Evaluating the performance of coupled MFC-MEC with graphite felt/MWCNTs polyscale electrode in landfill leachate treatment, and bioelectricity and biogas production

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Abstract

Purpose A bioelectricity producing system was configured by connecting to a microbial electrolysis cell producing hydrogen, in which both systems were without mediator, to treatment the landfill leachate of the and generate bioelectricity and hydrogen.

Methods The anode electrode was made with MWCNTs polyscale coating on graphite felt and the cathode electrode with activated carbon coating on carbon cloth. In the MFC-MEC coupled system, the electrodes were connected in series using copper wire. The system was set up in a fed-batch mode and the landfill synthetic leachate was injected into the anode MFC-MEC chamber as fuel.

Results In MFC, the highest voltage, current density and power density were 1114 mV, 44.2A/m³ and 49.24 W/m³, respectively. The maximum of the coulombic efficiency system was 94.10%. The highest removed COD, NH₄-N and P was 97.38%, 79.56% and 74.61%, respectively. In the MEC, the maximum of voltage input, current density and power density was 1106 mV, 43.88 A/m³ and 48.54 W/m³, respectively. The maximum coulombic efficiency system was 125.54%. Also the highest removed COD, NH₄-N and P was 97.46%, 78.81% and 76.25%, respectively. The highest biogas production rate and its yield were 39 mL/L.d, and 0.0118 L/g CODrem, respectively.

Conclusion This study found that the MFC-MEC coupled system had promising potential for strong wastewaters treatment, such as the leachate of landfill; and the in-site use of generated electricity and the production of useful fuels such as biogas.

Keywords Microbial fuel cell · Microbial electrolysis cell · Bioelectricity generation · Biogas production · Polyscale electrode · Leachate treatment

Introduction

Controlled landfills are still the most widely used waste disposal methods in developing countries, even if the waste management hierarchy considers this treatment to be the last

resort. Every year, hundreds of thousands of cubic meters of leachate is released from these places. However, the generation of leachates is a critical issue of this landfill. Leachate is commonly generated from precipitation, surface run-off, and infiltration of groundwater percolating through the landfill [1,

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2]. Landfill leachate contains large amounts of organic and inorganic compounds, nutrients, chemical pollutants and heavy metals such as Pb, Ni, Cd, Cr, etc. (many of the compounds are toxic and carcinogenic) in which the composition and concentration of pollutants depends on various factors such as age of burial site, precipitation, seasonal changes in climate, chemical and biological activity, temperature, type and composition of the waste and the amount of moisture in the waste [3, 4].

Landfill leachate due to the existence of different types of pollutants is a toxic and harmful wastewater that is highly polluting and is considered a major environmental pollutant at the landfill. Leachate is a major threat to the surrounding soil, groundwater, and even surface water. Therefore, landfill leachate has become one of the most important issues in sustainable landfill solid waste management due to the increasingly stringent requirements for controlling contamination and the problems encountered for its treatment; and the effective treatment, of especially freshly produced leachate (in the early stages of waste disposal or decomposition) has received more attention around the world. Therefore, sustainable economic and environmental solutions for treating this highly polluting wastewater are at increasing demand [5, 6].

Landfill leachate management is one of the key factors to eliminate the risk of environmental pollution, especially groundwater aquifers under the landfill. Many landfill leachate management options have been used, including recycling, evaporation, discharge to municipal wastewater collection networks, treatment and disposal, which in many cases will require pre-treatment or complete treatment [7, 8]. Different types of leachate treatment methods such as leachate recycling, simultaneous treatment with domestic wastewater, physical processes (membrane separation processes such as ultrafiltration, nanofiltration, reverse osmosis), chemical (precipitation, coagulation-clotting, chemical oxidation) and biological (aerobic and anaerobic digestion, submerged biological filters, anaerobic sequential batch reactors) or combined purification systems have been reported. But each of these methods has limitations in terms of efficiency, operating costs, and energy consumption [9–12]. It is necessary to choose easier and cheaper treatment options to minimize contamination caused by leachate and achieve satisfactory discharge quality standards.

Microbial Fuel Cell (MFC) is an electrochemical device that can directly convert the chemical energy in organic matter into electrical energy through the catalytic activity of microorganisms [13]. In an MFC, microorganisms in the anode, oxidize organic matter and produce electrons and protons. The electrons flow through an electrical circuit from the anode to the cathode and react with the protons in the cathode (passing through the proton exchange membrane from the anode chamber to the cathode chamber) and reacts with an oxidizer such as oxygen. As a result, electricity is generated

automatically. This technology, which uses microorganisms as catalysts for oxidation or reduction reactions in the vicinity of electrodes, has the potential to be used for wastewater treatment and energy recovery [14].

An important part of MFC is the electrodes, which play an important role in generating electricity. Also, the type of anode electrode material and its composition can directly change bacterial loading and electron transfer. Carbon-based materials such as graphite felt can increase the density power of MFC by their high specific surface area and power generation which is three times higher than other carbon materials [15]. However, such simple carbon materials show poor biocompatibility and poor electrocatalytic activity. Therefore, carbon material can be modified to increase the activity of such materials for microbial anode reaction, biocompatibility and improved performance. A nanostructure, such as multi-walled carbon nanotubes, is ideal for both biocatalytic and electrocatalytic processes due to its unique structural properties [14]. The unique electrical, mechanical, optical and chemical properties of MWCNTs allow them to be used in many fields, including materials science, electronics, mechanics, light and biology. MWCNTs are defined by two or more sheets of graphene coaxially arranged around a central hollow core with van der Waals forces between adjacent layers and varying in diameter from a few to ≥ 100 nm. The characteristics of these materials include high length to diameter ratio, large available external surface area, high porosity and optimal reactivity [16–18]. Therefore, they show excellent biocompatibility; and can be placed on graphite felt to increase surface area and electron transfer speed more than before. As a result, it further increases the MFC power density, reduces the system's internal resistance, and plays an important role in improving the MFC power density [19].

