was 124.16 mW/m^2 and was obtained 24 hours after the first urine addition; a control MFC showed a value of 65.40 mW/m^2 in the same period. The treated MFC produced an average power of 70.75 mW/m^2 up to 21 days after the initial urine addition; the control MFC gave an average value of 4.508 mW/m^2 over the same period. The average internal resistances of the treated MFC and the control MFC obtained after the initial treatment were 269.94 and 1627.89 Ω, respectively. This study demonstrates the potential of human urine to reduce internal losses in soil MFCs and to provide stable power densities across various external resistors. These results are propitious for future advancements in soil MFCs for power generation utilizing human urine (a readily available source of nutrients) as a substrate.

KEYWORDS
bacteria, losses, microbial fuel cell, polarization, power density, resistance, soil, urine

1 | INTRODUCTION

Microbial fuel cells are special bio-electrochemical converters capable of converting wet organic waste directly into electricity[1] with high efficiencies[2] for extended periods of time.[3] They do this through the activities of microorganisms.[4] One type of microbial fuel cells (MFCs) that is currently receiving increased research attention is soil-based microbial fuel cell (S-MFC). This is connected to the discovery of the potential of MFCs to enhance the bioremediation of contaminated soils[5,6]; coupled with their ability to activate devices such as sensors that run on low power.[7] S-MFCs are unique because of their numerous advantages over other types of MFC: they are comparatively easier to construct and install; cation exchange membranes (CEM) are normally not required because the gradient in the soil creates a natural potential difference that is necessary for the flow of electrons.[8] In S-MFC, the soil acts as a nutrient-rich anodic medium, as a source of electroactive microbes and as a CEM.[9,10] The abundance of electrogenic bacteria and redox mediators[11] in the soil makes it possible to use almost any soil type as an inoculum for MFCs to generate electricity.[12] Despite these advantages, S-MFCs are characterized by a continuous voltage drop when the nutrient-rich organic content available for soil microbial metabolism is used up.[13,14] This usually causes metabolic restrictions, which leads to high internal resistances of the MFCs.[15,16]

Two types of curves (polarization curves and power curves), usually derived from polarization data, are most often used for reporting MFCs data. A polarization curve shows the working voltage of the MFC as a function of the current or the current density. Although, these curves may not represent the performance of MFCs in the most useful form for technical design, they provide useful information for the characterization of the chemistry and the dynamics of MFCs' operation.[17] Polarization data can be obtained for the anode, the cathode or for the entire MFC with a potentiostat, a variable resistance box or external resistors that have been technically selected according to the system.[18] These are typically used to vary the external resistors across which voltage drops are measured. The voltage is obtained by periodically changing the resistors; while the current is determined according to Ohm's law.[19,20] A power curve, on the other hand, presents the power (or power density) as a function of the current or current density.[21] The power density curve is very useful for determining the point of maximum power transfer in MFCs or conventional fuel cells.[22] Because of the low ionic conductivity of most substrate solutions,[23] ohmic resistance is very important in determining the point at which the maximum power is achieved for many MFCs.[21] The performance curve of an MFC with high internal resistance is usually a symmetrical half-wave; in which the maximum achievable power (MAP) occurs at a point where the external resistance corresponds to the total internal resistance of the cell.[21]

Polarization and power density curves directly reflect MFCs' performances. They are the most common methods for determining internal losses and MAP of MFCs.[21] Polarization curves refer to the losses that normally occur in fuel cells and are generally described by three sections of decline: a first section with a rapid voltage drop, a second section of linear voltage drop, and another section with a fast voltage drop, in which the current density is maximum.[24] These three regions of decline are often attributed to the loss of activation, Ohmic, and concentration or mass transfer.[25] These losses are usually evaluated from different regions of the curves depending on their shapes. While activation losses appear in the first section, ohmic and mass transfer losses are manifested in the second and third (last) area of the polarization curve.[22]

