Study of corrosion inhibition of aluminum in acidic media by pineapple crown extract

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Abstract. The efficiency of pineapple crown extract as corrosion inhibitor of aluminum in $1M H_2SO_4$ acidic medium was tested using weight loss and potentiodynamic methods, at varied inhibitor concentration. Through the data from the weight loss method there was calculated the corrosion rate and pineapple crown extract's inhibition on aluminum corrosion in acidic medium, at varied inhibitor concentration. Also, with the data obtained from the potentiodynamic method, the polarization curves and Tafel tangents were constructed, while calculating the corrosion rate and inhibition efficiency of pineapple crown extract. Experimental measurements showed that pineapple crown extract acts as a mixed inhibitor and the inhibition efficiency increases with increasing the extract concentration.

Keywords: aluminum; pineapple crown extract; potentiodynamic method; green inhibitor; corrosion.

1. Introduction

Corrosion is a surface phenomenon between a metal and an aggressive medium. Usage of many metals and alloys nowadays, which are distinguished by their basic properties, such as: good electrical and thermal conductivity, resistance to traction, etc. has rendered the study of corrosion a special importance. Their instability towards air and water reduces corrosion resistance [1]. The use of new corrosion-resistant materials has been the focus of a great deal of research in recent years. Aluminum is a white silver-like metal, suitable for forging, light and a good conductor of electricity and heat [2]. It is widely used in industry [3]. Aluminum is resistant to corrosion due to the oxide layer, which in acidic and basic media breaks down, thus allowing the onset of corrosion [1, 4]. For this reason, the use of corrosion inhibitors in industry has taken on special importance, in order to reduce the degree of corrosion of various metals and metal alloys, which are in contact with aggressive media [5]. Numerous studies have been recently conducted so as to find suitable compounds to use as corrosion inhibitors. Most of these compounds are synthesized chemicals, which have high production costs and are harmful to both the environment and humans. Of utmost importance nowadays is the use of green inhibitors, which are easily produced and harmless to humans. Organic compounds which contain O, N, S, P atoms, hydrophobic hydrocarbon part, hydrophilic functional groups such as -OH, -COOH, aromatic rings are active centers that influenced the absorption on the surface of the metal [5-8]. They have resulted as good inhibitors against corrosion and suitable for the environment. Polyphenols as coumaric acid and ferulic acid are found in pineapple crown extract [9-11]. The purpose of this study is specifically to test the pineapple crown extract as an inhibitor on aluminum corrosion in acidic medium.

2. Experimental

To study the inhibition efficiency of pineapple crown extract, two methods were used: weight loss method and that of measuring corrosion current density.

2.1. Materials and reagents

The material under investigation was aluminum with the following chemical composition: Al (97.36%), Si (0.40%), Fe (0.7%), Cu (0.15%), Mn (0.15%), Mg (0.80%), Cr (0.04%), Zn (0.25%) and Ti (0.15%). The reagents was purchased from Sigma Aldrich. The pineapple fruits were imported from Tropical countries.

2.2. Extract preparation

The pineapple crown was dried in a thermostat at 40 °C, grinding it finely to increase the contact surface. To prepare the alcoholic extract, 200 ml of 70% ethyl alcohol was poured into 20 g of pineapple crown three times, then placed in a magnetic mixer for 6 hours and the extract was filtered.

The extract was then left to evaporate the alcohol to ¹/₄ of quantity and placed for refrigerated storage, as it should be stored at 4 °C and in the dark.

2.3. Corrosion medium

To prepare corrosive (blank) solutions, sulfuric acid (H₂SO₄) with a concentration of 96% and density of 1.830 g/cm³ was used. The concentrations of pineapple crown extract used are: 1 g/L; 2 g/L; 3 g/L; 4 g/L.

