



Effect of pH variation and oxygen presence on the cathodic recovery of copper in the microbial fuel cell with bioenergy generation and wastewater treatment

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Bio-electrochemical systems (BESs) are a novel, promising technology for the recovery of metals. Microbial fuel cells (MFC) have been widely investigated for wastewater treatment and simultaneous energy production as well as resource recovery. In this study, the effect of pH and oxygen presence on the reduction of Cu^{2+} ions in the cathode compartment was analyzed as oxygen act as a competitor for metal ions and can cause lower recovery of metal due to its higher reduction potential compared to most of the metals. It was observed that in the presence of oxygen, the power density was higher 35 mW/m^2 compared to 14 mW/m^2 in the absence of oxygen. The copper removal was 98.3% and 97.1% in the aerobic cathode and anaerobic cathode respectively. The COD removal was higher in the case of aerobic cathode system than the anaerobic cathode which was 86% and 80% respectively. At pH more than 4.5 Cu^{2+} precipitated instead of depositing on the cathode surface, while at lower pH, it was reduced to $\text{Cu}_{(s)}$ and deposits on the surface of the cathode. The reduction of Cu^{2+} ions in the absence of oxygen can help to reduce the complexity of the design but the higher performance in the case of aerobic environment was because of the parallel reduction of Cu^{2+} and oxygen.

Keywords: Copper recovery, microbial fuel cell, bio-energy, wastewater treatment, Cu^{2+} ions.

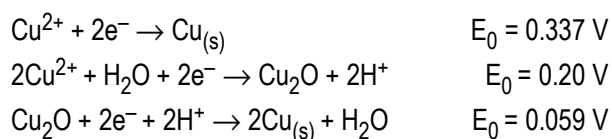
Introduction

The environment quality has been compromised due to the various human activities. The rapid digitalization has contributed to the huge demand for the electronic items and as a result, it increased the disposal quantity of heavy metal containing waste streams into the environment¹. It has an adverse effect on ecology and human health². Copper is widely used in a variety of products such as electrical appliances, water pipes, electrical and data cables due to its properties such as high electrical and thermal conductivity, malleability and ductility³. It is an important industrial metal having consumption of approximately 70% in the electrical appliance industry⁴.

In a microbial fuel cell (MFC) the wastewater is degraded in the anode compartment due to microbial action generating electrons, protons and CO_2 ². The electrons are transferred through the external circuit to the cathode giving bioenergy and protons migrated through the proton exchange

membrane to the cathode chamber where they react with electron acceptor (such as O_2)⁵. MFCs can be used for heavy metal recovery from wastewater if the terminal electron acceptor on the cathode side is a metal ion and it can be reduced.

The major challenges related to MFC studies are long-term application and stability of the system, high cost of electrodes and membrane, membrane fouling, higher internal resistances for electron transfer and lower current densities. In the cathode chamber if wastewater containing Cu^{2+} ions is fed then they will act as an electron acceptor and it can be recovered as pure copper, Cu_2O and $\text{Cu}(\text{OH})_2$ ⁶⁻⁸. The reduction of Cu^{2+} ions can be achieved on the cathode side due to its higher reduction potential than the redox potential of acetate⁹. This can result in the simultaneous recovery of copper with wastewater treatment and bio-energy generation. The reaction mechanism involved in the reduction of Cu^{2+} ions can be proposed by the following equations¹⁰:



The required pH for the better performance of cathode is 4.5 as above the pH 4.5 the Cu^{2+} may precipitate as Cu_2O or CuO .

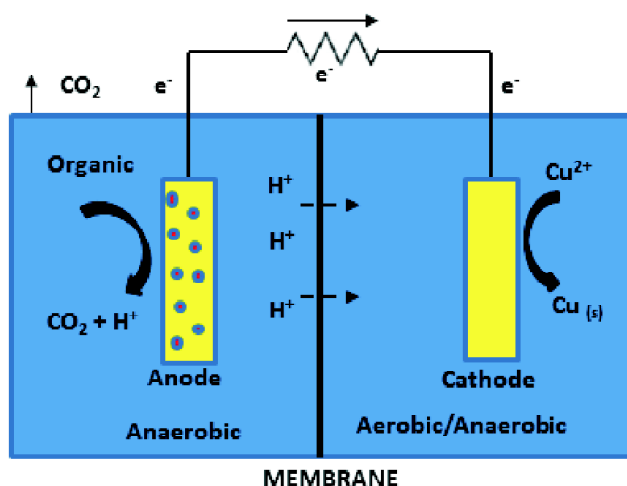


Fig. 1. Mechanism of copper recovery at pH less than 4.5.