Urine is an excellent raw material for MFC systems for real applications.[26] In addition to treating urine with MFC, the results of recent studies are promising for the direct recovery of bioelectricity from urine.[27,28] A system of MFCs inoculated with activated sludge and fueled with human urine has been practically applied in the lighting systems.[29] Urine has also been reported to boost an S-MFC with improved efficacy when its nutrient-rich properties are exhausted.[30,31] This approach of using urine in MFC systems is considered to be a total energy gain for the entire on-site treatment of human waste because it can reduce energy costs for waste treatment while generating electricity.[28] Soil MFC systems may be more practical to use because they are easy to implement. However, the high internal resistance of S-MFCs due to the low conductivity of the soil limits their use. Thus, the application of the right substrate to S-MFCs for improved performance is necessary. S-MFC systems that run on urine not only offer the option of using urine that is hitherto considered waste, but also prevent open urination by providing technology for the safe use of urine for energy production. Such technology will find useful applications in rural areas and refugee camps where access to electricity is limited and pollution from open urination is rampant.

Although urine has proven to be an excellent substrate for improving the performance of MFC, no specific study has provided information on the effects of urine on the performance and internal losses of soil-based MFCs. Hence, this study was designed to generate power, and polarization curves to provide information and results that allow an understanding and contextualization of the potentiality of urine as a suitable substrate to minimize some inherent losses in soil MFCs.

2 | MATERIALS AND METHODS

The step-by-step experimental studies are shown in Figure 1.

2.1 | Sample preparation, MFC setup, and operation

Soil was collected from an agricultural plot at the University of Ibadan, Nigeria. The soil was sieved, using a plastic sifter of 2 mm pore size, and saturated with distilled water to form mud as previously described.[30] Two MFCs

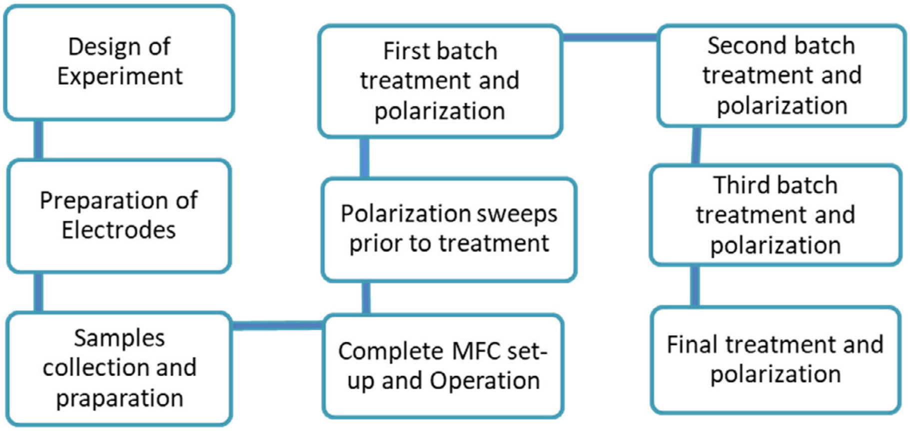

FIGURE 1 Experimental layout for the study [Colour figure can be viewed at wileyonlinelibrary.com]

(control MFC [cMFC] without treatment and test MFC [tMFC] for the urine treatment) were set up in graduated cylindrical plastic vessels, 8 cm high and 7 cm diameter. The two electrodes were made of porous carbon materials (Keego Technologies, LLC) and housed in the same vessel to form a single chamber configuration as shown (Figure 2). Mud was placed at the bottom of the vessel up to the 1-cm mark before the anode was inserted. Additional mud was deposited on top of the anode up to the 5-cm mark. Then, the cathode was made to rest on top of the mud to allow for oxygen interaction.[32] A detailed description of urine collection and utilization, MFC setup, and operation have been previously reported.[31]

