

The Inhibitory Effect of Amoxicillin on Aluminum Corrosion in a Gel Electrolyte

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In this study, the effect of amoxicillin as a green corrosion inhibitor on aluminum alloy 6061 in an agar medium containing sodium chloride (NaCl), as the gel electrolyte, was investigated using electrochemical impedance spectroscopy (EIS) and Tafel extrapolation method (TEM) at room temperature during immersion time intervals. The results revealed that the gel electrolyte reacted better than electrolyte solutions to reduce corrosion. Measured by EIS, it was demonstrated that inhibition efficiency (IE) increased during time. To ascertain investigation more, TEM was done just once on the last day of the measurements confirming the role of amoxicillin in reduction of corrosion activity in the gel electrolyte.

Keywords: Gel electrolyte, Corrosion inhibitor, Amoxicillin, EIS

1. INTRODUCTION

Corrosion has been far defined as destructive attacks by the environment on metals following chemical or electrochemical processes. It is notable to say that most kinds of corrosion occur in an electrochemical manner. In an aqueous solution, corrosion reactions are also similar to those in a flashlight cell such as the Leclanche cell consisting of a central carbon electrode and a zinc cup electrode separated by an electrolyte consisting essentially of ammonium chloride (NH₄Cl) solution [1]. In electrolyte environments, this process is also carried out by both negative and positive charge carriers called ions. The current carried by each ion also depends on its mobility and electrical charge. As well, metals might become inactive once they have contact with a medium containing chloride or other aggressive solutions [2, 3], which can be the effect of corrosion on their surfaces. Additionally, many metals exposed to fluids erode [1]. Corrosion on the surface of metals, which is of utmost importance in engineering, can correspondingly cause severe challenges [4].

For economic and safety reasons, corrosion engineers attempt to reduce metal waste and its financial losses in order to lower the economic impact of corrosion. Metal scraps also occur in the corrosion of pipes, tanks, ships, marine structures, etc [5]. Corrosion can further endanger car navigation systems and other devices such as cells by breaching their surfaces in the form of holes or gaps in the operating equipment.

In industry, some systems, which act as electrochemical cells commonly in contact with liquid electrolytes, can create problems, impeding the study of surfaces, joints, irregular angles, etc.[5]. Liquid electrolytes used in electrochemical cells mainly contain acids such as sulfuric acid or hydrochloric acid. Chemical materials are mostly corrosive and sometimes dangerous which can also be even toxic endangering human life and the environment. For example, lithium-ion batteries even when properly maintained in environmental conditions may explode over time. If lithium ion batteries in a liquid electrolyte are repeatedly and fast charged, the ions are generally accumulated after a while. In this way, an increase in the number of positive ions and electrons causes ions collision followed by a spark and final explosion. The main reason underlying this is using liquid electrolytes.

The more secure the cells are, the more suitable they are to use, resulting in less damage to the environment [6].

Gel electrolytes have been extensively studied due to their potential use in electrochemical devices, such as batteries, solar cells, fuel cells and electrochromic devices [7-10]. A portable corrosion cell based on the use of agar as a gelling agent have been proposed to perform non-destructive, in-situ electrochemical measurements for application in cultural heritage studies. To decrease corrosion, toxicity and general dangers and damages made to humans and the environment, gel electrolytes are suggested to be used instead of liquid electrolytes. Ions move much slower in gel electrolytes compared with electrolyte solutions[8]. These gel electrolytes are also more suitable to assess pitting corrosion on the surface of metals because crevice corrosion occurs less resulting in less pitting corrosion [11].

After the formation of the crevice, some microcells are formed where the metal inside the crevice acts as an anode. Moreover, after aeration, these microcells make some other cells such as pH cells and concentration cells which can increase corrosion. However, when using a gel electrolyte, the opposite is true even if there is electrolyte aeration. The region tends to act as a small cathode, with no interference with the measurement of pitting corrosion because the points most exposed to air enrichment are close to the electrolyte boundary [11].

