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Authors: I. Hossein Nejad Keivani, S. Mohammadi

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**Studying different solvent systems on extraction performance of pomegranate
peel extract as a green corrosion inhibitor for carbon steel in 15% HCl
medium**

Iman Hossein Nejad Keivani, Somayeh Mohammadi *

Department of Applied Chemistry, Faculty of Chemistry, University of Guilan,

P.O. Box: 41635-1914, Rasht, Iran.

*E-mail address: somaye.mohammadi32@guilan.ac.ir

Abstract

Corrosion inhibition properties of pomegranate peel extract (PPE) extracted by water, water/ethanol and water/acetonitrile were investigated for carbon steel in 15% HCl medium. According to the results of the total phenolic content (TPC) test, the highest TPC value was obtained in the extracted PPE with water-acetonitrile (1:2 V/V) compared to water and water-ethanol (1:2 V/V). The characterization of PPE was performed by TPC test, FT-IR and SEM/EDX. The corrosion protection efficiency was checked through weight loss, electrochemical impedance spectroscopy (EIS), polarization, absorption isotherm, attenuated total reflectance (ATR) and X-Ray diffraction (XRD) analysis. The concentrations of 0.5, 1, 1.5, and 2 g/L of the inhibitor were investigated that the best result was acquired at concentration of 2 g/L. The polarization data confirmed that the resulting inhibitor behaved as a mixed type inhibitor with a dominant cathodic effect. According to the EIS test, after 24 hours, the inhibitor efficiency at the optimal concentration was equal to 95 %. The SEM- EDX results confirmed the creation of a protective film on the metal surface. Also, in the presence of the green inhibitor,

XRD showed no rust products on the steel substrate.

Keywords: pomegranate peel; green corrosion inhibitor; acetonitrile; carbon steel, HCl.

1. Introduction

Corrosion is a chemical and often electrochemical reaction that causes a lot of damages every year by destroying especially widely used industrial metals, including steel and steel alloys. According to statistical studies, an average of 2.5 billion USD (about 3.4% of the global GDP) is lost annually in damages caused by metals corrosion [1]. One of the most considerable, affordable and practical ways to reduce the metals corrosion rate is using of corrosion inhibitors [2-4]. A corrosion inhibitor is a synthetic or natural compound that reduces a metal corrosion rate to an acceptable level by adding to the corrosive environment in low concentrations. In various industrial processes, mineral acids are used for descaling, acidization of oil wells, and acid pickling [5]. HCl and H₂SO₄ are the major common mineral acids in industries, but in most industries (including the oil industry) because of the formation of insoluble products in the presence of H₂SO₄ for descaling processes, 15% HCl is often used [5, 6]. In the use of 15% HCl, no insoluble product remains after acid washing of metals, but due to the high dissolution and corrosive nature of the acid for metals, appropriate corrosion inhibitors must be used [5]. Also, one of the ways to increase the extraction of oil from oil wells is to inject acid into the well in order to dissolve calcareous materials and facilitate the flow of oil [7]. In petroleum industry, in order to acidify oil wells for the enhanced recovery of oil, mineral acid (HCl that most is used in 15-28 %) and organic acid solutions (formic acid and

acetic acid) or a mixture of these (HCl-formic acid or HCl- acetic acid) are used [8-11].

But HCl is the most common acid in oil well acidification due to its cost-effectiveness, soluble reaction products and high dissolving power [2, 10, 11].

Organic corrosion inhibitors containing heteroatoms of N, O, S, as well as compounds containing heterocyclic and π - electrons are very effective corrosion inhibitors in acidic environments, especially 15 % HCl [5]. The important point in using corrosion inhibitors is that, a corrosion inhibitor must reduce corrosion and also be environmentally friendly [12]. Many synthetic chemical inhibitors cause problems to the environment and human health (due to the toxic nature) and strict restrictions apply to their use [13, 14]. As well as the high price of the chemical corrosion inhibitor products, leads the use of green inhibitors (as a new strategy environmentally friendly, cheap and renewable) for controlling the metals corrosion in different corrosive environments in recent years. In general, green corrosion inhibitors covering plant extracts with many organic molecules containing, heteroatoms, aromatic rings and polar groups [13-15]. Plant extracts are known to be an extremely wealthy parent of natural compounds that can be produced by simple and low cost methods [16]. Considerable research studies have done on the progress of corrosion inhibitors for steel alloys, particularly green corrosion inhibitors [13-17]. Plant extracts show promising results in various studies that sometimes these inhibitors have results comparable to commercial inhibitors [13, 15, 17]. Green corrosion inhibitors extracted from Plant extracts are good corrosion inhibitors that their inhibition efficiencies are above 80 % [17]. This high performance is affiliated to the high amount of certain phytochemical substances in their composition [17]. Because green corrosion inhibitors have high potentials for corrosion protection of steel alloys, therefore, further

studies are incumbent to reach the highest inhibition efficiency (close to 100 %) [17].

Extensive studies have been conducted on various plants as green corrosion inhibitors for steel corrosion protection in acidic media [18].

Pomegranate is one of the main fruits that are cultivated in Middle East, Iran, Turkey, America, etc. The chemical compounds in pomegranate are different depending on its different parts, seeds, pulp, peel and even leaves, as well as the type and origin of pomegranate [19, 20]. Pomegranate peel is about 50% of the whole fruit, which is often throw away without use, while being a wealthy source of polyphenolic combination, that are very cheap and readily available [19]. Various researches have shown that the highest amounts of bioactive compounds and antioxidants (compared to other portions of pomegranate fruit) are present in pomegranate peel [21]. Pomegranate peel has various remedial properties, such as anti-cancer, anti-inflammatory, etc [22-24]. Polyphenols, mainly allagitanins and ellagic acid in pomegranate peel, are known as antioxidant and anti-cancer compounds, also, having the ability to absorb free radicals in the body [21, 25]. The amount of polyphenol compounds in pomegranate peel is related to the amount and degree of antioxidant properties [25]. Although some polyphenol compounds can be chemically synthesized today, there are still challenges and concerns about their safety [21]. Therefore, pomegranate peel is of great interest as a reliable and healthy source for the preparation and extraction of natural polyphenol compounds used in the pharmaceutical, food, cosmetic and health industries [21]. Different works were done on evaluation of corrosion inhibition properties of different pomegranate components like, pomegranate leaf extract [14, 26] and pomegranate peel extract [27-29]. Gu et al studied the anti-bacterial feature and the effect of PPE in inhibiting the corrosion of Q235A steel

in 1 M HCl solution at temperatures of 30, 45 and 60. Based on the weight loss test, the highest efficiency was obtained (at 30 °C) equal to 92.7 %. According to the results of this group, in addition to polyphenols, which reduce the rate of oxygen reduction in cathodic sites by absorbing oxygen, hydroxyl and ether groups can reduce corrosion in the acidic environment by absorbing H^+ [27].

Aghzaf et al. results showed that PPE acted as a mixed type corrosion inhibitor in acidic environment [28]. The created organic layer on the metal substrate, plus to forming a hydrophobic physical barrier against the aggressive environment, also had a chemical antioxidant activity (probably because of polyphenolic compounds) [28]. According to their results, the extracted inhibitor at 10 % v/v, had an efficiency of 96 % [28]. In another work, marsol et al. studied the inhibition effect of a methanolic extract (by Soxhlet) of pomegranate peel for corrosion protection of carbon steel in 1M HCl solution [29]. The optimal inhibition efficiency equal to 88 % was acquired at amount of 1 g/L. Also, salim et al. inspected the effect of PPE for mild carbon steel in 1 M HCl solution. Polarization data confirmed that the behavior of the studied inhibitor was of a mixed type with an IE% of 90.1 % in the amount of 4 % by weight/volume [15]. Considering the importance of green and environmentally friendly corrosion inhibitors, as well as the availability and renewable nature of these inhibitors, along with the advantage of their cost-effectiveness, in this work, it has been tried to use different solvent systems to increase the corrosion protection efficiency of PPE by increasing the extract efficiency of the effective compounds (polyphenols). There are various methods for extracting PPE (including polyphenol compounds) such as simple solvent extraction with mixing, extraction with pressurized water, extraction with supercritical carbon dioxide, extraction

with the help of microwaves and ultrasonic waves [21, 30, 31]. The solvent extraction method is a simple and cheap method, but it is less efficient compared to the other methods, and the other methods are also limited in terms of the need for special equipment in industrial and high-scale applications [21]. Therefore, in this research, different solvent systems were used to increase the extraction efficiency of antioxidant compounds and inhibitor efficiency by simple solvent extraction method.

Considering the polarity of the antioxidant components in the pomegranate peel (especially polyphenols) water and alcoholic solvents such as ethanol, methanol, and their mixtures were often used in solvent extraction [14, 21, 32]. Therefore, the solvent type for extraction, determines the final chemical characteristics of the obtained extract [32]. For this purpose and in this work, water, water-ethanol and water-acetonitrile solvents were used in different proportions to extract PPE. The extraction efficiencies in different solvents were compared with each other by total polyphenolic content (TPC) test by the Folin-Ciocalteu spectrophotometric method. Also, the performance of the resulting green inhibitors in protecting of carbon steel corrosion in 15 % HCl solution was compared with each other by weight loss, electrochemical techniques like EIS and linear polarization, SEM/EDX, FT-ATR and XRD methods. In this study, for the first time, acetonitrile solvent was used in addition to water to increase the efficiency of extracting phytochemical compounds from pomegranate peels, and its results were compared with the conventional and widely used ethanol in this field. Also, the effectiveness of the resulting pomegranate peel extract was investigated in detail in the more corrosive environment (15% hydrochloric acid) for the first time, unlike the other performed studies that were done in HCl solution with a maximum concentration of 1 M.

