

Punica Plant extract as Green Corrosion inhibitor for C-steel in Hydrochloric Acid Solutions

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Punica Plant extract was studied as green corrosion inhibitor for carbon steel in 1 M HCl solutions by the potentiodynamic polarization, AC electrochemical impedance spectroscopy (EIS), potentiodynamic anodic polarization, scanning electron microscope (SEM). The obtained results showed that the inhibition efficiency of this extract increased by increasing the concentration and decreased by raising the temperature. Langmuir adsorption isotherm fits the experimental data for the studied extract. The effect of temperature on the corrosion rate was studied at temperature range 30 – 50°C. Thermodynamic parameters of activation and adsorption were calculated and discussed. The results showed that this extract acted as mixed type inhibitor but cathode is more polarized when an external current was applied. The mechanism of the inhibition process was determined using electrochemical techniques.

Keywords: Punica plant extract; carbon steel; HCl, EIS, Langmuir adsorption isotherm

1. INTRODUCTION

Formation of scales in machineries and equipment's is a common problem in industries and these remains as a major challenge to scientists and researchers. To prevent the formation of scales, cleaning of the equipment's by mineral acids is essential. But these acids are aggressive and to decrease the aggressiveness of the cleaning acids, inhibitors are often used. Schmitt [1] extensively discussed about the types of inhibitors recommended to protect metallic materials, especially ferrous metals and alloys from corrosion in acid solutions during pickling, acid cleaning, scale removing and oil and gas well acidizing. There are some requirements for the compound to act as corrosion inhibitor. Regarding the chemical structure and chemical behavior, an inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic

compound must have some features to act as a corrosion inhibitor. Among these, the molecule may have a large structure, double bonds, an active center or group, etc. These features make the molecule to cover a large area of a metal surface with a firmly attached film. Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the inhibitor used, must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly. One of the sources of these cheap and clean inhibitors is plants. Plant parts contain several compounds that satisfy the requirements of a good corrosion inhibitor. Many recent studies [2–11] have adopted this trend using naturally occurring substances.

This work is devoted to examine the corrosion inhibition ability of the aqueous extract of punica for the corrosion of carbon steel in 1 M HCl by electrochemical techniques and surface studies.

2. EXPERIMENTAL METHODS

Pure samples of carbon steel were used throughout the experiment have the following chemical compositions in weight n%: C 0.24, Mn 1.4, P 0.025, Si 0.45 and rest is Fe.

2.1. Electrochemical measurements

The electrodes used for such experiments were cut from a strip coupon to be with 1x1cm dimensions of a carbon steel sheet was fixed at one end by mechanical jamming, and the electrode was fixed into a Pyrex glass tubing of appropriate diameter by means of araldite (Ciba-Geigy-Switzerland) leaving the exposed length, 1x1 cm² to contact the solution. In all measurements mechanically polished electrodes were used, polishing was affected using emery papers of different grades, degreased with acetone, washed with double distilled water, and dried with filter papers, Electrodes treated in this way were found to give producible results. Standard ASTM glass electrochemical cell was used and platinum electrode was used as an auxiliary electrode. All potentials were measured against saturated calomel electrode (SCE) as a reference electrode. The potential increased with a speed of 1 mV/sec started from -800 mV to -200 mV. Potentiodynamic anodic polarization measurements by changing the electrode potential automatically from (-1000 to 1200 mV_{SCE}) vs. SCE with a scan rate of 1 mVs⁻¹ for studying pitting corrosion. The inhibition efficiency (% IE) and the degrees of surface coverage (θ) were defined by equation (2) [12]:

$$\% \text{ IE} = \theta \times 100 = [1 - (i_{\text{corr}} / i'_{\text{corr}})] \times 100 \quad (1)$$

Where i_{corr} and i'_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

2.2. Electrochemical impedance spectroscopy (EIS) measurements

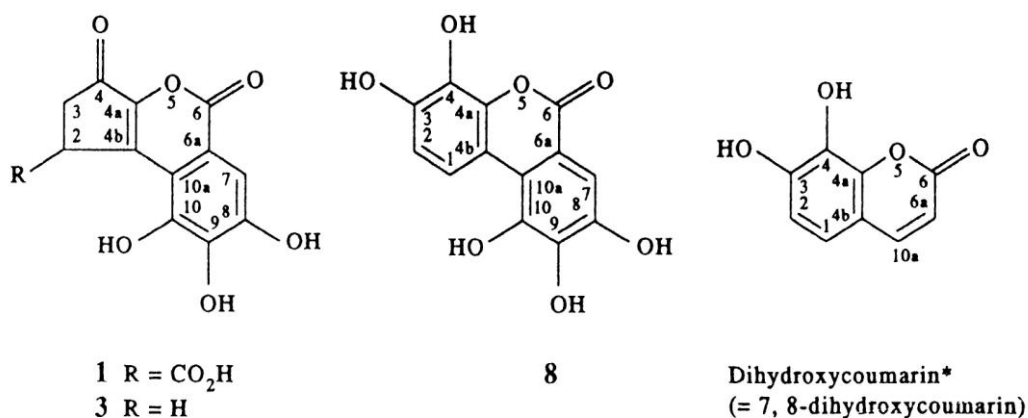
EIS measurements were carried out using ac signals 10 mV peak to peak at the open circuit potential in the frequency range of 100 kHz to 10 mHz. Time interval of 30 min. was given for a

steady state attainment of open circuit potential (OCP) then, the impedance measurements were carried out. The working electrode and the electrolytic solutions were prepared as described before. Impedance data through this work were represented by a simple equivalent-circuit model, which is equivalent to the well-known Randles cell [13]. The measurements were carried out at a constant room temperature of 25°C

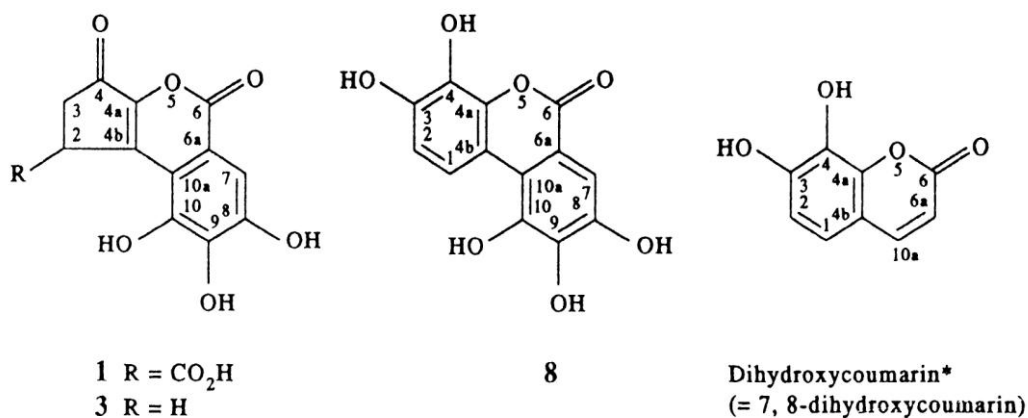
2.3. Scanning electron microscope (SEM) studies

Scanning electron microscope (Model Field Emission Scanning Electron Microscope (Philips XL-30) version -96) was used to examine the surface of the C-steel specimen immersed in test solution containing a certain concentration of plants extract compounds at 30°C. The SEM is equipped with an energy dispersive X-ray spectrometer (EDX) and has both back-scattered electron and secondary electron detectors for imaging. The SEM is operated through a PC based system. The procedure of surface treatment was the same as that of the weight loss experiments. After the surface treatment the specimens were stored in desiccators until required for examination.