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2.4. Weight loss method

It is a simple method through which the weight loss of the material under study is estimated by calculating its corrosion rate in mm/year and inhibition efficiency according to the relevant formulas 1 and 2 [12-14]:

$$V_{(mm/vit)} = \frac{87.6 \cdot \Delta m}{d \cdot A \cdot t} \tag{1}$$

where: Δm - the difference of weight, in mg; d - the density, in g/cm³; A - the surface of sample, in cm²; t - the time of exposure of the sample, in h.

Inhibitor Efficiency (%) =
$$\frac{CR uninhibited - CR inhibited}{CR uninhibited} x 100$$
(2)

where: CR uninhibited - is corrosion rate of the uninhibited system; CR inhibited - is the corrosion rate of the inhibited system.

For the weight loss method, aluminum cylindrical specimens $40 \pm 2 \text{ mm} \log \text{and} 5.5 \pm 0.3 \text{ mm}$ in diameter were prepared on a lathe. A hole was drilled in at the top of each specimen and marked. For each corrosive solution there are 2 parallel specimens. The samples were polished with P220-P1200 sandpaper, and then subjected to an ultrasonic bath, initially cleaned with benzene for 3 - 4 minutes, double distilled water, and finally with acetone for 3 - 4 minutes.



Figure 1. The sample of aluminum

They were then dried in a thermostat at 60 °C for 30 minutes. The specimens were heated and cooled again until constant weight was obtained and they are introduced in corrosive solution. After 5 days the specimens are removed from the corrosive solutions. They are rinsed with distilled water to remove corrosion products, then rinsed with acetone, dried in a thermostat, and reweighed up to a constant weight.

2.5. Potentiodynamic method

It consists in measuring the intensity of the corrosion current by means of a potentiometer, constructing the Tafel curves, finding the density of the corrosion current, and then calculating the corrosion rate based on the respective formula [12-14]:

$$V_{corr} = (K x A x i)/(n x \rho)$$
(3)

where: *A* - is the atomic weight of the metal (A = 26.98 g/mol); *i* - corrosion current density in (μ A/cm²); *n* - the number of electrons exchanged during metal dissolution (n = 3);

 ρ - the density in (g/cm³) (ρ = 2.7 g/cm³), *K* is a constant which equals to 0.00327 if the corrosion rate (V_{corr}) is calculated in [mm/y].

The inhibitor efficiency was calculated based on Eq. 2.

An electronic potentiostat of the TACUSSEL PJT 24-1 type was used for the experiment. The electrodes used were: working electrode (Al); Hg/HgSO₄ electrode as reference electrode; and platinum electrode for H₂SO₄ medium as counter electrode.

The circular shape was chosen for the working electrode because it avoids sharp or angled surfaces, thus avoiding the possibility of corrosion with cracks.

In the case of the electrode prepared for measurement, the contact surface is circular with a diameter of $\Phi = 6.1$ mm. Specimens are prepared on the lathe according to the scheme shown in Figure 2.



Figure 2. The sample of aluminum for potentiodymanic measurements

Before measurement, the solutions are initially deionized with a nitrogen sparge in order to remove dissolved oxygen.

Table 1. Solution for we	ight loss and	l potentiodynamic
mea	surements	

Nr.	Blank	Concentration of pineapple crown extract (g/L)			
		1	2	3	4
1	+				
2	+	+			
3	+		+		
4	+			+	
5	+				+

3. Results and discussion

3.1. Weight loss method

The results obtained from the weight loss method in the form of rate of corrosion in mm/year and inhibition efficiency in percentage are shown in Table 2.

Table 2. Corrosion rate and inhibition efficiency for aluminum in absence and presence of the inhibitor

Sample	Corrosion medium	V (mm/year)	Inhibition efficiency (%)
1	Blank (1M H ₂ SO ₄)	0.2604	0
2	1 g/L	0.2097	19.48
3	2 g/L	0.1708	34.42
4	3 g/L	0.1612	38.09
5	4 g/L	0.1517	41.76

The results obtained from the weight loss method show that the increase of the inhibitor concentration increases the coverage area, protective efficiency, and decreases corrosion rate expressed in mm/year. The lowest inhibitory efficiency is in the solution where the concentration of pineapple crown extract inhibitor is 1 g/l respectively 19.48%, whereas the highest inhibitory efficiency is for the 4 g/l pineapple crown extract solution, 41.76%. The corrosion rate is reduced from 0.2604 mm/year, the blank solution, to 0.1517 mm/year in the 4 g/l inhibitor concentration solution.

