Design and feasibility study of novel paraboloid graphite based microbial fuel cell for bioelectrogenesis and pharmaceutical wastewater treatment

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Abstract

The pharmaceutical industrial wastewater (PIW) is rising globally as one of the major health problems nowadays, not only for aquatic animals but also for human beings and the environment. Several conventional techniques including coagulation, filtration, biological membranes, and advanced oxidations have been used for the treatment of PIW, but all these techniques are limited with their applications and results. The present study aimed to build a cost-effective, high biodegradable, eco-friendly, and highly efficient PIW treatment technique to generate electricity and reduce the COD of wastewater. In the present study, the novel paraboloid of graphite-based microbial fuel cell (MFC) configuration has been designed, by

eliminating different types of casings and the membranes, for the bio-electrogenesis and the treatment of the PIW. Municipal solid wastewater (MSW) was used as the substrate for developing the biofilm in the paraboloid graphite-based MFC. The PIW treatment showed adequate bioelectricity generation including current, power, and voltage, and open-circuit voltage (OCV) of about 2.76 mA and 0.76 mW, 276 mV and 330 mV at 100 Ω respectively after five operating cycles. The cyclic voltammetry showed the maximum generation of 2.01 W/m^3 and 168 mA/m^2 of power and current densities respectively followed by a considerable reduction in internal resistance from 197 to 99 Ω. The results reported a significant amount of reduction in COD and TDS of 80.55% (5460 to 1060 mg/L) and 35.62% (800 to 515 mg/L) respectively of PIW by MFC. The reduction in the % removal efficiency of the COD (80.55%) suggested that the removal of organic compounds from PIW is parallel to bioelectrogenesis. Based on these major findings, it is recommended the novel membrane-less and paraboloid graphite-based MFC operation significantly drag concentration towards the feasibility of using pharmaceutical wastewaters for bio-electrogenesis.

Keywords: Paraboloid-shaped MFC; Bioelectrogenesis; COD reduction; Pharmaceutical wastewater; Open circuit voltage and Power density.

1 Introduction

With the increasing world population, industrialization, and urbanization the demand for a quality life is also increasing. Several industries are established to fulfil the requirement of human beings, but along with their benefits, there are several types of problems including the production of wastewater [1]. The whole world is encountering several types of industrial effluents, which can exert many harmful effects including cancer, reproductive disorder, and organ failure. Among them, the most important are fertilizer, food and dairy processing, petrochemical, textile, and pharmaceutical effluents [2]. The pharmaceutical effluent is quite different from the rest of the conventional effluents due to discharging of organic pollutants

and drugs components including antibiotics, vitamins, antiepileptics and cosmetic ingredients and their adverse effects on the environment are not well known and are becoming one of the major problems for the environment and its stakeholders [3].

The pharmaceutical effluents contain a large amount of waste products including organic solvents, solid and liquid wastes, contaminants hormones, antiepileptic drugs, and antibiotics, which carried high total dissolved solids (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids. The waste containing a high amount of COD, when discharged into the streaming water, immediately reduces the dissolved oxygen and contaminates the water for further use [4]. Therefore, there is a need to decontaminate the pharmaceutical waste before discharging [5, 6]. The treatment of pharmaceutical waste is a very challenging task due to its intractable behaviours. Conventionally several techniques including chemical coagulation, osmosis, membrane techniques, advanced oxidation, and electronic coagulation have been used for the treatment of pharmaceutical wastewater, but all of these strategies did not attain considerable importance due to their limitations including less efficiency, low biodegradability, less reduction in COD and BOD of wastewater, and high cost [7].

Chemical coagulation is a simple wastewater technique [8], which involves destabilizing the contaminated water by using chemicals like ferric salts, lime, and aluminium sulphate, but few important concerns are about the formation of aggregation of compounds during the physical transportation of particles, low removal of pathogens, use of lethal chemicals, and environmental challenges [9, 10]. Another, conventional pharmaceutical wastewater treatment method is the reduction/oxidation in the bio-electrochemical system, which provides a suitable environment for the treatment of trace organic compounds in pharmaceutical wastewater, but

its major concerns are about the high cost and being less eco-friendly, and low bio-degradability difficulties [11]. Furthermore, the biological pharmaceutical wastewater treatment is also considered an important key strategy to treat the water, the microorganisms are used in most of the biological methods to degrade the contaminants into harmless water and carbon dioxide. But in the biological degradation systems. some parameters including limited removal of suspended solids, high hydraulic retention time, insufficient removal of turbidity, and biological degradation constant need to be addressed (K_{biol} is not present for many of the pharmaceutically active compounds including carbamazepine and clofibric acid) to estimate the degradation efficiency of pharmaceutical wastewater [10, 12].

However, there is a need to develop a cost-effective, high degradable, and eco-friendly pharmaceutical wastewater treatment strategy. Recently, the microbial fuel cell (MFC) has attained considerable attention towards the treatment of wastewater including pharmaceutical wastewater due to its high degradation efficiency, multidirectional applications, the current generation, eco-friendly behaviour, and cost-effectiveness. Microbial fuel cell (MFC) technology is the bioreactor that depends on the electroactive bacteria, popularly known as exoelectrogens, to simultaneously produce electric power and treat wastewater by reducing the BOD and COD of effluents [13]. Design feasibility, energy production, power density, and scale-up of MFC are the major concerns of researchers to treat wastewater [14].

Initially, the double chamber microbial fuel cell was made which consisted of two compartments including anode and cathode. The anode chamber was filled with wastewater in which microbes break the organic compounds to produce the carbon dioxide along with hydrogen ions (proton) and electrons. Protons migrated to the cathodic chamber by proton exchange membrane (PEM) while electron transmitted to the cathode through an external

circuit where oxygen reduction occurs. The reactions between oxygen, hydrogen ion, and electron produce water (**Eqs.(1-(*3*))**. The oxidation occurs in the anodic chamber while reduction occurs in the cathodic chamber [15, 16].

$$Anodic\ reaction: \quad C_xH_yO_z + H_2O \rightarrow nCO_2 + nH^+ + ne^- \tag{1}$$

$$Cathodic\ reaction: \quad nO_2 + nH^+ + ne^- \rightarrow nH_2O \tag{2}$$

$$Overall\ reaction: \quad C_xH_yO_z + 2O_2 \rightarrow nCO_2 + nH_2O \tag{3}$$

The overall reaction involves the conversion of acetate into two components carbon-dioxide and water. According to emerging evidence, several types of MFC's including double chamber [15], cube and flat type [17], miniature, tubular [18], stacked [19], cylindrical [20], H-type [21], and single chamber [22] MFCs have been reported so far for the treatment of textile, dyes, and pharmaceutical wastewater. In cube and flat microbial fuel cells, the internal resistance is reduced by availing the large membrane area and inertly shorter distance between electrodes to increase the power production [17].

