Pomelo leaves extract as a green corrosion inhibitor for carbon steel in 0.5 M HCl

T.R. Ali, T.A. Salman^{ID}* and M.S. Shihab

Department of Chemistry, College of Science, Al-Nahrain University, P.O.Box: (64055)
Jadriah, Baghdad, Iraq

*E-mail: dr.tag_s@yahoo.com

Abstract

The current work presents a simple, low-cost, and eco-friendly method for carbon steel corrosion retardation in 0.5 M HCl in a temperature range of 293–313 K. The pomelo plant, which is widespread all over the world, is regarded as a rich source of phytochemical compounds. The maceration method was adopted for pomelo leaf extraction (PLE) and *n*-hexane was used as a solvent (HPLE). The extract components were identified using Gas Chromatography–Mass Spectroscopy (GC-MS) and Fourier transform infrared spectroscopy (FTIR). These characterization methods confirm that HPLE is a rich source of phytochemicals such as alcohols, esters, ethers, alkenes, and ketones. The corrosion investigation was accomplished by electrochemical measurements and scanning electron microscopy (SEM). Potentiodynamic polarization curves for different inhibitor concentrations (0, 25, 50, 75, and 100 ppm) showed that HPLE behaves as a mixed type inhibitor with a maximal inhibition efficiency of about 82% at 100 ppm. The metal surface study was carried out by scanning electron microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX). The data obtained from SEM and EDX data are compatible with those obtained from the electrochemical experiments. Metal surface studies proved the presence of a protective film that is constructed by adsorption of inhibitor molecules on the metal surface. Thermodynamic adsorption isotherm calculations show that the adsorption of HPLE on the mild steel surface obeys the Langmuir adsorption isotherm.

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Introduction

Carbon steel (CS) alloys consist fundamentally from iron and carbon with trace additives of other chemical elements. These alloys are widely used for several aspects of life owing to their attractive properties such as good electrical conductance, heat transfer capability, good magnetic properties, and soft texture. Corrosion of CS leads to wastage of most of its properties, which causes a great disadvantage.

In general, a corrosion process can be defined as a chemical or electrochemical reaction between matter (usually metals or alloys) and their environments, causing destruction of their properties. So the corrosion processes are divided into two types according to the

environment: chemical corrosion takes place when the metal corrodes in a non-electrolyte environment, such as metal oxidation in hot air, while electrochemical corrosion occurs in an electrolyte solution accompanied by charge transfer across the metal/solution interface [1].

In agreement with the thermodynamic laws, metals tend to access the oxidized state and return to the ore form, which represents a lower energy state. Therefore, the corrosion phenomenon is a spontaneous and irreversible process, Equation 1.

In conjunction with release of electrons from the metal (oxidation process or anodic reaction), electron consumption takes place from the other side (reduction process or cathodic reaction). In an acid environment, the released electrons are captured by protons (H^+), so the cathodic reaction occurs as shown in Equation 2:

In an alkaline or neutral environment, the cathodic reaction occurs by oxygen reduction as shown in Equation 3:

Both reactions (oxidation and reduction) occur on the metal surface at the same rate to ensure that the net current is equal to zero [2]. Since the 40 s of the past century, the issue of metal corrosion has received considerable interest from researchers because it is the largest destruction factor of equipment. In order to minimize corrosion effects, several trends with different methods have been adopted for prevention or reduction of corrosion processes, such as:

- electrochemical protection methods, such as cathodic or anodic protection;
- amelioration of the nature of metals by modifying the additives in such a way as to increase the corrosion resistance;
- building a protective layer on the surface of a metal or alloy;
- modification of the corrosive environment toward a non-aggressive state by addition of a small amount of a chemical substance, the so-called corrosion inhibitor.

Corrosion inhibition is the most widely used anti-corrosion method among such methods because of its simplicity, economic advantage, and effectiveness [3]. Green corrosion inhibitors are superior to synthetic organic inhibitors because they are eco-friendly, biodegradable, cheap, renewable, and readily available [3–5]. The pomelo plant belongs to the citrus family, which has evergreen leaves and is regarded as a rich source of phytochemicals [6, 7].

In this work, pomelo leaves were extracted by the maceration method with n-hexane as the solvent. Subsequently, this extract was examined as a corrosion inhibitor for carbon steel

in acid media using the potentiodynamic polarization method and a scanning electron microscope (SEM).

