

## BIO-ELECTROCHEMICAL RECOVERY OF COPPER FROM DILUTE ACIDIC SOLUTIONS AS A FUNCTION OF EXTERNAL RESISTANCE, COPPER AND IRON CONCENTRATIONS

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**Abstract.** Bioelectrochemical systems provide a promising tool for the copper recovery from the heap leaching solutions which usually contain low copper and high iron concentrations. In this study, the role of copper and ferrous ion concentrations, and external resistance in the removal of synthetic sulfuric acid solutions by a lab-scale Microbial Fuel Cell (MFC) was investigated and good results were obtained in the removal of copper.

**Keywords:** copper, heap leaching solution, bioelectrochemical systems, microbial fuel cell, external resistance.

### 1. Introduction

Low grade ores from abandoned and producing deposits, overburden rocks, mill tailings, and non-ferrous slag are considered to be one of the largest sources for non-ferrous metals production.<sup>1</sup> Heap leaching is a widely used extraction method for low-grade ores and minerals, including copper, gold, silver, and uranium.

Oxide copper ore, mixed oxide-sulphide ores and low-grade copper sulphide ore, which, for economic reasons, cannot be enriched by flotation, may be processed by heap leaching methods.<sup>2</sup> However, processing of a huge amount of low-grade ore causes serious problems such as lower copper-cathode-production efficiency from such a low-concentrated pregnant leach solution (PLS) in the solvent extraction and electro-winning (SX-EW) plants.<sup>3</sup> The PLS usually contains up to *ca.* 2 g/L of copper, while the iron concentration is up to *ca.* 5 g/L due to, *e.g.*, leaching of iron minerals.<sup>4</sup> Also, it contains an extensive area of elements, such as Cu, Fe, Ni, Zn, *etc.*

Almost 20 % of annual Cu production is carried out using electro-winning.<sup>5</sup> In industrial electro-winning, the typical operating conditions are cell voltage of *ca.* 2 V, copper ion concentration of *ca.* 50 g/L, current density of 0.02–0.045 A/cm<sup>2</sup>, temperature of 313–333 K, current efficiency of 89–94 % and specific energy consumption of 1.8–2.5 kWh/kg of copper.<sup>6</sup> The application of EW for dilute leaching solutions purification, specifically the removal of Cu, is actually a difficult approach, since the recovery of metals from dilute solutions is known to involve high operating expenses.

Microbial Fuel Cells (MFCs) are a novel technology to convert biodegradable materials directly into electricity. During the last years, applications of microbial fuel cells expanded from wastewater purification combined with electricity production to production of added-value components in the cathode, like H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>.<sup>7,8</sup> A new potential application of MFCs is the removal and recovery of metals from mining and metallurgical wastewaters and leachates. Compared to the electrowinning, the metallurgical MFC has the advantage of electricity production instead of electricity consumption, and the high removal efficiency leading to final copper concentrations <1.2 mg/L.<sup>9</sup> Later, Motos *et al.*<sup>10</sup> tried to improve the MFC performance by modifying the electrode materials, the membrane, and the distance between electrodes and mass transport within the system. Using a synthetic solution containing 2 g/L of Cu, high current density and power production were achieved in their improved cell. The current was enhanced from 3.2 to 23 A/m<sup>2</sup> while the power density increased from 0.8 to 5.5 W/m<sup>2</sup>.<sup>10</sup>

Metal recovery with Bio-Electrochemical Systems (BESs) was first illustrated with copper,<sup>11</sup> and, afterwards, some other metals, such as zinc, silver, and vanadium, have been successfully recovered.<sup>12–14</sup> Ter Heijne *et al.*<sup>9</sup> studied the recovery of copper in an MFC using a bipolar membrane. The catholyte consisted of 1 g/L of Cu<sup>2+</sup> as CuCl<sub>2</sub> at pH 3. Maximum power density of 0.8 W/m<sup>2</sup> and copper removal of 99.88 % were obtained.

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Zhang *et al.*<sup>15</sup> investigated the cathodic reduction of complex-state copper(II) in a microbial fuel cell. They used a synthesized solution containing 5 mM and 50 mM of Cu and NH<sub>3</sub>, respectively. Electrochemical reduction mechanism of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> was studied and copper removal efficiency of 96 % was obtained.

Fedje *et al.*<sup>16</sup> studied the washing of soil or ash (combusted soil/bark) with acidic waste liquids followed by electrolytic Cu recovery by means of bioelectrochemical systems. Copper with 99.7–99.9 wt.% purity was recovered from the acidic leachates, using BES. They also investigated the behavior of the main impurities in the solution. Co-deposition of Zn 0.1 %–0.3 % and Pb 0.01 %–0.03 % were measured.

Kaur *et al.*<sup>17</sup> studied the copper recovery in a bioelectrochemical system using synthesized and real distillery effluents (relatively high copper concentration, *i.e.*, 1 g/L followed by a lower concentration, *i.e.*, 50 mg/L). 60–95 % copper was recovered in the form of deposits depending on starting concentration. According to their results, better performance was observed at high Cu<sup>2+</sup> concentration with double metal removal efficiency. Initial Cu<sup>2+</sup> concentration, pH and external resistance were found to play an important role.