2. Experimental

2.1. Materials

Ethanol 96 %, Acetone and acetonitrile 99.99% were taken from Dr. Mojallali pharmaceutical chemicals industries complex Company (Iran). Acidic solution (15% HCl) was made by 37% HCl dilution. The inhibitor solutions with different concentrations (0.5, 1.0, 1.5 and 2.0 g/L) were made by adding certain values of the solid extracts in 25 mL of 15 % HCl. Carbon steel (CS) plates (ST37: with chemical composition in percent (wt. %): carbon (0.45), Oxygen (1.37) and iron (17.98) were obtained from Nama poushesh Etemad, Rasht (Iran). CS plates were de-rusted with various grade sandpaper and cleaned with distilled water and acetone, before immersing in the test solutions.

2.2. Extraction process of PPE

The dominant components in pomegranate peel extract are: gallic acid, gallic acid, ellagic acid, etc., which contain heteroatoms, electronegative functional groups, and π and lone pair electrons [33]. The structure of some of the most important polyphenol compounds found in pomegranate peel is shown in Figure 1. In order to prepare PPE, Shirazi pomegranate peel was used. In this way, after washing with water, the pomegranate peel was completely dried in an oven (temperature of 40 °C within 3 days. Then, it was crushed into a fine and uniform powder and kept in a closed container in the refrigerator away from light until use. 10 grams of the resulting powder were carefully weighed and 100 mL of the intended solvent added to it and stirred for 6 hours at a temperature of 55 °C by a magnetic stirrer at 200 rpm [31]. Then, in order to remove solids, the above mixture was filtered through filter paper and the resulting dark brown liquid extract

(Figure 2) was dried at 40 °C until it reached a solid and stored in dark glass containers with lids in the refrigerator. The extraction process was done by three types of solvents including water, water/ethanol mixture at volume ratios of (1:0.5), (1:1) and (1:2) and also water/acetonitrile mixture at volume ratios of (1:0.5), (1:1) and (1:2).

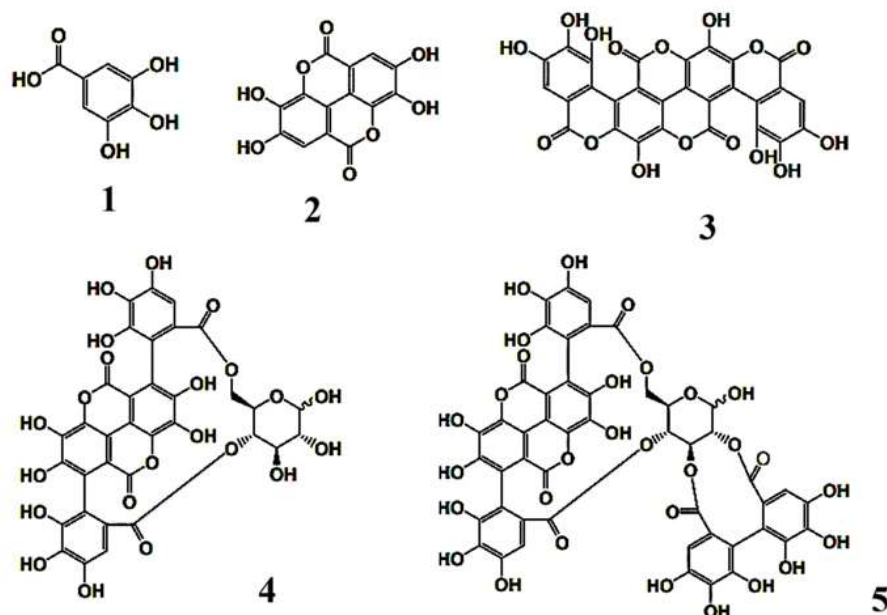


Figure 1: the chemical structure of polyphenolic compounds found in pomegranate: 1- Gallic acid 2- Ellagic acid 3- Gallgic acid 4- Punicalin 5- Punicalagin [33].



Figure 2: Preparation steps of PPE.

2.3. Methods

2.3.1. Spectral studies

FT-IR spectrum of the solid PPE in KBr pellets was recorded using Shimadzu FT-IR 4100 spectrophotometer with a resolution of 4 cm^{-1} , the number of 50 scans and the number of data points 8192 and data intervals of approximately about 1.93 cm^{-1} . To study the adsorption of the green corrosion inhibitor compounds on the metal substrate, two steel pieces after polishing and degreasing were immersed in 15 % HCl solution containing the green corrosion inhibitor and also in 15 % HCl solution without inhibitor (as a blank sample) for 24 hours. Then, the FT-ATR test was performed on the both mentioned plates using FT-ATR 4100 spectrophotometer with a resolution of 8 cm^{-1} and 16 co-added scans. The total polyphenolic content (TPC) of the extracts was estimated by the Folin-Ciocalteu spectrophotometric method. Gallic acid (0-100 mg/L) was used for

standard curve. The data were revealed as gallic acid milligrams in gram of the solid extract PPE (mg GAE/g PPE). All tests were examined at three times.

2.3.2. Electrochemical measurements

For studying the electrochemical impedance spectroscopy (EIS) and linear polarization, steel surfaces with an area of 7.5 cm^2 were used. These tests were executed by an Autolab potentiostat/galvanostat 84165 with Nova 1.6 software in a three-electrode cell, in which, steel plates, Ag/AgCl and platinum were used as working electrodes, saturated reference electrode and counter electrode, respectively. These tests were fulfilled at the open circuit potential (OCP) and the temperature of 25°C in 25 mL of acid solution, at the frequency range of 10 mHz–100 kHz (AC amplitude of 10 mV). ZsimpWin commercial software 3.22 (developed by Princeton Applied Research, TN, USA) was used for analyzing the empirical data. The linear polarization was done in the potential domain of -250 to +250 mV relative to the OCP with 1 mV/S scan rate.

2.3.3. Weight loss measurements

For this test, the steel fragments were cut in dimensions of $2 \times 2 \text{ cm}^2$, and they were de-rusted. In order to perform the weight loss test, all the steel pieces were weighed using a digital scale with an accuracy of 0.0001 grams. After that, the parts were transferred to glass containers containing 25 mL of 15 % HCl (a control) and also placed in 15 % HCl solution that contained various inhibitor concentrations. This test was done during 1, 3 and 7 days. After the desired times passed, the steel surfaces were cleaned by a plastic brush and water and after drying, they were weighed again. The carbon steel corrosion

rate ($\text{mg cm}^{-2} \text{ h}^{-1}$), the inhibition efficiency (IE %) and the surface coverage (θ) were estimated using equations 1-3.

$$C \cdot R = \frac{m_1 - m_2}{S \times t} \quad (1)$$

$$\text{IE}\% = \left(\frac{W_{\text{uninhibitor}} - W_{\text{inhibitor}}}{W_{\text{uninhibitor}}} \right) \times 100 \quad (2)$$

$$\theta = \left(\frac{W_{\text{uninhibitor}} - W_{\text{inhibitor}}}{W_{\text{uninhibitor}}} \right) \quad (3)$$

In equation 1, m_1 is the initial weight of the steel pieces (mg), m_2 is the final weight of the steel pieces (mg), S is the whole area of the piece (cm^2) and t is the immersion time (hour).

2.3.4. Metal substrate analysis by SEM/EDX

The metal surfaces were explored using a VEGA\\TESCAN-LMU SEM/EDX with an accelerating voltage of 30 KV. For this purpose, the plates were cut into a square shape with dimensions of $1 \times 1 \text{ cm}^2$ and cleaned as previously explained and placed in 25 mL of the relevant solution for 24 hours.

2.3.5. XRD analysis

The formed oxide compounds on the steel surface in the absence and the presence of the green inhibitors in acidic solution, XRD patterns were used. For this purpose, the steel pieces were cut into square shapes with dimensions of $1 \times 1 \text{ cm}^2$ and cleaned as previously mentioned. Then, they were put in 25 mL of acid solution (blank sample) and the acid solution containing the inhibitor for 24 hours. For the preparation of XRD patterns, Philips PW1730 device, (made in the Netherlands), was used with the wavelength of the

copper X-ray lamp 1.54056 angstroms, the voltage 40 kV and the current 30 mA.

2.3.6. Adsorption isotherm

A corrosion inhibitor performance depends on its kind of interactions with the metal substrate. Adsorption mechanisms mostly include chemical interactions and physical adsorption [34]. There are different types of surface adsorption isotherms, the most common of which are: Langmuir, Temkin and Frumkin. The Langmuir isotherm is the most important among the mentioned isotherms as it usually provides an acceptable explanation for the surface adsorption behavior according to equation 4 [35].

$$\frac{C_{inhibitor}}{\theta} = \frac{1}{K_{ads}} + C_{inhibitor} \quad (4)$$

In the equation 4, $C_{inhibitor}$ is the inhibitor concentration, θ is the amount of surface coverage (from the weight loss, equation 5) and K_{ads} is the equilibrium constant of the adsorption process.

$$\theta = \frac{W_{uninhibitor} - W_{inhibitor}}{W_{uninhibitor}} \quad (5)$$

3. Results and Discussion

3.1. Measurement of antioxidant activity of PPE (determination of total polyphenol content (TPC))

According to the studies, there is a close relationship between TPC and antioxidant activity [36, 37]. In order to make a preliminary comparison between different solvent systems in the antioxidant extraction from pomegranate peel and also to specify the best volume ratio between water: ethanol and water: acetonitrile solvents, the amount of TPC in the extracted PPE in different solvents measured. The obtained results were presented in Table 1. It was obvious that the extract/water had the minimum TPC level (22.85 mg

GAE/g) and the extract/water-acetonitrile (1:2) had the maximum amount (62.15 mg GAE/g). The amount of TPC in the extract/water-ethanol (1: 2) was 28.30 mg GAE/g. According to the table's results, increasing the ratio of ethanol and acetonitrile solvents to water resulted in an increment in TPC extraction efficiency. The results of this test confirmed that acetonitrile solvent was even more efficient than ethanol in extracting TPC like phenolic acids, tannins and flavonoids (with more than 2 times efficiency). The phenolic compounds are the main factors in the antioxidant property and the higher the amount of polyphenol and tannin, causes the higher antioxidant activity [36, 37]. The higher amount of TPC in the extract/water-acetonitrile (1: 2) could be due to the greater solubility of polyphenol compounds in pomegranate peel in the presence of acetonitrile rather than ethanol. Therefore, based on this test, for the next investigations, water was used as a control and water-ethanol (1:2 V/V) and water-acetonitrile (1:2 V/V) solvent systems were used as the selected solvents to extract PPE in this work.

