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Impact of Self-Fabricated Graphene–Metal Oxide Composite Anodes on Metal Degradation and Energy Generation via a Microbial Fuel Cell

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Abstract: Microbial fuel cells (MFCs) are thought to be ecologically friendly, despite electron transport and generation challenges. In order to address this, the efficiency of MFCs was investigated using two different anode electrodes made from biomass: graphene oxide (GO) and graphene oxide-metal oxide (GO-MO) (GO-ZnO). After 18 days of operation, the maximum power density for GO was 0.69 mW/m^2, whereas the maximum power density for GO-ZnO was 1.05 mW/m^2. Furthermore, the ability of MFCs to transform the soluble metal ions (Cd^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+}) into an insoluble state was investigated, which is a secondary use of MFCs with significant benefits. In the soluble state of metal ion transformation into an insoluble state, the rate of GO-ZnO was higher (92.71%) than that of GO (81.20%). The outcomes of material, analytical, and biological tests undertaken to validate the efficiency of anodes are presented. It has been shown that using innovative materials as electrodes in MFCs is a potential method for improving electron transport. Furthermore, as an organic substrate, food waste seems to be a viable alternative to more traditional options. In light of these discoveries, we investigate various unanswered issues and possibilities for MFCs. Organic substrate evaluation trials were also included in the present results to demonstrate that organic waste may be a reliable source of MFC performance. This article also has a thorough discussion of food waste oxidation, as well as challenges and future recommendations.

Keywords: energy transportation; microbial fuel cell; biomass; electrodes; wastewater treatment

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1. Introduction

A microbial fuel cell, also known as an MFC, is a developed type of bio-electrochemical system that generates electrical power by efficiently oxidizing organic substrates [1]. The bacterial species that have been introduced act as a catalyst, which speeds up the process of oxidizing the organic substrate [2]. An MFC may be used in a wide variety of contexts, and research on MFCs has become more popular in recent years [3]. Modern society faces wastewater treatment and energy problems. Thus, an MFC is becoming a popular method in the present era. Recent research has shown that metal ion degradation via MFCs is the most successful because electron acceptors can be used to boost energy production [4,5]. It is better to use MFCs for efficient metal ion recovery or remediation.

According to the literature, low energy performance makes the MFC unsuitable for industrial use. The low energy performance emphasized electron generation and electron transportation from anode to cathode electrodes. MFCs perform poorly due to insufficient electron transport from bacteria to electrodes [6]. The transportation of electrons is a major challenge. Anode electrodes directly influence electron production and transfer capability [7]. To perfect this process, the problem must be addressed by meeting the

aforementioned requirements [8]. Typically, carbon and pure metal materials were employed as electrodes, but during operation, the metal-based anodes demonstrated corrosion problems that harmed long-term stability as well as the development of bacteria [9]. The mild conductivity, large surface area, and easy availability of carbon materials led to their selection. The performance of MFCs derived from traditional carbon-based materials was insufficient [10].

According to a previous literature survey, it was proposed that graphene derivatives are the potential source for anode development [11,12]. The surfaces of waste-derived GO materials are strongly oxygenated, which may drastically modify Van der Waals interactions and result in a variety of water solubilities [13]. The edge plane nanobands on the heterogeneous surfaces of GO are primarily electroactive, while the basal plane islands are electrochemically inert [14]. The outstanding conductivity, surface area, biocompatibility, and mechanical stability of graphene derivatives were revealed. As a result, when compared to other materials, they may be regarded as great performers [15]. Graphene derivatives also have several flaws, including high manufacturing costs and a lack of resources. One solution to this problem is to synthesize graphene oxide (GO) from forest waste, notably oil palm material. This method is both affordable and readily accessible. It was previously reported that the GO made from forest debris was biocompatible, had a large surface area, and was an excellent conducting material [16]. Additionally, the GO generated from forest waste must be modified with metal oxide to boost the electron transfer efficiency (ETE), as this will increase its conductivity. It is preferred that the metal oxide be readily accessible, inexpensive, highly conductive, biocompatible, and exhibit excellent ETE. According to several studies, metal oxides were added to electrodes as modifiers to improve the performance [17,18]. Forest biomass-derived GO was enhanced with environmentally-friendly synthetic commercial zinc oxide (ZnO) nanoparticles (NPs) to increase the electron transport rate. According to previous evidence, ZnO was thought to be the most promising of all the metal oxides because of its exceptional electrical, semiconductor, and optical activities as well as its high electrocatalytic ability [19]. For example, Shakeel et al. [20] investigated the ZnO-coated polyindole-functionalized multiwalled CNTs and their use as a biofuel cell anode. The resulting output was high, but the biofilm was damaged due to the CNTs' cellular toxicity.

Another issue is the generation of electrons since there is not enough organic substrate available. Energy efficiency and metal reduction directly rely on the rate of electron production, making it amongthe key challenges [21]. While the production rate was determined to be low, some investigations suggested that carbon derivatives successfully transfer electrons from anode to cathode [22]. The high rate of electron production is inhibited by the bacterial species' limited access to organic substrate. Recent research by Fadzli et al. [21] shown that using highly carbohydrate-based organic substances is essential for enhancing energy efficiency. Additionally, they stated that using organic substrates obtained from waste, such as waste food, fruit waste, and sugar waste, is the best approach. Organic matter, which is generated by a variety of sources, includes food waste. Annual increases in food waste were observed [23]. As waste management grows more challenging, food waste is seen as a major concern. Thus, several studies supported more efficient food waste treatment and its advantages. Food waste as an organic substrate in MFCs is used in this study. Food waste serves as a source to generate energy and degrade the mixture of Cd^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+} ions in synthetic wastewater via MFCs. This research also provides new research for other researchers by investigating the effect of waste organic substrate with self-fabricated electrodes on MFC performance.

2. Methodology Details

2.1. Material and Reagent

Oil palm biomass waste (received a gift from Malaysia), sulfuric acid (97%, Sigma-Aldrich, Berlin, Germany), potassium permanganate (Sigma-Aldrich), hydrogen peroxide (30–32%,—Sigma-Aldrich), hydrochloric acid (37–38%,—Sigma-Aldrich), ethanol (95%,

QRec), zinc oxide (Sigma-Aldrich), polysulfones (PSF, Sigma-Aldrich), lead, cadmium, chromium, nickel nitrate (Sigma-Aldrich), dichloromethane (QRec), sodium nitrate (Sigma-Aldrich), commercial graphite rod (FUDA Lead, New York, NY, USA), glucose (AR grade) and distilled water (DW) were used in this research.

2.2. Preparation and Synthesis of Oil Palm Biomass-Derived GO

Carbon powder was produced by carbonizing the oil palm biomass. The dried oil palm biomass goes through carbonization by being heated up (800 °C) at a rate of 20 °C per minute while being continuously surrounded by argon gas for 3 h. The resulting carbonized flakes were put through a mortar and processed quickly to produce powder. The produced oil palm biomass-carbon is then subjected to the Hummer method to produce GO [24]. The oil palm biomass-carbon (10 g) and $NaNO_3$ (15 g) were mixed in 300 mL of H_2SO_4 with constant stirring. The mixture was then placed in an ice bath (0–5 °C). At this temperature, the mixture was agitated for two hours before $KMnO_4$ (25 g) was gently added to the suspension. After the stirring was finished, the mixture was taken out of the ice bath and left to stir continuously for two days so that the oxidation process could be completed at room temperature. When the color became violet, brown, DW (140 mL) was gradually added and stirred once more at 85 to 90 °C until a dark brown color was visible. By swirling continuously while 210 mL of DW was added, this solution was further diluted. A total of 15 mL of H_2O_2 is then added to the solution to cease the reaction. The stored mixture was further cleaned with ethanol and water by centrifugation, before being dried at 45 °C to produce the GO.

2.3. GO-ZnO Composites Preparation via Solvothermal Method

The solvothermal approach was used to produce the GO-ZnO composites. To make the GO-ZnO composite, 250 mL of ethanol and 5 g of GO along with 2.5 g of commercial ZnO were mixed at room temperature and agitated for 3 to 4 h. The particle size of the ZnO was less than 120 nm according to the manufacturing company. At 210 °C, the finished product was heated until it became powder (GO-ZnO composite).