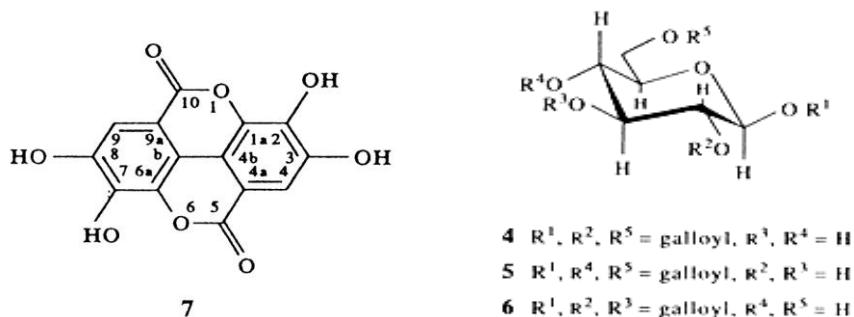
The chemical structure of components of punica plant extract is shown below:



* Numbering is for convenience



* Numbering is for convenience



3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements

The potentiodynamic polarization curves for carbon steel in 1 M HCl solutions containing different concentrations of punica plant extract at 30 °C are shown in Figure (1). The intersection of Tafel regions of cathodic and anodic branches gives the corrosion current density (i_{corr}) and the corrosion potential (E_{corr}). Table (1) shows the electrochemical parameters (E_{corr} , anodic and cathodic Tafel slopes, β_a , β_c , and i_{corr}) obtained from Tafel plots for the carbon steel electrode in 1 M HCl solution in the absence and presence of different concentrations of punica plant extract. Inspection of Figure (1) shows that the addition of punica has an inhibitive effect on both anodic and cathodic parts of polarization curves generally shifted the E_{corr} value towards the negative direction and decrease in i_{corr} value. In addition, parallel cathodic Tafel curves show that the hydrogen evolution is an activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor [14]. The anodic curves of carbon steel in 1 M HCl in the presence of punica extract show that the extract has no effect at potential higher than E_{corr} , this behavior may be the result of significant carbon steel dissolution leading to a desorption of the inhibiting layer. In this case, the desorption rate of the inhibitor is higher than its adsorption rate [15]. This limitation of inhibitory action on cathodic domain is found by different researchers [16, 17]. The data of Table (1) revealed that i_{corr} decreases considerably with increasing the inhibitor concentration, while no definite trend was observed in the shift of E_{corr} values. This indicates that this extract acts as mixed type inhibitor. The Tafel slopes show slight changes with addition of inhibitors, which suggests that the inhibiting action occurred by simple blocking of the available cathodic and anodic sites on carbon steel surfaces. The dependence of % IE versus inhibitor concentration is also presented in Table (1). The obtained efficiencies indicate that this investigated plant extract act as effective inhibitor.

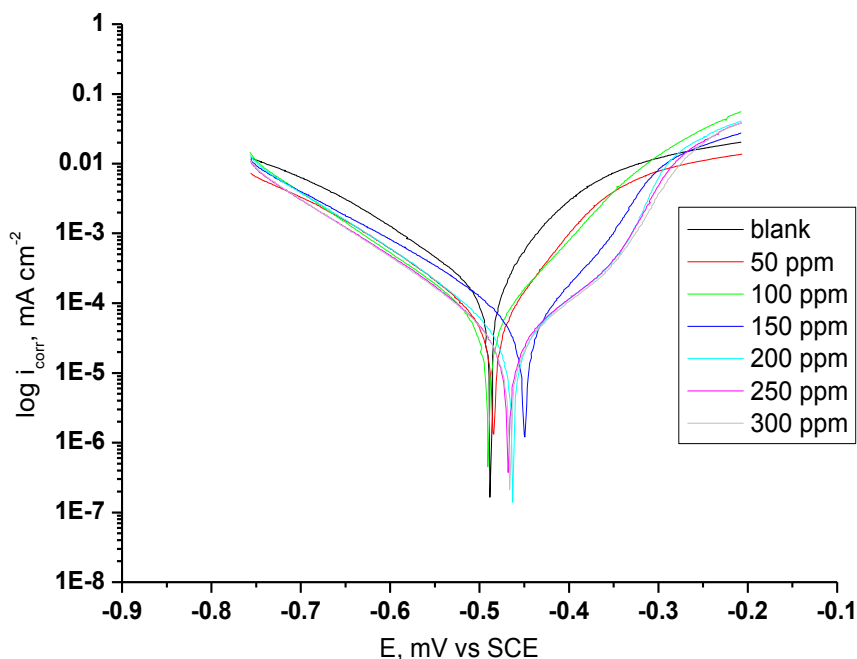


Figure 1. Anodic and cathodic polarization curves obtained at 30°C in 1 M HCl at different concentrations of punica extract

Table 1. The effect of concentration of punica on the electrochemical parameters calculated using potentiodynamic polarization technique for the corrosion of carbon steel in 1 M HCl at 30°C

Conc., ppm	-E _{corr} , mV vs SCE	i _{corr} , μA cm ⁻²	-β _c , mV dec ⁻¹	β _a , mV dec ⁻¹	R _p Ohm cm	C.R Mm y ⁻¹	θ	% IE
blank	488	148.5	149	128	201.5	1.723	----	----
50	485	64.66	144	116	430.4	0.751	0.565	56.5
100	491	47.08	121	91	479.4	0.546	0.683	68.3
150	450	39.50	136	84	569.2	0.459	0.734	73.4
200	463	15.32	105	78	1271	0.178	0.897	89.7
250	468	13.76	105	79	1425	0.160	0.907	90.7
300	467	12.73	104	79	1534	0.148	0.914	91.4

3.2 Electrochemical impedance spectroscopy (EIS) measurements

The corrosion behavior of C-steel in 1M HCl solution in the absence and presence of different concentrations of plants extract was investigated by the EIS technique at 30°C. Figure (2) shows the Nyquist plots (a) and bode plots (b) for C-steel in 1M HCl solution in the absence and presence of different concentrations of investigated punica at 30°C. The obtained Nyquist impedance diagrams in most cases does not show perfect semicircle, generally attributed to the frequency dispersion [18] as a result of roughness and in homogenates of the electrode surface. The data reveal that, each impedance diagram consists of a large capacitive loop with low frequencies dispersion (inductive arc). This inductive arc is generally attributed to anodic adsorbed intermediates controlling the anodic process [19, 20]. By following this, inductive arc was disregarded. The impedance spectra of the different