Microbial electrolysis cell (MEC) is a bio-electrochemical system that uses exo-electrogenic bacteria to oxidize organic compounds in the anode, as an electron acceptor and to produce a useful chemical such as hydrogen gas in the cathode. There is no oxidant in the cathode chamber in the MEC, so the electrons combine with the protons to produce hydrogen. Hydrogen production in these systems requires the entry of a small amount of electrical energy from an external power supply to circumvent thermodynamic constraints [20]. Theoretically, the voltage required for acetate MEC is approximately 0.14 V compared to 1.2 V for water electrolysis; but in practice a voltage greater than 0.2 V is required for the MEC and usually more than 0.5 V is used. The microbial electrolysis cell has a higher hydrogen recovery, than the hydrogen-producing reactor that uses waste fermentation. Less energy consumption and no need for expensive anodic catalysts are the most important benefits of using a MEC over a water electrolyzer [21].

A paired MFC-MEC system has been successfully developed by modifying the anode electrode for the treatment of

synthetic landfill leachate and the simultaneous generation of renewable energy (both electricity and biogas) from organic waste without the need for external energy input. In both systems, the anode electrode has been modified with the use of MWCNTs. In this coupled system, the electricity generated by the MFC is supplied for on-site use by the MEC, and therefore the production of biogas happens without an external power source. The need to adhere to sustainable development and environmental protection has made landfill leachate treatment an unavoidable dilemma. Therefore, the treatment of this type of wastewater requires the use of new methods. In this study, the treatment of synthetic landfill leachate by MFC-MEC combined technology using graphite felt/MWCNTs polyscale as the anode electrode and the direct production of bioelectricity and biogas were investigated.

Materials and methods

Electrodes preparation and their coating

The electrodes used in this study were graphite felt ($2.5\text{ cm} \times 2.5\text{ cm} \times 0.2\text{ cm}$) as the anode and carbon cloth ($2.5\text{ cm} \times 2.5\text{ cm}$) as the cathode, which was purchased from Arian Tajhiz Azma Company. MWCNTs with a purity of more than 98%, a diameter of 30–50 nm, length of 20 μm , ash of 1.5 wt%, and specific surface area of $60\text{ m}^2/\text{g}$ were purchased from the Aldrich (USA) company and before use, were purified and activated. The first step was sonicated MWNTs in a mixture of sulfuric acid and nitric acid ($\text{H}_2\text{SO}_4 - \text{HNO}_3$) in a volume ratio of 1: 3 for 4 h. It was then filtered and washed three times with ultrapure water obtained from a Millipore-MilliQ system. Finally, it was centrifuged at 3500 rpm and dried at room temperature [22].

MWCNTs were coated on graphite felt as follows: NH_2 -functionalized graphite felt was placed in a dried vacuum in 10 cc of dimethylformamide solvent (DMF) and 1 mg/L of MWCNTs was added. In the next step, 0.4 mg/mL 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (DCC) was added to each container; and was then placed on a 50 rpm shaker for 24 h, so that the COOH group of MWCNTs can get connected to NH_2 in graphite felt [23].

In this study, activated carbon powder based on bamboo was purchased from the Arian Tajhiz Azma (Iran) Company, and was used as a cheap catalyst. The surface area of 1 g of it was between 700 and 900 m^2 and its size was approximately 100 μm . For coating activated carbon on Carbon cloth, 250 mg of activated carbon was combined with 27.78 mg of carbon black in a 9:1 mass ratio, and a few drops of nafion solution were added to it and mixed thoroughly. In the next step, the carbon cloth was cut and weighed. Then, 10–15 drops of Merck ethanol were added to the mixture to make the dough mixture like, and by rolling method pressure

(pressure of 1 atm for 5 min) was performed on coating Carbon cloth. Then was exposed to open air to dry [24]. The final weight of carbon cloth coated was measured after drying, to achieve a mass loading rate was $17.6\text{ mg}/\text{cm}^2$.

Bio-electrochemical system configuration

Both bio-electrochemical systems (MFC and MEC) were designed with dual-chambers. The compartments were made of Plexiglas. Each anode and cathode chamber had $10 \times 7.5 \times 7.5\text{ cm}$ dimensions and an effective volume of 450 ml. The compartments were separated by a proton exchange membrane (NAFION117, DuPont Co USA, surface area 54 cm^2 and thickness 183 μm). To increase porosity, the membrane was purified with 5% sulfuric acid (v/v) at 80 $^\circ\text{C}$ for 2 h before use, and then cleaned with deionized water [25]. The membrane was then cut according to the chamber volume calculations, and placed on the joint surface and center of the two chambers, using two pieces of plastic as a support plate to prevent fluid pressure inside the chambers. The anode electrode was made of graphite felt/MWCNTs polyscale and the cathode was carbon cloth/ activated carbon. In the MFC-MEC coupled system, the connection of the electrodes was done in series using copper wire. The distance between the anode and cathode electrode was 3 cm. The Ag/AgCl reference electrode was placed near the anode electrode to measure the potential of the electrode. In order to record the voltage produced by MFC, a digital multimeter device (Model 2700, Keithley Instruments Inc., Cleveland, OH, USA) and voltage input to MEC a D.C. power source (IT6720, Itech, China) was used. A gas bag (0.5 L capacity; Cali-5-Bond, Calibrated Instruments Inc.) was also attached to the top of the MEC cathode chamber to collect the produced gas. A schema of the MFC-MEC coupled system is shown in (Fig. 1).

