Original Article

Electrochemical Studies of Aluminium-2014 Alloy in 1M Acetic Acid using pomegranate Extract as corrosion Inhibitor

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ABSTRACT

The inhibition performance of atenolol on Aluminium-2014 in 1 M Acetic Acid solution was studied by weight loss and electrochemical methods. The results show the inhibition efficiency was found to increase with increasing the concentration of the inhibitor from 50 to 300 ppm. The maximum inhibition efficiency 93.8% was observed in the presence of 300 ppm inhibitor (in case of potentiodynamic polarization). The inhibition action of atenolol was explained in terms of adsorption on the Aluminium-2014 surface. Electrochemical Impedance spectroscopic technique (EIS) exhibits one capacitive loop indicating that, the corrosion reaction is controlled by charge transfer process. Polarization measurements showed that the inhibitor is of a mixed type. The results obtained from the different methods are in good agreement. The surface morphologies of Aluminium-2014 were examined by scanning electron microscope (SEM).

KEYWORDS: *Corrosion, Pomegranate, Aluminium-2014, Acetic Acid, Electrochemical studies.*

1. Introduction

The environmental consequence of corrosion is enormous and its inhibition has been deeply investigated. Acetic Acid is widely used in various technological processes in industry, e.g., in pickling baths, in the extraction and processing of oil and gas and in other chemical and petrochemical industries. Also, in the technical cracking of petroleum, acids appear as a result of hydrolysis of salts and may have a destructive effect on the equipment. Corrosion in Aluminium-2014 is important and expensive problem in the industries and it represents a significant portion of loss as a result of lost production, inefficient operation, and high maintenance. It has been found that one of the best methods of protecting metals against corrosion involves the use of inhibitors which are substances that slow down the rate of corrosion and Therefore, the development of corrosion inhibitors based on organic compounds containing nitrogen, oxygen atoms is of growing interest in the field of corrosion and industrial applications. The corrosion inhibition is a surface process, which involves adsorption of the organic compounds on the metal surface. The adsorption depends mainly on the electronic structure of the molecule. The inhibition efficiency of organic compounds depends on the mode of interaction with the metal surface and molecular structure. However, there is increasing concern about the toxicity of most corrosion inhibitors. The toxic effects not only affect living organisms but also poison the environment. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors. Recently, several studies have been carried out on the inhibition

of corrosion of metals by. Moreover, the pharmaceutically active compound is big enough 3-aminopyridine-2-carbaldehyde thiosemicarbazone. Furthermore,3-aminopyridine-2-carbaldehyde thiosemicarbazone is very cheap, easily available, environmentally friendly and most importantly is nontoxic. In view of these favorable characteristic properties, atenolol drug was chosen for the corrosion studies.The main objective here is to investigate the corrosion process of Aluminium-2014 in 1 M Acetic Acid solution in the absence and presence of different concentrations of atenolol. It was also the purpose of the present work to test the various electrochemical studies and surface morphologies.

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Material and Methods

Aluminium-2014 materials used for the study were mechanically cut into specimen of sizes 4 × 1.5 × 0.2 cm. AR grade Acetic Acid was used for the preparation of aggressive solutions. Various (approximate) concentrations of acid with and without inhibitor were prepared using double distilled water.

The compound 3-aminopyridine-2-carbaldehyde thiosemicarbazone was purified by recrystallisation with ethanol. The inhibitor used in this study is non-toxic, with high molecular size, contains a large number of donating atoms (N, S, atoms) and easily available as pharmaceutical drug. Molecular structure of the used inhibitor is presented below
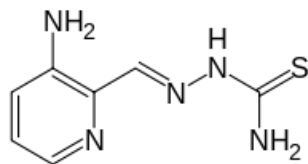
Figure 1: Structure of Pomegranate Extract

Electrochemical studies

The working electrode was polished with different grades of emery papers, washed with water and degreased with acetone. All electrochemical measurements were carried out using a CHI 608E electrochemical impedance analyzer model. Prior to the electrochemical measurement, a stabilization period of 30 min was allowed, which was proved to be sufficient to attain a stable value of open circuit potential (OCP). The electrochemical studies were made using a three-electrode cell assembly at room temperature with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was Aluminium-2014 with the exposed surface of 1 cm2 and the rest being covered with commercially available resin. The EIS measurements were carried out from Nyquist plot using AC signal of 0.01 V amplitude for the frequency spectrum from 100 kHz to 0.01 Hz. The potentiodynamic polarization curves were recorded in the potential range of +300 mV from the open circuit potential at a sweep rate of 0.01 mV/s.