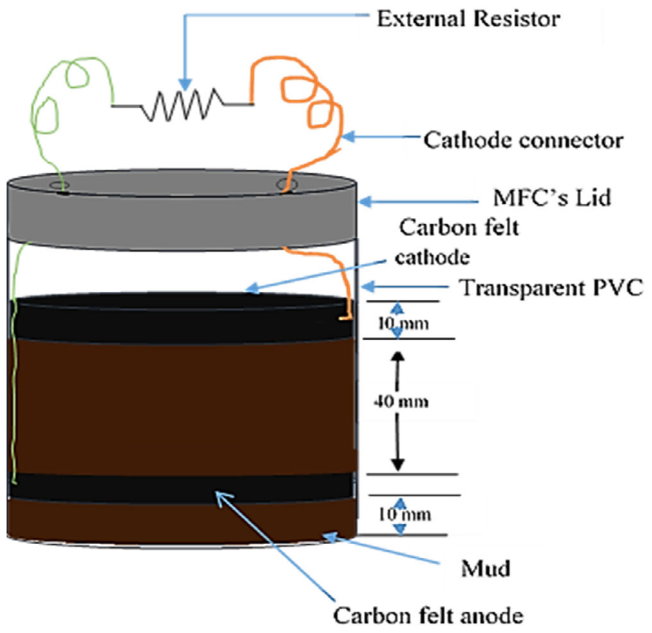

FIGURE 2 Schematic diagram of Microbial fuel cells set-up [Colour figure can be viewed at wileyonlinelibrary.com]

2.2 | Data acquisition and calculations

The voltage drop across various external resistors was measured with a digital multimeter (Kelvin 50LE), from which the currents were calculated in accordance with Ohm's law. The actual values of all resistors were also measured using the multimeter. Power and polarization data were obtained across external resistors varied between 47 and 4700 Ω ± 5% and the power densities curves were plotted from the polarization data normalized to the anode surface area (0.00385 m^2). This resistance range was chosen because the soil MFC prototype generated a maximum power between 220 and 1000 Ω in a previous experiment.[14] Prior to treatment, polarization sweeps were performed on days 5, 6, 9, 10, and 15 during the period of continuous operation of the MFCs. Then, further polarization sweeps were performed just before the substrate (urine) was fed into tMFC (days 19, 24, 32, and 36) and 24 hours after each batch treatment (days 20, 25, 33, and 37). To obtain an optimum external load for tMFC its power was estimated across seven different external loads every 24 hours. All resistances were estimated from the slopes of the different regions of the polarization plots, and the internal losses were evaluated in terms of resistance.

3 | RESULTS AND DISCUSSIONS

3.1 | Variation of voltage and power outputs of the MFCs with time and treatment

Figures 3 and 4 show typical plots of polarization and power density data obtained to compare the performances of tMFC and cMFC (days 6 and 19) before the initial treatment while Figures 5 and 6 respectively

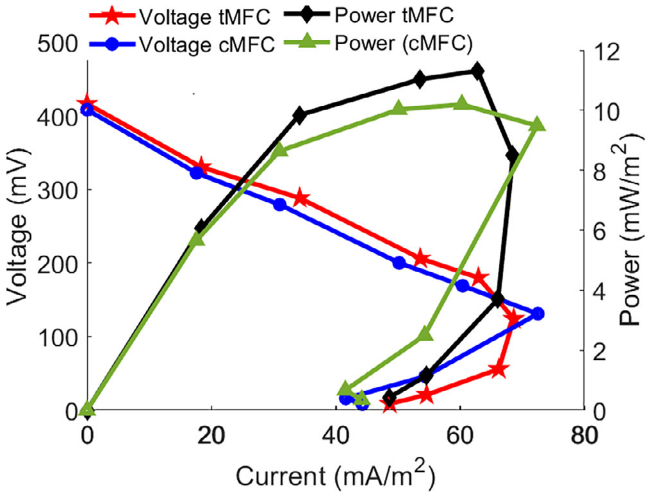

FIGURE 3 Polarization and power density curves of microbial fuel cells (day 6) before treatment with urine [Colour figure can be viewed at wileyonlinelibrary.com]