Preparation and pre-treatment of inoculated microbial consortia

In this study, anaerobic digestion sludge was used as a microbial consortium and was prepared from the municipal wastewater treatment plant located in Tehran. The sludge prepared, was sieved by a 1 mm sieve, to remove large debris. The sieved sludge was then poured into a beaker. To prevent the action of methanogenic bacteria, before use, beakers containing sieved sludge, went through combined pre-treatment, by first undergoing ultrasonication treatment (40 kHz and 120 W for 5 min) and then thermal treatment (100 $^\circ\text{C}$ for 15 min). Eventually the beakers were placed in room temperature before inoculation [26].

Fig. 1 Schematic diagram of the MFC–MEC coupled system

Startup and operation of the bio-electrochemical system

In this study, both bio-electrochemical systems were operated in fed batch mode. In order to start up the system, the MFC and MEC anode compartments with anaerobic digestion sludge (1:10), sodium acetate (1.5 g/L) as electron donor, phosphate buffer solution (100 mM, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ 11.54 g/L; $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ 2.27 g/L; NH_4Cl 0.31 g/L; KCl 0.13 g/L), trace minerals of 12 mL/L (per liter, 3.0 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 0.5 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$; 1.0 g NaCl ; 0.1 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; 0.18 g $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$; 0.1 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 0.18 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; 0.01 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 0.02 g $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$; 0.01 g H_3BO_3 ; 0.01 g $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; 0.03 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 0.30 mg $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$; pH 7.0), vitamins of 12 mL/L (per liter, d-biotin 0.002 g; folic acid 0.002 g; pyridoxine hydrochloride 0.010 g; thiamine HCl 0.005 g; riboflavin 0.005 g; nicotinic acid 0.005 g; d-pantothenic acid 0.005 g; vitamin B12 0.0001 g; p-Aminobenzoic acid 0.005 g; thiotic acid 0.005 g; pH 7.0.) and extracted yeast (0.5 g/l) were inoculated [27, 28]. The cathode chamber was filled with $\text{K}_3\text{Fe}(\text{CN})_6$ (50 mM) and phosphate buffer (100 mM, K_2HPO_4 and KH_2PO_4) as catalyze [29]. The MFC cathode chamber was aerobic and the MEC was anaerobic.

During the startup period, the MFC system was operated in open circuit voltage (OCV) mode. For the MEC system, in the acclimatization step, a constant voltage of 0.6 V with an external resistance of 10 Ω was applied by a DC power supply.

After this step, in MFC, when the output voltage dropped below 50 mV and in MEC, the current intensity dropped below 5 mA, the anolyte was refreshed.

After reaching steady-state conditions (achieving stable voltage generation in MFC and current in MEC), the influent of the anode chamber was changed to synthetic landfill leachate. At the beginning of the experimentation phase, the optimal external resistance (10–1000 Ω) was determined. Then, the MFC system with the optimal external resistance, was connected to the circuit close to enter the next stages of the experimentation phase. In the next step, the MFC and MEC systems were coupled by connecting the electrodes in series, to supply the required MEC voltage by the MFC and remove the external power supply. The MFC-MEC coupled bio-electrochemical system was changed from 0.178–11.428 kg COD/ $\text{m}^3 \cdot \text{d}$ for different organic loading of leachate; and in terms of treatment efficiency, the amount of voltage generated by the MFC for the MEC and the efficiency of the gas produced by the MEC were tested.

Table 1 Characteristics of the synthetic landfill leachate used as fuel for the bio-electrochemical system

Parameter	Concentration	Unit
COD	1000–64,000	mg/L
$\text{NH}_4\text{-N}$	100–6400	mg/L
P	2.3–147.2	mg/L
EC	21.61	ms/cm
pH	6.8–7.2	–

Sodium acetate ($C_2H_3NaO_2$), ammonium chloride (NH_4Cl), ammonium bicarbonate (NH_4HCO_3), monopotassium phosphate (KH_2PO_4) and mineral trace minerals were used to make synthetic landfill leachate, which was used as fuel to feed the reactors. The characteristics of synthetic landfill leachate are shown in Table 1. $NaHCO_3$ and H_2SO_4 solutions were used to adjust the pH of the input solution to 7 ± 0.2 , which was confirmed by a pH meter.

To remove oxygen and maintain anaerobic conditions in the anode chamber, highly pure nitrogen gas (99.998%) was injected into the anode chamber for 20 min, at the beginning of the process. To prevent the activity of methanogenic bacteria, in addition to pre-treatment processes of the microbial consortium, 0.5 mM BES solution (2 bromo-ethano-sulfonate) was added to the anode chamber. 5 mM Sodium molybdate was also added to prevent sulfate reduction [30]. The content in the anode chamber was agitated at 200 rpm by a magnetic stirrer. The gas samples produced at the MEC cathode and collected in the gas bag were removed using a gastight syringe (250 μ L, Hamilton, Sample-lock Syringe).

Measurement and analysis

Measurement of MWCNTs coating on graphite felt

To check if the anode electrode coating was well done, the surface of the electrodes was analyzed by Field Emission Scanning Electron Microscope (FESEM) (Model: Joel6335F) techniques before and after coating. To perform the FESEM test after the electrode coating, the electrode was placed in a rotary for 1 h to dry. The morphology of biofilm growth on the anode was also examined using FESEM technique after the experiments (startup) were completed.

