



Ferula hermonis Plant Extract as Save Corrosion Inhibitor for Zinc in Hydrochloric Acid Solution

O.A. Mohamed¹, H.M. Elabbasy², A. S. Fouda¹

¹Department chemistry, Faculty of Science, Mansoura University, Mansoura-35516, Egypt. Email: asfouda@hotmail.com, Fax: +2 050 2202271, Tel: +2 050 2365730

²Misr higher Institute for Engineering and Technology, Mansoura, Egypt. Email: helabbasy@hotmail.com

Received: 13/6/2021
Accepted: 17/6/2021

Abstract: The efficiency of Ferula hermonis plant extract, as inhibitor for zinc (Zn) corrosion in a 1 M HCl solution, has been tested by mass loss (ML), electrochemical measurements (potentiodynamic polarization (PP), and electrochemical impedance spectroscopy (EIS) procedures), in addition to surface examination analysis. The outcomes indicated that Ferula hermonis extract showed good efficiency to Zn corrosion, and displayed high inhibition efficiencies. The maximum value of the inhibition approached 90.6% within the presence of 300 ppm Ferula hermonis extract. The adsorption isotherm of Ferula hermonis extract on the Zn surface was found to follow Langmuir adsorption isotherm. The adsorption was a spontaneous, exothermic process accompanied by a decrease in the entropy. Thermodynamic parameters were determined and discussed. Also, the inhibition efficiency (%IE) was found to increase as the concentration of Ferula hermonis extract increases, and depresses as the temperature grows. The outcomes of the applied chemical and electrochemical techniques are in good agreement. The morphology of the surface of uninhibited and inhibited Zn was examined by atomic force microscopy (AFM), The results indicated that there is a protective film formed by Ferula hermonis plant extract on the Zn surface that protects it from to be corroded in the acid media .

keywords: Ferula hermonis extract, Zn, HCl, Corrosion inhibition, AFM

1.Introduction

Based on the nature of the environment, Zn can form a protective film that made up of basic oxides carbonates, or hydrated sulfates. After formation of the protective film, the rate of corrosion reduces. Generally, the corrosion of Zn is related to the dissolution from the surface. Also, air is only somewhat corrosive to zinc. Under 200°C the grown of the film is very slow and the formed film is very adherent to the surface. Steel coated with Zn acts likewise as pure Zn [1]. Presently, Zn alloys makes about 20% of Zn uses. In western countries, Zn alloy was applied as cover material for roofs, this way extends the average life from 5-10 years to 120-140 years and more. Therefore, in the extended run, at Zn consumption, the ratio of galvanization will reduce, while that of zinc alloy increases gradually. Also, Zn shows a good resistance to electromagnetic field. For

radio frequency interference, Zn plate considered as a very shielding material. As Zn does not produce any sparks, if it was alone or in contact with

other metals, it is appropriate for making explosion-proof apparatus. In addition, it was discovered that Zn resists abrasive, corrosion, and shows some mechanical properties at room temperature. Zn forms various alloys with many other metals. Alloys of Zn and Zn oxide are uses in the automobile, building and shipbuilding industries, together with light industry, batteries, and home electrical machines industries. Presently, consumption of Zn among non-ferrous metals is the second after aluminum and copper, thus preventing the Zn metal dissolution in aqueous solutions is of great importance. Corrosion inhibitor can be used for this purpose. Corrosion inhibitor

compound can be added to a corrosion aqueous medium by small amount

2. Experimental Measurements

2.1. Metal composition and preparation

The Zn sample contains the following components as weight percentage: Cd 0.52, Fe 0.035, Mn 0.005, Pd 0.18, Sn 0.07 and Zn the rest. The Zn sheet of thickness 0.1 cm used for this study is cut mechanically to 2 x 2 cm coupons [7]. These coupons were used as provided, with a great polishing using different emery papers 400, 600, 1200, and 2000. However, surface treatment of the coupon involved rinsing in distilled water, degreasing in acetone. Then the coupons can be stored in a moisture-free desiccator to avoid contamination before their use in the corrosion studies [8].

2.2 Plant preparation method

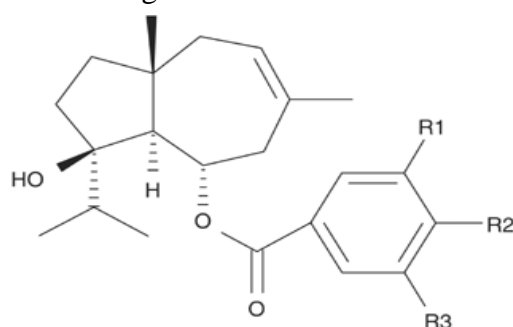
Definite amount (300 gm) of *Ferula hermonis* plant powder was drenched in 1200 ml of ethyl alcohol solvent (80% BDH), at a proportion of 1:4. Electric blender was used to agitate the mixture to ensure blending the powder and the solvent [9], after that the mixture is putted in air-tight plastic vessel. The mixture vessel, can then retained in the refrigerator at 40 °C 2 days [10]. The filtration of the mixture is done firstly using cheesecloth, thereafter by Whatman grade 1 filter paper. The filtrate concentrating can be done in vacuity employing Rotary Evaporator (Model RE52A, China) until reaches 10% of its authentic volume at temperature between 37 °C and 40 °C. The concentrating process is carried out until complete dehydration in water bath [11]. The concentrated extract can be kept in a refrigerator until usage [12].

