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Simultaneous electricity generation and sulfide removal via a dual chamber microbial fuel cell

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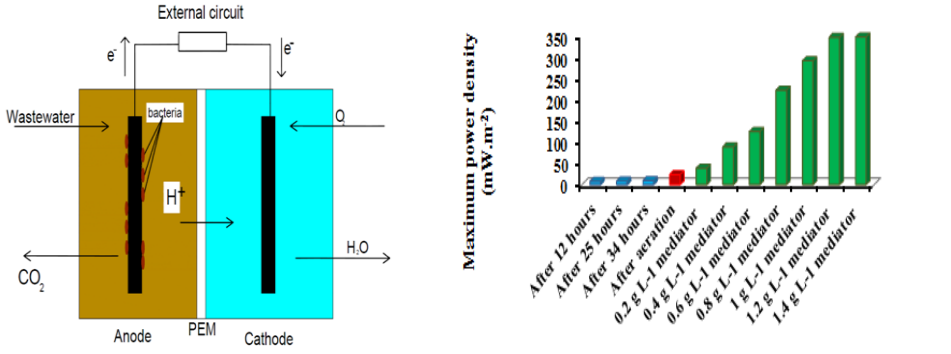
HIGHLIGHTS

- Transfer of produced electrons to anode is one of the main parts in MFCs.
- Some MFCs needs artificial electron acceptors in their aerobic cathode compartment.
- Cyclic voltammetry was used to study of anodic electrochemistry analysis.
- Hexacyanoferrate was used as cathodic solution in different concentrations.
- Maximum generated voltage and power density were 988.9145 mV, 346.746 $mW.m^{-2}$, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Microbial fuel cells (MFCs) have recently been used to alter different sources of substrates to produce bioelectricity. MFCs can also be used for wastewater treatment and electricity generation simultaneously. Sulfur compounds such as sulfides commonly exist in wastewater and organic waste. In this study a dual chamber MFC was constructed for power production. Sulfide was used as the electron donor in the anaerobic anode compartment. A mixed culture of microorganisms was used as an active biocatalyst to convert the substrate into electricity. The obtained experimental results illustrated that the MFC can successfully alter sulfide to elementary sulfur while generating power. The initial concentration of sulfide in the anode compartment was 0.4 g l^{-1} and it was completely removed after 3 days of MFC operation. The influence of oxygen was examined in the cathode chamber and the cell voltage gradually increased during aeration, reaching 480 mV after 1200 s. Hexacyanoferrate was added to the cathodic solution in different concentrations and its effects were investigated. The maximum generated voltage, power and current density were 988.9145 mV, 346.746 $mW.m^{-2}$, 1285.64 $mA.m^{-2}$, respectively and they were obtained in the presence of 1.4 g l^{-1} of mediator.

1. Introduction

The reduction in the earth's fossil fuels and the environmental problems associated with them are two important issues which have attracted researcher's attention to fuel cells (Bagotzky et al., 2003). Fuel cells are a suitable alternative to fossil fuels; however their use has some disadvantages such as harsh reaction conditions and expensive catalysts (Rodrigo et al., 2007). Accordingly, renewable bioenergy is viewed as one of the ways to decrease the current crisis. A microbial fuel cell (MFC) is a biological system which converts biodegradable organic substances to electricity using bacteria as its biocatalyst (Katuri and Scott, 2011). An MFC generates electricity from bio-convertible substrates. Bacteria change natural electron acceptors, such as oxygen into an insoluble acceptor, such as the MFC anode (Rabaey and Verstraete, 2005). The advantages of this technology include non-pollution, high energy efficiency, mild operating conditions, strong biocompatibility and great application potential in various areas, which have received a great deal of attention from scientists.