Experimental

Specimen preparation

The chemical components in weight percentage (wt.%) in a commercial rectangular plate of carbon steel were determined to be as follows: C = 0.370%, Si = 0.230%, S = 0.014%, Mn = 0.670%, Cu = 0.160%, Ni = 0.059%, Ti = 0.013%, Co = 0.009%, Cr = 0.078% and the remainder iron (Fe). Afterward, the steel plate was segmented into circular specimens with dimensions of ($2 \times 20 \text{ mm}^2$) and they were polished with emery papers 180, 320, 1000, 2500, and 4000. Subsequently, the polished specimens were degreased with ethanol and etched with acetone, then washed with distilled water and left to dry at room temperature.

Solution preparation

1 L of 0.5 M HCl to be used as the corrosive solution was prepared by adding 41.75 ml of 36% HCl (11.975 M) to the appropriate volume of distilled water.

Inhibitor preparation

Pomelo leaves were collected from the orchards of Diyala Governorate, specifically from Baquba city, and afterward extracted by n-hexane through the following steps:

- the pomelo leaves were washed by tap water in order to remove all dust and other impurities and left for about 72 h to dry under the sun, thereafter ground by an electric grinder;
- twenty grams of PL powder were macerated in 125 ml of n-hexane and refluxed with stirring for about 72 h at 40°C. Then, the mixture was filtrated through Whatman filter paper and the solvent was evaporated at 40°C, then stored at 4°C for the subsequent steps;
- solutions (25, 50, 75, and 100 ppm of HPLE) were prepared by dissolving the appropriate quantity in 20 ml of DMSO, then decanting into 1 L of 0.5 M HCl.

Gas Chromatography – Mass Spectroscopy (GC-MS) measurement

The chemical components of HPLE were identified by the GC-MS technique, where a computerized control apparatus (QP 2010 Plus SHIMADZU) was used. The analysis process started with the injection of 2 μl of HPLE using a micro syringe at 70 eV and helium gas as a carrier. After 30 min (the run time), the data of the unknown sample was compared with the database library.

Fourier Infrared Spectroscopy

Functional groups that exist in HPLE were identified through FTIR spectroscopy within the spectral range of $4000\text{--}500 \text{ cm}^{-1}$ using a Shimadzu IR Affinity 1 (Japan) spectrometer.

Electrochemical polarization measurement

The ability of HPLE to provide corrosion inhibition was estimated by the potentiodynamic polarization method. In this method, three fundamental parts that were used:

1. Corrosion cell: a flat-bottomed container made of Pyrex glass containing three types of electrodes immersed in the solution of corrosion. The three electrodes are:
 - A working electrode (WE) was a circular carbon steel specimen under study with a hole surface area of 1 cm that permits the solution to contact the metal specimen.
 - A saturated calomel electrode (reference) (RE) to measure the working electrode potential.
 - A platinum electrode (axillary) to complete the cell circuit.
2. Potentiostat/galvanostat at 200Mlb (2007) Germany apparatus. This device controlled the applied potential on the WE relative to the RE, and measured the current between the WE and the auxiliary electrode.
3. A computer connected to the potentiostat for data processing and recoding all the corrosion parameters.

In the polarization test, the open circuit potential (OCP) is achieved first, where the working electrode is kept for about 15 min to attain a steady state. Secondly, starting from the OCP potential, the polarization test is performed by polarizing the WE in the range of 200 mV at a scan rate of 2 mV/s, and then the electrochemical parameters are recorded.

Scanning electron microscope (SEM)

The FEI Inspect-S50 apparatus (Japan) was used to study the metal surface morphology and assure the adsorption of inhibitor molecules on it.

Result and Discussion

Gas Chromatography–Mass Spectrometry (GC-MS)

The GC-MS chromatogram of HPLE exhibits that about eighteen phytochemicals are present in this extract. Comparison of the chemical library with this chromatogram reveals there are many organic compounds with various functional groups in the extract. The presence of heteroatoms, heterocyclic and multiple-bond organic compounds provides a rich electronic density which enhances the interaction with metal orbitals, whereas improving the adsorption on the metal surface [3, 8]. The GC-MS chromatogram of HPLE is shown in Figure 1.