and in the same time reduce the metal dissolution in high rate. There are some necessities for the compound to applied as corrosion inhibitor. Concerning the chemical structure and chemical performance, a compound of inorganic nature has the ability to oxidize the metal to form a passive film on the metal surface. Conversely, the organic compounds must have some features to be applied as corrosion inhibitors [2]. The organic molecule has π electrons of aromatic ring and unshared pairs of electrons of O, S and N atoms. The main features of employing of plant extracts as metal corrosion inhibitors is money

considerations and safety as they are cheap and safe for environment [3]. The important compounds in the plant extract are hydroxyl and carbonyl groups. The use of plant extracts to inhibit the metal corrosion in several aqueous solutions was carried out by several authors [4]. *Ferula hermonis* is a medicinal plant that grow in the Mediterranean region belongs to the carrot family, its original home is Syria and Lebanon. The word hermonis is taken from the name of Mount Hermon on the boundary between Syria and Lebanon. Common names of *Ferula hermonis* are Zallouh and Lebanese Viagra. The last name refers to the general usage of the *Ferula hermonis* roots as a purported aphrodisiac. The study aims to investigate the efficiency of *Ferula hermonis* extract as inhibitor for Zn corrosion in 1 M HCl solution by applying chemical and electrochemical techniques, together with examination of the uninhibited and inhibited metal surface, and confirming the study through computing some quantum chemical factors for the principle constituents in the used extract [5,6].

2.3 Chemical constituents found in the *Ferula hermonis* plant

The major components recognized in the herb and roots of *F. hermonis* were daucane sesquiterpene esters: ferutinol p-hydroxybenzoate (ferutinol), ferutinol benzoate (teferdin), ferutinol vanillate (teferin) and epoxyferutinol benzoate [13,14]. Chemical structures of ferutinol, teferdin and teferin are presented in Fig. 1.



R1	R2	R3	Trivial name
H	OH	H	Ferutinol
H	H	H	Teferdin
H	OH	OCH ₃	Teferin

Fig. (1): Chemical structures of Ferutinol, Teferdin and Teferin

2.4. Mass loss (M L) method

The prepared coupons were immersed into aggressive solutions of 1 M HCl includes diverse concentrations (50 - 300 ppm) of Ferula hermonis extract for identified period of time. Then the mass loss after the acid exposure is computed. Cleaning the corroded specimens, to eliminate the corrosion product and determining the weights, must be done carefully. The tested temperatures involved 25°C, 30,35,40, and 45 °C. All measurements were done for triplicated. Rate of corrosion (k_{corr}) can be determined as follows:

$$k_{\text{corr}} = (m_1 - m_2) / A.t \quad (1)$$

where the mass of the specimen before and after exposure to the acid media are m_1 , m_2 , respectively, the specimen area in cm^2 is A and t is the corrosion time (in min). Inhibitor efficacy (% IE) and metal surface coverage (θ) by Ferula hermonis extract were computed as follows:

$$\% \text{ IE} = \theta \times 100 = [(\Delta W_1 - \Delta W_2) / \Delta W_1] \times 100 \quad (2)$$

with ΔW_1 and ΔW_2 as the M L without and with Ferula hermonis extract respectively [15].

2.5. Electrochemical techniques

The procedures of electrochemical were done in a tripartite electrodes cell with Potentiostat/ Galvanostat (Gamry PCI 300/4), organized by DC 105, EIS 300 and EFM 140 software. Linked to a computer for data read and store. Besides the Zn working electrode; a saturated calomel electrode (SCE) and platinum electrode were employed as reference and counter electrodes, respectively. The Zn electrode was of 1 cm diameter and was connected to a copper wire from one aspect, that was necessary for connection the electricity. The Zn electrode was abraded with several class (400 to 2000) of emery paper, scrubbed utilizing acetone and rinsed utilizing distilled water. All measurements were done in deaerated solutions at 25.0 ± 0.1 °C by applying ultra-circulating thermostat. The measurements were started after a steady state of 30 minutes, which is necessary to decrease the pre-immersion oxide film from the Zn surface. No trials were made to deaerated solutions and each experiment was performed on a newly abraded electrode using a freshly prepared

electrolyte. The PP procedures were recorded at a scan rate of 0.5 mV s^{-1} from -500 to +500 mV. The % IE and θ from PP test were computed as follows.

$$\% \text{ IE} = \theta \times 100 = [1 - (i_{\text{corr}} / i_{\text{corr}}^0)] \times 100 \quad (3)$$

with i_{corr}^0 and i_{corr} as the corrosion current densities without Ferula hermonis extract and with it, respectively [16].