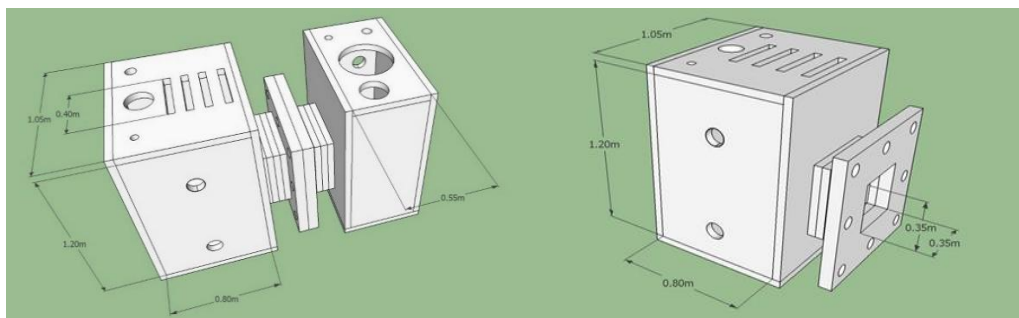
Thus, the first purpose of this study was to determine the effect of external resistance and initial Cu<sup>2+</sup> concentration on the removal of copper, power and current generation in the MFC. The empirical findings in this study provide further insights into the correlation of operational variables such as external resistance and Cu<sup>2+</sup> concentration in the catholyte. The second aim of this study was to investigate the impacts of major impurities, such as iron, in the process of copper removal and recovery. Indeed, most of the studies reported so far in the literature have focused on simple synthetic solutions, which contain only free Cu ions (Cu<sup>2+</sup>) in the catholyte. By contrast, real wastewater and particularly acidic heap leaching solutions, typically contain a complex mixture of metals, such as Cu<sup>2+</sup>, Fe<sup>2+</sup> and other ionic and non-ionic constituents. Therefore, the viability of copper removal and recovery from synthetic binary solutions containing Cu<sup>2+</sup> and Fe<sup>2+</sup> ions was herein examined.

Furthermore, main attention was also placed at analyzing the influence of catholyte composition on the performance of a copper-reducing MFC, primarily in terms of current density and power density.

## 2. Experimental

### 2.1. Microbial Fuel Cell

A rectangular-shape bioreactor consisting of two joint chambers made from plexiglass sheets, were used in this study as shown in Fig. 1. Each reactor consisted of an anode and a cathode chamber (400 and 600 mL effective working volume for cathode and anode compartment, respectively), which were separated by a proton exchange membrane (PEM-Nafion™ N117-Dupont Co., USA) with an available surface area of 12.25 cm<sup>2</sup>. Both anode and cathode electrodes were made of stainless-steel mesh with the same geometrical surface area of 14 cm<sup>2</sup> (both sides). BES reactor was connected to a computer equipped with a data logger (DGHS-EL20101-R3, Danesh Gostar Co., IRI); a saturated calomel electrode (SCE, +0.244 V vs. SHE, Metrohm Co., Switzerland) was used as a reference electrode to record the individual anode and/or cathode potential during the various experiments. Throughout the study, all potentials were reported with respect to the SHE. The external circuit consisted of copper wires (about 2 mm, outer diameter). Both compartments were air proofed in order to prevent O<sub>2</sub> leaking into the anaerobic chambers, being toxic to anaerobic bacteria thriving at the anode and competing with Cu<sup>2+</sup> ions as terminal electron acceptors at the cathode. The membrane was preconditioned prior to being used. To this aim, it was sequentially soaked and boiled in a hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30 %), deionized (DI) water, and then sulfuric acid solution (H<sub>2</sub>SO<sub>4</sub>, 0.5M); each step taking one hour. Prior to being used, the PEM was immersed and boiled in deionized water for one hour.<sup>18</sup> Before making the electrical connection, the steel meshes were first cleaned by soaking in pure acetone or ethanol overnight.



**Fig. 1.** A scheme of the experimental apparatus

## 2.2. Materials

All chemicals used for the experiments were analytical grade and were used as received without any extra purification. The aqueous solutions and reagents were prepared by using distilled water (DI). Anaerobic sludge, collected from the industrial town sewage (Yazd, Iran), was used as inoculum in the anode compartment. Culture medium contains the following ingredients (all per liter of DI water): 1.36 g/L  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ , 1.05 g/L  $\text{NH}_4\text{Cl}$ , 1.5 g/L  $\text{KH}_2\text{PO}_4$ , 2.2 g/L  $\text{K}_2\text{HPO}_4$ , and 0.2 g/L yeast extract.<sup>19</sup> Phosphate buffered-saline (PBS) solution includes (per liter):  $\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$  (4.77 g),  $\text{Na}_2\text{HPO}_4$  (2.75 g),  $\text{NaCl}$  (2.93 g) (to increase solution conductivity). Also, copper (II) sulfate (with 99 % purity) solution in desired concentrations, sulfuric acid (with 98 % purity) and nitric acid (with 65 % purity) were used in the experiments. All of the chemicals used were purchased from Merck (Germany).

## 2.3. Inoculation and Operation of the MFC

To start up the experiment, the anodic chamber of the MFC was filled with a 60 mL inoculum and 540 mL of culture medium, prepared as described in Section 2.2. During this initial phase, the cathode chamber was filled with phosphate buffered-saline (PBS) solution (400 mL, pH 7) and was kept constantly aerated at the approximate flowrate of 80 mL/min. The experiments were performed under fed-batch process conditions, in a temperature-controlled incubator ( $308\pm 2$  K). A fixed external resistance was connected between the anode and cathode to close the circuit (500  $\Omega$  in all experiments, except where otherwise noted) and to check the electricity generation. After acclimation phase and voltage stabilization, the air injection into the cathode compartment was stopped and the buffer solution was replaced with 400 mL of the copper sulfate ( $\text{CuSO}_4$ ) solution, containing the desired initial concentration of  $\text{Cu}^{2+}$ . The initial catholyte pH was adjusted to 2 using concentrated  $\text{HNO}_3$  solution. A magnetic stirrer was used to mix the anolyte and catholyte, so as to minimize the occurrence of substrate and biomass concentration gradients. Prior to starting the bioelectrochemical experiments, the anode and cathode chambers were purged with nitrogen ( $\text{N}_2$ ) gas (80 mL/min) to eliminate the dissolved oxygen and establish anaerobic conditions. Eventually, the reactor was operated instantly for the recovery of copper and the related experiments as shown in Fig. 2.

