Application of Some Natural Plants Extracts as Green Inhibitors for Corrosion Protection of steel in 1 M HCl

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Abstract

The inhibitive action of Costus speciosus (*Crep ginger*) and Lawsonia alba (*Henna*) on mild steel corrosion in 1 M HCl solution was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Surface analysis such as scanning electron microscope (SEM), Atomic Force Microscopy (AFM) techniques confirmed the formation of protective layer on mild steel surface in the presence of plants extract. Results obtained showed that these investigated compounds are functioned as good inhibitors for mild steel corrosion in 1 M HCl solution. Polarization data revealed that the plants extract act as mixed type inhibitors .The inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from different tested techniques were in good agreement.

Keywords Crep ginger **,** Henna, mild steel, HCl

1- Introduction

Corrosion of metals is a major industrial problem that has attracted much investigations and researches. This is because some industrial processes such as acid cleaning, pickling and etching facilitate contact between metal and aggressive medium (such as acid, base or salt), consequently the metal is prone to corrosion. A corrosion inhibitor is a substance which, when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment. Thus, inhibitors are one of the most practical methods for protection from corrosion ,especially in acid solutions to prenent unexpected metal dissolution and acid consumption [1,2]. A common classification of inhibitors is based on their effects on the electrochemical reactions involved in the corrosion process [3,4]. Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or as cathodic and anodic inhibitors, nevertheless, as a general rule, act through a process of surface adsorption, designated as a film - forming. These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal [5]. The researchers have been focused on the use of ecofriendly compounds such as plant extracts which contain many organic compounds. Amino acids, alkaloids, pigments and tannins are used as green alternatives for toxic and hazardous compounds, due to biodegradability, eco-friendliness, low cost and easy availability the extracts of some common plants and plant products have been studied as corrosion inhibitors for various metals and alloys under different environmental conditions[6]. Mild steel (MS), X80, J55 steel are commonly used in construction of oilfield line pipes, casing and storage facilities. Their corrosion behavior was investigated in 1 M HCl solution in absence and presence of seed extracts of Griffonia simplicifolia(SEGS) at 303 K [7]. The inhibition efficiency of Tinospora crispa extracts as corrosion inhibitor of mild steel in 1 M HCl was determined using weight loss, potentiodynamic polarization and EIS [8]. Abou Shahba et al [9] investigated the corrosion inhibition of mild steel by Catharanthus roseus (Vince rosea) and Turmeric (Curcuma longa) extracts as green inhibitors in 1 M HCl solution. The application of extracts of henna, thyme, bgugaine and inriine was investigated for their anticorrosion activity [10-13]. The effect of addition of bgugaine on steel corrosion in HCl is patented [14].The inhibition and adsorption effects of the aqueous extracts of Musa paradisica (Banana) peels on mild steel corrosion in 1 M HCl as well as change in inhibition efficiency with ripening of the peels are investigated [15]. The corrosion inhibition effect of red apple (Malus domestica) fruit extract for mild steel in HCl was investigated by gravimetric and electrochemical methods at 30 – 60 °C [16]. The inhibition efficiency of acid extract of Nicotiana leaves on mild steelin 1 M HCl has been evaluated by weight loss method [17]. Ibrahim et al [18] using traditional weight loss measurements and various electrochemical techniques to investigate the inhibition effect of Fig leaves extract on corrosion of mild steel in 2 M HCl solution.

This work focuses on the inhibitory effect of Costus speciosus (*Crep ginger*) and Lawsonia alba (*Henna*) extracts as green inhibitors for mild steel in 1 M HCl solutions at room temperature using different techniques.

2- Experimental.

2.1. Materials and solutions

2.1.1. Composition of material sample

Table (1): Chemical composition (wt%) of the mild steel

Element	**Fe**	**C**	**Si**	**Mn**	**P**	**Ni**	**Al**	**Cu**	**S**	**Ti**	**Co**	**Mo**	**Cr**
Weight (%)	**99.66**	**0.068**	**0.022**	**0.169**	**0.004**	**0.011**	**0.033**	**0.045**	**0.006**	**0.001**	**0.005**	**0.005**	**0.004**

2.1.2. Test solutions

The solution of 1M hydrochloric acid (Test solution) were prepared for each experiment using analytical grade of hydrochloric acid (37%) and diluting concentrated HCl to a required concentration with bidistilled water. The concentration range of inhibitor was 50 to 300 ppm.

