RESEARCH ARTICLE

Corrosion Inhibition of Pure Aluminum in Acidic Media Using Expired Drug Deoxycyclin

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ABSTRACT

Weight loss, technique were used to investigate the inhibitory effect of expired drug molecules, deoxycyclin, on aluminum pure corrosion in 0.5 M H_2SO_4 solution, at (293.15, 303.15, 313.15 K). When the concentration of inhibitor is increased, the inhibition efficiency improves. The Langmuir isotherm model governs adsorption. So the inhibition efficiency depends on absence and presence of the inhibitor. the highest inhibition efficiency of 93.25% was obtained at the highest inhibitor concentration and highest temperature.

Keywords: Acidic solution, Aluminum, Corrosion, Deoxycyclin, Inhibitor.

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INTRODUCTION

Corrosion is an interfacial and irreversible reaction between a material and its environment that results in its dissolution and consumption. In many cases, corrosion causes results that are harmful to the material in question.[1] The reaction usually starts at a metal surface, which can be identified by the weight of the metal or the change in chemical or physical properties over time.[2] Corrosion is an undesirable phenomena that occurs naturally when metals and their temporarily unstable forms, such as ores or natural minerals, have a strong inclination to change to a more thermodynamically stable state. Metals exist in various forms, such as oxides, hydroxides, and other forms, because of their environment.[3] Aluminum and its alloys are among the most cost-effective and dependable metals available today, thanks to their superior strength-to-density ratio. Transportation, aviation, two-wheelers, hiking gear, inline skating frames, and hang glider frames are just a few applications.[4] The nonferrous metal aluminum is the most extensively utilized. It is critical to keep this metal from corroding. Corrosion inhibitors are a common approach for preventing corrosion.[5] At a corrosive environment, an inhibitor is a chemical substance or mixture of chemicals that effectively prevents or lowers corrosion without causing substantial reactivity with the environment's components.[6] The focus of corrosion inhibition research has shifted to human health and safety concerns. The researchers have focused on utilizing environmentally acceptable chemicals such as plant extracts, which contain a variety of organic chemicals, for this aim. Green alternatives to poisonous and dangerous substances include amino acids, alkaloids, pigments, and tannins. Extracts of some common plants and plant products have been examined as corrosion inhibitors for various metals and alloys under diverse environmental circumstances due to biodegradability, eco-friendliness, low cost, and accessible availability.[7] The results of employing expired medications were unexpected, as they turned out to be perfect and cost-effective corrosion inhibitors rather than a pharmaceutical ingredient that had to be discarded.[8] This distinguishing property drives research into the potential of pharmaceuticals as corrosion inhibitors all around the world. Drugs, which are eco-friendly and non-toxic, are better suited to environmental standards than hazardous inhibitors. As a result, various studies have employed both new and expired drugs as corrosion inhibitors.[9]

The following are some of the most significant characteristics that must be present in inhibitors:

- It must provide good corrosion protection at low inhibitor concentrations.
- It must prevent corrosion from attacking all exposed materials.
- It must remain efficient in extreme operating conditions (higher temperature and velocity).
- Corrosion rate should not increase dramatically if inhibitor dosage is too low or too high.
- It should suppress both uniform and localized corrosion.
- It should be effective for a lengthy period of time.
- It should not be a source of toxicity or contamination.

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EXPERIMENTAL PART

Extraction of Expired Drugs

Current corrosion inhibitors were derived from expired pharmaceuticals with a higher water solubility. The molecular structure of deoxycyclin used is shown in Figure 1. Moreover, the chemical properties of deoxycyclin shown in Table 1. The expired drug was selected to obtain the active material of the green inhibitors that include Deoxycyclin. The drug is crushed through a pestle, mixed with distilled water, left for 24 hours, filtered for 36 hours, and then dried in oven at 80ºC for 4 hr/da.[10]

Some inspections and tests, including high-performance liquid chromatography (HPLC) to determine the amount of active substance in the extract, were completed to recover materials from expired medications to ensure the existence of effective aggregates in the extract and fourier transform infrared spectroscopy (FTIR).