Flat plate type MFC with Nafion PEM (proton exchange membrane) and anode assembly provides a larger surface area for membrane and cathode. The proton exchange membrane in cells significantly helped in transfer the chemical energy into electrical energy produced by the electrochemical reaction of oxygen and hydrogen, and also oppose the direct combustion of oxygen and hydrogen into thermal energy. The anodic chamber is usually fed with organic biomass while air is pumped through a cathodic chamber without using any liquid catholyte [23]. Single chamber microbial fuel cell has an external cathodic wall that is exposed to the atmosphere and eliminates the cost of oxygen (aeration) pumping to the cathodic chamber [22]. A stacked microbial fuel cell consists of more than two chambers that can be applied in series or parallel form in order to increase the power up to 35 V [19]. The voltage reversal and limited power density are the major problems in the conventionally used MFC, in addition, these

135 microbial fuel cells have the lowest columbic efficiency and used membrane for ion exchange
136 that provides greater resistance and cost as well [24].
137
138 Nayak and Ghosh [16] reported that photosynthetic microbial fuel cells showed the maximum
139 COD removal of about 87.8% with an efficiency of 95% for pharmaceutical wastewater. They
140 also revealed that pharmaceutical wastewater treatment produces maximum power density and
141 voltage of 838.68 mW/m^2 and 740.13 mV respectively. Zhuang et al., [19] performed an
142 experiment to treat real wastewater by parallel stack microbial fuel cell (PSMFC) at two
143 different organic loading rates as 1.2 and 4.9 kg COD/m^3 d. They stated that PSMFC removed
144 up to 90.8 and 83.8% of NH_4^+-N and COD of wastewater at 1.2 kg COD/m^3 d and 80.7 and
145 77.1% NH_4^+-N and COD at 4.9 kg COD/m^3 d. They also observed maximum power density
146 and voltage of 175.7 W/m^2 and 1.8 V respectively at 4.9 kg COD/m^3 d. Mohanakrishna et al.,
147 [20] investigated the treatment of Labanah whey wastewater using cylindrical graphite
148 microbial fuel cell and observed the maximum substrate deprivation efficiency of 72.76% with
149 maximum power and current generation of 1.02 mW and 3.2 mA respectively at 100 Ω. Prasad
150 and coworkers reported the maximum COD reduction of 91.50% with power generation of 335
151 mV during pharmaceutical wastewater treatment by microbial fuel cell after a hydraulic
152 retention period of 12 days [25]. Similarly, Amari and his research group observed the
153 maximum COD reduction of 93 and 78%, and power density of 20.5 and 6.5 W/m^3 for real and
154 synthetic wastewater respectively by dual-chambered microbial fuel cell [26].
155
156 In recent years, the pharmaceutical effluent is continuously increasing in its bulk and strength
157 too. However, there is a need to develop a new and revolutionary technique to identify the
158 complex mixture in pharmaceutical effluents and treat them effectively with high accuracy and
159 less costly. To the best of our knowledge, for the first time, the present study evaluates the

formation of graphite-based, paraboloid shaped microbial fuel cell to generate greater electricity and reduce the total dissolved solids (TDS) and chemical oxygen demand (COD) of pharmaceutical wastewater. Moreover, for the first time, the substrate degradation rate (SDR) and organic loading rate (OLR) of pharmaceutical wastewater is discussed for a better understanding. The present study investigates the production of open-circuit voltage (OCV), current, power density, voltage, and current density from the pharmaceutical industrial wastewater by MFC.

2. Materials and methods

2.1. Sample collection

This pharmaceutical wastewater samples were taken from NabiQasim Pharma Industries, Karachi, Pakistan. Wastewater having the COD of 5460 mg/L and pH 7.4–7.7 was taken to the laboratory and quickly stored at 4 ºC in the refrigerator. The aim of storing at 4 ºC was to preserve the nature of the wastewater and to avoid any sort of biological change. Paraboloid shaped graphite based MFC was constructed for the treatment of pharmaceutical wastewater. Sodium acetate (99.9% purity) and phosphate buffer (pH 7) were purchased from the SIGMA-Aldrich Chemical Co. (USA).

2.2. MCF configuration and inoculation

The microbial fuel cell (MFC) was designed with a novel configuration that has a paraboloid shape. The paraboloid MFC was composed of two cups, one is the inner paraboloid cup named as a cathode and the other is the outer paraboloid cup named as the anode. Both anode and cathode were fabricated with the graphite material to remove any substrate effect. The anode and cathode were adjusted in one another in such a way that they showed truncated. The smaller paraboloid cup (cathode) was placed inside the larger paraboloid cup (anode), in such a way that the cathode placed epi-centrically in the anode. The anode electrode had the dimensions

of 108 mm height and 66 mm face diameter, while the cathode electrode had the dimensions of 85 mm height and 58 mm face diameter. The base of an anode (7 mm thick) and a cathode (3.5 mm) was made of graphite.

The open portion of space between the anode and the cathode (at the top) was closed with an acrylic plastic plate type ring, as shown in **Fig. 1**. The acrylic made plastic ring (lid) of the anode has two openings, one opening is used for the sampling purpose, and the second opening used for the feeding purpose. Both openings are of 1.5 mm in diameter, through which the tube of white plastic (1.5 mm diameter) inserted into the anode, and the opening of the tubes was kept closed throughout the operation for ensuring the anaerobic condition in the anode. The outer surface of the anode which is open to air was insulated with the paraffin layer to stop the environmental interference to the anolyte or the bioactivity inside the anode. This novel design of the MFC gives the dual truncated membrane-less MFC.

The apparent volume of the anode was 186 mL and the geometric surface area was measured as 189 cm^2, while the apparent volume of the cathode was 111 mL with 132 cm^2 geometric surface area. The novel design was also optimized in the way that the distance between the anode and cathode also lowered. As the spacing is a major factor in the performance of the MFC, the lower the spacing between the anode and cathode, the higher will be the efficiency of the MFC assembly. Being the favourable factor for the performance of the MFC, the spacing between the anode and cathode has adjusted at 5.5 to 6 mm. The surface-to-volume ratio of anode and cathode was 1.017 and 1.194 respectively. The copper wire was used as the connector between the two electrodes (anode and cathode). The copper wire was used due to its minimum current resistance and maximum level of conductivity as compared to other wires like titanium and stainless steel.

For regular electrochemical analysis, copper wire is extensively used for the outside connection between the two paraboloid cups [27-29]. The voltage and the current of the MFC assembly were measured by the multi-meter and cyclic voltammetry. In Microbial Fuel Cell (MFC) the mixed liquor or the mixed microbial consortia was developed from the Municipal Solid Wastewater (MSW) to develop biocatalyst and biofilm for bio-electrogenic activity in the wastewater. The MSW contains the mixed microbial consortia which were collected from the domestic wastewater tank (NFC-IET Multan) with 545 mg/L COD and pH 7.4–7.7. Prior to the use of MSW into the MFC for the inoculation, 1 L MSW was taken into a beaker and left it to settle for a certain time at room temperature. When the sewage water was settled down, the 900 mL of supernatant was removed out and the rest of 100 mL of MSW containing the sludge was taken into the anode chamber as inoculum. The specific amount of sodium acetate (3 g/L) was also added in the anode to settle the sludge, which acts as the substrate in the anode and helped in increasing the growth rate of the bacteria [30, 31].

The opening of the anode was closed to ensure the anaerobic condition inside the anode, which was operated for 8 days to enrich the biofilm that will be developed on the inner walls of the anode in the anodic compartment. The same media which was formulated for the initial step was also prepared for the next two more cycles with new anodic liquid. The three cycles ensured a considerable growth of the biofilm inside the anode. On completing the three cycles, and the formation of the biofilm in the anode, the cathode was introduced into the anode to receive the electrons from anode without rupturing or disturbing the biofilm.