2.2. Preparation of plants extracts

Costus speciosus (*Crep ginger*) leaves and flowers and Lawsonia alba (*Henna*) leaves plants were purchased from the local market and ground into a fine powder to give 200 gm of powdered materials which extracted separately by soaking in 70 % methanol (300 ml) for 48 hr. at room temperature. Then the methanolic extract of the sample was concentrated to nearly dryness under reduced pressure by using the rotary evaporator at 45 ^{o}C to achieve the crude methanolic extract which kept for further investigation [19].

2.3. Preparation of mild steel specimens

All specimens were mechanically cut into sizes with 2 cm x 2 cm x 2 cm dimensions and abraded by emery paper of different grads, then washing with acetone and bidistilled water and finally dried.

2.4. Measurements Techniques

Electrochemical measurements

A three-electrode cell including a working electrode, an auxiliary electrode and a reference electrode was used for the electrochemical measurements. The working electrodes were made of mild steel.The auxiliary electrode was a platinum foil, the reference electrode was a saturated calomel electrode (SCE) with a fine Luggin capillary tube positioned close to the working electrode surface in order to minimize ohmic potential drop. Each specimen was successive abraded by using SiC emery papers up to 1200 grit size, washed with bidistilled water and degreased in acetone and finally dried. The polarization curves were determined by changing the electrode potential automatically from – 0.1 to 0.2 V with respect to the free corrosion potential (E vs. SCE) at a scan rate of 1 mV/s. Stern-Geary method [20] used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines to a point which gives log i_{corr} and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then i_{corr} was used for calculation of inhibition efficiency (%IE) and surface coverage (θ) as in equation 4 [21]:

$$\% \text{ IE} = \theta \times 100 = [1 - (i_{corr(inh.)/}\, i_{corr(free)]} \times 100 \quad (1)$$

where $i_{corr(free)}$ and $i_{corr(inh)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

Electrochemical impedance spectroscopy measurements EIS were carried out in a frequency range of 1 Hz to 100 kHz with amplitude of 10 mV peak-to-peak. . The experimental impedance was analyzed and interpreted based on the equivalent circuit. The main parameters deduced from the analysis of Nyquist diagrams, are the charge transfer resistance R_{ct} (diameter of high-frequency loop) and the double layer capacity C_{dl}. The inhibition efficiencies and the surface coverage (θ) obtained from the impedance measurements are calculated from equation 5 [22]:

$$\%\text{IE} = \theta \text{x} 100 = [1-(R^{\circ}_{ct}/R_{ct})] \times 100 \quad (2)$$

where R^{o}_{ct} and R_{ct} are the charge transfer resistance in the absence and presence of inhibitor, respectively

2.5. Surface Investigation Techniques

2.5.1. Scanning Electron Microscopy (SEM)

The mild steel specimens were immersed for 24 hr. in 100ml 1M HCl solution containing optimum concentrations (300 ppm of inhibitors). After 24 hr., the specimens were taken out and dried. Examination of mild steel surface after 24 hr. exposure to 1 M HCl solution without and with inhibitors was carried by using (JEOL JSM-5500,JAPAN) scanning electron microscope.

2.5.2. Atomic Force Microscopy (AFM)

The mild steel specimens were immersed for 24 hr. in 100ml 1M HCl solution containing optimum concentrations (300 ppm of inhibitors) at room temperature. After 24 hr., the specimens were taken out and dried. The nature of the protective film formed on the surface of mild steel surface after 24 hr. exposure to 1 M HCl solution without and with inhibitor was carried by using a Pico SPM2100 AFM device operating in contact mode in air at Nanotechnology Laboratory, Faculty of Engineering Mansoura University.