Table 1. Total polyphenol content in PPE, of the dried extract samples.

extract sample	TPC (mg GAE/g)
extract/water	22.8
extract/water-ethanol (1: 0.5)	25.30
extract/water-ethanol (1: 1)	26.10
extract/water-ethanol (1: 2)	28.30
extract/water-acetonitrile (1: 0.5)	47.87
extract/water-acetonitrile (1: 1)	53.34
extract/water-acetonitrile (1: 2)	62.15

3.2. Evaluation of the green inhibitor's performances by weight loss

Table 2, show the weight loss results of the steel plates after immersion times of 1, 3 and 7 days in blank acid and acid with different concentrations (0.5, 1.0, 1.5 and 2.0 g/L) of the extracted PPE in water (extract/water), water-ethanol solvent (1:2 V/V) (extract/water-ethanol) and in water-acetonitrile solvent (1:2 V/V) (extract/water-acetonitrile)) are given. According to the obtained results, it was clear that the extracted PPE showed different corrosion protection efficiencies in different concentrations and the corrosion protection efficiencies (IE %) enhanced with the increasing of the PPE amount from 0.5 g/L to 2.0 g/L. The IE % of extract/water-acetonitrile was significantly higher than the extract/water and extract/water-ethanol at all three times. This greater efficiency in the water/acetonitrile solvent system could be due to the presence of more polyphenolic compounds extracted from pomegranate peel by the acetonitrile solvent (according to TPC test).

The extracted polyphenol compounds are able to protect the metal from corrosion by adsorbing on the metal surface and forming a protective film on the metal substrate. Based on the results, by passing time, the values of IE % of the inhibitions for the extracted PPE by all the solvents showed a decrease. After one week, the maximum decrease was observed in the case of extract/water about 21.5 % and the minimum decrease in IE% was observed for the extract/water-acetonitrile (about 10 %). This confirmed that due to the higher extraction of polyphenolic compounds from pomegranate peel by acetonitrile, a protective film with greater adhesion and thickness was formed on the metal substrate, which provided more effective corrosion protection of the metal substrate. Among the reasons for the decrease in IE% after one week, the

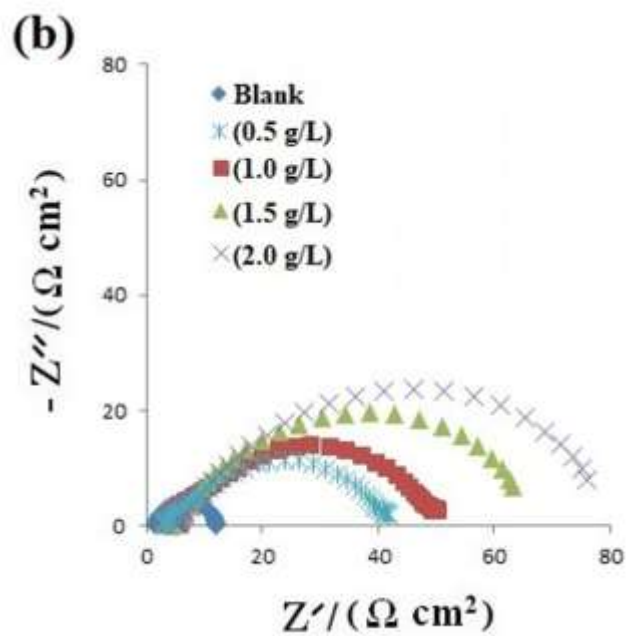
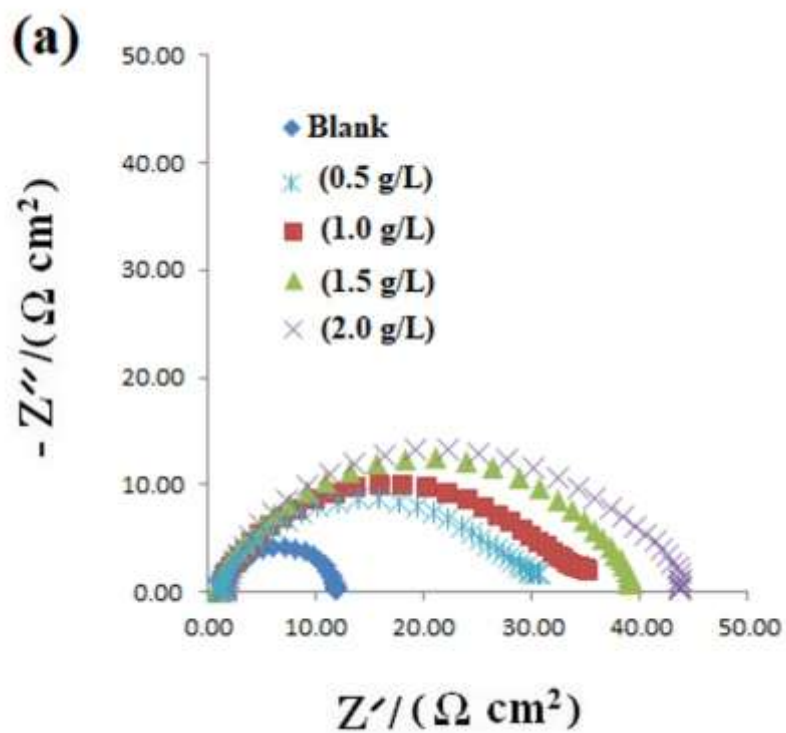
desorption of some of inhibitor molecules from the metal substrate and also the rust products formation can be mentioned. However, after one week, the extract/water-acetonitrile green corrosion inhibitor (2.0 g/L), indicated acceptable IE % compared to the other studies samples in this test.

Table 2. Weight loss data of the immersed carbon steel plates in 15% HCl solution containing different concentrations of the green corrosion inhibitors.

Inhibitor name	Con.(g/L)	1 day			3 days			7 days		
		CR (mg.cm ⁻² .h ⁻¹)	θ	IE%	CR (mg.cm ⁻² .h ⁻¹)	θ	IE%	CR (mg.cm ⁻² .h ⁻¹)	θ	IE%
blank	-	-	-	2.86	-	-	-	2.12	-	-
extract/water	0.5	0.278	0.653	65.3	0.316	0.496	49.6	0.412	0.413	41.3
	1.0	0.245	0.722	72.2	0.290	0.585	58.5	0.386	0.492	49.2
	1.5	0.227	0.756	75.6	0.226	0.613	61.3	0.354	0.558	55.8
	2.0	0.220	0.788	78.8	0.214	0.668	66.8	0.317	0.573	57.3
extract/water-ethanol	0.5	0.136	0.746	74.6	0.198	0.665	66.5	0.248	0.523	52.3
	1.0	0.109	0.821	82.1	0.174	0.748	74.8	0.216	0.646	64.6
	1.5	0.091	0.856	85.6	0.142	0.762	76.2	0.191	0.693	69.3
	2.0	0.062	0.897	89.7	0.111	0.805	80.5	0.171	0.749	74.9
extract/water-acetonitrile	0.5	0.095	0.846	84.6	0.128	0.756	75.6	0.187	0.683	68.3
	1.0	0.059	0.916	91.6	0.072	0.844	84.4	0.145	0.779	77.9
	1.5	0.042	0.947	94.7	0.067	0.887	88.7	0.100	0.824	82.4
	2.0	0.036	0.978	97.8	0.061	0.902	90.2	0.087	0.878	87.8

3.3. Electrochemical impedance spectroscopy (EIS)

Figures 3 and 4 present the Nyquist and Bode plots for various inhibitors in concentrations of 0.5 g/L, 1.0 g/L, 1.5 g/L and 2.0 g/L.