Various studies have been done for the recovery of heavy metals. But when oxygen is present with the metal ions at the cathode then there is a possibility of competition between metal ions and oxygen for getting reduced especially if the metal ions are having lower reduction potential than oxygen. In such situations there is a need to study the effect of oxygen presence on the recovery of metal ions which can assist to decide the condition requirement at the cathode in terms of aerobic and anaerobic.

In the literature, the reduction of the Cu^{2+} ions under aerobic condition is reported but in this case oxygen may act as a competitor against the Cu^{2+} ions to accept the electrons as oxygen has higher reduction potential than Cu^{2+} which may cause lower copper recovery in the microbial fuel cell. Therefore, the main aim of this study was to carry out the reduction of the Cu^{2+} ions under anaerobic condition and its comparison with aerobic conditions as well as the effect of pH on the MFC performance in terms of COD removal, copper recovery, bio-energy generation as well as the analysis of various internal resistances and losses occurring in the system.

Materials and methods

Materials:

The analytical grade chemicals required for the experiments were purchased from the viable sources. Distilled water was produced by the Milli-Q filter (Millipore, USA). Carbon felt and Nafion 117 was provided by Vinpro Technologies, Hyderabad. The synthetic wastewater was prepared with acetate 1000 mg L^{-1} , protein 80 mg L^{-1} , NaHCO_3 24 mg L^{-1} , KH_2PO_4 14 mg L^{-1} , NH_4Cl 60 mg L^{-1} , CaCl_2 18 mg L^{-1} , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ mg L^{-1} and was used as an anolyte¹¹. The 500 ppm Cu^{2+} ion solution was prepared from CuSO_4 .

MFC configuration and operation:

Four different configurations of dual-chamber MFCs were constructed and inoculated with 100 mL anaerobic sludge from the local municipal sewage wastewater treatment plant. The dual-chamber MFCs were fabricated with the anode and cathode compartments ($\text{dxH} = 4 \times 8 \text{ cm}$, 120 mL) as shown in Fig. 2, two ports that allow feed inlet/outlet and gas inlet/outlet, and electrode connection parts. Carbon felt (0.0028 m^2) was used as electrodes in both the compartments. The membrane Nafion 117 (DuPont, USA) was used to separate anode and cathode compartments. The electrodes were coupled with SS wire as a current collector.

The feed solution of the anode was 5% sludge with prepared anolyte and in the cathode compartment, there was Cu^{2+} ion solution having concentration of 500 ppm . The initial chemical oxygen demand (COD) of the feed was 1000 mg/L . The anode compartments were initially purged with nitrogen to remove dissolved oxygen.

Table 1. Various configurations in the installed MFCs

Set	Description
A1	Aerobic cathode with no pH control
A2P	Aerobic cathode with pH maintained below 4.5
C1	Anaerobic cathode with no pH control
C2P	Anaerobic cathode with pH maintained below 4.5

The pH in A2P and C2P was maintained below 4.5 by adding HCl to avoid precipitation of copper.

The systems were operated in open circuit condition for

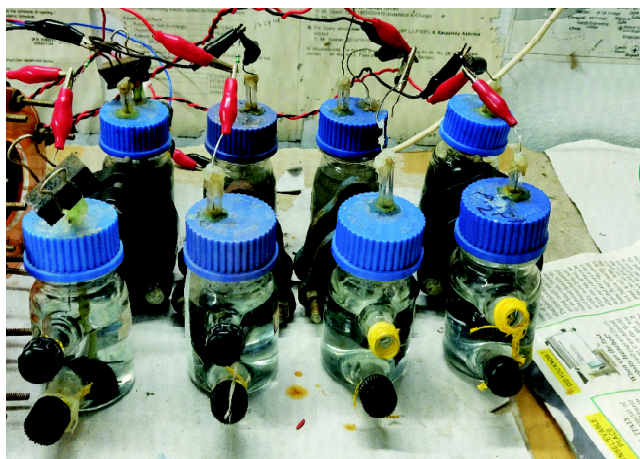


Fig. 2. Reactor setups (left to right C1, C2P, A1, A2P).