Researchers have recently used agar to make an electrolyte gel, a dry extract of red algae that does not dissolve in cold water but dissolves in boiling water and then turns into a gel at 35 to 40 degrees Celsius or less. Agar is derived from the agarose, a neutral polysaccharide, which is a linear polymer composed of repeating agarobiose units. Fig. 1 shows the chemical structure of agar. In this respect, an agar, used as a gel electrolyte, is a complex mixture of polysaccharides found in the cell-matrix of red algae Rhodophyta (*Gracilaria*, *Gelidium*, and *Pterocladia*) [12-15].

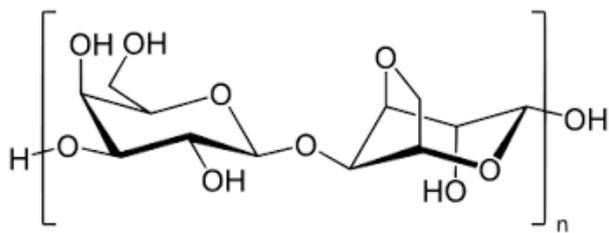


Figure 1. Structure of agarose polymer

Agar can form hard gels even at very low concentrations (0.004%) [8]. Low cost, biodegradability, high degree of biocompatibility, and reproducibility of experiments in electrochemical measurements [16] led researchers to use agar in the preparation of electrolyte gels. That is why gel polymer electrolytes (GPEs) have been extensively experimented and potentially utilized in electrochemical devices such as batteries [17, 18], solar cells [19, 20] and fuel cells [12, 14].

The gel prepared from pure agar is not compatible enough with irregular surfaces and angles due to the lack of softeners. To stabilize this gel electrolyte and to make it conductive, glycerol and a substance containing ions such as NaCl are added to agar [21].

Hydrogen bonds are formed between the hydroxyl glycerol and agarose groups [22]. The ions, most of which are added from salt, are transported through hydrogen bonds in the gel. Thus, this gel which is rich in water becomes conductive [23]. Studies on gel electrolytes have shown that the addition of glycerol to these gels inhibits the anodic reaction while having little effect on the cathodic reaction. Gel electrolytes have a neutral pH close to aqueous solutions containing 0.5% NaCl. Here, very little acidification is observed due to the addition of glycerol whose effect on pitting corrosion is not considerable [11].

Abdullah has studied the inhibitory effect of amoxicillin and other antibiotics in 2 M hydrochloric acid solution on aluminum surface [24]. Also, Golestani et al. reflected on the effect of amoxicillin and other antibiotics on the corrosive behavior of mild steel in 1.0M HCl solution [25]. Tuan et al also used a sustainable gel electrolyte containing Pb^{+2} as the corrosion inhibitor in a hybrid blue battery [26]. All the above highlights the role of antibiotics and gel electrolytes to reduce corrosion.

In the current study, we aimed at reducing corrosion on aluminum alloy 6061 surface. In this respect, agar was used as the gel electrolyte containing NaCl and amoxicillin as the inhibitor. To this end electrochemical impedance spectroscopy (EIS), Tafel extrapolation method (TEM) and FTIR spectroscopy were used.

2. MATERIALS AND METHODS

2.1. Materials

Amoxicillin was obtained from Sigma-Aldrich Co. (Germany) and used without any further purification. Fig. 2 shows the chemical structure of amoxicillin with the molecular formula of $C_{16}H_{19}N_3O_5S$.

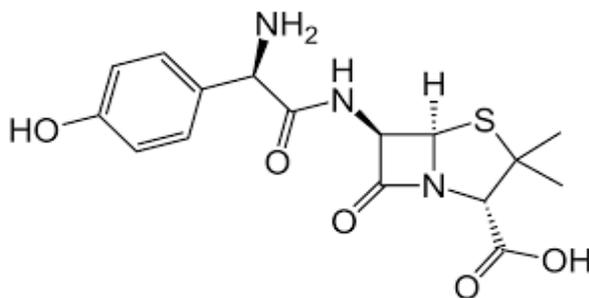


Figure 2. Molecular structure of amoxicillin

The working electrodes (WEs) were prepared from aluminum alloy 6061 with the surface area of 100 mm². Table 1 presents the chemical composition of the alloy.