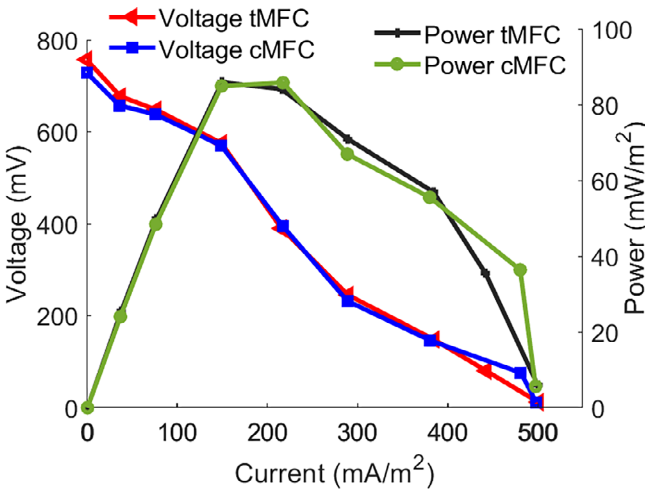

FIGURE 4 Polarization and power density curves of microbial fuel cells (day 19) before treatment with urine [Colour figure can be viewed at wileyonlinelibrary.com]

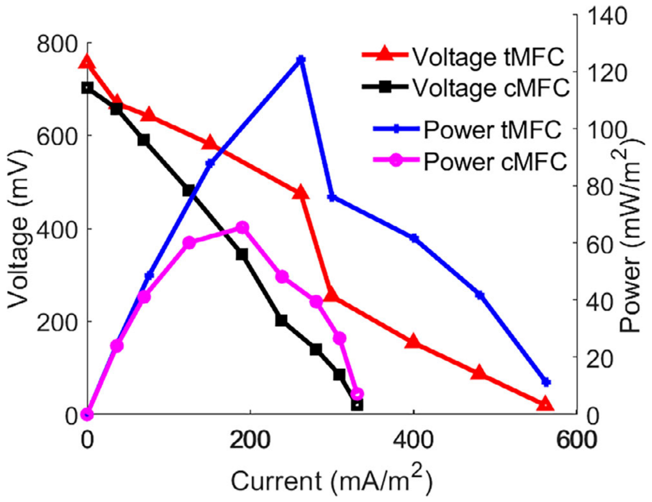

FIGURE 5 Polarization and power density curves of microbial fuel cells 24 hours after the first batch treatment [Colour figure can be viewed at wileyonlinelibrary.com]

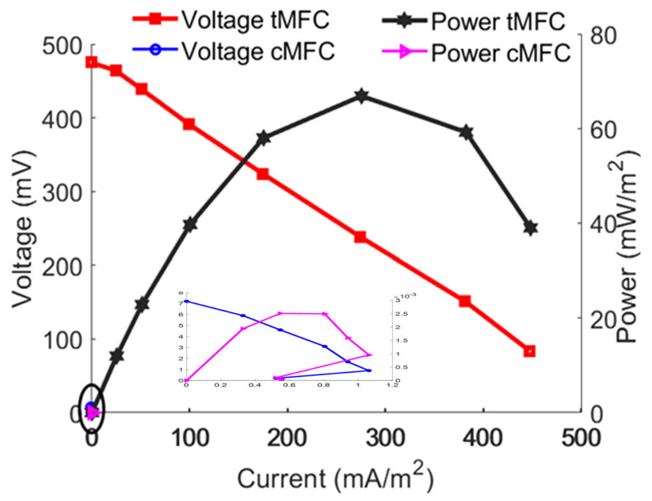

FIGURE 6 Polarization and power density curves of microbial fuel cells (MFCs) 24 hours after the last batch treatment. The circled portion represents cMFC with near zero performance on day 37. The inset is the expanded view of the circled portion [Colour figure can be viewed at wileyonlinelibrary.com]

compare the MFCs' performances after the initial and final treatments with urine.

The tMFC and the cMFC showed similar polarization trends and power characteristics prior to the addition of urine (Figures 3 and 4). This argues that the conditions of operation and the microbial communities of both cells were similar, since the same soil was used. The apparent difference between the data shown in Figures 3 and 4 is related to the exponential growth of the electroactive bacteria, since MFCs' outputs follow the trend of the phases typical for the bacterial growth.[33,34] This observation is also evidence that the soil used in this experiment was rich in nutrients to support the normal metabolism of the microorganisms without initial treatment with urine. The first treatment was performed when a voltage drop was observed after stability was attained for both MFCs between day 17 (results not shown here) and day 19.[31]

As can be deduced from Figure 5, the tMFC performed better after the first treatment with urine, while the cMFC output became almost zero toward the end of the experiment (Figure 6). The continued generation of electricity from tMFC was apparently due to the treatment with urine, which served as an appropriate substrate for the sustained metabolism of the electroactive bacteria.

