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SUSTAINABLE INDUSTRIAL AND ENVIRONMENTAL BIOPROCESSES

Simultaneous bioelectricity generation from cost-effective MFC and water treatment using various wastewater samples

Sweta Naik[1] · Satya Eswari Jujjavarappu[1]

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Abstract

Worldwide, the requirement of electrical energy has increased with an increase in population. Thus, there is a need to develop an alternative source of sustainable energy, such as microbial fuel cell (MFC). MFC is a better option of energy generation and can provide a renewable resource which utilizes wastewater into power by the help of microorganisms. MFC is one of the advanced methods for treating wastewater and simultaneously producing current and voltage. Dual-chambered MFC was prepared using two plastic boxes (500 ml) by using wastewater as an anolyte. Different types of mediators are used in MFC including methylene blue, potassium ferricyanide, and EDTA to facilitate and higher the efficiency of electron transfer from the MFC to the electrode. Maximum OCV and current output of sample 1 (Budha Talab pond water) were 0.86 V and 75.1 mA and of sample 2 (Jaypee cement plant) were 1.42 V and 122 mA. The maximum current output of sample 3 (sugar industry, sewage waste, NIT canteen) was 1.3 V. Various physiochemical parameters such as dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) were analyzed which affect the power output. The obtained result concluded that wastewater should be feed at a certain time interval to avoid the loss of substrate for organisms in the anodic chamber which lead to the death of the microorganism. Among all, sugar industry wastewater has a high potential for power generation as their physiochemical results are suitable for better power output.

Keywords Salt bridge · Electrical energy · MFC · Wastewater treatment · Mediators · DO · BOD · COD

Introduction

Nowadays, renewable energy for sustainable development is one of the major concerns as the demand and need for energy is increasing day by day which is much greater than the produced energy. Various traditional wastewater treatment methods are available but it was assessed that approximately 9 times more energy is needed to treat the wastewater than its amount (Dannys et al. 2016). Therefore, novel renewable energy sources and technologies should be developed with high energy potential and significant benefit. MFC technology allows the generation of electricity along with wastewater treatment. MFC uses electrogenic microbes from wastewater to oxidize the organic compounds present in the water and separate electron from protons. The electrons move through the anodic chamber to the external circuit for the current generation. The separated protons move through the proton-exchange membrane (PEM) or salt bridge in the cathodic chamber where they combine with the electrons to form water. In order to control pollution and discover a novel energy source, MFC technology can be suggested (Rahimnejad et al. 2015; Rahimnejad et al. 2015). For electricity generation, MFCs can provide a better option in terms of high efficiency, safe, clean, and quiet performance. MFC with wastewater treatment has the potential benefits for the environment, specifically to decrease stress on wastewater treatment facilities. MFC technology benefits from the natural metabolism of man microorganisms present in the wastewater for power generation (Dannys et al. 2016). To resolve these challenges, this work is proposed to provide an inexpensive energy source with high yield efficiency for energy generation. Prasad et al. (2015) studied the removing efficiency of contaminants through MFC. It was observed that organic matters present in wastewaters can be used for bioelectricity generation and simultaneous wastewater treatment. It was found that for

Responsible editor: Philippe Garrigues

✉ Satya Eswari Jujjavarappu
satyaeswarij.bt@nitrr.ac.in; eswari_iit@yahoo.co.in

[1] Department of Biotechnology, National Institute of Technology Raipur, Raipur, India

removal of TDS, TSS, BOD, COD, sulfates, and chlorides from wastewater, MFC is a very effective and cheaper method. The batch-type anaerobic treatment plant was constructed for the treatment of wastewater from the pharma industry. After every 72 h, treated samples were collected for testing their pH, TSS, TDS, COD, BOD, sulfates, and chlorides to calculate the productivity of the plant. The results showed that COD was reduced to 91.5% and a small quantity of 335 mV was produced. The study revealed that MFC was successful in treating the pharma industry wastewater and microbes present in the wastewater for the removal of COD, BOD, and other parameters (Prasad et al. 2015). Harshitha et al. (2019) used fabricated MFC for voltage production with different biowastes such as cow dung, sludge, and soil mixture in the anode chamber. They also studied the changes in voltages created by using varied pH, organic matter, length of time, and temperature on the MFC. Salts of different concentrations were used in the salt bridge-like sodium chloride, sodium bicarbonate, and sodium carbonate. Around 230 mV of voltage was generated by using 0.85% of cow dung in a solution of drain water; the same composition with respect to time and temperature showed a voltage output of 223 mV and 215 mV. Similarly, 330 mV of voltage was generated using a pH solution of 1 M Na2CO3 salt. The above data support further use of this MFC in the process of electricity generation from wastewater (Harshitha et al. 2019).