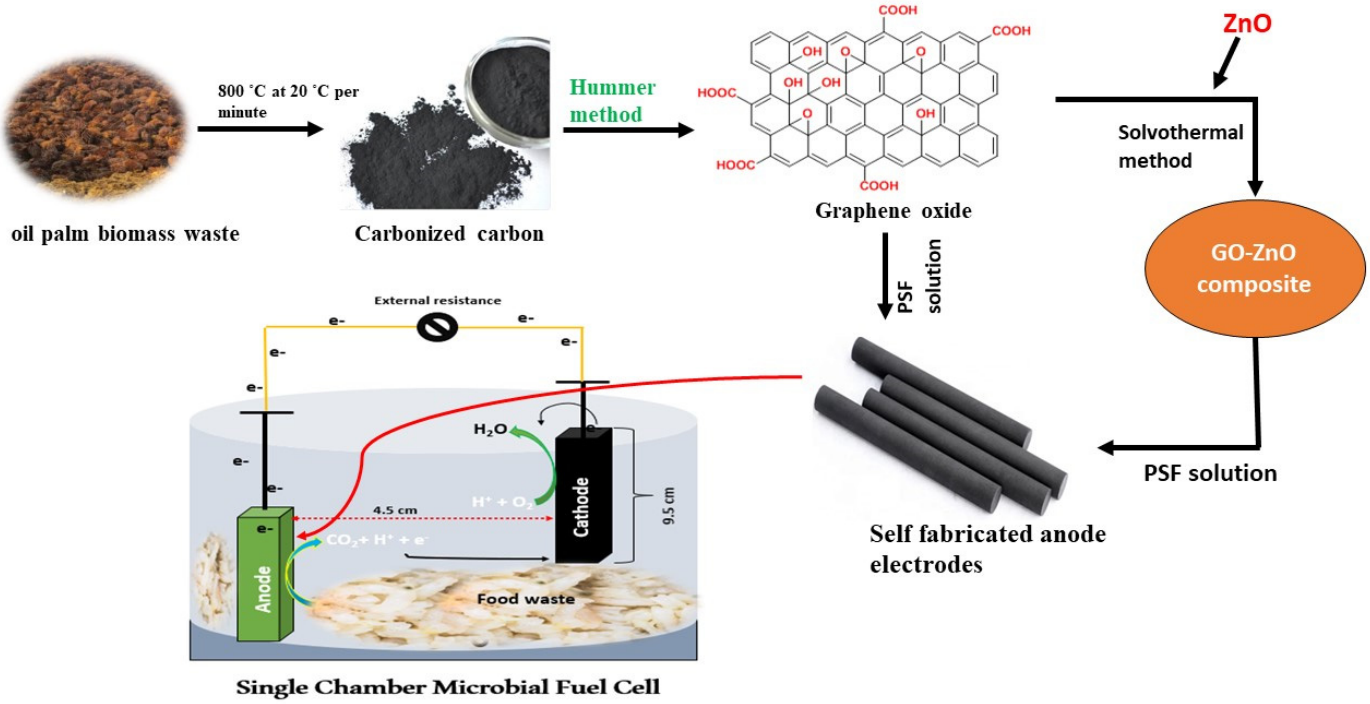
2.4. Material Characterizations

Multiple approaches were used to characterize the synthesized materials (GO and GO/ZnO composite). The functional groups and morphology of the synthesized material were investigated using the Fourier Transform Infrared (FTIR; Perkin Elmer model System 2000) and scanning electron microscope (SEM) (SEM-Zeiss, model DSM-960, Germany). The atomic force microscopy (AFM-SII Sciko Instrument INC SPI 3800N Probe station), which was also used to assess the material's surface roughness. Most often, in material science, the X-ray diffraction (XRD; Philips PW 1710 X-ray diffractometer) method is employed to determine the crystalline structure of produced material. The primary purpose of the XRD is to determine a material's structure from its diffraction pattern.

2.5. Fabrications of Self-Fabricated Anodes

For the fabrication of two different kinds of electrodes in MFC operations, the prepared materials were used. The performances of two electrodes were investigated using various electrochemical methods. A 2.2 mm graphite rod served as the substrate and current collector for each experiment while fabricating anodes. To produce the GO anode, PSF solution (3.5 g solution in 10 mL dichloromethane), 5 g of GO powder was thoroughly mixed. The graphite rod was wrapped in the resulting paste-like substance, which was then heated at 45 °C for two to three days to reinforce it mechanically. Similar to this, to produce the paste-like materials, 5 g of GO-ZnO composites was mixed individually with 3.5 g PSF solution. To produce the rod-shaped anodes, the paste-like ingredients were applied all around the graphite rods. Next, both electrodes were heated at 400 °C for 24 h. Again, both electrodes were briefly immersed in PSF solution prior to MFC operations. The PSF serves as a supporting and protecting material in electrode fabrication. The PSF

not only helps to bind the synthesized material, but it also reduces the Zn leakage during the MFC operation [25]. All the prepared anodes were 8 cm in length, 1 cm in radius, and had 56.52 cm^2 of surface area. The biomass conversion to GO-ZnO composite for anode electrode fabrication is shown in Scheme 1.



Scheme 1. The conversion of oil palm biomass to GO results in the formation of a GO-ZnO composite for the fabrication of anode electrodes for single-chamber MFCs.

2.6. Organic Substrate, Inoculation, Assembly and Operation of Microbial Fuel Cell

The food waste was collected from the local restaurants. For the experiment, 500 g of food waste was used. Fish, rice, sweet cake, and curry were among the foods that were thrown away as food waste. The food waste was separated from the plastic and bones before being processed for 5 min in a blender. For the electrical pulverizer to grind the food waste to perfection, distilled water (50 mL) was supplied. To minimize clogging issues, the food waste was subsequently filtered using a stainless-steel sieve to remove the coarse elements. The concept of gravity helped to remove any oil that was floating on the surface of the filtered liquid. The wastewater was collected from the local pond, and then a concentration of 10 mg/L of Cd^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+} was added to the wastewater. On the basis of suggestions from the literature, a supplement of 10 mg/L was added to the effluent [26]. In this research work, the wastewater that has metal ions added to it is referred to as "synthetic wastewater". Table 1 presents a comparison of the characteristics of local pond water with those of synthetic wastewater.

Table 1. Recorded characteristics of local pond and synthetic wastewater.

Parameters	Local Pond Wastewater	Synthetic Wastewater
pH	6.97	6.40
Color	Light yellow	Light black yellowish
Temperature	24 ± 1 °C	24 ± 1 °C
Metal ions	O mg/L	10 mg/L
Odor	Bad smell	Bad smell

In this study, an MFC with a single chamber was used. A single-chamber MFC has the following components: a container with a capacity of 1000 mL for water; graphite rods serving as the cathode; GO, GO-ZnO serving as the anode; resistance; and crocodile clips. The graphite rod's length was measured at 9.5 cm, and its width was determined to be 1 cm. The anode-cathode were split by a distance of 4.5 cm. The chamber of the MFC had a total weight of 1 kg worth of food waste put into it. In addition to the food waste, there was a total of 700 mL of synthetic wastewater. The anode was immersed into the food waste, which served two purposes: it was the location where the bacteria attached themselves, and it was also the location where electrons were generated. However, the cathode rod was placed into the topmost layer of wastewater. The graphite rods were outfitted with crocodile clips to secure various items. The external resistance was 1000 Ω. Internal and external resistance should normally be equivalent. Due to the formation of the biofilm surrounding the anode at the beginning of the operation, the internal resistance steadily decreased. As a result, using a certain external resistance is not a strict rule. Anode to cathode distance and surface area are two factors that often affect a cell's internal resistance [27]. The 1000 external resistor is preferred for MFC operation while operating at room temperature and a pH of 6 to 7, according to a prior research on the influence of external resistance that was published by Igboamalu et al. [28]. Additionally, 1000 was used prior to the operation for a few days to validate the accurate selection of the external resistance, and it was noted that the closed-circuit voltage was lower than the open circuit voltage when loaded by the external resistance, but that it later slowly recovered. In general, larger resistance should be used if it cannot be recovered, and lower resistors should be used in open circuit voltage if there was no appreciable voltage drop [29]. In the Microbiology Teaching Laboratory, the temperature was allowed to remain at room temperature. A mix of cultural bacterial species were present in the wastewater. To always keep the appropriate amount of oxygen in the reactor, an air pump was put there. During this technique, 2 mL of a glucose solution (15 g in 250 mL of liquid) was infused daily to make up for the water that was lost as a result of evaporation. The glucose has a dual use: it replaces the water that was lost, and it also provides the nutrients that are necessary to stimulate the activity of the bacteria. The glucose also functions as an electron donor when the substance is subjected to electrochemical oxidation. It is possible that the MFC's performance will improve significantly as a result of this modification. The whole experiment took place in a continuous trend at room temperature for a period of 30 days. In addition, the experiment was carried out not once, not twice, but three times to guarantee that the outcomes would be the same each time.

2.7. Analytical Measurements

To evaluate the anodes' efficiency in energy production, electrochemical characterizations were carried out. Various external resistance values (100 to 5000 Ω) were connected to monitor the voltage production trend or polarization behavior. A digital multimeter was employed to record the measurements, and the Ohm law was then used to compute the current density (C.D.) and power density (P.D.) The P.D, C.D. and current calculation formulas are provided elsewhere [30]. In each experiment, the first measurement was made using a new supply of inoculum with a constant concentration. Each resistance value fluctuation needed 30 min to settle before the next resistance measurement could be taken. To examine the redox potential of the cells, a cyclic voltammogram (CV) using a three-electrode setup was used. The electrodes were composed of Pt wire, glassy carbon electrodes, and reference electrodes made of Ag/AgCl (counter electrode). Up until the reaction was finished, the CV analysis was carried out every 10 days. Within the potential range of +0.8 to 0.8 V, the pace of the CV scan was 10 mV/s. The CV peaks at various time intervals were further analyzed using specific capacitance (C_p) to assess the bioelectrochemical performances of the bacterial population during MFC operation. C_p is often defined as the integration

across the whole set of statistics per unit area of both the cathode and the anode. C_p is measured in F/g. To determine C_p, the following Equation (1) was used.

$$C_p = \frac{A}{2mk(\Delta V)} \quad (1)$$

where A = CV area, m = load, k = scan speed, and V is the whole voltage range of the CV analysis.

2.8. Biological Characterizations and Parameter Optimizations

The degradation of metal ions was measured using a PerkinElmer AAnalyst 400 atomic absorption spectrometer after 5 days, as per the anticipated timetable, using a sample of 2 mL liquid taken from the MFC. From the findings of the AAS, the degradation efficiency rate was evaluated using Equation (2).

$$RE = \frac{T_{intial} - T_{final}}{T_{intial}} \times 100 \quad (2)$$

where RE = degradation efficiency, T_{final} = final concentration and $T_{initial}$ = initial concentration.

SEM evaluates bacterial species' compatibility with anode electrodes. SEM images revealed the presence of bacteria on the anode. Only organic substrate factors, using GO and GO-ZnO as anodes, were the focus of our research as we examined the direct influence these parameters had on the performance of MFCs. In general, it is necessary to tune the settings for GO and GO-ZnO anodes since these factors directly impact electron transport and the development of bacteria. To get the most accurate results possible for both the GO and the GO-ZnO, several experimental runs were carried out. Other factors, such as external load, temperature, and electrodes, were held constant throughout the experiment. In this study, commercial glucose and food waste were used as comparisons to demonstrate that food waste is superior as an effective organic source of sugar. After ten days, measures of energy consumption and the efficiency of deterioration were recorded. Throughout the process of optimizing the organic substrate, we continued to use the same inoculation source for operation.

3. Results and Discussion

3.1. Synthesized Material Analysis

The investigation of FTIR spectroscopy shows the GO and GO-ZnO formation in Figure 1. FTIR spectroscopy clearly showed that material oxygen functional groups were representative GO's. These functional groups were ascribed to C–O–H deformation, C–O vibrations, C–OH stretching vibrations, and the C=O stretching of COOH groups by peaks at 1230, 1090, 1400, and 1700 cm^{-1}. The 1050 cm^{-1} band represented C-O stretching vibrations combined with C–OH bending. Bands near 1690 cm^{-1}, which were related to the C=C skeletal vibrations of GO, were also observed with ease. In addition to this, a wide peak appeared at approximately 3400 cm^{-1}, and it was thought that this peak corresponded to the C–OH groups; hydroxyl stretching vibrations exist [31]. These findings are comparable with those that have been reported in the literature, which have demonstrated that the existing oxygen groups significantly increase the hydrophilic properties of GO as well as the interlayer spacing. These findings are supported by these results. The presence of another strong peak at approximately 560 cm^{-1}, which can be attributed to the characteristic stretching vibration modes of Zn-O and which confirmed the attachment of ZnO nanoparticles to GO following solvothermal treatment, was evidence that ZnO nanoparticles had been successfully attached to GO [32].