2.3. MFC operation

After the formation of truncated MFC and the development of biofilm in the anodic section, the operation of MFC started for the treatment of the real wastewater or the effluent of the

pharmaceutical industry. The designed MFC was operated for the pharmaceutical wastewater which contained several wastage constituents of drugs, organic pollutants, syrups and the residues of the multi-vitamins with COD of 5460 mg/L. The nitrogen gas was supplied for 10 min to the anode to maintain the anaerobic condition [32]. The 65 mL of wastewater (based on the available volume of the anode that was 70 mL) was taken into the anodic chamber along with 2 mL of the nutrient solution (the acetate solution) through the sampling opening on the lid of anode using the syringe. In the cathode chamber, 100 mM of the phosphate buffer solution having the neutral pH (pH 7) was added as the catholyte to increase the conductivity (M1000 Benchtop; Thomas Scientific, USA) and maintain the pH for electricity-generating bacteria [33].

The cathode was remained open to the air so that the catholyte could have the excess supply of air to accomplish the reduction reaction which must take place in the cathodic chamber. The MFC was operated in both modes at the room or ambient temperature (22 ± 2 ℃). The MFC was operated for 4 days (HRT, the hydraulic retention time), after which the anodic feed of the first cycle was removed carefully from the anodic chamber with the help of a syringe and the fresh feed of the same media was added to start the next bath cycle. The operated feed, which was taken out, was stored in the refrigerator (4 ℃) to persevere the actual nature of the treated feed, and to evaluate the operating performance of the whole system. The MFC reactor was operated up to 5 cycles in total at the same operating conditions, for evaluating the performance of the MFC assembly for pharmaceutical wastewater treatment.

2.4. Bio-electrochemical analysis

The performance evaluation of the MFC was considered based on the parameters including potential difference, open-circuit voltage (OCV), voltage and the current (at different applied resistances), power (mW), current density (mA/m^2) and the volumetric power density (W/m^3).

The output parameters such as potential difference or the open-circuit voltage (OCV), voltage, and the currents were recorded by using the multi-meter [34]. The power density (W/m^3) was calculated with the help of a reaction (**Eq. (4)**). The power density is the amount of power that is generated per unit area. The power density was measured at anode because all the biological activities were acquired at the anode.

$$P = \frac{I \times V}{A} \quad (4)$$

where P represents the power density (W/m^3), A is the area of the anode (m^2), V is the voltage (mV) and I represent the flowing current (mA). The current density (mA/m^2) was calculated by following the **Eq. (5)** [35].

$$J = \frac{I}{A} \quad (5)$$

where J represents the current density (mA/m^2), A is the area of the anode (m^2), and I represent the flowing current (mA). The COD was calculated at the end of each cycle in such a way that, when the feed sample was removed from the MFC, the 50 mL of the sample of PIW was taken to the COD bottles for measuring the COD of a sample. The COD and TDS were calculated by using the closed reflux method [36, 37]. Organic loading rate (OLR) is used to calculate the quantity of influent substrate that enters the digester per unit time and determined using **Eq. (6)**, whereas the substrate degradation rate (SDR) was determined to study the pattern and rate of COD removal during cycle operation and calculated using the **Eq. (7)**. Both OLD and SDR have the same units as kg COD/m^3 day [38].

$$OLR = COD_{initial}/HRT \quad (6)$$

$$SDR = CRE \times OLR \quad (7)$$

where HRT is the hydraulic retention time (days), $COD_{initial}$ is the chemical oxygen demand (mg/L), and CRE is the COD removal efficiency (%).

In the end, the power yield was calculated by relating the maximum power with that of the total amount of COD which was removed at the end of each cycle.

2.5. Cyclic voltammetry

Cyclic voltammetry (CV) was accompanied for evaluating the behaviour of the biocatalyst or the bio-anode and the electrode interference [39] using the potentiostat model CHI700E (CH Instruments, USA). The CV experiments were performed using a potentiostat configuration and five different experimental scenarios. On applying the potential ramp (scan rate and scan range are specified) the graphs of loop-shaped were obtained when the applied potential was taken as the values of x-coordinate and the values of open circuit potential were taken as y-coordinate. In the system, the anode was used as a working electrode and the cathode as a counter electrode [40], while the wastewater was used as the electrolyte. To measure the polarization behaviour of the MFC, the current density was taken across the wide range of the external resistance ranging from 10 Ω to 30 KΩ. This polarization behaviour was evaluated twice, in the first cycle and then in the fifth cycle of operation. The pH and the TDS were calculated at the end of each cycle [41].

3. Results and discussion

The results for pharmaceutical wastewater in paraboloid MFC are much impressive. This assembly effectively removed up to 80.50% of the COD of pharmaceutical wastewater, generated up to 2.76 mA current, and the voltage of 0.80 mV. This unique design has given more area to volume ratio, which is also one of the uniqueness of this design as described in the following sections.

3.1. Pharmaceutical wastewater treatment

Pharmaceutical industry waste contains the phosphate of aminophylline, ammonium chloride, methanol, certain salts of glycerophosphate, organics and other antiseptics including chlorhexidine, permanganates, and quaternary ammonium compounds. According to emerging evidence, the chemical oxygen demand (COD) of the pharmaceutical industry wastewater (PIW) ranges from 1600–7000 mg/L, this range of (COD) shows the higher amount of the organics present in the wastewater which has to be treated before discharging out [7]. The paraboloid shaped microbial fuel cell (MFC) provides the efficient treatment of this effluent anaerobically.

3.1.1. COD and TDS reduction

The initial COD of collected pharmaceutical wastewater was 5460 mg/L. To reduce the COD of PIW by MFC, five cycles were performed up to 8 days. During the operation of five cycles, the minimum 26.92% COD reduction (5460 to 3990 mg/L) was achieved in the first cycle and maximum COD reduction (5460 to 1060 mg/L) efficiency of about 80.55% of PIW was achieved in the fifth cycle by MFC. These findings give remarkable pharmaceutical wastewater treatment efficiency as presented in **Fig. 2**. The findings of **Table.1** reported that during the first operating cycle, the total 1470 mg/L of COD was removed, and clearly stated that by increasing the operation cycle the reduction efficiency of COD also increased from 1470 to 4400 mg/L after fifth cycles.

The findings of the substrate degradation rate (SDR) were improved from 0.36 to 1.09 kg COD/m^3 day as presented in **Table.1**. The SDR has followed the same trends as COD reduction, it was improved by increasing the operation cycle. The results are also in agreement with previously reported findings, Mohan et al., [42] observed the maximum SDR value of

0.88 kg COD/m^3 day with 62.9% COD removal for chemical wastewater by dual-chambered MFC. They also reported the maximum voltage of about 304 mV at an organic loading rate (OLR) of 1.40 kg COD/m^3 day. Abbasi et al., [18] showed that Perspex glass made MFC effectively reduced the COD of chemical industry wastewater from 452 to 60 mg/L. They also revealed that MFC reduced the phosphate concentration in the chemical industrial wastewater from 52.7 to 35.7 mg/L. Similarly, Amari et al., [33] reported that the 78 and 93% of COD of synthetic and pharmaceutical plant wastewater was reduced by dual-chamber constructed MFC (Plexiglas sheet). Furthermore, Ismail and his research group observed that Perspex glass made microbial fuel cell (MFC) with granular activated carbon (GSC) as biofilm successfully reduced up to 83% of pharmaceutical wastewater after continuous operation of 45 days [32].