Nayak et al. (2018) prepared H-type two-chamber MFC by using sewage wastewater and distillery wastewater to investigate its efficiency. Microalgae (*Scenedesmus abundans*) were used for the generation of electricity. This study showed a higher power density of 836 mW/m^2 and OCV of 745.13 mV. On degrading organic and inorganic compounds, CO_2 will be produced which can be consumed by microalgae for growth and oxygen generation at the cathode. The adaptation of algae and bacteria separately in both chambers and high dilution of organic distillery wastewater with sewage wastewater have increased the efficiency of MFC. Their study recommends that high power generation by MFC can be fulfilled by adequate dilution of distillery wastewater and suitable condition for microalgal growth (Nayak et al. 2018). Rahman et al. (2018) used sugar beet plant wastewater in MFC for power generation. No catalyst was used and cheap materials were used for MFC construction. After several dilutions of the raw wastewater, it was fed in batch mode and a power density of 14.9 mW/m^2 was observed. In the anodic chamber, methanogenesis, fermentation, and diffusion of oxygen by cation exchange membrane are taking place, which shows the Coulombic efficiency (CE) of 6.21% to 0.73%. An active microbial consortia community was found on the anode by scanning electron microscopy (SEM), which was responsible for wastewater treatment and electricity generation. This study confirmed that in MFC, sugar beet processing wastewater can also be used to generate electricity as well as for pollutant removal (Rahman et al. 2018). Mahendra and Mahavarkar (n.d) studied dairy and domestic wastewater and compared it with the single-chamber (MFC-1) and double-chamber (MFC-2) for electricity generation. A 0.84 mA and 1.02 mA current were produced by MFC-1 and 0.84 mA and 1.02 mA of current by MFC-2 from 100% domestic and dairy wastewater concentrations; this showed that MFC-1 is more efficient than MFC-2 (Mahendra and Mahavarkar n.d). Samuel (2013) constructed soil MFC and used dye industrial effluent soil and agriculture soil samples for bioelectricity generation. 0.93 V electricity was generated for 650 h by dye industrial effluent soil whereas 0.82 V for 400 h by agricultural soil. It was found that, in the industrial dye, effluent soil has active and high electrogenic bacterial anode community, which increased the efficiency of soil MFC and was able to produce electricity for continuous 650 h. This showed the significance of soil type in MFC bacterial communities and will help in future research for long-term electricity production by soil MFC (Samuel 2013). Luo et al. (2017) aimed to investigate MFC in alkaline conditions using yogurt wastewater as a substrate for electricity production. A single-chamber air cathode MFC was used, and the pH of 10.5 was maintained. A maximum power density of 1043 ± 100 mW/m^2 was observed. The NH_4-N and COD removal efficiencies were more than 87% and 74%, respectively. There was a decrease in electricity production and the viability of bacteria also decreased in anode biofilm, as there was an increase in internal resistance and COD concentration. These results expressed that more research has to be done for the application of MFC in alkaline conditions (Luo et al. 2017). Abdul and Beigh (2016) prepared MFC with sewage sludge as the substrate which is rich in high organic compounds and is today's major environmental pollution source. *Saccharomyces cerverciae* sp. is used as a biocatalyst for the conversion of sewage sludge into electric current and methylene blue as a mediator. Agarose concentrations in the salt bridge were changed to check the efficiency of MFC. Agarose salt concentration ranging from 7 to 12% was used, only 10% concentration gave the best noticeable voltage generation of 0.97 V and a current of 0.98 mA. Thus, it shows that to increase voltage generation, the optimal concentration of agarose should be used to make the salt bridge (Abdul and Beigh 2016).

Aswin et al. (2017) prepared an economical MFC experiment in two phases. In the first phase, no mediators were used in dairy and leather effluent as a substrate, and in the second phase, ferroin as a mediator is used in dairy, leather, and sewage wastewater as the substrates with ferroin. MFC is using *Saccharomyces cerevisiae* for the treatment of effluent; its physiochemical characteristics such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), and total suspended solids (TSS) were determined before and after treatment. In the first phase, BOD and COD removal

were found to be 64.3% and 83.4% for dairy and 59.3% and 80.4% for leather effluent, and in the second phase, BOD and COD removal efficiency were found to be 47% and 65% for domestic wastewater, 79% and 85.4% for dairy effluent, and 64% and 80% for leather effluent. Dairy and leather wastewater produced a maximum power of 385.25 μW and 304.5 μW in the first phase and in the second phase; domestic, leather, and dairy wastewater generated 1.28 mW, 1.95 mW, and 1.98 mW of power. In both phases, the power generated during the treatment of dairy wastewater is more. The results showed that dairy wastewater is producing more electrons as it is being degraded efficiently compared with domestic wastewater and leather effluent (Aswin et al. 2017). MDC and TMN (2017) successfully represent that the MFC can be used for off-grid electricity generation and for treatment of wastewater. Stainless steel was used as electrode and the proton-exchange membrane was Agar-NaCl salt bridge, which produced 37.651 μW of power and 0.0677 W of electricity. Various parameters were measured like TDS, BOD, COD, EC, and oil and grease which are 72.66%, 90.63%, 93.98%, 73.06%, and 83.82%; this showed the efficiency of the water treatment (MDC and TMN 2017). Sanath Kondaveeti et al. prepared two types of MFC, i.e., single-chambered and dual-chambered. The entire study of MFC had taken place in three different stages. They got maximum current of up to 545 mV in single-chamber MFC and 643 mV in dual-chambered MFC. In single-chambered MFC, the maximum COD removal was up to 55.25% and 60.63% in the dual-chambered MFC in the first phase compared with others (Kondaveeti et al. 2019).

Lastly, it can be concluded that for the treatment of dairy waste and energy production simultaneously, MFC is the best. In this study, we have prepared MFC using five types of wastewater, i.e., from Budha Talab pond water, sewage waste, wastes from a local sugar industry and National Institute of Technology canteen located at Raipur, and Jaypee Cement plant at Durg; we have analyzed all the wastewater treatment physiochemical parameters which affect the power output.

Experimental methodology

Wastewater sampling from various sources

Sample 1 (Budha Talab pond water)

The wastewater samples were collected from Budha Talab pond water, located at Raipur (21.2514° N, 81.6296° E) district, Chhattisgarh, India, and stored at room temperature. The physicochemical characterization of waste samples was performed by the reported method detailed and given in APHA, 2005 (Eaton et al. 2005).