Sample Preparation

To investigate the corrosion test (loss weight), pure aluminum Specimens were first created. Cutting the specimen is a critical parameter in corrosion resistance, and it is vital to establish a uniform surface. Square specimens (3 cm, 3 cm, 1 nm) were cut with an electrical saw and then shaped into a final specimen with a hole drilled on one side for simple suspension in the corroding solution.

The second thing grinding and polishing the specimens were then ground with paper of various in sequence of (220, 400, 600, 800, 1000, 1500 and 2000) to obtain a flat and scratch-free surface. The samples were polished with alumina suspension. After that, distilled water was used to rinse the samples. Acetone was used to decrease the polished samples, then dried and stored in a plastic container. A four-digit electronic balance was used to weigh the samples, and an electronic vernier was used to measure their dimensions.[11]

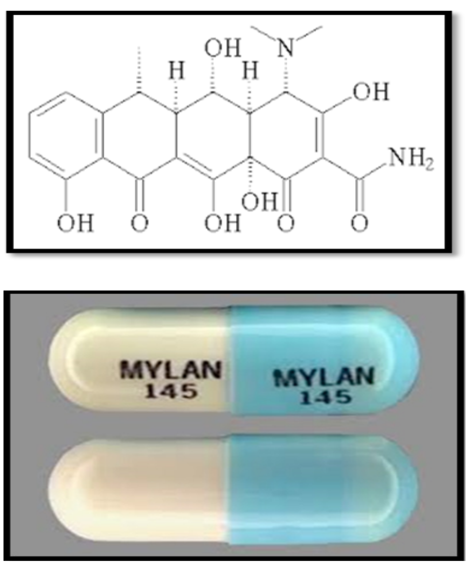

Figure 1: Appearance and chemical structure of Deoxycyclin

Table 1: Chemical properties of Deoxycyclin

Color	*Light yellow*
Molecular Formula	$C_{22}H_{24}N_2O_8$
Molecular Weight	444.4 g/mol

Preparation of Corrosion Medium

This study used corrosion media, including a 0.5M H2SO4 solution. This media was produced in distilled water and placed in flasks with 500 mL capacities filled with various drug concentrations.

Fourier Transform Infrared Spectrum (FTIR)

The FTIR technique is used to determine the active groups in pharmaceuticals after they have been extracted by combining a sample of the extract with KBr and recording the spectra Perkin Elmer spectrum a model (65).

Atomic Force Microscopy (AFM)

The topography of the surface was displayed and the roughness was measured using AFM.

Scanning Electron Microscope (SEM)

Following the necessary research, the surface morphology of pure aluminum was assessed using SEM.

RESULTS AND DISCUSSION

Weight Loss Measurement

To determine how much weight had been lost, pure aluminum specimens were used. The specimens were fully immersed in 200 mL of 0.5M H_2SO_4 after being washed and dried. A solution with and without an inhibitor (deoxycyclin) was tested for 3 hours. After cleaning, the samples were dried using an electric drier and weighed with an analytical balance. Weight loss was measured in experiments with different inhibitor concentrations (50, 100, 150, 200, 250, 300) ppm and at different temperatures (293.15, 303.15, 313.15) (K). Corrosion rate (CRcorr) was calculated using the following expression.[12]

$$CR\ (gmd) = \frac{\Delta wt}{At} \tag{1}$$

Where (CR) is the corrosion rate, (W) is the weight loss in grams, (A) is the sample area in (t), m^2 is the immersion time in days, and the corrosion rates are determined in units of g/m^2 day and symbolized by (gmd) Given the corrosion rate, the efficiency ratio is determined using the equation below:[13]

$$\%IE = \frac{CRuninhibit - CRinhibit}{CRuninhibit} \times 100 \tag{2}$$

Where ($CR_{uninhibit}$) and ($CR_{inhibit}$) are the corrosion rates in the absence and presence of different concentrations of inhibitory, the rate and potency of damping were examined under varied implementation circumstances temperature and concentration, and the results were collected in Table 2.

It explains why the rate of corrosion increases with temperature and decreases with increasing inhibitor concentration. In terms of efficiency inhibition, it increases as the inhibitor concentration rises and as the temperature rises.