Nyquist plots (Fig. 2) were analyzed by fitting the experimental data to a simple equivalent circuit model, which includes the solution resistance R_s and the double layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance R_{ct} [21]. In 1M HCl with the presence of various concentrations of Punica, the impedance diagrams show the same trend (one capacitive loop), however, the diameter of this capacitive loop increases with increasing concentration. The main parameters deduced from the analysis of Nyquist diagram are: The resistance of charge transfer R_{ct} (diameter of high frequency loop). The capacity of double layer C_{dl} which is defined as:

$$C_{dl} = 1/2\pi f_{max} R_{ct} \tag{2}$$

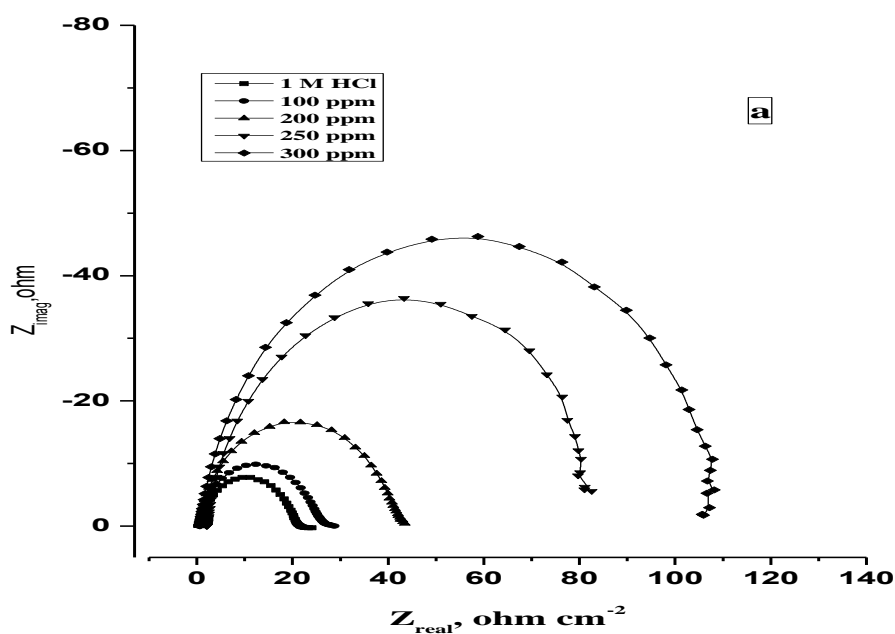
Where f is the frequency.

The inhibition efficiency (% IE) and the surface coverage (θ) of the used inhibitor obtained from the impedance measurements can be calculated from equation (3):

$$\% IE = \theta \times 100 = \left[(R_{ct} - R_{ct}^0) / R_{ct} \right] \times 100 \tag{3}$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance in the absence and presence of different concentrations of inhibitor, respectively. The impedance data such as C_{dl} , R_{ct} , θ and % IE were calculated by assuming Randles circuit (Fig. 3) and are given in Table 2. From the impedance data given in Table (2), we conclude that:

The value of R_{ct} increases with the increasing the concentration of the extract and hence, the increase in the corrosion inhibition efficiency in acidic solution. This can be attributed to the formation of protective film on the metal solution interface [22].



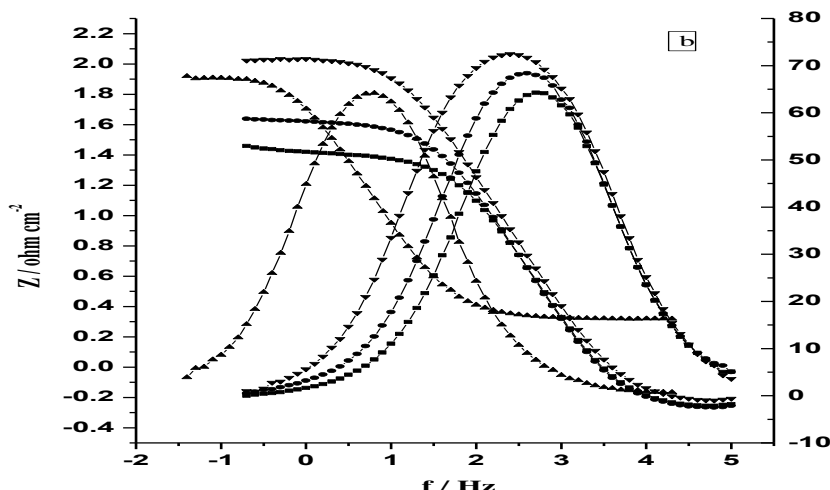


Figure 2. The Nyquist (a) and Bode (b) plots for corrosion of C-steel in 1M HCl in the absence and presence of different concentrations of punica at 30°C

The existence of single semicircle showed that single charge transfer process occurred during dissolution of C-steel which unaffected by the presence of the extract. The value of double layer capacitance decreases by increasing the extract concentration. This is attributed to increase in thickness of electronic double layer [23]

The % IE obtained from EIS measurements are nearly close to those obtained from polarization and weight loss methods.

Table 2. Electrochemical kinetic parameters obtained from EIS technique for the corrosion of C-steel in 1M HCl at different concentrations of punica at 30°C

Conc., ppm	C _{dl} , μF cm ⁻²	R _{ct} , ohm cm ²	θ	% IE
Blank	97.46	18.82	----	----
100	95.42	26.32	0.285	28.5
200	93.31	43.68	0.569	56.9
250	89.80	84.98	0.779	77.9
300	85.80	121.40	0.845	84.5

3.3 Pitting corrosion of carbon steel in NaCl and its inhibition

Pitting corrosion of carbon steel as other metals and alloys occurs when passivity break down takes place on the surface exposed to the corrosive environments at which anodic dissolution proceeds whilst the major part of the surface remains passive. The dependence of the pitting corrosion potential of carbon steel electrode on the concentration of Cl⁻ ion can be clearly seen from Fig. (3). This Figure

represents the plot of pitting potential E_{pitt} vs. the logarithm of chloride ion concentration. Straight line relationship was obtained satisfying the following equation:

$$E_{\text{pitt}} = a_1 \pm b_1 \log C_{\text{Cl}^-} \quad (4)$$

where a_1 and b_1 are constants depend on both the nature of the electrode and type of aggressive anions. As the concentration of chloride ions increases the pitting potential is shifted to more negative direction indicating the destruction of passive film and initiation of pitting corrosion. The differentiation between pit initiation and pit propagation is well explained by Aziz and Godard [24].

Plants extracts have been successfully applied for the inhibition of general corrosion of materials; the development of organic inhibitors for pitting corrosion of carbon steels has not received much attention. In the case of the inhibition of general corrosion, inhibition efficiency is assumed to be proportional to the adsorption of organic components present. The pitting corrosion, however, is a complicated localized corrosion phenomenon and the relationship between adsorption and inhibition is not obvious. The primary step in the action of corrosion inhibitors in NaCl solution usually is the adsorption of inhibitors on the metal surface [25]. The adsorption process depends upon electronic characteristic of the inhibitors, the nature of surface, temperature and pressure of the reaction, steric effect, multiplayer adsorption and the degree of surface activity. Figure (3) represents the effect of the addition of increasing concentrations of some punica on the potentiodynamic anodic polarization curve of carbon steel electrode in 0.1M NaCl at a scanning rate of 1mV/sec. It was found that the pitting potential of the carbon steel electrode is shifted to more positive (noble) direction with increasing the concentration of additives. This indicates that increased resistance to pitting attack. An increase of inhibitor concentration causes the shift of the pitting potential into more positive values in accordance with the following equation:

$$E_{\text{pitt}} = a_2 + b_2 \log C_{\text{inh}} \quad (5)$$

Where a_2 and b_2 are constants which depend on both the composition of additives and the nature of the electrode. Inhibition afforded by these additives using the same different concentrations of the additives decreases as decreases the concentration of inhibitor. Most of the well-known inhibitors are Punica as plant extract containing nitrogen, sulphur and oxygen atoms. The influence of plants extracts such as amines on the corrosion of carbon steel has been investigated by several workers [26, 27]. Most of organic inhibitors act by adsorption on the metal surface. This phenomenon is influenced by the nature and surface charge of metal, by the type of aggressive electrolyte and the chemical structure of inhibitors [28]. The most important prerequisites for additives to be efficient inhibitors are that substance should chemisorb on the surface, having a high energy on the metal surface, and the barrier layer formed should increase the inner layer thickness.