The EIS procedures were performed by using an AC potential to an electrochemical cell and recording the current at the frequency ambit (100 kHz - 0.1 Hz) in 10 mV peak-to-peak capacity. Charge transfer resistance (R_{ct}) and constant phase element (CPE) can be gotten from Nyquist plots. %IE and θ from EIS measurements were calculated as below:

$$\% \text{ IE} = \theta \times 100 = [1 - (R_{\text{ct}}^0 / R_{\text{ct}})] \times 100 \quad (4)$$

with R_{ct}^0 and R_{ct} as the charge-transfer resistance without Ferula hermonis extract and with it, respectively .

2.6. Surface analysis

Atomic force microscopy (AFM) test

Atomic force microscope is considered a new select to examine the effect of inhibitor on the corrosion process at the metal surfaces, by analyzing the surface morphology at nano- to micro- scale. The key advantage of this technique is that the surface roughness can be determined. AFM test was performed for Zn specimen after 24 hr of immersion of 1 M HCl without and with 300 ppm of the extract.

3. Results and Discussions

3.1. Mass loss (M L) estimations

Mass loss of Zn metal in (mg cm^{-2}) without and with various concentrations (50 -300 ppm) of the Ferula hermonis extract can be determined at various time periods The curves were obtained and shown in Fig. 2. As indicated from the figure, there is a significant fall of the extract curves below the curve of free acid. The k_{corr} of Zn specimens after immersion in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract was computed. In all cases, the efficiency of the extract raises with growing concentration of the extract but k_{corr} reduces. The decrease in the k_{corr} might be because the increase of adsorption and coverage of Ferula

hermonis on Zn surface with growing concentration of Ferula hermonis extract. These results indicated that, the extract was a very good inhibitor for Zn dissolution in HCl solution.

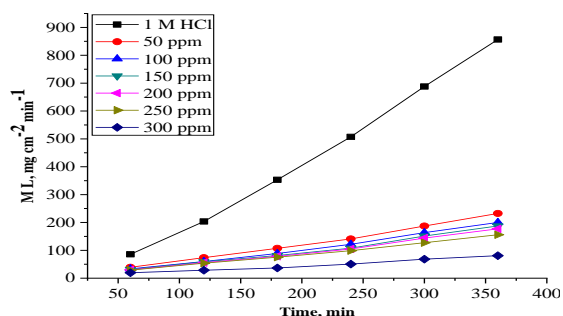


Fig. (2): M L- time curves at 25 °C for Zn corrosion in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract

3.1.1. Effect of temperature

M L of Zn in solutions of 1 M HCl had been studied in the temperature ambit (25- 45 °C) without and with various concentrations of Ferula hermonis extract and the results were tabulated in Table 1. The inhibition efficiency (%IE) for Zn corrosion in inhibited 1 M HCl solutions increase with a growth in the extract concentration. This indicates that Ferula hermonis extract molecules were adsorbed on Zn- solution interface forming a protected layer on the Zn surface that prohibits its corrosion. A decrease in the extract efficiency with increasing temperature indicates physical adsorption of the extract species on Zn surface.

The estimation of activation energy (E_a^*) can be calculated using Arrhenius equation:

$$k_{\text{corr}} = A \exp(-E_a^*/RT) \quad (5)$$

with R as the universal gas constant and A as the Arrhenius pre-exponential multiplier. The plots of $\log k_{\text{corr}}$ with $1/T$ for Zn in uninhibited and inhibited 1 M HCl solutions must give straight lines (Fig. 3) with slopes equals $(-E_a^*/2.303R)$. Eq. (7) was used to determine the enthalpy (ΔH^*) and entropy (ΔS^*) of activation for the Zn in uninhibited and inhibited 1 M HCl solutions.

$$k_{\text{corr}} = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (6)$$

with N represents Avogadro's number and h represents Planck's constant. Plotting of $\log k_{\text{corr}}/T$ with $1/T$ presented straight lines (Fig. 4) with slopes of $-\Delta H^*/2.303R$ and intercepts of

$(\log(R/Nh) + (\Delta S^*/2.303R))$. The computed activation data (E_a^* , ΔH^* and ΔS^*) were provided in Table 2. Inspection of Table 2 indicated that the values of E_a^* of Zn corrosion in 1 M HCl with Ferula hermonis extract were higher than it for blank solution. The values of ΔS^* were negative, which means that in the rate determining step, the activated complex show step of association instead of step of dissociation. Indication of the positive sign of enthalpy is that adsorption of Ferula hermonis extract on Zn surface is endothermic [17].