Figure 1. GC-MS Chromatogram of HPLE.

As it is noticeable in Figure 1, the highest intensity among these lines is found for line 3 which belongs to *o*-xylene, whereas the other lines vary from medium to weak intensity. The nomenclature, retention time, chemical formula, molecular weight and structure of characteristic compounds are demonstrated in Table 1.

Table 1. The major compounds identified in HPLE.

No.	Name of compound	RT (min)	Chemical formula	MW (g/mole)	Structure
1	butan-1-ol	2.108	C ₄ H ₁₀ O	74.12	
2	cyclohepta-1,3,5-triene	2.650	C ₇ H ₈	92.14	
3	<i>o</i> -xylene	4.025	C ₈ H ₁₀	106.17	
4	hepta-2,5-diyn-4-one	4.400	C ₇ H ₆ O	106.12	
5	6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane	5.842	C ₁₀ H ₁₆	136.24	
6	(<i>E</i>)-2-(hydroxyimino)ethyl acetate	6.175	C ₄ H ₇ NO ₃	117.10	
7	1-(<i>p</i> -tolyl)pentan-1-one	6.642	C ₁₂ H ₁₆ O	176.26	
8	prop-2-yn-1-ylcyclopentane	7.242	C ₈ H ₁₂	108.18	
9	vinyl methacrylate	13.317	C ₆ H ₈ O ₂	112.13	
10	methyl 2-hydroxy-2-methylbutanoate	19.350	C ₆ H ₁₂ O ₃	132.16	
11	2-(propylsulfonyl)acetonitrile	21.158	C ₅ H ₉ NO ₂ S	147.19	
12	2-(3-(oxiran-2-yl)propyl)-3-(oxiran-2-ylmethyl)oxirane	21.300	C ₁₀ H ₁₆ O ₃	184.24	

No.	Name of compound	RT (min)	Chemical formula	MW (g/mole)	Structure
13	allyl butyl oxalate	21.542	C ₉ H ₁₄ O ₄	186.21	
14	butyl propyl oxalate	22.450	C ₉ H ₁₆ O ₄	188.22	
15	(E)-undec-2-en-4-ol	23.317	C ₁₁ H ₂₂ O	170.30	
16	(E)-2-(hydroxyimino)ethyl acetate	24.150	C ₄ H ₇ NO ₃	117.10	
17	2,3,4-trimethylheptane	24.683	C ₁₀ H ₂₂	142.29	
18	(2E,7E)-4,6-dimethylnona-2,7-dien-5-one	27.733	C ₁₁ H ₁₈ O	166.26	

Fourier Infrared Spectroscopy

FTIR spectroscopy was used to detect the functional groups that belong to phytochemicals that have been diagnosed previously in GC-MS chromatograms. As it is evident in Figure 2, FTIR analysis gave results that agreed with those obtained by the previous method, where HPLC encompassed an assortment of phytochemicals. The broad peak in the range between 3600–3320 cm⁻¹ is assigned to the alcoholic OH group, whereas the more intense peak at 1762.28 cm⁻¹ indicates the presence of carbonyl compounds [9]. The other important peaks are listed in Table 2.

Figure 2. FTIR spectrum of HPLC.

Of significant functional groups in Figure 2, there is an alcoholic OH group which is represented by a broad peak in the range from 3736–3200 cm^{-1} . A peak at 1718.24 cm^{-1} is assigned to the carbonyl group in ester [9]. The other peaks are shown in Table 2.

Table 2. The main bands in HPLE.

No.	Peak number, cm^{-1}	Bond	Group assignment
1	3600–3200	O–H	Alcoholic
3	2921.13	C–H	Asymmetric $-\text{CH}_3$
4	2854.88	C–H	Symmetric $-\text{CH}_2-$
5	1726.28	C=O	Carbonyl compounds
8	1451	C–H	Asymmetric bending $-\text{CH}_2-$
9	1372	C–H	Symmetric bending $-\text{CH}_3$
11	1243.43	C–O	Stretching of C–O bond in ester
12	1169.81	O–C	Stretching of O–C bond in ester
14	977.86	=N–O	C=N–O stretching in oxime
15	522.77	O–H	Bending O–H (alcohol)

Corrosion study

Potentiodynamic polarization (PDP) curves

Figure 3 illustrates the polarization curves of potential E (mV) against $\log(i)$ (i is the current density in $\mu\text{A}/\text{cm}^2$) for carbon steel in 0.5 M HCl in the absence and in the presence of various concentrations of the inhibitor in the temperature range of 293–313 K.