Table 1. Typical composition of aluminum alloy 6061

| Component | Al | Mg | Si | Fe | Cu | Zn | Ti | Mn | Cr | others |
|----------------|---------|---------|---------|---------|-----------|----------|----------|-----------|-----------|--------|
| Amount (Wt. %) | Balance | 0.8-1.2 | 0.4-0.8 | Max.0.7 | 0.15-0.40 | Max.0.25 | Max.0.15 | Max. 0.15 | 0.04-0.35 | 0.05 |

The agar was obtained from German company Merck. Glycerol as a clear, colorless, odorless, and non-toxic liquid is a simple polyol compound with a molecular formula of C₃H₈O₃. NaCl was purchased from Merck Co.

2.2. Methods

EIS, as a method to measure corrosion, was practiced to study corrosion behavior in the gel electrolyte containing NaCl and glycerol with and without the corrosion inhibitor. WEs made up of aluminum with the surface area of 100 mm² were sealed with copper wire on one side and epoxy resin on the other side. Before starting the experiments, the surfaces of the WEs were polished with wet abrasive papers, 600-2500 grades, washed with distilled water, and finally dried in ambient air. The EIS experiment was later conducted using a potentiostat/galvanostat Autolab 302N (Ecochemia, Netherlands) and supported by a frequency response analyzer FRA-2 and Nova 1.11 software. The measurements were also taken in a conventional three-electrode cell. The counter electrode (CE) was made of a platinum rod with the surface area of 100 mm², and the reference electrode was a saturated (KCl) Ag/AgCl electrode. To obtain the stabilized open circuit potential (OCP), the WEs were immersed and fixed in the gel electrolyte which reached the temperature of 40°C before starting EIS. A sinusoidal potential perturbation of 10 mV versus OCP in the 10 mHz to 100 kHz frequency range was further used in EIS. The Nyquist plots of the EIS data were subsequently analyzed using Nova 1.11 software. Potentiodynamic polarization curves were additionally recorded at a scan rate of 1mV/s.

For gel preparation, the first step was to place the container in an oven (obtained from Shimi Fan Co. Iran) at 180 °C for 1 hour; then agar, NaCl, glycerol, and water were added, mixed, and placed in an autoclave (purchased from Zain Medical Ltd. UK) for 15-20 minutes at 121°C and at a pressure

of 1.5 atm. Once the temperature of the gel reached 40°C, the electrodes were immersed and fixed inside the gel without any corrosion inhibitors to be used as the blank.

In order to prepare another gel electrolyte containing the corrosion inhibitor, agar, glycerol, distilled water and amoxicillin with concentration of 100 mM were stirred on a heater near a flame for 10 minutes at a temperature of 90°C. When the gel electrolyte reached 40°C, the WEs were placed inside the gel. Then, a sinusoidal potential perturbation of 10 mV versus open circuit potential (OCP) in the 10 mHz to 100 kHz frequency range was used in EIS in both gel electrolytes on days one, two, five, and fifteen to control corrosion on the surface of aluminum electrodes. After that, TEM was used on the 15th day to control the test results.

Also on the last day, the 15th day, FTIR method was performed to further examine the surface of the working electrodes. The powdered sample was made into tablets with the help of KBr and the test was performed by an infrared spectrometer made by the German company Bruker, Tensor 27 model.

3. RESULTS AND DISCUSSION

3.1. EIS Results

Nyquist and Bode presentations of EIS for the aluminum 6061 in the gel electrolytes in the presence and absence of amoxicillin are shown in Figs. 3 and 4.