Table (1): Variation of inhibition efficiencies (IE %), surface coverage (Θ) and corrosion rate (k_{corr}) for several concentrations of Ferula hermonis extract at different temperatures

Temp, °C	Conc. (ppm)	k_{corr} (mg/cm ² min)	Θ	%IE
25	Blank	2.380	-----	-----
	50	0.646	0.729	72.9
	100	0.556	0.767	76.7
	150	0.521	0.781	78.1
	200	0.492	0.793	79.3
	250	0.433	0.818	81.8
	300	0.224	0.906	90.6
30	Blank	2.670	-----	-----
	50	0.792	0.703	70.3
	100	0.708	0.735	73.5
	150	0.635	0.762	76.2
	200	0.572	0.786	78.6
	250	0.529	0.802	80.2
	300	0.273	0.898	89.8
35	Blank	3.135	-----	-----
	50	1.061	0.661	66.1
	100	0.897	0.714	71.4
	150	0.777	0.752	75.2
	200	0.715	0.772	77.2
	250	0.639	0.796	79.6
	300	0.369	0.882	88.2
40	Blank	3.625	-----	-----
	50	1.713	0.528	52.8
	100	1.366	0.623	62.3
	150	1.255	0.654	65.4
	200	1.192	0.671	67.1
	250	1.069	0.705	70.5
	300	0.880	0.757	75.7
45	Blank	3.762	-----	-----
	50	1.977	0.475	47.5
	100	1.939	0.485	48.5
	150	1.830	0.514	51.4
	200	1.698	0.549	54.9
	250	1.573	0.582	58.2
	300	1.201	0.681	68.1

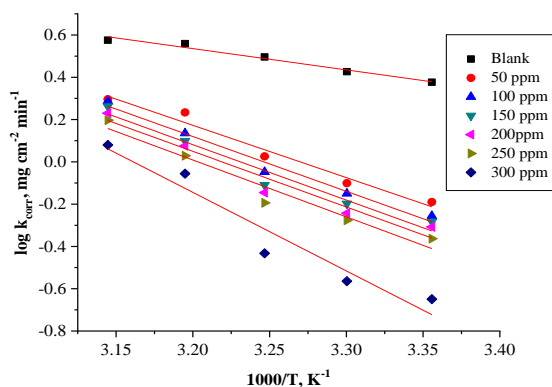


Fig. (3): Plotting of $\log k_{\text{corr}}$ with $1/T$ for Zn in 1M HCl without and with Ferula hermonis

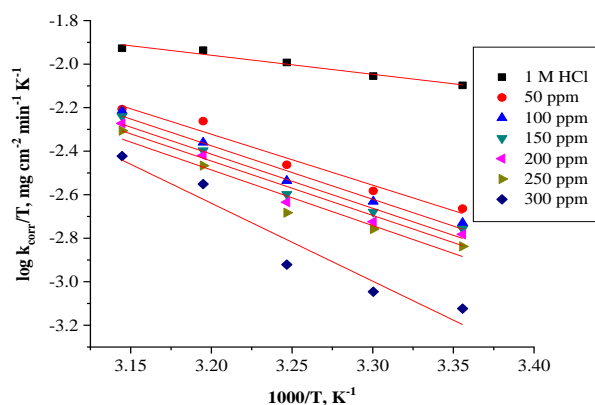


Fig. (4): Plotting of $\log k_{\text{corr}} / T$ with $1/T$ for Zn in 1 M HCl without and with Ferula hermonis

Table (2): Activation parameters for Zn in 1 M HCl without and contain several concentrations of Ferula hermonis extract

Conc., ppm	E_a^* kJ mol ⁻¹	ΔH^* kJ mol ⁻¹	$-\Delta S^*$ J mol ⁻¹ K ⁻¹
0	19.3	16.72	181.48
50	47.4	44.79	98.58
100	49.6	47.07	92.33
150	50.2	47.58	91.43
200	50.4	47.82	91.24
250	51.5	48.94	88.47
300	71.1	68.54	28.66

3.1.2. Adsorption isotherms

In order to study the metal surface coverage with Ferula hermonis extract, different adsorption isotherms were applied. The most suitable one is that of Langmuir adsorption isotherm equation. This isotherm expected that the adsorption is done in a monolayer at certain adsorption sites and there is no side interaction between adsorbed species at the surface. The relationship between the part of Zn surface covered with Ferula hermonis extract, θ , and the extract concentration, C , as indicated from Langmuir equation was as follows.

$$C/\theta = 1/K_{\text{ads}} + C \quad (7)$$

with K_{ads} as the adsorption equilibrium constant and obtained from of the intercept. According to this equation, plots of straight lines must be obtained (Fig. 5) with slopes nearly equal to unity.