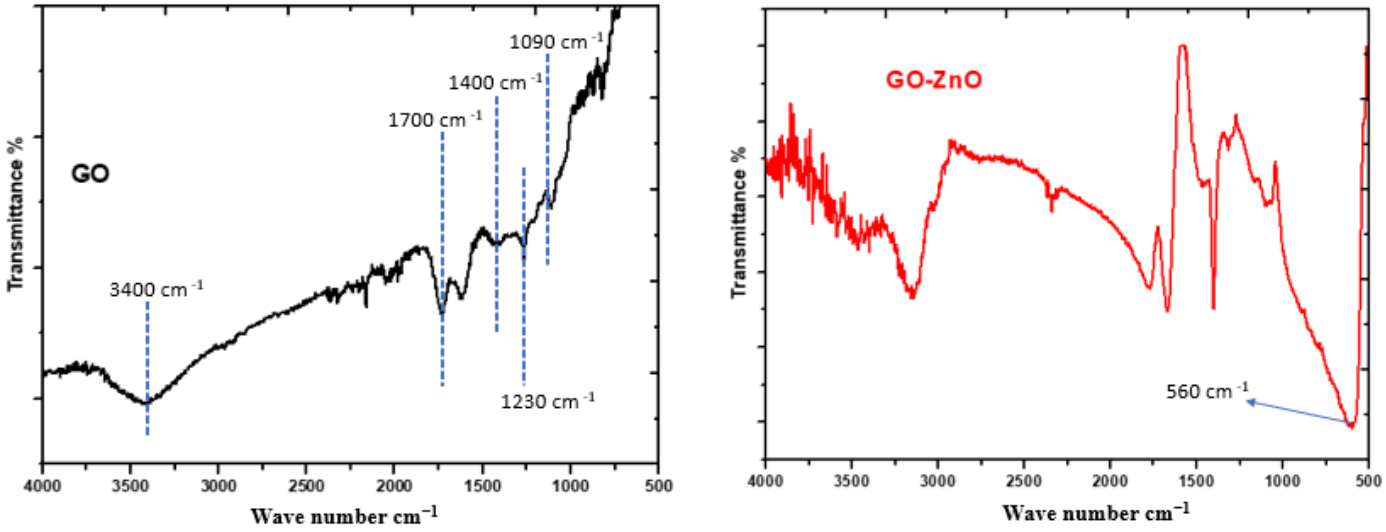


Figure 1. FTIR spectra of the synthesized material.

In addition to this, the crystalline nature of the synthesized composite, which was shown by XRD examination as presented in Figure 2, provided further evidence that GO was synthesized. The reason for this was a strong peak at 2θ = 10°. This peak was precisely matched with GO's (001) reflection. A diffraction peak at 2θ = 24.2° showed successful graphite oxidation [33]. According to the literature, the strong peak at 2θ = 10° indicated the successful synthesis of the GO material [33–35]. At the same time, the GO-ZnO XRD model was compatible with the hexagonal wurtzite ZnO structure [36]. The most prominent peaks were found at 2θ values of 33.70°, 36.101°, 38.141°, 47.02°, 56.602°, 59.761°, and 68.02°, respectively. These values corresponded to the lattice planes (001), (100), (002), (101), (102), (110), and (112); additionally, the XRD results showed that the ZnO particles were successfully embedded on GO [37].

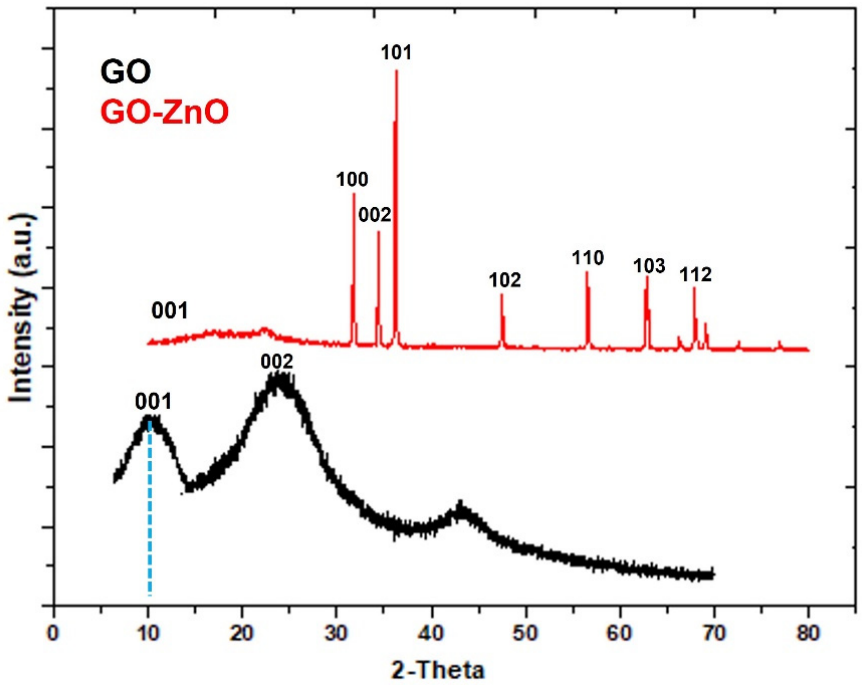


Figure 2. XRD spectra of (i) GO and, (ii) GO-ZnO composite.

As can be seen in Figure 3, SEM was applied to investigate the surface morphology of both graphene oxide (GO) and the GO-ZnO composite. SEM pictures demonstrate the

simple form of the GO that may have been exfoliated as well as the particle size range between 100 and 200 nm. The SEM scan reveals that the average size of the ZnO was less than 120 nm. In addition, a disk-like structure of ZnO NPs in the form of a hexagon was seen in the SEM picture. This structure was surrounded by six uneven edges. The review of the relevant prior literature led to this conclusion [38]. The ZnO particles presence on the GO surface was shown by the GO-ZnO composite. The composite surface showed the presence of hexagonal crystal ZnO particles, along with a particle size of less than 200 nm. The SEM from this investigation were compared to previously published data, and the results were interpreted appropriately [38].

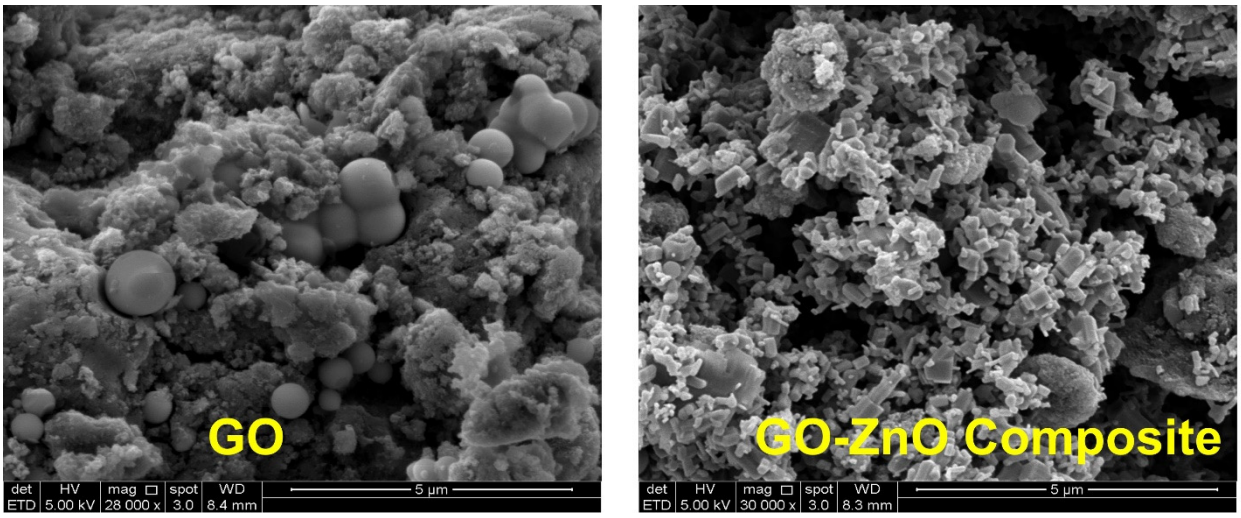


Figure 3. SEM analysis of (i) GO and, (ii) GO-ZnO composite.

Figure 4 presents the results of an investigation performed with an AFM on GO and GO-ZnO. The picture obtained by AFM of GO revealed a few layers of carbon with an uneven composition of GO particles with a smooth surface. The GO-ZnO composite AFM picture showed, without a doubt, the influence that the ZnO particles had on the surface of the GO sheet. This indicates that the GO in the composite exhibited positive exfoliation behavior. According to the research that was performed in the past, the surface roughness that was shown by the GO-ZnO composite may serve as confirmation that the material is an appropriate location for the development of bacteria [39].

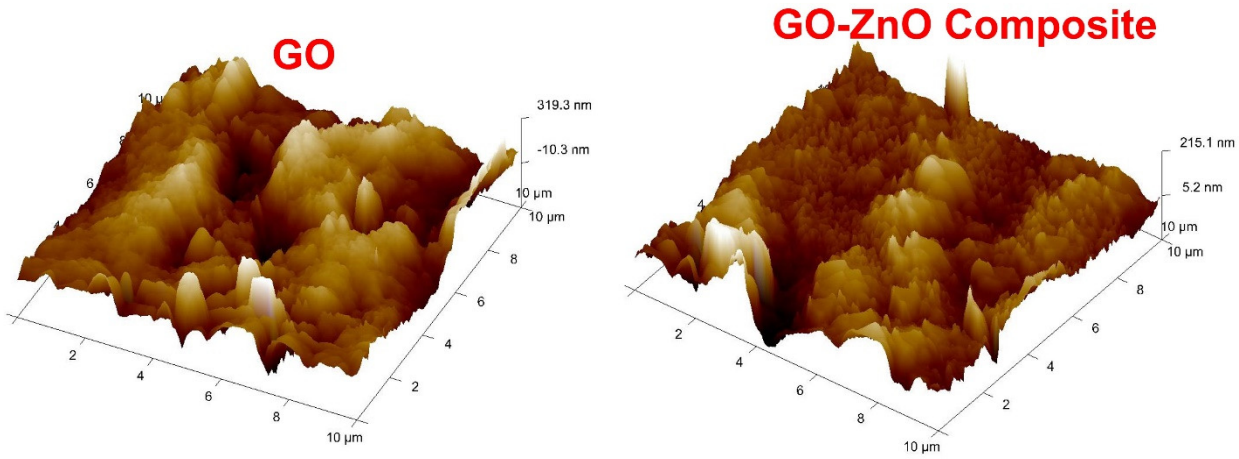


Figure 4. AFM image of (i) GO and, (ii) GO-ZnO composite.