The organic contents which degraded in the anodic chamber anaerobically produced some gases including CO_2 as intermediate. The anaerobes (*Shewanella putrefaciens and Aeromonas hydrophila*) which were present in the anode utilizes these organic matters through metabolism. The degradation of the organic matter results in COD reduction that interprets as the function of treatment of wastewater and is called as wastewater treatment efficiency of MFC. Like COD, the TDS is also an important factor in the wastewater. During five cycles of operation TDS of the PIW was also calculated, which was recorded as 800 at an initial stage. The results of **Table.2** showed the maximum TDS removal efficiency was recorded as 35.64% (800 to 515 mg/L) at the fourth operation cycle whereas the minimum of 33% (800 to 536 mg/L) efficiency was recorded during the fifth cycle.

The TDS removal efficiency during the first cycle was recorded as 33.75% (800 to 530 mg/L) that improved up to the fourth cycle (35.64%). This trend may be due to the complexity of organic solvents in the actual pharmaceutical wastewater. These results are also in correlation

with previously reported findings, Prasad et al., [25] showed the TDS removal from 2600 to 2150 mg/L (17.31%) for pharmaceutical wastewater using dual-chambered MFC. Similarly, Mahendra and co-workers observed the significant TDS removal from 1000 to 250 mg/L using MFC [43]. Padmaja et al., [5] reported that the chemical coagulation method using Alum and $FeCl_3$ removed the TDS of active pharmaceutical ingredients like 14% (16290 to 14000 mg/L) and 26.30% (16290 to 12000 mg/L) respectively. Nikhil et al., [44] observed that aerobic nitrification treatment (ANT) operation on pharmaceutical wastewater treatment effectively removed the TDS, phosphates and sulfates of about 24.5, 49.6, and 43% respectively. They also reported that the maximum TDS removal efficiency in the denitrification treatment (DNT) operation system was recorded as 24.2% during pharmaceutical wastewater treatment. Palani et al., [45] stated that the membrane bioreactor successfully reduced the Total Dissolved Solids (TDS) of pharmaceutical wastewater of about 70% at 300 kPa with 35% increased flux.

3.2. Bioelectricity generation by MFC

Municipal solid wastewater (MSW) is used for the development of the biofilm, as it contains the mixed microbial consortium which develops the biofilm on the anode's inner surface effectively. The COD of the collected MSW was 545 mg/L with a pH 7.4–7.7. The formation of electroactive bacteria (*Shewanella oneidensis, Shewanella putrefaciens* and *Aeromonas hydrophila*) at the anode surface is the basic source of the current generation in MFC, as these bacteria are in the form of a nano-pili forming sessile layer which helped in the movement of bacteria via external force. When the metabolism activity of the bacteria starts, it extracts the electrons to degrade the organic waste present in pharmaceutical wastewater. Cyclic voltammetry is an electrochemical technique for evaluating out the redox reaction at the surface of the electrode.

Bioelectrogenesis and substrate degradation, both can be illustrated using electrochemical reaction in the MFC. The response of the biofilm was interpreted as a function of current generation with applied potential, which gradually increases from the first cycle to the fifth cycle; thus, this improvement in current is the function of bacterial biofilm (*Shewanella oneidensis*, and *Aeromonas hydrophila*) as presented in **Fig. 3**. The discharge rate of the electrons during the metabolism can be determined by the oxidation and reduction peaks, so Forward Sweep (FS) and Reverse Sweep (RS) is responsible for it. The cyclic voltammetry of PIW during all five cycles shows the development of the electroactive biofilm with increasing the concentration of anolyte and catholyte due to the diffusion. The sharp peaks during the FS and RS demonstrate the reaction occurring as a result of a redox reaction. Velvizhi and Mohan [46], stated that the anaerobic operation (ANO) of pharmaceutical wastewater showed the maximum reduction current of -2.81 mA as compared to the oxidation current as 0.65 mA. But they also revealed that the bio-electrochemical treatment operation of wastewater showed the maximum oxidation current of 24.98 mA in contrast to reduced current 23.25 mA.

The amount of current generation depends on the surface area of an anode, organic content, and the types of microorganisms. MFC is operated for 5 cycles up to 8 days. **Fig. 4** illustrated that the maximum open-circuit voltage (OCV) was recorded as 330 mV after 96 h (4 days) wastewater treatment by MFC. The initial OCV was measured as 134 mV after 8 h treatment that effectively increased up to 330 mV after 96 h treatment (4 days), but suddenly it decreased to 133 mV after 184 h treatment. Sun and co-workers revealed that the actual pharma wastewater contains much complexity as compared to acetate-containing wastewater because acetate acts as a simple substrate in the growth of electroactive bacteria [47].

Velvizhi and Mohan [48] revealed that the maximum 242 mV production of OCV with 54.28 mW/m^2 power density was achieved with DSW (designed synthetic wastewater) as a substrate during pharmaceutical wastewater treatment by a single-chambered MFC (Perspex glass). They also reported that the production in open-circuit voltage (OCV) and power density increased as 290 mV and 118.89 mW/m^2 by increasing the organics load, this may be due to the availability of higher substrate for the anodic biocatalyst that improved the anolyte conductivity. The current efficiency (mA), power (mW), and voltage (mV) were evaluated up to five operating cycles, and each cycle comprises for 4 days. Each parameter was recorded after every 8 h.

The maximum amount of current generation in the first, second, third, fourth, fifth cycle was achieved as 1.94, 2.13, 2.35, 2.56, 2.76 mV, respectively as presented in **Fig. 5** and **Fig. 6,** which illustrates the production of voltage during PIW treatment in MFC. The maximum voltage in the first cycle was recorded as 194 mV, followed by 213, 235, 256, and 276 for second, third, fourth, and fifth cycles respectively. The results clearly showed that the overall maximum voltage as 276 mV was produced in the 5^{th} cycle after 440 h treatment. The current and voltage that are produced during the five cycles are the function of biofilm growth, which depends on the thickness of the biofilm. The more thickness of biofilm, the more will be the current and voltage produced. As the biofilm thickness increases on the anodic surface, the current and voltage produced also increase, which is called the electroactive enrichment.

Similarly, **Fig. 5** illustrate the production of power, the maximum power during the 1^{st}, 2^{nd}, 3^{rd}, 4^{th} and 5^{th} operated cycle was achieved as 0.37, 0.45, 0.55, 0.65 and 0.76 mW respectively. These results are also in agreement with previous reported MFC and conventional methods for pharmaceutical wastewater treatment. Huggins et al., [49] reported that graphite made

microbial fuel cell (aeration reactor) generated the maximum power of 0.36 Wh equivalent to 24 Wh per cubic meter pharmaceutical wastewater treatment followed by 135 mV voltage and 193 mA/m^2 power density production. Naik et al., [35] demonstrated that duel chambered MFC effectively produced the voltage of 0.8 V for 144 h treatment of wastewater. They reported that the maximum 68 mA current was also produced till 168 h.