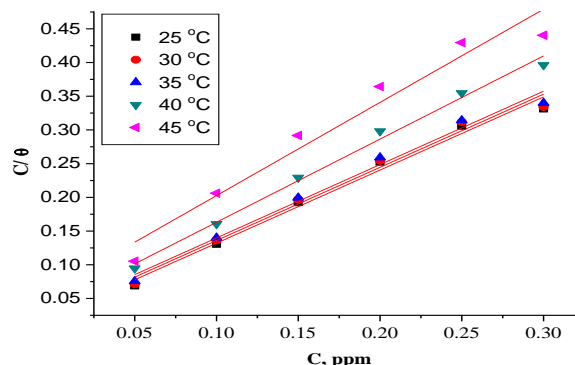


Fig. (5): C/θ with C for Zn in solutions of 1 M HCl with Ferula hermonis extract at diverse temperatures

The free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$, is obtained as follows:

$$K_{\text{ads}} = (1/55.5)\exp(\Delta G_{\text{ads}}^{\circ}/RT) \quad (8)$$

with 55.5 represents the water conc. in the solution bulk (mol/lit.). The calculated $\Delta G_{\text{ads}}^{\circ}$ values were tabulated in Table 3. The sign of $\Delta G_{\text{ads}}^{\circ}$ is negative which means that the adsorption of Ferula hermonis extract on Zn surface was spontaneous. The adsorption is considered physical when $\Delta G_{\text{ads}}^{\circ}$ values are around (-20 kJ mol^{-1}) whilst it is considered chemical when $\Delta G_{\text{ads}}^{\circ}$ values are around (-40 kJ mol^{-1}). For the present work, the $\Delta G_{\text{ads}}^{\circ}$ values were lies between $-17.9 \text{ kJ mol}^{-1}$ and $-19.3 \text{ kJ mol}^{-1}$, indicating physical adsorption. The enthalpy of adsorption, $\Delta H_{\text{ads}}^{\circ}$, was calculated through applying the following Van't Hoff equation.

$$\log K_{\text{ads}} = \Delta H_{\text{ads}}^{\circ}/2.303RT + \text{constant} \quad (9)$$

Figure 6 displays plotting of $\log K_{\text{ads}}$ with $1/T$ for Zn in 1 M HCl with Ferula hermonis extract. The $\Delta H_{\text{ads}}^{\circ}$ value (shown in Table 3) was (-37.422), which proves that the adsorption process is an exothermic. Finally, $\Delta S_{\text{ads}}^{\circ}$ can be attained using the following equation.

$$\Delta S_{\text{ads}}^{\circ} = (\Delta H_{\text{ads}}^{\circ} - \Delta G_{\text{ads}}^{\circ})/T \quad (10)$$

The $\Delta S_{\text{ads}}^{\circ}$ values were listed in Table 3. The negative sign of $\Delta S_{\text{ads}}^{\circ}$ values means that there is a decrease in the order of the adsorbed molecules at the solid/liquid interface.

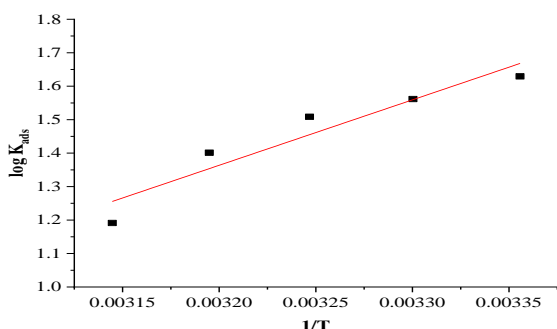


Fig. (6): Plotting of $\log K_{ads}$ with $1/T$ for Zn in solutions of 1 M HCl with Ferula hermonis extract

3.2. Electrochemical measurements

3.2.1. Potentiodynamic Polarization

Figure 7 displays the anodic and cathodic PP curves for Zn in 1.0 M HCl solution without and with different concentrations of Ferula hermonis extract at 25 °C. The electrochemical parameters calculated by using PP technique were listed in Table 4. The PP curves shown that, the shift the anodic and cathodic curves to the lower values of corrosion current densities in the presence of Ferula hermonis extract. This causes decreasing in the corrosion rate. It means that, the cathodic and anodic reactions were both retarded by Ferula hermonis extract. The shape of the curves is alike in both the cathodic and anodic sides. The outcomes demonstrated that the anodic and the cathodic

Tafel slopes (B_a and B_c) were faintly changed on increasing the concentration of the examined extract. This displayed that the Zn dissolution and hydrogen reduction mechanisms with and in absence of Ferula hermonis extract remain unchanged, meaning that Ferula hermonis extract was considered as a mixed type inhibitor, i.e. exhibits cathodic and anodic inhibition effects. However, the cathode was most polarized. The constancy of cathodic slope acquired from the PP results demonstrate that the process of hydrogen evolution was under activation control and inserting the extract does not vary the mechanism of this process. This result displays that the inhibition of Zn corrosion by Ferula hermonis extract was done by the adsorption process on the surface.