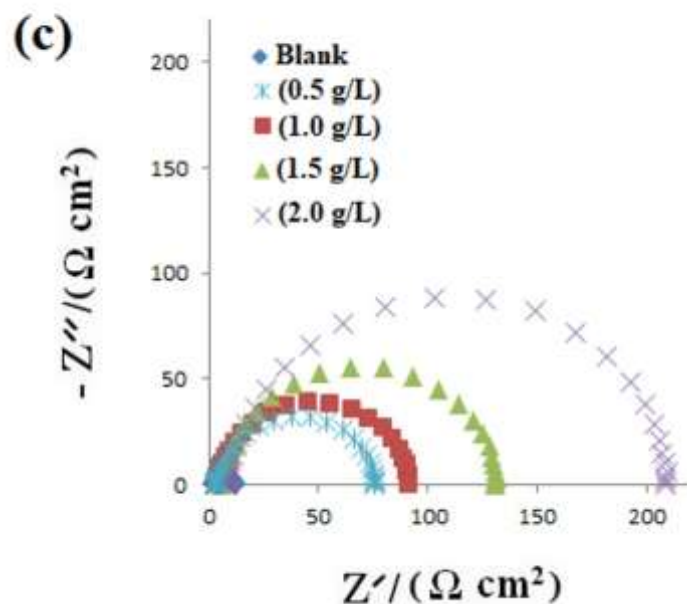
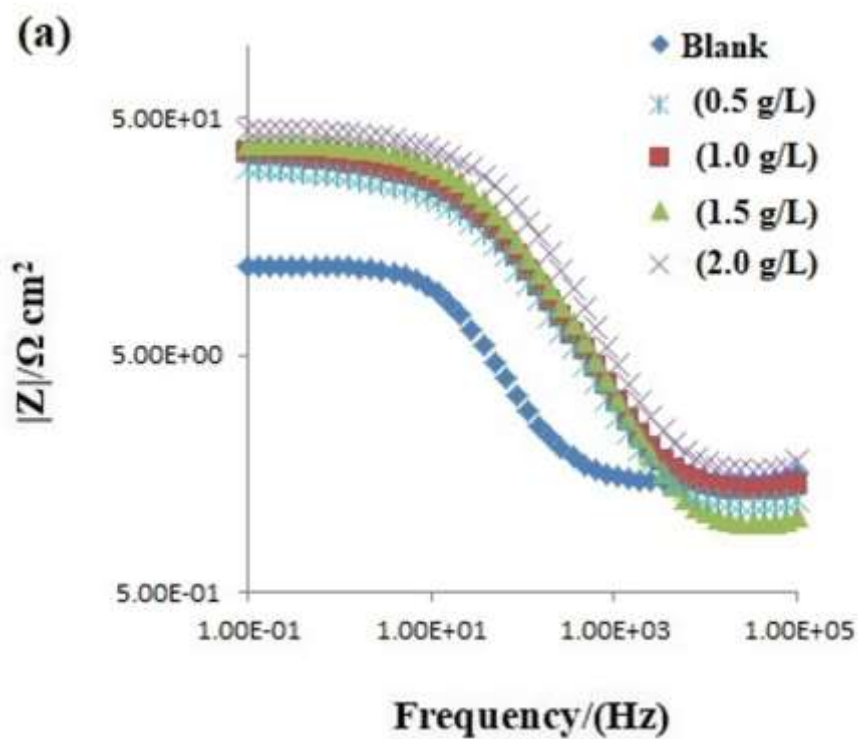


Figure 3: Nyquist diagrams of carbon steel after 24 h immersion in blank acid and acid with different amounts of (a) extract/water, (b) extract/water-ethanol and (c) extract/water-acetonitrile corrosion inhibitors.



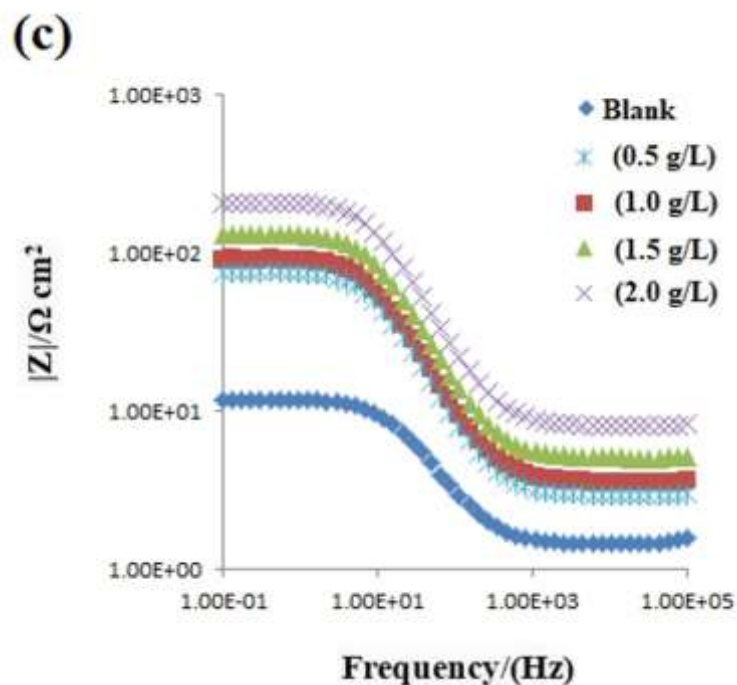
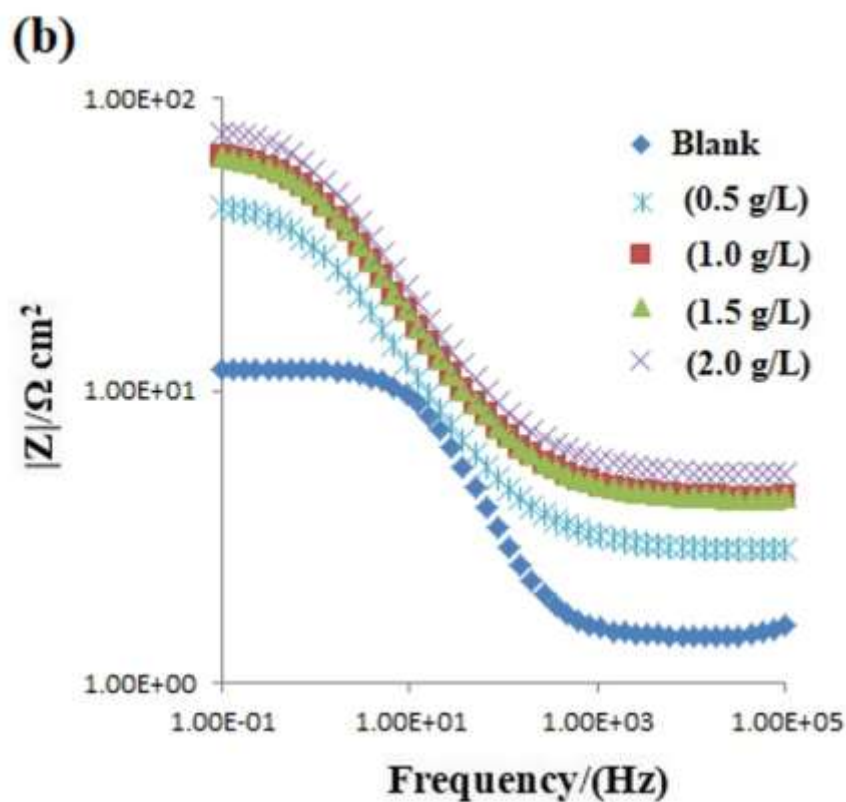


Figure 4: Bode diagrams of the samples after 24 h immersion in blank acid and acid with different amounts of (a) extract/water, (b) extract/water-ethanol and (c) extract/water-acetonitrile corrosion inhibitors.

The most suitable fit of the Nyquist diagrams was gained by the equivalent circuits shown in Figure 5. The impedance parameters were shown in Table 3. The offered circuits had a solution resistance (R_s) which is negligible compared to other resistances, a polarization resistance (R_p) and a constant phase element (CPE) that replaces the ideal capacitor element to better match the data in the software. The reason for this deviation from the perfect capacitor is typically due to the roughness of the electrode surface or surface inhomogeneity caused by inhibitor absorption [29, 38]. The obtained magnitude of the constant phase element (Y_0) from the Zsim software can be converted into a capacitor element (C_{dl}) by equation 6. The C_{dl} parameter was used for a better investigation of the capacitive behavior of corrosion systems that show non-ideal capacitive behavior [39, 40].

In general, in the Nyquist diagrams, the real impedance difference in the minimum and the maximum frequencies is charge transfer resistance (R_{ct}) that in this project was replaced by (R_p) (Figure 5 and Table 3) [39]. For the immersed steel sample in acid solution without the inhibitor, R_p includes the sum of the resistances containing of R_{ct} , the diffusion layer resistance (R_d) and the resistance related to all kinds of accumulated in the steel/electrolyte interface (R_a) (Figure 5). R_{ct} indicated the corrosion rate, while other resistances, including R_d and R_a , were simple resistances on the flow path. In the inhibited solution, the inhibitor film resistance (R_f) was also added to the set of R_p resistors (Figure 5) [39].

$$C_{dl} = (Y_0 R_{ct}^{1-n})^{1/n} \quad (6)$$

A semicircle in these plots displayed that the reaction was only under the charge transfer control. For initiation of corrosion, a charge transfer must be carried out among the

corrosive solution and the metal surface, but binding the inhibitor molecules to the metal surface, block the anodic positions and prevent the corrosion reaction.

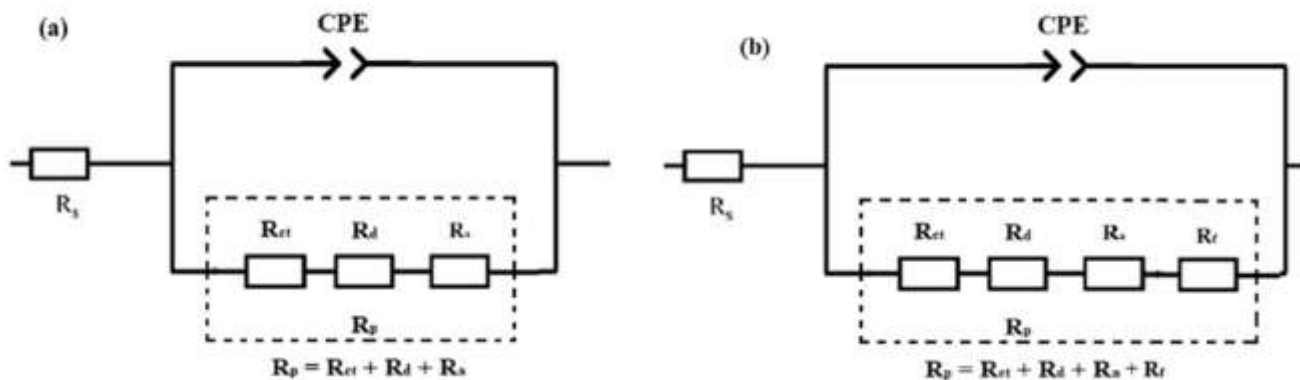


Figure 5: The equivalent circuit resulting from matching the EIS data for a) metal immersed in acidic medium without inhibitor and b) metal immersed in acidic medium containing inhibitor.

