Surface Interaction and Corrosion Inhibition of Carbon Steel in Sulphuric Acid Using Punica granatum L. extract

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Abstract: Corrosion inhibition of carbon steel in aqueous 1 M H_2SO_4 was examined in the absence and presence of (Punica *granatum) plant* extract as a green corrosion inhibitor with potentiodynamic polarization (PP), electrochemical frequency modulation (EFM), electrochemical impedance spectroscopy (EIS) and mass loss techniques. The effect of temperature and inhibitor concentration was calculated using mass loss method. The data gained indicated that the plant extract solution could serve as an effective inhibitor for steel corrosion in sulphuric acid media. With increasing plant extract concentration, the inhibition activity was found to increase. As temperature and concentration increase higher inhibition activity was obtained 91.7% for Punica granatum at higher level of inhibitor concentration and temperature. Measurements of PP have shown that this extract is of mixed type and chemically adsorbed on carbon steel surface following Temkin isotherm. The film formed on the metal surface has been analyzed by Fourier transforms spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analyses. The statistics from various tests seem to agree.

1.Introduction

C-steel is alloy of iron that contains up to 2.1 % (as weight percentage) carbon. C-steel is considered the most useful substance used in several manufacture.

because of its excellent mechanical features and a very low price. In the metal finishing industry, acid solutions are widely used for the reduction of unwanted scale and corrosion, boiler cleaning, and heat exchangers [1-3]. Therefore, inhibitors can eventually be used in the treatment process to avoid unexpected metal dissolution and excess acid in the cleaning process [4]. In fact, Organic compounds are most well-known acid inhibitors. Effectual corrosion inhibition with N, O and S [5-6]. However, most of these chemicals are not only costly but also poisonous to living beings. For several decades, the development of a novel corrosion inhibitors for plant extracts has attracted some interest as an environmentally friendly corrosion inhibitor [7]. Plant extracts are an extremely rich source

of natural chemical compounds that can be processed at low cost and are biodegradable in nature by simple processes. Corrosion inhibition of extract of garcinia kola [8], kopsia singapurensis [9], Nyctanthes arbortristis leaves [10], Black pepper [11], were studied as corrosion inhibitors in H_2SO_4 medium. Punica granatum (PG) is commonly used in respiratory ailments and in preparation of tinctures, cosmetics and other medicinal formulae [12]. PG is very abundant in ellagitannins which are high molecular weight water-soluble phenolic compounds. Ellagitannin hydrolysis generates hexahydroxy diphenic acid, which naturally rearranges into ellagic acid (EA) [13-14]. EA [Fig. 1] is an incredibly thermodynamically stable molecule reflecting the four-ring lipophilic domain., The hydrophilic component is composed of four phenolic (hydroxyl) and two groupings of lactone (which can act as a donor or acceptor of the hydrogen bond)PG peels contain a significant numbers of such

polyphenols As flavonoids attached to sugar, quercetin, kaempferol [15], flavonoid Di glycoside[16], organic acid[17] ellagic acid and ellagic tannin[18].On the other hand, it was confirmed that steroid hormones like estrone[19], estradiol [20] and testosterone have also been found in PG extract [21]. Tannic acid (TA) (Fig. 1) is the standard hydrolyzing tannin consisting of a combination of various gallic acid (GA) esters of glucose. TA occurs in barks and many plant fruits contain PG, chelates of iron due to their 10 galloyl groups and decreases non-heme iron intestinal absorption [22-23]. The purpose of this research is to study the inhibitive effect of PG extract in 1 M H_2SO_4 solutions as an inexpensive, green, and naturally occurring substance on the corrosion behavior of C- steel. The study is performed through methods of mass loss (ML), and electrochemical techniques, FT-IR