In many studies, oxygen was used as the final electron acceptor in the

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cathode compartment (Reddy et al., 2010). The consumption of electrons and protons that are combined with oxygen, eventually create water, and end this transfer cycle. Oxidized mediators, can also accelerate the reaction of water formation in the cathode chamber. Substrate as nutrient source of the cell played an important biological role and other factors such as mediator, microorganisms and nutrients affected the bioelectricity production pattern (Sun et al., 2010).

MFCs are capable of producing clean energy, apart from their effective treatment of waste material such as wastewater (Liu et al., 2004). The active microorganisms in the anaerobic anode compartment have the ability to use the organic matter which exists in the wastewater as a source of energy and generate protons and electrons, through which electricity can be recovered (Zhang and Liu, 2010). Wastewater treatment by MFC was first done by Habermann and Pommer (1991). Wastewaters include various organic compounds, so they can be consumed in MFCs as fuel. After Habermann and Pommer, many other researchers also used this application of MFC but with different substrates. Food processing wastewater, hygienic wastes, and swine wastewater were used as biomass sources for MFCs because of their rich organic matters (Liu et al., 2004; Min et al., 2011; Oh and Logan, 2005). MFC can be used to treat organic and inorganic matters as well as oxidized metal pollutants in the cathode and anode chambers and many studies have been related to this topic (Du et al., 2007). Table 1 shows a list of MFCs which have been examined for the elimination of different pollutants and electricity generation.

Table 1
Different elimination of substrate via MFC.

Elimination of	Cathode Material	Anode Material	Maximum power	Removal at	Removal efficiency (%)	Reference
Carbon	Granular graphite	Granular graphite	34.6 W.m-3	Anode chamber	100	(Virdis et al., 2008)
COD	Graphite felt	Graphite felt	7.6 mW	Anode chamber	90	(Moon et al., 2005)
Dye	Graphite plate	Graphite plate	15.73 mW.m-2	Anode chamber	93.15	(Yadav et al., 2012)
Nitrogen	Granular graphite	Granular graphite	34.6 W.m-3	Cathode chamber	67	(Virdis et al., 2008)
Copper	Graphite plate	Graphite plate	339 mW.m-3	Cathode chamber	96	(Tao et al., 2011)

Organic molecules in wastewaters can be biodegraded in the anode compartment of MFCs (Du et al., 2007). Sulfide is a common organic molecule which is found in wastewaters by the action of anaerobic bacteria on organic substances. High levels of sulfide ions in waters are perilous for living creatures and so should be treated from wastewater before they are released into the environment (Rahimnejad et al., 2012). Exploring new energy sources is an important issue in achieving sustainable development and circulation economy (Najafpour et al., 2011). Techniques such as physical, chemical and electrochemical methods have been used for sulfide treatment but they are expensive and high operated (Lee et al., 2012). Microbial fuel cell is a new technology which can be used for power production and sulfide removal simultaneously. Many literatures have focused on sulfide treatment in MFCs (Cai and Zheng, 2012). Sulfide removal in MFC using certain microbes such as Alcaligenes sp., Paracoccus sp. and Pseudomonas sp. C27 was investigated before (Lee et al., 2012); but few studies have considered using this process in mixed cultures. Microbial communities used in MFCs for power generation and sulfide alteration have been probed (Rahimnejad et al., 2012). Sulfide can be oxidized to different sulfur species depending on its surrounding condition and redox potential. Polysulfides, sulfates, thiosulfates and elemental sulfur are the results of sulfide oxidation in different redox potential (Sun et al., 2009). Also it has been indicated that sulfide oxidation plays a key role in power production in sedimentary MFCs (Tender et al., 2002).

In this study, a two chamber MFC was designed and fabricated for power production and sulfide removal. A mixed culture of microorganisms was used for this aim. The effects of different concentrations of oxidizer agent and aeration on MFC performance, power generation, and voltage and sulfide removal efficiency of MFC were investigated.

