



Investigation of the Corrosion Behavior of Selected Metal Electrodes used in a Microbial Fuel Cell for Clean Energy Production

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Abstract

The electrodes material plays an important role in the amount of electricity produced in microbial fuel cells (MFCs). Metal electrodes used in MFCs are subject to biological and concentration cell corrosion which leads to a decrease in the cell efficiency. In the present work, the corrosion behavior of three selected electrode materials, namely, stainless steel, copper, and zinc under different operating conditions was investigated and discussed. In anode chamber, the microorganism (MO) used was *Saccharomyces cerevisiae* (yeast) with sodium acetate as a substrate forming the microbial corrosive solution. In the cathode chamber, the corrosive solution is aerated water. The effects of different operating parameters on the corrosion rate (CR) of these electrodes were studied such as: microorganism concentration, aeration of cathode chamber, and flow velocity in cathode chamber. The potential of the each electrode was measured to understand the corrosion behavior of electrodes and the produced current was also investigated. It was found that the corrosion rate of the electrodes in both anode and cathode chambers increases with increasing MO concentration in anode chamber and with increasing agitation speed in cathode chamber. The bio-corrosion is an important part of the corrosion occurring in microorganism chamber. The stainless steel exhibited the lowest corrosion rate for the whole investigated range of operating parameters followed by copper. The zinc electrode was found to be poor as an electrode in MFC as its corrosion rate was very high in all conditions investigated. In addition, this study showed that the air pumping in water chamber causes an appreciable increase in the corrosion rate in both chambers and an increase in the produced current.

Keywords: Microbial Fuel Cell, Electrode Material, Corrosion, Microorganism, Agitation Velocity, Aeration

1. Introduction

Due to a growing global population, domestic and industrial energy demands are on rise. Fossil fuels meet the needs of energy but because of pollution, global warming has increased research on alternative energy sources. Microbial fuel cells (MFCs) have recently been intensively researched in many academic laboratories as a potential bioenergy production technology from organic carbon sources such as wastewater, sludge and others [1, 2]. The performance of MFC is depending on the electrode materials, electrode potential, microorganism concentration and substrate concentration. According to Jack et al. [3], microorganisms were accountable for 34% of localized corrosion at an oil company. Microbial

impacts are thought to be responsible for roughly 20% of all corrosive environments to metallic surfaces. Microorganism influenced corrosion (MIC) is the result of a microbiologically induced change that promotes the formation or preservation of physiochemical interactions that would not normally occur under essentially similar circumstances. It is important to remember that in essence, these microorganisms' procedures need not act in solitude, but instead in live show with electrochemistry forces inside the particular setting. The metal degradation is recognized as biocorrosion, or microbially-influenced corrosion [4, 5]. The electrodes material has a significant impact on the electrochemical performance of MFCs. As a result, electrode testing is crucial in this

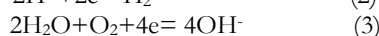
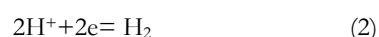


industry. The fundamental and particular characteristics of MFC electrodes materials are numerous. Electrochemical solid terminal materials ought to have high reactivity, biocompatibility, chemical stability, dimensional stability, and also safely effective or caustic in particular [6]. Metal electrodes are widely used in previous works to serve as electrodes in MFC and are recommended for providing acceptable level of power generation [7, 8]. Despite the several advantages of metal electrode such as high electrical conductivity, high mechanical properties, availability and cost-effective prices, the important limitation is the corrosion. The formation biofilm and the formed compounds due to the bacterial activity affects the electric current generated and the corrosion rate of metal electrode in MFCs. In MFC, the presence of microorganism and substrate and the produced compounds due to bacterial activity increases the concentration cell effect which leads to increase the current produced by electrode corrosion. The potential difference between the two terminals may cause an enhanced corrosion of the electrode in the compartment of high potential that leads to decrease the MFC efficiency. Zhu and Logan [9] showed a decrease in power generation of MFC due to corrosion of copper anode. Guerrini et al [10] noticed slight localized corrosion attack on stainless steel anode in MFC. No systematic evaluation of corrosion rate of copper nor stainless steel was reported in that studies. Bensalah et al [11] enhanced the copper anode performance in MFC by reducing its corrosion rate via coating with carbon based material.