3.2. Energy Generation Analytical Measurement Studies

Experiments using the GO and GO-ZnO composites were carried out in MFCs for the purpose of analyzing the trends in voltage production at the anodes. Each experiment lasted for a period of 30 days. During the first few days of operation, a considerable variation in the voltage generation was seen, with GO producing 1 mV and the GO-ZnO composite anode delivering 2 mV, respectively. The voltage that was produced by GO was 111 mV, whereas the voltage that was generated by the GO-ZnO composite was 137 mV on day 18. The next day, the GO-ZnO composite produced 137 mV, which was more than GO's previous output of 111 mV. In both instances, there was a consistent upward trend in voltage; however, the GO-ZnO composite produced a far higher voltage than GO. In the beginning, the bacterial colony slowly oxidized the organic substrate that was fed, and as a result, the voltage steadily grew. According to the findings of the GO-ZnO composite, the addition of ZnO improved electron transport and made the material biocompatible since it did not have any adverse effects on living bacteria. Up until the point when the voltage production stopped, both electrodes were functioning normally. After 18 days, there was a clear decreasing trend in the voltage generation of both electrodes, and later it was very low. The initial fresh growth of bacterial species in the anode chamber caused this continuous rise when the bacteria quickly began oxidation and electron transport was strong. During the process of oxidation of the organic substrate, the newly constructed anode made it possible for electrons that were produced by bacteria to be transported more quickly. Later, voltage dropped as a result of the fact that all bacterial species ultimately reach the death phase of their life cycle and that both electrodes began to operate less effectively after a particular point in time. This result implies that the biocatalyst was only useful for a limit voltage production of 30 days before reaching a state of low oxidation, at which time the creation of electrons was at a low level. According to earlier studies, organic substrates lead to a voltage drop during the operation. If the bacteria are to survive for a period of time, the organic source should be enough to offer energy for their activities [21,40]. Because electrodes are what are utilized to transport the electrons, the two electrodes that were employed in this investigation both exhibited great performance. During operation, the capacity to generate electrons without experiencing a decreasing trend is contingent on bacterial activity as well as the stability of organic substrates [41]. Figure 5 demonstrates how the voltage trend increased gradually before starting to fall on the 30th day of the MFC.

In order to shed light on the connection that exists between current and resistance in MFCs, this study considered polarization behavior. To analyze the polarization study and find the ideal current–resistance bond. On day 18, when the voltage was high, polarization behavior was analyzed. On the other hand, a low exterior resistance suggested a high voltage production but imprecise voltage stability, while a high external resistance indicated a restricted capacity to generate voltage. At 1000 Ω in the GO anode, the maximum CD was measured at 28.94 mA/m^2, whereas the highest PD was measured at 0.69 mW/m^2. The internal resistance of the solution was measured at 581 Ω in that particular anode. The GO showed a growing trend in CD as it went from higher to lower external resistance; for instance, its high external resistance corresponded with 5.23 mA/m^2 at 5000 Ω, and 28.94 mA/m^2 at 100 Ω. In a manner analogous, the current density (CD) of the GO-ZnO composite anode was high (38.15 mA/m^2) when the external resistance was 1000 Ω and the internal resistance effect was 497 Ω. Figure 6 demonstrates that the highest PD for the composite anode was 1.05 mW/m^2. A comparative profile with previous literature is presented in Table S1. Energy efficiency at the anode was lower because of the high external resistance, but it may now be allowing electrons to flow to the cathode. In addition, since electrons could not get through the bacteria to the anodes, the internal resistance was lower than it would have been otherwise. Experiments on polarization have shown a pattern that has been compared to this one before [42,43].

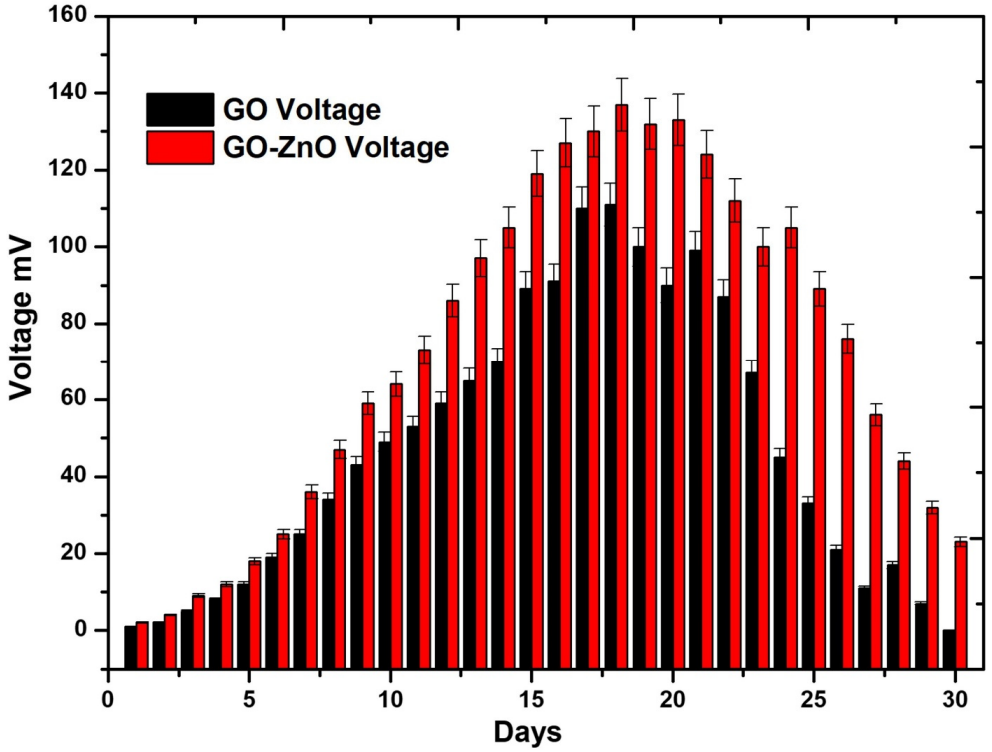


Figure 5. Voltage generation trend through the MFC operation in the presence of self-fabricated anodes.

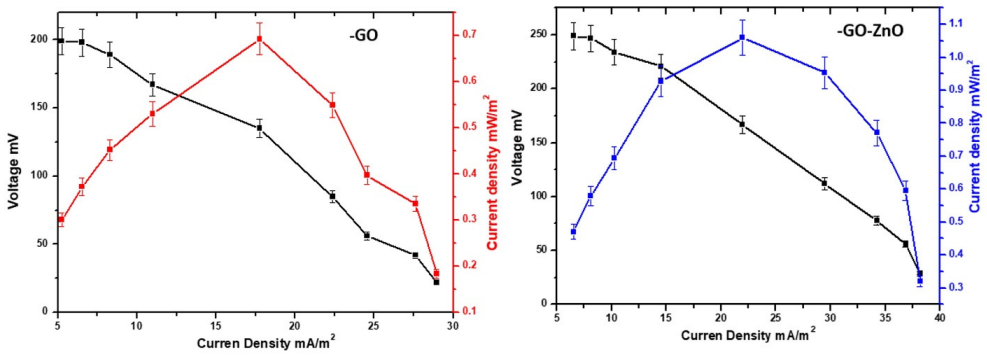


Figure 6. Polarization curves of GO and GO-ZnO anode during the operation.

Next, we determined the rate of electron transport by performing CV throughout a potential window range of 0.8 V in both positive and negative directions. The examination of the CV at various intervals demonstrated the bacterial biomass catalytic activity that is connected to the electrodes. The redox reactions that occurred throughout the process represented this activity. Figure 7 demonstrates the CV behavior at different intervals while the MFC is operating. GO's CV curves were scanned both forward (FS) and reversely (RS); the FS was 1.0×10.0^{-5} mA on day 10, 2.6×10.0^{-5} mA on day 20 and 4.3×10.0^{-5} mA on day 30. However, the RS on days 10, 20, and 30 was -0.4×10.0^{-5} mA, 0.8×10.0^{-5} mA and -1.4×10.0^{-5} mA, respectively. Days 10, 20, and 30 were used to test the FS and RS for the GO-ZnO composite; the FS findings were 1.7×10.0^{-6} mA, 2.4×10.0^{-5} mA and 5.9×10.0^{-5} mA, respectively, while the RS values were -0.5×10.0^{-5} mA, -1.8×10.0^{-5} mA, and -2.4×10.0^{-5} mA. The high RS for the GO-ZnO composite was -2.4×10.0^{-5} mA, while the FS was 5.9×10.0^{-5} mA. The FS or RS may be used to depict the oxidation and reduction rates at various times throughout the MFC's operation. Day 30 found strong oxidation peaks for both GO and the GO-ZnO composite, and that day reverse electron transport accounted for most of the decrease in rate. On

day 30, oxygen in the cathode chamber increased electron discharge and neutralized electrons before reaching the anode, boosting oxidation and reduction. GO's biological process took longer than GO because in ZnO, there were no oxidation or reduction currents on the 10th day, leading to poor metal ion degradation. The analysis of the pattern of biofilm formation at the GO and GO-ZnO composite anodes during the reaction took into account a wide range of other factors. Utilizing the CV curve and the corresponding Equation (1), C_p may be determined. Biofilm strength during the reaction was reflected by the high C_p values. If the C_p value was high, the biofilm appeared to be well formed and stable. On day 30, GO displays 0.00006 F/g, whereas GO-ZnO displays 0.00009 F/g. The results of these and other studies provide an explanation for and suggest the presence of substantial biofilm growth. It has been observed that similar patterns exist for other materials [44]. Other days results are shown in Table 2.