3.2.1. Power and current densities

In MFC, some amount of total produced power can be lost more than one source, that can minimize the total ideal voltage production, and cause activation and concentration losses, which are termed as internal resistance [50]. Internal resistance was calculated by using the polarization curve. The polarization curve was drawn by varying the external resistance from OCV (open circuit voltage) to the SCV (short circuit voltage) when a steady state of voltage was reached across 100 **Ω** resistance. The internal resistance of the MFC was equal to the external resistance when maximum power density reached (1.47 W/m^3) or by the slope of the V-I graph ($R=\Delta V/\Delta I$).

The polarization curve was recorded at the end of two cycles (1^{st} and 5^{th} cycle) with the external resistance of 10 to 30 k**Ω**. The polarization curve which was recorded during the first cycle, gives the maximum power density of 1.47 (W/m^3), with a maximum current density of 37.18 (mA/ m^2) across 197 **Ω** resistor, as the internal resistance of the MFC in the first cycle was recorded 197 **Ω**, as shown in **Fig. 7**. Initially, the power density increased from 0 to 1.47 W/m^3 but after it starts to decrease from 1.47 to 1.15 W/m^3 but current density increased from 0 to 146.5 mA/m^2 with reducing the resistance from 3000 to 10 **Ω**. **Fig. 8** demonstrate the production of current density and power density. The polarization curve which was recorded during the 5^{th} cycle gives the maximum power density of 2.01 (W/m^3), a maximum current

density of 168.05 (mA/m^2) across 99 **Ω** resistor, as the internal resistance of the MFC in 5^{th} cycle was recorded 99 **Ω**, as presented in **Fig. 8**.

The overall findings indicate that the maximum power and current densities of about 2.01 W/m3 and 168.05 mA/m2 were achieved after the 5^{th} operation cycle of MFC in PIW treatment, which may be due to the availability of acetate as a substrate that gives more biodegradability. Velvizhi and his co-workers showed that bio-electrochemical treatment (BET) operation of pharmaceutical wastewater generated a maximum of 81.67 mW/m^2 and 371 mA/m^2 power density (PD) and current density (CD) respectively at lower organic load. They stated that total PD (157.60 mW/m^2) and CD (508.60 mA/m^2) production increased by increasing the organic load. They also reported that the anaerobic operation of pharmaceutical wastewater treatment only produced current with electron membrane assembly during bio-electrochemical analysis [46].

Chang et al. [51] reported that the maximum power density (PD) and coulombic efficiency (CE) of about 162.74 mW/m^2 and 7.09% were recorded after 8 h of HRT (hydraulic retention time) by MFC (plain-graphite plate) during pharmaceutical wastewater treatment containing PPs. They also revealed that the total PD and CE production decreased to 29.12 mW/m^2 and 2.23% respectively after 5 h HRT in sewage water. Nayak and his research group reported that the MFC wastewater treatment system generated the maximum power density of about 560.81 mW/m^2 and voltage of about 610 mV after 21 day treatment [52]. The power density of paraboloid shaped-designed MFC is the function of the cathode surface area (0.023 m^2), electrode spacing, and the growth of biofilm. The spacing between the electrodes was 6 mm. The polarization curves during all the five cycles show that the volumetric power density has increased from 1.46 to 2.01 W/m^3 and reduced the internal resistance from 197 to 99 **Ω** due to

the enrichment of the biofilm. Under the current scenario of environmental pollution [53, 54], there is serious need to develop and apply eco-green technologies [55] to tackle the pollution [56] therefore, microbial fuel cells could be an excellent options for the treatment of diverse type of wastewater micropollutants as well as to generate bioelectricity.

4. Conclusions

With the growing world population, the environmental regulatory agencies have put the researchers on the way to evolve or to present some unique methods and technologies for the better development of human beings. In the present study, the novel graphite-based paraboloid shaped Microbial Fuel Cell (MFC) was built to treat the pharmaceutical wastewater and generate electricity. The MFC analysis was performed up to five operating cycles for 8 days for the treatment of pharmaceutical industrial waste. The newly designed, truncated paraboloid MFC gives a higher surface area of about 0.023 m^2 per unit volume with the minimum electrode spacing which was found to be the feasible and favourable technology for energy production and wastewater treatment. The results demonstrated that the MFC analysis significantly reduced the COD and TDS of pharmaceutical wastewater of about 80.55 and 35.23% respectively. The cyclic voltammetry findings reported that the truncated paraboloid MFC successfully generated a power density of 2.01 W/m^3 along with reducing the internal resistance from 197 to 99 Ω after the five operating cycles. The MFC technique effectively generated the maximum open-circuit voltage (OCV) of 330 mV after 96 h treatment, followed by current, power, and voltage of about 2.76 mA, 0.76 mW, and 276 mV after 440 h treatment respectively. Moreover, biofilm development during the five cycles with reducing the internal resistance along with COD removal and substrate degradation rate showed the upscaling viability of the microbial fuel cell (MFC) also at the commercial level. However, it is recommended that the current density and the power density should be increased, by using the natural or the synthesized mediators, these mediators might increase the electron extract ratio

from the cell of microbes. In pharmaceutical industrial wastewater along with various organic chemicals, the effluent also contains antiseptics. So, it is also suggested that researchers should have to work on these antiseptics, for enhancing the efficiency of the microbial fuel cell (MFC).

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List of Tables

682 **Table.1.** The COD removal, OLR, and SRD efficiencies of pharmaceutical wastewater
683 treatment by MFC after five operating cycles.

Cycle	$COD_{initial}$	COD_{final}	CRE (%)	HRT (day)	OLR (kg COD/m^3 day)	SDR (kg COD/m^3 day)	COD_R
1	5460	3990	26.92	4	1.37	0.37	1470
2	5460	2980	45.42	4	1.36	0.61	2480
3	5460	2100	61.54	4	1.35	0.83	3360
4	5460	1500	72.53	4	1.35	0.97	3960
5	5460	1060	80.58	4	1.36	1.09	4400

684 COD: chemical oxygen demand; OLR: organic loading rate; SDR: substrate degradation rate;
685 CRE: COD removal efficiency.
686

687 **Table.2.** The TDS percentage removal efficiency of pharmaceutical industrial wastewater
688 (PIW) by MFC up to five operating cycles.