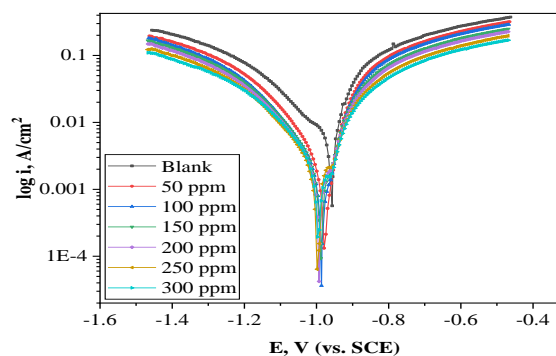


Fig. (7): Anodic and cathodic PP curves at 25 °C for Zn in solutions of 1 M HCl without and with Ferula hermonis extract

Table (3): Thermodynamic adsorption parameters for Zn in solutions of 1 M HCl with Ferula hermonis extract at diverse temperatures

Temp., °C	R^2	$K_{ads} M^{-1}$	$-\Delta G_{ads}^0 kJ.mol^{-1}$	$\Delta H_{ads}^0 kJ.mol^{-1}$	$-\Delta S_{ads}^0 J.mol^{-1} K^{-1}$
25	0.983	42.6	19.3	37.4	61.0
30	0.981	36.4	19.2		60.2
35	0.984	32.3	19.2		59.2
40	0.992	25.2	18.9		59.3
45	0.948	15.5	17.9		61.5

Table (4): Influence of Ferula hermonis extract concentration on PP technique parameters at 25 °C for Zn in solutions of 1 M HCl

Conc., ppm	$-E_{OCP}, mV$	$-E_{corr}, mV$	$j_{corr}, mA.cm^{-2}$	$-\beta, mV.dec^{-1} c$	$\beta, mV.dec^{-1} a$	$R_p, \Omega.cm^2$	C.R mm/yr	θ	%IE
Blank	962.4	-959.0	10.70	298.0	126.0	3.59	6296	-----	-----
50	964.8	-977.0	2.690	162.2	108.4	10.49	1.588	0.749	74.9
100	967.1	-986.0	2.210	157.8	107.4	12.56	1.305	0.793	79.3
150	968.8	-989.0	2.110	145.9	103.0	12.42	1.242	0.803	80.3
200	968.7	-993.0	1.750	125.4	101.0	13.88	1.032	0.836	83.6
250	969.4	-997.0	1.360	121.2	99.70	17.47	802.3	0.873	87.3
300	968.2	-995.0	1.310	93.90	98.00	15.89	774.9	0.878	87.8

3.2.2. Electrochemical impedance spectroscopy (EIS)

Nyquist and Bode diagrams for Zn in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract are displayed in Figs. 8 &9, respectively. The circuit that represent Ferula hermonis extract and electrolyte is presented in Fig. 10, with R_s as the solution resistance. Parameters of EIS test were calculated and set in Table 5. Figure 9 displayed that Nyquist spectrum has by a single full half-circle, indicating that the Zn corrosion control can be done by a charge transfer process. The increase of the diameters of the capacitive loop with Ferula hermonis extract indicating the increase of the inhibition process. The impedance of a CPE is explained through the following equation [18,19]:

$$Z_{CPE} = Y_0^{-1}(j\omega)^{n-1} \quad (11)$$

with Y_0 as the CPE magnitude, ω as the angular frequency of the maximum impedance for the imaginary constituent, n as the phase shift and j as the imaginary number. Generally, n equals 0 indicates the resistance, n equals 1 indicates the capacitance, n equals -1 indicates the inductance and n equals 0.5 indicates the Warburg impedance. As presented in Table 5, n values lie between (0.902-0.974) with and without the Ferula hermonis extract. This deviancy from ideal performance (from unity) illustrates the occurrence of surface heterogeneity and surface roughness. The values of interfacial double layer capacitance (C_{dl}) can be attained using Nyquist plot through the formula:

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1} \quad (12)$$

with f_{max} as the maximum frequency of AC and R_{ct} as the charge transfer resistance. Inspection of Table 5 designates that R_{ct} rises and C_{dl} reduces with the growing in the concentrations of Ferula hermonis extract. Increasing R_{ct} values leads to rising of the inhibition efficiency, that due to the progressive exchange of water by the adsorbed molecules over the Zn surface forming an adherence film. This covered film will decrease the double layer thickness. The decrease of C_{dl} with the increase in the extract concentration can also resulted from the lower in local dielectric constant, which indicates the adsorption of

Ferula hermonis extract on both anodic and cathodic sites on the Zn surface. The surface smoothness with of extract can be also improved via Bode plots. The ideal capacitor is described by -1 for a constant value and 90° for phase angle. The deviation from the ideality occurs because the surface roughness. This deviation is higher in the nonexistence of extract as gotten by Bode plots (Fig. 10). The phase angle rises with growing the concentration of the Ferula hermonis extract and will be more effective at higher extract concentration.