72 h to achieve a stable voltage and then the polarization curve was prepared to get an idea about optimum resistance to be used in the system which was 1000Ω . The open circuit potential was measured by the data logger system. After connecting the systems with external resistance, they were connected to the data acquisition system and the voltage was measured at an interval of 30 min.

Parameters and measurement:

Open circuit potential (mV) was measured and stored in the data logger system (34972A, Keysight Technologies, USA). Ohm's law was used to calculate current (I) and power. The polarization curve was prepared by varying various external resistances ($100 \text{ k}\Omega$ to 1.5Ω) in the external circuit and voltage was measured at each resistance. The current was calculated as $I = V/R_{\text{ext}}$ or the current density normalizing by an electrode surface area, and by plotting voltage versus current to obtain the polarization curve¹². The closed reflux method as per APHA was applied for the analysis of COD¹³. Atomic absorption spectroscopy was used to measure the remaining Cu^{2+} ion concentration in the catholyte. The MFC performance was evaluated in terms of voltage (V) and current (I). The Tafel plots and electrochemical impedance spectroscopy (EIS) were performed to determine various losses. The copper recovery was calculated by equation $((\text{Cu}^{2+}_{\text{initial}} - \text{Cu}^{2+}_{\text{final}})/\text{Cu}^{2+}_{\text{initial}}) \times 100$ and COD removal was calculated by equation $((\text{COD}_{\text{initial}} - \text{COD}_{\text{final}})/\text{COD}_{\text{initial}}) \times 100$.

Results and discussion

The open circuit potential (OCP) was measured using a data logger and the set-ups were kept in the open circuit mode for 72 h to achieve stable voltages as shown in Fig. 3. The stable open circuit potentials achieved were 0.82 V, 0.509 V, 0.302 V and 0.471 V for reactors A1, A2P, C1 and C2P respectively.

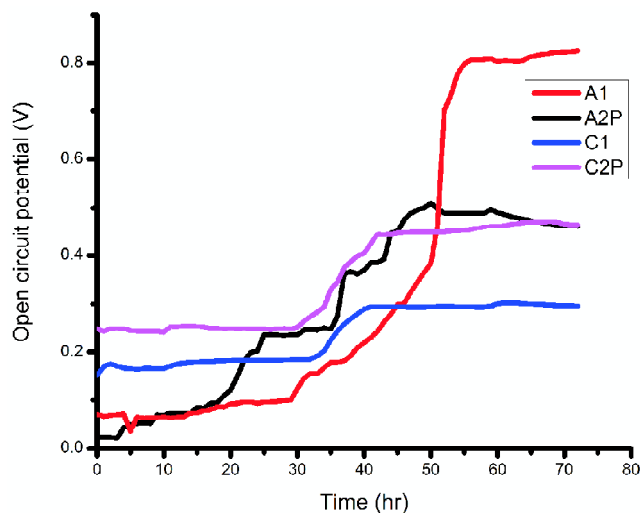


Fig. 3. Open circuit potential.

The highest power density observed was 35 mW/m^2 in the case of A1 and 22 mW/m^2 in the case of C1 as shown in Fig. 4.