As it is seen in these curves, with addition of HPLE, the corrosion potential varies in the active or noble direction. This indicates that HPLE retards both the hydrogen evolution process and metal dissolution. So, the HPLE can be classified as a mixed corrosion inhibitor [10]. The kinetic parameters of corrosion, such as E_{corr} , i_{corr} , cathodic and anodic Tafel slopes, corrosion rate, and penetration rate, that are obtained from the polarization curves are listed in Table 3.

Figure 3. Polarization curves of carbon steel in 0.5 M HCl without and with different concentrations (25, 50, 75, 100 ppm) of HPLE in the temperature range of 293–313 K.

Table 3. Corrosion parameters of carbon steel in 0.5 M HCl without the inhibitor and in the presence of different concentrations (25, 50, 75 and 100 ppm) of HPLE in the temperature range of 293–313 K.

Inh. (ppm)	<i>T</i> (K)	$-E_{\text{corr}}$ (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	<i>CR</i> (g/m ² d)	<i>PR</i> (mm/Y)
0	293	508	42.6	10.8	0.51
	298	500	43.3	10.9	0.56
	303	494	53.2	13.3	0.615
	308	495	64.2	16.3	0.755
	313	487	96.3	23.8	1.100
25	293	491	16.56	4.12	0.192
	298	489	17.11	4.25	0.197
	303	486	21.9	5.45	0.253
	308	489	28.05	6.89	0.32
	313	493	47.8	11.88	0.55
50	293	473	13.07	3.25	0.151
	298	479	14.9	3.7	0.172
	303	479	19.01	4.73	0.22
	308	492	24.51	6.1	0.283
	313	500	43.6	10.84	0.5
75	293	473	8.6	2.14	0.1
	298	486	10.7	2.7	0.125
	303	483	13.51	3.36	0.156
	308	484	18.92	4.7	0.22
	303	489	36.4	9.1	0.422
100	293	472	3.2	0.8	0.037
	298	479	5.5	1.4	0.065
	303	480	8.75	2.2	0.1
	308	481	13.98	3.5	0.16
	313	484	27.3	6.8	0.32

As it is noticeable in the above table, at certain inhibitor concentrations the inhibition efficiency decreases, the electrochemical impedance of the metal decreases, the corrosion potential shifts to more negative values, and the corrosion rate increases. In contrast, as

inhibitor concentration increases at certain temperatures, the corrosion potential shifts in the noble direction and the corrosion rate decreases [11, 12].

Effect of temperature

The temperature effects on carbon steel corrosion in the range of 293–313 K was studied in the absence and in the presence of different HPLE concentrations. Throughout this study, the kinetic parameters of corrosion were calculated through Arrhenius Equation 4.

$$\log i_{\text{corr}} = \frac{-E_a}{RT} + \log A \quad (4)$$

Where, i_{corr} is the corrosion current, E_a is the activation energy of the corrosion process, R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature (K), and A is the preexponential factor [12]. The slope of the straight line that arises by plotting $\log(i)$ against $1/T$ represents the fraction of ($E_a/2.303R$), while the intercept of the straight lines with the y axis is equal to $\log(A)$. From this diagram, the activation energy E_a and the preexponential factor were calculated and listed in Table 4. As seen from the activation energy values shown in Table 4, it increases with an increase in the inhibitor concentration, which is evidence of the corrosion process inhibition. The protective film formed upon adsorption of inhibitor molecules on the metal surface could increase the energy gap (E_a) between the reactant and the activated complex that exists in the pathway of corrosion products formation, consequently the corrosion process is hindered [13].

The enthalpy of activation ΔH_a and the entropy of activation ΔS_a could be calculated by application of an alternative formula of the Arrhenius equation:

$$i_{\text{corr}} = \left(\frac{RT}{Nh}\right) \cdot \exp\left(\frac{\Delta S_a}{R}\right) \cdot \exp\left(\frac{-\Delta H_a}{RT}\right) \quad (5)$$

Where N is Avogadro's number and h is Planck constant ($h = 6.626 \cdot 10^{-34}$ J·s). The last formula of Arrhenius equation can be rewritten as the equation below [13]:

$$\log\left(\frac{i_{\text{corr}}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right) \quad (6)$$

By plotting $\log(i_{\text{corr}}/T)$ against $1/T$ (as seen in Figure 5), the enthalpy of activation ΔH_a and entropy of activation ΔS_a can be calculated [14].