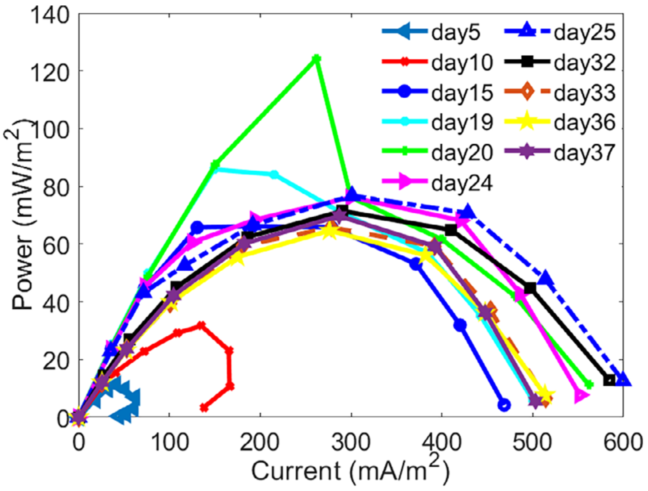

FIGURE 7 Power densities of test microbial fuel cell [Colour figure can be viewed at wileyonlinelibrary.com]

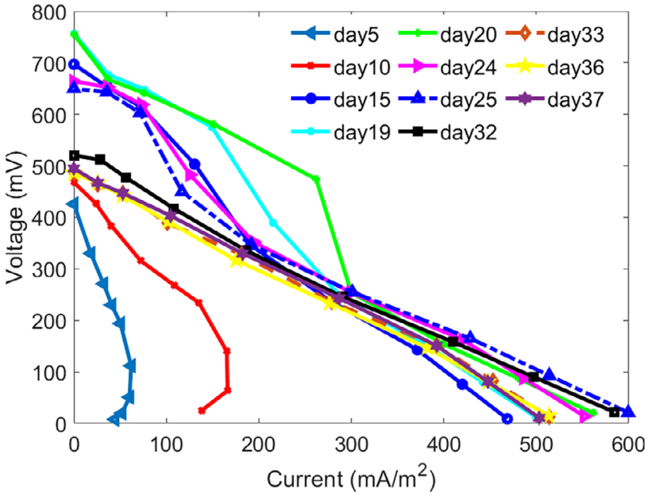

FIGURE 8 Polarization of test microbial fuel cell [Colour figure can be viewed at wileyonlinelibrary.com]

Figures 7 and 8 presents, respectively, the power density and polarization trends of the tMFC on days 5, 10, 15, and 19 (before the initial treatment), 24, 32, 36 (before each batch treatment) and days 20, 25, 33, 37 (24 hours after each batch treatment with fresh urine).

The maximum power density achieved from tMFC prior to urine addition was 84.056 mW/m^2 at a current density of 215.53 mA/m^2 and cMFC yielded a corresponding value of 85.76 mW/m^2 at a current density of 217.1 mA/m^2 (Figure 4). The overall maximum power density of tMFC was 124.16 mW/m^2 at a current density of 261 $\text{mA/m}^{2,}$ and it was obtained 24 hours after the first addition of urine (Figure 7); whereas cMFC yielded 65.40 mW/m^2 at a current density of 190.11 mA/m^2. Although the maximum power of tMFC obtained 24 hours after the initial urine injection was due to overshoot,[22] it produced an average power of 70.75 mW/m^2 after the initial treatment for up to 21 days; in the same period cMFC achieved an average value of 4.508 mW/m^2. The overshoot may indicate limitations to electrons transfer at the anode arising from a sharp increase in the anode potential when the resistance to the flow of current reduced.[35] On the other hand, the overshoot might be due to the initial reaction of microbes and their adaptation to the new urine-enriched environment as subsequent polarization tests did not show the overshoot phenomenon. This observation depicts a typical lag phase (in technical microbiology) in which microbial consortia adapt to a changing environment.