Cycle	$TDS_{initial}$	TDS_{final}	TDS_R	TDS removal (%)
1	800	530	270	33.75
2	800	521	279	34.87
3	800	528	272	34.00
4	800	515	285	35.62
5	800	536	264	33.00

689 TDS: Total dissolved solids.

690

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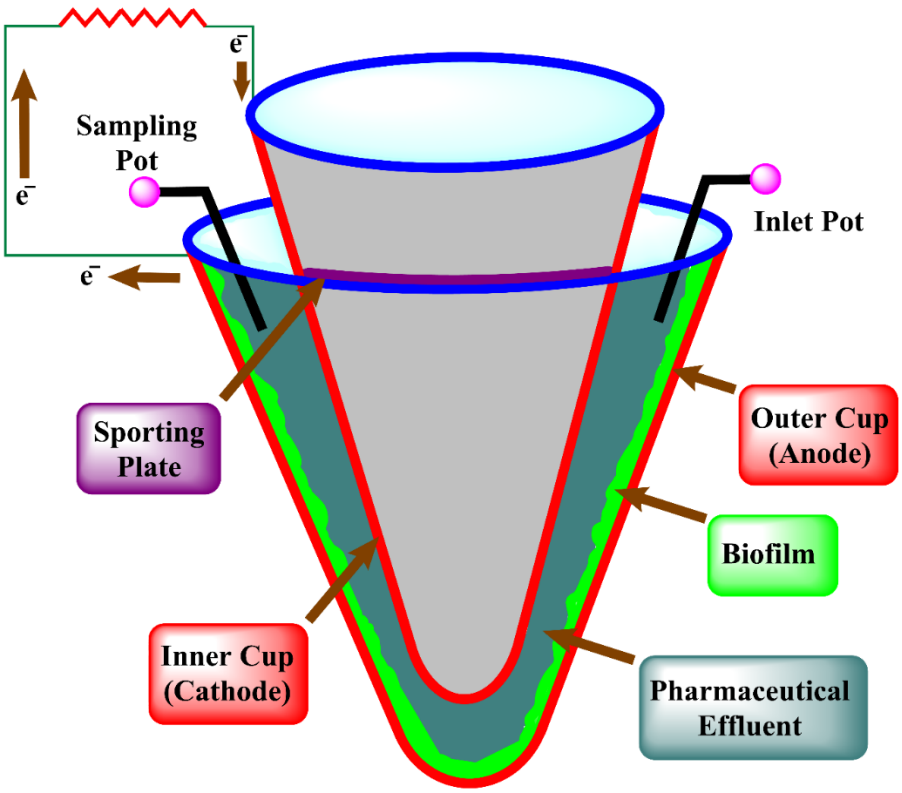

711

712 **Fig. 1.** The novel configuration of graphite-based paraboloid microbial fuel cells for
713 pharmaceutical wastewater treatment and bioelectrogenesis.
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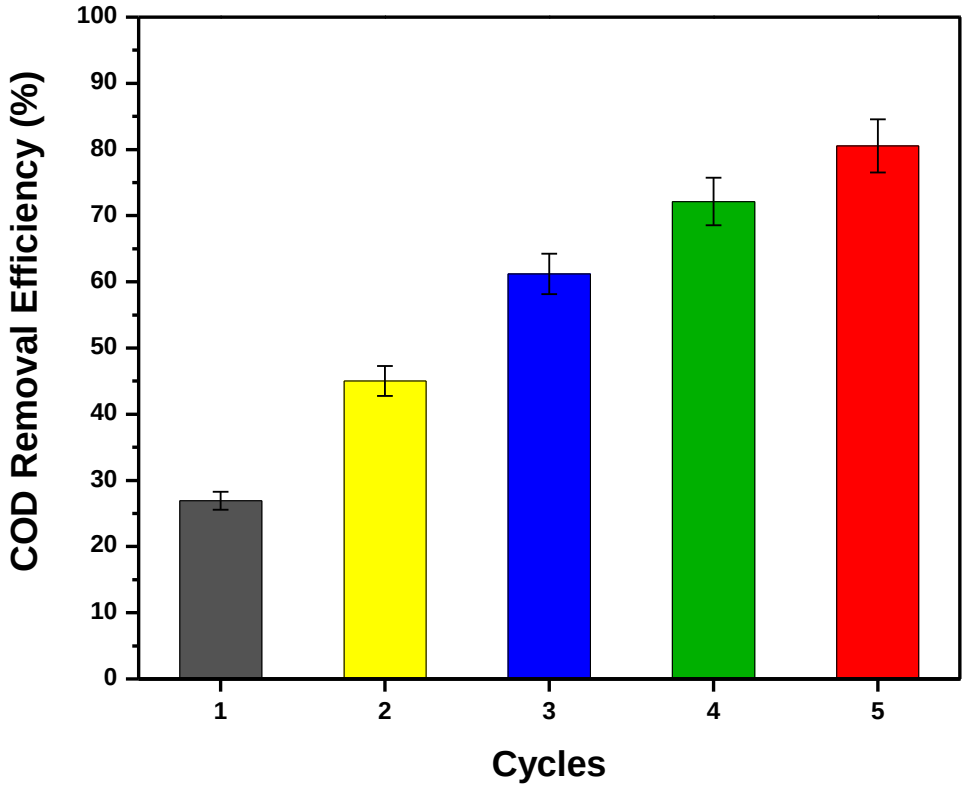

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716 **Fig. 2.** The COD percentage removal efficiency of pharmaceutical wastewater by MFC up to
717 five operating cycles.
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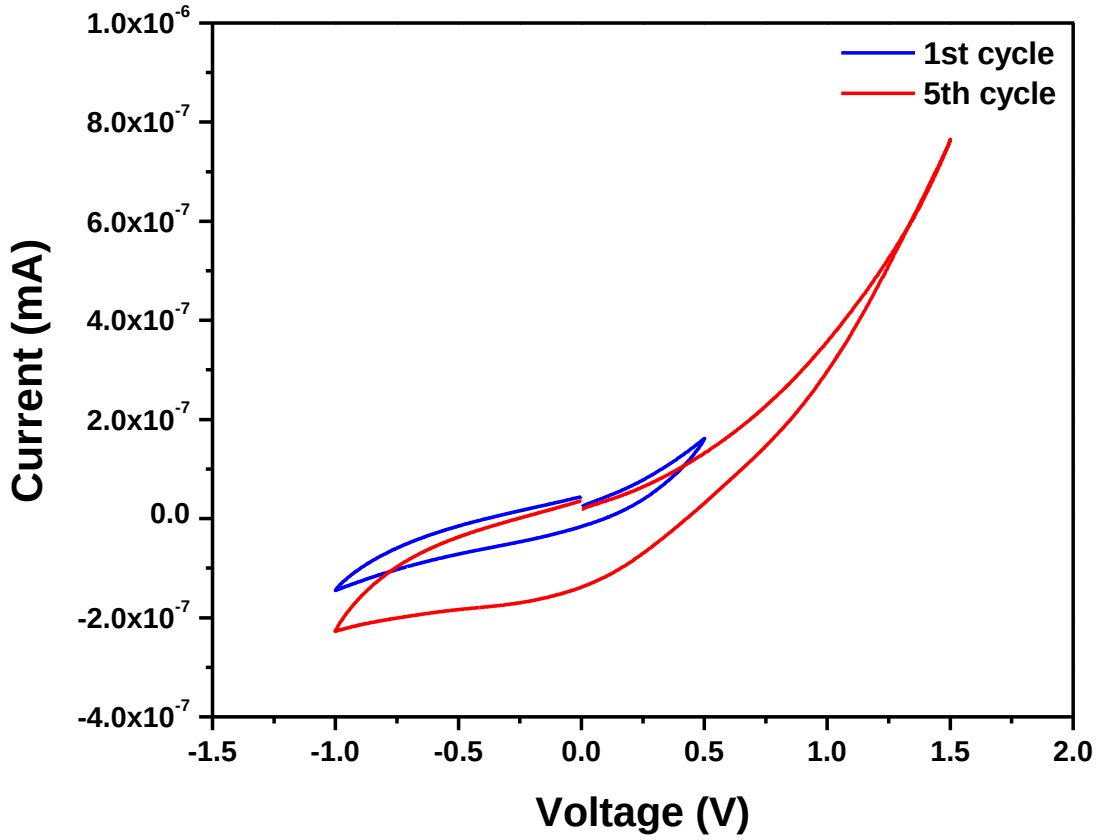

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720 **Fig. 3.** The cycle voltammetry analysis of PIW during the 1st and 5th operating cycles by MFC

721 at bacterial biofilm.