Weight loss measurements

All the tests were conducted in 100 ml aerated 1 M AA solution at room temperature with different concentrations of 3-aminopyridine-2-carbaldehyde thiosemicarbazone for 3 h immersion period. These samples were polished with emery paper of 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0 grades, washed thoroughly with doubled distilled water, degreased with acetone and finally dried. At the end of the tests, the specimens were carefully washed in distilled water, dried and then weighed. Duplicate experiments were performed in each and the mean value of the weight loss has been reported. From the weight loss measurements, the corrosion rate (W) was calculated using the following equation,

$$CR = W = \frac{m_1 - m_2}{St}$$

where, m1 is the mass of the specimen before corrosion, m2 is the mass of the specimen after corrosion, S is the total area of the specimen, t is the corrosion time, and W is the corrosion rate. The (IE%) was determined using the following equation,

$$\%IE = W = \frac{W_0 - W_i}{W_0} \times 100$$

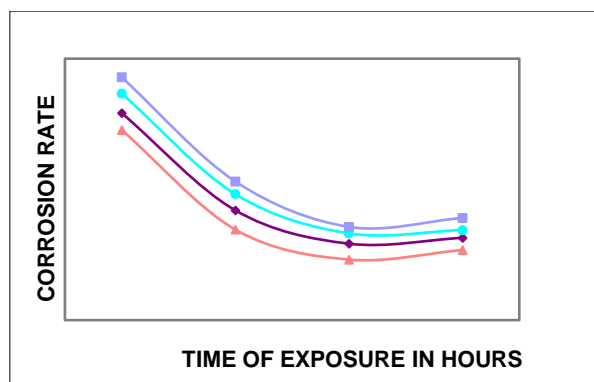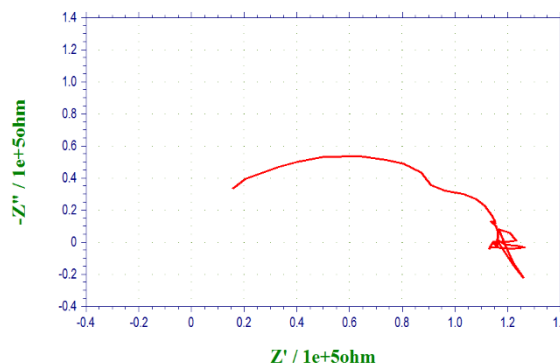where, Wo is the corrosion rate in the absence of inhibitor and Wi is the corrosion rate in the presence of inhibitor

Figure 2: Weight loss Corrosion Test in 1M AA using different Concentration of Inhibitor

Surface studies

The scanning electron microscopy (SEM) VEGA3TESCAN model was used to study the morphology of the corroded surface in the presence and absence of 3-aminopyridine-2-carbaldehyde thiosemicarbazone for the immersion of 3 h at room temperature. The SEM images were taken from that portion of the specimen where better information was expected.