2. Materials and methods

2.1. Material

The MFC used in this paper was constructed by using two 750 ml cubic Plexiglas chambers as its anode and cathode compartments (figure 1). The two chambers were separated by a PEM (3.0cm× 3.0 cm, Nafion-117, Sigmae Aldrich, USA) and assembled using stainless steel studding, nuts and washers. Graphite plates were used as anode and cathode electrodes. The anode was placed in the center of the anodic chamber (area, 21cm^2) and it was connected to the cathode (area, 18 cm^2) to provide the connections for the external circuit with wire copper. Both electrodes were parallel to the PEM. The voltage was measured by using data logger (fabricated analog digital data acquisition to record data point) and recorded through a personal computer. The MFC was operated in the fed-batch mode and at room temperature between 16 ◦C and 22 ◦C. The cathode solution contained 500 ml of deionized water.

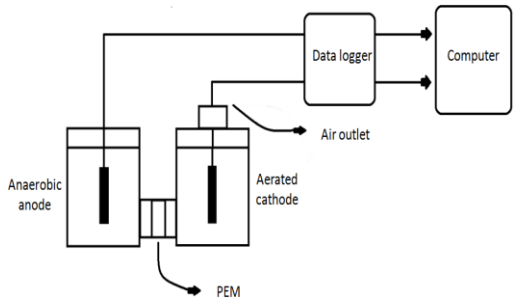

Fig.1. Schematic diagram of the dual chamber MFC for bioelectricity production

2.2. Experimental procedure

Activated sludge was used as inoculums and it was collected from the anaerobic process tank operated at the Ghaemshahr wastewater treatment center located in northern Iran. Sulfide was used as the sole electron donor. The conductivity and pH of the wastewater were 1093 µS cm^{-1} and 6.5, respectively. Wastewater containing 0.4 g l^{-1} sulfide was used as the anode solution and the total liquid volume was 600 ml. The anode chamber was purged with nitrogen gas for 10 min to remove dissolved oxygen so as to maintain anaerobic conditions.

2.3. Analysis

All chemicals and reagents used for the experiments were analytical grades and supplied by Merck (Darmstadt, Germany). The sulfide concentration was determined by using electrochemical methods. A cyclic voltammetry was performed at room temperature using the potentiostat/galvanostat electrochemical analysis system Ivium (Netherlands, V11100) with a voltammetry cell in a three electrodes configuration. An anode electrode, platinum wire and Ag|AgCl|KCl (3 M) were used as working, auxiliary and reference electrodes, respectively. Scanning electronic microscopy (SEM, VEGA2−TESCAN) techniques were applied to provide surface and morphological information for the used electrodes in the anode compartment.

The voltage was measured by using data logger and polarization curves were obtained through an adjustable external resistance, measured when the voltage was kept constant. The power and current were calculated based on the following equations:

$$P = I^2.R \quad (1) \qquad P = E^2/R \quad (2)$$

In these equations P represents produced power, E is measured cell voltage; R is external resistance and I indicate the produced current. The

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current and power generation density was normalized to the geometric area of membrane (9 cm^2).

3. Results and discussion

3.1 MFC performance

Microbial fuel cell (MFC) is a new technology that can produce electricity and treat wastewater concurrently. After inoculation of 0.4 $g.l^{-1}$ sulfide in the anode chamber with an active mixed culture as electrically active bacteria, data logger was used to obtain data in the form of an open circuit voltage until reaching a steady state condition.

The fabricated MFC was operated in the batch mode at room temperature. The performance of the microbial fuel cell was then evaluated by using a polarization curve. A maximum power density of 7.867 $mW.m^{-2}$ was obtained for MFC after 12 hours. For the latter, the power density remained around 8.134 $mW.m^{-2}$ until the 25th hour. The steady-state conditions were achieved after 34 hours of operation time. At the steady-state conditions, the maximum produced power and current density were 9.758 $mW.m^{-2}$ and 134.487 $mA.m^{-2}$, respectively. The maximum power and current density of the MFC in these 34 hours have been shown in table 2.