## 2.4. Chronoamperometry of Copper Electrowinning from Mixed Solutions

Chronoamperometry (CA) tests were performed in a typical three-electrode cell with a working volume of

150 mL which was continuously stirred and operated at pH 2. The working electrode, consisting of a titanium plate (purity of 99.95 %) of 14  $\text{cm}^2$  surface area, was controlled at  $-0.1$  V vs. SCE by means of a potentiostat (Ivium Model, Series V11108, Netherlands). The counter electrode was a platinum sheet (purity of 99.95%). The distance between the working and the counter electrode was kept constant at  $3.0 \pm 0.1$  cm. All measurements were performed at 298 K. During electrowinning, the cell voltage was monitored with a digital multimeter.

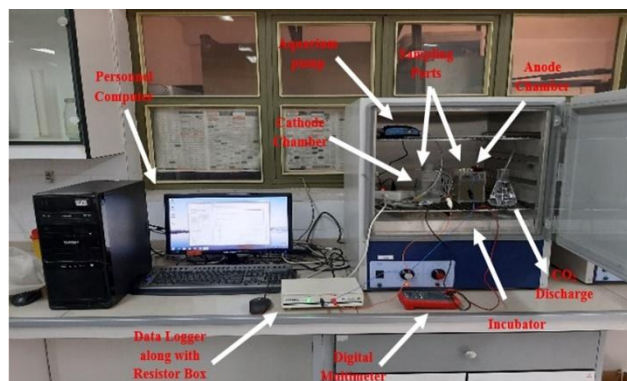


Fig. 2. Experimental setup of double chambered MFC

## 2.5. Analytical Procedures and Electrochemical Measurements

The  $\text{Cu}^{2+}$  concentration was determined using an Atomic Absorption Spectrometer (Young Lin AAS-8000 Series, 8020 Model, Korea). Observation of reduced product formed on the cathode surface was carried out by Scanning Electron Microscopy (SEM) (TESCAN, VEGA3, Czech Republic). The cell voltage ( $E_{\text{cell}}$ ) was measured across an external resistor ( $R_{\text{ext}}$ ) through a data logger with constant current at 2 hours intervals. When the cell voltage output was stable, a stepwise change of external loads using a variable resistor box (10-10,000  $\Omega$ ) was used to obtain a polarization curve and identify the maximum power generation. The internal resistance ( $R_{\text{int}}$ ) of the cell was calculated from the slope of cell voltage (V) versus  $I$  using Eq. (1):

$$V = E - I \cdot R_{\text{int}}, \quad (1)$$

where  $E$  is electromotive force of the cell.<sup>20</sup>

Power density ( $P_{\text{density}}$ ), normalized by the anode surface area, was computed by using Ohm's law as Eq. (2):

$$P_{\text{density}} = \frac{E_{\text{cell}}}{R_{\text{ext}} A} \quad (2)$$

The copper removal efficiency was calculated as Eq. (3):

$$RE_{\text{Cu}} = \frac{C_0 - C_t - C_{\text{diff}}}{C_0} 100 \% \quad (3)$$

In the above equations,  $P$  is the power density ( $\text{mW}/\text{m}^2$ ),  $E_{\text{cell}}$  is the measured cell voltage (mV),  $R_{\text{ext}}$  is the external resistance,  $I$  is the current calculated by  $E_{\text{cell}}/R_{\text{ext}}$  (mA),  $A$  is the geometrical surface area of the anode electrode.  $C_0$  is the primary  $\text{Cu}^{2+}$  concentration of the catholyte fed into the cathode chamber (g/L).  $C_t$  is the residual  $\text{Cu}^{2+}$  concentration in the catholyte at time  $t$  (g/L), and  $C_{\text{diff}}$  is the  $\text{Cu}^{2+}$  concentration in the anolyte at time  $t$  (g/L). For total Cu analysis, 5 mL samples were removed from the cathode chamber.

### 3. Results and Discussion

#### 3.1. Analysis of the Open Circuit Voltage (OCV) of the MFC

The MFC was run for about 36 days and the cell performance was monitored measuring OCV. During an initial startup phase, the cathode chamber of the MFC was filled with PBS and was kept aerated, while the anode was filled with the inoculum and supplied with acetate as electron donor. During this phase, the anode and cathode were open-circuited (the MFC was operated without a load or a resistance in the external circuit) in order to maximize the substrate conversion rate and in turn accelerate the development of an electroactive biofilm on the anode surface. After approximately 4 days of operation, the Open Circuit Voltage (OCV) of the MFC stabilized at approximately 0.3 V, indicative of the presence of an active electric current-generating anodic biofilm. Subsequently, aeration was stopped, and the cathode chamber was replaced with 3 g/L of copper solution.