Results and Discussion

Electrochemical impedance spectroscopy The experimental results obtained from EIS measurements for the corrosion of Aluminium-2014 in the presence of atenolol at room temperature. The impedance spectra for Aluminium-2014 in 1 M AA solution without and with optimum concentration of atenolol are presented as Nyquist plots Clearly, the impedance spectra exhibit a large capacitive loop at high frequencies followed by a small inductive loop at low frequency values. The capacitive loop indicates that the corrosion of steel is mainly controlled by a charge transfer process, and usually related to the charge transfer of the corrosion process and double layer behavior. On the other hand, the inductive loop may be attributed to the relaxation process obtained by adsorption of inhibitor on the electrode surface. The diameter of the capacitive loop in the presence of inhibitor is bigger than in the absence of inhibitor (blank solution) and increases with the inhibitor concentration.
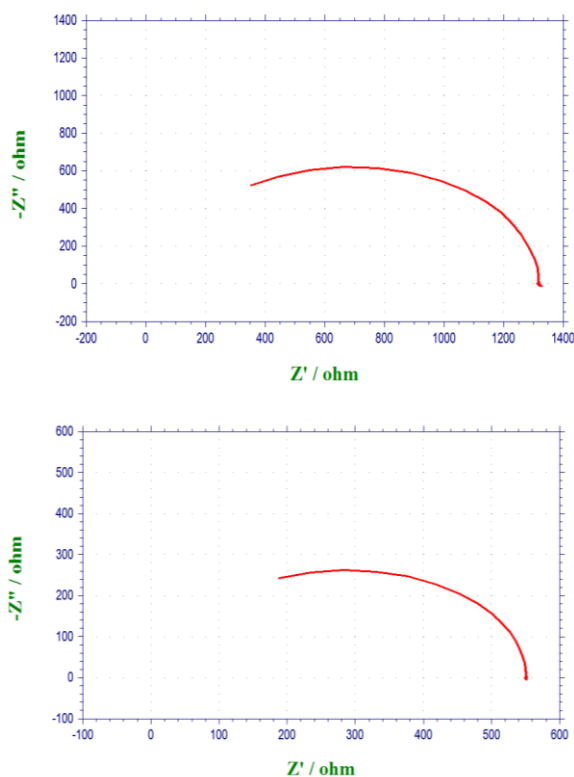
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anodic and cathodic regions of the Tafel plots. The corrosion current density (Icorr) can be obtained by extrapolating the Tafel lines to the corrosion potential and the inhibition efficiency (IE%) values were calculated from the relation.

$$IE(\%) = \frac{I_{corro} - I_{corroi}}{I_{corro}} \times 100$$

where, Icorro and Icorri are the corrosion current densities in the absence and presence of inhibitor, respectively represents all corrosion parameters including inhibition efficiency of the atenolol obtained from potentiodynamic polarization studies. The polarization curves for Aluminium-2014 in 1 M AA containing with and without inhibitor are given in. The parallel cathodic Tafel lines suggested that the addition of inhibitors to the 1 M HCl solution do not modify the hydrogen evolution mechanism and the reduction of H+ ions at the Aluminium-2014 surface, which occurs mainly through a charge transfer mechanism.

The change in the values of βc in the presence of inhibitor clearly indicates the effect of the inhibitor compound on the kinetics of hydrogen evolution.

BLANK (Without Inhibitor)

Figure 3: a-c,EIS Studies of Al 2014 in Different Cocentration of Inhibitor

This indicates that the impedance of inhibited substrate increases with the inhibitor concentration. Noticeably, the Nyquist plot does not present perfect semi-circles (non ideal); they indicate a depressed capacitive loop. These deviations known as frequency dispersion were attributed to surface roughness and inhomogeneities of the solid surface Electrochemical impedance parameters for Aluminium-2014 in 1 M AA containing different concentrations of 3-aminopyridine-2-carbaldehyde thiosemicarbazone.

Nyquist plots of Aluminium-2014 in 1 M AA solution with different concentrations of 3-aminopyridine-2-carbaldehyde thiosemicarbazone with equivalent circuit model.
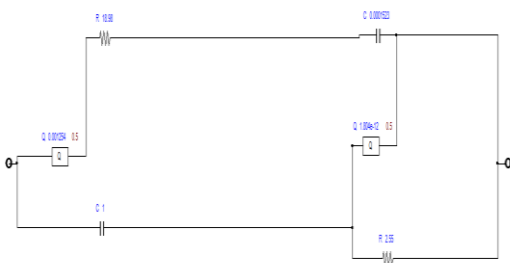