Sample 2 (Jaypee Cement Plant)

The wastewater samples were collected from Jaypee Cement Plant, located at Durg (21.1904° N, 81.2849° E) district, Chhattisgarh, India, and stored at room temperature. The physicochemical characterization of waste samples was performed by the reported method detailed and given in APHA, 2005 (Eaton et al. 2005).

Sample 3 (sugar industry, sewage waste, NIT canteen)

The wastewater samples were collected from sewage waste and wastes from a local sugar industry and from the National Institute of Technology canteen located at Raipur (21.2514° N, 81.6296° E) district, Chhattisgarh, India, and stored at room temperature. The physicochemical characterization of waste samples was performed by the reported method detailed and given in APHA, 2005 (Eaton et al. 2005).

MFC construction

Generally, MFC consists of two chambers, i.e., anode and cathode chambers, two electrodes as an anode and cathode, and a salt bridge. The anodic chamber contains a substrate and biocatalyst at the anaerobic condition. The aerobic environment is maintained at the cathode chamber. The salt bridge acts as a bridge between the anodic and cathodic chamber and enables the transfer of protons. Graphite sheet and carbon cloth were used as electrodes in anodic and cathodic chambers, respectively. Schematic representation of MFC is illustrated in Fig. 1.

Methodology for water sample 1 (Budha Talab)

MFC setup preparation

Two-chambered MFC was prepared by using two plastic boxes. Two plastic boxes of 500 ml capacity each with a diameter of 9 cm were taken and marked as an anode and cathode. The volume of cathodic and anodic chamber was 508.94 cm^3 (r = 4.5 cm and h = 8 cm). A hole with a diameter of 2 mm was made on each lid for the insertion of electrodes. In the anodic chamber, 300 ml of wastewater as an anodic inoculation was used whereas 300 ml of potassium hydroxide solution was used as a cathodic solution in the cathodic chamber. A hole with a diameter of 3 cm was made in the middle of each of the plastic boxes to attach a salt bridge, linking the anodic and cathodic chamber. To maintain anaerobic condition, the anodic chamber was closed air-tightly and sealed with tape and hot glue gun as shown in Fig. 2. A total of four setups were prepared.

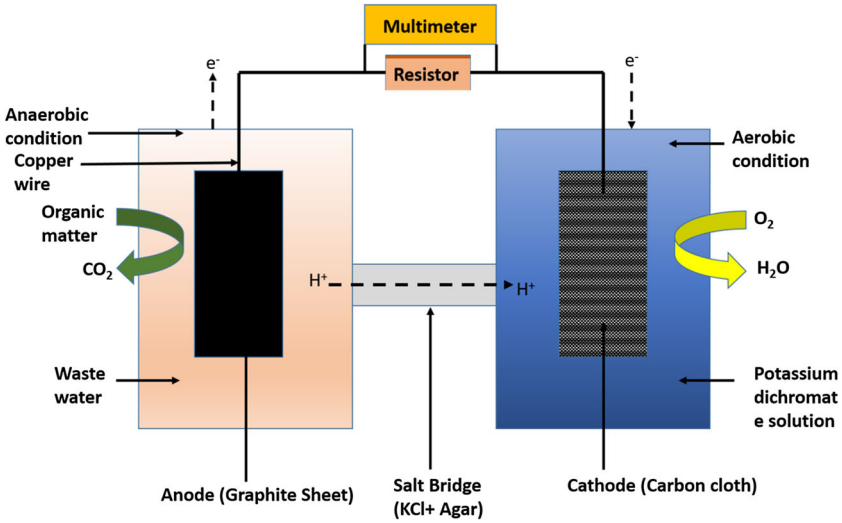

Fig. 1 Schematic representation of dual-chambered microbial fuel cell

Salt bridge preparation

The salt bridge was prepared by using potassium chloride and 5% agar, which was boiled for 5–10 min. The solution was then sucked into a falcon tube having a diameter of 3 cm and allowed to solidify. The prepared salt bridge was then inserted into the corresponding MFC set up and sealed with a hot glue gun.

Electrodes used as anode and cathode

Graphite sheet (1 cm × 1 cm) was used as the electrode at the anodic chamber and carbon cloth (1 cm × 1 cm) as an electrode at the cathodic chamber to collect electrons. Copper wires were used to connect the electrodes on each side of the chamber. These electrodes were preferred as they are cost-effective and easily available. Before use, electrodes were decontaminated with 100% ethanol, 1 M HCl, followed by 1 M NaOH each, kept for 1 h to neutralize to remove the probable contaminants, and stored in distilled water. A 100 Ω resistor was connected to both anode and cathode copper wires.

Anodic and Cathodic Chamber All the waste samples were prepared by adding 3 gm/l glucose to 300 ml of waste. This was transferred to the anodic chamber with an aerobic condition. Approximately 10-ml waste sample containing 1% glucose was replaced in the anodic chamber at an interval of 3 days. The first setup was for control, in the second, third, and fourth setup, mediators were added and they were methylene blue, potassium ferricyanide, and EDTA (100 μm). In the cathodic chamber, 300-ml KOH solution was added.