3. Results and Discussion

3.1. Potentiodynamic polarization

Potentiodynamic polarization measurements are depend on the nature of inhibitor such as anodic or cathodic or mixed-type inhibitor, mode of action and mechanism of the inhibitor reaction. The inhibition action of compound extracts on the electrochemical corrosion behavior of mild steel in 1 M HCl solution in the absence and presence of various concentration (50- 300) ppm of inhibitors in 1 M HCl solution at room temperature were studied and the polarization curves are shown in Figures (1-2). The inhibition efficiency (% IE) of the used inhibitors values and the degree of surface coverage (ϴ) were calculated using the equation (1). The important electrochemical corrosion parameters such as corrosion potential (E_{corr}), corrosion current density(i_{corr}), anodic (β_a) and cathodic (β_c) Tafel plots and the inhibition efficiencies (% IE) are given in Tables (2-3). Inspection the data of these Tables it is shown that:

i. The cathodic and anodic curves obtained exhibited Tafel-type behavior.

ii. The cathodic and anodic potential values slightly shifted towards both negative and positive direction in the presence of different concentration of the compounds extracts in 1 M HCl, indicating the inhibitors acted as a mixed type inhibitor [23, 24] as it shown from Figures (4-6) where both cathodic and anodic polarization curves are influenced by the presence of the inhibitive compounds in the corrosive media.

iii. The corrosion current density (i_{corr}) values are decreased, while the inhibition efficiency (% IE) increased with increase in the concentration of the inhibitors, indicating that these compounds retard the dissolution of mild steel in 1 M HCl solution and degree of inhibition depends on the concentration and type of the inhibitor. This implies that these compounds were acting as good adsorption inhibitors.

iv. The inhibitive action of these compounds was discussed in terms of blocking the electrode surface by adsorption the inhibitors molecules through the active centers.

v. The values of anodic (β_a) and cathodic (β_c) Tafel plots for the inhibitors were shifted slightly, the slightly variation in Tafel slope suggested that the inhibitors is blocking the cathodic and anodic sites without changing the mild steel dissolution mechanism [25,26].

vi. The order of inhibition efficiency for the additives is:

Costus speciosus > Lawsonia alba

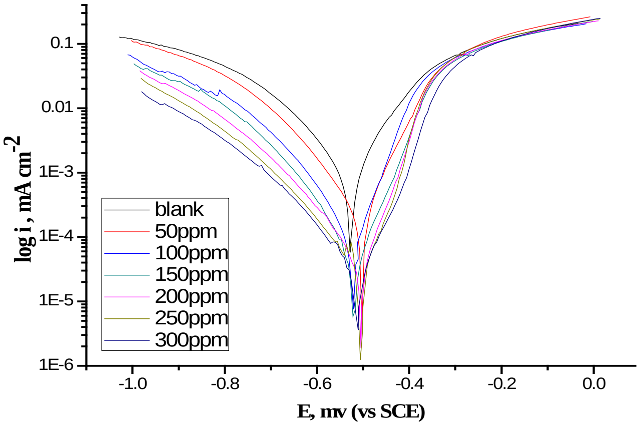

Figure (1): Potentiodynamic polarization curves for the corrosion of mild steel in 1 M HCl in the absence and presence of various concentrations of Costus speciosus at 25^{o}C.

Table (2): potentiodynamic data for mild steel in 1M HCl in the absence and presence of different concentrations of Costus speciosus extract at 25^{o}C.

[inh.] ppm	- $E_{corr,}$ mV vs. SCE	$i_{corr,}$ µA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R, Mpy	θ	% IE
0	528	1250	132	94	445	-	-
50	498	388	98	70	110	0.690	69
100	501	335	102	67	90	0.732	73.2
150	492	258	108	65	87	0.794	79.4
200	488	220	110	72	81	0.824	82.4
250	475	192	115	75	76	0.846	84.6
300	490	157	118	63	71	0.874	87.4

Table (3): potentiodynamic data of mild steel in 1M HCl in the absence and presence of different concentrations of Lawsonia alba extract at 25^{o}C.