The adsorption of organic additives may be due to: i) Electrostatic attraction between charged metal ii) Interaction of unshared electron pair in the molecule with the metal, iii) Interaction of electron with the metal and iv) a combination of the above. The adsorbed molecule can then retard the anodic and cathodic corrosion reaction. Also, the adsorbed molecule may be inhibiting the pitting corrosion by shifting the critical pitting potential to more noble value by one or a combination of the following mechanisms: Forming a physical barrier layer between metal and coordinate, or Reducing the metal reacting through an alteration in the nature of metal surface or changing the structure of the metal solution interface. However, inhibition efficiency of organic additives depends on many factors [29],

including the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes. From the sequence of the inhibition efficiency it is clear that, the electron donation increases the electron density at bulk stricter. So, as the number of electron donating group increases, the electron density at the ring increases. So, from the results obtained in this part revealed that inhibition of pitting corrosion of carbon steel by plant extracts as indicated from potentiodynamic anodic polarization was found to depend on the concentration and nature of inhibitor. The values of pitting corrosion potential ($E_{\text{pitt.}}$) were shifted to more noble value as the concentration of inhibitor increases. These results indicated the inhibiting effect of such additives toward the pitting corrosion [30]. Also, the inhibition of pitting corrosion by plant extracts is assumed to occur as a result of the following processes: a) Competitive adsorption sites on the metal surface occurs, a shift of the pitting potential to noble direction which required to enable the chloride ions to reach a concentration in the double layer sufficient to overcome the inhibiting action of ketone group, there by destroying the passivity and initiation of pitting corrosion occurs. b) The presence of oxygen atom makes the adsorption take place through the transfer of its lone pair of electron to the metal surface forming coordinate type linkage. The increase resistance for pitting corrosion of carbon steel in Cl^- ion in presence of planets extracts can be explained on the basis that, these additives contain oxygen atom, the lone pair of electron on the oxygen atom is assumed to combine with H^+ ion produced from the water to form corresponding organic cation. So, the adsorption of planets extracts at the surface of the metal takes place via the lone pair of terminal oxygen atom of planets extracts.

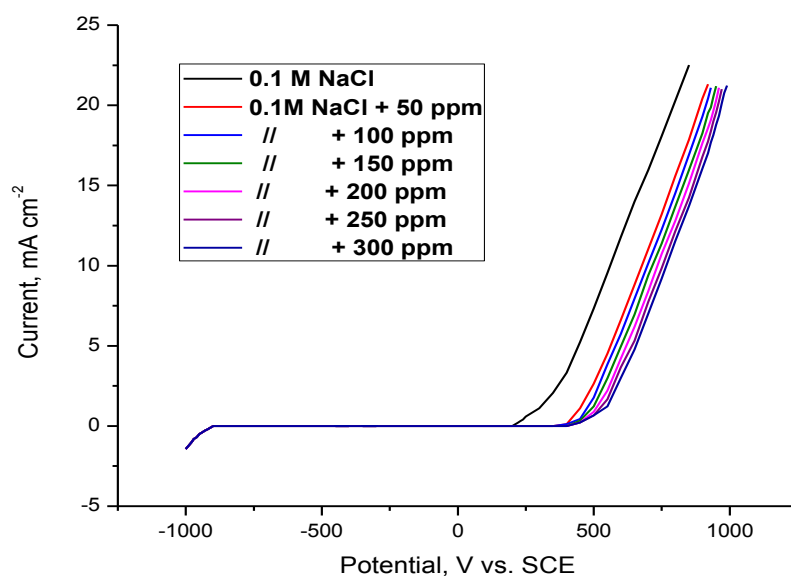


Figure 3. Potentiodynamic anodic polarization curves of carbon steel in 0.1M NaCl containing different concentrations of punica extract

3.4 Surface examination

Scanning electron microscope (SEM) was used to examine the surface of the original mechanically polished C-steel specimen and surface of the C-steel samples which had been naturally

immersed for 48 hours in test solution containing each 1 M HCl, 1 M HCl + 300 ppm from punica plant extract . After removing the individual specimens from the test solution, they were washed with bidistilled water. SEM micrographs for the mechanically polished C-steel specimen presented in Figure (4), the micrographs revealed the presence of coarse and fine polishing marks, the micrograph shows a characteristic inclusion which probably an oxide inclusion. Also, the surface was damage strongly and the grain boundaries edges appear clearly. Figure (5) shows the micrographs for the C-steel immersed in 1M HCl for 48 hours. The tested samples show an extensive etching composed of white and dark areas. According to Villamil et al [31], the white areas represent the ferrite phase and the dark areas represent the pearlite (mixture of ferrite and cementite (Fe₃C) in a lamellar form). Figure (6) shows scanning electron micrographs of the C-steel immersed in 1 M HCl + 300 ppm punica extract. This figure shows less extensive attack in the presence of the extract than in the uninhibited acid. It could be concluded that the extract components absorbed on the metal surface to form a thin layer by which metal was protected from corrosion.

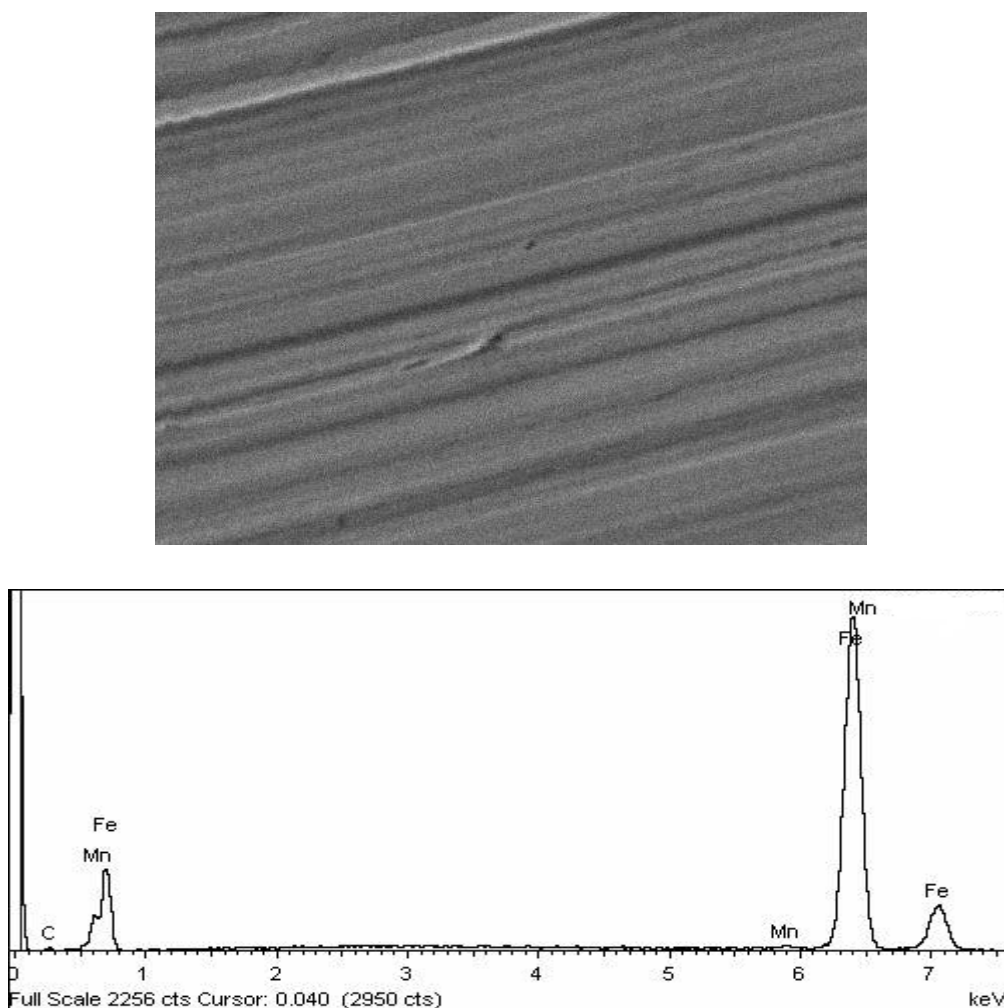


Figure 4. SEM and EDX images obtained for the freshly polished surface of carbon steel without any additives at 30°C