spectroscopy, X-ray-photoelectron spectroscopy (XPS) analyses.
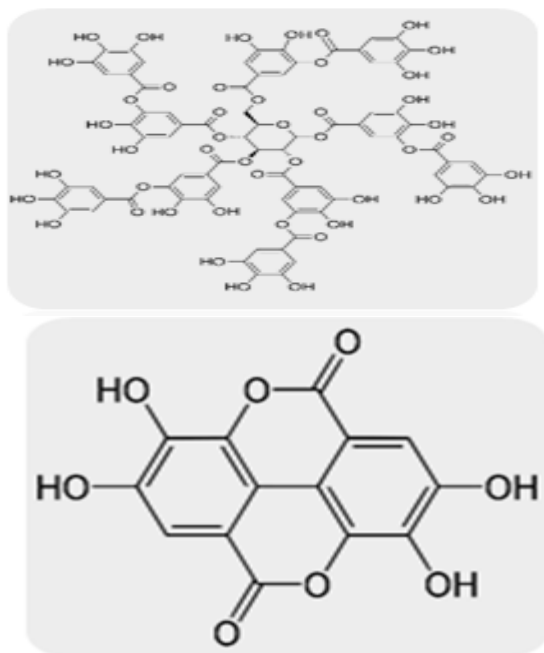
Ellagic acid Tannic acid

Fig. 1. Chemical structure of ellagic acid and tannic acid

2-Experimental techniques

2.1. Materials and solutions

C-steel specimens used in the study have the next compositions (as weigh percentage): 0.14 C, 0.1 Cr, 0.01 Ni, 0.024 Si, 0.5 Mn, 0.05 P, 0.05 S, and the rest is Fe. C-steel specimens of measured (1.9 x 1.9 x 1) cm in triplicate were mechanically polished. Samples were abraded using emery papers ranging in grade from 250 to 1200, then cleaned with distilled water. Acetone was used to brush the surface and filter sheets were used to dry it. The acid medium used for this process is the solution of 1 M H_2SO_4 obtained by dilution with bidistilled water. H_2SO_4 was from analytical reagent grades (96%).

2.2- Preparation of plant extract

At room temperature, the Pongamia Pinnata plant product was dried in shade. Using electric mills, ground into fine powder and extracted by soaking in methanol. The solvent extract was isolated by rotary evaporation and vacuum-dried at 60-65°C. The extract solid was prepared utilized ethanol (1 g/L). Until using, crude extracts had been refrigerated [24].

2.3-Mass loss (ML) method

For measurement of ML, samples with dimensions (1.9x1.9x1) cm have been used. Successively, the specimens had been abraded with various series of variable grade emery papers beginning with coarse (250) grade and going to the finest (1200) grade. ML analyses were carried out without and with different concentrations of the extract tested in 100 ml 1M H_2SO_4 solutions. The concentration level for Punica granatum extracts ranged from 50 to 300 ppm. The immersion time is between 30 and 180 minutes. The weight of the specimens was measured before and after immersion with the following relationship [25]. , the corrosion rate of metal specimens (CR) was calculated.

$$CR = \Delta W/AT \quad (1)$$

ΔW is the reduction in mass (mg),

A is the surface area (cm^2) and t is the time (min). The ML was used to calculate the percentage inhibition Activity (% IE) and surface coverage (Ө) using Eq. (2):

$$IE\% = 100 \times Ө = 100 \times [(1-(\Delta W_1/\Delta W_2)] \quad (2)$$

Where ΔW_1 and ΔW_2 are the weight loss of carbon steel in 1 M H2SO4 in the absence and presence, respectively of various inhibitor concentrations.

2.4- Electrochemical Techniques

Electrochemical calculation was performed by three-electrode cell. They were arranged in a cell of glass. The reference electrode is the

Saturated Calomel Electrode (SCE), Platinum counter electrode as an electrode auxiliary, Square C-steel sample with 1 cm2 region It was used as the working electrode. Since immersion of the electrode for 30 minutes in the test solution, all electrochemical measures at the OCP have been performed at 25°C. Electrochemical studies were produced by using the Potentiostat/Galvanostat, ZRA(PCI4-G750), DC105 and EIS300 Gamry instruments, which connects to computer to record and analyses data using Echem analyst V.6.03.

PP tests

By applying a scan of 0.5 mV s−1 in the range of potential of -700 to +700 mV, we have achieved Tafel polarization plots about the open circuit potential (E_{ocp}). There have been recorded both catholic and anodic polarization curves. For measurement of inhibition activity and surface coverage (θ), as seen below, the density of the corrosive current (i_{corr}) was used.

%IE = θ x100 = [1- ($i_{corr(inh)}$ / $i_{corr(free)}$)] x 100 (3)

Where $i_{corr(inh)}$ and $i_{corr(free)}$ are corrosion currents densities in presence and absence of Punica granatum L. extract, respectively.

EIS measurements.