[inh.] ppm	- $E_{corr,}$ mV vs. SCE	$i_{corr,}$ μA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R, mpy	θ	% IE
0	528	1250	132	94	445	-	-
5	507	698	122	85	130	0.442	44.2
10	498	644	123	80	124	0.485	48.5
15	488	367	126	87	118	0.706	70.6
20	492	332	111	78	112	0.734	73.4
25	505	305	118	73	105	0.756	75.6
300	492	217	120	70	98	0.826	82.6

3.2. Electrochemical Impedance Spectroscopy (EIS) Measurements

Impedance measurement is a good technique in monitoring corrosion process. It is a non-destructive test because the magnitude of potential applied is small. Also, surface modification and errors associated with large deviations from electrochemical equilibrium are also reduced [27]. Information derived can be related to the kinetics of the electrode process, mechanism and surface properties at the metal/solution interface. Therefore, EIS tests were conducted. Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. The EIS instrument records the real (resistance) and imaginary (capacitance and inductance) components of the impedance response of the system. Study systems in which multiple electrochemical reactions are occurring gives some insight into the capacitive nature of electrochemical cells and has been proven to be powerful and accurate method for measuring corrosion rate.

The impedance spectra obtained for mild steel in 1 M HCl solution in the absence and presence of various concentrations of tested inhibitors at room temperature are presented as Nyquist plots (a) in Figures (3-4).

Upon the shape of the Nyquist plots (a) the diameter of the capacitive loops in the presence of inhibitors is bigger than in the absence of inhibitor and increases with the inhibitor concentration. This indicate that the impedance of inhibited substrate increases with the inhibitor concentration. Noticeably, these capacitive loops are not perfect semicircles which can be attributed to the frequency dispersion effect. In general, this imperfections behavior is attributed to surface roughness and inhomogeneity of the mild steel [28-30].

The impedance spectra of the different Nyquist and Bode plots Figures (3-4) were analyzed by fitting the experimental data to a simple equivalent circuit model.

The corrosion parameters from impedance measurements are shown in Tables (4-5). The obtained results show that:

i. The value of R_{ct} increases with increasing the concentration of the inhibitors and hence, the increase in the corrosion inhibition efficiency in acidic solution. This is due to the formation of protective film on the metal surface [31].

ii. The values of C_{dl} decrease on addition of inhibitor. This decrease could have been caused by an increase in the thickness of electrical double layer (adsorbed protective film) [32-34].

iii. The (%IE) obtained from EIS measurements are nearly closed to those obtained from polarization and weight loss methods.

iv. The order of the inhibition efficiency obtained from EIS measurements is as follows:

Costus speciosus > Lawsonia alba

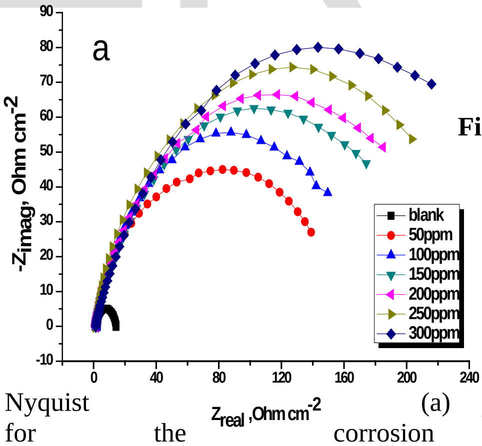

Figure (3): The Nyquist (a) plots for the corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of Costus speciosus extract at 25°C

Table (4): EIS parameters for the corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of Costus speciosus at 25°C.

[inh.] ppm	R_{ct}, Ω cm^2	C_{dl}, μFcm^{-2}	θ	%IE
0.0	12.3	47.16	-	-
50	29.4	34.4	0.592	59.2
100	40.9	29.2	0.699	69.9
150	54.5	27.9	0.774	77.4
200	60.1	26.3	0.795	79.5
250	64.3	24.7	0.808	80.8
300	77.9	22.1	0.842	84.2

Table (5): EIS parameters for the corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of Lawsonia alba at 25^{o}C.

[inh.] ppm	R_{ct}, Ω cm^2	C_{dl}, μFcm^{-2}	θ	%IE
0.0	12.3	47	-	-
50	20.2	30.3	0.391	39.1
100 0	22.2	23.6	0.446	44.6
150	35.0	21.2	0.648	64.8
200	36.7	19.9	0.664	66.4
250	44.5	16.2	0.723	72.3
300	64.8	14.8	0.810	81.0

3.3. Surface Examinations

3.3.1. Scanning Electron Microscopy (SEM)

In order to evaluate the surface morphology of the mild steel after exposure to 1 M HCl solution for 24 h immersion in the absence and presence of investigated compound extracts at optimum concentration (300ppm), a surface analysis was carried out by using Scanning Electron Microscopy after the corrosion tests as shown in Figures (5-7). The Inspections of the SEM images reveal that there is severe damage and cavities on the surface of mild steel in the absence of compound extracts Figures (5), because the metallic material is affected by the corrosive environment. However in the presence of the compound extracts there are very few pits and cracks observed in the inhibited mild steel surface Figure (6-7). The SEM studies confirm that a good protective film formation by the adsorbed inhibitor molecules on the mild steel surfaces [35].