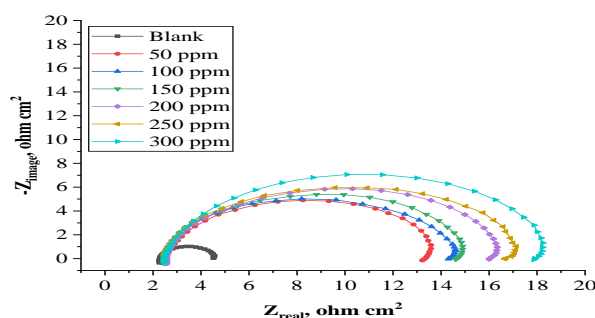


Fig. (8): Nyquist plots at 25 °C for Zn in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract

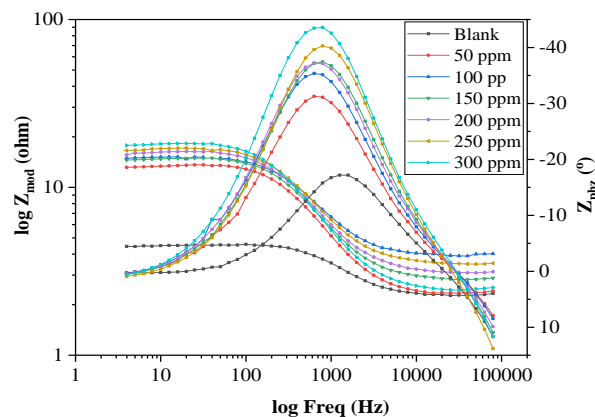


Fig. (9): Bode plots at 25 °C for Zn in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract

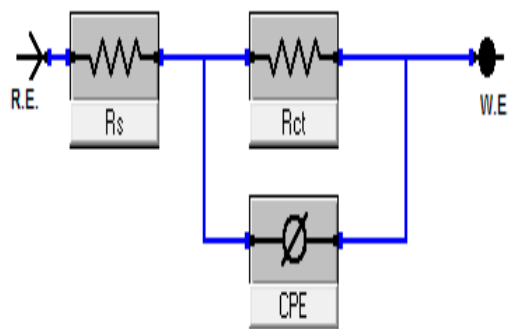


Fig. (10): Electrical circuit model that applied for proper EIS results

3.3. Surface examinations

Atomic force microscopy (AFM) test

Figure 11 (a-c) shows three dimensional AFM image for Zn specimen before & after exposure to a solution of 1 M HCl and after exposure to a solution of 1 M HCl contains 300 ppm of Ferula hermonis extract, respectively. Roughness data obtained for Zn surface by AFM were listed in Table 6. Inspection of Table 7 shows that there is lowering in the surface roughness value when Ferula hermonis extract was added to the solution. The lower roughness was noticed on the free metal (Fig. 11 (a)). The higher surface heterogeneity was noticed on Zn surface exposed to 1 M HCl only (Fig. 11 (b)). 3D explanations present great valleys and peaks. Fig. 11 (c) showed the lower corrosion destruction of Zn in 1 M HCl with 300 ppm of the Ferula hermonis extract with only small spikes and low roughness, representative that the inhibitive film is adsorbed over the surface of the metal [20].

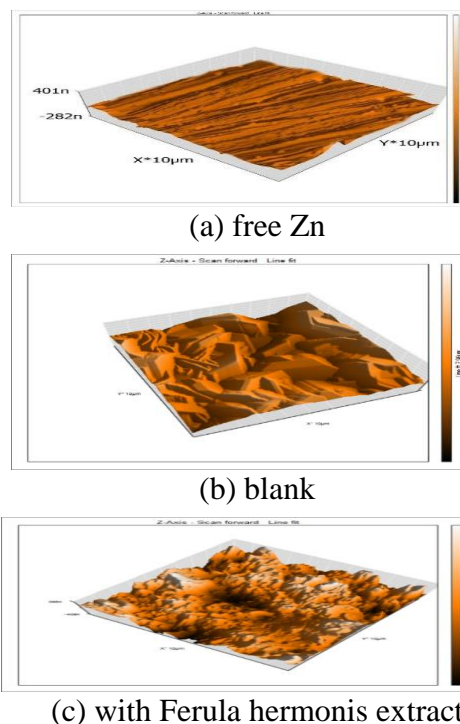


Fig. (11): Two and three dimensional AFM image of Zn specimen in 1 M without and with Ferula hermonis extract

Table (5): Parameters of EIS test at 25 °C for Zn in solutions of 1 M HCl without and contain several concentrations of Ferula hermonis extract

Extract conc., ppm	$R_{ct}, \Omega \text{ cm}^2$	$R_u, \Omega \text{ cm}^2$	$Y_0, \mu\text{S}^n/\Omega \text{ cm}^2$	alpha	$C_{dl}, \mu\text{F}/\text{cm}^2$	Θ	%IE
Blank	2.223±0.054	2.304±0.020	93.51±18.43e-6	0.974±0.022	74.84	-----	-----
50	11.37±0.129	2.350±0.019	55.67±4.036e-6	0.938±0.008	34.33	0.804	80.4
100	11.49±0.185	3.924±0.036	71.19±7.101e-6	0.905±0.011	33.84	0.807	80.7
150	12.28±0.148	2.851±0.023	63.35±4.870e-6	0.918±0.009	33.34	0.819	81.9
200	13.47±0.158	3.122±0.025	67.19±5.084e-6	0.909±0.009	33.46	0.835	83.5
250	13.87±0.178	3.523±0.028	69.55±5.565e-6	0.903±0.009	32.96	0.840	84.0
300	16.07±0.175	2.472±0.020	60.89±3.845e-6	0.918±0.007	32.84	0.862	86.2