Measuring electrochemical impedance, the potential of Open Circuit (OCP) and current signals for impedance measurements have been used at frequency ranges between 100 kHz and 10 Hz. The θ and % IE have been determined using the following Eq.

% IE=100 x Θ = 100 x [(1-$R_{ct\ (free)}$ /$R_{ct\ (inh)}$] (4)

Where $R_{ct\ (free)}$ and $R_{ct(inh)}$ as resistances of charge transfer without and with extract, respectively

2.5-Surface examinations

Atomic force microscopy (AFM) analysis. The determination of the metal surface roughness is regarded as the most important aspect of the AFM test. The acidic solutions with the highest dosage (300 ppm) of Punica granatum L. extract have been used in AFM testing with prepared specimens before and after immersion for 24 hours.

FTIR and XPS analyses

Fourier transforms spectroscopic (FTIR) spectra for Punica granatum L. extract before and after adsorption on C-steel surface for 24 hours were studied in spectral range 4000 to 500 cm^{-1} with the technique of Attenuated Total Reflectance (ATR) using FTIR-Spectrometer iS 10 (Thermo Fisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) analysis The XPS examination for C-steel surface was performed after 24 hours of immersion in free acid solution that includes 300 ppm of Punica granatum L. extract using apparatus ESCALAB 250Xi, Thermo-Scientific, United States American.

3. Result and Discussion

3.1. ML method

ML of C-steel was tested at 25 ±1°C after three hours of flood in 1M H_2SO_4 solution without and with varying concentrations of Punica granate is shown in Fig. [2]. The ML decreased as the concentration of extract increased and 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 Punica granate on C-steel surface with growing concentration of Punica granate extract [25]. the type of layer on the adsorbed molecule C-steel surface isolating metals from acidic solution and inhibiting corrosion sites [26].
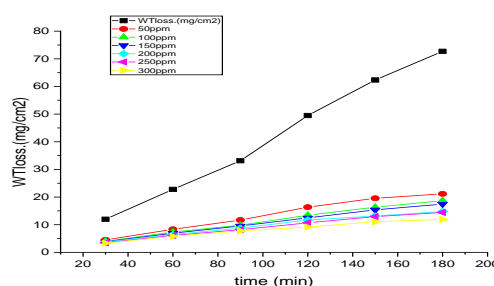
Fig. 2. Mass loss vs. time for C-steel in 1 M H_2SO_4 solution without and with varying concentrations of Punica granate at 25°C

3.1.2. Effect of temperature and thermodynamic parameters

Table 1 offers evidence from C.R, θ and IE percent of C0steel in H2SO4 (1M) in the different concentrations of Punica granate extract. By increasing the concentration of Punica granate and increasing the temperature, the percentage of IE and θ are increased. While C.R decease this indicates that the extract molecules were adsorbed on Cs- solution interface forming a protected layer on the Cs

surface that prohibits its corrosion. An increase in the extract efficiency with increasing temperature indicates chemically adsorption of the extract species on Cs surface.

Table 1. CR, θ and percent IE of C-steel in H_2SO_4 (1 M) solution in different Punica granate L. extract concentrations at different temperatures

Temp. (^{o}C)	[Extract] ppm	CR (mg cm^{-2} min^{-1})	θ	% IE
	Blank	0.412	----	----
	50	0.136	0.669	66.9
	100	0.112	0.728	72.8
25	150	0.104	0.748	74.8
	200	0.097	0.764	76.4
	250	0.089	0.784	78.4
	300	0.076	0.815	81.5
	Blank	0.443	----	----
	50	0.140	0.684	68.4
	100	0.122	0.726	72.6
30	150	0.107	0.757	75.7
	200	0.106	0.761	76.1
	250	0.098	0.78	78.0
	300	0.076	0.827	82.7
	Blank	1.080	----	----
	50	0.279	0.742	74.2
	100	0.256	0.763	76.3
35	150	0.229	0.788	78.8
	200	0.212	0.804	80.4
	250	0.182	0.832	83.2
	300	0.134	0.876	87.6
	Blank	1.568	----	----
	50	0.371	0.763	76.3
	100	0.32	0.796	79.6
40	150	0.302	0.807	80.7
	200	0.268	0.829	82.9
	250	0.231	0.852	85.2
	300	0.169	0.892	89.2
	Blank	1.854	----	-----
	50	0.387	0.791	79.1
	100	0.325	0.824	82.4
45	150	0.258	0.861	86.1
	200	0.250	0.865	86.5
	250	0.236	0.872	87.2
	300	0.152	0.917	91.7