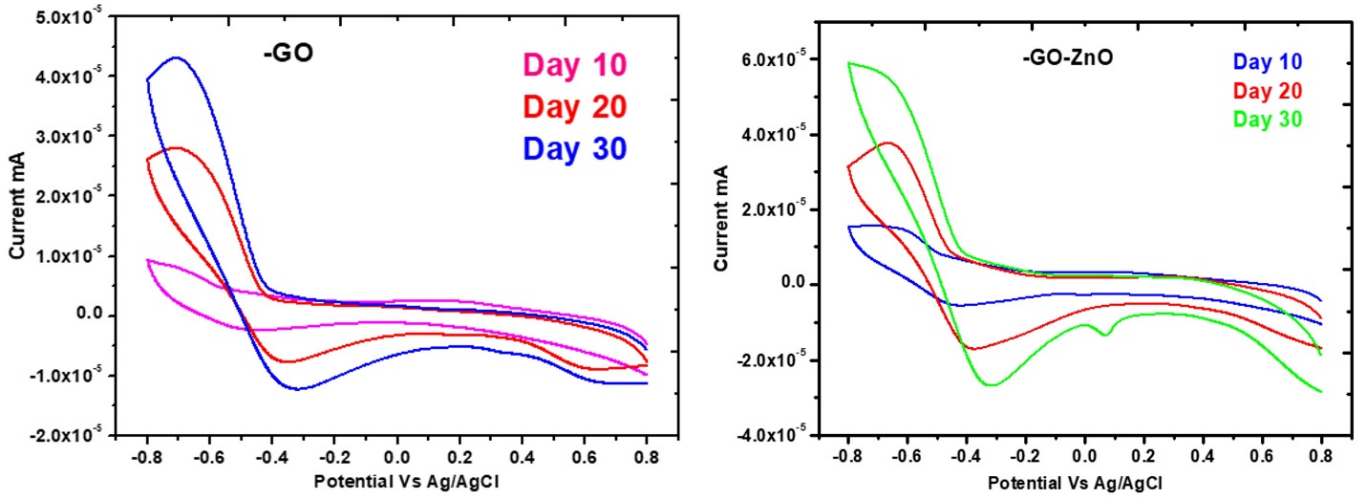


Figure 7. CV study of the GO and GO-ZnO.

Table 2. C_p values of GO and GO-ZnO anode CV curves.

Days	Specific Capacitance (F/g)	
	GO	GO-ZnO
10	0.00001	0.00004
20	0.00004	0.00005
30	0.00006	0.00009

3.3. Durability Study of GO and GO-ZnO Electrode

The durability of MFC electrodes is important for energy generation and wastewater treatment. The present study examined the anodes' stability (biocompatibility and durability). SEM images of anode biofilm after 30 days of MFC operation showed biocompatible and stable anodes. Durability was tested by cycling the anodes three times at 1000 Ω. Figure 5 reveals that the high voltage for GO was observed on the 18th day, while the maximum voltage for GO-ZnO was achieved on the same day. The sudden increasing trend in voltage could be attributed to the introduction of new inoculum as well as the quick electron transfer. After that phase, the voltage continued to drop in two scenarios, and the GO-ZnO anode revealed a more gradual decline than the GO anode. The GO anode was the control in both scenarios. This indicates that the GO-ZnO anode provided a surface area that was more conducive to the growth of bacteria in comparison to the GO anode. The biofilm that was found on GO-ZnO had a higher density than the biofilm that was detected on GO. This demonstrated that the continual feeding of organic substrate gave the bacterial colony the ability to produce electrons. Both electrodes demonstrated constant

performance throughout the operating cycles, with no evidence of biofilm or other material being destroyed. The performance of the GO-ZnO electrode was superior to that of the GO electrode due to the fact that ZnO contributed to enhanced electron transit and minimized the buildup of elements that were not acceptable. Nevertheless, both produced anodes exhibited excellent endurance for a period of 30 days. Several studies also investigated the durability via electrochemical methods of the prepared electrodes during continuous operation [45–47]. On the other hand, Senthilkumar et al. [48] revealed that waste-derived anodes had a durability span of 15 days. Table 3 provides a comparison of the several systems that have been suggested.

Table 3. A profile comparison of prepared anodes with previous work.

Anode Electrode	Inoculation	Durability (Days)	Current Density (mA/m^2)	References
Fe_3O_4/C_p [e]	Mix culture bacteria species	16.5	-	[49]
C_p [e]/HAPNW [f]	*Shewanella loihica*	2.1	2.90 mA/cm^2	[50]
Fe_3O_4/AC [1]/ SSM [2]	Pre-acclimated effluent	5.0	1.90 mA/m^2	[51]
AC [1]/PANI [3]/D-CSA [4]/ GF [5]	Mix culture bacteria	6.2	110 mA/m^2	[52]
CNT [6]/CC [7]	Mix culture bacteria	8–9	65 mA/m^2	[53]
NGNS [8]	*Escherichia coli*	4.1	-	[54]
Graphene/PEDOT [9]/ C_p [10]	*Escherichia coli*	24	3.59 mA/m^2	[55]
PEI [11]/GF [12]	*Saccharomyces cerevisiae*	5	-	[56]
GO	Mix culture bacteria	30	28.94 mA/m^2	Present study
GO-ZnO	Mix culture bacteria	30	38.15789 mA/m^2	Present study

[1] Activated carbon. [2] Stainless steel meshes. [3] Polyaniline. [4] D-camforsulfonic acid. [5] Graphite felt. [6] Carbon nanotubes. [7] Carbon cloth. [8] N-doped graphene nanosheets. [9] Poly(3,4-ethylenedioxythiophene). [10] Carbon paper. [11] Polyethyleneamine. [12] Hydroxylated and aminated polyaniline nanowire.

3.4. Degradation and Biological Studies

The most recent method for expanding MFC applications is to incorporate MFCs into the degradation of inorganic contaminants in water. For this reason, we set out to utilize MFCs to get rid of the bulk of the Cd^{2+}, Cr^{3+}, Pb^{2+}, and Ni^{2+} in synthetic wastewater, since their presence might induce diseases that can be lethal to people. The bacterial species surrounding the electrodes were fed by the food waste, and the biofilm was solely accountable for the high rate of degradation. According to Table 4, the electrodes significantly aid in degradation due to the thick biofilm that coats the anodes. The GO-ZnO composite anode was superior to GO in terms of degradation efficiency (81.20% vs. 92.71%). The degradation efficiency of the GO-ZnO composite increased in both situations. ZnO demonstrated better biocompatibility than GO did. However, the organic substrate ran out of energy too quickly for the bacteria to continue respiration after being used for a while. Bacterial species entered the death phase due to a lack of organic substrate, which also inhibited the metal ions from transforming into an insoluble form. Previous research by Singh et al. [57] examined the impacts of different organic sources and concluded that a deficiency of access to such a source might reduce the effectiveness of MFCs. That said, although the organic sources used are sufficient for bacterial activity in the sense of metal ion degradation, more force is necessary for high electricity production. For the sole purpose of monitoring metal concentrations, AAS has no further applications. Previous studies have shown that once an MFC operation is performed, the soluble metal ions become insoluble (sludge develops). The mechanisms of MFCs (electrons generated and transported) have been well described in prior research [26,58]. In an electrochemical reaction, soluble metal ion forms are reduced to solids by accepting electrons created throughout the process (precipitates) [26,58].

Table 4. Overview of the degradation of metal ions with the GO and GO-ZnO via MFCs.

Organic Matter	Concentration of Metal Ions	Electrode		Operational Days	Degradation Efficiency (%)
		Anode	Cathode		
Food waste	10	GO	Graphite rod	0	0.00
				10	40.45
				20	76.10
				30	81.20
		GO-ZnO	Graphite rod	0	0.00
				10	43.89
				20	79.04
				30	92.71

The anode-treated surfaces were analyzed by SEM to determine the kind of bacterial colonies that had colonized them (Figure 8). After 30 days, many distinct bacterial colonies were seen on the surface of the treated anodes (GO and GO-ZnO composite), and they were thought to be responsible for the generation of energy and metal ion degradation. The findings suggested that a controlled amount of biofilm growth is beneficial to power production. Sasaki et al. [59] also showed that a small amount of biofilm on the surface of anodes improves energy generation and degradation rates. The composition of the EPS was impacted by the increased biomass on the surface of the anode, which resulted in decreased energy generation. Therefore, it seems that MFCs result in clean energy technologies that do not release harmful emissions or waste products. Furthermore, in accordance with previous studies [60,61], the treated anodes' SEM image showed rod-shaped filament appendages, which indicates the existence of conductive pili types of bacterial species. This means that they used conductive pili to transfer the electrons to the anode electrode. The most prominent conductive pili types of bacterial species are *Escherichia*, *G. bacter*, *Klebsiella*, *Bacillus*, and *Actinobacillus*. Therefore, the present SEM images and previous evidence show that there is a great possibility that there are conductive pili types of bacterial species, as mentioned above.

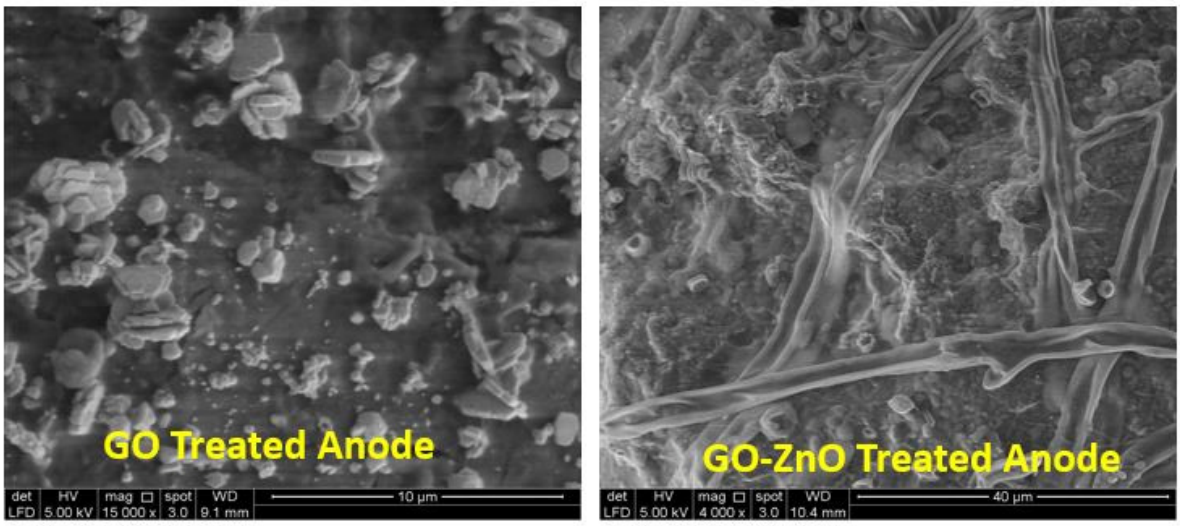


Figure 8. SEM images of treated anodes.