The corrosion reactions in MFC occur due to the activity of microorganism that produces oxidizing chemicals which are metabolism products or indirect consequences of metabolic products acting on the metal. An anodic reaction causes a metal in liquid to ionize:



The following cathodic reactions occurs on in one or both compartment of MFC:



Hydrogen ions and oxygen are the main the oxidizers in these reactions. Biological corrosion is merely the activation of these electrochemical reactions, which can contribute to bacterial activity or start corrosion by producing different free radical substances. It also can for differential aeration (different O_2 Concentration) or chemical concentration cells corrosion. Certain anaerobic microorganisms that can activate and use hydrocarbons can eliminate hydrogen (electrons) from metal substrates, promotion the electrochemical reaction (Eq. 2). Interaction by microorganisms with the creation or destruction of natural or applied protective layers, as well as the degradation of corrosion protection in closed systems, may all contribute in the corrosion rate. The microorganism activity can produce different corrosive product of organic and inorganic acids which promote corrosion under aerobic parameters [12,13].

Amongst all metals, stainless steel, copper and zinc have been recently proposed as electrode for MFC operation. In fact, most studies used these materials does not pay enough attention to the corrosion problem of such metals in MFC environment. The conditions in both compartments of MFC are different and can become considerably corrosive due to the formation of corrosive compounds in anode compartment and due to the aeration and flow in cathode compartment. The electrical connection between the two electrodes in MFC causes the corrosion phenomena to become more complicated due to mutual effect of electrodes on each other, i.e, galvanic effect. Although the corrosion phenomenon in MFC has a significant effect on the cell efficiency, studies concerning this issue are limited in literature. Most of the literature focuses on the maximization of the produced current without evaluation of the consequences on the electrode corrosion damage. Some studies used two different materials as electrodes in MFC without evaluation of the galvanic corrosion effect that was the reason for the production of important part of the cell current.

Accordingly, studying the corrosion behavior of the commonly used metals electrode in microbial fuel cell under different operating conditions is of a scientific and practical significance for recommending the successful metals for this application. Therefore, this current work is focused to study the corrosion behavior of different metals commonly used as electrodes in MFC for a range of microorganism concentration under the effect of flow velocity and aeration in cathode chamber.

2. Materials and Methods

2.1 Materials

Three electrode materials were used: stainless steel (SS316), copper and zinc, as an electrode for bio-electricity production in MFC to study their corrosion behavior. These materials were selected because of their use in literature for MFC electrode. Figure 1 shows photos of the 3 electrodes used. The dimensions of each electrode were 50 mm × 50 mm × 0.3 mm. One face was exposed to the solution, while the other was taped shut.

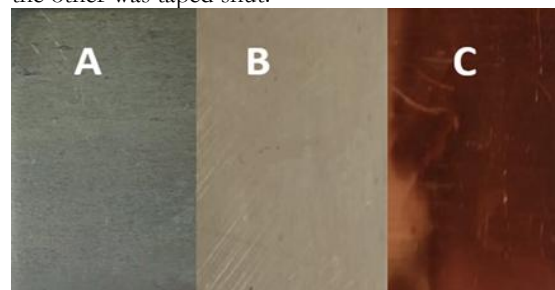


Figure (1): Three electrodes, (a) zinc, Zn, (b) stainless steel, SS 316 and (c) copper, Cu.