The preparation steps of the electrode samples were as follows: first small pieces of anode electrodes were taken. Samples in 2.5% glutaraldehyde were fixed for 2 h and washed with 0.1 mol/L PBS (pH 7.0, twice and 10 min each time). After that, the samples were dehydrated in a series of ethanol grades of 30%, 50%, 70%, 90%, once, and in 100% twice, for 20 min for each step, and were finally dried in a desiccator. The dried samples were coated with a 5-nm-thick layer of gold and examined with FESEM at 20 kV, and the images were captured digitally [31].

Measurement of voltage, current density, power density and coulombic efficiency

Voltage produced during experiments was measured using digital multimeters (UNI-T brand, Digital Multimeter 1000 V). The polarization curve was plotted to measure stable voltage for various external resistors (10–1000 Ω) to determine the optimal external resistance. The Current was

calculated according to Ohm's law (Eq. 1). The power was calculated using the Eq. 2 [32].

$$I = V/R \quad (1)$$

where, I (A) = current intensity, V (V) = voltage and R (Ω) = external resistance.

$$P = V \times I \quad (2)$$

The current density was calculated based anolyte volume as follows: $CV (A/m^3) = I/(\text{anolyte volume})$. The power density was determined by dividing the calculated power by the anolyte volume as follows: $PV (W/m^3) = P/(\text{anolyte volume})$. Also coulombic efficiency was calculated using the Eq. 3 [33].

$$CE(\%) = (M \times I)/(F \times b \times q \times \Delta COD) \quad (3)$$

in which M is the molecular weight of oxygen (32), I is the current intensity (A), F is the constant of Faraday (96,485 C/mol), b is the number of electrons exchanged per mole of oxygen (4), q is the flow rate of incoming wastewater (L/s); and ΔCOD is the difference between the input and output COD (g/L).

Measurement of treatment efficiency

To investigate the efficiency of synthetic leachate treatment entering the bio-electrochemical system as fuel, the samples taken from the MFC and MEC anode chamber were filtered by a 0.45 μ m membrane and chemical Oxygen Demand (COD) was measured using a portable spectrophotometer according to the factory method (DRB200 & DR2800, HACH Co., USA), ammonium nitrogen (NH_4-N) and phosphorus (P) in accordance with Standard Methods [34], pH using portable meter (sension1, HACH Co., USA) and electrical conductivity using a conductivity meter (FE-30 K, Metter-Toledo). The MFC-MEC performance in substrate removal during operation was calculated using Eq. 4 [13]:

$$\xi COD = \frac{CS_o - CS}{CS_o} \times 100 \quad (4)$$

In which, the ξCOD = percentage of substrate removal efficiency, CS_o = initial COD concentration and CS = COD remaining concentration. Organic loading rate (OLR) in Kg COD/ $m^3 \cdot d$ is also obtained from Eq. 5 [35]:

$$OLR = \frac{CS_o \times \text{feed rate}}{\text{reactor volume}} \quad (5)$$

Measurement of produced biogas

The yield of the produced gas (Y in L/g CODrem) from the MEC is also expressed based on the amount of COD removal and is calculated from the following equation [35]:

$$Y = V_{\text{gas}}/V_r(CS_o - CS) \quad (6)$$

In which V_{gas} is the total volume of produced gas (hydrogen or methane) and V_r is the volume of the reactor.

Results and discussion

Characterization of the anode and morphological analysis

Figure 2 (a, b, c) shows the FESEM image of plain graphite felt, MWCNTs, and graphite felt coated with MWCNTs, before they are used. As shown in Fig. 2 (a), the carbon fibers in the graphite flat were randomly twined. Fig. 2 (b) shows the smooth morphology of the outer surface of MWCNTs, which have diameters of about 47 nm. As shown in Fig. 2 (c), the MWCNTs are located on the surfaces of the graphite felt carbon filaments.

When the cell function became stable, the anode electrodes used in MFC and MEC were cut and observed to determine biofilm growth. Figure 2 (d) shows the FESEM images of biofilm growth on the anode. FESEM observations show that different types of bacteria are effectively attached to the surface of the electrodes in a dense manner. The bacteria attached to the anode are also often coccylgeal, and to a lesser extent rod-shaped bacteria, and appear to have a uniform morphology. Also shows the exoelectrogenic bacteria that evolved during the experimental period and play the role of biocatalysts in the transfer of electrons to the anode electrode through their nanowires. Apart from these species, there are other types of

microorganisms in biofilm, and this shows that the grown biofilm is not a pure environment. This high density of microorganisms from their binding to the electrodes can also be attributed to the high porosity of flat graphite, the more open, accessible architecture, and the high surface area of the electrode coated with MWCNT. In addition, the substrate, which contains the nutrients needed for microbial growth, can be easily and rapidly distributed in the biofilms present in flat graphite with sufficient mixing intensity.

MFC-MEC performance

MFC-MEC startup

The MFC-MEC pairing system began with the acclimation of electrogenesis bacteria in the anode chamber with sodium acetate as a carbon source in an open circuit voltage (OCV). At this stage, in the MFC system, when the voltage was reduced to about 50 mV, the growth medium of the bacteria was replaced with a new medium in the anode chamber, which is defined as an MFC cycle (Fig. 3a). As shown in Fig. 3a, the first cycle lasted about 19 days, and the voltage showed four separate phases, including the delay phase (0–0.056 V at 72 h), the logarithmic phase (0.057–0.67 V in 168 h), fixed phase (0.66–0.67 V from 168 to 216 h), and death phase (0.66–0.013 V from 216 to 348 h). Such a trend indicates that it is consistent with the four-phase pattern of normal bacterial growth [36]. The span of each period for cycles 2 and 3 significantly decreased to 15 and 11 days, respectively. At this stage, the MFC system has reached a stable state, and the voltage after the three cycles, for about 45 days during the

Fig. 2 FESEM images of (a) plain graphite felt, (b) MWCNTs (c) graphite felt coated with MWCNTs, (d) biofilm attached to anode after 45 days of operation

Fig. 3 a) MFC voltage output during startup stage b) Current generation in MEC startup span c) gas production rate in the in MEC Startup span

adjustment period has shown good reproduction, which means that the formation of biofilm on the surface of the anode electrode has been done well.

