Using Low Cost Membrane in Dual-Chamber Microbial Fuel Cells (MFCs) for Petroleum Refinery Wastewater Treatment

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Abstract. There are enormous methods to treat petroleum refinery wastewaters (PRW) that contain water-soluble hydrocarbons which cannot be separated by physical methods. Using microbial fuel cell (MFC) is a new PRW treatment method. Using potassium permanganate as cathodic electron acceptors in the cathode apartment of MFC with cheap proton exchange membrane instead of expensive Nafion was used in this work to treat PRW from Al Dura refinery. Potassium permanganate was used as cathodic electron acceptor to enhance MFC power production. So the effects of potassium permanganate amount on the MFC performance and PRW treatment results were investigated. Maximum power production at the room temperature of 1.0032 W/m² using 0.125 g/L of permanganate concentration, the maximum COD removal efficiency was 71.24 % during 48 hours.

1. Introduction.
In the past 30 years, research had expanded to find renewable energy sources rather than fossil fuels. Developments in the various fuel cell systems that benefit from bioenergy and renewable energy have been consistent with general trends to find these alternatives to these cells are microbial fuel cells.

Microbial fuel cells are electrophysiological cells of the Calvinistic type. The cells that have the potential to generate electricity from the chemical and biological reactions in which they occur. It usually consists of two chambers of anode and a cathode connecting them between a brine bridge or an ion exchange membrane (e.g. Nafion).

Figure 1 shows a typical microbial fuel cell consisting of two chambers of anode and cathode separated by an ion exchange membrane that allows protons to pass while oxygen and other compounds are obscured [1].

![Figure 1. Schematic diagram showing a preferred design for microbial fuel cell, PEM (e.g: Nafion) [1]](image-url)
The microbes adhering to the anode electrode dissolve the organic matter present in the anodized solution producing electrons, protons and carbon dioxide. The electrons and protons produced by the microbes move to the opposite side of the cell (cathode) through the outer circle and the ion exchange membrane respectively. In the cathode chamber, the protons and electrons react with the existing oxygen to form the water and an electric current as described in the following reactions [2].

\[
\begin{align*}
\text{Anodic reaction:} & \quad \text{CH}_3\text{COOH} + 2\text{H}_2\text{O} & \rightarrow 2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & (1) \\
\text{Cathodic reaction:} & \quad 8\text{H}^+ + 8\text{e}^- + 2\text{O}_2 & \rightarrow 4\text{H}_2\text{O} & (2) \\
\text{Overall reaction:} & \quad \text{CH}_3\text{COOH} + 2\text{O}_2 & \rightarrow \text{2H}_2\text{O} + 2\text{CO}_2 & (3)
\end{align*}
\]

PRW has two aqueous and oily phases. Two PRW treatment stages were traditionally used. Physical methods to separate oily phase. The main output of the physical process is aqueous phase that contains suspended oil and also solid particles. Then, during the second treatment stage, the suspended particles are separated by coagulation. The output is a homogenous aqueous phase containing water dissolved hydrocarbons including phenol, benzene, xylenes, and other pollutants, which failed to separate by physical methods. Biological approaches are traditional methods to treat this wastewater [3]. Traditional biological process utilizes microorganisms to oxidize organic matter to simple products (\(\text{CO}_2\), \(\text{H}_2\text{O}\), and \(\text{CH}_4\)) [4]. In the recent years, biological PRW treatment process based on direct oxidation of dissolved hydrocarbons have been developed with aid of photocatalytic and photo-Fenton methods [5-6].

All of the mentioned methods, however, require catalyst, large amount of oxidant, and high energy consumption. PRW treatment by microbial fuel cell as an indirect oxidation method can be considered as a cost effective method not only because of low energy demands but also due to its power output to supply energy for treatment unit [7]. Degradation of hydrocarbons soluble in PRW using dual-chamber MFC has been investigated by Luoa [8].

In the present work, a dual-chamber microbial fuel cell with low cost membrane was used to treat petroleum refinery wastewater from Al Dura, Iraq. In the MFC, As a result of degradation process, electrons travel through external resistance and protons pass through membrane. The corresponding protons migrate to the cathodic chamber. At the cathode, an electron acceptor is reduced by the electrons via the circuit and the protons via the membrane [9]. The effects of potassium permanganate amount on treatment of PRW and MFC performance were investigated.