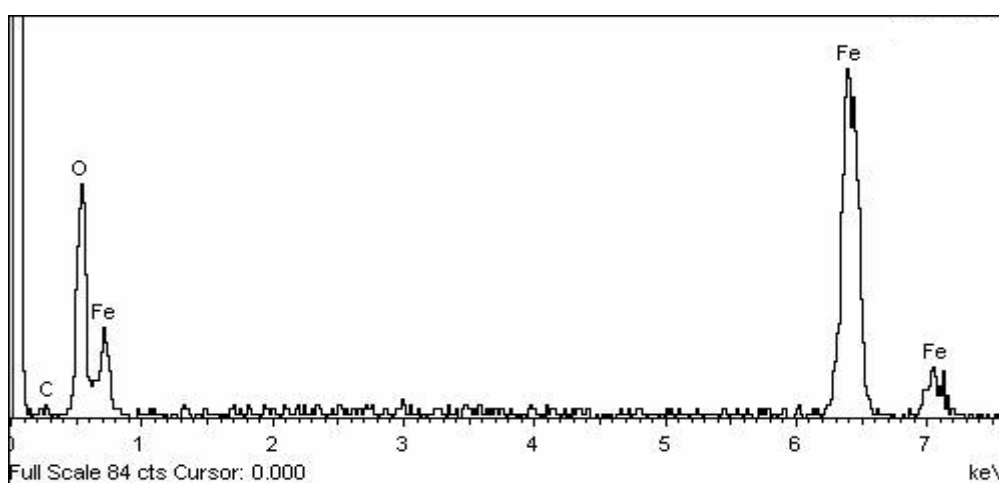
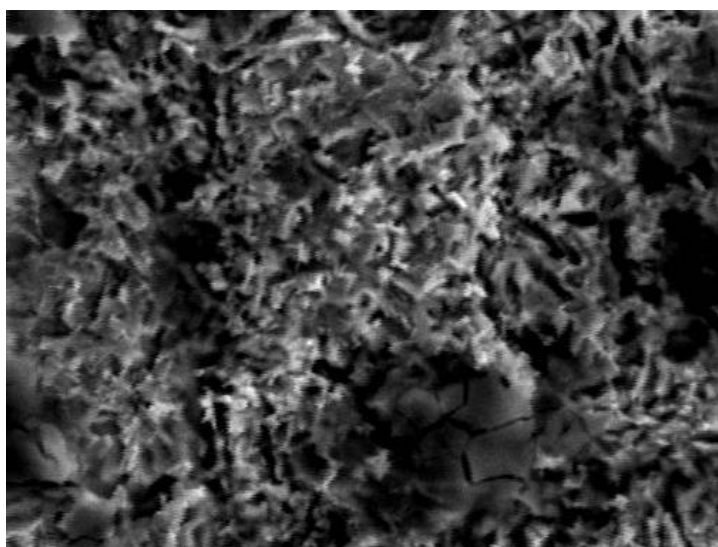
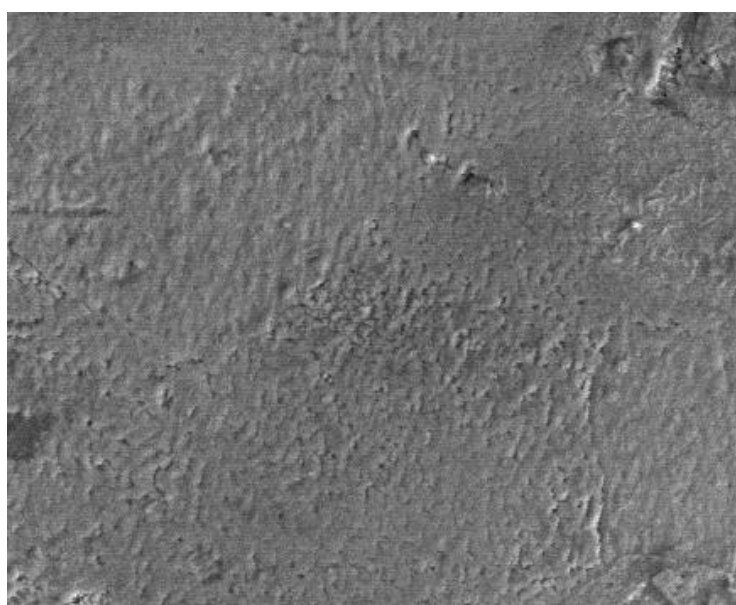


Figure 5. SEM images and EDX analysis obtained for the carbon steel surfaces immersed for 48 hours in aggressive solution (1 M HCl) at 30°C



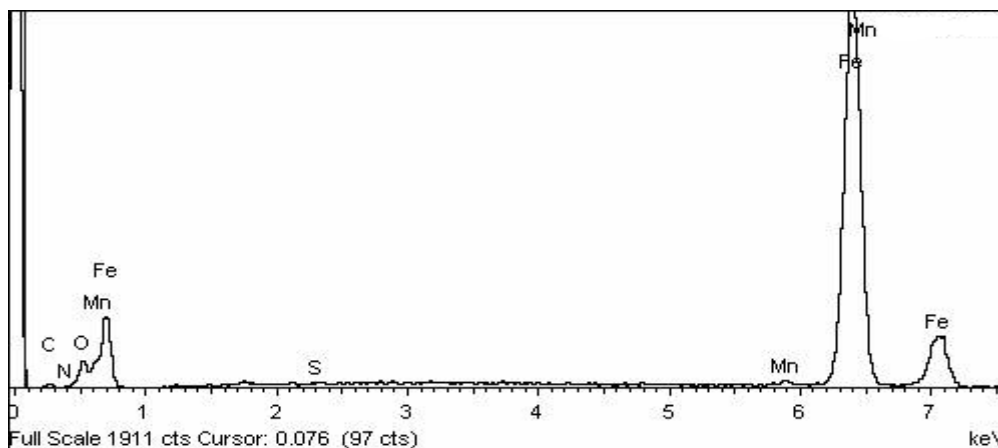


Figure 6. SEM and EDX images obtained for the carbon steel surfaces immersed for 48 hours in 300 ppm punica extract + (1 M HCl) at 30°C

3.5 Adsorption isotherms

Adsorption isotherms are very important for the understanding of the mechanism of organo-electrochemical reactions[32].The most frequently used isotherms are Langmuir, Frumkin, Temkin, parsons ...etc [33]. Assuming that corrosion inhibition was due to the adsorption of plants extracts, the degree of surface coverage, θ , was calculated from polarization method. Adsorption of organic adsorbate at the metal/solution interface can be represented by a substitutional adsorption process between organic molecules in the aqueous solution $Org_{(sol)}$ and water molecules on the metallic surface $Org_{(sol)}$ [34].



where $Org_{(sol)}$ and $Org_{(sol)}$ are the organic molecules in the aqueous solution and those adsorbed on the metallic surface, respectively, $H_2O_{(ads)}$ are water molecules on metallic surface , x is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate.