The Effect of Inhibitory Concentration on Corrosion of Pure Aluminum

As demonstrated in Table 2, adding deoxycyclin drug extracts greatly reduces the corrosion rate, and aluminum's corrosion rate normally increases with temperature. The lower the corrosion rate in deoxycyclin, the higher the concentration (0.5M H2SO4). As a result, deoxycyclin slowed the corrosion of aluminum in (0.5M H_2SO_4), indicating that it might be employed as a corrosion inhibitor for that metal, as shown in Figures 2 and 3.[14]

Inhibitor Performance and Adsorption Studies

It has been demonstrated that raising the inhibitor concentration from 50 to 300 ppm reduces the corrosion rate to extremely low levels. When the inhibitor concentration is low, the corrosion rate approaches its minimal value (300 ppm). This could be because the inhibitor concentration (300 ppm) is sufficient to cover the metal surface at the temperature range of (293.15,303.15 and 313.15 K). When analyzing adsorption characteristics, the surface coverage (θ) data is extremely important. Equation is used to calculate the surface coverage

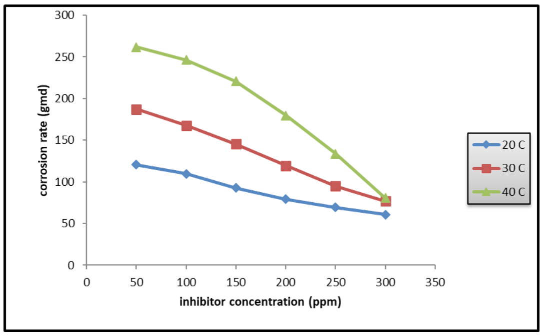

Figure 2: Effect of inhibitor concentration deoxycyclin extract on the corrosion rate of aluminum immersed in (0.5M H2SO4) for 3 hours.

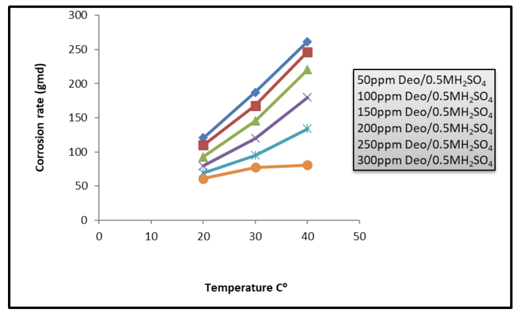

Figure 3: Effect of temperature on the corrosion rate of aluminum in (0.5M H_2SO_4) at different inhibitor concentration (Deoxycyclin extract).

Table 2: Effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum pure in (0.5M H_2SO_4) in absence and presence of Deoxycyclin extract as a corrosion inhibitor

Time (3 hours)					
Run	*C_{inh} (ppm)*	*Temperature (°C)*	*CR (gmd)*	*θ(surface coverage)*	*IE%*
1	Blank	20	312.042	0	0
2		30	549.068	0	0
3		40	1193.310	0	0
4	50	20	120.674	0.6133	61.33
5		30	187.305	0.6589	65.89
6		40	261.745	0.7806	78.06
7	100	20	109.791	0.6482	64.82
8		30	167.679	0.6946	69.46
9		40	246.531	0.7934	79.34
10	150	20	92.791	0.7026	70.26
11		30	145.429	0.7351	73.51
12		40	220.605	0.8151	81.51
13	200	20	79.309	0.7458	74.58
14		30	119.545	0.7823	78.23
15		40	179.811	0.8493	84.93
16	250	20	69.249	0.7781	77.81
17		30	94.970	0.8270	82.70
18		40	133.819	0.8879	88.79
19	300	20	60.730	0.8054	80.54
20		30	77.085	0.8596	855.98
21		40	80.589	0.9325	93.25

of an inhibitor at a particular concentration (3). The adsorption mechanism can be studied using the corrosion rate data.

$$\theta = \frac{IE}{100} \qquad (3)$$

Langmuir Adsorption Isotherm

The equation is used to calculate it (4). According to equation (4), graphs of (Ci/θ) versus.(Ci) for (deoxycyclin) extract inhibitors in (0.5M H2SO4) at (293.15,303.15, and 313.15 K) are shown in Figure 4. (3). Inhibitors are adsorbed according to the Langmuir adsorption isotherm, as the results fit straight lines. It could also explain the rise in inhibitory efficacy resulting from an increase in the amount of solvent molecules that adsorb on the aluminum surface, preventing active sites from direct acid assaults and therefore protecting metals from corrosion.[15]

$$\frac{Ci}{\theta} - \frac{1}{Kl} + \mathrm{Ci} \qquad (3)$$

where (Θ) is grade of surface coverage, C is the concentration inhibitor, k_{ads} is the adsorptive static equilibrium, and the molecular interaction parameters.