2.2 Microbial Fuel Cell (MFC)

Configuration and Operation

2.2.1 Microbial Fuel Cell (MFC) Configuration

The electrochemical cell constructed in this work was a double chamber microbial fuel cell operates in a batch mode under agitation and aeration in cathode



chamber. The experimental set up is shown schematically in Figure 2. The electrode was placed in the middle of a solution containing different concentrations of microorganism (MO) which was yeast (*Saccharomyces cerevisiae*, yeast) and sodium chloride 0.1N to facilitate the electrons transfer in the circuit. This compartment is the MO compartment which also contains sodium acetate (SA) as a substrate of 2g/l. The other compartment (water compartment, the cathode) also contained 0.1N NaCl. The two solutions were connected with a salt bridge containing saturated salt solution of 0.5N NaCl used to transfer the ions between the microorganism (MO) compartments and water compartment. The electrodes were connected by external copper wire to

transfer electricity and complete the circuit. The temperature was kept constant at 30 °C using a water bath. Air pump was used to pump the air into water chamber at a rate of 2.51 l/min. A mechanical agitator was used for agitating the solution with different stirring speeds in the water chamber. The work investigated the effect of microorganism concentration; *Saccharomyces cerevisiae* (3, 6, and 10 g/l), dissolved oxygen (DO) concentration by air pumping into the water (cathode) chamber, and the agitation of the solutions with different speeds (150, 300 and 450 rpm) with air pumping in water chamber on the corrosion rate and on the cell current and electrode potentials.

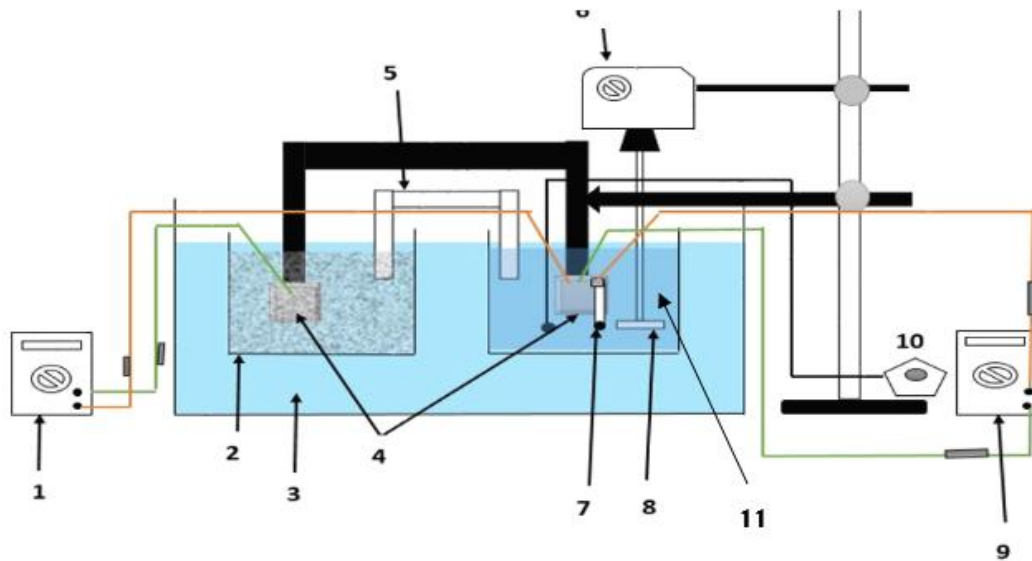


Figure (2): Sketch diagram of the MFC (1) Ampere meter, (2) MO chamber, (3) Water bath, (4) Specimens, (5) Salt bridge, (6) Stirrer, (7) Calomel Electrode, (8) Impeller, (9) Voltmeter, (10) Air pump, (11) Water chamber.

2.2.2 Experimental Procedure

Before each run, the electrode specimen was washed and cleaned to standard procedure [14]. Then the specimens were weighed to the 4th decimal of gram (w_1) by using digital balance. One face of the electrodes was completely insulated by tape and the electrodes were placed in the middle of the compartments. Water with 0.1N NaCl was used as a base solution in the two compartments. The MO chamber is the anode chamber because most of the reactions in this chamber are oxidation reaction [15] [Potter, 2011]. The sodium acetate salt of 2 g/l was added in microorganism solution a substrate to enhance MFC energy generation. The other compartment, containing water with NaCl, is the cathode chamber that include the cathodic reactions especially oxygen reduction reaction. The two solutions were connected with a salt bridge containing saturated salt solution used to transfer the ions between the microorganism (MO) compartment and the water compartment. The electrodes are connected by external copper wire to transfer electricity and complete the circuit. The temperature was kept constant at 30 °C by using a water bath. The measurements of the electrode potentials were performed using two saturated calomel electrodes. The Lugging capillaries were positioned at 2 mm from