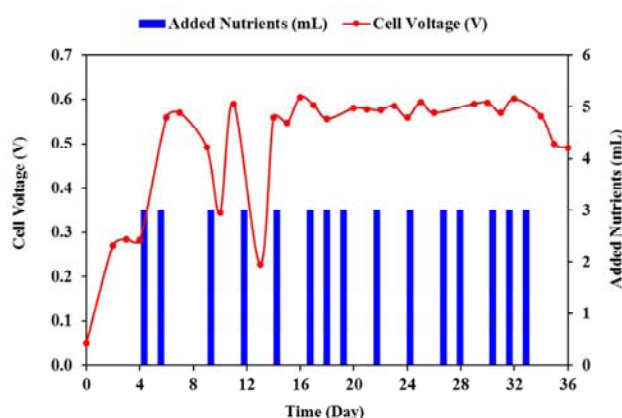


Fig. 3. Time course of the open circuit voltage (OCV) curve and spikes of nutrient solution

The catholyte replacement resulted in a sharp increase of the OCV, up to nearly 0.600 V (Fig. 3), a value which is only slightly lower than the theoretical cell voltage of 0.660 V. Importantly, upon reaching its maximum value, the OCV remained nearly constant throughout the whole experimental period, except on day 10 and 13 when it temporarily dropped, probably due to the shortage of organic substrates at the anode, yet it immediately resumed to the previous values as soon as nutrients were supplied again (3 mL of a 15 g COD/L solution), as shown in Fig. 3.

#### 3.2. Influence of the External Resistance on the MFC Performance

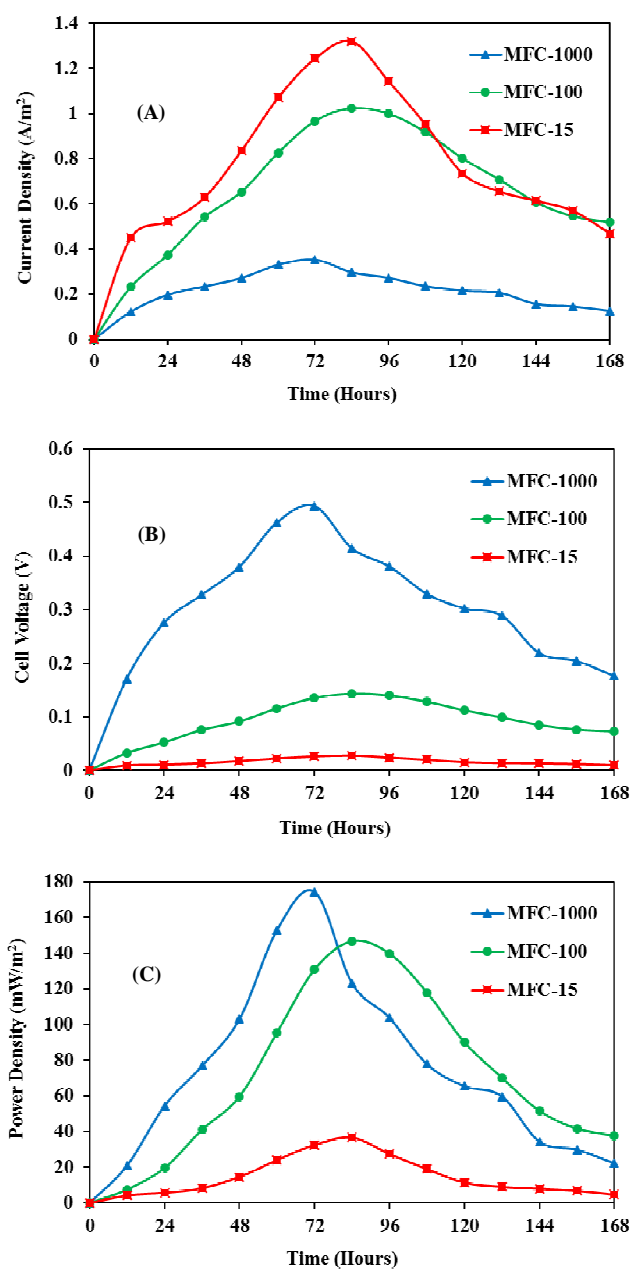
Effect of external loading on the MFC performance was studied. Three MFCs were run for 7 days using external resistors of 15, 100, and 1000  $\Omega$  at an initial  $\text{Cu}^{2+}$  concentration of 0.5 g/L. The current and voltage across these resistors were monitored. The obtained results are shown in Fig. 4.

When the external resistance was decreased from 1000 to 15  $\Omega$ , the current density increased from about 0.38 to 1.3  $\text{A}/\text{m}^2$  in day 3 which indicates high electron transfer from the anodic to cathodic chamber. Similarly, Lyon *et al.*,<sup>21</sup> Zhang *et al.*<sup>22</sup> and Koók *et al.*<sup>23</sup> observed that a conventional MFC with a lower external resistance showed a higher current generation.

According to the results, the maximum voltage was on day 3 with 0.5 V across 1000  $\Omega$  resistor with maximum power density of 178  $\text{mW}/\text{m}^2$  at 0.38  $\text{A}/\text{m}^2$ . The least power (40  $\text{mW}/\text{m}^2$  at 1.3  $\text{A}/\text{m}^2$ ) was attained by the 15  $\Omega$  resistor. The high values across 1000  $\Omega$  are attributed to the high amount of work to be done to overcome the high resistance.<sup>24</sup>

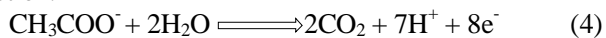
Polarization tests were carried out after the acclimation and voltage stabilization which corresponded to days 2, 3, and 4 for 15, 100, and 1000  $\Omega$ , respectively. Fig. 5 displays the voltage-current and power-current plots of the MFCs with the various external resistances, determined according to the method described in Section 2.5.