According to the impedance data (Table 3) and the Nyquist plots, the R_p value enhanced with increasing the inhibitor concentrations from 0.5 g/L to 2.0 g/L, and the highest corrosion IE% was 95 % at 2.0 g/L concentration for the extract/water-acetonitrile. The value of R_p increased from $11.6 \Omega \text{ cm}^2$ (in blank) to $207.8 \Omega \text{ cm}^2$ (in the inhibited solution) and the related C_{dl} , decreased from $869 \mu\text{Fcm}^{-2}$ to $198 \mu\text{Fcm}^{-2}$. This was mostly related to the inhibitor adsorption on the metal surface and creating a protective film [41]. In Table 3, the parameter n is a measure of the roughness and smoothness of the metal substrate [41, 42]. In the presence of an inhibitor, its value is closer to 1, indicating the formation of an inhibitor film on the metal substrate. But as can be seen in the blank sample, its value is far from 1 ($n = 0.9619$), indicating the formation of corrosion products on the metal surface. Generally, adding an inhibitor to an acidic solution causes an enhancement in the thickness of the double layer and decrease in capacitor capacity, due

to the presence of the inhibitor molecules instead of the water molecules [42]. Based on the results, the value of 2.0 g/L was selected as the optimal concentration. Also, the performance of the extracted PPE in the presence of acetonitrile was quite evident compared to ethanol. The surface images of the steel plates after the impedance test are shown in Figure 6. The steel surface was completely oxidized and darkened in the blank acid solution. In the samples containing extract/water and extract/water-ethanol inhibitors, the amount of the surface darkness is much lower, but the shiny surface was related to the sample containing extract/water-acetonitrile, which was a sign of greater corrosion protection.

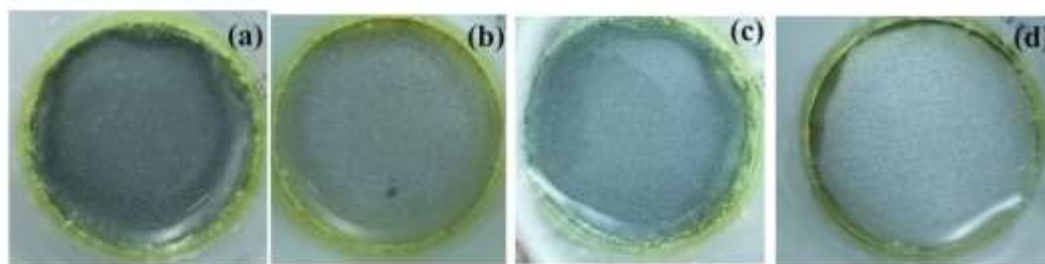


Figure 6: The digital photos of steel surfaces after completion of impedance test (24 hours immersion) in a) acid solution, b) acid solution containing extract/water, c) acid solution containing extract/water-ethanol and d) acid solution containing extract/water-acetonitrile inhibitor.

Table 3. EIS data of the carbon steel corrosion, after 24 hrs immersion in acid solutions (25 °C).

Inhibitor name	Cone(M)	$R_s(\Omega.cm^2)$	$R_p(\Omega.cm^2)$	$Y_0(\Omega^{-1}S^n cm^{-2})$	n	$C_{dl} (\mu F cm^{-2})$	IE%
blank	-	1.24	11.6	782	0.9619	869	-
extract/water	0.5	1.36	30.6	429	0.9726	489	64.6
	1.0	1.40	35.2	405	0.9746	456	69.3
	1.5	1.37	38.7	296	0.9871	365	72.2
	2.0	1.70	43.8	282	0.9890	331	75.4

extract/water- ethanol	0.5	1.56	41.3	324	0.9740	359	73.9
	1.0	1.52	50.1	243	0.9820	279	78.7
	1.5	1.66	63.4	246	0.9752	263	83.2
	2.0	1.71	76.0	232	0.9815	241	86.0
extract/water- acetonitrile	0.5	1.36	76.3	286	0.9813	305	86.2
	1.0	1.45	91.0	210	0.9835	226	88.4
	1.5	1.52	130.4	196	0.9887	212	92.0
	2.0	1.59	207.8	1176	0.9823	198	95.0

3.4. Investigation the effect of the inhibitors by polarization method

The polarization plots of the steel plates in acid solutions are shown in Figure 7. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion rate (r_{corr}) polarization resistant (R_p), anodic and cathodic Tafel slopes (β_a and β_c) and corrosion current density (I_{corr}) are given in Table 4. R_p and r_{corr} were calculated using equations 7 and 8 [40-43].

$$R_p = \frac{\beta_a \cdot \beta_c}{2.303 \cdot i_{\text{corr}} \cdot (\beta_a + \beta_c)} \quad (7)$$

$$r_{\text{corr}} = \frac{0.0032 \cdot i_{\text{corr}} \cdot M}{n \cdot d} \quad (8)$$

where in equation 7, i_{corr} is corrosion current density ($\text{A} \cdot \text{cm}^{-2}$) and in equation (8), i_{corr} is corrosion current density ($\mu\text{A} \cdot \text{cm}^{-2}$), M is atomic mass of steel (55.85), d is the density of steel (7.87 g/cm^3 for iron) and n ($n=2$) is the number of transferred electrons across the metal. According to the polarization results, the corrosion current density (I_{corr}) has decreased by the inhibitors, which indicated the development of a protective inhibitor film on the metal surface. The absorption of the phytochemical compounds of the extract on the metal/solution interface, blocked the anodic active sites and the corrosion processes were inhibited [26, 41, 43]. According to scientific literature, if the corrosion

potential of steel in the presence of an inhibitor shifts about ± 85 mV or more, the inhibitor is considered as cathodic or anodic, while if this shift be less than 85 mV, it is mixed type [29, 39]. Based on Table 4, the values of E_{corr} did not show any remarkable changes in the presence of the different extracts, which showed that they behaved as mixed type corrosion inhibitor in the acid solution [26]. The maximum alteration in E_{corr} for extract/water was 10 mV and for the extract/water-alcohol and extract/water-acetonitrile, they were equivalent to 30 mV in the direction of negative potentials. As a result, it can be concluded that the obtained inhibitor in this research was a mixed type inhibitor by a dominant cathodic effect. From Table 4, in the optimal concentration, the values of IE% were in the following order of extract/water < extract/water-ethanol < extract/water-acetonitrile, which they matched with the obtained results from the weight loss and EIS methods.

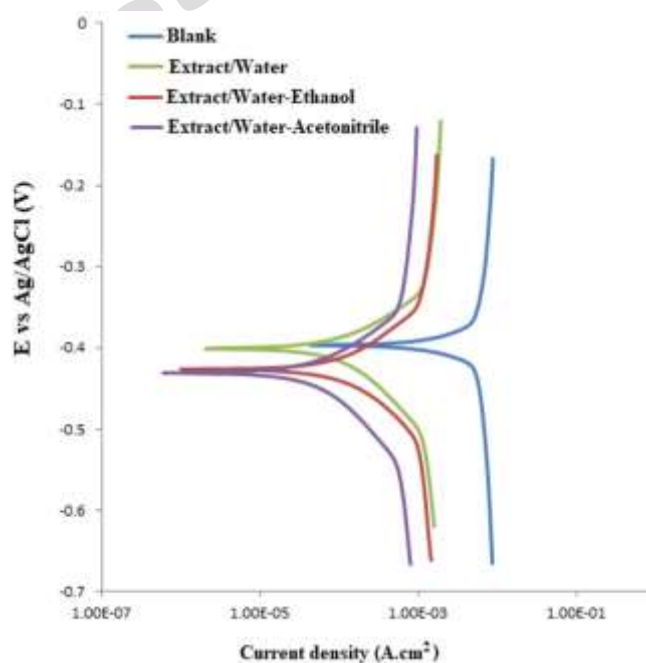


Figure 7: Polarization diagrams of carbon steel in blank acid solution and acid solution with 2 g/L of the green inhibitors after 24 hours of immersion.

Table 4. Polarization data of the steels in acid solution and acid solutions containing the green inhibitors (2.0 g/L) after 24 hours of immersion.

sample	(OCP)/V	β_a (V/dec)	β_c (V/dec)	R_p ($\Omega \cdot \text{cm}^2$)	i_{corr} (mA/cm ²)	r_{corr} (mm/y)	IE%
Blank	-0.39	9.00	8.23	3.4	0.54	6.12	-
Extract/water	-0.40	12.77	15.00	18.82	0.16	1.8	70.0
Extract/water-ethanol	-0.42	16.00	12.3	27.4	0.11	1.24	79.5
Extract/water-acetonitrile	-0.42	17.35	20.5	85.1	0.048	0.54	91.1

3.5. Examining the effect of temperature

A weight loss test was conducted to explore the rising temperature effect on the proficiency of the best green inhibitor. The data are displayed in Table 5. The green inhibitor's efficiency decreased by about 20 to 25 % at low concentrations and by about 12 % at higher concentrations at 40 °C, as can be observed. At 60 °C, the efficiency reduction was about 35% for low concentrations, and about 30 % for higher concentrations. The results of this test revealed that the corrosion rates grew with the enhancement of the temperature and also with decreasing the inhibitor concentration. The detachment of the inhibitor molecules from the substrate often caused to a decrease in antioxidant activity and inhibitor efficiency at high temperatures [39, 44].

Table 5. The obtained data from the test of the rising temperature effect on steel corrosion.