The MAP obtained from this study compare favorably with the values earlier reported by Liu and Logan[36] using wastewater as a substrate in a membrane-less single chamber MFC. Heilmann and Logan[37] also reported similar results in a single chamber MFC (SCMFC) using protein as the substrate. However, Greenman et al[38] reported about 75% lower power densities for a Square SCMFC utilizing leachate from a landfill. These lower power densities reported for an SCMFC could be due to the larger scale MFC and the different inoculants and substrates used.

The maximum electricity generation was generally reached on days 1 and 2 after the treatment of the tMFC with urine. This is an indication that the amount of urine used in this experiment was enough for sustained power production beyond 2 days. At that point, the MFC's output gradually declined and returned to the level of performance that it produced before the addition of urine. This corresponds to the findings of Ieropoulos et al[4] who reported that 25 mL of urine placed in the anode of a two-chamber MFC made of carbon-based material was sufficient to continuously generate energy over 3 days.

3.2 | tMFC daily performance with different external loads

Figure 9 presents the performance of tMFC across seven external loads before treatment with urine while Figure 10 presents its performance across the loads during treatment.

The results presented in Figures 9 and 10 depict the ability of S-MFC to deliver power across various external loads which is an indication of its versatility in application. Before treatment, the MFC produced varying power across various external resistances during the transition from one phase of microbial growth to another (Figure 9). The fairly constant power densities across different external resistances during treatment between days

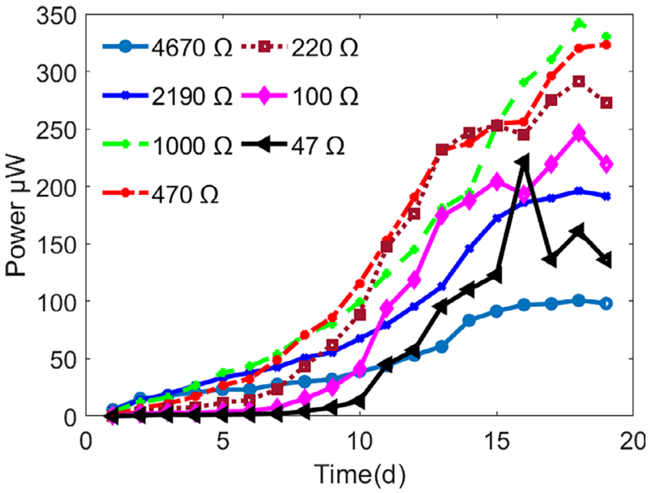

FIGURE 9 Test microbial fuel cell power prior to treatment [Colour figure can be viewed at wileyonlinelibrary.com]

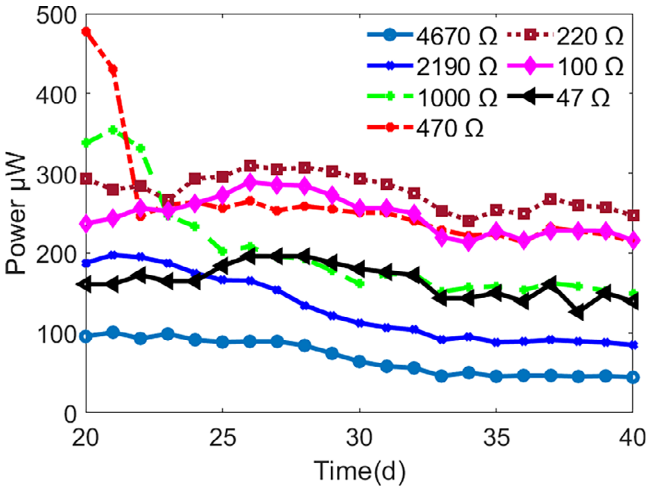

FIGURE 10 Test microbial fuel cell power during treatment [Colour figure can be viewed at wileyonlinelibrary.com]

23 and 40 of tMFC (Figure 10) show that urine has the potential to stabilize S-MFC power output. Stability of MFCs' output is not only crucial for the normal operation of low power appliances like sensors, but also significant for the development of power boosters for increasing the very low MFCs' power outputs. This stability observed with tMFC during treatment is obviously due to the availability of chemical compounds in urine capable of sustaining the microbial metabolism and consequently a reduction in the MFC's internal resistance. This result is in tandem with the report of Santoro et al[39] who studied a treatment process for human urine in a membrane-less one-chamber MFC and showed that human urine is degradable in single-chamber MFCs resulting in increased solution conductivity and stable power generation.