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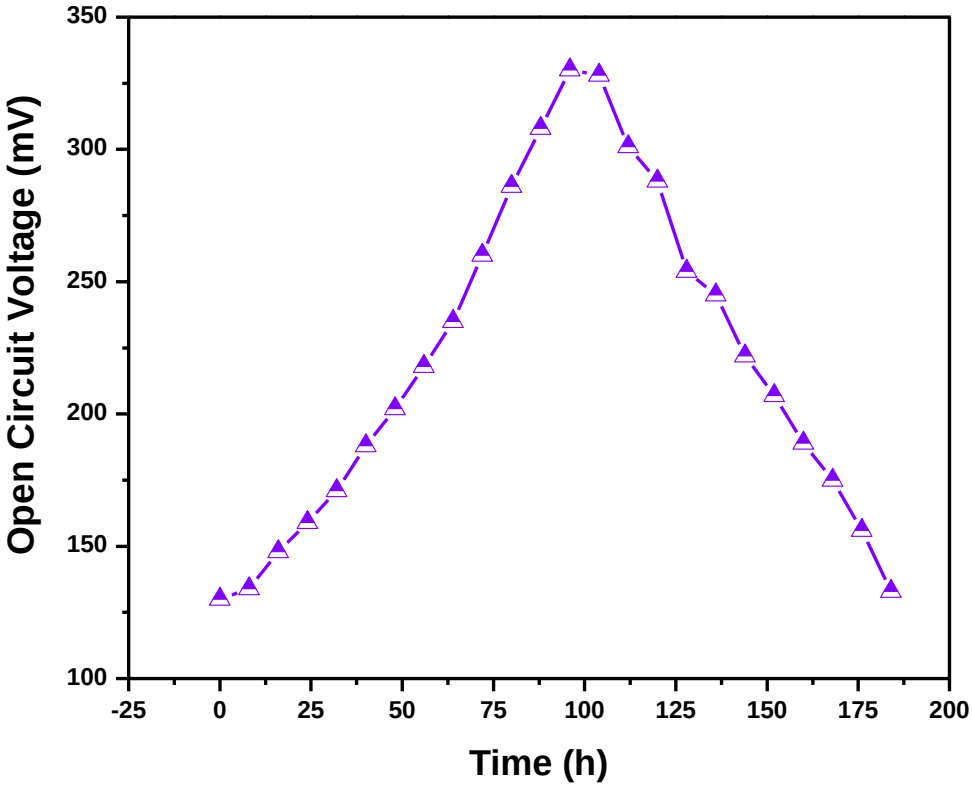

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724 **Fig. 4.** The open-circuit voltage (OCV) generation during the municipal solid wastewater
725 treatment by a microbial fuel cell.
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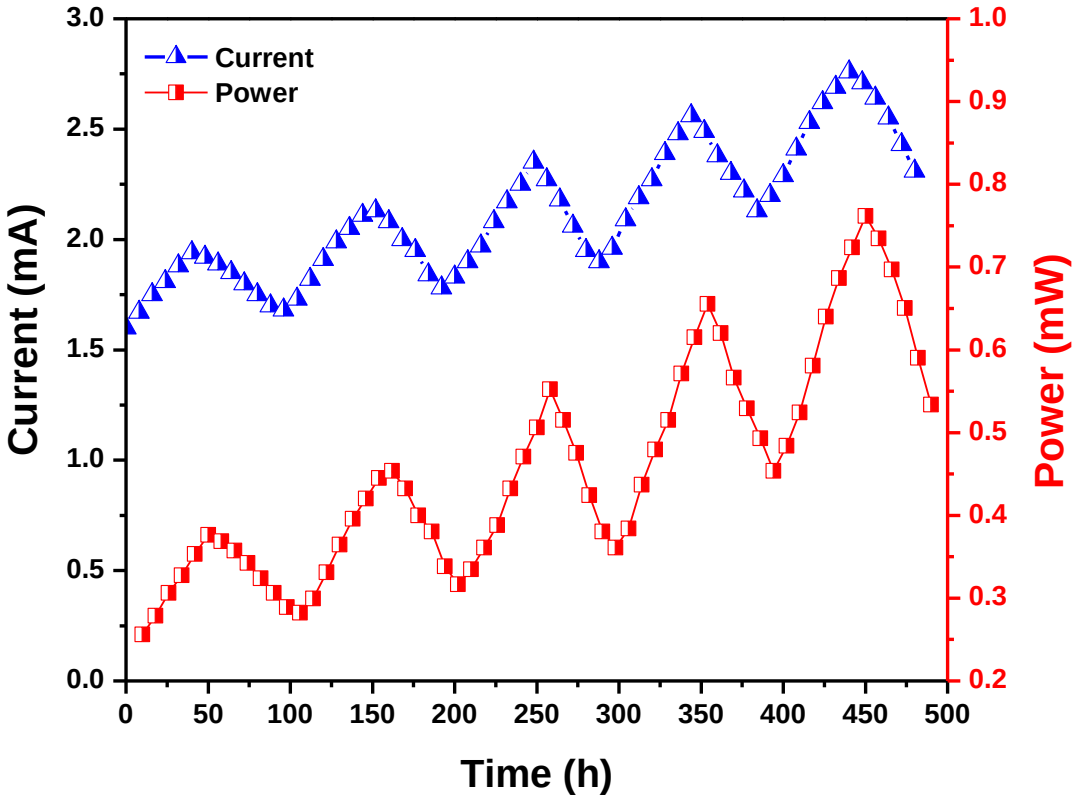

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728 **Fig. 5.** The power and current generation with time during the municipal solid wastewater
729 treatment by microbial fuel cell after five operation cycles.
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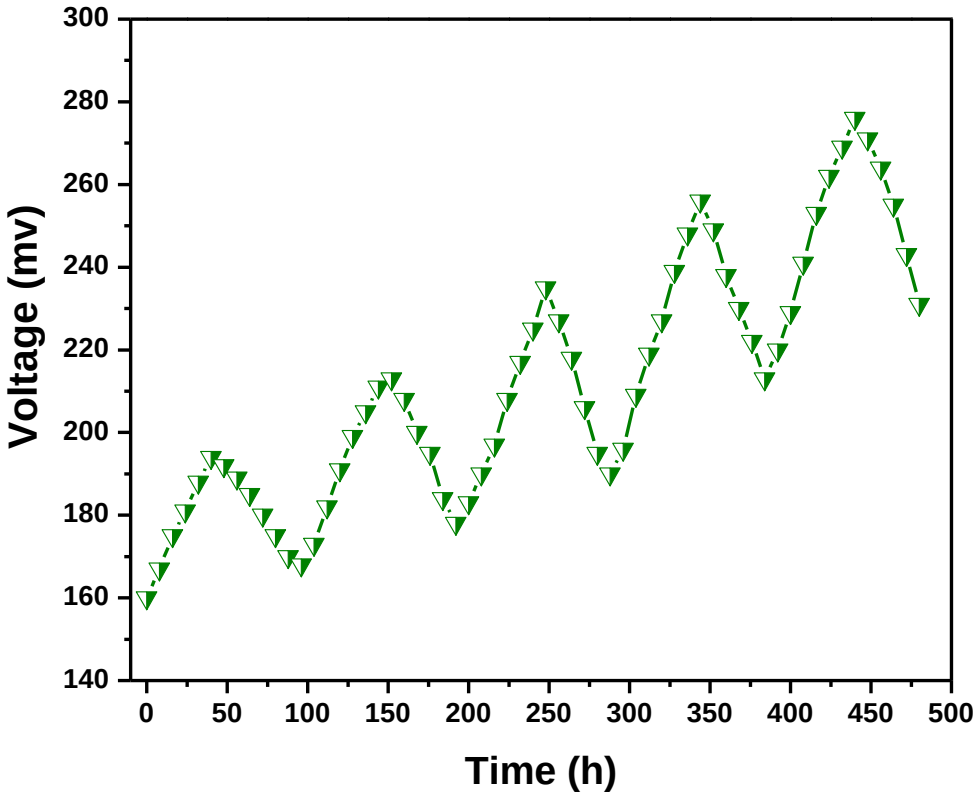