50PPM

Figure 4: Circuit Diagram for Impadence

Potentiodynamic polarization measurement
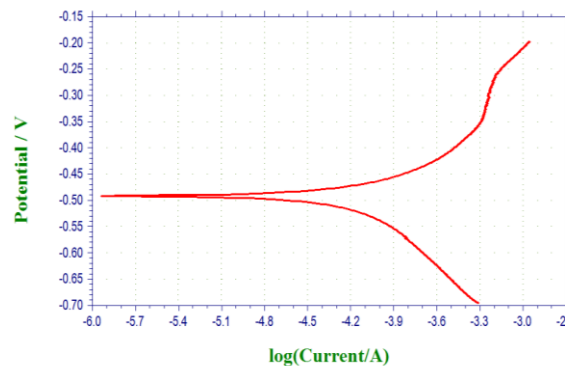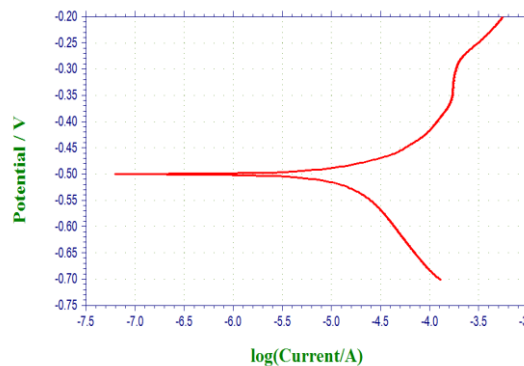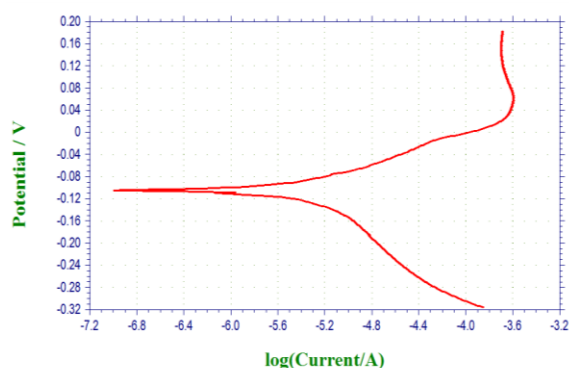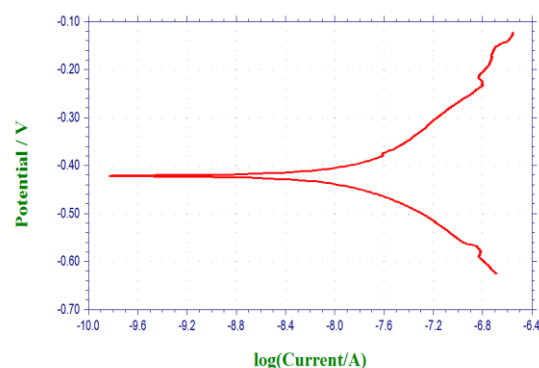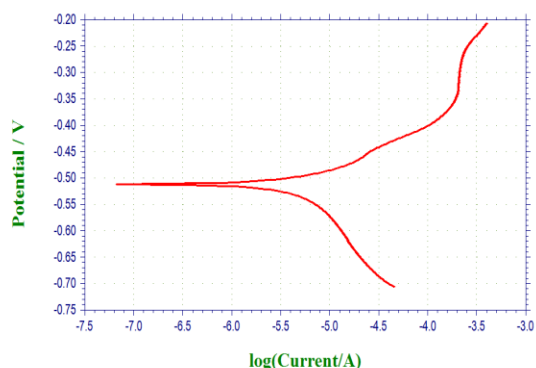The corrosion potential (Ecorr), corrosion current density (Icorr), and anodic (βa) and cathodic (βc) slopes are obtained by the

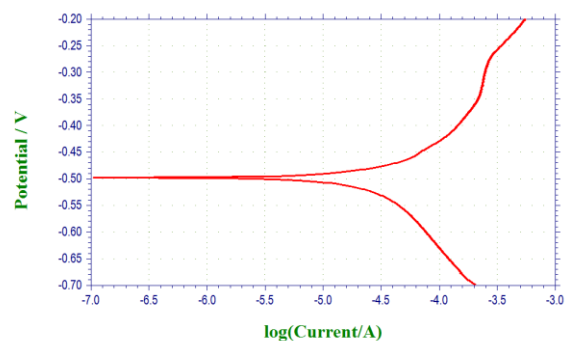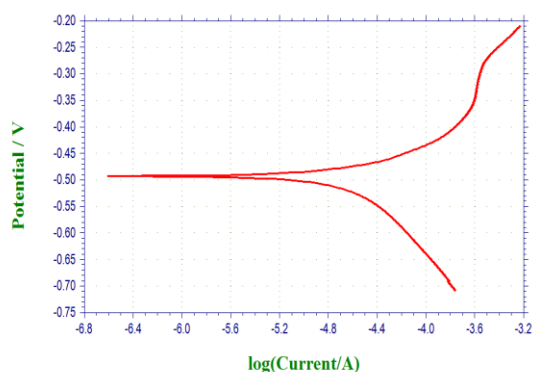**© 2020, AJAN. All Rights Reserved**