The Arrhenius equation calculate the activation energy (E_a^*) as follows:

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

R is the universal gas constant (8.314 Joule/mol K), A as Arrhenius pre-exponential multiplier. Fig. (3) indicates plotted between log CR against the reciprocal of temperature 1/T for C-steel in 1 M H_2SO_4 solution in the presence of different concentrations of Punica granatum. The E_a^* values can be determined from the slopes of straight lines based on the

figure. Another type of transition state expression can be used to measure Enthalpy and entropy of the activation mechanism (ΔH^* and ΔS^*) as following:

Log k/T = log (R/ Nh + ΔS^*/ 2.303R) + (-ΔH^*/ 2.303R) 1/ T   (6)

Where h is the Planck's constant and N is the Avogadro's number. The plots of (log k_{corr}/T) versus (1/T) (Fig. 4) should give a straight line with a slope = (- ΔH^*/ 2.303 R) and an intercept =Log (R/Nh +ΔS^* /2.303 R). Which from those relations obtain (ΔH^* and ΔS^*). Thermodynamic activation parameters were given in Table 2. The E_a^* values for inhibited solutions were lower than those for blank solution as illustrated in Table 2. The reduction in E_a^* means that extract particles on the C-Steel surface are chemisorption. A positive sign of ΔH^* means that the mechanism of activation is endothermic. Compared with the blank solution, the reduction in values of ΔH^* in inhibited solutions suggests that the energy barrier in the corrosion reaction reduces. The negative value of ΔS^* indicates that the activated complex is the step that decides the rate and reflects association rather than dissociation. Indicating that there is a reduction in the disorder, going from the reactant to the activated complex [27-28]

$$k_{corr} = A \exp(-E_a^* /RT) \qquad (5)$$
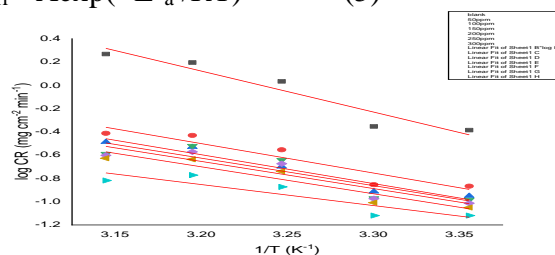
Fig. 3. Log CR vs. 1/T curves for various concentration of Punica granatum L. extract for corrosion of C-steel in 1 M H_2SO_4.
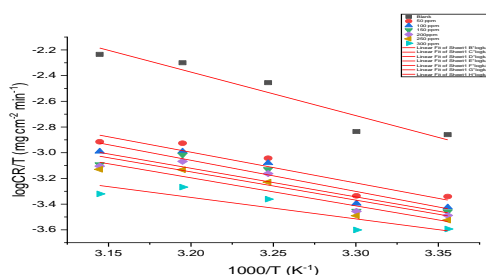
Fig. 4. Log (CR/T) vs 1/T diagram for various concentration of Punica granatum L extract for corrosion of C-steel in 1 M H_2SO_4.

Table 2. Parameters for thermodynamic activation of C-steel corrosion at various Punica granatum L extract concentrations in 1 M H2SO4 solution.

Conc, ppm	E_a^* kJ /mol	ΔH^* kJ /mol	ΔS^*,J /mol.K
Blank	67.394	64.80	-35.52
50	48.404	45.82	-108.19
100	47.466	46.35	-107.71
150	45.195	42.62	-120.84
200	44.632	42.07	-123.14
250	44.374	41.80	-124.89
300	34.572	32.00	-159.16

3.1.2. Adsorption isotherm

By using of adsorption isotherm provide some important information regarding the corrosion inhibition mechanism. The best fit was obtained with the Temkin isotherm which is in agreement with Eq.

$$a \, \Theta = \ln K_{ads} \, C \qquad (7)$$

Where C=concentration of extract and K_{ads}= adsorption constant. That appear in fig (5). It is possible to acquire the free adsorption energy ($\Delta G°ads$) by applying the following Eq.