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732 **Fig. 6.** The total voltage production after five operation cycles during the treatment of PIW by
733 MFC up to 492 h.
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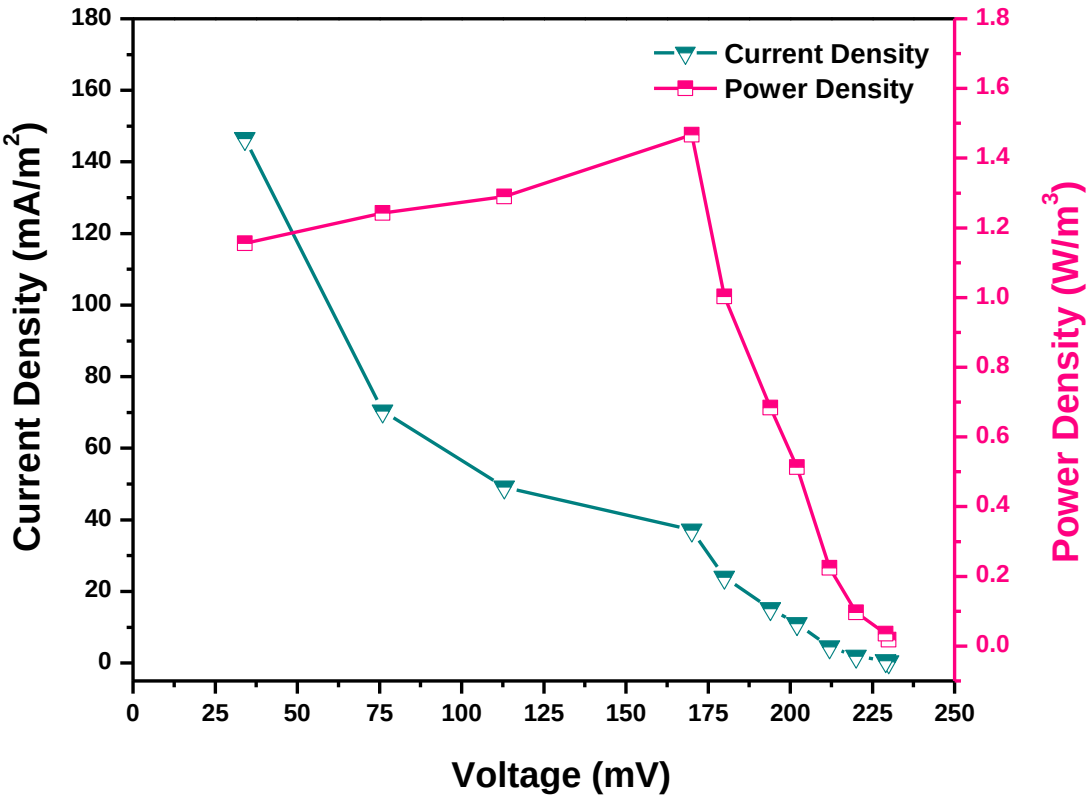

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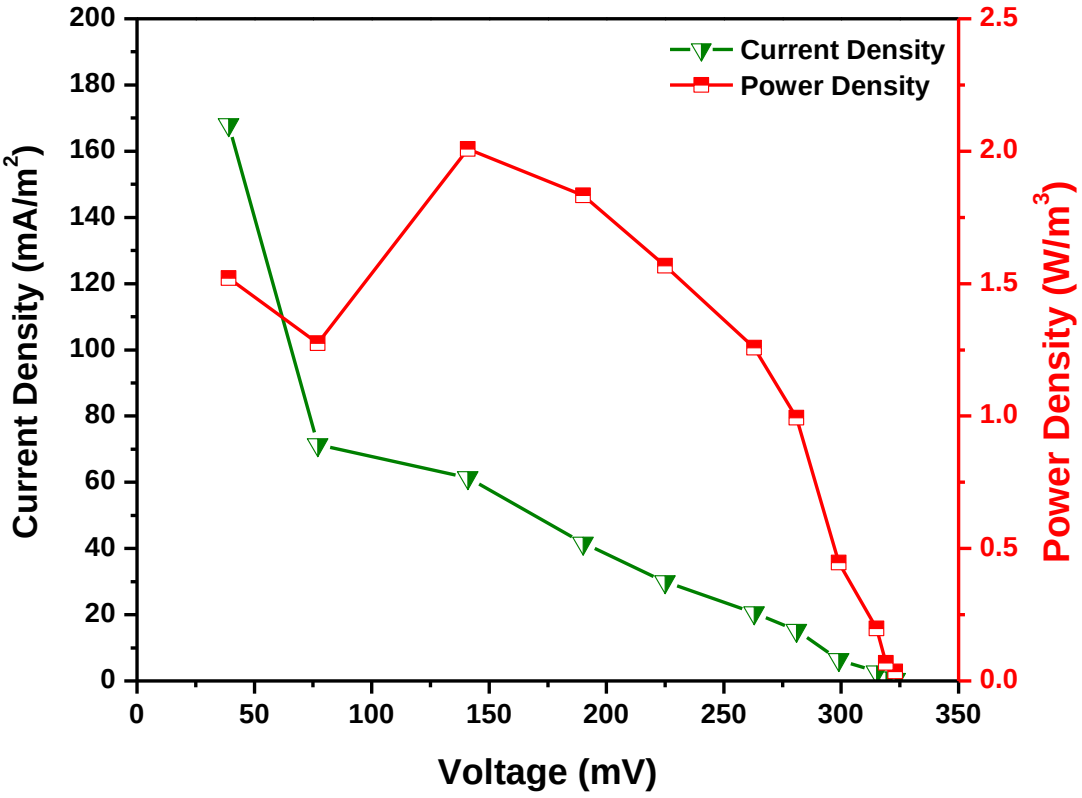
736 **Fig. 7.** The production of power density, current density, and voltage by the 1st operation cycle
737 during the bioelectrogenesis of PIW by MFC.
738



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740 **Fig. 8.** The production of power density, current density, and voltage by the 5th operation cycle
741 during the bioelectrogenesis of PIW by MFC.
742