3.5. Oxidation of Food Waste

The action of microorganisms is necessary for the high performance of MFCs in the transportation of electrons and the degradation of contaminants. In the scientific literature [60,61], several microbial species, such as *Escherichia*, *G. bacter*, *Klebsiella*,

Bacillus, and *Actinobacillus*, have been revealed to be exoelectrogens. In this experiment, several species of microorganisms were grown on food waste, which served as an organic substrate. Food waste was a disaccharide in its original form. However, it was subsequently changed into glucose and then oxidized by bacteria, which caused the waste to produce electrons. The investigation's findings on the –processes are summarized as follows (Equations (3)–(5)):

$$\text{Oxidation: Food waste} \rightarrow C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (3)$$

$$\text{Reduction: } 24H^+ + 24e^- + 6O_2 \rightarrow 12H_2O \quad (4)$$

$$\text{General: } C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Electricity} \quad (5)$$

Moving electrons from the anode electrode (where they are generated) to the cathode electrode (where they are reduced) is a key step in the oxidation process. Since there was only a single chamber in the MFC employed in this work, moving the protons from the anode to the cathode chamber was significantly easier [62,63]. The electrons are transferred via the provided outer circuit that is located outside. Before electrons can be moved to the cathode electrode in bacterial cells, they must first go to the cathode electrode through the anode electrode. A systematic presentation has been shown in Figure 9, it was modified according to the present study to show how electrons are generated and transferred to the anode electrode.

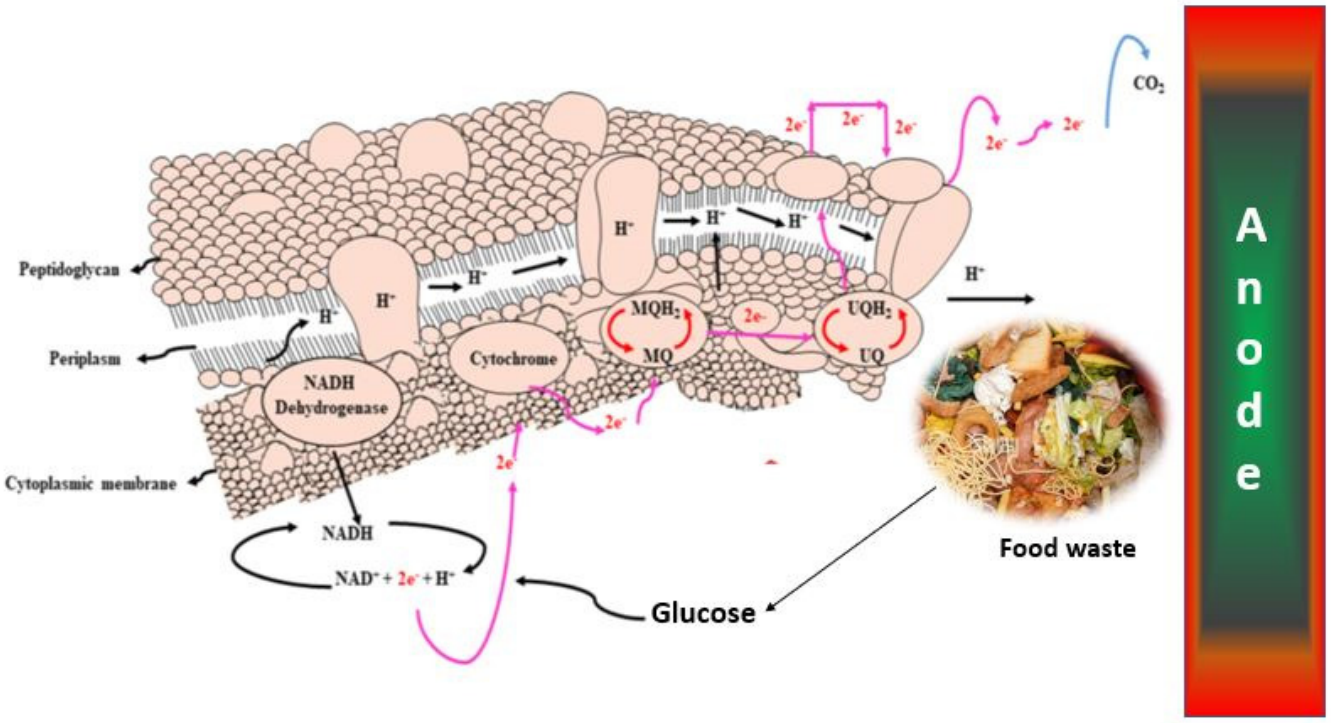


Figure 9. Food waste microbiologically oxidized in a single-chamber MFC (figure modified from [64] with Elsevier's permission).

3.6. Assessment of Food Waste as an Organic Substrate

When trying to maximize the performance of MFCs, among the most important factors to take into account is the organic substrate. Numerous studies have produced distinctive findings by making use of a wide variety of natural organic substrates [65]. Any source of carbohydrate that is used as an organic substrate in the process of operating MFCs has the potential to provide bacteria with the energy necessary to carry out their oxidative respiration activity. However, in the previous research that has been conducted, there have only been a very small number of attempts to use natural organic substrates in MFCs [66].

These substrates include rotten rice, biomass waste, vegetables, chocolate waste, and fruits. Among these researchers, Salvin et al. [67] used mangroves as an organic substrate in MFCs in order to increase the devices' energy performance. In contrast, food waste was used as an organic substrate in our experiment alongside glucose. This was performed to examine the relative performance of the food waste in comparison to the other commercial substrates even though its carbohydrate-based organic substrates contain a maximum concentration of bacterial nutrients than food waste. Table 5 summarizes the performance of all of the organic substrates, and it reveals that the best performance was achieved by the food waste. This means that glucose is a simple sugar that is easily and rapidly oxidized, which reduces the operation's durability as well as the transportation rate.

Table 5. Performance of commercial glucose and food waste as an organic substrate.

Electrode	Organic Substrate	Voltage (mV)	Operation Duration (Days)	Degradation Efficiency (%)
GO	Glucose	24	10	18.00
GO-ZnO	Glucose	38	10	31.20
GO	Food waste	49	10	40.45
GO-ZnO	Food waste	64	10	43.89

4. Comparative Profile with Pervious Literature

A recent subject in MFCs is the preparation of the high-quality, low-cost base material for anode fabrication. The development of anodes considers several variables to improve their conductivity, durability, mechanical, thermal, and chemical biocompatibility toward the operating microorganism in MFCs. The current findings indicate that both anodes exhibit high mechanical, chemical, and biological compatibility as described in the preceding sections. The chemical compatibility for bacterial growth is evident in the SEM photos of the biofilm around both anodes. Similarly, Figure 5 shows the rate of electron transit, demonstrating the good results. Both anodes were found to last 30 days when used continuously. Within 18 days, each electrode produced a maximum voltage of 110 mV (GO) and 130 mV (GO-ZnO). According to the most recent research, as shown in Table 3, the rate of electron transmission from anode to cathode was determined to be excellent. The highest CD was 28.94 mA/m^2 (GO) and 38.15 mA/m^2 (GO-ZnO), while the PD was 0.692 mW/m^2 (GO) and 1.059 mW/m^2 (GO-ZnO), respectively. The maximum CD and PD indicated that electron transportation was efficient for 30 days, which is consistent with the longevity of the anodes. Several studies used the same strategy to explain the durability and comparative profile of the self-fabricated anodes [7,8,45,46,54]. For example, Senthil et al. [48] fabricated the waste-derived 3D-carbon aerogel-ceria-nitrogen-doped reduced graphene oxide-based anode electrode. Their anode was advertised as having a 360-h continuous batch life. Similar to this, Table S2 presents a comparative profile on the degradation of toxic metal. In comparison to earlier literature, the current archival degradation efficiency was 92.71%, which is much higher. The presence of a conductive, biocompatible electrode and a very advantageous organic substrate in the form of food waste is what accounts for the high degradation efficiency and energy generation/transport.

Present Challenges and Future Perfectives

The potential for MFCs to be employed in a wide range of applications, including the bioremediation of wastewater, is now receiving a lot of attention [68]. Despite this, MFCs are still struggling to overcome limitations brought on by the design and composition of the electrodes. The generation of highly conductive electrodes and subsequent modifications to those electrodes have the potential to raise the standing of MFC technology in the context of the biodegradation of contaminants and the treatment of wastewater. The MFC is a revolutionary technology that could provide clean, safe, sustainable energy and help preserve the environment [40]. However, MFCs are a very new topic of research in the

scientific world; for this reason, it will need a considerable amount of effort and time before it can be regarded as commercially feasible. The developing problem with MFCs is that the organic substrate and electrode material are both prone to instability [21]. In the current investigation, favorable outcomes were achieved; nevertheless, it was challenging to maintain the system throughout the course of the whole research project. The scaling up of MFCs requires a long-lasting organic substrate. Recently, food waste has been used as a substrate in MFCs, which has extended the duration of the process to 30 days. To contemplate the scaling up of MFC dimensions, the requirements for a functioning organic substrate over the long term include a high level of stability as well as a significant quantity of carbohydrates. Another crucial aspect of the MFC that must be taken into account is the material that will be used for the electrodes. The MFC was not capable of producing an appropriate quantity of energy because of the material that was used for the electrodes. Anode material should transfer electrons effectively and create a biocompatible environment for bacteria to grow a biofilm on the anode surface [69,70]. Due to their affordability and high performance, electrode materials made from biomass have attracted a lot of interest. Many studies have already been conducted on the conversion of biomass to produce the electrodes [71]. A potentially fruitful strategy for the future may include the alteration of material obtained from biomass using polymers coupled with metal oxide.