Electrical measurements The MFC voltage was noted against time by a digital multimeter (Mastech DT830D, India) after every 24 h. The current was calculated by using Ohm's law $V=I \times R$, where V is the voltage across the resistance connected to the electrodes, I is the current generated, and R is the external resistance

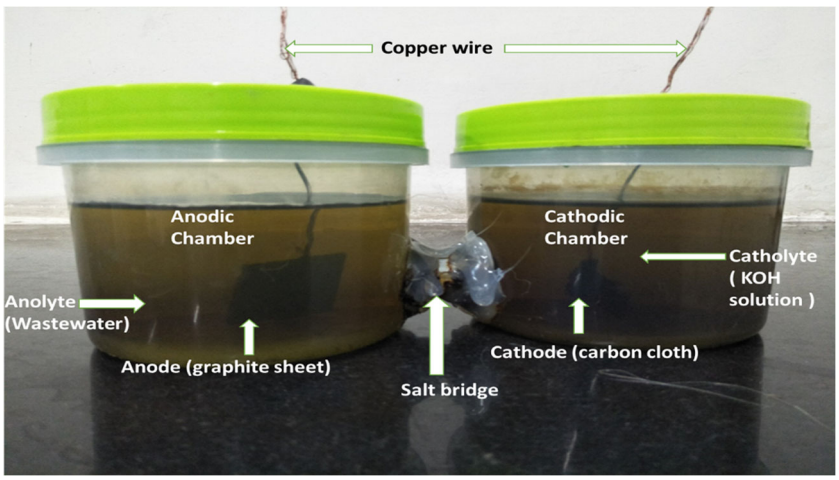

Fig. 2 Laboratory scale MFC system setup

Physicochemical parameters of wastewater The wastewater sample was analyzed for various physicochemical parameters such as dissolved oxygen (DO), biochemical oxygen demand (BOD), and chemical oxygen demand (COD). These parameters were measured by SensoDirect-150 multimeter instrument and by using Winkler's method and closed refluxed method (Shriwastav et al. 2010).

Methodology for water sample 2 (Jaypee Cement Plant)

The methodology is the same as the abovementioned water sample 1. In these three setups made, the first setup was control and the other two setups have methylene blue and potassium ferricyanide (10 mm) as mediator.

Methodology for water sample 3 (sugar industry, sewage waste, NIT canteen)

The methodology is the same as the abovementioned water sample 1. In these three setups made, these setups are control of the sugar industry, sewage, and NIT canteen.

Results

Analysis of results for water sample 1 (Budha Talab)

Voltage and current generation in an MFC

The voltage of sample A was constant till 144 h but after that, there was a sudden increase in voltage and we got the maximum voltage of up to 0.8 V as shown in Fig. 3a. In sample B, there is a sudden increase in voltage till 24 h but that there is a drop in voltage which could be due to feeding after every 24 h and then there is a very slow increase in voltage. In sample C, the highest voltage was at 144 h, i.e., 0.72 V; there is a very slow rise and drop in the voltage. In sample D, there is a constant voltage at every fed time, and after 168 h, there is a vigorous increase of 0.86 V in the voltage. The voltage drops in samples B, C, and D; it could be due to the mediators, and the chemicals might be inhibiting the microbial growth. The current of sample A is rising slowly and at a maximum current of up to 68 mA till 168 h but after that, it has decreased as shown in Fig. 3b. In sample B, the current has increased to 59.32 mA to 72 h, but after that, it has a constant current due to feed and changes in the organic content. In sample C, the current has increased up to 71.34 mA till 120 h after feeding but after that, it has decreased drastically. In sample D, the current has increased spontaneously till 74.23 mA to 96 h and after that, the current has remained constant. The current drops in samples B and C which may be due to the fact that wastewater was not supplied at regular intervals which lead to the loss of substrate for microorganisms to feed on and hence resulting in the death of organisms.

Current density and power density

Current density is defined as the amount of current flowing through per unit area. Here, the area of anode is taken, as all the biological activity takes place at the anode. Its formula is

$$J = \frac{I}{A}$$

where J is the current density, I is current, and A is the area of the anode. The current density of Budha Talab wastewater sample is given in Table 1. As the area of anode is 1 cm^2, the values of current and current density are similar.

Power density is defined as the amount of power generated per unit area. For the calculation of power density, the anode surface area is used because all the biological reactions like degradation and anion production happen at the anode (Logan and Schröder 2006). It's S.I. unit is W/m^3. Its formula is

$$P = \frac{I.V}{A}$$

where I is the current, V is the voltage, and A is the area of the anode surface. The power density of Budha Talab wastewater sample is mentioned in Table 2.

Effect of dissolved oxygen

DO analysis measures the quantity of free, non-compound oxygen (O_2) dissolved in wastewater. The dissolved oxygen is one of the essential parameters as it is directly correlated with the water bodies, microbial growth and activity, and their nutritional availability. The dissolved oxygen for sample A initially is 5.78 mg/l and after144 h, it was 1.70 mg/l. For sample B, the initial DO was 4.98 mg/l and after 144 h, it was 0.35 mg/l. For sample C, the initial DO was 5.23 mg/l and after 144 h, it was 1.25 mg/l. The DO for sample D was initially 5.19 and after 144 h, it was 1.40 mg/l. Low value resulted due to the consumption of oxygen during the decomposition of organic materials present in wastewater. This leads to the generation of high voltage and current (Oh et al. 2009).