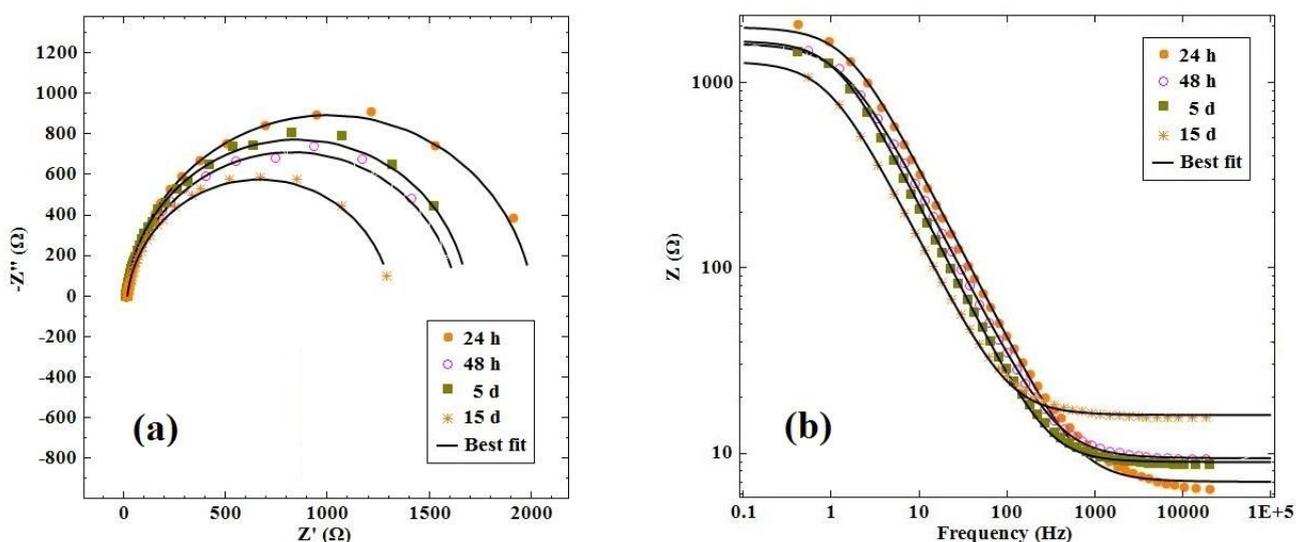


Figure 3. (a) Nyquist and (b) Bode plots for aluminum in gel electrolyte at 25°C at immersion time intervals in the absence of amoxicillin (blank).

According to Fig. 3(a), between 24 h to 48 h, the value of R_{ct} decreased but from 48 h to the fifth day its value increased slightly, which increased the diameter of the semicircle of the Nyquist

chart. This means that corrosion increased from 24 hours to 48 hours and decreased slightly on the fifth day. This might be due to the formation of corrosion product $\text{Al}(\text{OH})_3$ which functions as a coating on aluminum surface. However, on the 15th day, the R_{ct} value decreased resulting in an increase in corrosion after 15 days from immersion time. The data of EIS for the blank control is provided in Table 2.