Table 2
Maximum power and current density generated in 34 hours after incubation of MFC by active microorganisms.

Time (h)	Maximum power ($mW.m^{-2}$)	Maximum current ($mA.m^{-2}$)
12	7.867	108.890
25	8.134	121.191
34	9.758	134.487

Power density and polarization curves of the MFC used during the steady state condition have been presented in Figure 2. The maximum power density obtained without aeration and optimization were 9.758 $mW.m^{-2}$ (see Figure.2).

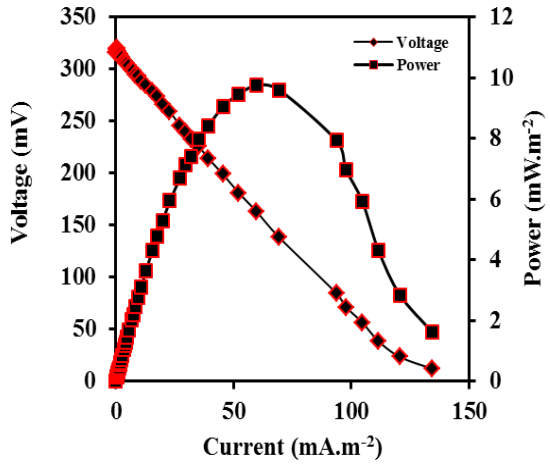

Fig. 2. Polarization curve of MFC in batch mode (34 hours after MFC operation).

According to prior studies, oxygen is an appropriate electron acceptor; therefore an increment of oxygen concentration in MFC can improve its performance (Gil et al., 2003). In this study, the influence of oxygen in the cathode chamber on OCV and the generated bioelectricity in the steady-state condition has been examined. While OCV results showed a stable value, the air supply with a constant flow rate was used to aerate the cathode chamber.

Figure 3 shows the performance of the MFC in terms of OCV improvement and with respect to time in the presence and absence of aeration in the cathode compartment. It can be observed that during aeration, the cell voltage rapidly increased, reaching 480 mV, leading to an increase in the MFC's performance and power generation. The maximum produced power and current density in the presence of aeration in the cathode chamber were 23.78 $mW.m^{-2}$ and 212.77 $mA.m^{-2}$, respectively.

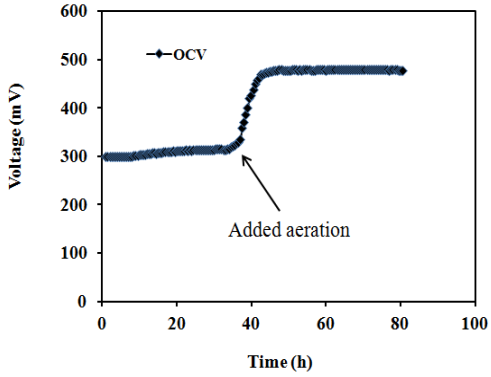

Fig.3. Open circuit voltage produced in MFC at steady-state condition and after aeration.

In each power supply, the main parameter is to enhance power and then to acquire the highest current density under maximum power density. The effect of mediators in the cathode compartment on MFC performances was investigated. Hexacyanoferrate was used as a mediator in the cathode chamber. The effect of aeration and lowest concentration of oxidizer agent on MFC performance have been shown in figure 4. When 0.2 g l^{-1} hexacyanoferrate was added to the cathode solution, the produced power density increased up to 38.773 $mW.m^{-2}$.

Hexacyanoferrate increases the conductivity of the system and is a suitable oxidizer agent in the MFC. This is the main reason behind the improvement seen in the performance of the MFC after the addition of a mediator (Jang et al., 2004). Also mediators such as hexacyanoferrate play a significant role in decrement of internal resistance (Zhang and Liu, 2010). Internal resistance is an important parameter in MFC performance and affects the output power.