Effect of biochemical oxygen demand

BOD is the amount of oxygen required for microbes in water. This requirement varies depending upon the temperature, concentration of nutrient, and availability of enzyme to the microbial populations. BOD can be defined as the amount of oxygen required to oxidize the organic compounds into carbon dioxide and water by microbial growth, decay, and death. The BOD value for all the four samples was initially 6.7 mg/l, 6.4

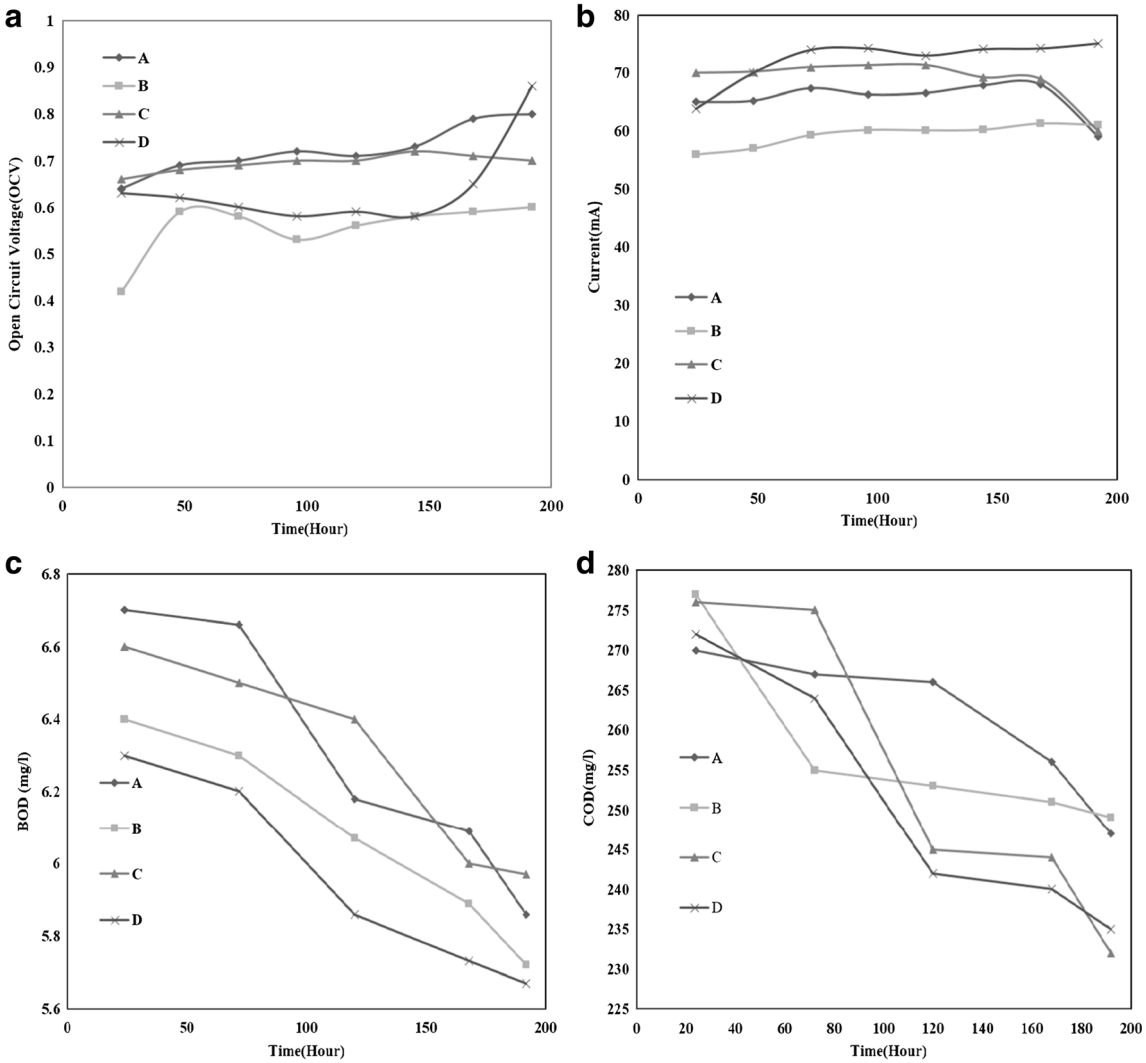

Fig. 3 **a** OCV of Budha Talab wastewater analyzed through MFC with different mediators. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. M FC setup with potassium ferricyanide as mediator. D. MFC setup with EDTA as mediator. **b** Current of Budha Talab wastewater analyzed through MFC with different mediators. A. Control (wastewater with no mediator). B. MFC setup with methylene blue mediator. C. MFC setup with potassium ferricyanide as mediator. D. MFC setup with EDTA as mediator. **c** BOD variation with respect to time. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as mediator. D. MFC setup with EDTA as mediator. **d** COD variation with respect to time. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as mediator. D. MFC setup with EDTA as Mediator

Table 1 Current density of wastewater from Budha Talab

Time (h)	A (mA/cm^2)	B (mA/cm^2)	C (mA/cm^2)	D (mA/cm^2)
24	65	56	70	63.8
48	65.23	57.012	70.2	70
72	67.39	59.32	71	74
96	66.28	60.19	71.3	74.23
120	66.56	60.12	71.34	73
144	67.89	60.23	69.2	74.11
168	68	61.29	68.9	74.23
192	59	61	60	75.1

Table 2 Power density of wastewater from Budha Talab

Time (h)	A (mW/cm^3)	B (mW/cm^3)	C (mW/cm^3)	D (mW/cm^3)
24	41.6	23.52	46.2	40.194
48	45.0087	33.63708	47.736	43.4
72	47.173	34.4056	48.99	44.4
96	47.7216	31.9007	49.91	43.0534
120	47.2576	33.6672	49.938	43.07
144	49.5597	34.9334	49.824	42.9838
168	53.72	36.1611	48.919	48.2495
192	47.2	36.6	42	64.586

mg/l, 6.6 mg/l, and 6.3 mg/l as shown in Fig. 3c. After 8 days, the value has decreased to 5.86 mg/l, 5.72 mg/l, 5.97 mg/l, and 5.67 mg/l. This indicates the rate of microbial activity and oxidation of organic matter present in the wastewater on to which the microbes can feed (Sagar 2015).