5. Conclusions

This article shows how waste derived MFC anodes transport the electrons and degrade the hazardous metal ions in synthetic wastewater. Our results show that an anode made from oil palm tree material may improve electron transport with GO and GO-ZnO, leading to superior energy performance. The MFC's use of waste food as an organic source is an ideal situation. A little study on the use of natural organic substrates has investigated the effectiveness of MFCs in producing electricity and treating wastewater. In our research, it was found that the prepared electrodes were extraordinarily biocompatible and stable for the operation of MFCs, as shown by several material characterizations and results. GO and GO-ZnO anodes generated a solid biofilm, proving their safety and chemical stability for 30 days. The metal ion degradation also occurred, and significant progress was made in a short amount of time. As an organic substrate, food wastes were used to energize the bacterial activities in MFCs. It took 30 days to finish each MFC operation, but only 18 days to reach peak energy efficiency. The composite anode was superior to the GO in terms of energy efficiency and electron transport. The MFC's organic substrate was still not highly stable, but the produced electrodes improved electron transportation. Therefore, future studies should concentrate on the durability of organic substrates in MFCs at the industrial scale.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr11010163/s1, Table S1: Comparative analysis of previously published research and the current work in MFC. Table S2: A comparison of the degradation of metal ions using various anodes in MFC.

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References

1. Heilmann, J.; Logan, B.E. Production of electricity from proteins using a microbial fuel cell. *Water Environ. Res.* **2006**, *78*, 531–537. [CrossRef] [PubMed]
2. Logan, B.E.; Regan, J.M. Microbial fuel cells—Challenges and applications. *Environ. Sci. Technol.* **2006**, *40*, 5172–5180. [CrossRef]
3. Khatoon, A.; Mohd Setapar, S.H.; Parveen, T.; Rafatullah, M. Outlook on the role of microbial fuel cells in remediation of environmental pollutants with electricity generation. *Catalysts* **2020**, *10*, 819.
4. Parkhey, P.; Sahu, R. Microfluidic microbial fuel cells: Recent advancements and future prospects. *Int. J. Hydrogen Energy* **2021**, *46*, 3105–3123. [CrossRef]
5. Choudhury, P.; Ray, R.N.; Bandyopadhyay, T.K.; Basak, B.; Muthuraj, M.; Bhunia, B. Process engineering for stable power recovery from dairy wastewater using microbial fuel cell. *Int. J. Hydrogen Energy* **2021**, *46*, 3171–3182. [CrossRef]
6. Ahmad, H.; Parveen, T.; Ahmad, A.; Oves, M.; Ismail, I.M.; Qari, H.A. Recent advances in metal decorated nanomaterials and their various biological applications: A review. *Front. Chem.* **2020**, *8*, 341.
7. Kirubaharan, C.J.; Yoo, D.J.; Kim, A.R. Graphene/poly (3, 4-ethylenedioxythiophene)/Fe_3O_4 nanocomposite–An efficient oxygen reduction catalyst for the continuous electricity production from wastewater treatment microbial fuel cells. *Int. J. Hydrogen Energy* **2016**, *41*, 13208–13219.
8. Kirubaharan, C.J.; Kumar, G.G.; Sha, C.; Zhou, D.; Yang, H.; Nahm, K.S.; Raj, B.S.; Zhang, Y.; Yong, Y.-C. Facile fabrication of Au@ polyaniline core-shell nanocomposite as efficient anodic catalyst for microbial fuel cells. *Electrochim. Acta* **2019**, *328*, 135136. [CrossRef]
9. Han, D.; Wu, S.; Zhang, S.; Deng, Y.; Cui, C.; Zhang, L.; Long, Y.; Li, H.; Tao, Y.; Weng, Z. A Corrosion-Resistant and Dendrite-Free Zinc Metal Anode in Aqueous Systems. *Small* **2020**, *16*, 2001736. [CrossRef]
10. Rodríguez-Couto, S. Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): An overview. *Biochem. Eng. J.* **2020**, *164*, 107779.
11. Idris, M.O.; Noh, N.A.M.; Yaqoob, A.A. Sustainable microbial fuel cell functionalized with a bio-waste: A feasible route to formaldehyde bioremediation along with bioelectricity generation. *Chem. Eng. J.* **2022**, *1*, 140781.
12. Idris, M.O.; Guerrero-Barajas, C.; Kim, H.-C. Scalability of biomass-derived graphene derivative materials as viable anode electrode for a commercialized microbial fuel cell: A systematic review. *Chin. J. Chem. Eng.* **2022**, *in press*.
13. Fu, C.; Zhao, G.; Zhang, H.; Li, S. Evaluation and characterization of reduced graphene oxide nanosheets as anode materials for lithium-ion batteries. *Int. J. Electrochem. Sci.* **2013**, *8*, 6269–6280.
14. Kurra, N.; Jiang, Q.; Nayak, P.; Alshareef, H.N. Laser-derived graphene: A three-dimensional printed graphene electrode and its emerging applications. *Nano Today* **2019**, *24*, 81–102. [CrossRef]
15. Thepsuparungsikul, N.; Ng, T.; Lefebvre, O.; Ng, H. Different types of carbon nanotube-based anodes to improve microbial fuel cell performance. *Water Sci. Technol.* **2014**, *69*, 1900–1910. [CrossRef] [PubMed]
16. Cai, T.; Meng, L.; Chen, G.; Xi, Y.; Jiang, N.; Song, J.; Zheng, S.; Liu, Y.; Zhen, G.; Huang, M. Application of advanced anodes in microbial fuel cells for power generation: A review. *Chemosphere* **2020**, *248*, 125985. [CrossRef]
17. Chiu, W.-T.; Chang, T.-F.M.; Sone, M.; Tixier-Mita, A.; Toshiyoshi, H. Roles of TiO_2 in the highly robust Au nanoparticles-TiO_2 modified polyaniline electrode towards non-enzymatic sensing of glucose. *Talanta* **2020**, *212*, 120780. [CrossRef]
18. Deng, C.; Ma, C.; Lau, M.L.; Skinner, P.; Liu, Y.; Xu, W.; Zhou, H.; Ren, Y.; Yin, Y.; Williford, B. Amorphous and crystalline TiO_2 nanoparticle negative electrodes for sodium-ion batteries. *Electrochim. Acta* **2019**, *321*, 134723. [CrossRef]
19. Baratto, C.; Ferroni, M.; Rocco, D.; De Angelis, C.; Faglia, G. Chemical sensing with ZnO nano and microwires. *Nano-M&D* **2019**, *2019*, 28.
20. Shakeel, N.; Ahamed, M.I.; Kanchi, S.; Kashmery, H.A. Green synthesis of ZnO nanoparticles decorated on polyindole functionalized-Mcnts and used as anode material for enzymatic biofuel cell applications. *Sci. Rep.* **2020**, *10*, 5052.
21. Fadzli, F.S.; Bhawani, S.A.; Adam Mohammad, R.E. Microbial fuel cell: Recent developments in organic substrate use and bacterial electrode interaction. *J. Chem.* **2021**, *2021*, 4570388. [CrossRef]
22. Rafatullah, M.; Chua, Y.S.; Umar, K. Recent advances in anodes for microbial fuel cells: An overview. *Materials* **2020**, *13*, 2078.
23. Ghisellini, P.; Ulgiati, S. Circular economy transition in Italy. Achievements, perspectives and constraints. *J. Clean. Prod.* **2020**, *243*, 118360. [CrossRef]
24. Paulchamy, B.; Arthi, G.; Lignesh, B. A simple approach to stepwise synthesis of graphene oxide nanomaterial. *J. Nanomed. Nanotechnol.* **2015**, *6*, 1.
25. Fahmey, M.S.; El-Aassar, A.-H.M.; Abo-Elfadel, M.M.; Orabi, A.S.; Das, R. Comparative performance evaluations of nanomaterials mixed polysulfone: A scale-up approach through vacuum enhanced direct contact membrane distillation for water desalination. *Desalination* **2019**, *451*, 111–116. [CrossRef]