the surface of each electrode. The run duration was 5 h. Each experimental run was carried out twice for checking reproducibility and accuracy. At the end of experiments, the electrodes were cleaned according to a standard procedure for specimen preparation [14] and then weighted (w_2). So that the corrosion rate (CR) can be determined using the Equation 4:

$$CR = \Delta W / At \quad (4)$$

where CR is the corrosion rate in gmd, Δw is weight loss (gram), A is area (m^2), and t is time (day). After each experiment, the electrodes cleaned according to standard procedure and microscopic images of corroded electrodes were taken for different conditions.

Table 1 lists the values of pH in both MO (yeast) and water chambers for different as measured experimentally using pH meter and Table 2 lists the values of oxygen concentration for different solutions. Table 1 shows that the pH is lower in microorganism solution (anode chamber) and decreases with increasing yeast concentration. Table 2 shows that the O₂ concentration decreases considerably with increasing MO concentration and increases with air pumping (aeration).



Table (1): Measured values of pH for different solutions.

Concentration	pH
0.1N NaCl solution	6.3
MO solution (yeast 3 g/l + 2 g/l SA)	4.8
MO solution (yeast 6+ g/l2 g/l SA)	4.6
MO solution (yeast 10 g/l+2 g/l SA)	4.3

Table (2): Measured concentration of dissolved oxygen

Solution	concentration of dissolved oxygen, mg/l
Distilled water + 0.1 N NaCl	6.1
Distilled water + 3 g/l yeast + 2 g/l sodium acetate	2.4
Distilled water + 6 g/l yeast + 2 g/l sodium acetate	2.1
Distilled water + 0.1N NaCl + air pumping	7.2

3. Results and Discussion

3.1 Effect of Microorganisms Concentration

Figure 3 shows typical microscopic images of copper before corrosion and after corrosion in water chamber and in MO chamber. It can be seen that both solutions caused clear corrosion damage to the surface. Figure 4 shows a comparison between corrosion rates of three electrodes at different MO concentrations in anode chamber (MO chamber) and cathode chamber (water chamber) in running MFC (closed circuit). In both MO and water chambers, Figs. 4 present the corrosion rate for different electrodes in both chambers (each material is used as anode as cathode in each experimental run). It is evident that the corrosion rate of SS is lowest followed by copper, while, Zn showed high corrosion rate. This indicates the corrosion resistance of SS is high in these environments in both MO and water chambers. Comparing Figs. 4 indicates that the corrosion rate of each electrode material is dependent on the solution. The Zn exhibits higher corrosion rate in cathode chamber (water) than in MO chamber. Whereas, Cu and SS exhibit higher corrosion rate in MO chamber. This indicates that the more acidic environment (according to Table 1) attacks Cu and SS, while Zn is most attacked in water chamber. This behavior is for short circuited MFC but for free corrosion (open circuit; which is beyond the scope of present work), the corrosion behavior may be different as has been studied by various works in literature [15, 16, 17].

Figures 5 show the potentials versus time of three electrodes in anode and cathode chambers at the microorganism's concentration of 3 g/l. For copper the electrode potential of anode (MO chamber) is more positive than that of cathode (water chamber). For SS there is no considerable difference between the two chambers. For Zinc the potential in cathode chamber is more positive than that in anode chamber. The potential difference is dependent on the solution and the oxidation and reduction reaction, formed MO

film, and formed corrosion product layer if any. In general, the higher the O₂ concentration is the higher the potential.