100PPM

250PPM

150PPM

300PPM

Figure 5: (a-f),Tafel plots of Aluminium-2014 in 1 M AA solutions with various concentrations of Inhibitor

The shift in the anodic Tafel slope (βa) values may be due to the adsorption of inhibitor molecules onto the Aluminium-2014 surface. The studied inhibitor compound acts as a corrosion inhibitor suppressing both anodic and cathodic reactions by getting adsorbed on the Aluminium-2014 surface blocking the active sites, and these results suggested that the addition of inhibitor reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction, indicating that this inhibitor exhibits cathodic and anodic inhibition effects. Therefore, the atenolol can be classified as a mixed inhibitor in 1 M HCl solution.

200PPM

Table 1: Potentiodynamic polarization values for the corrosion of Aluminium-2014 in 1 M AA in the absence and presence of different concentrations of Inhibitor

Conc. (ppm)	β_a (1/V)	β_c (1/V)	E_{corr} (mV/SCE)	I_{corr} (mA/cm²)	R_p (Ohm)	IE (%)
Blank	4.722	6.558	−536.3	1.736	22.2	–
50	8.539	7.965	−487.0	0.5325	50	69.3
100	7.403	8.042	−504.1	0.3961	71	77.2
150	7.686	8.410	−514.0	0.2156	125	87.6
200	7.700	9.071	−486.9	0.1666	156	90.4
250	7.655	7.530	−508.2	0.1241	231	92.9
300	7.348	8.555	−508.8	0.1071	255	93.8

Weight loss measurements

The values of corrosion rate and percentage inhibition efficiency were calculated from weight loss method at different concentrations of atenolol in 1 M HCl after three hours immersion at room temperature. They are summarized in. It was observed that atenolol inhibits the corrosion of Aluminium-2014 in 1 M HCl solutions at various concentrations used in the study. It is evident from that the inhibition efficiency is increased from 61.4% to 92.8% with the addition of 50–300 ppm of atenolol. The maximum inhibition efficiency was shown at 300 ppm concentration of atenolol and further increasing inhibitor concentration does not change IE%. Indeed, the corrosion rate values of Aluminium-2014 decrease from 93.333 mmy−1 to 6.738 mmy−1 on the addition of 50 ppm to 300 ppm of atenolol.

Table 2: Weight loss values of various concentrations of Pomegranate in 1 M AA solution

Concentration (ppm)	Weight loss (mg cm^{-2})	Corrosion rate (mm y^{-1})
Blank	39.2	93.333
50	15.14	36.048
100	9.20	21.905
150	5.97	14.214
200	4.34	10.333
250	3.90	9.286
300	2.83	6.738

The increased inhibition efficiency (IE%) and decreased corrosion rate (CR) might be due to the result of increased adsorption and increased coverage of atenolol on the Aluminium-2014 surface with increasing concentration of atenolol . The variation of inhibition efficiency with various immersion times from 1 h to 5 h at 300 ppm atenolol is shown in. The IE% increased from 80.1% to 92.8% when immersion time increases from 1 h to 3 h and thereafter no deep change in IE% was noted (92.8–92.0%). This is due to the increased corrosion rate of metal with immersion time. It is clear that atenolol showed good inhibition for Aluminium-2014 corrosion in 1 M AA solution.

Scanning electron microscopy
In order to evaluate the conditions of the metal surface in contact with acid solution in the absence and presence of inhibitor, a surface analysis was carried out, using scanning electron microscope, immediately after the corrosion tests. The Aluminium-2014 samples in 1 M AA solution with and without optimal concentration of the atenolol were subjected to analysis. SEM images are shown in a–c. It shows, surface corrosion of Aluminium-2014 decreased remarkably in the presence of the