2. Experimental work: MATERIALS AND METHODS

A. Materials

- Two PVC pipe chosen as a cathode and anode chambers for MFC with the volumes of 300 ml and 7 cm diameter. Each pipe contain 5 and 3 mm holes for solution addition and wires inlets respectively. The holes in anode side were sealed with small cup to prevent air admittance.
- Cathode: 6 cm diameter anodizing aluminum.
- Anode: the MFC used in this experiment utilized non-catalyzed graphite sheet 2*4 cm.
- Membrane: 38.5 cm\(^2\) hydrophobic LowDensity Polyethylene LDEP as a low cost material utilized in this MFC between the two chambers.
- Solution containing organic matter at anaerobic anode side received from wastewater treatment lab, 7 pH and 500 mg/L COD (chemical oxygen demand).
- Potassium permanganate aqueous solution used in cathode side as an electron acceptor, with 0.0625, 0.125, and 0.25 g/l concentrations.
- In conventional MFC platinum coated carbon cloth and carbon cloth and activated with biofilm were used as cathodes and anodes respectively. In most MFCs expensive cost Naftion®, Agar and Gore-Tex membranes were used as membrane materials.
B. Fuel cell configuration
The dual-chamber fuel cell used in the present paper constructed by joining the cathode and anode chambers between two square Perspex glasses by 4 screws. The distance between anode and cathode electrodes was constant in all experiments (3 cm). Copper wires were used for contact with electrodes after sealing the contact area with 'epoxy' material. A 38.5 cm² proton exchange membrane was embedded between two chambers. Voltage recorder using data logger, Hantek365A embedded parallel to external resistance, 10 Ω. All the experiments carried out at room temperature.

C- Electric parameters calculations
Current and power densities are the most important parameters that should be measured. Ohm law: used to calculate current intensity [10].

\[ I = \frac{V}{R} \]  

(4)

Where V and R denote, respectively, potential difference and external resistance. In addition, power obtained using the following equation:

\[ P = IV \]  

(5)

Power density (W/m²) and current density (A/m²) are calculated by dividing power and current intensity to the anodic surface area (m²).

D- Chemical oxygen demand measurements
COD is the main characteristic of the wastewater, evaluated as an index of MFC performance. In the present research, APHA standard method was used to measure COD concentrations.

3. Results and Discussions
A-Operational MFC power generation
Immediately after cell filling with wastewater and potassium permanganate aqueous solution voltage reached 685, 657, and 100 for cells with cathode side contain 0.25, 0.125, 0.0625 g/L potassium permanganate aqueous media. The proper selection of aluminum and graphite electrodes according to their difference potential in their solutions and oxidizing of the organic matter by microorganisms assumed to be the chemical and the biological factors might have been the reason of the high initial voltage results. Thereafter, the voltage rapidly increased due to biological activity. The instability that can be attributed to the instability of the biofilm on the anode surface during the working period that include growth and degradation [11]. Cell voltages stabilized at 823, 836, and 782 mV after 48 hours, voltage variation as shown in Fig 2. Increasing potassium permanganate concentration in cathode side increase electrolyte conductivity and decrease ohmic and activation losses [10], that increase power density 0.3292, 1.0032, and 0.7038 W/m² with potassium permanganate concentration as shown in Fig.3. Decreasing power density at 0.25 g/l potassium permanganate concentration related to the formation of Al–KMnO₄ as the main product of the aluminum surface and potassium permanganate, cathode solution, reaction that limits electron transfer to the solution and complete the cell reaction to generate electricity.
Voltage inclined when using the cell after few months without new solutions injection into the chambers, as shown in Figure 4 for the cell with cathode contain 0.25% g/L potassium permanganate aqueous media, this attributed to the formation of brown layer over aluminum surface consist from Al–KMnO₄ complex [12] which classified as a protective film. As well as a fully degradation of organic matter in the PRW, as COD measurement confirmed, reducing electron generation and increasing the system resistance.

Under typical atmospheric conditions, a native oxide or passive film naturally forms on aluminum. The native oxide layer is nonuniform, thin and noncoherent. The native oxide film imparts a certain level of corrosion protection. Anodizing aluminum is capitalizing on the natural phenomenon of passive film formation on aluminum in a production environment. Anodizing yield a uniform and continuous protective oxide film. It is highly ordered columnar nanoscale structure with central pore [13]. Pores reactivity enables adsorption of the electrolyte ions, as the immersion period increases, the protective film is ruptured and a complex Al–K MnO₄ formed that closed the pores and a thick, nonconductive, inhibitor layer formed. Formation of the nonconductive layer increase the double layer and the whole system resistance that have great effect on the cell potential.

**B- Chemical oxygen demand COD removal**

COD is amount of required oxygen to convert total organic matter present in wastewater into carbon dioxide and water. Treatment process reduces COD. Figures 4 show, COD removal of PRW versus time using potassium permanganate as cathodic electron acceptors, with 100 Ω of external resistance. As can be seen in Figures 5, COD removal efficiencies were 69.254% and 71.24 % and 69.75% during 48 hours in the presence of 0.0625, 0.125, and 0.25 g/l concentrations potassium permanganate respectively.
During PRW treatment into MFC, COD was found to be reduced extensively in the first day. To explain COD rapid reduction in the first day return back to the variation of voltage with time, it was instable during the first 24 hours that referred to the biofilm instability. Biofilm degradation and rebuilding consume the organic matter to produce electron during adhering of the microorganisms on the electrode. When the biofilm became stable after that time it resist electron transferring to the anode surface through its thickness and inhibit COD reduction. Increasing potassium permanganate concentrations in cathode chamber, as electron acceptor, enhance the electron flow from the anode to the cathode through the external circuit and the protons through the membrane that increasing organic matter degradation reaction and reducing COD.