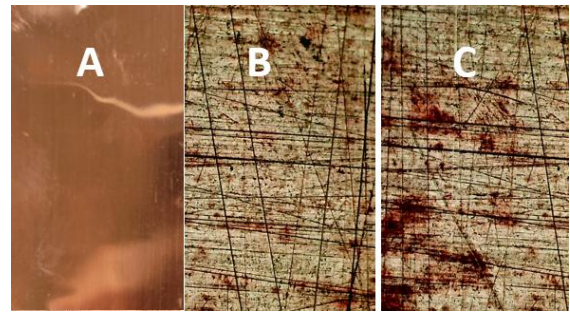


Figure (3): A. clear copper electrode, B. corroded copper in water compartment, C. corroded copper in MO compartment electrode at C= 3 g/l, the magnification is 500.

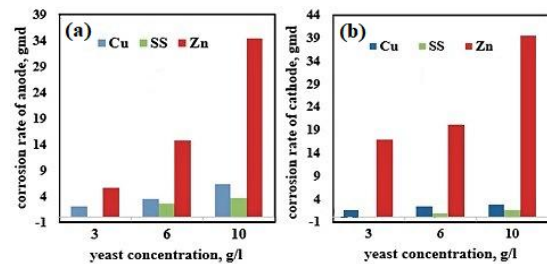
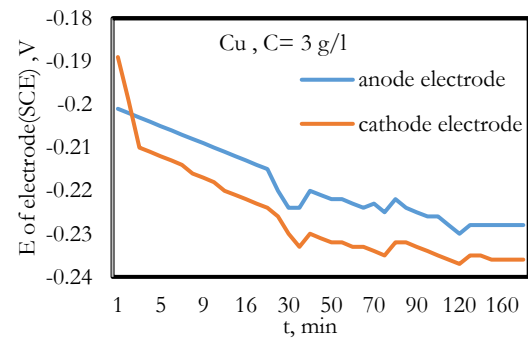
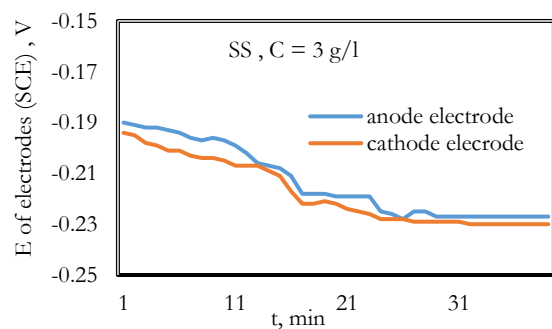


Figure (4): The comparison between corrosion rates of three electrodes at different MO concentrations, (a) CR in the anode chamber (b) CR in the cathode chamber.

It can be noted from Figures 5 that there is a large difference between zinc potential and copper and stainless-steel potentials in both chambers. This is because zinc is more active and weaker in neutral and acidic solutions, thus its corrosion rate is high, and it is not recommended for microbial fuel cell construction.



(a)



(b)

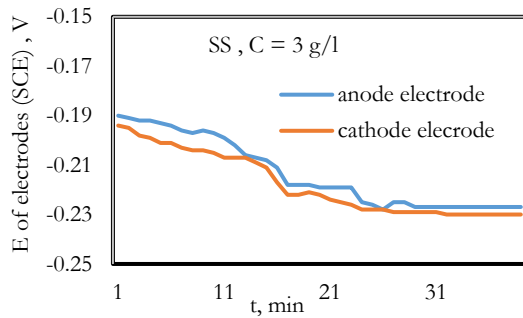


Figure (5): Potential vs. time in both chambers for (a)Cu, (b)SS, (c)Zn electrodes.