When equilibrium is reached in equation (6), it becomes possible to obtain different expressions for the adsorption isotherm plots. Data of θ were found to fit with the Langmuir [35] isotherm, given by:

$$C/\theta = 1/K_{ads} + C \tag{7}$$

$$\text{with } K_{ads} = 1/55.5 \exp (- \Delta G^o_{ads}/RT) \tag{8}$$

C is the concentration of the inhibitor in the bulk solution, K_{ads} the adsorption equilibrium constant, ΔG^o_{ads} the free energy of adsorption. Figures (7) show the plot of C/θ vs. C for punica extract. These plots give straight lines with slopes very close to unity. The regression is 0.9995. This means that there is no interaction between the adsorbed species on the electrode surface [36]. It is clear that the adsorption free energies are negative values, meaning that adsorption of thiazolodine-5-one derivatives onto the C-steel surface in HCl is spontaneous. On the other hand, it is found that kinetic-thermodynamic model of El-Awady et al [37] which has the formula:

$$\log (\theta / 1 - \theta) = \log K' - y \log C \tag{9}$$

Is valid and verify the present adsorption data Fig (8). The equilibrium constant of adsorption $K = K^{(1/y)}$, where $1/y$ is the number of the surface active sites occupied by plants extracts molecule and C is the bulk concentration of the inhibitor. Plotting $\log \frac{\theta}{1-\theta}$ vs $\log C$ for the punica extract is given in Fig. 8, where straight line relationship was obtained suggesting the validity of this model for the studied case. The values of K_{ads} , $1/y$ and ΔG°_{ads} calculated by the kinetic model and K_{ads} and ΔG°_{ads} calculated from Langmuir isotherm are given in Table (4) for plants extracts, respectively. The value of equilibrium constant obtained from this isotherm is about $9 \times 10^4 \text{ M}^{-1}$, suggesting a chemically adsorbed film on C-steel surface. The large values of ΔG°_{ads} and its negative sign indicate that the adsorption of the plants extracts on C-steel surface is proceeding spontaneously and is accompanied by a highly efficient adsorption [38]. It is noting that the value of y is less than unity. This means that the given inhibitors molecules will form multi-layer on C-steel surface. In general the values of ΔG°_{ads} obtained from El-Awady *et al.* model are comparable with those obtained from Langmuir isotherms. From Table (4) it is noted that ΔG°_{ads} values have a negative sign indicating that the adsorption process proceeds spontaneously and increase as the percentage inhibition increases.

Table 4. Inhibitor binding constants (K_{ads}), free energy of binding (ΔG°_{ads} , kJ mol^{-1}), and number of active sites ($1/y$) for inhibitor at 30°C

Inhibitor	Kinetic Model			Langmuir isotherm	
	$1/y$	$K_{ads} \times 10^{-4} \text{ M}^{-1}$	$-\Delta G^{\circ}_{ads}$, kJ mol^{-1}	$K_{ads} \times 10^{-4} \text{ M}^{-1}$	$-\Delta G^{\circ}_{ads}$, kJ mol^{-1}
Punica extract	1.25	6.6	38.0	12.6	39.7

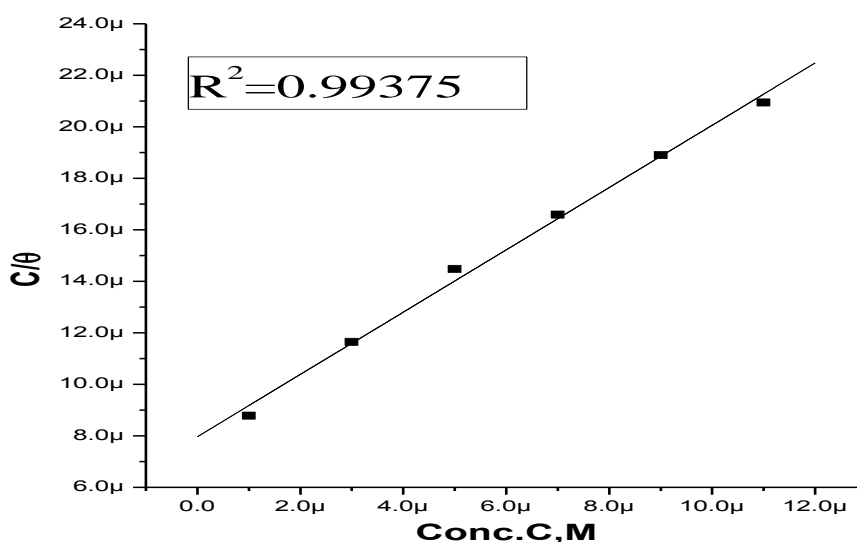


Figure 7. Langmuir adsorption isotherm for punica extract on C-steel in 1 M HCl at 30°C

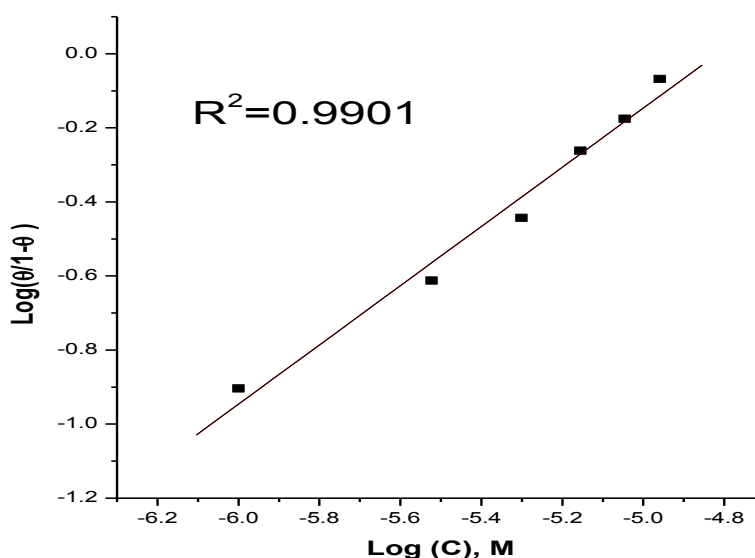


Figure 8. Curves fitting of corrosion data for C-steel in 1M HCl in presence of punica extract of inhibitors to the kinetic model at 30°C

3.6. Effect of Temperature

In this part the effect of temperature on the corrosion rate of carbon steel in 1 M HCl solution in the absence and presence of Punica as plants extract was studied. The behavior at different temperatures (30-50°C) was investigated by polarization measurements given in Table (5). The values of corrosion rate obtained at different temperatures permit the calculation of the Arrhenius activation energy, E_a^* , according to the following equation:-

$$\text{Log (corrosion rate)} = - E_a^*/2.303RT + A \tag{10}$$

Where A is the Arrhenius pre exponential factor, it is a constant depends on a metal type and the electrolyte, R is the universal gas constant and T is the absolute temperature. This form of Arrhenius equation is applicable in our case when we plot the (log corrosion rate) ($\text{mg cm}^{-2} \text{min}^{-1}$) against the reciprocal of absolute temperature, (1/T), are shown graphically in Figure (9). The values of the activation energies, E_a^* , were calculated from the slopes of these lines in the absence and presence of plants extracts in 1 M HCl solution and are given in Table (5). These values indicate that the presence of plants extract increases the activation energy of the metal dissolution reaction and that the process is activation controlled. It is clear that the value of E_a^* in the presence of inhibitors are higher than those in uninhibited acid solution. The results agreed with that of previous study reported by Fouda *et al.* for C-steel in 1 M HCl [39]. Ateya *et al.*[40] found that the activation energy of free acid equals 51.4 kJ mol^{-1} for iron in 5N H_2SO_4 solution which was identical to that reported by Hudson *et al.*[41]and by selim *et al.*[42], on the other hand Maitra and Singh [43] found that the activation energy of low carbon steel in 1N H_2SO_4 solution is equal to 4.81 kJ mol^{-1} .