Effect of chemical oxygen demand

The chemical oxygen demand analysis defines the amount of oxygen required for oxidation of organic matter into carbon dioxide and water in the presence of a strong chemical oxidant. The COD is used to measure pollution of wastewater in terms of oxygen required for oxidation of organic matter. The COD value for all the four samples was initially 270 mg/l, 277 mg/l, 276 mg/l, and 272 mg/l as shown in Fig. 3d. After 8 days, the value has decreased to 247 mg/l, 249 mg/l, 232 mg/l, and 235 mg/l. This indicates the microbial function present in a waste sample in metabolizing the carbon source as an electron donor (Luo et al. 2017).

Analysis of results for water sample 2 (Jaypee Cement Plant)

Voltage and current generation in an MFC

The voltage of sample A is stable till 96 h and then there is a slight decrease in voltage and then a maximum voltage is measured at 192 h up to 1.42 V; after that, there is a drastic decrease as shown in Fig. 4a. Sample B shows a slow increase in voltage and a slight decrease; after that, there is a constant increase of up to 0.7 V. Sample C shows a decrease in voltage but after fed with glucose, it shows a maximum increase in voltage of up to 1.22 V and the voltage decreases, due to a decrease in substrate leading to the death of microbes. The voltage drops in samples A and C; it could be due to the mediators, and the chemicals might be inhibiting the microbial growth. The current of samples A and B in Fig. 4b shows a consistent current graph, both showing a maximum current of 15.51 mA and 32 mA after which the current decreases. Sample C in the figure initially shows a drop in current but after 96 h, it rises drastically up to a maximum of 122 mA and drops down. The current drop may be due to the fact that wastewater was not supplied at regular intervals which lead to loss of substrate for microorganisms to feed on and hence resulting in the death of organisms.

Current density and power density

Current density is defined as the amount of current flowing through per unit area. Here, the area of the anode is taken, as all the biological activity takes place at the anode. Its formula is

$$J = \frac{I}{A}$$

where J is the current density, I is current, and A is the area of the anode. The current density of Budha Talab wastewater sample is given in Table 3. As the area of anode is 1 cm^2, the values of current and current density are similar.

Power density is defined as the amount of power generated per unit area. For the calculation of power density, the anode surface area is used because all the biological reactions like degradation and anion production happen at the anode (Logan and Schröder 2006). It's S.I. unit is W/m^3. Its formula is

$$P = \frac{I.V}{A}$$

where I is the current, V is the voltage, and A is the area of anode surface. The power density of Budha Talab wastewater sample is mentioned in Table 4.

Effect of dissolved oxygen

DO analysis measures the amount of free, non-compound oxygen (O_2) dissolved in wastewater. The dissolved oxygen is one of the important parameters as it is directly correlated with the water bodies, microbial growth and activity, and their nutritional availability. The dissolved oxygen for sample A is initially 6.25 mg/l and after144 h, it was 5.32 mg/l. For sample B, the initial DO was 5.42 mg/l, and after 144 h, it was 0.97 mg/l. For sample C, the initial DO was 5.36 mg/l, and after 144 h, it was 1.78 mg/l. Low value resulted due to the consumption of oxygen during the decomposition of organic materials present in wastewater. This leads to the generation of high voltage and current.

Effect of biochemical oxygen demand

BOD is the amount of oxygen required for microbes in water. This requirement varies depending upon the temperature, concentration of nutrient, and availability of enzyme to the microbial populations. BOD can be defined as the amount of oxygen required to oxidize the organic compounds into carbon dioxide and water by microbial growth, decay, and death. The BOD value for all the three samples as shown in Fig. 4c was initially 4.2 mg/l, 4.27 mg/l, and 4.54 mg/l. After 8 days, the value has decreased to 3.89 mg/l, 4.01 mg/l, and 3.9 mg/l. This indicates the rate of microbial activity and oxidation of organic matter present in the wastewater on to which the microbes can feed.

Effect of chemical oxygen demand

The chemical oxygen demand analysis defines the amount of oxygen required for oxidation of organic