Freundlich Adsorption Isotherm

Equation is used to calculate it (5) The values of (n") and (KF) are obtained by plotting (ln) versus (lnCi) with slope and intercept, respectively. Because the correlation coefficient values are low, Freundlich does not appear to apply well to this system. However, because the correlation coefficient values are high, the Langmuir isotherm applies and gives the adsorption isotherm system more fitness.[16]

$$Ln\theta = LnKf + n''LnCi \qquad (3)$$

Timken Adsorption Isotherm

The adsorption of the extracts on the aluminum metal surface was described using equation (6), which was determined. Surface coverage (θ) versus (ln Ci) was plotted in Figure 6, with slope and intercept yielding the values of (a) and (KT), respectively. Because the correlation coefficient values are smaller, it is clear that the Timken isotherm does not apply well to this system. The Langmuir adsorption isotherm is the best since the correlation coefficient values are high[17].

$$\theta = \frac{1}{2\mathrm{a}}Ln - \mathrm{KT} - \frac{1}{2\mathrm{a}}LnCi \qquad (3)$$

Where; a is the molecular parameter of interaction, K_T is the equilibrium, (Timken adsorption isotherm) constant, (L/gm) equation (6) can be plotted as surface coverage (Θ) versus (lnC_i), where slope and intercept yield a and K_T values, respectively.[17]

Table 3 shows the kinematic data. The inhibition obeys the Langmuir adsorption isotherm description in their model of action more than the Freundlich adsorption isotherm and even more than the Timken adsorption isotherm, implying that corrosion-inhibiting compounds function on the metal's surface, Using the Langmuir isotherm adsorption, the highest correlation coefficients (R2) were achieved with monolayer formation according to adsorption. Because G°ads is less than 20 $kJ.mol^{-1}$ and has negative values, the type of adsorption is physical.

FTIR Studies

The peak at 3389.2 cm^{-1} was attributed to (OH) stretching, and the peak at 2929.2 cm^{-1} was allocated to (C-H) stretching, as shown in Figure 7. The (C=C) stretching peak was found at 1615.9 cm^{-1}, while the (C-N) stretching peak was found at 890.08 cm^{-1}. At 1247–1040, the aromatic in plane and out plan deformation peaks emerged. Aromatic (C-H) bending of 8 cm^{-1} was observed. The aromatic in plane and out plan deformation peaks were appeared at 1247–1040.8 cm^{-1}, aromatic (C-H) bending was appeared at1457.2 cm^{-1}.

Atomic Force Microscope Studies

The AFM technology was used to examine the surface aluminum pure morphology in the absence and presence of deoxycyclin extract. Higher extract resulted in more inhibition.[18] For distractions taken into account, microscopic analysis of the atomic force (AFM) provides a measure of rate roughness Ra (mean deviation from all points of profile roughness from the average streak along the rating), root–mean–squared roughness (Rq), the mean height measured, and length of valuation measured from average line (Figures 8 to 10 and Table 4).[19]

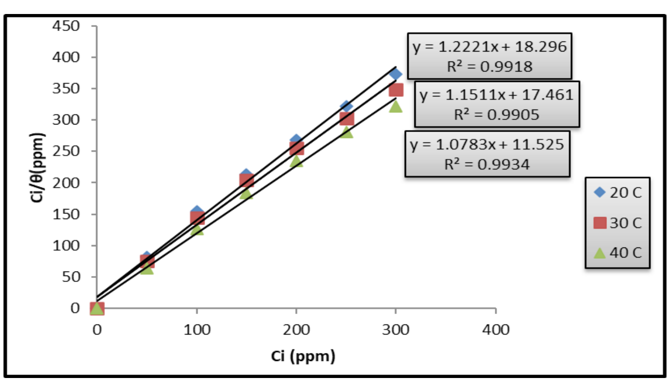

Figure 4: Langmuir adsorption isotherm of (deoxycyclin extract) for aluminum corrosion in (0.5M H_2SO_4).