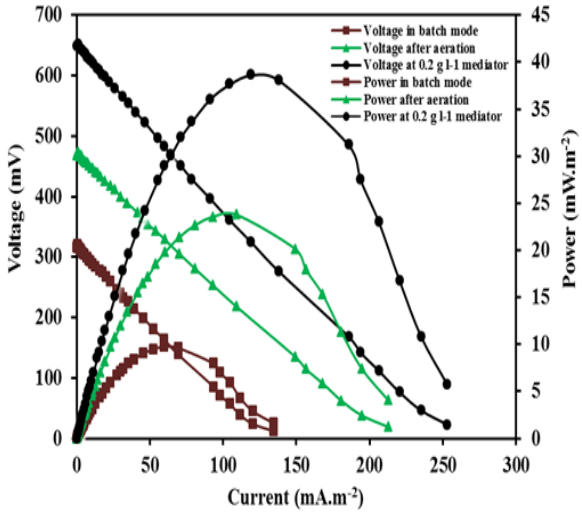

Fig.4. Variation of polarization curves in batch mode, after aeration and while using 0.2 g L^{-1} hexacyanoferrate as mediator in cathode chamber.

Different concentrations of hexacyanoferrate were examined in the cathode solution. At each concentration the polarization data was obtained when the voltage output became stable (after 2 h). Maximum power densities and open circuit voltages have been shown in table 3. Concentrations of oxidizer agent those were greater than 1.2 g l^{-1} showed no positive impact for the additional current and power (See Table 3).

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Table 3
Maximum power and current density and OCV of MFC in different concentration of hexacyanoferrate in cathode chamber as mediator.

Hexacyanoferrate concentration in cathode chamber (g l^{-1})	OCV (mV)	Maximum power (mW.m^{-2})	Maximum current (mA.m^{-2})
0	480.3073	9.782	99.392
0.2	648.1525	38.773	253.268
0.4	814.0657	88.727	442.238
0.6	836.7671	124.732	588.015
0.8	929.2631	221.841	855.273
1	968.9145	291.127	1063.141
1.2	984.9145	346.220	1257.51
1.4	988.9145	346.746	1285.64

Figure 5 shows the polarization, power density and open circuit voltage curves obtained after addition of the highest concentration of the mediator (1.4 g l^{-1}) in the MFC.

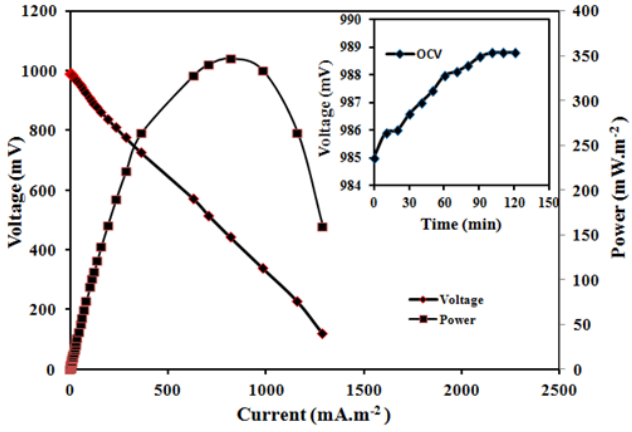

Fig.5. Polarization and power density curves after addition of 1.4 g L^{-1} hexacyanoferrate in the cathode compartment. Inset: open circuit potential curve in two hours after addition of 1.4 g L^{-1} hexacyanoferrate.

The initial concentration of sulfide in wastewater was determined. 0.4 g l^{-1}sulfide was consumed by the microorganisms to produce bioelectricity. Sulfide was detected after 3 days and almost 98% of the sulfide disappeared from the MFC. Our obtained results were very similar to the findings of previous researches; Zhao and coworkers used sulfur compounds as substrates in the MFC and sulfur compounds removal was attained (Zhao et al., 2009). Ryckelynck et al. produced electricity in the MFC by sulfide oxidation and they too achived 98% sulfide removal (Rabaey et al., 2006). Nearly complete sulfide removal was also obtained in the past e (Cai and Zheng, 2012).