A maximum power density ( $P_{\text{max}}$ ) of 156  $\text{mW}/\text{m}^2$  was achieved with the 15  $\Omega$  circuit load, while lower power densities of 136 and 96  $\text{mW}/\text{m}^2$  were obtained with the 100 and 1000  $\Omega$  resistors, respectively. The estimated internal resistance ( $R_{\text{int}}$ ) of the MFC operated with an external resistance of 15  $\Omega$  was 348  $\Omega$ , while it was slightly higher (*i.e.*, 356 and 429  $\Omega$ ) when the applied external resistances were 100 and 1000  $\Omega$ , respectively. The lower performance of the MFC with a 15  $\Omega$  resistor might be due to the significant ohmic loss resulting from the existence of void spaces in the interior of the biofilm.



**Fig. 4.** Effect of external resistances on (A) current density, (B) cell voltage and (C) power density generation (Initial  $\text{Cu}^{2+}$  concentration of 0.5 g/L, catholyte pH=2, and external resistances of 15  $\Omega$ , 100  $\Omega$  and 1000  $\Omega$ )

It is well known that the electrochemical oxidation of acetate is an acid-producing process. In the anode compartment, acetate is oxidized according to the following reaction:



As shown in the above equation, the oxidation of every mole of acetate produces 7 moles of proton, which can result in a pH decrease within the biofilm microenvironment. This can lead to an increase in the potential for

acetate oxidation and an inhabitation of microbial metabolism, both negatively influencing the MFC performance.<sup>25</sup> When an MFC was operated at a high current density or a low resistance, this problem becomes more serious due to the higher proton production rate. Koók *et al.*<sup>23</sup> reported cyclic voltammetry measurements which confirm that the anode surfaces of a low-resistance MFC could have been better enriched in redox-active components and thus, covered by a thicker biofilm.

A suitable biofilm structure is crucial for the maximum power density and sustainable current generation of the MFCs. Previous studies showed that the biofilm established at a higher external resistance tended to form a compact structure with a less active biomass and a lower EPS content.<sup>22,23</sup> This led to an increase of the maximum power density with the decrease of external resistance. However, when the external resistance became lower than the optimum value, a loose biofilm structure with a less active biomass and a higher EPS content was developed, resulting in more void spaces beneficial for proton and buffer transport and reduction of the electrical conductivity within the biofilm. Therefore, a lower maximum power density and higher maximum sustainable current generation can be obtained.

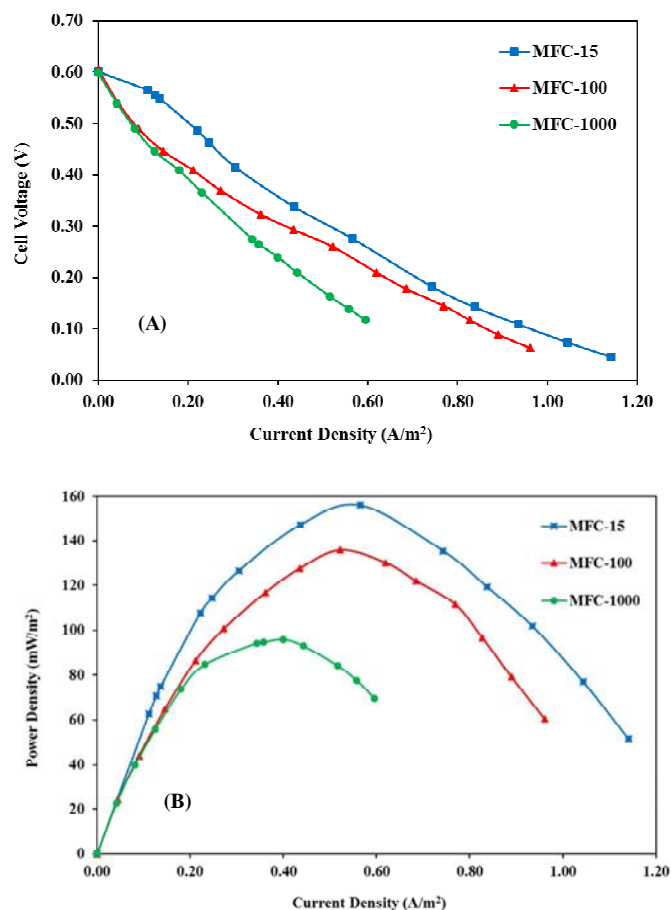
### 3.3. Influence of Initial Copper Concentration on the MFC Performance

In order to evaluate the effect of the  $\text{Cu}^{2+}$  concentration on the MFC performance (*i.e.*, current and power generation), various initial  $\text{Cu}^{2+}$  concentrations of 0.5, 1,

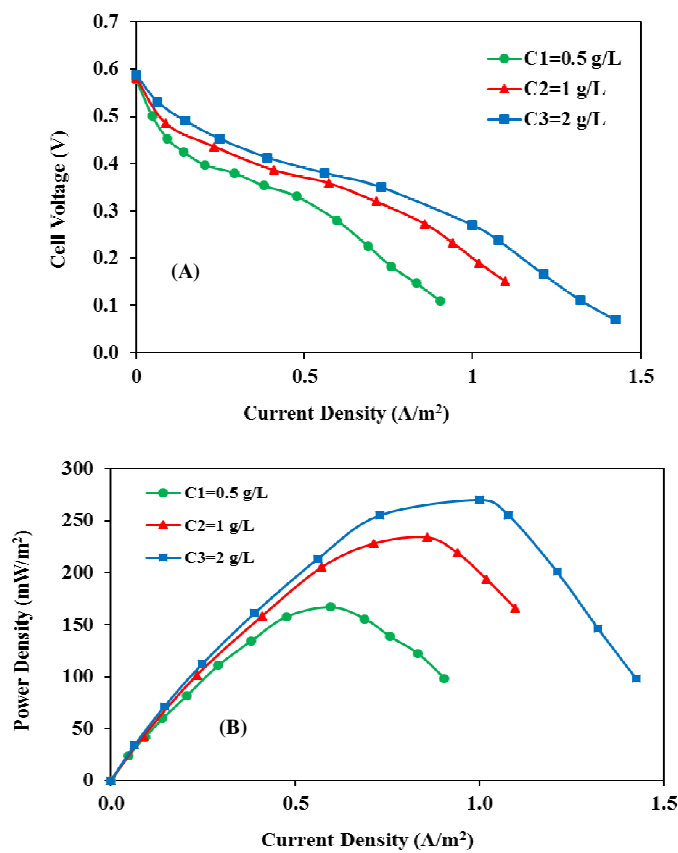
and 2 g/L were applied to the cathode chamber of the MFC. The low external resistance of 15  $\Omega$  was used to maximize the electric currents to the cathode. After reaching a pseudo-steady state condition, polarization curves were determined (Fig. 6).