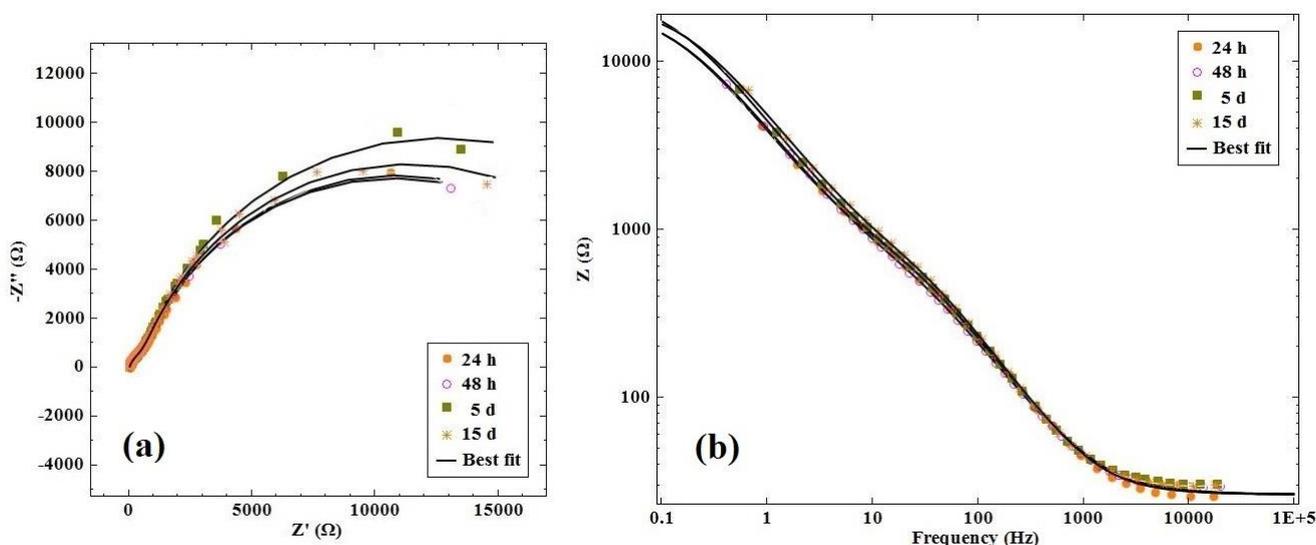


Figure 4. (a) Nyquist and (b) Bode plots for aluminum in gel electrolyte at 25°C at immersion time intervals in the presence of amoxicillin.

Table 2. Impedance parameters for aluminum in gel electrolyte at 25°C over time for blank.

| Time | R_{ct} kΩ | n | Y_0 ($\text{Fcm}^{-2} \text{s}^{n-1}$) | C_{dl} $\mu\text{F.cm}^{-2}$ |
|----------|-------------|-------|--|--------------------------------|
| 24 hours | 2 | 0.92 | 64.3 | 559.863 |
| 48 hours | 1.58 | 0.919 | 83.5 | 559.791 |
| 5 days | 1.6 | 0.949 | 89.7 | 605.488 |
| 15 days | 1.4 | 0.928 | 153 | 745.621 |

Considering Fig. 4(a), it can be observed that in the presence of the inhibitor, the Nyquist diagram semicircle diameter increased. As shown in Table 3, the R_{ct} value slightly increased, considered somehow constant, while the C_{dl} value decreased over time. This means that these changes in the values of C_{dl} were the result of the inhibitor adsorption on the surface of aluminum followed by a decrease in corrosion. The data of EIS for the presence of the inhibitor is shown in Table 3.

Table 3. Impedance parameters and IE values for aluminum in gel electrolyte in the presence of amoxicillin 100 Mm at 25°C over time.

| Time | R _{ct} kΩ | n | Y ₀ (Fcm ⁻² s ⁿ⁻¹) | C _{dl} μF.cm ⁻² | IE _{EIS} % |
|----------|--------------------|-------|--|-------------------------------------|---------------------|
| 24 hours | 3.55 | 0.7 | 54.5 | 57.398 | 43.66 |
| 48 hours | 3.56 | 0.71 | 53.4 | 45.887 | 55.61 |
| 5 days | 3.57 | 0.74 | 41.2 | 34.975 | 55.18 |
| 15 days | 3.6 | 0.771 | 32.2 | 33.745 | 61.11 |

In order to review this trend, there was a need to calculate inhibition efficiency (IE). Table 3 shows the values of corrosion IE. The IE% was calculated via the following formula:

$$IE\% = \frac{R' - R}{R'} \times 100 \tag{1}$$

where R and R' represent charge transfer resistance before and after adding the corrosion inhibitor, respectively [27].

As seen in Table 3, R-values remained somehow constant over time while C-values decreased. After calculating the IE%, the IE-values obtained from EIS (Table 3) increased. This might be due to the coverage on the surface made by the inhibitor, which led to a rise in IE [28].

Various equivalent circuits have been proposed to analyze the Nyquist data obtained from EIS. In most papers, EIS data from metals coated with a polymer that are exposed to a corrosive environment have been analyzed by the equivalent circuit shown in Fig. 5 [8]. The electrolyte gel used in the current study was a good coating film between the metal surface and the environment. Therefore, we used the equivalent electrical circuit seen in Fig. 6 to analyze the EIS data on the aluminum surface. The equivalent circuit included R_s, R_{ct} and CPE. The value of n was less than one, which had non-ideal capacitive behavior. Due to the non-ideal behavior of the coating capacitor where the gel functioned as a coating between the metal surface and the environment, CPE was used instead of the capacitor.