Figure 6 shows the current density flowing in microbial fuel cell for the three different electrodes at the microorganism's concentration of 10 g/l. The steady state current density of electrodes is 16, 4, and 70 mA/m² for copper, stainless steel, and zinc respectively. Therefore, the highest current is provided by Zn, but a major part of this current is produced by the corrosion of Zn in both compartments. The SS produced the lowest current density indicating the high corrosion resistance. In MFC, the produced current is dependent on several factors such as the adhesion of biofilm on the electrode surface, the thickness of that film, the electrochemical and corrosion properties of the electrode, and the ability of the microorganism for the oxidation) [18, 19] Accordingly, this difference in the values of produced current for the three electrodes is ascribed to those reasons. The high corrosion rate of Zn shown in Figures 4 indicates that, the reason for high current produced by zinc electrodes is due to the corrosion of zinc not because zinc is successful electrode for energy production. Therefore, Zn cannot be used as electrode in MFC due to its high corrosion rate. Cu and SS produces lower current but major part of this current is due to the bacterial activity not corrosion.

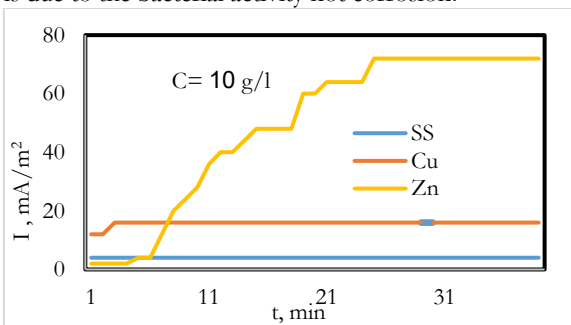


Figure (6): Current density for three electrodes at the microorganism's concentration of 10 g/l.

3.2 Effect of air pumping

Figure 7 shows a comparison between the corrosion rate of three electrodes under air pumping in the water compartment at 3g/l MO concentration. It can be seen in the presence of aeration; SS results in the lowest CR and Zn results in the highest for all MO concentrations. Figures 8 a and b compare the corrosion rate of different electrodes in both compartment in the presence and absence of air pumping in water compartment. It is clear that the corrosion rate of electrodes increases in both compartments with air pumping for all yeast

concentrations. The aeration of cathode chamber causes an increase in the O₂ concentrations in this compartment. In addition, the O₂ concentration in MO is also slightly increases due to the transfer of O₂ from cathode compartment to MO compartment through the salt bridge as has been reported by previous work [19]. The increase in O₂ concentration in both chambers leads to an increase in the corrosion rate as the O₂ is the major oxidizing species. The average percent increase in the CR with aeration of copper is 11%, of SS is about 53% , and of Zn is 9%. Air bubbling in cathode chamber under stirring causes an increase in the dispersion of air bubbles because the large bubbles breaks up into smaller ones due to the shearing effect and high turbulence level provided by the impeller [20]. The increased dispersion increases the interfacial area (surface area) of contact between the air bubbles and the solution leading to increase the concentration of O₂ which in turn increases the resection reaction enhancing the corrosion rate. In addition, air pumps in shifts the potential to more positive which also increases the CR.

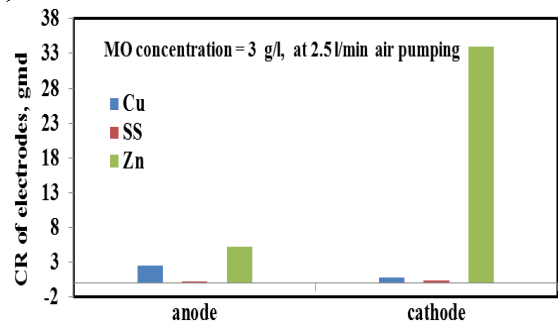


Figure (7): Comparison of the corrosion rate of three electrodes when air pumping in the water compartment at 3 g/l MO concentration.

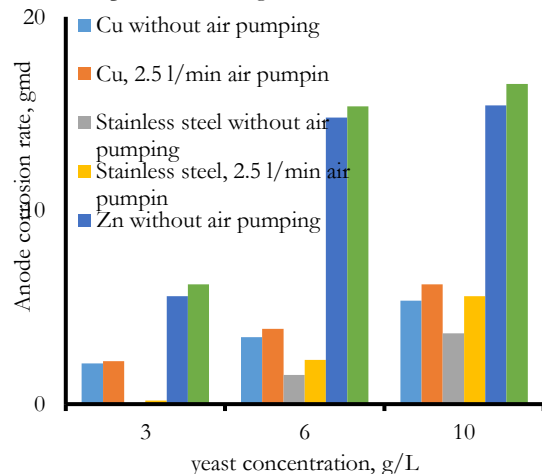


Figure (8a): Corrosion rate of electrodes in the anode compartment with air pumping into the cathode chamber for different MO concentrations