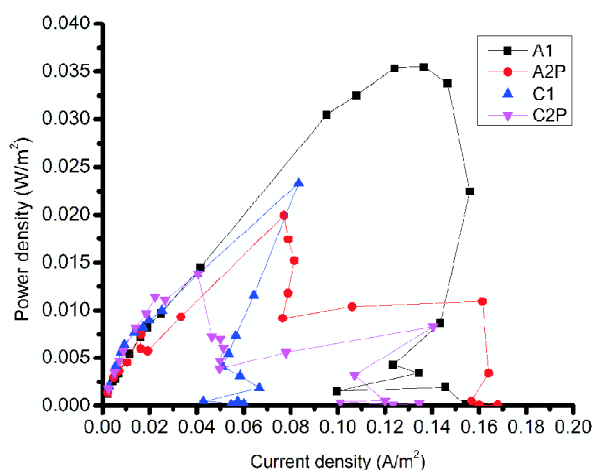


Fig. 4. Power density curves for all the MFC reactors.

The polarization curve shown in Fig. 5 represents a voltage decrease in the system due to electrode overpotentials and ohmic losses. The highest current density 0.15 A/m^2 was observed in the case of aerobic cathode A1 system and 0.08 A/m^2 in the case of anaerobic cathode system C1.

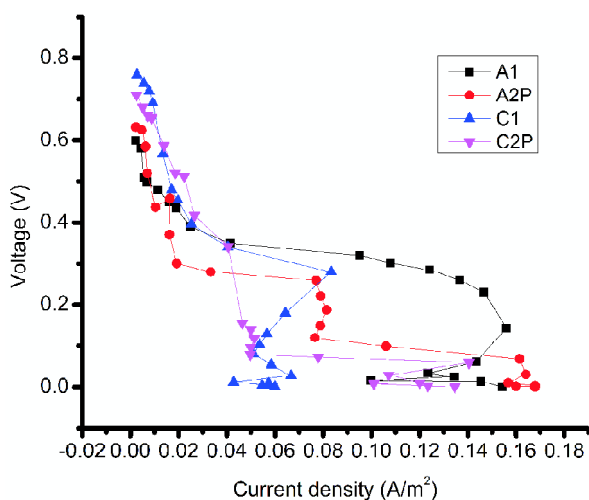


Fig. 5. Polarization curve for the installed MFC reactors.

Electrochemical impedance spectroscopy (EIS):

To evaluate various internal resistances that influence the electron transfer in the system like charge transfer resistance, double-layer capacitance, ohmic losses, etc., the Nyquist plots are used by using EIS¹⁴. Based on that, performance of any change is measured and selected like electrode coatings, catalyst application, change in electrolyte, conditions, etc.

EIS was used for our system to find out internal resistances due to faradic and non-faradic components influence the power performance of the system and it comprises of series resistance (R_s) which can be further divided into polarization resistances and ohmic resistances. The three-electrode system arrangement was used with CH instruments electrochemical workstation to carry out EIS studies shown in Fig. 6. The smallest semicircle shows lowest resistance. The reference electrode was Ag/AgCl.

The minimum ohmic resistance (R_s) and charge transfer resistance (R_{ct}) were observed in A1 (Table 2) in which the cathode was aerobic and pH was not maintained less than 4.5.

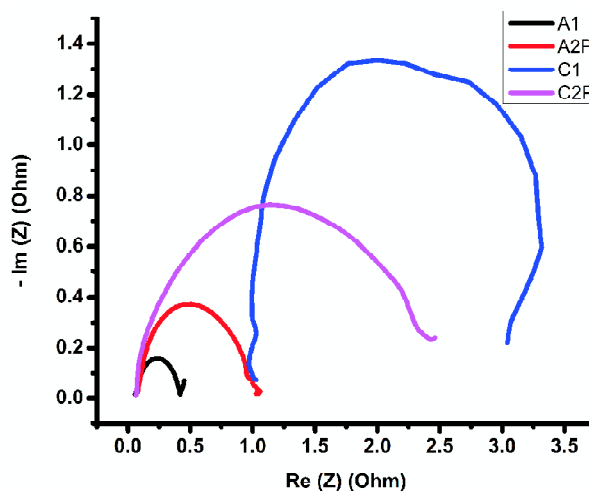


Fig. 6. Comparative Nyquist plot for the installed MFC reactors.

Table 2. Various internal resistances for various electrodes

Set	R_s (Ω)	R_{ct} (Ω)
A1	21.94	86.14
A2P	27.56	114.8
C1	380	720
C2P	33.92	235.2

Tafel plot:

The Tafel analysis can lead to the estimation of two important physical parameters: the Tafel slope and the exchange current density¹⁵.