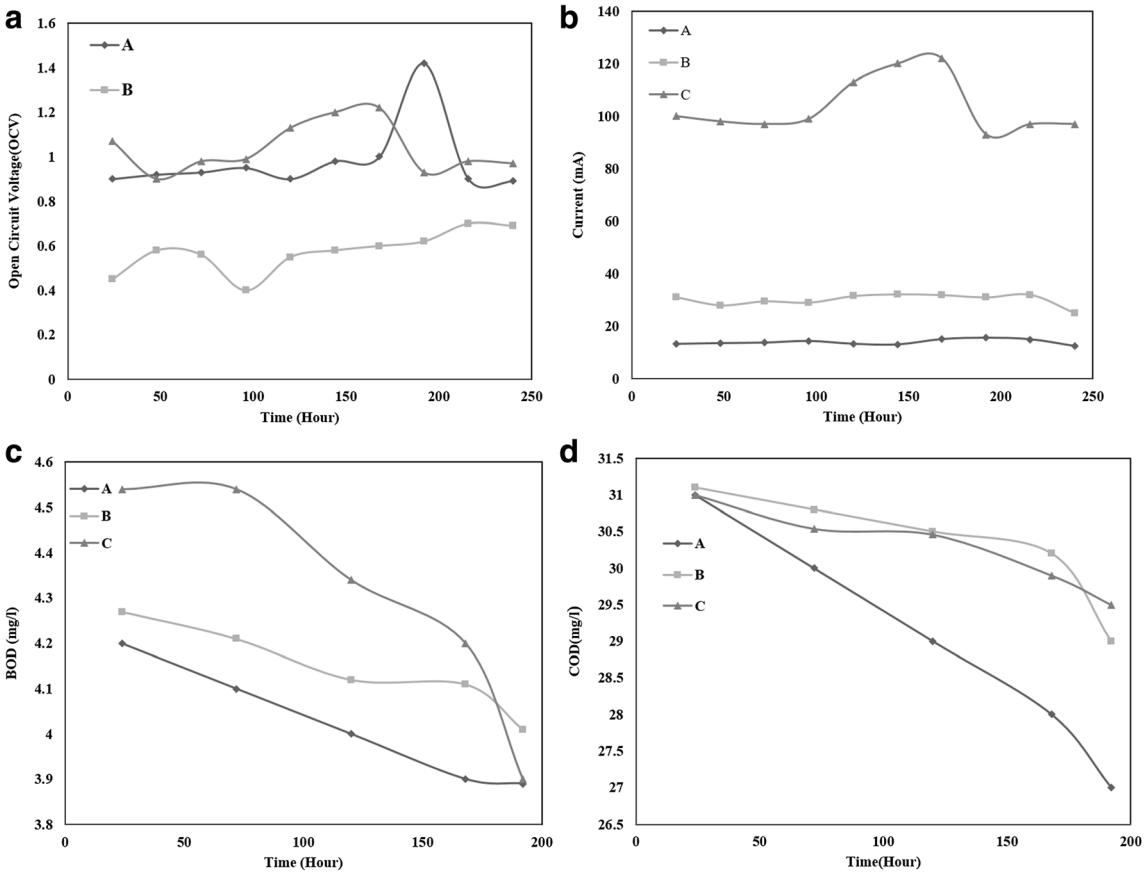

Fig. 4 **a** OCV of Bhilai Jaypee Plant industrial wastewater analyzed through MFC with different mediators. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as mediator. **b** Current of Bhilai Jaypee Plant industrial wastewater analyzed through MFC with different mediators. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as Mediator. **c** BOD variation with respect to time. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as mediator. **d** COD variation with respect to time. A. Control (wastewater with no mediator). B. MFC setup with methylene blue as mediator. C. MFC setup with potassium ferricyanide as a mediator

matter into carbon dioxide and water in the presence of a strong chemical oxidant. The chemical oxygen demand is used to measure the pollution of wastewater in terms of oxygen required for oxidation of organic matter. The COD value for all the three samples as shown in Fig. 4d was initially 31 mg/l, 31.1 mg/l, and 31 mg/l. After 8 days, the value has decreased to 27 mg/l, 29 mg/l, and 29.5 mg/l. This indicates the microbial function present in a waste sample in metabolizing the carbon source as an electron donor.

Table 3 The current density of wastewater from Jaypee Cement Plant

Time (h)	A (mA/cm^2)	B (mA/cm^2)	C (mA/cm^2)
24	13.2	31.1	100
48	13.49	28	98
72	13.69	29.5	97
96	14.29	29	99
120	13.23	31.5	113
144	13	32.2	120
168	15	31.9	122
192	15.51	31	93
216	14.93	32	97
240	12.39	25	97

Table 4 Power density of wastewater from Jaypee Cement Plant

Time (h)	A (mW/cm^3)	B (mW/cm^3)	C (mW/cm^3)
24	11.88	13.995	107
48	12.4108	16.24	88.2
72	12.7317	16.52	95.06
96	13.5755	11.6	98.01
120	11.907	17.325	127.69
144	12.74	18.676	144
168	15	19.14	148.84
192	22.0242	19.22	86.49
216	13.437	22.4	95.06
240	11.0271	17.25	94.09

Analysis of results for water sample 3 (sugar industry, sewage waste, NIT canteen)

After analyzing the control and with mediator samples of sample 1 and sample 2, there was no vast difference seen in the results. So, in sample 3, no mediators are used.

Voltage generation in an MFC

Sample A has shown a consistent drop in voltage as shown in Fig. 5 measuring the lowest voltage of 0.34 V. Sample B shows a constant voltage but after 144 h, there is a drop in voltage of up to 0.8 V; it could be due to the loss of substrate for microbes and their death started. In sample C, there is a slow rise in voltage but after 168 h, voltage increases rapidly because of feed, which made an increase in organic matter which is necessary for the microbes to grow.

Effect of dissolved oxygen

DO analysis measures the amount of free, non-compound oxygen (O_2) dissolved in wastewater. The dissolved oxygen is one of the important parameters as it is directly correlated with the water bodies, microbial growth and activity, and their nutritional availability. The dissolved oxygen for sample A is the highest with 1.70 mg/l and the lowest for sample B with 0.35 mg/l. Low DO value resulted due to the consumption of oxygen during the decomposition of organic materials present in wastewater. This leads to the generation of high voltage and current.