inhibitor (b). Inspections of the figures reveal that there is severe damage, clear pits and cavities on the surface of Aluminium-2014 in the absence of inhibitor (c) than in its presence and polished metal (a). There are fewer pits and cracks observed in the inhibited surface. It conforms that the metal surface is fully covered with the inhibitor molecules and a protective inhibitor film was formed.
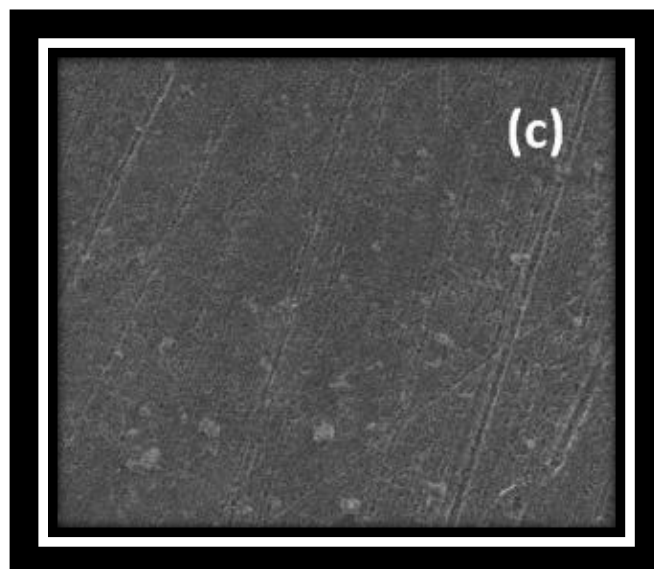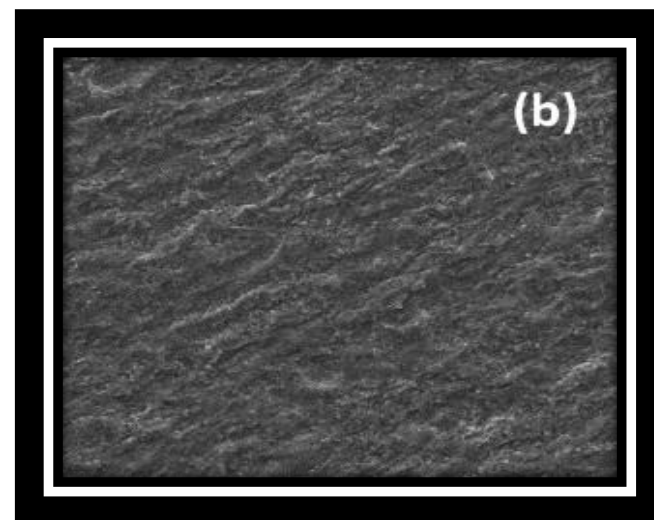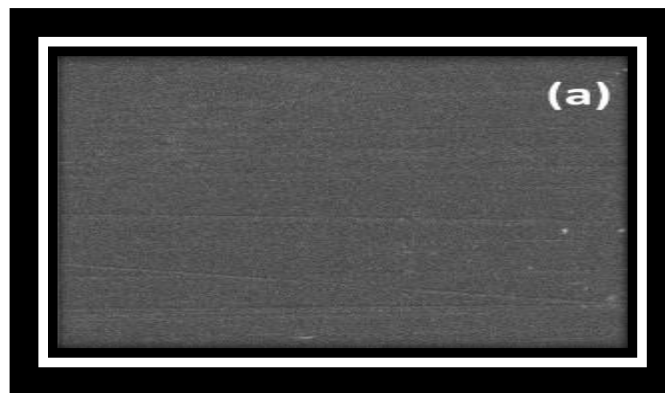
Figure 6: SEM images of Aluminium-2014 (a) Polished surface (b) 1 M AA solution (c) 1 M AA solution with optimum concentration of Pomegaranate (300 ppm)

Conclusion

On the basis of the above results the following conclusion can be drawn.

- The results obtained lead to the conclusion that Pomegranate effectively inhibits the corrosion of Aluminium-2014 in 1 M AA solutions.
- The corrosion process was inhibited by adsorption of the inhibitor molecule on the Aluminium-2014 surface.
- The inhibition efficiency of these compounds increases with the increase of the pomegranate concentrations.
- Polarization curves demonstrated that the atenolol is a mixed-type inhibitor for Aluminium-2014 surface corrosion in these solutions. EIS measurements also indicate that the inhibitor increases the charge transfer resistance and show that the inhibitive performance depends on an adsorption of the molecules on the metal surface.
- The SEM images confirm the formation of the protective layer on the metal surface.

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