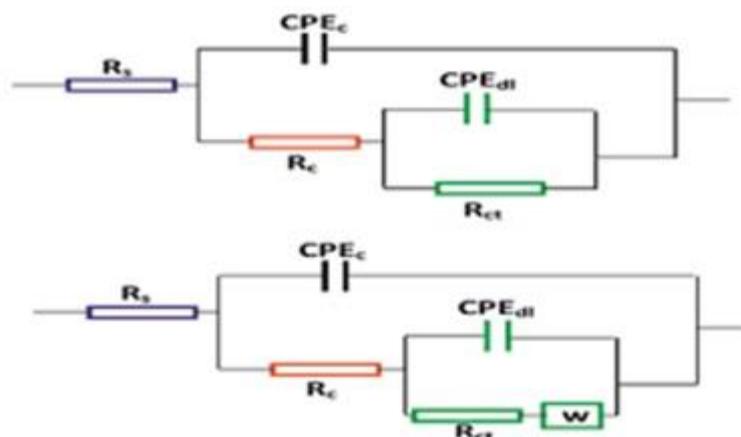


Figure 5. Equivalent circuit used to fit EIS data from metals coated with a polymer

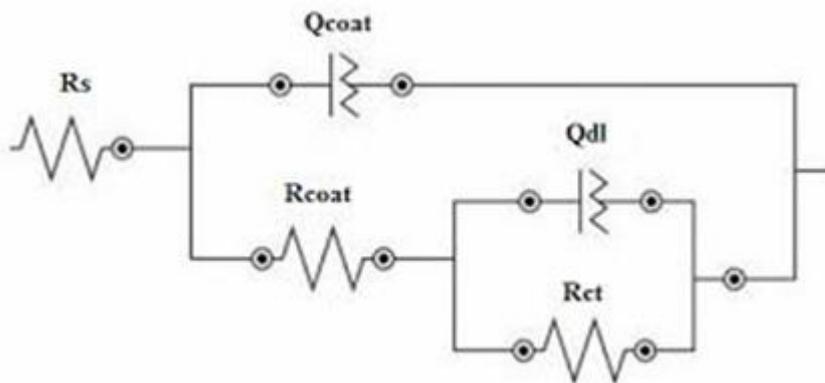


Figure 6. Equivalent circuit used to fit experimental data

Reviewing the Nyquist diagram in the presence of a corrosion inhibitor shows that addition of amoxicillin as an inhibitor increased the ring diameter without affecting the properties of amoxicillin [29]. Although our results are in line with those obtained by Ahamad [29], in the current study, the use of gel electrolyte as a coating instead of electrolyte solution played an important role in decreasing corrosion.

The impedance of the constant phase element (CPE) is as follows [27, 28]:

$$Z_{CPE} = \frac{1}{Y_0 (j\omega)^n} \tag{2}$$

where Y_0 is CPE constant ($F\text{ cm}^{-2}\text{s}^{n-1}$ or $\text{s}^n\ \Omega^{-1}\text{cm}^{-2}$), j refers to $\sqrt{-1}$, ω shows angular frequency, and n represents phase shift. For $n = 0$, Z_{CPE} indicates resistance with $R=Y_0^{-1}$. Such resistance for $n=1$ is a capacitance with $C=Y_0$, a Warburg element for $n=0.5$ and an inductive with $L = Y_0^{-1}$ [30] for $n=-1$. The correct equation for the relationship between Y_0 and CPE is as follows [31]:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \tag{3}$$

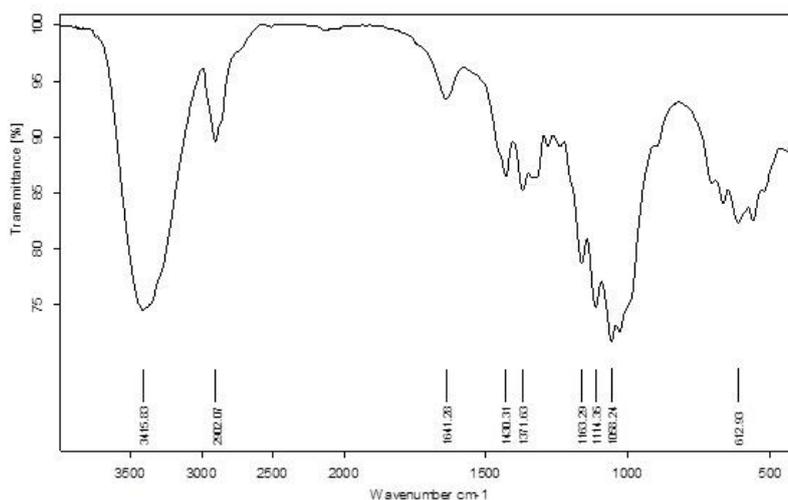
where ω_{max} shows maximum angular frequency indicating that the imaginary component of the impedance is at its maximum. Here, to obtain ω_{max} , the following equation was used:

$$\omega_{ma} = 2\pi f_{max} \tag{4}$$

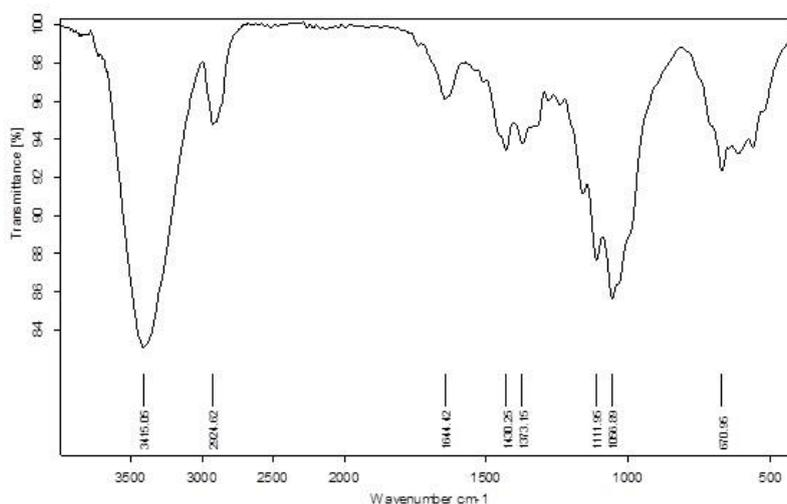
where f_{max} is considered the maximum frequency of the EIS plots.

3.2. FTIR and TEM analysis

After a long immersion time of the aluminum in the electrolyte gel, the FTIR spectrum was taken from the aluminum surface in the presence and absence of the inhibitor in the gel electrolyte. Fig. 7(a) shows the FTIR spectrum of the aluminum surface, based on which, the presence of a strong spectrum in the range of 3400 with a relatively good elongation indicated the alcoholic OH group. And the spectra in the range of 1050-1300 confirmed the existence of the C-O group. According to the range obtained from the surface of the aluminum alloy, the presence of agar on the surface was confirmed, which could indicate the coating between the metal surface and the environment. Fig 7(b) shows the FTIR spectrum of the aluminum surface in the presence of the inhibitor in the gel. Compared to Fig. 7, there was no difference between them. The FTIR spectra in the presence and absence of the inhibitor could also confirm its physical adsorption on the metal surface.



(a)



(b)

Figure 7. FTR spectrum of the aluminum surface after immersion in the gel electrolyte for 15 days in (a) the absence and (b) presence of inhibitor..

Fig. 8 presents potentiodynamic polarization plots for aluminum immersed in gel electrolyte in the absence (blank) and presence of amoxicillin after 15d. In our study, the maximum displacement of E_{corr} was 4 mV which was much less than ± 85 mV. Also, the data [31-33] specifies that when corrosion potential (E_{corr}) is higher than ± 85 mV regarding E_{corr} of the blank, the inhibitor can be considered distinctively as either cathodic or anodic. All of these suggest that amoxicillin is a mixed type inhibitor.