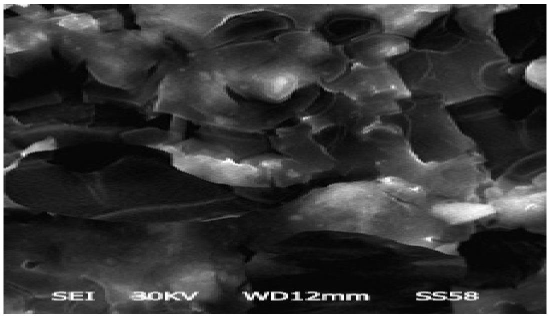

Figure (5): SEM micrographs of mild steel surface after 24 h of immersion in 1 M HCl

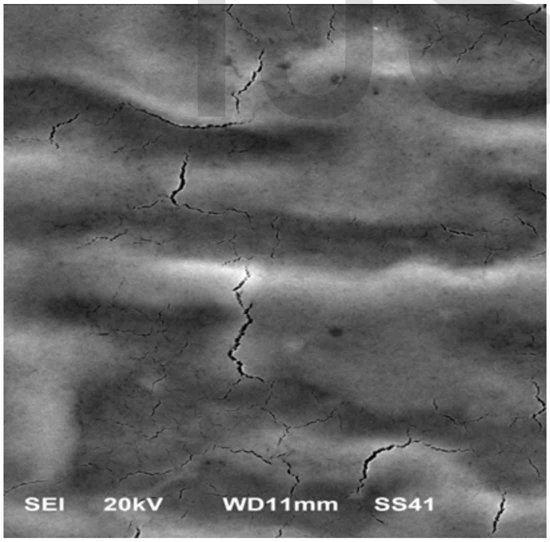

Figure (6): SEM micrographs for mild steel surface after 24 h of immersion in 1 M HCl + 300 ppm of Costus speciosus extract at 25^{o}C.

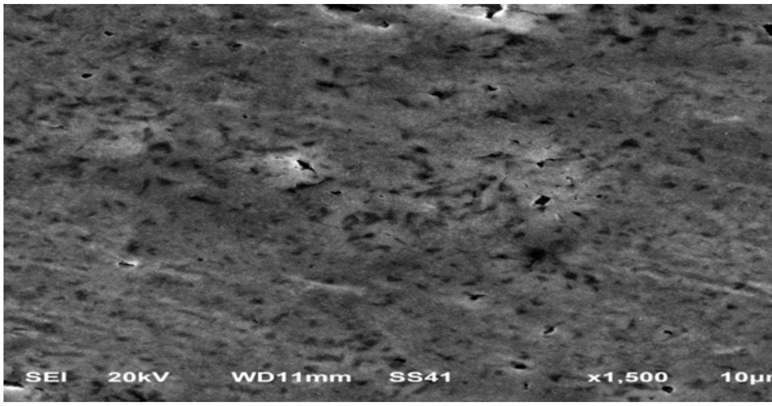

Figure (7): SEM micrographs for mild steel surface after 24 h of immersion in 1 M HCl + 300 ppm of Lawsonia alba extract at 25^{o}C.

3.3.2. Atomic Force Microscopy (AFM)

AFM is a powerful tool to investigate the surface topography at nano-to-micro scale. It has become a new choice of study to influence the inhibitor on the generation and the progress of the corrosion at the metal or glass/solution interface [36, 37]. AFM is becoming an accepted method for investigation of the roughness of metals, alloys and glasses [38]. The three-dimensional (3D) surface topography of the polished mild steel in 1 M HCl solution in the absence and presence of investigated compounds extracts at optimum concentrations (300ppm) are shown in the Figures (8-11). The scanning area of all the AFM images like polished mild steel, blank and inhibited mild steel is 4 µm × 4 µm.