The Tafel plot was prepared (Fig. 7) to calculate the exchange current density by normalizing with the cathode area.

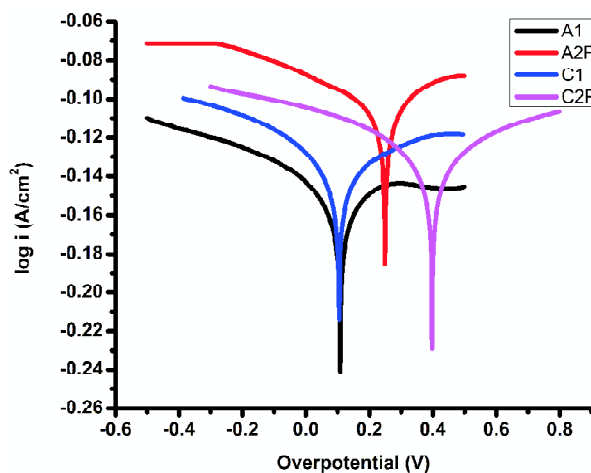


Fig. 7. Comparative Tafel plots for different MFC reactors.

The highest exchange current density was observed for A1 (Table 3) which was an aerobic cathode without any pH control which shows lower activation losses and internal resistances.

Table 3. Exchange current density for various electrodes

Set	Exchange current density (i_0) (mA/cm ²)
A1	4.08E-05
A2P	1.38E-06
C1	3.66E-06
C2P	4.24E-06

The maximum COD reduction and Cu²⁺ reduction were observed in A1 and the lowest in the C2P. The maximum power density was observed in the A1 which was 35 mW/m². The maximum COD reduction of 86% and Cu²⁺ reduction of 98.3% were observed in A1 and the lowest in the C2P.

Table 4. MFC performance

Parameter	A1	A2P	C1	C2P
COD reduction (%)	86	83	85	80
Cu ²⁺ reduction (%)	98.3	98.1	97.8	97.2
Power density (mW/m ²)	35	22	23.2	14.9

Anaerobic and aerobic Cu²⁺ reduction and pH variation:

The Cu²⁺ ions reduction under aerobic condition was higher than the anaerobic condition. This is due to the parallel reduction processes of oxygen and Cu²⁺ ions which lead to a higher rate of electron transfer from anode to cathode. This causes higher availability of electrons for copper ions to reduce and higher power density. The brownish mass of copper was observed on the cathode surface. This might also indicate that there was very little or no effect of oxygen presence on the reduction of the Cu²⁺ ions. The internal resistances were lower and exchange current density was higher in case of the aerobic environment with no pH control. This indicates lower resistances for electron transfer to the cathode and lower activation loss. Although, at higher pH, Cu²⁺ ions can precipitate as Cu₂O or CuO in the solution, but as stated above, there is a possibility for the conversion of Cu₂O

to Cu_(s). When the pH was maintained by external input, it might imbalance the natural flow of protons from the anode to the cathode resulting in lower microbial activity at the anode which in turn affected the electron generation and transfer in the microbial fuel cell system.

Conclusion

The effect of pH and oxygen presence on the reduction of Cu²⁺ ions and COD removal as well as reactor performance in terms of energy output was studied in MFCs. It was observed that in the case of A1 aerobic environment the power density was higher (35 mW/m²) and a lower value of 14.9 mW/m² was observed in the case of C1 under anaerobic environment. Similarly COD removal was also higher in case of aerobic cathode system (86%). The copper removal was 98.35% and 97.2% in the aerobic cathode and anaerobic cathode respectively. The pH of Cu²⁺ ions solution below 4.5 favors the reduction of Cu²⁺ ions to Cu_(s) but due to imbalance in proton transfer it has negative effect on the performance of MFC in terms of energy generation as well as it also increases internal resistances which obstructs electron transfer from anode to cathode especially in anaerobic condition. The internal resistances were lower in the case of aerobic cathode reactors indicating ease of electron transfer from anode to cathode.

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