Generally one can say that the nature and concentration of electrolyte affect greatly the activation energy for the corrosion process. the addition of 300 ppm of punica plant extract to the solution increases the activation energy (E_a^*), as shown in Table (5) and the extent of the increase is

proportional to the inhibition efficiency of the inhibitor, indicating that the energy barrier for the corrosion reaction increases in the presence of these additives. This means that by addition of the inhibitor in the acid solution, the corrosion reaction will be further pushed to surface sites that are characterized by higher values of activation energy E_a^* indicating that carbon steel corrosion occurs at the uncovered part of the surface. Thus, adsorption of the inhibitor was assumed to occur on the higher energy sites [44], the presence of inhibitor, which results in the blocking of the active sites, must be associated with an increase in the activation energy, E_a^* which indicates the physical adsorption or weak chemical bonding between the inhibitor molecules and C-steel surface [45].

An alternative form of Arrhenius equation is the transition state equation:

$$\text{Rate} = \frac{RT}{Nh} \exp(\frac{\Delta S^*}{R}) \exp(-\frac{\Delta H^*}{RT}) \quad (11)$$

where h is Planck's constant, N is the Avogadro's number, ΔS^* is the entropy of activation, ΔH^* is the enthalpy of activation. A plot of $\log(\text{Rate}/T)$ vs. $(1/T)$ (Fig. 10) gives a straight line with a slope of $(-\Delta H^*/2.303R)$ and an intercept of $(\log R/Nh - \Delta S^*/2.303R)$. The calculated values are given in Table (5). The values of ΔH^* are positive indicating that the process is endothermic one. The values of E_a^* are larger than the analogous values of ΔH^* indicating that the corrosion process must involve a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume. Moreover, the average value of difference $(E_a^* - \Delta H^*)$ is about 2.8 kJ mol^{-1} which approximately around the average value of RT (2.69 kJ mol^{-1}), indicating that the corrosion process is uni-molecular reaction as it is characterized by the following equation [46]:

$$E_a^* - \Delta H^* = RT$$

ΔS^* in the absence and presence of additives is larger and has negative values meaning that a decrease in disordering takes place in going from reactants to the activated complex [46-49]. It is obviously that the ΔS^* shifts to more negative values (more ordered behavior) with increasing protection efficiency. This can be explained that the inhibitor species may involve in the activated complex of the corrosion reaction leading to more ordered systems.

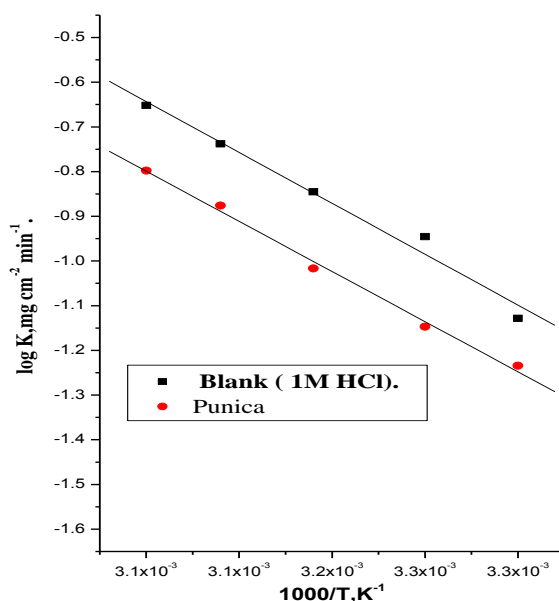


Figure 9. log corrosion rate vs.1/T for C-steel in presence of punica extract at210 min.

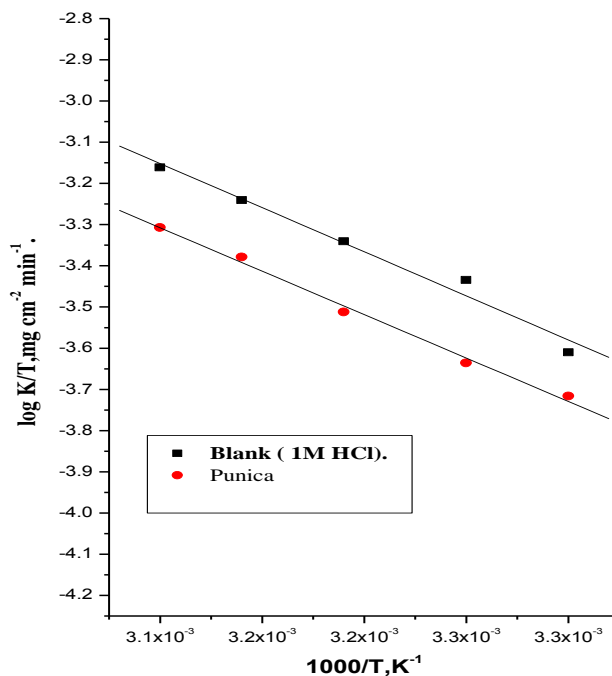


Figure 10. log corrosion rate/T vs.1/T for C-steel in presence of punica extract at 210 min

Table 5. Activation parameters of the dissolution of C-steel in 1 M HCl in the absence and presence of 300 ppm of punica extract

Inhibitor	Activation parameters		
	-E _a [*] , kJ mol ⁻¹	ΔH [*] , kJ mol ⁻¹	-ΔS [*] , J mol ⁻¹ K ⁻¹
Free acid	43.3	40.5	130.8
Punica	46.1	43.3	135.8

3.7. Chemical Structure of Inhibitor and Corrosion Inhibition

Inhibition of corrosion of carbon steel in 1M HCl solution by the investigated punica as measured by chemical and electrochemical measurements was found to depend on both the concentration and the nature of the extract. The observed corrosion date in presence of the extract, namely. The decrease of corrosion rate with increasing the concentration of the extract, The linear variation of weight loss with time, The parallel shift in Tafel lines to higher potential values, and the decrease in corrosion inhibition with increasing temperature. These observations indicate that the corrosion inhibition is due to adsorption of the extract components at the solution/interface. The nature of extract interaction on the metal surface during corrosion inhibition can be explained in terms of its adsorption characteristics; however, inhibition efficiency of extract components depends on many factors, which include the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes. The inhibition activity was due to the adsorption ability of the extract which was

confirmed by Langmuir adsorption isotherms. The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the extract. The anodic inhibition may be due to the adsorption of principle phytochemical constituents present in the extract through ring oxygen atom and oxygen atoms of –OH group in dihydroxycoumarins and forms a protective coating on the metal surface, thus prevents the contact between the metal and corrosive acid. The protonated species of the principle constituents may compete with H⁺ ion reduction and may control the cathodic reaction.