As analyzed from the inhibited sample Figure(10-11), there are very less pits, cracks and damage on the surface of mild steel with the optimum concentrations (300ppm) of compound extracts. The average roughness value of polished mild steel Figure (8) surface is 33.431nm. The slight roughness observed on the surface of polished mild steel is due to atmospheric corrosion and some streaks made on the surface of mild steel during polishing with emery papers. The average roughness value of mild steel surface in 1M HCl solution Figure (9) in the absence investigated compound extracts are 667.5 nm. The greater roughness is due to the acid attack on the surface of mild steel in the corrosion test period 24 h. therefore, the surface of mild steel in 1 M HCl solution had a considerable pores structure with deep cracks. However, in the presence of optimum concentrations (300ppm) of investigated compound extracts the average roughness's are reduced to 102.64, 91.724, 118.64, 103.65, and 107.97, respectively. The lower value of roughness reveals that the investigated compound extracts protects the surface of mild steel effectively.

Figure (8): AEM micrographs of mild steel surface before immersion in 1M HCl

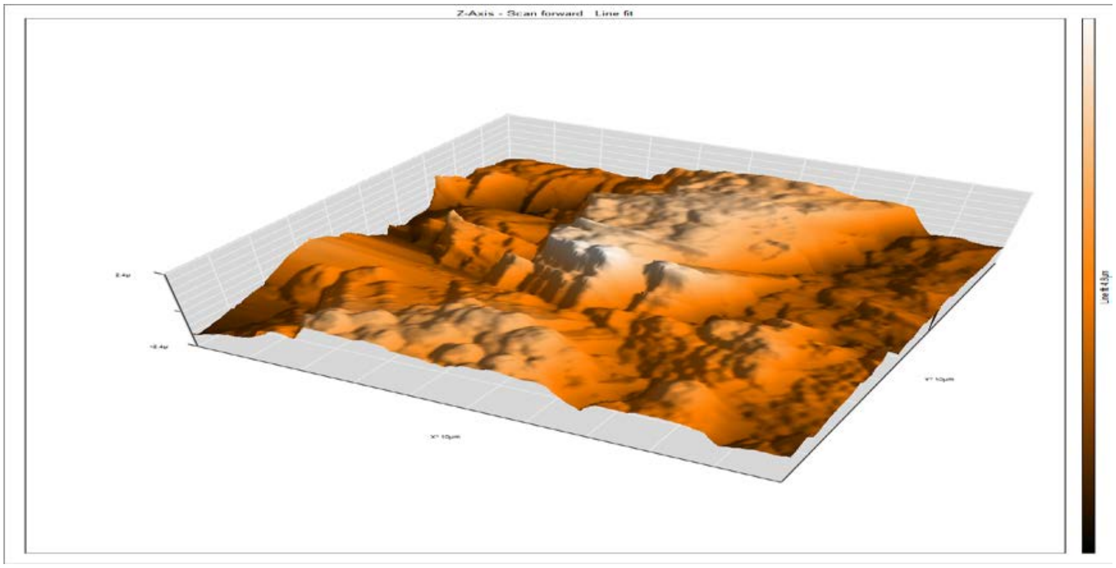

Figure (9): AEM micrographs of mild steel surface after 24 h of immersion in 1M HCl