Interestingly, the peak power density of the MFC increased from 167  $\text{mW}/\text{m}^2$  (at about 0.6  $\text{A}/\text{m}^2$ ) to 234  $\text{mW}/\text{m}^2$  (at 0.8  $\text{A}/\text{m}^2$ ) as the  $\text{Cu}^{2+}$  concentration was increased from 0.5 to 1 g/L, and it further raised up 270  $\text{mW}/\text{m}^2$  (at 1  $\text{A}/\text{m}^2$ ) as the applied  $\text{Cu}^{2+}$  concentration was 2 g/L. In accordance, the internal resistance of the cell decreased from 335 to 227  $\Omega$ , and finally 198  $\Omega$ , by increasing the applied  $\text{Cu}^{2+}$  concentration from 0.5 to 2 g/L, as shown in Fig. 6.

Taken as a whole, the reported results clearly highlight that the MFC performance is improved by increasing the  $\text{Cu}^{2+}$  concentration, most likely as a result of a decrease in the concentration polarization in the cathode. Analogously, the observed decrease of the internal resistance, which likely resulted from the increased electrical conductivity of the catholyte, may also have contributed to the improved MFC performance.



**Fig. 5.** Effect of external resistance on (A) polarization and (B) power density curves (Initial  $\text{Cu}^{2+}$  concentration of 0.5 g/L, catholyte pH=2, and external resistances of 15  $\Omega$ , 100  $\Omega$  and 1000  $\Omega$ )



**Fig. 6.** Effect of  $\text{Cu}^{2+}$  concentration on (A) polarization and (B) power density curves (Initial  $\text{Cu}^{2+}$  concentration of 0.5, 1, and 2 g/L, catholyte pH=2, external resistance of 15  $\Omega$ )

So far, the MFC performance with a  $\text{Cu}^{2+}$  catholyte was examined only by few researchers. However, the results of this study are fully in agreement with the conclusions drawn by Tao *et al.*,<sup>26</sup> Zhang *et al.*,<sup>27</sup> and Sumisha *et al.*<sup>28</sup>

### 3.4. Anaerobic Cathodic Copper Reduction

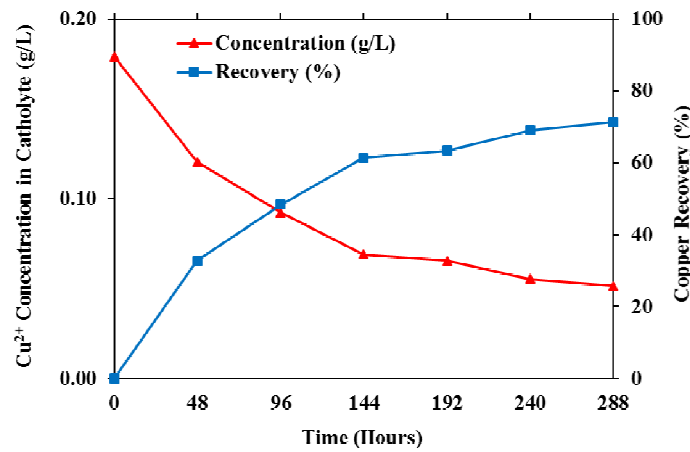
In order to consider the possibility for copper removal and recovery, an experiment was conducted under anaerobic conditions in which the catholyte contained 0.18 g/L of  $\text{Cu}^{2+}$  as  $\text{CuSO}_4$  at pH 2. An external resistor of 15  $\Omega$  was employed in order to maximize current generation and in turn copper reduction. The experiment lasted 12 days. During the MFC operation, an average current density of 0.52  $\text{A}/\text{m}^2$  was achieved. Over time, as the copper concentration gradually decreased, the current density diminished, down to values as low as 0.15  $\text{A}/\text{m}^2$ , at the end of the 12-day operational period. According to Ter Heijne *et al.*,<sup>9</sup> at low copper concentrations (less than 0.2 g/L in their work), mass transfer limitations causes small current densities.

A decrease in copper concentration resulted in a decrease in cathode potential. As a result, cell voltage and current density decreased as well. The reduction of  $\text{Cu}^{2+}$  ions in the catholyte and the corresponding copper removal vs. time is shown in Fig. 7.