In the MEC system, during the start-up period, the current began to increase after 14 days, and after 45 days of operation, a reproducible current (Fig. 3b) was obtained. When the maximum reproducible current intensity for the four batch cycles was obtained, the MEC reactor was considered to have launched successfully. This means that the startup of both bio-electrochemical systems (both MFC and MEC) was successful and ready for leachate treatment tests. The amount of gas produced in the four MEC start-up cycles was also measured, as shown in Fig. 3c. As it can be seen, the amount of biogas production in the first cycle was very low (maximum

0.26 mL/L.d) and in the next cycles with more biofilm growth on the anode, the amount of biogas production increased (second cycle 9 mL/L.d, third cycle 12 mL/L.d and fourth cycle 17 mL/L.d). The results obtained in this section are consistent with the study of Call and Logan (2008) and Carrera et al. (2013) [37, 38].

Operation MFC-MEC

At this stage of the experiments, the MFC system was inoculated and tested with an input COD concentration of 1000–64,000 mg/L. Figure 4 shows the OCV for different COD concentrations with respect to time, and it was observed that the MFC system gives different OCVs in different COD

Fig. 4 Performance of MFC during open circuit voltage with different COD concentration

inputs. As can be seen, the highest voltage given by MFC was 1.114 V, which was obtained at a COD concentration equal to 8000 mg/L. After that, with the increase of COD to 32,000 mg/L, the voltage decreased slightly, but with the increase of COD from this value (64,000 mg/L), the voltage decreased significantly. This is because high concentrations of COD may affect the microbial activity of the anode chamber, leading to an increase in the internal resistance of the anode chamber and may increase the load transfer resistance [39]. In the present study, the OCV of MFC was almost four times higher than that of Goud et al. (2011) in relation to food waste as fuel for electricity generation and Puig et al. (2011) in relation to leachate treatment by MFC [40, 41]. It was also observed that it took approximately 4 days for stable OCV to form with different concentrations of COD. Therefore, it was decided to operate the MFC system for 4 days retention time.

In the next step, the circuit was closed using an external resistor in different values of 10–1000 Ω to test the cell close circuit voltage (CCV) with a concentration of COD equal to 8000 mg/L and to determine the optimal external resistance; and this was done by drawing a polarization curve because the polarization curve is useful for determining the dependence of the microbial fuel cell function on resistance (Fig. 5). Figure 5 shows that when the external load was reduced from 1000 to

56 Ω , the close circuit voltage was almost constant. When the resistance varied from 56 to 10 Ω , there was a sudden drop in voltage. The relatively effective electron discharge observed at lower resistances may be a possible reason for the higher potential drop and lower voltage stability at low resistances [42]. The maximum close circuit voltage was approximately 1.071 V, which was obtained at a resistance of 56 Ω . This means that the bio-electrochemical system has come to a stable state, and due to the possibility of a slight decrease in OCV, by maintaining the external load at 56 Ω , we can obtain a good current from the treatment of synthetic leachate. Therefore, the external resistance of 56 Ω was considered optimal and in the next steps, the external resistance of 56 Ω was placed in the system.

Figure 6 also shows the change in voltage and power density with the current density for a fixed resistance of 56 Ω . As can be seen in the figure, at COD concentration and optimum external resistance, the current density reached 37.14 A/m². Also, the power density increased to 34.76 W/m² and then decreased. Also, as the current density increases, the voltage decreases. This is due to various reasons such as membrane clogging, potential losses such as activation polarization, ohmic losses and concentration polarization [43]. According to the results of the experiments and the voltage-density curve,

Fig. 5 Performance of MFC during close circuit voltage for different external resistance in the optimum COD concentration

Fig. 6 Variation in Voltage and power density generation as a function of current density

this curve can be divided into three stages: activation polarization, ohmic drop and concentration polarization. In the first stage, the current was relatively low, the activation resistance caused by the kinetic reaction plays an important role, which causes a rapid decrease in voltage (the slope of the voltage drop in this part is sharp). As the current increases, the polarization curve shows a linear relation between voltage and current, which is called ohmic polarization and is due to ionic resistance and electronic resistance [36].

At this stage, when the external resistance is equal to the internal resistance, non-ohmic polarization also occurs, which according to Ohm's law in this case the power density has reached a maximum (34.76 W/m^3). With the steady increase in current density, the distribution of concentration became apparent. At low resistances, the fuel cell allows more electrons to pass through the circuit to neutralize the protons in the cathode chamber. For this reason, at low resistances, we see a higher power density. Also, due to the higher speed of electron transfer from the external circuit than the speed of electron consumption in the cathode, some electrons are consumed by mechanisms other than the cathode reaction and as a result the current produced in low resistors is higher than high resistors. Therefore, in order to achieve maximum production capacity, it is necessary to increase the rate of proton transfer and reduce the internal resistance of the system [27, 44].