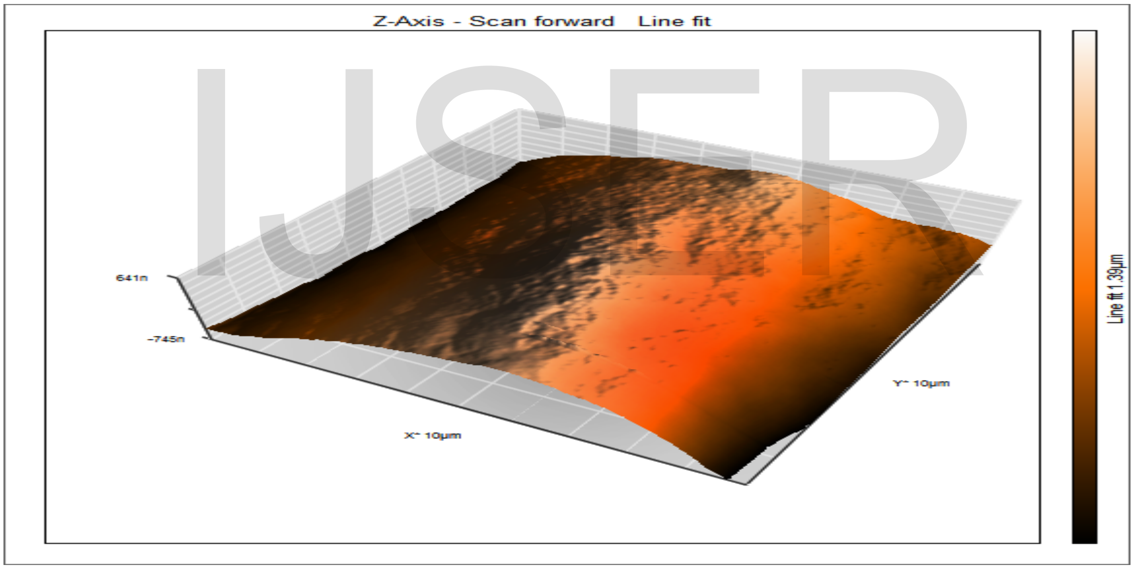

Figure (10): AFM micrographs for mild steel surface after 24 h of immersion in 1 M HCl + 300 ppm of Costus speciosus extract

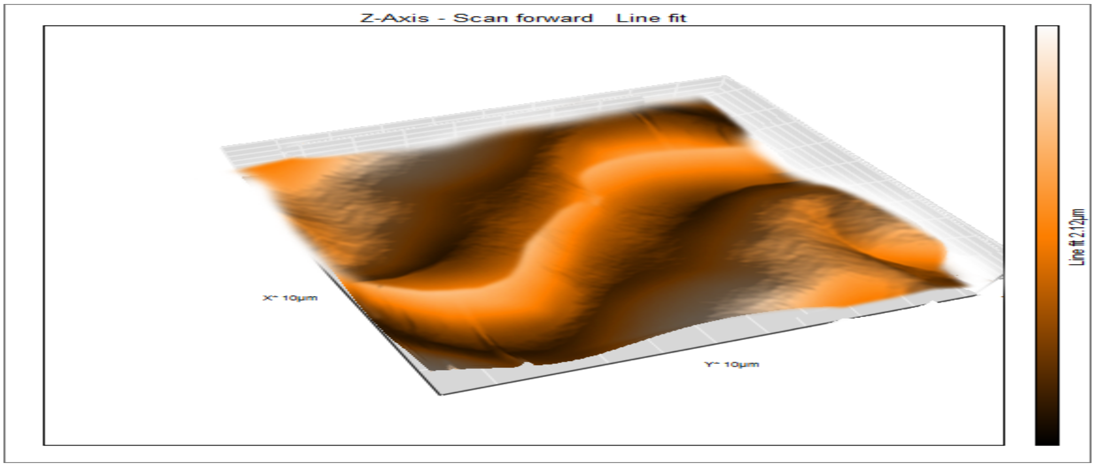

Figure (11): AFM micrographs for mild steel surface after 24 h of immersion in 1 M HCl + 300 ppm of Lawsonia alba extract

Conclusions

On the basis of this study the following conclusions can be drawn:

(1) Costus speciosus and Lawsonia alba extracts acts as inhibitors for mild steel corrosion in acidic medium.

(2) Inhibition efficiency of Costus speciosus and Lawsonia alba extracts increases with increase in concentration of the inhibitors.

(3) The values of inhibition efficiency indicate that, Costus speciosus extract more effective than Lawsonia alba extracts.

(4) The corrosion inhibition is probably due to the adsorption of the plant extracts on the metal surface and blocking its active sites by phenomenon of physical and chemical adsorption.

(5) SEM reveals the formation of a smooth surface on mild steel in presence of Costus speciosus and Lawsonia alba extracts probably due to the formation of an adsorptive film of electrostatic character.

(6) Also the results indicate that, Costus speciosus and Lawsonia alba extracts acts as mixed type inhibitors.

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