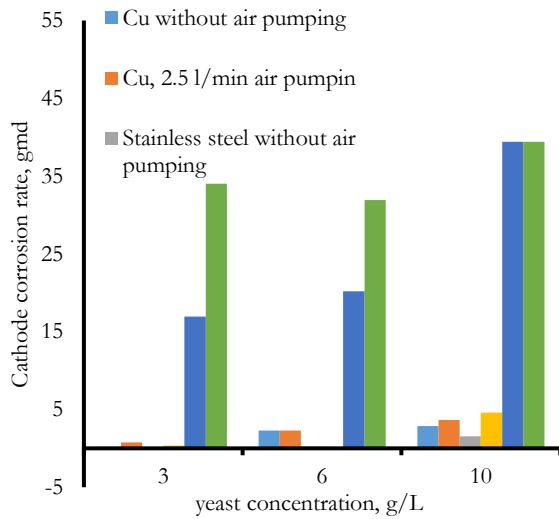


Figure (8b): Corrosion rate of electrodes in cathode compartment with air pumping into the cathode chamber with different MO concentrations.

3.3 Effect of flow velocity

Figures 9a and 9b show the effect of agitation speed in cathode chamber on the CR of anode and cathode respectively. It can be seen that the increased flow velocity causes a considerable increase in the CR for the three electrodes for the range of MO investigated. The average percent increase in CR in MO chamber when the velocity increases from 0 to 450 rpm is 186% for copper, 40% for SS, 290% for zinc. Accordingly, the flow velocity in water chamber caused an appreciable increase in corrosion rate of the electrodes in MO chamber. This high influence of velocity is ascribed to the galvanic effect between the two terminals of the cell that the corrosion behavior of first pole considerably affects the other pole. The same observation has been reported in the galvanic corrosion study of Ali and Hasan [2020]. Montanes et al [2009], in galvanic corrosion study of Cu/SS, reported that copper corrosion increases rapidly when the flow velocity (represented by Re) increases due to the SS galvanic effect. They showed that there is a synergy between the galvanic effect and the flow of fluid.

The average percent increase in CR of the electrodes in water chamber velocity increases from 0 to 450 rpm is 300% for copper, 20% for SS, 120% for zinc. Comparing the percent increase in CR with flow velocity between the two chambers indicates that the increase in CR of SS with velocity in water chamber is much lower than that in MO chamber, although the agitation is in water chamber. This can be reasoned to the occurrence of a partial passivation of SS surface at high flow velocities as has been reposted by several previous works [21, 22, 23]. This passivation increases the potentials difference between the two terminals leading to enhance the corrosion in other terminals of the cell [24].

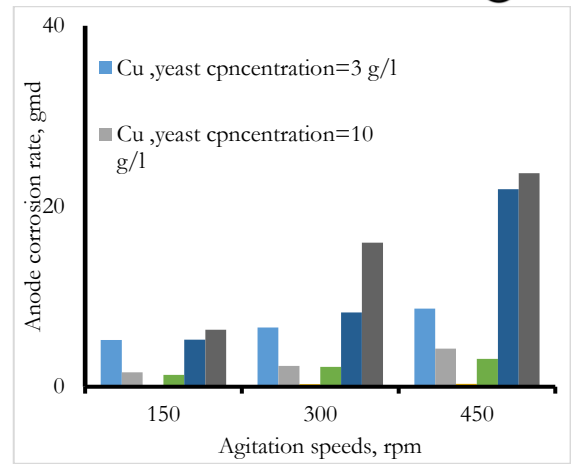


Figure (9a): Corrosion rate of electrodes in the anode compartment at different agitation speeds in the cathode chamber with different MO concentrations