Inhibitor name	Con.(g/L)	20 °C			40 °C			60 °C		
		CR (mg.cm ⁻² .h ⁻¹)	θ	IE%	CR (mg.cm ⁻² .h ⁻¹)	θ	IE%	CR (mg.cm ⁻² .h ⁻¹)	θ	IE%
blank	-	1.15	-	-	2.12	-	-	2.86	-	-
extract/water-	0.5	0.084	0.88	88	0.496	0.682	68.2	3.62	0.550	55.0
	1.0	0.054	0.92	92	0.472	0.763	76.3	3.21	0.578	57.8

acetonitrile	1.5	0.047	0.94	94	0.469	0.820	82.0	2.74	0.623	62.3
	2.0	0.039	0.97	97	0.458	0.860	86.0	2.25	0.650	65.0

3.6. Examination of adsorption isotherm parameters

The efficiency and performance of an inhibitor in an acidic environment are estimated by its adsorption onto the metal surface [39]. The resulting curves are very useful for detecting the absorption behavior of corrosion inhibitors. Fig.8. shows the isothermal plots of extract/water-acetonitrile absorption on the steel surface at temperatures of 20 °C, 40 °C and 60 °C. According to the adsorption isotherm plots, because the slope of the line in the C/θ graph in terms of C was very close to one, indicated that the inhibitor adsorption correlated to the Langmuir isotherm. This means that the extract adsorption on the substrate is a single layer [39].

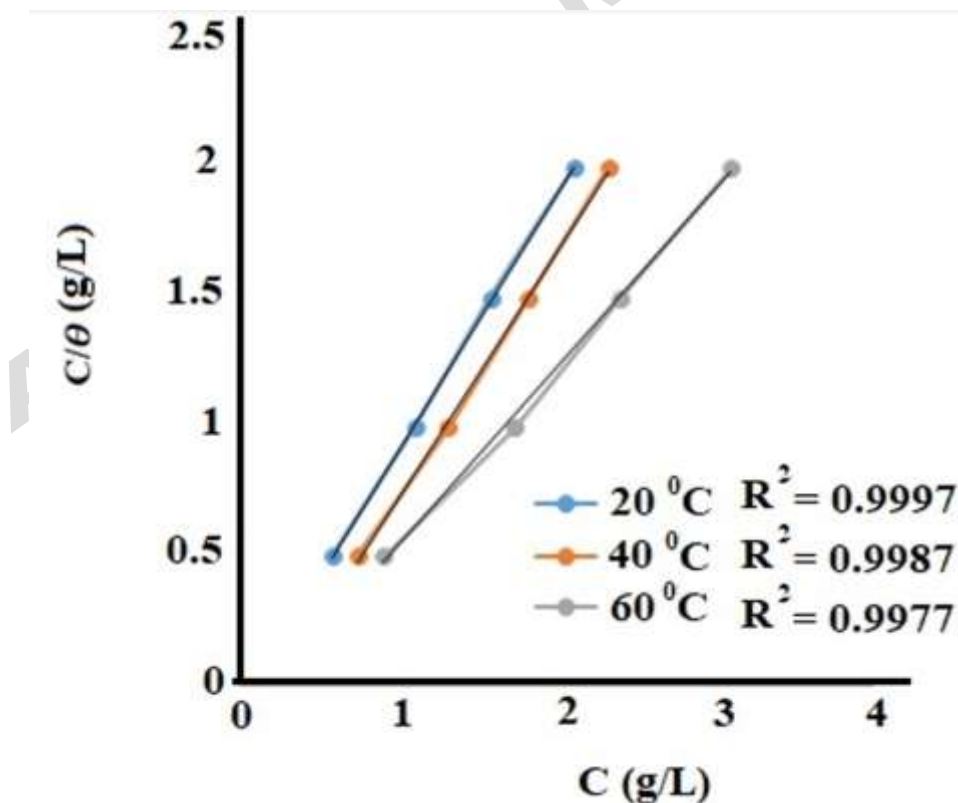


Figure 8: Langmuir isotherm diagram for carbon steel in acidic solution containing extract / water-acetonitrile at different temperatures.

3.7. Investigation of FT-IR test on the dry extract of pomegranate peel

What is generally present in a plant extract with corrosion inhibition ability are various organic natural components that make a dense layer on the metal substrate and create corrosion inhibition properties. Natural compounds those are capable of acceptable protection of the metal surface without the need for complex synthesis methods or their optimization in the final formulation. Most of the compounds identified in pomegranate peel include aldehyde, ketone, amino, alcoholic, aromatic or phenolic compounds [15]. The existence of electron-rich unsaturated bonds and aromatic rings in the natural compounds in pomegranate peel, increases its inhibitory properties [15]. Figure 9. shows the normalized FT-IR spectrum of extracted PPE (in solid state) in water and water-acetonitrile (1:2 V/V). The wide and intense stretching band in the area of 3300 cm^{-1} to 3424 cm^{-1} was related to the bonded -OH groups of polysaccharide compounds, flavonoids, gallic acid, ellagic acid, fatty acid compounds and generally phenolic compounds in the extract [44, 45]. The peak in 2935 cm^{-1} was representative of the stretching vibrations, and the observed peak in 1342 cm^{-1} was the bending vibration of the -CH₃ and -CH₂ groups of the carbon skeleton of various compounds including polysaccharides [28, 46]. The observed peak in 1615 cm^{-1} was linked to the C-O-C or C=C bond in aromatic compounds, which was consistent with what other researchers in this field, had reported [15, 28, and 46]. The peak in 1727 cm^{-1} was representative of the carbonyl group and generally ester carboxylic acid in the compounds [28, 47]. The observed bands at 1500 cm^{-1} and 1442 cm^{-1} were related to the symmetric and asymmetric bending vibrations of the carboxylic group [31]. In the region of 900 cm^{-1} to 1200 cm^{-1} , the observed bands were C-O and C-O-C vibrations, which were again a sign

of the presence of polysaccharide compounds and flavonoids [28]. The strong peak in the 1056 cm^{-1} region was also related to the C-OH stretch of the alcoholic group [47].

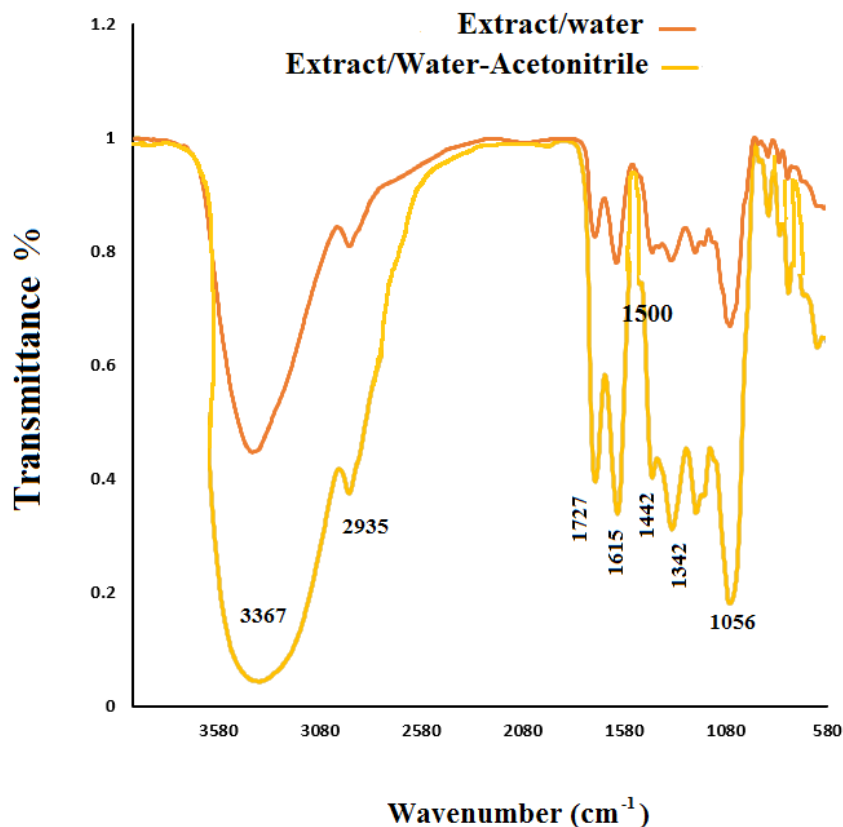
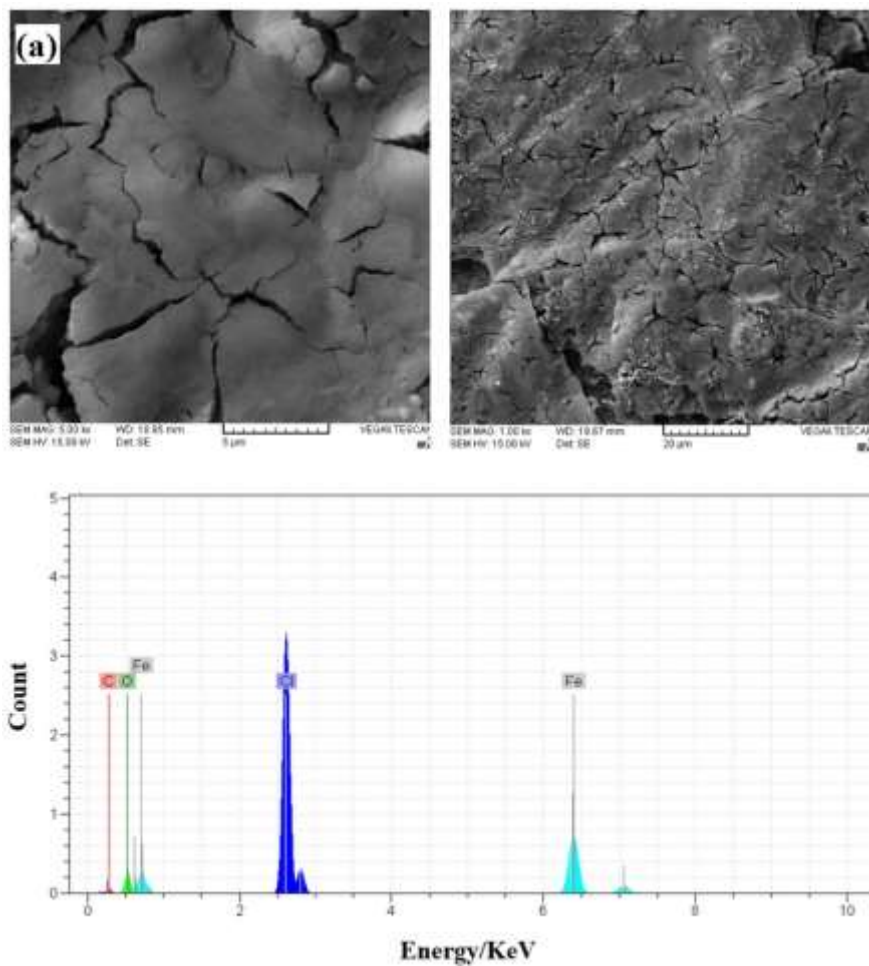


Figure 9: The normalized FT-IR spectra of the solid extracts.