In connection with the MEC system, with the increase of the applied voltage from 0.5 to 1 V, the maximum current increased and the fed-batch cycle period is shortened (Fig. 7a). The average current increased from 5 to 32 mA with applying voltages from 0.5 to 1 V. Biogas production from applied voltages also increased from 12 to 44 mL/L.d (Fig. 7b). The increase in current production and the production of biogas with the used voltages showed that the production of biogas is proportional to the production of current. The high current output and the amount of biogas production in the MEC with the Grafite Felt/MWCNTs polyscale electrode are partially attributed to the low internal resistance of the system. These results were consistent with the study of Hou et al. (2015) on wastewater treatment and methane production

by MEC and Hernández-Flores et al. (2017) on harvesting energy from leachates in microbial fuel cells [45, 46].

While generating power in the operation of bio-electrochemical systems, we are looking to extract the largest number of electrons stored in biomass as much as possible, as well as recover as much energy as possible from the system. If all of the calculated substrate removal causes electricity, the coulombic efficiency (CE) is defined as the ratio of the total number of coulombs transferred to the anode from the substrate to the maximum coulomb. Therefore, coulombic efficiency is a direct measure of competition between electrogens (electrogenic bacteria) and methanogens (methanogenic archaea) at sufficiently low hydrogen pressure [42]. Figure 8 show the coulombic efficiency changes with current density at 56Ω for the MFC and MEC systems. In the MFC system, it is observed that since the current density has increased to 37 A/m^3 , CE has also increased from 13.43 to 87.62%. In the MEC system, with increasing current density up to 18 A/m^3 , CE has increased from 19.46 to 96.18%. This increase in CE was attributed to higher conductivity levels as well as more synthetic leachate conduction. Also, high coulombic efficiency for synthetic leachate indicates that a much higher percentage of removed organic matter is decomposed in anode-dependent processes [47]. At higher current densities, there may be a synthetic limit or cell mass transfer that leads to unstable voltage efficiency. It may sometimes occur due to the release of oxygen into the anode chamber, which leads to the waste of electrons for reviving (reducing) the released oxygen. The results of the present study are comparable to the research of Hassan et al. (2017) on landfill leachate treatment using electrofenton and MFC processes with coulombic efficiency of 28–40% and Zhang et al.'s (2012) study of biocathode microbial fuel cell for electricity recovery from dairy fertilizers with a coulombic efficiency of 39.8% [48, 49].

Voltage, current density and power density at different OLRs

Tables 2 and 3 shows the output voltages produced by MFC for MEC input and both bio-electrochemical system current

Fig. 7 (a) Steady state current generation with different applied voltages (b) Average current and biogas production rate as a function of applied voltages

density and power density at different OLRs (0.178–11.428 kg COD/m³.d) of the landfill synthetic leachate. With increasing organic loading rate to 1.428 kgCOD/m³.d, the output voltage increased to more than 1100 mV, current density to 44 A/m³ and power density to 49 W/m³; and with increasing organic loading rate to 5.714 kgCOD/m³.d, production voltage slightly decreased and the current and power density decreased more; but with increasing organic loading rate to 11.428 kgCOD/m³.d, the generated voltage dropped to less than 500 mV, the current density decreased to below 20 A/m³ and the power density decreased to below 10 W/m³. In

general, the voltage generated by the MFC varies at different organic loadings rate. This may be attributed to minor changes in the concentration of the input solution. In general, the voltage generated in MFC is related to the concentration of the carbon source and the efficiency of their use by anaerobic microorganisms [29]. The results show that the highest OLR leads to low voltage generation, power density and current density. The higher OLRs of the anode chamber may lead to a higher risk of membrane clogging and severely affect the bio-electrochemical behavior of the system, which may adversely affect voltage generation [50]. Higher OLRs may also

Fig. 8 Coulombic efficiency from the MFC and MEC with variation in current density

Table 2 Voltage, current density, power density generation, coulombic efficiency MFC and landfill leachate treatment efficiency at different OLRs

MFC								
OLR (kg COD/m ³ .d)	Voltage output (V)	Current density (A/m ³)	Power Density (W/m ³)	COD removal (%)	NH ₄ -N removal (%)	P removal (%)	CE (%)	
0.178	0.768	30.47	23.4	92.8	37.6	33.9	94.10	
0.357	0.845	33.55	38.36	92.35	57.5	52.17	82.05	
0.714	0.954	37.86	36.13	89.35	72.5	59.13	60.36	
1.428	1.114	44.2	49.24	90.8	84.37	74.61	46.27	
2.857	1.021	40.54	41.42	95.13	79.56	76.49	37.029	
5.714	1.064	42.25	44.98	97.38	72.65	63.75	23.34	
11.428	0.497	19.74	9.82	44.43	34.53	25.27	10.98	

lead to the accumulation of volatile fatty acids (VFAs), which may not facilitate voltage generation in MFC. On the other hand, the activity of methanogenic microorganisms increases due to higher OLR, which in turn weakens the voltage generation capacity of electrogenic bacteria [51]. The results of studies by Juang et al. (2011) and Ye et al. (2019) show that MFC can obtain the maximum amount of voltage generated in a safe OLR, and if the OLR increases, its value decreases [52]. In the present study, it can be observed that increasing the OLR from 0.178 to 1.428 kg COD/m³.d has simply increased the voltage generation from 700 to more than 1000 mV. This is because higher OLRs can clearly provide more substrates for electrogenic bacteria, which improve the recovery of chemical energy [21].

The input voltage to the MEC varied depending on the amount of voltage efficiency from the MFC at different organic loadings rate. As shown in Table 3, the input voltage to the MEC ranged from 700 to 1100 mV. By increasing the OLR of the MFC system to 1.428 kg COD/m³.d, the amount of produced voltage increased and this increased the input voltage to the MEC system. The higher the input voltage to the MEC, the maximum current density was achieved in a

shorter time. The maximum produced current density was from MEC was 43.88 A/m³ at voltage 1100 mV. The results of the present study comply with the study of Kargi et al. (2011) about the production of hydrogen gas from anaerobic sludge by electrohydrolysis, and Escapa et al. (2015) about household wastewater treatment by MEC [53, 54]. Also Table 4 presents a brief comparative evaluation of BES performance with other studies dealing with inoculation source used.