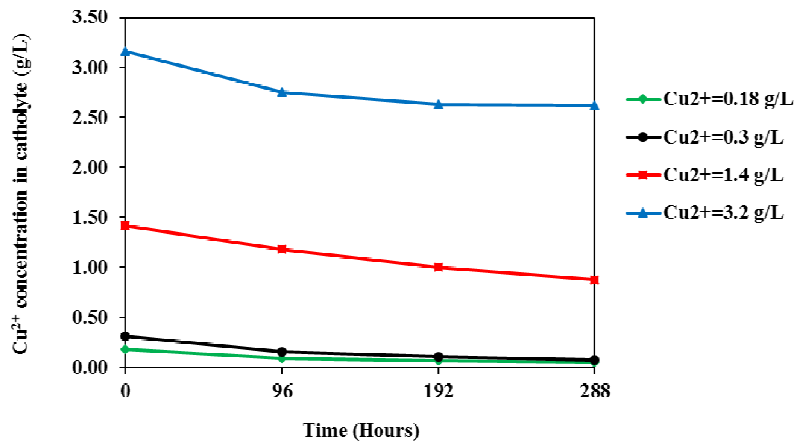
At the end of the experiment, the  $\text{Cu}^{2+}$  concentration in the cathode compartment was 0.05 g/L, with a corresponding removal efficiency of 71.3 %.

The effect of the initial  $\text{Cu}^{2+}$  concentration on copper removal was also evaluated by performing experiments in which the concentration of  $\text{Cu}^{2+}$  was increased to 0.3, 1.4 and finally 3.2 g/L. After 12 days, copper removal of 75.27 %, 37.91 %, and 17.04 % was obtained, respectively.

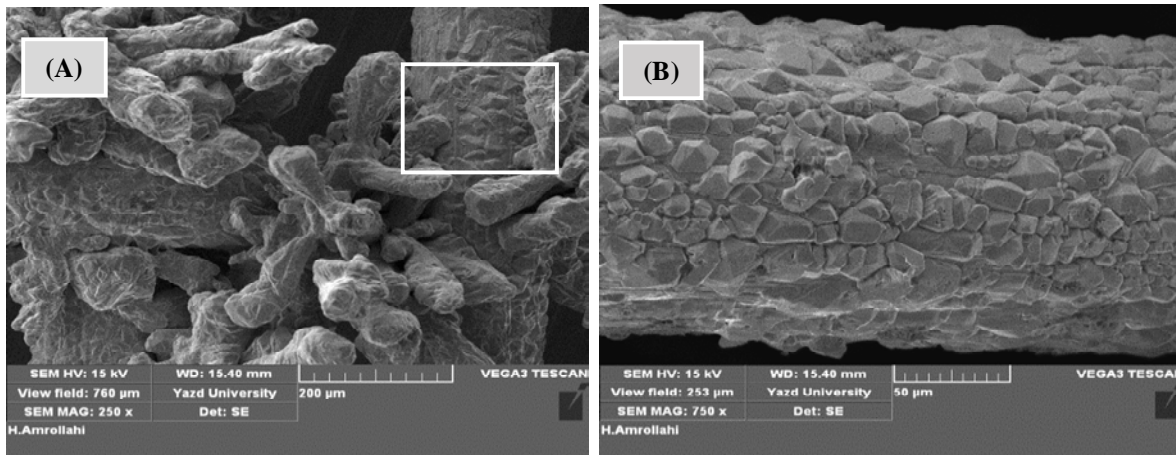
According to the Fig. 8, at the first 4 days, increasing the initial  $\text{Cu}^{2+}$  concentration in the catholyte from 0.18 to 3.2 g/L resulted in an increase in the precipitation rate from 0.9 to 4.27 mg Cu/h. After that, the copper deposition rate remained almost constant for the solution containing 1.4 g/L of Cu, while it reduced to 0.67 mg Cu/h for the solution containing 3.2 g/L of  $\text{Cu}^{+2}$ .



**Fig. 7.** Reduction of Cu<sup>2+</sup> ions and copper removal vs. time in the catholyte (Initial Cu<sup>2+</sup> concentration of 0.18 g/L, catholyte pH=2, and external resistance of 15 Ω)



**Fig. 8.** Effect of the initial Cu<sup>2+</sup> concentration on copper recovery (Initial Cu<sup>2+</sup> concentration of 0.18, 0.3, 1.4 and 3.2 g/L, catholyte pH=2, external resistance of 15 Ω)



**Fig. 9.** SEM images of the cathode electrode after deposition (A) cathode after the reaction, and (B) a magnification of the framed portion in (A) (reaction time of 288 hours)

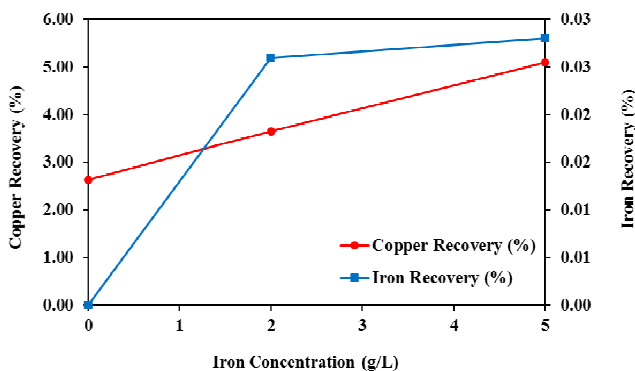


Fig. 9 shows the surface of the cathode after 12 days of MFC treatment using a solution containing 1.4 g/L of  $\text{Cu}^{2+}$ . The copper deposit displays octahedral habit that eventually connects to form a dense layer. This may be attributed to the slow growth of copper. The denseness of the copper product allowed for strips of copper to be peeled off the electrode for recovery.

### 3.5. The Impact of $\text{Fe}^{2+}$ Concentration on the Copper Recovery in the MFC

Effect of ferrous ion presence on the copper removal was studied using a solution containing 1.4 g/L of  $\text{Cu}^{2+}$ . Firstly, chronoamperometry experiments were performed in the presence of 2 and 5 g/L of  $\text{Fe}^{2+}$ . Fig. 10 shows the results.