26. Yaakop, A.S.; Ahmad, A. Application of microbial fuel cells energized by oil palm trunk sap (OPTS) to remove the toxic metal from synthetic wastewater with generation of electricity. *Appl. Nanosci.* **2021**, *11*, 1949–1961.
27. Timmers, R.A.; Strik, D.P.; Hamelers, H.V.; Buisman, C.J. Characterization of the internal resistance of a plant microbial fuel cell. *Electrochim. Acta* **2012**, *72*, 165–171. [CrossRef]
28. Igboamalu, T.E.; Bezuidenhout, N.; Matsena, M.T.; Chirwa, E. Microbial fuel cell power output and growth: Effect of pH on anaerobic microbe consortium. *Chem. Eng. Tran.* **2019**, *76*, 1–16.
29. Katuri, K.P.; Scott, K.; Head, I.M.; Picioreanu, C.; Curtis, T.P. Microbial fuel cells meet with external resistance. *Bioresour. Technol.* **2011**, *102*, 2758–2766. [CrossRef]
30. Yaqoob, A.A.; Yaakop, A.S. Modified graphene oxide anode: A bioinspired waste material for bioremediation of Pb^{2+} with energy generation through microbial fuel cells. *Chem. Eng. J.* **2021**, *417*, 128052. [CrossRef]
31. Durmus, Z.; Kurt, B.Z.; Durmus, A. Synthesis and characterization of graphene oxide/zinc oxide (GO/ZnO) nanocomposite and its utilization for photocatalytic degradation of basic Fuchsin dye. *ChemistrySelect* **2019**, *4*, 271–278. [CrossRef]
32. Anandhavelu, S.; Thambidurai, S. Single step synthesis of chitin/chitosan-based graphene oxide–ZnO hybrid composites for better electrical conductivity and optical properties. *Electrochim. Acta* **2013**, *90*, 194–202. [CrossRef]
33. Chen, C.-H.; Chung, T.-Y.; Shen, C.-C.; Yu, M.-S.; Tsao, C.-S.; Shi, G.-N.; Huang, C.-C.; Ger, M.-D.; Lee, W.-L. Hydrogen storage performance in palladium-doped graphene/carbon composites. *Int. J. Hydrogen Energy* **2013**, *38*, 3681–3688. [CrossRef]
34. Feng, J.-X.; Zhang, Q.-L.; Wang, A.-J.; Wei, J.; Chen, J.-R.; Feng, J.-J. Caffeine-assisted facile synthesis of platinum@ palladium core-shell nanoparticles supported on reduced graphene oxide with enhanced electrocatalytic activity for methanol oxidation. *Electrochim. Acta* **2014**, *142*, 343–350. [CrossRef]
35. Bikkarolla, S.K.; Cumpson, P.; Joseph, P.; Papakonstantinou, P. Oxygen reduction reaction by electrochemically reduced graphene oxide. *Faraday Discuss.* **2014**, *173*, 415–428. [CrossRef] [PubMed]
36. Li, X.; Sun, P.; Yang, T.; Zhao, J.; Wang, Z.; Wang, W.; Liu, Y.; Lu, G.; Du, Y. Template-free microwave-assisted synthesis of ZnO hollow microspheres and their application in gas sensing. *CrystEngComm* **2013**, *15*, 2949–2955. [CrossRef]
37. Umar, K.; Adnan, R.; Rashid, M. Graphene oxide–ZnO nanocomposite: An efficient visible light photocatalyst for degradation of rhodamine B. *Appl. Nanosci.* **2021**, *11*, 1291–1302.
38. Serrà, A. Self-assembled oil palm biomass-derived modified graphene oxide anode: An efficient medium for energy transportation and bioremediating Cd (II) via microbial fuel cells. *Arab. J. Chem.* **2021**, *14*, 103121.
39. Rodríguez-Couto, S.; Ahmad, A. Preparation, characterization, and application of modified carbonized lignin as an anode for sustainable microbial fuel cell. *Process Saf. Environ. Prot.* **2021**, *155*, 49–60.
40. Yaqoob, S.B.; Bhawani, S.A.; Ismail Abdulrahman, R.M. Utilization of Mangifera indica as Substrate to Bioremediate the Toxic Metals and Generate the Bioenergy through a Single-Chamber Microbial Fuel Cell. *J. Chem.* **2021**, *2021*, 8552701. [CrossRef]
41. Daud, N.N.M. Application of rotten rice as a substrate for bacterial species to generate energy and the removal of toxic metals from wastewater through microbial fuel cells. *Environ. Sci. Pollut. Res.* **2021**, *28*, 62816–62827. [CrossRef] [PubMed]
42. Sajana, T.; Ghangrekar, M.; Mitra, A. Application of sediment microbial fuel cell for in situ reclamation of aquaculture pond water quality. *Aquac. Eng.* **2013**, *57*, 101–107. [CrossRef]
43. Sajana, T.; Ghangrekar, M.; Mitra, A. Effect of presence of cellulose in the freshwater sediment on the performance of sediment microbial fuel cell. *Bioresour. Technol.* **2014**, *155*, 84–90. [CrossRef] [PubMed]
44. Fadzli, F.S.; Rashid, M. Electricity generation and heavy metal remediation by utilizing yam (*Dioscorea alata*) waste in benthic microbial fuel cells (BMFCs). *Biochem. Eng. J.* **2021**, *172*, 108067. [CrossRef]
45. Senthilkumar, N.; Pannipara, M.; Al-Sehemi, A.G. PEDOT/$NiFe_2O_4$ nanocomposites on biochar as a free-standing anode for high-performance and durable microbial fuel cells. *New J. Chem.* **2019**, *43*, 7743–7750. [CrossRef]
46. Gnana Kumar, G.; Kirubaharan, C.J.; Udhayakumar, S.; Karthikeyan, C.; Nahm, K.S. Conductive polymer/graphene supported platinum nanoparticles as anode catalysts for the extended power generation of microbial fuel cells. *Ind. Eng. Chem. Res.* **2014**, *53*, 16883–16893. [CrossRef]
47. Yaakop, A.S.; Rafatullah, M. Utilization of biomass-derived electrodes: A journey toward the high performance of microbial fuel cells. Appl. *Water Sci.* **2022**, *12*, 99–112.
48. Senthilkumar, N.; Aziz, M.A.; Pannipara, M.; Alphonsa, A.T.; Al-Sehemi, A.G.; Balasubramani, A. Waste paper derived three-dimensional carbon aerogel integrated with ceria/nitrogen-doped reduced graphene oxide as freestanding anode for high performance and durable microbial fuel cells. *Bioprocess Biosyst. Eng.* **2020**, *43*, 97–109. [CrossRef]
49. Kim, J.R.; Min, B.; Logan, B.E. Evaluation of procedures to acclimate a microbial fuel cell for electricity production. *Appl. Microbiol. Biotechnol.* **2005**, *68*, 23–30. [CrossRef]
50. Zhao, Y.; Nakanishi, S.; Watanabe, K.; Hashimoto, K. Hydroxylated and aminated polyaniline nanowire networks for improving anode performance in microbial fuel cells. *J. Biosci. Bioeng.* **2011**, *112*, 63–66. [CrossRef]
51. Peng, X.; Yu, H.; Ai, L.; Li, N.; Wang, X. Time behavior and capacitance analysis of nano-Fe3O4 added microbial fuel cells. *Bioresour. Technol.* **2013**, *144*, 689–692. [CrossRef] [PubMed]
52. Scott, K.; Rimbu, G.; Katuri, K.; Prasad, K.; Head, I. Application of modified carbon anodes in microbial fuel cells. *Process Saf. Environ. Prot.* **2007**, *85*, 481–488. [CrossRef]
53. Tsai, H.-Y.; Wu, C.-C.; Lee, C.-Y.; Shih, E.P. Microbial fuel cell performance of multiwall carbon nanotubes on carbon cloth as electrodes. *J. Power Sources* **2009**, *194*, 199–205. [CrossRef]

54. Kirubaharan, C.J.; Santhakumar, K.; Senthilkumar, N.; Jang, J.-H. Nitrogen doped graphene sheets as metal free anode catalysts for the high performance microbial fuel cells. *Int. J. Hydrogen Energy* **2015**, *40*, 13061–13070. [CrossRef]
55. Wang, Y.; Zhao, C.-e.; Sun, D.; Zhang, J.-R.; Zhu, J.-J. A graphene/poly (3, 4-ethylenedioxythiophene) hybrid as an anode for high-performance microbial fuel cells. *ChemPlusChem* **2013**, *78*, 823. [CrossRef]
56. Christwardana, M.; Frattini, D.; Accardo, G.; Yoon, S.P.; Kwon, Y. Effects of methylene blue and methyl red mediators on performance of yeast based microbial fuel cells adopting polyethylenimine coated carbon felt as anode. *J. Power Sources* **2018**, *396*, 1–11. [CrossRef]
57. Singh, S.; Songera, D.S. A review on microbial fuel cell using organic waste as feed. *CIBTech J. Biotechnol.* **2012**, *2*, 17–27.
58. Al-Zaqri, N.; Yaakop, A.S. Potato waste as an effective source of electron generation and bioremediation of pollutant through benthic microbial fuel cell. *Sustain. Energy Technol. Assess.* **2022**, *53*, 102560.
59. Sasaki, D.; Sasaki, K.; Tsuge, Y.; Kondo, A. Less biomass and intracellular glutamate in anodic biofilms lead to efficient electricity generation by microbial fuel cells. *Biotechnol. Biofuels* **2019**, *12*, 72. [CrossRef]
60. Li, M.; Zhou, M.; Tian, X.; Tan, C.; McDaniel, C.T.; Hassett, D.J.; Gu, T. Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity. *Biotechnol. Adv.* **2018**, *36*, 1316–1327. [CrossRef]
61. Idris, M.O.; Kim, H.C. Exploring the effectiveness of microbial fuel cell for the degradation of organic pollutants coupled with bio-energy generation. Sustain. *Energy Technol. Assess.* **2022**, *52*, 102183.
62. Yaqoob, A.A.; Mohamad Ibrahim, M.N.; Umar, K.; Bhawani, S.A.; Khan, A.; Asiri, A.M.; Khan, M.R.; Azam, M.; AlAmmari, A.M. Cellulose derived graphene/polyaniline nanocomposite anode for energy generation and bioremediation of toxic metals via benthic microbial fuel cells. *Polymers* **2021**, *13*, 135. [CrossRef] [PubMed]
63. Yaqoob, A.A.; Idris, M.O.; Ahmad, A.; Daud, N.N.M.; Ibrahim, M.N.M. Removal of Toxic Metal Ions from Wastewater Through Microbial Fuel Cells. In *Microbial Fuel Cells for Environmental Remediation*; Springer: Singapore, 2022; pp. 299–325.
64. Umar, M.F.; Rafatullah, M.; Ibrahim, M.N.M.; Ismail, N. Bioelectricity production and xylene biodegradation through double chamber benthic microbial fuel cells fed with sugarcane waste as a substrate. *J. Hazard. Mater.* **2021**, *419*, 126469. [CrossRef]
65. Huang, L.; Chai, X.; Quan, X.; Logan, B.E.; Chen, G. Reductive dechlorination and mineralization of pentachlorophenol in biocathode microbial fuel cells. *Bioresour. Technol.* **2012**, *111*, 167–174. [CrossRef] [PubMed]
66. Sharma, Y.; Li, B. The variation of power generation with organic substrates in single-chamber microbial fuel cells (SCMFCs). *Bioresour. Technol.* **2010**, *101*, 1844–1850. [CrossRef] [PubMed]
67. Salvin, P.; Ondel, O.; Roos, C.; Robert, F. Energy harvest with mangrove benthic microbial fuel cells. *Int. J. Energy Res.* **2015**, *39*, 543–556. [CrossRef]
68. Fadzli, F.; Yaakop, A. Benthic microbial fuel cells: A sustainable approach for metal remediation and electricity generation from sapodilla waste. *Int. J. Environ. Sci. Technol.* **2022**, *14*, 1–14.
69. Yaqoob, A.A.; Ibrahim, M.N.M.; Guerrero-Barajas, C. Modern trend of anodes in microbial fuel cells (MFCs): An overview. *Environ. Technol. Innov.* **2021**, *23*, 101579. [CrossRef]
70. Serrà, A.; Bhawani, S.A.; Ibrahim, M.N.M.; Khan, A.; Alorfi, H.S.; Asiri, A.M.; Hussein, M.A.; Khan, I.; Umar, K. Utilizing Biomass-Based Graphene Oxide–Polyaniline–Ag Electrodes in Microbial Fuel Cells to Boost Energy Generation and Heavy Metal Removal. *Polymers* **2022**, *14*, 845.
71. Yaqoob, A.A.; Guerrero–Barajas, C.; Umar, K. Local fruit wastes driven benthic microbial fuel cell: A sustainable approach to toxic metal removal and bioelectricity generation. *Environ. Sci. Pollut. Res.* **2022**, *29*, 32913–32928. [CrossRef]