Biogas produced by MEC and its yields in various OLRs

The production of useful gases such as hydrogen and methane is considered a key indicator for the efficiency of the MEC system [60]. For this reason, the volume and composition of gas produced from the MEC system during operation as well as its yields was measured (Table 3). The rate of gas production in the whole reactor has been varied in different OLRs, and when the OLR was 1.428 kg COD/m³.d, gas production has increased sharply and its maximum production was 39 mL/L.d. The gas yields were also 0.0118 L/g CODrem.

Table 3 Voltage input, current density, power density generation, coulombic efficiency MEC and landfill leachate treatment efficiency at different OLRs

MEC									
OLR (kg COD/m ³ .d)	Input voltage (V)	Current density (A/m ³)	Power Density (W/m ³)	COD removal (%)	NH ₄ -N removal (%)	P removal (%)	Gas production rate (mL/L.d)	Gas yield (L/g) L/ g CODrem	CE (%)
0.178	0.764	30.31	23.16	90.1	33.2	28.26	32	0.0789	125.54
0.357	0.839	33.32	27.98	87.6	51.5	53.47	37	0.0469	108.96
0.714	0.943	37.42	35.28	85.97	73.75	55.21	34	0.0219	94.59
1.428	1.106	43.88	48.54	91.36	80.12	76.25	39	0.0118	70.88
2.857	1.003	39.83	39.98	95.33	78.81	72.17	28	0.0040	58.86
5.714	1.028	40.79	41.93	97.46	71.15	59.87	23	0.0016	34.29
11.428	0.489	19.42	9.50	44.14	29.23	21.87	15	0.0011	13.56

Table 4 Comparison of this work with other studies dealing with inoculation source in BES

BES	Reactor configuration	Anode electrode	Inoculation source	Removal Efficiency	Maximum power or current density	Applied voltage (V)	CE (%)	Source
MFC-MEC	two chamber	Graphite felt/MWCNT	Synthetic landfill leachate	97% of COD	49.24 W/m ³	–	94	This Study [55]
MFC-MEC	two chamber	graphite	Azo dye synthetic wastewater	98% of dye	–	–	98	
MFC-MEC	two chamber	carbon paper	synthetic wastewater	84 of COD	338 mW/m ²	–	56	
MFC	Single chamber	graphite	landfill leachate	37 of COD	334 mW/m ³	–	–	
MFC	Two chamber	graphite fiber brushes	Dairy wastewater	45 of COD	15 W/m ³	–	39	
MFC	Single chamber	Activated carbon/MWCNT	Sodium acetate	94% of COD	3.5A/m ²	–	47	
MEC	Two chamber	Graphite felt	Synthetic wastewater	78% of COD	0.09A/m ³	0.9	69	
MEC	Two chamber	carbon felt	domestic wastewater	85% of COD	–	0.4	94	
MEC	Single chamber	carbon cloth	Synthetic wastewater	76% of COD	46A/m ³	0.95	150	

The difference is in the composition of the biogas produced by the MEC system with different biological or bio-electrochemical reactions. For MEC, the production of CH₄ can be from hydrogenotrophic methanogenesis of hydrogen; and CO₂ produced by bio-electrochemical process, acetoclastic methanogenesis from sodium acetate, as well as electromethanogenesis of CO₂ in the MEC cathode [35]. The results of this study are comparable to those of other researchers. Hydrogen production (0.53 L/L.d) and its decrease with increasing operating time and increasing methane (0.118 L/L.d) by Rader et al. (2010), gas production up to 40% by Cho et al. (2018); and biogas production (0.8–1.8 m³/m³.d) has been reported by Tenca et al. (2013) [35, 61].

Coulombic efficiency of the MFC-MEC system at different OLRs

The highest coulombic efficiency from MFC was 94.1%, and MEC was 125.54%, which in both OLR was equal to 0.178 kgCOD/m³.d. The minimum coulombic efficiency of MFC was 10.98% and MEC was 13.54% in OLR equal to 11.428 kg COD/m³.d (Tables 2 and 3). In both bio-electrochemical systems in high OLRs, the coulombic efficiency decreased. This is because the anode surface with high saturation may induce side-populations such as methanogens and heterotrophs to compete with electrogene bacteria for substrates. Therefore, it weakens the activity of electrogenic microorganisms [62].

A decrease of CE in high OLRs indicates the loss of substrate in a nonelectricity production process, and non-current processes are dominant in reactors, and the removal of COD occurs mainly in a non-electrogenic way. Also, low coulombic efficiency suggests that electron transfer bacteria are

unable to convert most of the available carbon fuel into electricity. The maximum value of coulombic efficiency in the present study was higher than that obtained from the study of Ichihashi et al. (2012), Callegari et al. (2018), and Elakkiya et al. (2013) and was mainly due to the effectiveness of the sewage source and electrode material [63–65], but as shown in Table 4, was lower than that obtained from the study of Yanping Hou et al. (2015) [45].