3.8. SEM- EDX analysis

In order to a better view to the effects and inhibition power of the PPE used in this research, SEM images were taken along with EDX elemental analysis of the steel substrates. Figure 10, indicates the images of SEM/EDX spectra of steel surfaces, at the end of 24 hours immersion in blank and acid solution containing inhibitor. It was obvious that the steel surface in acidic environment in the absence of the green inhibitor (Figure 10a), was a surface containing of many cracks and porosity. While according to Figure 10b, a cohesive layer on the substrate was quite evident, which had caused its protective

effect in the acidic environment. In fact, the extract compounds by forming a hydrophobic film on the substrate surface preserved the metal surface to a large extent against corrosion. According to the EDX analysis, the steels elements composition was listed in Table 6. A higher percentage of carbon in the inhibited environment was a sign of the surface absorption of the inhibitor on the steel surface. Generally, an increment in the oxygen content and a decrement in the iron content in a sample without an inhibitor is a sign of oxidation of the surface and dissolution of iron in the lack of an inhibitor [39]. By using the inhibitor, the amount of oxygen in the substrate showed a significant decrease, which was a sign of its proper performance in protecting the metal substrate. The phenolic compounds in the PPE reduced the acidic strength and its corrosive nature, and their deposit layer on the substrate, was an excellent barrier for effective metal protection [13, 28, 40].



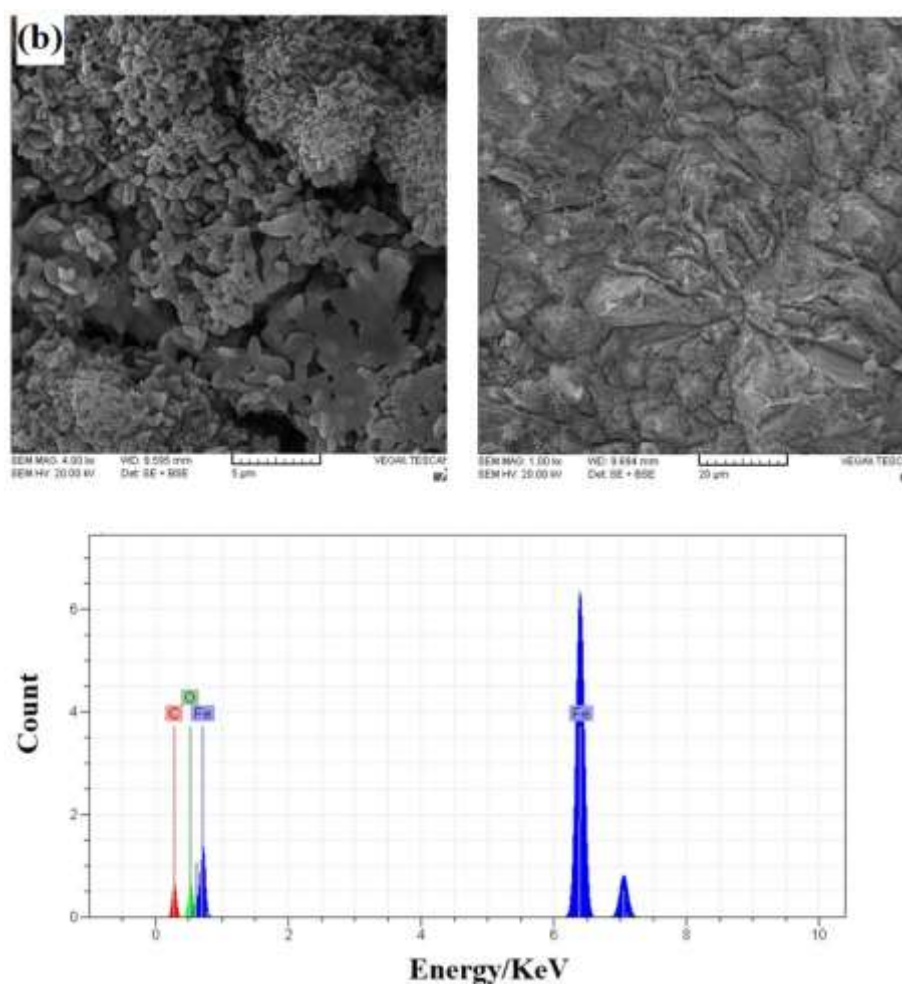


Figure 10: SEM / EDX data of (a) steel in 15% HCl, (b) steel in 15% HCl with extract/water-acetonitrile after 24 hours immersion.

Table 6. EDX data of carbon steel, in 15% HCl and 15% HCl with the extract/water-acetonitrile after 24 hours immersion.

Element	CS in HCl (wt.% - atm.%)	CS in HCl + inhibitor (wt.% - atm.%)
Fe	48.43 - 31.35	85.17 - 58.28
C	2.59 - 7.81	7.92 - 25.21
O	8.79 - 19.86	6.91 -16.51
Cl	40.19- 40.98	-

3.9. FT-ATR

In this test, two steel pieces after polishing and degreasing were placed in 15 % HCl with

2.0 g/L of inhibitor and also in 15% HCl (blank) for 24 hours. Afterwards, the ATR test was conducted on the both pieces. The FT-ATR spectrum obtained from the both samples is shown in Figure 11. Based on this test, the observation of some absorption bands related to the inhibitor compounds in the spectrum of the inhibited steel and the absence of these bands in the blank sample was a sign of the extract molecules absorption on the substrate. The strong observed peak in the immersed sample in acid solution containing the inhibitor was related to -OH groups of different compounds of PPE, which was slightly shifted to a higher wave number (3392 cm^{-1}) [48]. The stretching vibration band of the C=O carbonyl group of the compounds in the extract was also observed at the wave number of 1678 cm^{-1} , which was shifted to a lower wave number compared to the spectrum of the pure extract (Figure 11 in the area of 1727 cm^{-1}) [49].

The appeared peak in the wave number 1635 cm^{-1} was related to the C=C bond adsorbed on the metal substrate, which was shifted to a higher frequency compared to the pure extract spectrum in Figure 11 (1615 cm^{-1}). Based on the pure extract FT-IR spectrum (Figure 9), a broad observed band in 1220 cm^{-1} of the metal FT-ATR spectra in the inhibited acid solution, was considered as C-O, C-OH alcoholic and C-O-C vibrations. The bands that were viewed as a broad peak were caused by transitions, displacements, and overlapping. Comparing the ATR spectrum of the steel sample immersed in the acid solution containing the inhibitor with the FT-IR spectrum obtained from the extract/water-acetonitrile in Figure 9., showed that some peaks have completely disappeared. On the other hand, some peaks have shifted to higher wave numbers and some have moved to lower ones and some were disappeared that means some interactions between the extract and the substrate [26, 48-51].

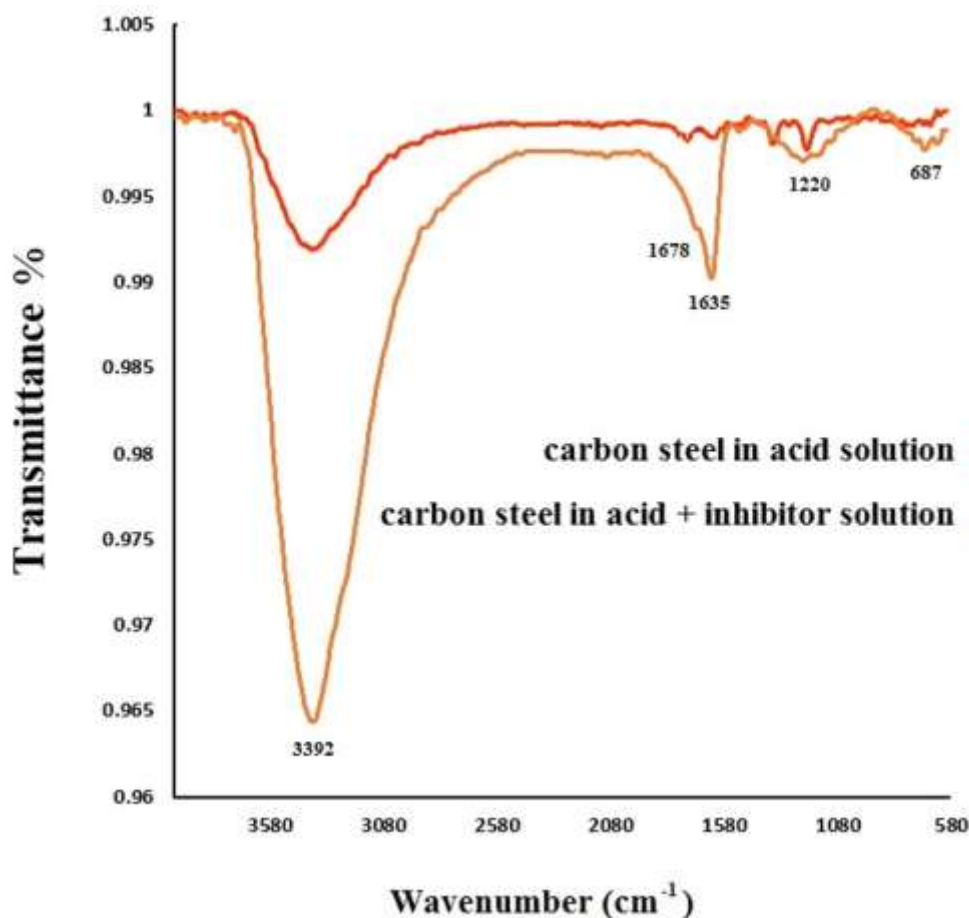


Figure 11: FT-ATR spectrum of the steel in acid solutions.