Figure 4. Arrhenius plot of $\log i_{\text{corr}}$ vs. $1/T$ for carbon steel corrosion in 0.5 M HCl in the presence and in the absence of different concentrations (25, 50, 75 and 100 ppm) of HPLE in the temperature range of 293–313 K.

Figure 5. Arrhenius plot of $\ln (i_{\text{corr}}/T)$ vs. $(1/T)$ for carbon steel corrosion in 0.5 M HCl in the presence and in the absence of different concentrations (25, 50, 75 and 100 ppm) of HPLE in the temperature range of 293–313 K.

The activation enthalpy and entropy were calculated and listed in Table 4. Obviously, as it is seen in this table, the activation enthalpy is endothermic and it increases as the inhibitor concentration increases, which delays the corrosion process. Additionally, there is an increase in activation entropy with an increase in inhibitor concentration, which means an increase in irregularity. It is worthwhile to note that the regularity (entropy decrease)

conforms to the transformation of reactants to activated complexes in the rust formation pathway. Where the activated complex exemplifies the associated state more than the dissociated state, consequently, the increase in entropy refers to the waning of the corrosion process [15].

Table 4. Arrhenius parameters for carbon steel corrosion in 0.5 M HCl with and without different concentrations of HPLE in the temperature range of 293–313 K.

<i>Inh.</i> (ppm)	E_a (kJ·mol ⁻¹)	A (molecules·cm ⁻² ·s ⁻¹)	ΔH_a (kJ·mol ⁻¹)	$-\Delta H_a$ (J/K·mol)
0	13	$6.3 \cdot 10^{23}$	28	233
25	17	$1.3 \cdot 10^{24}$	37	202
50	19	$1.8 \cdot 10^{24}$	42	197
75	23	$2.6 \cdot 10^{24}$	50	172
100	35	$5 \cdot 10^{24}$	77	87

Inhibition efficiency (%E) and surface coverage (θ)

The inhibition efficiency (%E) of HPLE in 0.5 M HCl solution was studied by application of Equation 7:

$$\%E = \left[1 - \frac{i}{i^0}\right] \cdot 100 \quad (7)$$

Where i and i^0 are the corrosion current densities in the presence and absence of HPLE, respectively [14]. The surface coverage (θ) is calculated by the relationship below [15, 16]. The inhibition efficiency and surface coverage (for different inhibitor concentrations) are listed in Table 5.

$$\theta = \left[1 - \frac{i}{i^0}\right] \quad (8)$$

Table 5. Inhibition efficiency %E and surface coverage θ of HPLE at a different concentration in the temperature range of 293–313 K in 0.5 M HCl.

<i>T</i> (K)	25 ppm		50 ppm		75 ppm		100 ppm	
	%E	θ	%E	θ	%E	θ	%E	θ
293	61.12	0.6112	69.32	0.6932	79.8	0.798	92.31	0.9231
298	60.48	0.6048	65.59	0.6559	75.3	0.753	87.3	0.873
303	58.83	0.5883	64.27	0.6427	74.6	0.746	82.7	0.827
308	56.31	0.5631	61.82	0.6182	70.53	0.7053	78.2	0.782
313	50.36	0.5036	54.7	0.547	62.2	0.622	71.6	0.716

The results in Table 5 confirm the previous investigations that the inhibition efficiency of the inhibitor, and the surface coverage of the metal decreased with an increase in temperature. This can be interpreted by the fact of the decrease in thermal stability of inhibitor adsorption on the metal surface with an increase in temperature. On the other hand, ionic mobility and hydrogen diffusion have a considerable role in enhancing the corrosion process. These factors are directly proportional to temperature, so they increase as the temperature increases. Meanwhile, the corrosion increases and the inhibition efficiency decreases [17].