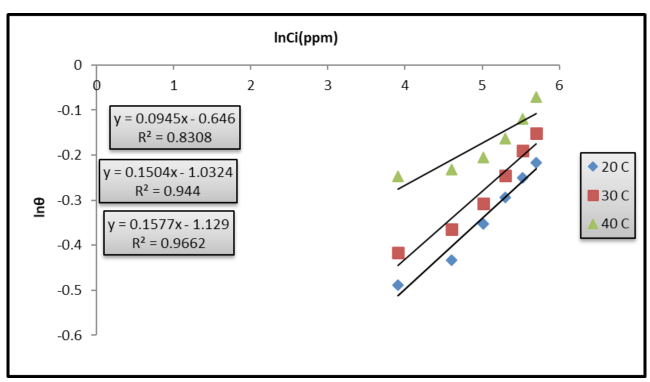

Figure 5: Freundlich adsorption isotherm of (deoxycyclin extract) for aluminum corrosion in (0.5M H_2SO_4).

Table 3: Parameters of the adsorption of luminum corrosion in inhibited 0.5 M H_2SO4.

T,K	*Langmuir isothermal adsorption*			*Freundlich adsorption isotherms*			*Timken adsorption isotherm*		
	K_L (L/mg)	*ΔG°ads (kJ/mol)*	*R^2*	*K_F (L/mg)*	*n*	*R^2*	*K_T (L/mg)*	*A*	*R^2*
293.15	0.0547	-2.7065	0.991	0.323	0.157	0.996	1.0121	0.139	0.992
303.15	0.0573	-2.9159	0.990	0.356	0.150w	0.944	1.0151	0.148	0.990
313.15	0.0868	-4.0934	0.993	0.524	0.094	0.830	1.0356	0.160	0.970

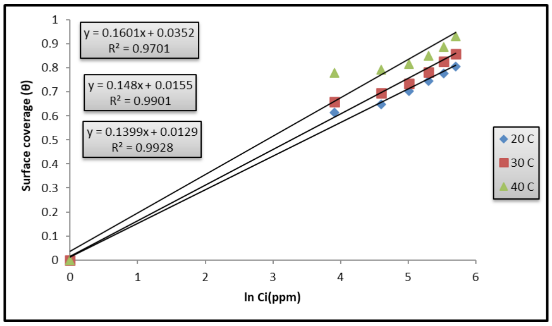

Figure 6: Timken adsorption isotherm of (deoxycyclin extract) for aluminum corrosion in (0.5M H_2SO_4).