COD removal efficiency at different OLRs

The MFC-MEC system developed in this study was able to continuously generate electricity and purify leachate simultaneously. In bio-electrochemical cell evaluation, as a bio-electrochemical device capable of generating an electric current from the oxidation of an organic substance, the concentration of COD in the cell output is valuable to be evaluated as an important parameter [33]. The rate of COD removal in the cell depends mainly on the oxidation of organic matter in the leachate by microbial activity. Tables 2 and 3 shows the efficiency of COD removal and COD concentrations of MFC and MEC output effluents in the OLR range of 0.178–11.428 kg COD/m³.d, which work as fed batch-mode. The amount of COD removal in the anodic chamber of MFC and MEC was observed in the range of 44–97% in different OLRs. During the days of operation, various fluctuations were observed due to the complexity of the bio-electrochemical reactions that occur in the anode chamber.

According to these tables, it was clear that when the OLR increased from 0.178 to 1.428 kg COD/m³.d, the efficiency of COD removal in MFC and MEC was more than 85%. However, when the OLR was very high (11 kgCOD/m³.d) this scenario led to a reduction in the efficiency of COD

removal in MFC and MEC by about 44%. A similar result has been reported on the effect of OLR on the removal of organic matter in MFC in the study conducted by Liu et al. (2016) [55]. In contrast, Molognoni et al. (2016) argued that higher carbon removal efficiency could be achieved under substrate limiting conditions (1000 gCOD/L.d) [66]. This contradiction may be attributed to the different types of anaerobic microorganisms used in wastewater treatment plants. In addition, Tamilarasan et al. (2017) reported that methanogenic microorganisms are the reason for deleting COD in higher OLR [67]. Excessive organic matter creates a good position for methanogens, and where OLR is higher than the maximum electron transfer rate from MFC, it leads to methanogenesis. These findings highlight the importance of OLR for COD removal in wastewater treatment, because optimized OLR can help anaerobic microorganisms to use substrates effectively [53]. In two chamber MFC, COD removal was performed with the combined effects of electrogenic and non-electrogenic microorganisms in the anode chamber for microbial decomposition. In fact, there are many influential factors, including sewage and inoculation resources, MFC configuration, and electrode properties in COD removal by MFC, which make it difficult to compare MFC studies about COD removal [68].

Ammonium and phosphorus removal efficiency at different OLRs

Another important parameter for MFCs and MECs in connection with wastewater treatment is the removal and conversion of nutrients (nitrogen and phosphorus). Nitrogen was determined as ammonium (NH_4) and phosphorus (P) ions, as total phosphorus and was measured at different OLRs for 4 days of operation. As shown in Tables 2 and 3, the removal of ammonium nitrogen with an input of 100–6400 mg/l, in different OLRs by MFC, varied from 34% to 84% and MEC from 29 to 80%. In MFC and MEC close circuit tests, ammonium nitrogen depletion may be due to microorganism's consumption for growth and reproduction, emission of ammonium ions from the anode chamber to the cathode chamber, or ammonium evaporation [69]. Removal of $\text{NH}_4\text{-N}$ in bio-electrochemical systems is the result of complex biological and physicochemical processes that require deeper research to better understand the mechanism of nitrogen removal and transformation in these systems [70]. The results of the present study are in line with studies conducted by Lu et al. (2009) in relation to electricity generation from starch processing wastewater, Mansoorian et al. (2013 and 2016) about electricity generation from food and dairy processing wastewater and their treatment, and Kim et al. (2015) about anaerobic digestion and paired

MFC for COD removal and ammonia recovery [50, 71–73].

Phosphorus, with an input of 2.3–147.2 mg/l, was removed by MFC by 76.49%, and MEC by 76.25%, at a OLR equal to 2.857 kgCOD/m³.d and 1.428 kgCOD/m³.d, respectively (Tables 2 and 3). This removal of P was probably the result of the consumption of nutrients with the growth of bacteria and the precipitation of struvite. Previous studies have shown that P is mainly removed by the sedimentation of phosphate ions in combination with metals such as magnesium, calcium, and potassium ions in the form of struvite and hydroxy apatite salts [74]. The pH of the anolyte, which is maintained in the range of 7 ± 0.2 , also increases salt sedimentation. Similar results have been reported on phosphorus removal in MFC in the study of Tao et al. (2014), [75] Santoro et al. (2014) [76] and Liu et al. (2020) [9]. In a previous study, Mansoorian et al. (2016) argued that with increasing exploitation time, not only the amount of phosphorus removal did not increase, but even in some cases it slightly increased, due to low redox potential, which stimulated microorganism to release phosphorus or convert organic phosphorus in wastewater to orthophosphate [50].

Conclusions

In this study, in order to significantly improve the treatment of synthetic landfill leachate, a coupled MFC-MEC system was built with an anode electrode, based on graphite felt/MWCNTs polyscale to simultaneously generate electricity and biogas. The electricity generated by the MFC easily supplied the required MEC voltage and the external source was removed. The excellent bio-electrochemical performance obtained can be due to the easy electron transfer mechanism through the connection of MWCNTs on Graphite felt and the unique characteristics of MWCNT such as high electrical conductivity and stability. MFC gave 1114 mV of voltage and 49.24 W/m³ of power density along with the substrate removal of 97% in terms of COD. The voltage input to MEC was 1106 mV along with the output power density 48.54 W/m³ and substrate removal of 97% in terms of COD. The maximum amount of biogas produced was 39 mL/L.d, and biogas yields was 0.0118 L/g CODrem. In terms of the treatment and energy parameter, MFC-MEC system upto 5.714 kgCOD/m³.d organic loading was effective in treatment efficiency and energy generation. This study shows that the MFC-MEC coupling system had a promising potential to enhance cost-effectiveness, efficiency landfill leachate treatment and the biogas production generation of renewable bioenergy from wastes especially without added mediator and catalysts expensive.

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Compliance with ethical standards

Conflict of interests The authors declare that they have no conflict of interests regarding the publication of this paper.

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