$$K = 1/ 55.5 \exp (-\Delta G_{ads}/ RT) \qquad (8)$$

$$\log K = - \log 55.5 - \Delta G_{ads}/ 2.303RT \qquad (9)$$

Where 55.5 is the molar concentration of water in the solution. The Van't Hoff plot is the method used to quickly determine the enthalpy of adsorption process (ΔH^o_{ads}) both qualitatively and quantitatively according to the following equation:

$$\log K_{ads}=(−\Delta H^o_{ads}/2.303RT) +\text{constant} \qquad (10)$$

The plot between log K_{ads} and 1/T is seen in Figure (6). The value of ΔH^o_{ads} from the slope of the line can be determined. The entropy of adsorption (ΔS^o_{ads}) can be calculated using the basic thermodynamic principal equation as follows.

$$\Delta G^o_{ads}=\Delta H^o_{ads}-T\Delta S^o_{ads} \qquad (11)$$

Table 3 described the received adsorption parameters. Values of ΔG^o_{ads} are negative and increased as the % IE increased which indicates that this investigated extract is strongly adsorbed on the C-steel surface and shows the spontaneity of the adsorption process and stability of the adsorbed layer on the C-steel surface. The values of ΔG^o_{ads} obtained were approximately equal to -51.7 ± 1 kJ mol^{-1}, indicating that the adsorption mechanism of the

(Punica *granatum* on C-steel in 1 M H$_2$SO$_4$ solution involves chemisorption. The K_{ads} follows the same trend in the sense that large values of K_{ads} imply better more efficient adsorption and hence better inhibition efficiency. The negative sign of $\Delta H°_{ads}$ reveals that adsorption of the inhibitor on C-steel surface from 1M H$_2$SO$_4$ solution is an exothermic process, which indicates that %IE for the plant extract increases with the rise in temperature. Such behavior can be explained on the basis that temperature rise causes adsorption of some adsorbed inhibitor molecules on the c-steel surface and hance higher protection was observed. Entropy of adsorption (ΔS^o_{ads}) were found to have negative signs, which indicated that adsorption reaction is attended by decrease in the disorder.
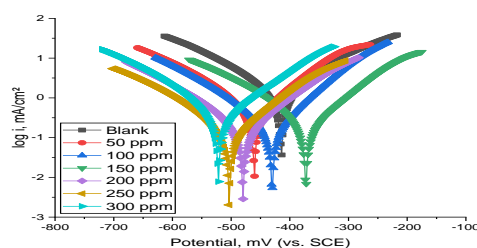
with Punica granatum extract.
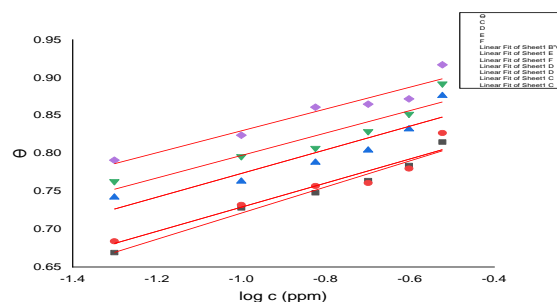
Fig. 5. Temkin adsorption model of Punica granatum L. extract on C-steel surface at different
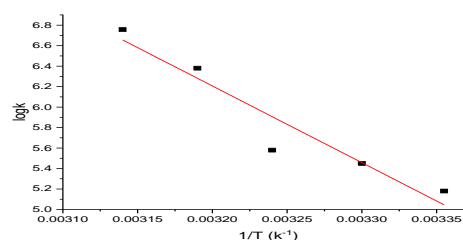
Fig. 6. Log K_{ads} vs. 1/T curve for adsorption of Punica granatum L. extract on C-steel surface.

Fig. (7): Anodic and cathodic PP curves at 25°C for c-steel in solutions of 1 M H$_2$SO$_4$ without and with Punica granatum extract

Table 3. Punica granatum L. extract thermodynamic adsorption parameters. Extract at varying temperatures on C-steel Surface.