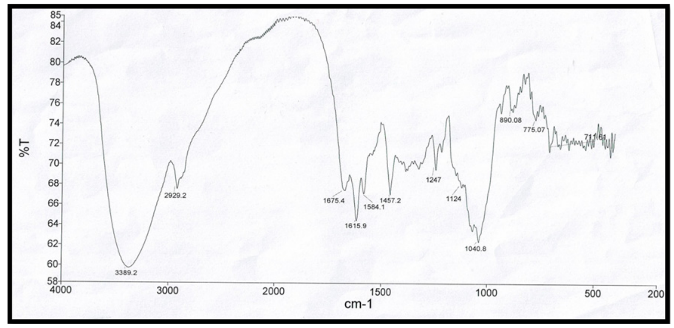

Figure 7: FTIR spectra of Deoxycyclin extract

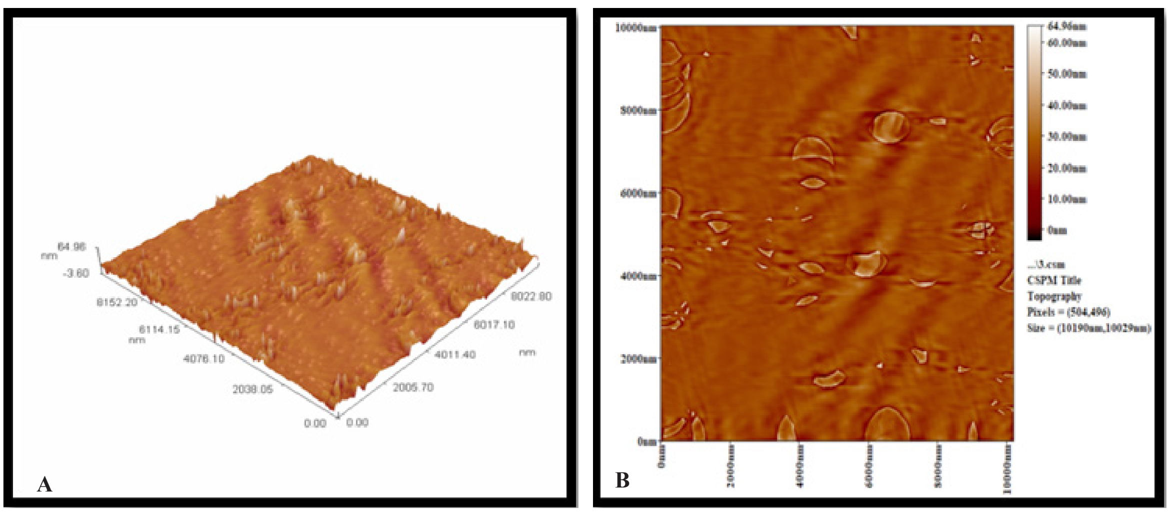

Figure 8: 2D and 3D images of AFM for the polished aluminum surface.

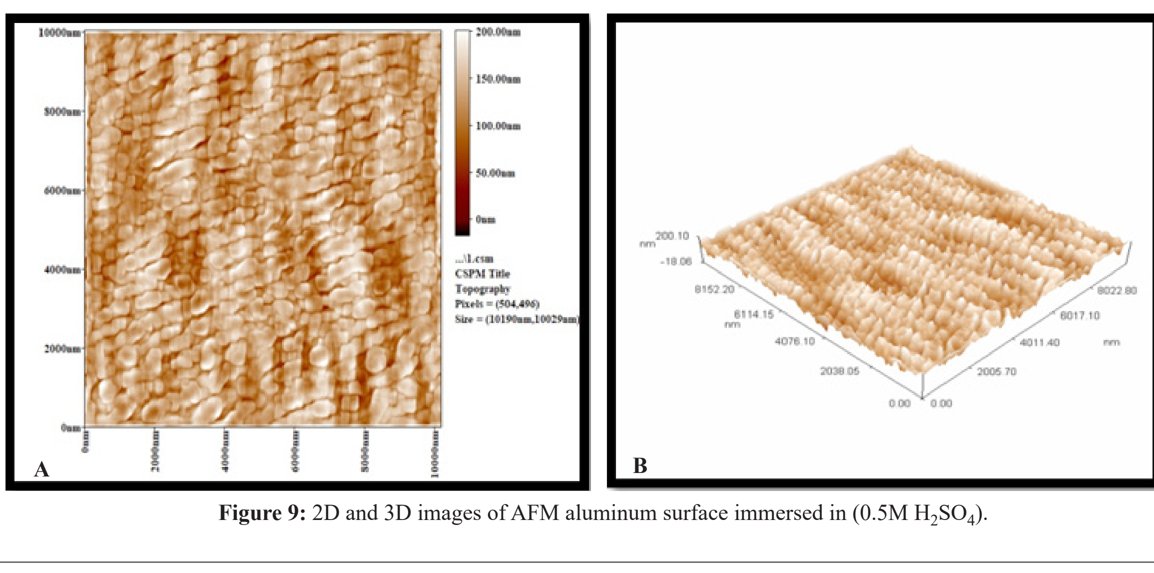

Figure 9: 2D and 3D images of AFM aluminum surface immersed in (0.5M H_2SO_4).