4. CONCLUSIONS

The investigated punica plant extract is good inhibitor and act as mixed type inhibitor for carbon steel corrosion in HCl solution. The results obtained from all measurements showed that the inhibiting property increases with increasing inhibitor concentration. Double layer capacitances decrease with respect to blank solution when the plant extract is added. This fact confirms the adsorption of plant extract molecules on the carbon steel surfaces. The adsorption of extract on carbon steel surfaces in HCl solution follows Langmuir isotherm. The negative values of ΔG°_{ads} show the spontaneity of the adsorption process. The values of inhibition efficiencies obtained from the different independent techniques showed the validity of the results. The plant extract shift the pitting potential to more positive values, indicating the inhibiting effect of these compounds. Quantum-chemical calculations are in a good agreement with the experimental data obtained by potentiodynamic polarization and EIS techniques.

References

1. G. Schmitt, *Br. Corros. J.*, 19(4) (1984) 165.
2. A. Y. El-Etre, *Appl. Surf. Sci.* 252 (2006) 8521.
3. A. Bouyanzer; Hammouti, B.; Majidi, L. *Mater. Lett.* 60(2006) 2840.
4. M Benabdellah; M.Benkaddour; B.Hammouti; M. Bendahhou; A.Aouniti, *Appl. Surf. Sci.* 252(2006) 6212.
5. E. Chaieb, A. Bouyanzer, B. Hammouti, M. Benkaddour, *Appl. Surf. Sci.* 246(2005) 199
6. B.Müller, *Corros. Sci.* 44(2002) 1583.
7. Y. Zhao; Q. Li; B. Liang; P. Hou *Appl. Surf. Sci.* 252(2005) 1245
8. A. Y. El Etre, M Abdallah; Z. E El-Tantawy, *Corros.Sci.*, 47(2005), 385.
9. H. Ashassi-Sorkhabi; B.Shaabani; D.Seifzadeh, *Electrochim.Acta* 50 (2005) 3446.
10. A.S.Fouda, S.Rashwan, Y.K.Elghazy, *Inter.J. Adv. Res.* 1(10) (2013) 568-589
11. A.S. Fouda, G.Y. Elewady, K.Shalabi, S. Habbouba, *J. Mater. Environ. Sci.* 5 (3) (2014)
12. F. Bentiss, M. Lebrini and M. Lagrenee, *Corros. Sci.*, 47(2005) 915.
13. M. Willars, N.A. Hampson, A. Atkinson and A. Marshall. *Surf. Technol.*, 4(5) (1976) 465.
14. G. Schmitt and B. Olbertz *Werk Stoffe. Korros.* 29 (1978) 45.
15. J.M. Saveant and Sukhac Binh, *J. Org. Chem.*, 42 (1977) 124.
16. A. Veres, G. Reinhard and E. Kalman, *Br. Corros. J.*, 27 (1992) 147.
17. S. Kertit and B. Hammouti, *Appl. Surf. Sci.*, 93(1) (1996) 59.

18. M. Elachouri, M.S. Hajji, M.Salem, S. Kertit, J. Aride, R. Coudert and E. Essassi, *Corrosion*, 52(2) (1996) 103.
19. A.M.S. Abdennabl, A.I. Abdullhadi, S.T. Abu-Orabi and H. Saricimen, *Corros. Sci.*, 38(10) (1996) 1791.
20. MS. Muralidharan, B. Ramesh Babu, S. Venkatakrishna Iyer and S. Rengamani, *J. Appl. Electrochem.* 26(3) (1996) 291.
21. A.E. Stoyanova, E.I. Sokolova and S.N. Raicheva, *Corros. Sci.*, 39(9) (1997) 1595.
22. D.D. Macdonald, *Transient Techniques in Electrochemistry*, (New York, NY: Plenum Press) (1977).
23. W. J. Lorenz, and F. Mansfeld, *Corros.Sci.*, 21 (1981) 647.
24. P. M. Aziz, H. P. Godard; *Corrosion Ind. Eng. Chem.*, 44, (1952), 179.
25. I. L. Rozenfeld; "Corrosion Inhibitors", New York Mc Graw-Hill Inc., (1981).
26. F. Bentiss, M. Lagreeneel, B. Mernariand, H. El Attri; *J. Appl. Electrochem.*, 29 (1999)1073.
27. J. M. Shyes; *Br. Corros. J.*, 25 (1990) 175.
28. J. G. N. Thomas; *Proceedings 5th European symposium on corros. Inhibitors. An n Univ. Ferrara, N. S sez, V. Suppl. No. 8 (1980) 453.*
29. W. F. Bogaerts, A. A. Van Hauteand; *J. Nucl. Mater*, 115, (1983) 339.
30. S. Samkarapapavinasam, M. F. Ahmed; *J. Appl., Electrochem.*, 22 (1992) 390.
31. R.F.V. Villamil, P. Corio, J.C. Rubin and S.M.I. Agostinti *J. Appl. Electrochem.*, 535 (2002)75
32. S. Bilgic and N. Caliskan, *Appl. Surf. Sci.*, 152 (1999) 107.
33. G.B. Ateya, B. El-Anadouli and F.El-Nizamy, *Corros. Sci.*, 24 (1984) 509.
34. I. Langmuir, *J. Am. Chem. Soc.*, 39 (1947) 1848.
35. A.J.Bard, L.R.Faulkner, *Electrochemical Method*, John Wiley&Sons, NY, 1980, P.517.
36. Y.A. El-Awady and A.I. Ahmed, *J. Ind.Chem.*, 24A (1985) 601.
37. R.F.V. Villamil, P. Corio, J.C. Rubin and S.M.I. Agostinti, *J. Appl. Electrochem.*, 535 (2002) 75.
38. O.L. Riggs, K.L. Morrison and D.A. Brunzell, *Corrosion NACE*, 35 (1979) 356.
39. A.K. Mohammed, H.A. Mostafa, G.Y. El-Ewady and A.S. Fouda, *Port. Electrochim. Acta* 18(2000) 99.
40. B.G. Ateya, B.M. Abou El Khair and R. Al-Qamimi, *Corros. Sci.*, 22 (1982) 717
41. R.M. Hudson, T.J. Buther and C.J. Warning, *Corros. Sci.*, 17 (1977) 571
42. M. Selim, A. Yassin and B. Ateya, *Corros. Sci.*, 17 (1977) 923.
43. A. Maitra and G. Singh, *Indian J. Chem.*, 29 (1981) 338
44. O.L. Riggs and R.M. Hurd, *Corrosion*, 23 (1967) 252
45. X.H. Li and G.M. Mu, *Appl. Surf. Sci.*, 252 (2005) 1254.
46. M.K. Gomma and M.H. Wahdan, *Materials Chemistry and Physics*, 39 (1995) 209.
47. J.M. Bastidas, A.J. Dedamborenea Vazquez, *J. Appl. Electrochem.*, 27(3) (1997) 345-349.
48. J.M. Bastidas, J.L. Polo, E. Cano, *J. Appl. Electrochem.* 30(10) (2000) 1173
49. J.M. Bastidas, J.L. Polo, E. Cano, C.L. Torres., *J. Mat. Sci.*, 35(1) (2000).