Notably, results shown in Fig. 10 indicate that the removal of copper was slightly improved in the presence of  $\text{Fe}^{2+}$  ions. The increase in  $\text{Fe}^{2+}$  concentration, corresponded to an increase in the current density from 1.2 to 2.1  $\text{A}/\text{m}^2$ . The presence of ferrous ions in the system may produce a background current as a result of  $\text{Fe}^{2+}$  reduction. The combination of  $\text{Fe}^{2+}$  reduction and copper reduction resulted in higher current densities. In spite of that, however, the co-presence of iron caused iron impurities entering into the copper deposits (data not shown).

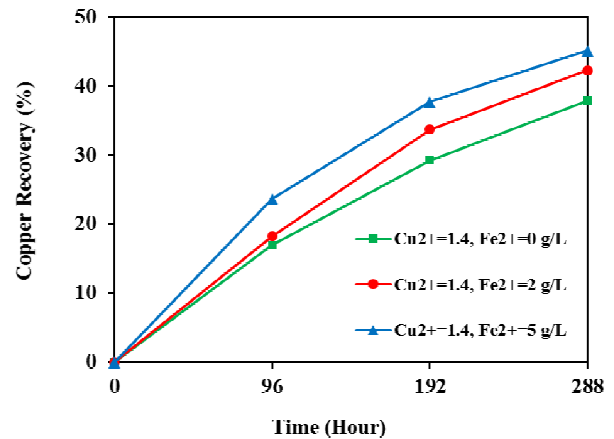


**Fig. 10.** Effect of different  $\text{Fe}^{2+}$  concentrations on the copper electrowinning by chronoamperometry technique ( $\text{CuSO}_4$  solution,  $\text{Cu}^{2+}=1.4$  g/L,  $\text{pH}=2$ , and 2 hours)

Secondly, two MFCs were run in the presence of ferrous ions concentrations of 2 and 5 g/L. The MFCs were operated using a 15  $\Omega$  resistance for 12 days. Fig. 11 shows the results. In agreement with the chronoamperometry results, the presence of  $\text{Fe}^{2+}$  also improved the performance of the MFC. Indeed, the average current density increased from 0.8 to 0.95  $\text{A}/\text{m}^2$  after adding  $\text{Fe}^{2+}$  at concentrations of 2 and 5 g/L. Notably, a 7.23 % increase was obtained over a period of 288 hours.

The findings obtained from the biological fuel cell in terms of current density and copper deposition are in a

good agreement with the results obtained from the chronoamperometry tests.



**Fig. 11.** Effect of  $\text{Fe}^{2+}$  concentrations on the copper recovery using an MFC ( $\text{CuSO}_4$  solution,  $\text{Cu}^{2+}=1.4$  g/L, and  $\text{pH}=2$ )

## 4. Conclusions

Copper production industry faces the need of processing of low-grade ores and tailings. Heap leaching is one of the main methods to reach this goal. However, the heap leaching PLS usually contains low copper and high iron concentrations but also extensive amounts of elements, such as Mg, Mn, Ni, Zn, etc. While almost 20 % of annual Cu production is carried out using electro-winning, its application for dilute leaching is difficult and involves high operating expenses. Bioelectrochemical systems provide a promising tool for the recovery of copper from the heap leaching solutions which usually contain low copper and high iron concentrations.

In this research, the role of copper and ferrous ion concentrations, and external resistance in the removal of synthetic sulfuric acid solutions by a lab-scale microbial fuel cell was investigated. According to the findings, higher external resistance results in a higher power density (in example 180  $\text{mW}/\text{m}^2$  for the 1000  $\Omega$ ). However, copper metal recovery needs higher current density so that lower external resistance should be used. In this study, current density of 1.3  $\text{A}/\text{m}^2$  was obtained when the 15  $\Omega$  resistor was connected to the MFC. Results showed that the peak power density of the MFC increased from 167  $\text{mW}/\text{m}^2$  (at about 0.6  $\text{A}/\text{m}^2$ ) to 270  $\text{mW}/\text{m}^2$  (at about 1  $\text{A}/\text{m}^2$ ) as the  $\text{Cu}^{2+}$  concentration was increased from 0.5 to 2 g/L. The  $\text{Cu}^{2+}$  elimination performance was 71.34 %, 75.27 %, 37.91 %, and 17.04 % for  $\text{Cu}^{2+}$  concentrations of 0.18, 0.3, 1.4 and 3.2 g/L, respectively. Chronoamperometry tests showed that addition of ferrous ions to the

solution enhances the current density but also copper removal. Similarly, the increasing of  $\text{Fe}^{+2}$  concentration from 2 to 5 g/L increased both current density (about 20 %) and copper extraction (about 7 %). The results of this study confirm the ability of the MFCs for the metallurgical recovery of copper from impure dilute sulfuric acid solutions obtaining from heap leaching processes.

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## БІОЕЛЕКТРОХІМІЧНА РЕКУПЕРАЦІЯ МІДІ З РОЗВЕДЕНИХ КИСЛОТНИХ РОЗЧИНІВ ЯК ФУНКЦІЯ ЗОВНІШНЬОГО ОПОРУ, КОНЦЕНТРАЦІЇ МІДІ ТА ЗАЛІЗА

**Анотація.** Біоелектрохімічні системи є перспективним інструментом для рекуперації міді з розчинів купчастого вилугування, у яких переважно низька концентрація міді та висока концентрація заліза. У цій роботі досліджено роль концентрації іонів міді та заліза, а також зовнішнього опору у видаленні синтетичних розчинів сірчаної кислоти за допомогою лабораторного мікробного паливного елемента (MFC). Отримано хороші результати видалення міді.

**Ключові слова:** мідь, розчин купчастого вилугування, біоелектрохімічні системи, мікробний паливний елемент, зовнішній опір.