T, K	log K_{ads}	$-\Delta G^o_{ads,}$ kJ mol^{-1}	$-\Delta H_{ads,}$ kJ mol^{-1}	$-\Delta S_{ads,}$ J mol^{-1}K^{-1}
298	4.9	38.1	117.3	526
303	5.31	40.9		522
308	5.87	44.9		526
313	6.04	46.6		523
318	6.5	50.1		526

3.2. Electrochemical measurements

3.2.1. PP tests

The PP curves for C-steel in 1 M H_2SO_4 are seen in the Fig. [7] in the absence and presence of Punica granatum extract. The anode and cathode current potential curves are extrapolated from the point of corrosion current density (i_{corr}) to their intersection point, Polarization measurements have obtained cathodic and anodic Tafel slopes (β_c and β_a), corrosion potential (E_{corr}) and inhibition efficiency and the degree of surface coverage (θ) was determined and given in Table 4. It is found that the presence of extract decreases i_{corr} due to the adsorption of extract materials on the carbon steel surface. There is no noticeable improvement in the inhibited solution relative to the uninhibited solution in the E_{corr} and Tafel slopes. The addition of the analyzed extract did not substantially alter the values for E_{corr} and suggested that the inhibitor functions as a mixed mode inhibitor [29]. In addition, it is noted that both the cathodic (βc) and anodic (βa) slopes were moved to more negative and positive directions by Tafel lines. This shows that the corrosion reaction process is established and the simple adsorption approach stops the corrosion reaction [30].

Table (4): Influence of Punica granatum extract concentration on PP technique parameters at 25°C for C-steel in solutions of 1 M H_2SO_4

| Conc., ppm	$-E_{corr}$, mV vs SCE	j_{corr}, mA.cm^{-2}	β_a , mV/dec	$-\beta_c$,mV/dec	Θ	%IE
Blank	414.8	0.943	122.5	139.2	----	-----
50	-460.7	0.5102	128.4	-156.6	0.459	45.9
100	-429.5	0.4039	97.1	-126.9	0.572	57.2
150	-372.7	0.3171	118.8	-142.2	0.664	66.4
200	-479.1	0.1949	123.8	-137.0	0.793	79.3
250	-503.2	0.1183	121.7	-143.8	0.875	87.5
300	-394.3	0.0484	157.9	-166.9	0.949	94.9

3.2.2. EIS tests

In corrosion studies, EIS is an effective and useful method. A lot of details can be obtained from impedance diagrams, such as kinetic parameters, surface properties, and mechanistic information [31-34]. Figure. 8 shows Nyquist plots obtained at open-circuit potential without and with varying concentrations of Punica granatum extract their respective corrosive potential after 30 minutes of immersion in 1 M H_2SO_4 at 25.0 ± 0.1 °C. As a result of the increase in the number of extracts molecules, the results indicate an increase in the diameter of every semicircle of the Nyquist plot when the concentration was increased between 50 and 300 ppm. The electrical circuit equivalent model used to conform the EIS results was seen in the Figure. 9. Different parameters are included in Table 5, such as R_{ct}, double layer capacitance (C_{dl}) and (percent IE). It found

that there is increase in (R_{ct}) values while there was a gradually decrease in (C_{dl}) values as concentration of Punica granatum extract increases. This can be due to the progressive substitution of water molecules by the adsorption on the metal surface of the extract molecules or increasing the the double layer thickness. As indicated in Table 5, n values lie between (0.985- 0.972). The deviation from unity can be illustrated on the bases of heterogeneity and roughness occurred on the C-steel surface [35].
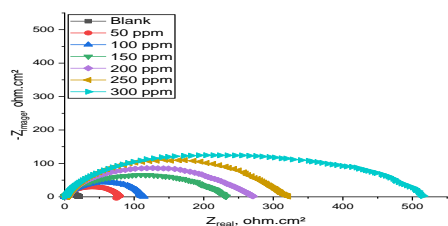
Figure 8. Nyquist plots for corrosion of the C-steel in the used acid medium without and at various doses of Punica granatum extract
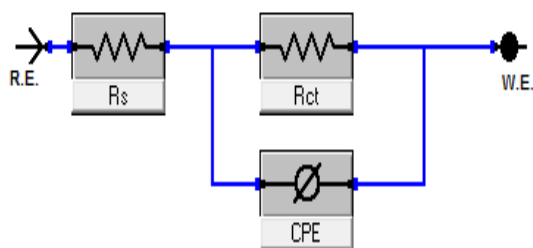
Figure 9. The circuit used to analyze the EIS values

Table 5. EIS parameters for corrosion of the C-steel in the used acid medium without and at various doses of Pc L. extract

| Extract conc., pm	Rs, ($\Omega c2$)	n	C_{dl},($\mu F/^2$)	R_{ct}, (Ωc^2)	Θ	%IE
Blank	2.521	0.985	608.7	25.12	-	-
50	3.605	0.992	437.4	60.24	.58	58.30
100	1.905	0.989	384.5	87.48	.71	71.28
150	3.338	0.994	296.4	143.3	.82	82.45
200	3.481	0.955	208.3	197.7	.87	87.29
250	3.879	0.911	145.7	302.6	.917	91.70
300	4.048	0.972	65.31	516.1	.95	95.13