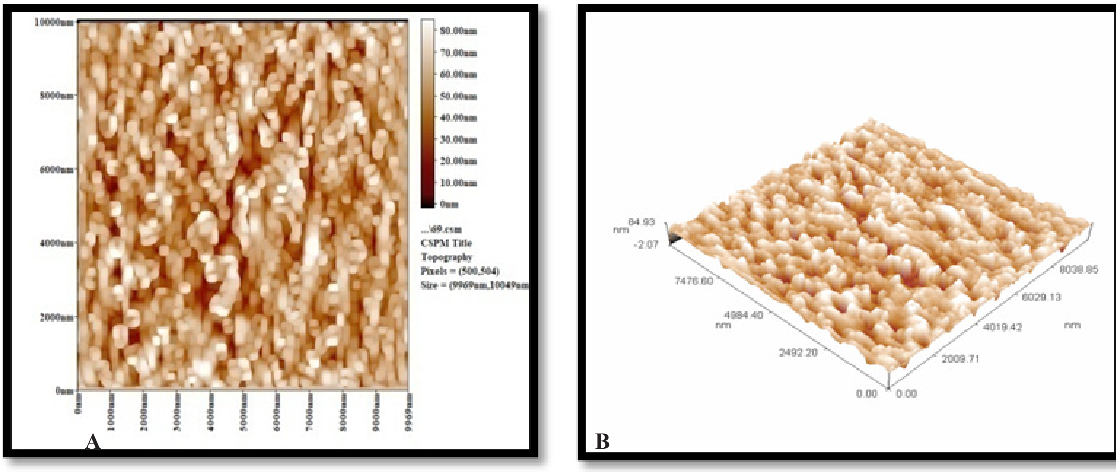

Figure 10: 2D and 3D images of AFM aluminum surface immersed in (0.5M H_2SO_4) presence (300 ppm) of deoxycyclin extract

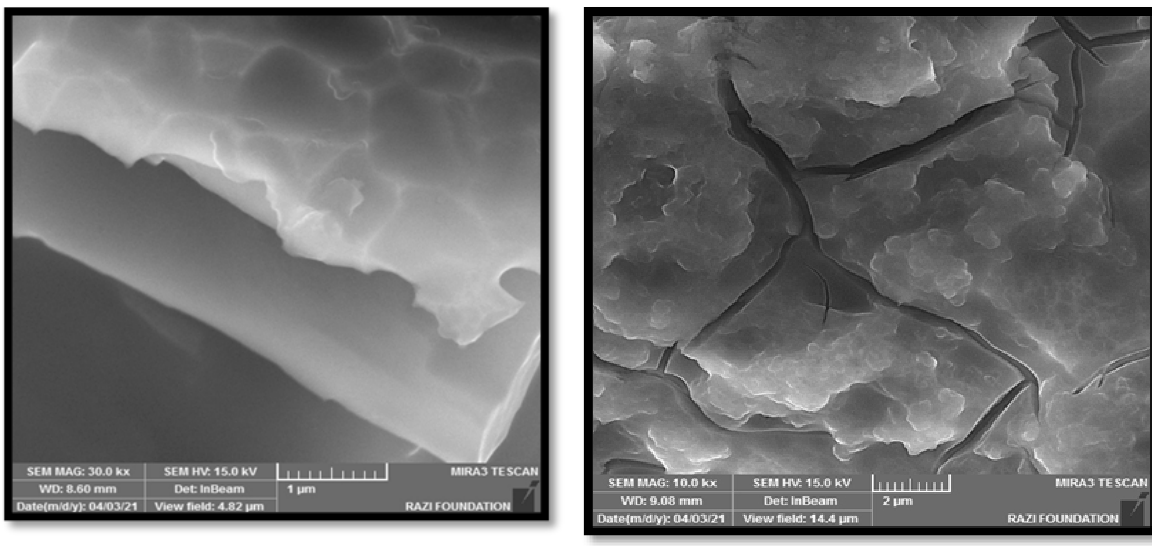

Figure 11: SEM images of (a) Aluminum pure surface after immersion in a corrosion solution(0.5M H_2SO_4) for (3h) at (313.15K), (b) aluminum surface after immersion in (0.5MH_2SO_4) and in presence of inhibitor (Deoxycyclin).

Table 4: Average roughness and average diameter for all cases.

Case	*Ra(nm)*	*Rq(nm)*	*Average diameter(nm)*
Corroded aluminum pure in H_2SO_4	22.3	27.8	238.04
Inhibited aluminum pure by deoxycyclin	11.6	14.8	335.40

Scanning electron microscope (SEM)

A scanning electron microscope (SEM) was used to study the morphology of aluminum (Figure 11).

CONCLUSIONS

In a 0.5 MH_2SO_4 media, the deoxycyclin extract is a good and efficient inhibitor of aluminum corrosion. The extract's maximum inhibitory efficacy was found to be 93.25 percent at the optimal concentration of 300 ppm at 313.15 k. The adsorption of various concentrations of the drug extract on the surface.

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