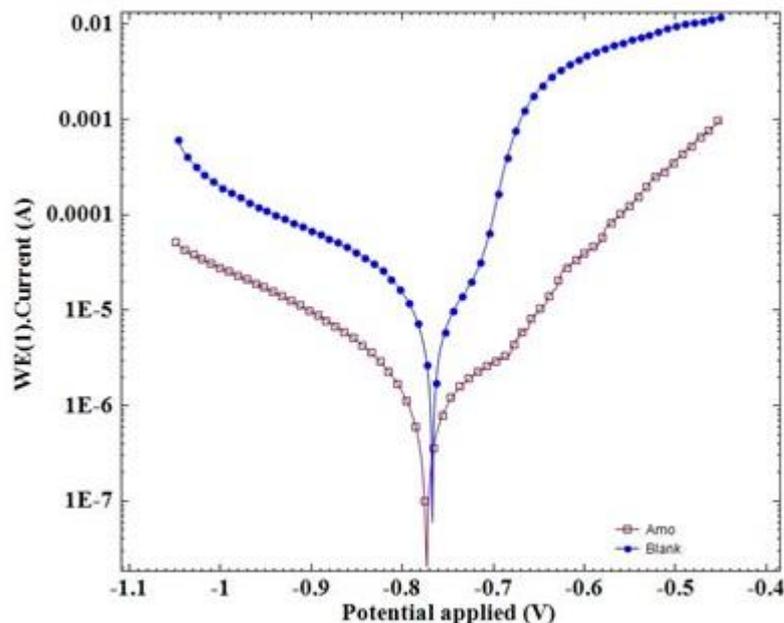


Figure 8. Potentiodynamic polarization curves for aluminum in gel electrolyte at 25°C in the absence (blank) and presence of amoxicillin (Amox) after 15d.

Fig. 9 shows images of WEs surfaces from an optical microscope in the presence and absence of inhibitor on the aluminum surface perfectly certifying the inhibitory effect of amoxicillin.

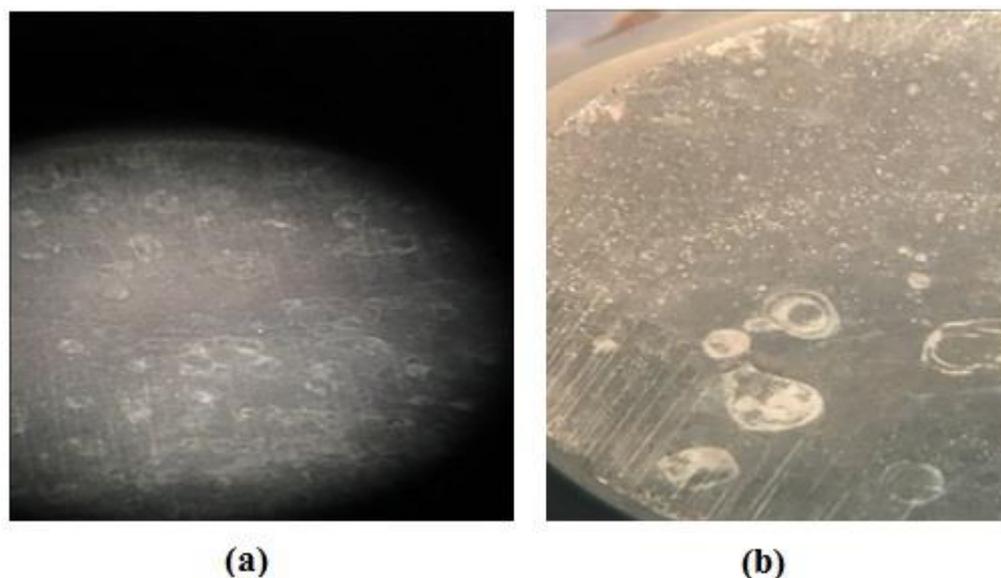


Figure 9. Optical microscopic images of the aluminum surface after immersion in the gel electrolyte for 15 days in (a) the presence and (b) of absence inhibitor

4. CONCLUSION

The inhibitory effect of amoxicillin on the corrosion behavior of aluminum alloy 6061 in the gel electrolyte was studied using EIS. The EIS data showed that amoxicillin, an inhibitor, in the gel

electrolyte reduced corrosion. The use of this inhibitor minimized the pitting corrosion of the aluminum surface. The IE% values further showed acceptable compatibility with the data acquired. Examination of the Potentiodynamic polarization spectrum also showed that the inhibitor was of the mixed type and reduced corrosion over time. The TEM results also confirmed the EIS findings. Moreover, based on the FTIR spectrum, the absorption phenomenon was also a physical one. All in all, the inhibitory effect of amoxicillin as well as its non-toxic and green characteristics seems to make it one of the best candidates to reduce corrosion. The use of a gel electrolyte can also be a good alternative to conventional aqueous electrolytes in corrosion studies on metal surfaces. However, further studies are to be conducted on other green inhibitors and gel electrolytes.

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