C- MFC efficiency and performance calculations

We depend in our design and electrodes materials selection into their electrochemical properties into the chamber solutions. For theoretical calculations the anode polarization potential found using eq.6 [14]

\[ E_{anode} = E_{anode}^0 - \frac{RT}{8F} \ln \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{HCO}_3^-][\text{H}^+]} \right) \]  

(6)

Where \( E_{anode}^0 = 0.187 \) V.

Calculation produces a potential of -0.296 V. Permanganate redox potential is a function of its concentration in cathode chamber and pH. By using Nernst equation and theoretical potential \( (E^0) \) of 1.51 V, polarization potential of cathode can be described as follows [15]:

\[ E_{cathode} = E_{cathode}^0 + 0.0052 \log [\text{MnO}_4^-] - 0.0422 \cdot \text{pH} \]  

(7)

\[ \text{MnO}_4^- + 8\text{H}_2\text{O} + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 12\text{H}_2\text{O} \]  

(8)

\[ E_{cathode} = 1.662 \text{ V} \]

Calculation produces a potential of 1.197, 1.199, and 1.2 V for 0.0625, 0.125, and 0.25 g/l of potassium permanganate aqueous solution used in cathode side.

\[ E_{\text{emf}} = E_{\text{cathode}} - E_{\text{anode}} \]  

(9)

Theoretical \( E_{\text{emf}} \) were calculated using eq. 9 were found to be 1.493, 1.49, and 1.496 V for 0.0625, 0.125, and 0.25 g/l of potassium permanganate aqueous solution used in cathode side. In practice, increasing the permanganate concentration increases the electrolyte conductivity and decreases ohmic and activation losses that increase power of MFC. Also, manganese dioxide is the main product of redox reaction and its reaction with cathode electrode, as discussed above, limits electron transfer and MFC performance.

In practice, due to irreversible losses, the actual output voltage is less than the one resulted from the ideal equation. The significant losses that affect MFC operation are activation loss \( \eta_{act} \), ohmic loss \( \eta_{ohmic} \), and mass transfer loss \( \eta_{conc} \) that take place in both the anode and cathode. The operational
voltage output as a function of current density can be calculated as follows [16], taking open circuit voltage VOC into account:

\[ V = OCV - \eta_{act} - \eta_{ohmic} - \eta_{conc} \]

MFC efficiency measured by equation 10

\[ \eta_{MFC} = \frac{V_{measured}}{E_{emf}} \cdot \frac{(n \cdot F)}{(n \cdot F)} = \frac{V_{measured}}{E_{emf}} \quad (10) \]

Efficiency for cells with different KMnO₄ concentrations, 53.44, 54.28 and 50.77%. It was found that the optimum power generation efficiency with cathode side contain 0.125 g/l KMnO₄.

Columbic efficiency is defined as the ratio between the charge transported to anode and maximum charge, which might be obtained from total substrate degradation. This parameter is evaluated as follows [17]:

\[ CE = \frac{\int_{0}^{t_b} \frac{dt}{dt}}{F} \frac{V_{an} \cdot \Delta(\text{COD})}{V_{an} \cdot \Delta(\text{COD})} \quad (11) \]

Where I is the electrical current intensity, F the Faraday's constant, Vₐₙ the anaerobic chamber volume, and Δ (COD) the overall removal of substrate during tₖ.

Using Eq. (11), the values of Columbic Efficiency (CE) with 100 Ω external resistance were 7.56%, 22.05%, and 16.89% during 48 hours with cathode side contain 0.25, 0.125, 0.0625 g/L potassium permanganate aqueous media respectively. Thus, it is obvious that using permanganate as electron acceptor has advantages such as higher values of removal COD and CE. As pointed earlier, the reason is that the rate of oxidation of wastewater by microorganisms is higher due to effective e’ discharge and higher current generation using permanganate as electron acceptor [18].

4. Conclusions.
Petroleum wastewater from Al Dura Refinery (COD = 500.125 mg/L, pH = 7) treated in a dual-chamber microbial fuel cell MFC using potassium permanganate as cathodic electron acceptors. To increase the values of columbic efficiency and wastewater treatment, it is essential to use MFC with optimum potassium permanganate amount. Selecting the electrodes materials with high electrochemical potential difference play a big role in the power generated form MFC. Long time exposure of Aluminum electrode into permanganate aqueous media will produce resistance layer on its surface which increase whole system resistance and reduce the generated power.

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