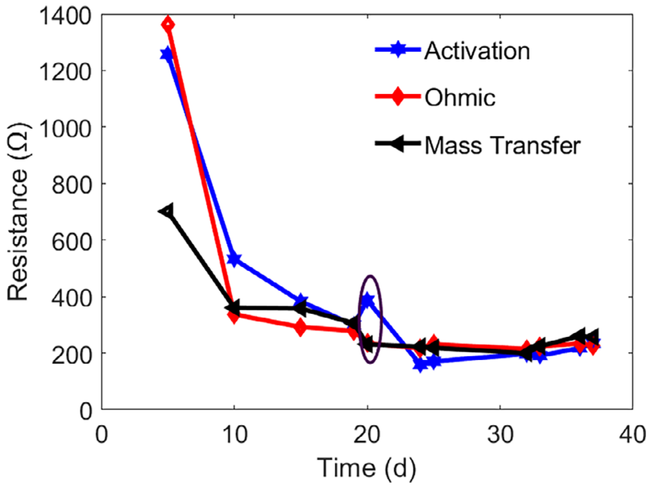

FIGURE 11 Test microbial fuel cell losses with time. The circled portion shows the effect of the initial treatment on the different losses [Colour figure can be viewed at wileyonlinelibrary.com]

3.3 | Variation of the losses and total internal resistance of tMFC with time and treatment

Figure 11 presents activation, Ohmic, and mass transfer losses as evaluated in terms of resistance from the slopes of the different regions of the polarization plots in Figure 8. The total internal resistances obtained from the slope of the linear sections of the polarization curves are presented in Figure 12.

All the typical inherent losses common to most MFCs were observed in the MFCs of this study before the addition of urine (Figures 3 and 4). The initial addition of urine resulted in more of activation loss than mass transfer loss (Figure 11). The initial increase in activation loss may be due to the microbes' reaction to a change in their environment as urine was added. The initial high ohmic loss was apparently due to the resistance of the flow of electrons through the electrodes and their connectors, including the limitation caused by the low ionic conductivity of the mud. Ohmic and activation losses were dominant in the test MFC up to day 20 (24 hours after the initial treatment). The loss of mass transfer appeared to be overcome from the first addition of urine, since the values obtained coincided with the ohmic resistances. The reduction of these losses did not appear to be an anomaly as it indicated enhanced microbial activities as a result of their acclimation to the new urine-enriched environment. It is also a proof of the ability of

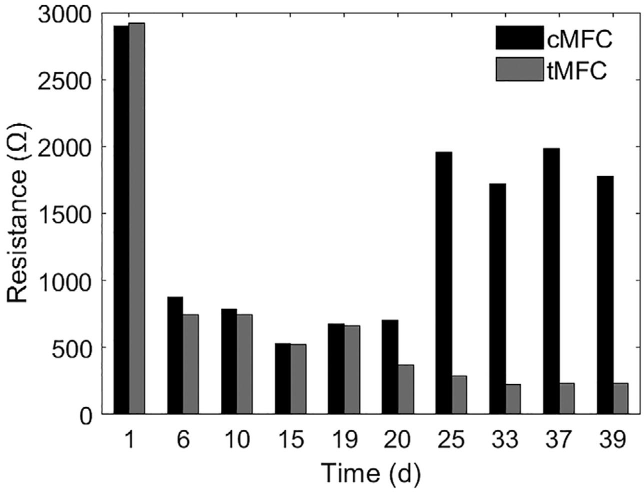

FIGURE 12 Internal resistance of test microbial fuel cell

electrogenic microbes to degrade the organic components of urine and utilize them as a substrate. Ohmic losses, probably due to the resistance between the connecting wires and the electrodes were predominant and thus one of the main limitations for the performance of the urine-treated S-MFC's configuration used in this study. Conversely, all these losses were present throughout the period of operation of cMFC as can be deduced from the results presented in Figure 6.