Table (6): Roughness data obtained for Zn surface by AFM technique

Specimen	Average roughness (Sa) [nm]
Zn	79.72
Zn in 1 M HCl	617.30
Zn in HCl+300 ppm extract	111.31

5. References

- Prasad AS (1991) Discovery of human zinc deficiency and studies in an experimental model. *Am J Clin Nutr.* **53(2)**:403-12
- Chaieb E, Bouyanzer A, Hammouti B, Benkaddour M (2005) Inhibition of the corrosion of steel in 1 M HCl by eugenol derivatives. *Appl Surf Sci.* **246(1-3)**: 199-205
- Chauhan LR, Gunasekaran G (2007) Corrosion Inhibition of Mild Steel by Plant Extract in Dilute HCl Medium. *Corrosion Science.* *Corros Sci* **49**: 1143–1161
- Fouda AS, Shalabi KS, Nofal AM, El-zekred MA (2018) Methanol extract of Rumex Vesicarius L. as eco-friendly corrosion inhibitor for carbon steel in sulfuric acid solution. *Chem Sci Trans* **7(1)**: 101-111
- Fouda AS, Abdel Haleem E (2018) Berry leaves extract as green effective corrosion inhibitor for Cu in nitric acid solutions. *Surf Eng Appl Electrochem* **54(5)**: 498-507
- Fouda AS, Rashwan SM, Darwish MMK, Arman NM (2018) Corrosion inhibition of

- Zn in a 0.5 M HCl solution by Ailanthus Altissima extract. *Port Electrochim Acta* **36(5)**: 309-323
- 7 Elabbasy HM, Fouda AS (2019) Olive leaf as green corrosion inhibitor for C-steel in sulfamic acid solution. *Green Chem Lett Rev* **12(3)**: 332-342
 - 8 Fouda AS, El-Ewady GY, El-Abbasy HM, Zidan SM (2018) Vitex Agnus Castus plant extract as safe corrosion inhibitor for carbon steel 1018 in 1 M hydrochloric acid. *J Chem Biol Phys Sci* **8(3)**: 469-491
 - 9 Fouda AS, Elabbasy HM (2019) Corrosion inhibition effect of methanol extract of nerium oleander on copper in nitric acid solutions. *Int J Electrochem Sci* **14**: 6884-6901
 - 10 Elabbasy HM (2019) Investigation of Withania Somnifera extract as corrosion inhibitor for copper in nitric acid solutions. *Int J Electrochem Sci* **14**:5355 – 5372
 - 11 Sobhi M (2013) Marjoram extract as corrosion inhibitor for dissolution of zinc in 1.0 M HCl. *Int J Corros* **2013(1)**: 1-7
 - 12 Chetouani A, Hammouti B (2003) Corrosion inhibition of iron in hydrochloric acid solutions by naturally henna. *Bull Electrochem* **19(1)**: 23–25
 - 13 Muhammad I, Mossa JS, El-Ferally FS (1996) Additional Antibacterial Diterpenes from the Bark of Juniperus procera. *Phytother. Res* **10(7)**: 406-407
 - 14 Trease GE, Evans WC (1989) *Pharmacognosy*. 13th edition. English Language Book Society, Bailliere Tindall, Britain, London
 - 15 Akpanabiatu MI, Umoh IB, Udosen EO, Udoh AE, Edet EE (2005) Rat serum electrolytes, lipid profile and cardiovascular activity on Nauclea latifolia leaf extract administration. *Indian J Clin Biochem* **20(2)**: 29-34
 - 16 Eyong UE, Agiang MA, Atangwho IJ, Iwara IA, Odey MO, Ebong PE (2011) Phytochemicals and micronutrients composition of root and stem bark extracts of Vernonia amygdalina Del. *J Med Med Sci* **2(6)**: 900-903
 - 17 Farnsworth NR, Akerele O, Bingel AS, Soejarto DD, Guo Z (1985) Medicinal plants in therapy. *Bull World Health Organ* **63(6)**: 965-981
 - 18 Gabriel A, Agbor DK, Julius EO (2007) Medicinal plants can be good sources of antioxidants: case study in Cameroon. *PJBS* **10(4)**, 537-544
 - 19 Galal A (2000) Sesquiterpenes from Ferula hermonis Boiss. *Pharmazie* **55**: 961–962
 - 20 Abourashed EA, Galal AM, El-Ferally FS, Khan IA (2001) Separation and quantification of the major daucane esters of Ferula hermonis by HPLC. *Planta Med* **67**: 681–682.