Discussion

Analysis of voltage and current fluctuation of sample 1 in MFC

The power output in the control was good enough for lighting a lamp compared with others as some mediators may have reverse or toxic effects. The OCV and current resulted from methylene blue was least among all the mediators including control, which may be due to irreversible behavior of the mediator. During an experiment with methylene blue, a green-colored solution was observed after few days that indicates that there are some gram-negative bacteria which are known for ethanol degradation which reacts with methylene blue to form the metallic green color solution due to metachromatic properties of the dye (Adebule et al. 2018). The performance of potassium ferricyanide mediators in MFC was more or less than stable throughout the experiment as the initial voltage and current of 0.68 V and 70 mA, in the final 0.7 V and 60 mA. The reason behind these results may be due to the high diffusibility nature of potassium ferricyanide. It was also observed that the ferrous component of the mediator was reduced by the reversible reaction that takes place in the anodic chamber and simultaneously the redox potential of the solution also increases. Moreover, little bit fluctuation observed in between initial and final day value is only due to the continuous replacement of fresh media and substrate to initiate the growth of microorganism in the anodic chamber. The OCV and current results from EDTA were showing that it continuously decreases with increase in time, which indicates that the EDTA has been totally used up by the microbes.

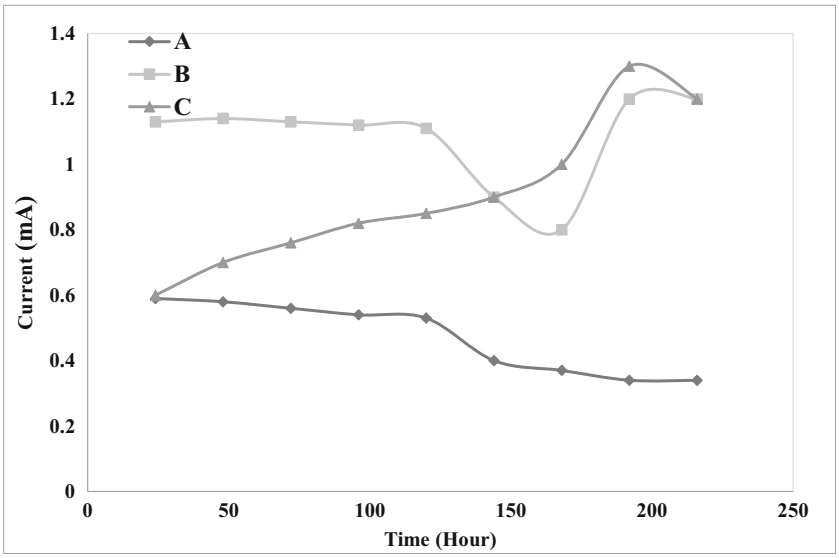

Fig. 5 Currents of wastewater from different sources were analyzed through MFC setup. A. Sugar industry. B. Sewage. C. Canteen NIT RAIPUR

Analysis of voltage and current fluctuation of sample 2 (Jaypee Cement Plant) in MFC

Among all, methylene blue was the least performer where potassium ferricyanide showed good result. It may be due to the high concentration of methylene blue applied in the MFC that affects the microbial growth and leads to a decrease in OCV and current, i.e., 0.69 V and 31.9 mA. As we already discussed earlier, potassium ferricyanide due to high diffusibility in nature gives a good result, i.e., 113 mA and 1.22 V, current and OCV. Without a mediator, the MFC also possesses good result as an industrial waste rich in a high amount of organic pollutant, which leads to good electricity generation in OCV and current, i.e., 1.42 V and 14.93 mA.

Analysis of voltage and current fluctuation of sample 3 (sugar industry, sewage waste, NIT canteen) in MFC

In these samples, mediators are not used for the preparation of MFC; still, it showed good results, as all the three wastewaters are enriched with a good amount of organic pollutants. Among all, NIT canteen wastewater in MFC performed better than the sugar industry and sewage wastewater. NIT canteen generated a current of 1.3 V, the sugar industry generated 0.59 V, and sewage waste generated 1.2 V.

Mashkour et al. (2017) constructed a dual-chambered MFC; they used modified cathodes of titanium oxide and hybrid graphene; the power density observed was 80 mW/m^3 and 220 mW/m^3 and got a power density output in the range of, i.e., 36.6 mW/cm^3 to 148.84 mW/cm^3 (Mashkour et al. 2017). Pant et al. (2016) used four different industrial wastewaters and Zirfon® was used as a proton-exchange membrane; 419 mW/m^2 power density was generated. Colombo et al. (2017) used air cathode in which they used spirulina in the cathodic chamber and obtained power densities in the range of 0.8 to 1 W/m^2 (Colombo et al. 2017). Pasupuleti et al. (2016) constructed three different MFC modes, i.e., batch mode, semi-continuous, and continuous mode and obtained a maximum power density in semi-continuous mode, i.e., 20.54 mW/m^2 followed by continuous mode 17.22 mW/m^2, and batch mode 0.75 mW/m^2 (Pasupuleti et al. 2016).

Conclusions

In the present work, five types of wastewater samples were taken as anolytes for MFC construction and their physicochemical properties were also characterized. From the above discussion, it was concluded that wastewater should be feed at a certain time interval to avoid the loss of substrate for organisms in the anodic chamber which lead to the death of the microorganism. From our study, we have observed that mediators can increase the efficiency of MFC, but if the concentrations of mediators are high, they could work as a toxic and lead to the death of microorganism and low power output. All the physicochemical properties were also directly correlated with electrical conductivity. Among all, sugar industry wastewater has the highest potential for power generation as DO, BOD, and COD results are appropriate for the better output.

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