3.3. Surface examinations

3.3.1. AFM analysis

AFM is a very powerful measure for the estimation of the roughness of the sample surface in the order of the nanometer fraction at a high resolution [36]. In the absence and presence of 300 ppm of Punica granatum L. Extract the surface morphology of C-steel was studied using AFM experiments after immersion in 1 M H2SO4 for 24h. The AFM images are seen in Figure 10, three dimensional (3D) with 300 ppm Punica granatum L. extract In uninhibited system, Due to dissolution in the corrosive medium with a roughness of (993.76) nm, the C-steel surface was fairly damaged. The roughness of inhibited C-steel surface was (113.92 nm) the creation of a protective coating on the surface allows the surface roughness to

decrease which effectively prevents it from corrosion.

.3.3.2. FT-IR analysis

To identify the functional groups found in the Punica granatum extract using liquid samples, Fourier transformation infrared spectroscopy studies (FT-IR) have been employed. The FT-IR spectrum of the Punica granatum extract and the corrosion products present are shown in Fig. 11. Where (Fig. 11a) represent before adsorption on carbon steel and (Fig. 11b) after adsorption. As demonstrated in Fig. 11a, there are broad peaks of the extract at (3328-2975-1718-1613-1343 cm-1) which correspond to O-H, aliphatic C-H
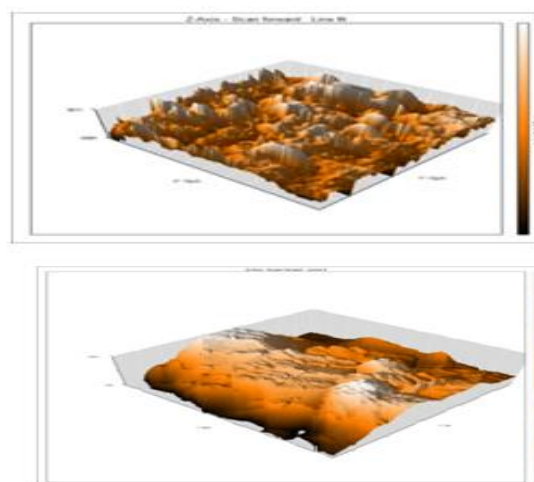
(A)Blank with (b) 300 ppm Punica granatum L. extract.

stretching vibration frequencies, C=O, C-O symmetric stretch, and C-H. It is obvious that some peaks are moving or disappearing, some peaks are also less significant between Punica granatum spectra in Fig. 11a and Adsorbed molecules of an extract on the surface of the C-steel in (Fig. 11b) This suggests that the Punica granatum extract was adsorbed by the functional groups present in the extract molecules on the C-steel surface, which generated the inhibition process.
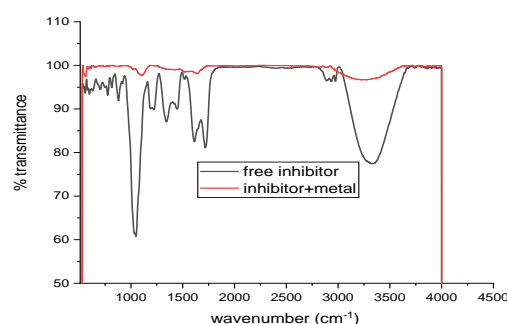
4. Conclusions

In a solution of 1 H_2SO_4, the Punica granatum L. extract seems to have a strong inhibitory efficiency for corrosion of C-steel. And the inhibition was clarified by the adsorption fundamental. Punica granatum L. extract adsorption on a C-steel surface followed the Temkin adsorption isotherm. The adsorption is chemisorption. The percentage of IE rises with increased extract dosage and increased temperature. Potentiodynamic polarization procedures indicate that Punica granatum L. extract exhibits cathodic and anodic inhibition effects. As Punica granatum L. extract increases, reduction occurs in C_{dl}, while the raise in R_{ct} was attained with rising the extract dose. AFM results for C-steel surface with Punica granatum L. extract indicates low roughness, meaning that the inhibitive film is formed on the metal surface.

4. References

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