The total internal resistance (Figure 12) obtained from the slope of the linear sections of the polarization curves[40] is a clear indication that human urine can effectively reduce the internal resistance of S-MFC. The initial internal resistances of cMFC and tMFC were respectively 2896.2 and 2917.5 Ω prior to addition of urine. The internal resistances of both MFCs decreased drastically by the 15th day, which indicates the formation of an active biofilm on the anode[41] of the MFCs. This resulted in an increase in performance for both MFCs and this trend continued till day 18. The internal resistances of cMFC and tMFC were 676.43 and 659.47 Ω on day 19 and 702.56 and 368.56 Ω, respectively, 24 hours after the first treatment. The internal resistances for both MFCs started increasing on day 19 before urine was added; which indicated substrate or nutrient depletion in the systems.[42] Five days after the initial treatment, the internal resistance of cMFC increased drastically, while that of tMFC decreased slightly. The average internal resistances of tMFC and cMFC obtained between days 20 and 37 were 269.94 and 1627.89 Ω, respectively. The increased internal resistances observed with cMFC is attributed to higher anode overpotentials at the same working current and the death of the electroactive microbes due to the depletion of the available nutrient for continued metabolism, as previously discussed.[30] The reduction in the internal resistance of tMFC is attributed to an enhancement of the microbial metabolism which increases the rate of electron transfer between the electrodes. Apart from serving as a suitable substrate for the electrogenic bacteria, some components of urine contain oxygen atoms. These atoms in combination with atmospheric oxygen, which enters into the cell upon opening, favor the cathodic reactions as they increase the rate of electron acceptance and oxygen reduction at the cathode.[43] In addition, injection of urine into the cell increases its conductivity due to an increased ionic strength, which is responsible for the reduction in tMFC's internal resistance.[44] Although treatment with urine obviously resulted in reduced internal resistance and, consequently, better performance of tMFC, this reduction in internal resistance did not result in a proportional increase in power since the daily voltage generated by the MFC also decreased slightly with continuous treatment. This shows that urine oxygen components did not equally benefit the anodic reactions as it is known that continuous aeration of SMFC leads to oxygen diffusion into the anodic region, which leads to the growth of non-electroactive aerobic bacteria that compete for the substrate and consequently reduces MFC's Power.[16,45,46]

4 | CONCLUSIONS

Polarization and power density curves were created for a urine-treated soil MFC. Extrapolations from these curves revealed that the maximum power from the urine-treated MFC was 124.16 mW/m^2 and was obtained 24 hours after the first urine addition. A control MFC produced 65.40 mW/m^2 in the same time. The treated MFC (tMFC) produced an average power of 70.75 mW/m^2 for 21 days after the initial urine addition; and the control MFC (cMFC) gave a corresponding value of 4.508 mW/m^2. The mean internal resistances of the tMFC and the cMFC obtained after the initial treatment was 269.94 and 1627.89 Ω, respectively. In this study, urine not only improved MFC power generation by reducing its internal losses but also demonstrated its potential to stabilize SMFC power output through various external loads and extend the life of the cell. These results showed that human urine is a cheap fuel for MFC that can reduce the losses associated with S-MFC. In addition, we have provided additional information and evidence that paves the way for the practical use of urine in S-MFCs for real application. The main limitations of this study are high Ohmic resistance, probably due to the resistance between the connecting wires and the electrodes, and oxygen diffusion into the anodic area of the single chamber configuration. For this reason, the initial performance achieved after the first treatment was not maintained during the entire study period. Therefore, further studies are recommended to determine the best urine volume and feeding rate, the best electrode spacing, the best electrode and connectors material, the best cell configuration and the best operating conditions for optimal performance of the urine-treated S-MFC.

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