Thermodynamics of Corrosion

Inhibitor adsorption

The inhibition mechanism is implemented through adsorption of inhibitor molecules on the metal/solution interface from the corrosive medium. The electronic density centers in these molecules play a vital role in the adsorption process. However, adsorption may occur via one of the four types of metal-inhibitor interactions: 1) the charged parts on the metal surface and inhibitor molecules interact through electrostatic attraction; 2) the donor-acceptor interactions between the metal and the uncharged electron pair that exists in the inhibitor molecules; 3) interaction between the metal and the π -electrons present in the inhibitor; 4) a combination of 1 and 3 [14].

Thermodynamic adsorption isotherm

The effect of concentration on the adsorption on the metal surface can be investigated through equations describing the variation of the adsorbed quantity as a function of inhibitor concentration by different adsorption models. There are a variety of adsorption models, such as Langmuir, Frumkin, Temkin, and Freundlich [18]. These models offer a linear relationship between the adsorption of inhibitor molecules on the metal surface and the inhibitor concentration. In this study, the Langmuir adsorption isotherm has been adopted because it suggests a monolayer adsorption and homogenous adsorption in which each molecule has a constant enthalpy and sorption activation energy [19]. Furthermore, the Langmuir adsorption isotherm (Equation 9) shows the best linear relationship among them, with a correlation coefficient R^2 of up to 0.996 [15].

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (9)$$

Where C_{inh} and K_{ads} are the inhibitor concentration and the equilibrium adsorption constant, respectively [14]. The equilibrium adsorption constant is readily calculated by plotting (C_{inh}/θ) vs. C_{inh} , where the intercept is equal to $(\text{intercept}=1/K_{\text{ads}})$, Figure 6.

Figure 6. Langmuir adsorption isotherm plots for adsorption of different concentrations (25, 50, 75 and 100 ppm) of HPLE on carbon steel surface in 0.5 M HCl in the temperature range of 293–313 K.

From the intercept of the straight line with y axis in the diagram above, the values of K_{ads} were calculated. By introducing K_{ads} values into Equation 10, the values of Gibbs free energy for adsorption ΔG_{ads} were calculated.

$$\Delta G_{\text{ads}} = -RT \ln(10^3 \cdot K_{\text{ads}}) \quad (10)$$

Where 1000 denotes the water concentration in g/L, R is the universal gas constant (8.34 J/mol·K), and T is the temperature in Kelvin degrees [20].

In practice, it's relatively difficult to classify the adsorption of inhibitor molecules as a purely physical or purely chemical phenomenon. This is because chemical adsorption is typically paired with physical adsorption via charge interactions between two charged centers on the inhibitor molecules and the metal surface [21]. Through the values of Gibbs free energy (ΔG_{ads}), it can be ranked as an adsorption process, whether physical or chemical adsorption.

When $\Delta G_{\text{ads}} = -20$ kJ/mol or less negative, adsorption occurs through charge interactions between the metal surface and inhibitor molecules, and physical adsorption predominates (physisorption).

In contrast, when $\Delta G_{\text{ads}} = -40$ kJ/mol or more negative, adsorption occurs via donor-acceptor interactions (charge transfer) between the metal surface and the inhibitor molecules, and chemical adsorption (chemisorption) predominates [17].

The enthalpy of adsorption ΔH_{ads} and the entropy of adsorption ΔS_{ads} are evaluated by the Gibbs Equation:

$$\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T \cdot \Delta S_{\text{ads}} \quad (11)$$

Through a plot of ΔG_{ads} vs. temperature T , the enthalpy ΔH_{ads} is represented by the intercept of the straight line with the y axis while the slope is the entropy ΔS_{ads} [22] (Figure 7).

Figure 7. Plot of Gibbs free energy vs. temperature for adsorption of different concentrations (25, 50, 75 and 100 ppm) of HPLE on carbon steel surface in 0.5 M HCl in the temperature range of 293–313 K.

All adsorption thermodynamic parameters are listed in Table 6. From the ΔG_{ads} values in this table, it can be concluded that the adsorption process is spontaneous and within the range of physical adsorption.

Table 6. Adsorption thermodynamic parameters for adsorption of different concentrations (25, 50, 75 and 100 ppm) of HPLE on carbon steel surface in 0.5 M HCl in the temperature range of 293–313 K.