3.2 Electrochemical behavior of MFC

Cyclic voltammetry (CV) is an electrochemical analysis method which can investigate the electrochemical behavior and activity of microbes in MFC (Zhang et al., 2009). In this study, cyclic voltammograms have been plotted using platinum wire and Ag/AgCl as auxiliary and reference electrodes, respectively. As can be seen, Figure 6 is depicted for anolyte in three different compositions. The electrochemical activity in anolyte has been examined with no inoculums, with just microorganism and with a mixture of inoculums and sulfide.

When there were no inoculums in the anode chamber, voltammograms had no sensible peak. They confirmed that there were no electrochemical activities in the anode chamber. Voltammogram (b) had one oxidation-reduction peak at approximately 0.265 V (vs Ag/AgCl) which indicated the electrochemical activity of the attached microorganisms on the anode electrode. Voltammograms (c) had two oxidation-reduction peaks which were approximately at -0.19 V (vs Ag/AgCl) and 0.29 V (vs Ag/AgCl). The first peak was attributed to sulfide oxidation and the second, implied the microorganisms' activity.

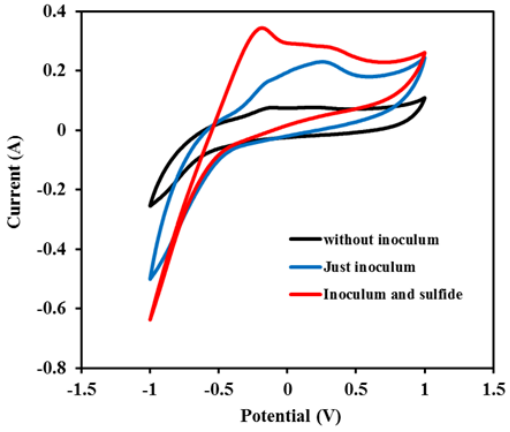

Fig.6. CV scans in the anode solution.

As can be seen in figure 7 scanning electronic microscopy demonstrates surface and morphological information about the used electrode in the anode compartment. A piece of the anode electrode (1×1cm) was analyzed by scanning electronic microscope before (7.a) and after (7.b) usage in the two chambers of the MFC with magnification of 2000. These obtained images demonstrated microorganisms grown on the graphite surface

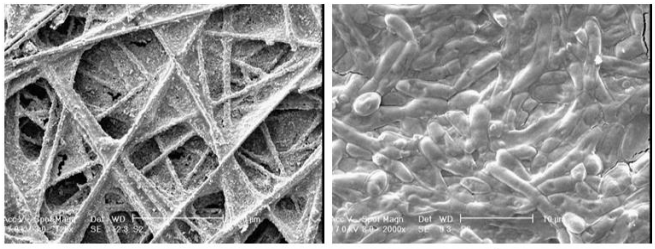

Fig.7. SEM image of carbon paper before (a) and after (b) using in MFC.

4. Conclusions

In this study a fabricated MFC was successfully operated to treat sulfide in the wastewater and simultaneously generate bioelectricity. The system used sulfide as a substrate at a concentration of 0.4 g l^{-1}. This was almost completely removed from the wastewater during the MFC operation and oxidized to elemental sulfur. Aeration in the cathode chamber increased the power density approximately 2 times. Hexacyanoferrate was used with several concentrations as an oxidizing agent in the cathode chamber to enhance the performance of the MFC. The maximum obtained power and current density were 346.746 mW.m^{-2} and 1285.64 mA.m^{-2}, respectively in the presence of 1.4 g l^{-1} of the mediator. The electrochemical activity of microorganisms and sulfide oxidation were confirmed using cyclic voltammetry.

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