3.10. XRD analysis

XRD patterns of the samples are displayed in Figure 12 a and b. XRD patterns showed the carbon steel surface in an acidic environment was mostly covered with Fe_3O_4 , FeOOH , Fe_2O_3 (iron corrosion products) and Fe. The appearing peaks at 2θ : 14.73, 21, 22.4, 26.7, 33.3, 34.44, 37, 52.3, 58.84, 61, 64.8 can be attributed to iron oxides, including Fe_3O_4 and FeOOH [52]. The main peak related to iron element can also be seen at $2\theta = 44.4$ [26, 52, 53].

As can be seen, in the sample without inhibitor (a), there was a more crowded pattern in terms of the appeared peaks numbers, which showed that the amount of the oxide phase

on the metal substrate was higher. In Figure 12b, the intensity and the number of the related peaks to the corrosion products showed a decrease in comparison with the blank, but the intensity of the main peaks related to iron increased significantly. These observations showed efficient performance of the inhibitor [14, 26]. On the other hand, the comparison of the two XRD patterns showed that in the pattern of the inhibited steel, the metal surface had wider peaks and lesser crystallinity structure than the control sample. This indicated the inhibitor absorption on the substrate and the creation of complex compounds with iron cations [53].

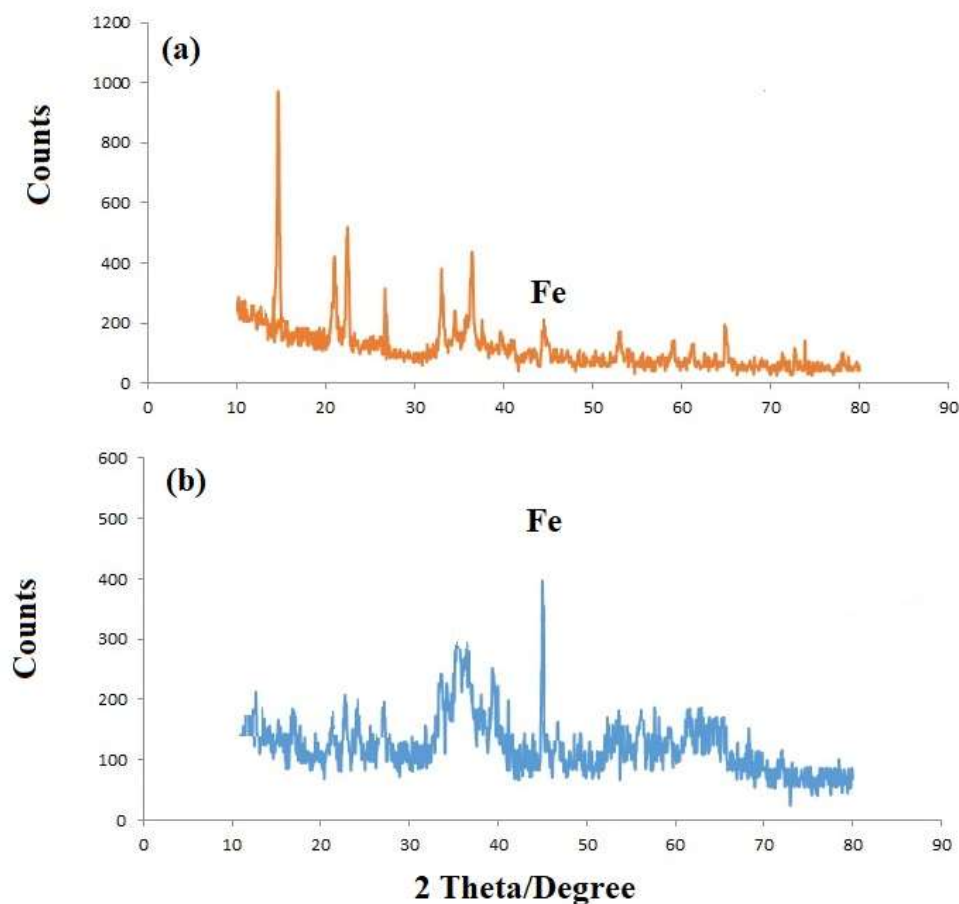


Figure 12: XRD pattern of the oxide phases on the steel surface exposed to acid solution (a) blank (b) in the presence of extract/water-acetonitrile.

3.11. Corrosion inhibition mechanism of PPE

PPE has high potential in corrosion protection of steel in acidic environments owing to various polyphenols compounds [44]. One of the most important polyphenol compounds in PPE is ellagic acid, that easily coordinate with iron atoms of the metal surface [44].

Ether and hydroxyl groups in polyphenols including ellagic acid, via many non-bonding pair electrons and also π electrons, are able to absorb H^+ ions through hydrogen bonds.

As a result, they reduce the corrosive nature of the HCl solution [44, 54].

Also, polyphenols are reducing agents and can be oxidized to benzoquinone via the soluble O_2 in acidic media [44, 54]. Therefore, PPE can effectively prevent the steel corrosion created by H^+ and O_2 . In this regard, acetonitrile is a relatively polar aprotic organic solvent in extraction and absorption methods. Unlike the mixtures of alcohol and ether with water, the combination of acetonitrile with water has little viscosity and high penetration power into natural materials for extraction [55]. Therefore, the mixture of acetonitrile and water acts as an excellent solvent system in the extraction of phytochemical compounds in PPE compared to water/alcohol and water/ether mixtures [55]. According to some researches, the main and major polyphenol compounds in PPE, are ellagic acid and gallic acid [44, 56, 57]. In Figure 13., the interaction of ellagic acid with H^+ and O_2 is presented.

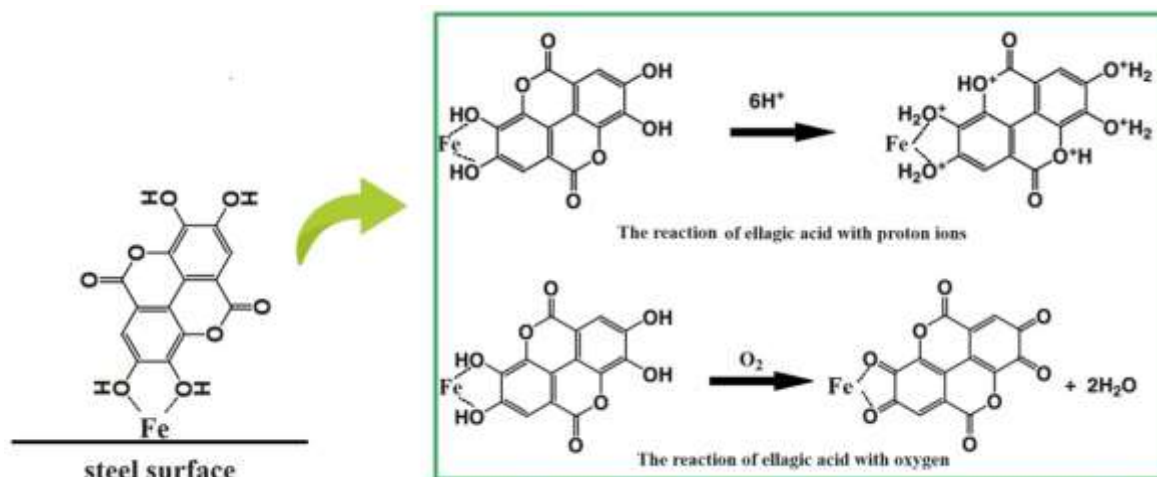


Figure 13: The proposed mechanism of corrosion protection of ellagic acid in PPE for steel in acidic medium.

4. Conclusion

- In general, the results of this work indicated that PPE is a suitable green corrosion inhibitor for steel in 15% HCl environment.
- The results of total phenol content (antioxidant) test showed that the lowest amount of total polyphenol was in the extracted PPE with water and the highest amount was in the extracted PPE with water-acetonitrile solvent system with volume ratio of 1:2.
- The results of the total polyphenol determination test showed that acetonitrile solvent was more efficient than ethanol in extracting polyphenol compounds.
- Based on weight loss test, IE% for extract/water-acetonitrile (1:2) was equal to 97.8% and according to EIS, it was 95%. Also, based on the weight loss and EIS test, the amount of 2.0 g/L was chosen as the optimal concentration.
- Polarization test confirmed that the performance of the PPE was a mixed kind with the dominant cathodic effect.

- According to the temperature effect investigation, at 40 °C, the IE% of the PPE declined about 20-25% at low concentrations and by 12% at higher concentrations, and at 60 °C it decreased by 35% for low concentrations. In higher concentrations, this reduction was about 30%.
- Based on the adsorption isotherm results, the inhibitor adsorption on the substrate followed the Langmuir isotherm.
- SEM/EDX confirmed creation of a dense film of the green inhibitor on the metal surface.
- According to the XRD pattern, the inhibited steel surface showed a decrease in the intensities and the number of the related peaks to corrosion products compared to the control sample.

What needs to be explained here is that the amounts of polyphenol components in different pomegranates are different, that affect their corrosion inhibition efficiency. But the point that was important in this research was to show the effect of acetonitrile in increasing the extraction efficiency of these compounds compared to water and alcohol, which was obtained based on the results of this research.

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