T (K)	K_{ads} ($\text{g}^{-1}\cdot\text{L}$)	ΔG_{ads} ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH_{ads} ($\text{kJ}\cdot\text{mol}^{-1}$)	$-S_{\text{ads}}$ ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
293	43.85965	26.0378	2.624	80.4
298	45.05050	26.5482		
303	47.84689	27.1457		
308	47.84689	27.5936		
313	47.65451	27.8910		

As it has been seen in the table above, the values of Gibbs energy were in the physical adsorption range, and they became more negative with an increase in temperature. Also, the negative sign of enthalpy indicates that the inhibitor adsorption is an exothermic process [23]. On the other hand, the positive sign of entropy refers to an increase in randomness; this may be attributed to the replacement of water molecules by inhibitor molecules, which leads to an increase in disorder and, consequently, entropy [24].

Scanning electron microscopy (SEM)

A metal surface morphology test was performed by scanning electron microscopy (SEM) technique. Figure 8 shows the surface morphology images of carbon steel samples before and after soaking in 0.5 M HCl solutions for 24 h at room temperature in the absence and presence of HPLE. In Figure 8-a, a polished CS sample is shown that is flat without any pits or appearances of corrosion. Figure 8-b shows the image topography of a CS sample after being immersed in an uninhibited solution. It is evident from this picture that the pits and cavities are appreciable on the metal surface. In Figure 8-c, an image of the topography of a CS sample after being immersed in an inhibited solution, it is obvious that inhibitor molecules have been adsorbed on the CS surface and the protective film was formed to act as a physical barrier between the metal surface and the environment.

Figure 8. SEM micrographs of carbon steel: a) polished specimen; b) after immersion in aggressive 0.5 M HCl for 24 h at r.t.; c) the same conditions as in (b) in the presence of 100 ppm HPLE inhibitor.

Energy Dispersive X-ray spectroscopy (EDX)

EDX analysis was accomplished in order to identify the assortment of elements on the metal surface for three samples in different states, *i.e.*, (a) polished dry specimen; (b) specimen after immersion in 0.5 M HCl for 24 h; and (c) the same conditions as in (b) in the presence of 100 ppm HPLE inhibitor.

As it is obvious from Figure 9, the peaks of Cl and O appear in the blank solution, Figure 9b, while they are absent in Figure 9a, which indicates the rust formation on the metal surface. Also in Figure 9c, there is a decrease in the Cl and O peaks in comparison with Figure b, which indicates a decrease in the corrosion process.

Furthermore, the appearance of *N* and *S* peaks in Figure c refers to the presence of HPLE molecules adsorbed on the MS [25]. The mass element ratios obtained from the EDX spectra are listed in Table 7.

Figure 9. EDX spectrum of carbon steel: a) polished specimen; b) after immersion in aggressive 0.5 M HCl for 24 h at r.t.; c) the same conditions as in (b) in the presence of 100 ppm HPLE inhibitor.

Table 7. The wt.% of the elements in the EDX spectrum.

Figure	Element Percentage in wt. %						
	Fe	Co	C	Cl	O	S	N
Figure 9-a	74.28	22.06	3.66	—	—	—	—
Figure 9-b	44.95	12.56	4.19	35.24	3.06	—	—
Figure 9-c	41.53	13.09	7.33	18.82	2.01	14.69	2.53

Conclusion

In this study, the pomelo leaves were extracted with n-hexane by the maceration extraction method. The chemicals in crude extract were diagnosed by GC-MS and FTIR spectroscopy. Esters are considered the most important among several organic compounds that exist in this extract. Afterward, the HPLE was investigated as a corrosion inhibitor for CS in 0.5 M HCl in the temperature range of 293–313 K. Four concentrations (25, 50, 75, and 100 ppm) of this extract were utilized for CS corrosion studies. Potentiodynamic polarization curves indicate that HPLE is a mixed-type inhibitor and that it shows a prominent anti-corrosion performance of up to 82.32% at 100 ppm concentration. The mechanism of inhibition

operates through adsorption of HPLE molecules on the metal surface. This adsorption is compatible with the Langmuir adsorption isotherm and occurs fundamentally as physical adsorption. The calculated Gibbs energy indicates that the adsorption process occurs spontaneously. In addition, surface morphology (SEM) and element composition of the metal surface (EDX) tests confirm the formation of a protective film on the metal surface by adsorption of inhibitor molecules.

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