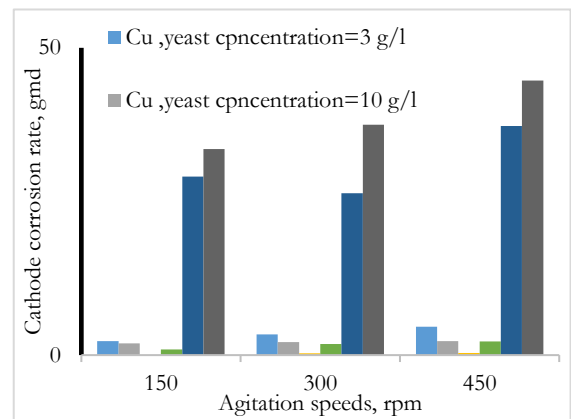


Figure (9b): Corrosion rate of electrodes in the cathode compartment vs. agitation speeds in the cathode chamber with different MO concentrations

Figure 10 shows a typical example of cell current density vs time for Cu, SS, and Zn electrodes at agitation velocity of 150 rpm. According to this figure, the lowest current of cell is for SS electrodes and the highest is for Zn. Because all the used electrodes in this work are metal, thus all are of high conductivity and the reason behind the large difference in the produced current cannot be attributed to the difference in the electrode conductivity. Another reason for producing current in MFC is bacterial activity in anodic region which produces oxidizing substances that leads to increase the cell current. Because the cell current is high in the case zinc electrodes, the expected reason for this high cell current is the high corrosion rate of zinc as has been indicated by weight loss experiment.

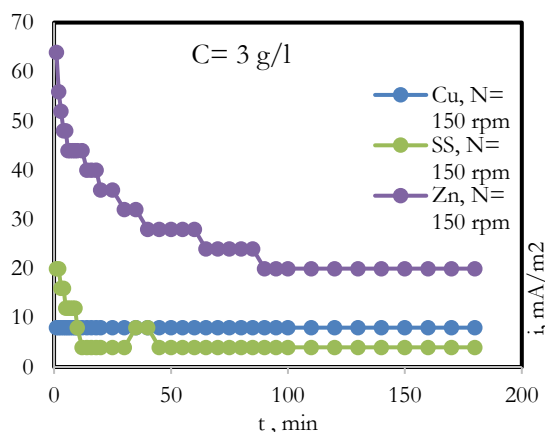


Figure (10): Current density vs. time in MFC for the three electrodes at 150 rpm agitation velocity and 3 g/l of MO concentration.

4. Conclusions

The selection of the electrode material (metals properties) is crucial for the performance of MFCs in terms of corrosion resistance, bacterial adhesion, electron transfer and electrochemical efficiency. Zinc is not suitable electrode to be used in MFC neither in the MO (anode) compartment nor in the water (cathode) compartment because it exhibits high corrosion rate in both compartments. The microorganism concentration increases the corrosion rate of electrodes in both anode and cathode compartments in MFC due to the metabolism and concentration cell effect. The biofilms that attached to the surfaces are useful for providing longer time of contact between the bacteria and surface but at the same time, it can cause a considerable corrosion rate of anode electrodes by biological corrosion. The current produced in the MFC cell is a result of two contributions. Part of this current is bio-current generated by MO and part is due to the corrosion of electrodes. The air pumping in the water compartment increases the corrosion rate of electrodes in both MO and water compartments and increases the cell current. The agitation velocity of catholyte increases the corrosion rate of electrodes in both MO and water compartments. It increases the cell current too. In general, the potential in the MO compartment is dependent of electrode material and the prevailing conditions. The MO activity in anode chamber increases the potential due to the formation of acidic environment. Stainless steel and copper exhibited higher potential in both compartments (comparing with zinc electrode) leading to high corrosion resistance. Overall, the stainless steel is a successful electrode from corrosion standpoint in MFC, but the energy generated by such electrodes is low, followed by copper. Due to high corrosion rate of zinc electrode in both chambers, it is not recommended at all to be used in MFC.

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