The pineapple crown extract contains coumaric acid and ferulic acid, which must have been adsorbed onto the aluminum surface through the lone pair of electrons on the oxygen atoms and the π -electrons of the phenyl and the carbonyl groups [15]. So, the surface area that is available for the attack by the aggressive medium is reduced. The decrease of corrosion rate and the increasing of the inhibition efficiency with the increasing of the concentration of pineapple crown extract confirmed the inhibition effect of pineapple crown extract on aluminum.



Figure 4. Diagram of inhibition efficiency in % for aluminum in 1M H₂SO₄ solution in absence and in presence of pineapple crown extract.

3.2. Potentiodynamic polarization

Figure 5 shows anodic and cathodic Tafel curves for aluminum in solution with and without of pineapple crown extract as inhibitor.



Figure 5. Potentiodynamic polarization curves for aluminum in 1M H₂SO₄ solution in absence and presence of pineapple crown extract.

The results obtained from the potentiodynamic method in the form of E_{corr} , corrosion potential, i_{corr} , corrosion current, corrosion rate in mm/year, and inhibition efficiency for solutions with and without inhibitor are given in Table 3.

Table 3. Corrosion potential, corrosion current density,
corrosion rate and inhibition efficiency of aluminum in
presence and absence of inhibitor

Medium	E _{corr} (mV)	i _{corr} (μA/cm²)	V _{corr} (mm/year)	Inhibition efficiency (%)
Blank	-599	95.6	1.33	-
1 g/L	-625	59.1	0.64	51.9
2 g/L	-642	41.2	0.45	66.2
3 g/L	-649	40	0.44	67.2
4 g/L	-649	38.5	0.42	68.5

From the results of Table 3, it turns out that increasing the inhibitor concentration decreases the corrosion current, and reduces the corrosion rate. The results of Table 3 show the values of inhibitory efficiency, which increases by increasing the inhibitor concentration: namely, the inhibitory efficiency reaches the highest value of 68.5% when 4 g/l inhibitor is in 1M H₂SO₄ acidic solution. The inhibitory effect of pineapple crown extract is directly related to the inhibitor ability to be adsorbed on the aluminum surface, due to the presence of polyphenols, hydroxyl groups, and double bonds in benzene rings [9, 16, 17]. The presence of pineapple crown extract in 1M H₂SO₄ acidic medium at four different concentrations does not significantly change the value of corrosion potential as shown in Figure 5 and Table 3. This shows that pineapple crown extract in 1M H₂SO₄ acidic medium acts as a mixed inhibitor, simultaneously controlling anodic and cathodic reactions on the aluminum surface [18, 19]. The increasing of the concentration of the inhibitor reduces cathodic current significantly, so it is predominantly cathodic inhibitor [20].

4. Conclusions

The weight loss method shows that the pineapple crown extract in $1M H_2SO_4$ solution mitigates the corrosion rate of the aluminum from 0.2604 mm/year to 0.1517 mm/year, with a protection efficiency 41.76%.

From the potentiodynamic measurement, the pineapple crown extract mitigates the corrosion rate of the aluminum from 1.33 mm/year to 0.42 mm/year with a protection efficiency 68.5%.

The results obtained from two methods shown that protection efficiency increases with the increasing of concentration of inhibitor, so the pineapple crown extract is a good inhibitor for aluminum in $1M H_2SO_4$ solution.

Conflict of interest

Authors declare no conflict of interest.

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Received: 20.04.2022 Received in revised form: 04.07.2022 Accepted: 09.07.2022