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The Synergistic Effect of Pomegranate Peel Extract with Zn^{2+} , Ce^{3+} , and KI Inhibition of Mild Steel Corrosion in Hydrochloric Acid: A Comparative Electrochemical and Surface Study

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Abstract: This study aims to evaluate the efficacy of pomegranate peel extract. The study investigated the effect of (PPE) in reducing the corrosion of mild steel in a 1 M hydrochloric acid solution, as well as the effect of adding Zn^{2+} , Ce^{3+} and KI enhances inhibition efficiency. Weight loss tests were conducted at various temperatures and immersion times, along with electrochemical measurements using open-circuit potential (OCP), potential polarization, and electrochemical impedance spectroscopy (EIS). Surface characterization was performed using scanning electron microscopy (SEM), atomic force microscopy (AFM), and four-dimensional infrared (FTIR) spectroscopy. The weight loss results showed that increasing the PPE concentration from 200 to 600 ppm improved inhibition efficiency, reaching approximately 30.03% at 600 ppm. Combining PPE with additives also resulted in a significant improvement in inhibition efficiency. The best result was achieved with the PPE-KI system at a concentration of 600 ppm PPE and 2 mM KI, reaching an inhibition efficiency of 74.77%. This was followed by the PPE- Ce^{3+} system and then the PPE- Zn^{2+} system. The study of the effect of temperature and immersion time showed that 25 °C and 24 hours represented the optimal conditions for the PPE-KI system under investigation. Electrochemical measurements supported this trend; the PPE-KI system recorded the highest charge transfer resistance (R_{ct}) of 107.20 $\Omega \cdot \text{cm}^2$, with an EIS-calculated inhibition efficiency of 69.22%. Furthermore, surface images showed improvement in the presence of PPE, particularly with the addition of KI, while FTIR spectra revealed changes in the environment of some functional groups after immersion. Overall, the results suggest a potential synergistic effect between PPE and KI.

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1. Introduction

Metal corrosion is a long-standing and prominent issue facing many industrial sectors, especially when dealing with acidic environments. This causes a gradual loss of metal and a deterioration in the properties of materials and equipment, in addition to the resulting economic losses. Mild steel is widely used in industrial applications due to its favorable mechanical properties, low cost, and ease of manufacturing. However, it is clearly susceptible to corrosion when exposed to acidic solutions, including hydrochloric acid used in cleaning, descaling, and acid treatment processes [1,2].

Mild steel corrodes in acidic environments as a result of electrochemical reactions. Iron dissolves at the anodic sites and hydrogen ions are reduced at the

cathodic sites. To reduce these reactions, corrosion inhibitors are used to slow the reaction rate between the metal surface and the aggressive medium. Interest in organic inhibitors derived from natural sources has increased due to the need for alternatives that are more compatible with the principles of green chemistry and have less impact on the environment compared to some conventional inhibitors [1,3].

Plant extracts and biomass residues have garnered increasing attention as natural sources of organic compounds capable of adsorbing onto metal surfaces and forming a protective layer that limits the interaction of the aggressive environment with the metal surface. The effectiveness of these compounds is linked to the presence of functional groups and donor atoms, such as oxygen and nitrogen, as well as aromatic systems and electrons. π , which can contribute to the interaction of inhibitor molecules and their adsorption onto the metal surface [2,3,4].

Pomegranate peels (*Punica granatum* L.) is a plant waste product rich in phenolic and polyphenolic compounds. It also contains functional groups such as hydroxyl and carbonyl groups and aromatic systems, along with a number of other organic compounds. These components can help pomegranate peel extract adhere to the steel surface and form a protective layer that reduces corrosion [6,5].

Pomegranate peel extract has been studied as an environmentally friendly inhibitor of mild steel corrosion in hydrochloric acid. One study showed Ashassi-Sorkhabi et al., using weight loss, electrochemical polarization, and electrochemical resistivity techniques, demonstrated that pomegranate peel extract possesses a clear ability to inhibit the corrosion of mild steel in HCl solution. This inhibitory effect was attributed to the adsorption of organic compounds present in the extract onto the metal surface [5]. Ait Aghzzaf et al. also showed that crude pomegranate peel extract acts as a mixed-type inhibitor in HCl, and its effect is linked to the formation of an organic layer on the steel surface, providing a protective barrier against the aggressive medium [6], Salim et al. likewise evaluated pomegranate peel extract as a green inhibitor for mild carbon steel in 1 M HCl [7].

Although plant extracts can provide significant protection against corrosion, their inhibitory efficiency can be affected by the extract's composition, concentration, the nature of the medium, and the experimental conditions. For this reason, some studies have investigated the use of other additives alongside organic inhibitors to enhance the absorption of the inhibitor components, increase surface coverage of the metal, and improve the performance of the protective coating. The term 'synergistic effect' is used when combining two substances results in a higher inhibitory efficiency than either substance achieves individually, and the presence of this effect is determined through appropriate experimental comparison. The synergism parameter (S) proposed by Aramaki and Hackerman is commonly used to quantify this effect, with $S > 1$ indicating synergism [8].

It is considered ions iodide one from Additions that Done Her study in area inhibition Erosion. Showed study he and his colleagues impact Synergistically between extract vegetable and ions iodide in inhibition corrosion steel The soft Q235 in solution HCl With focus 1M. She pointed the study to presence cooperation between ions iodide and molecules Abstract, Which Improve efficiency inhibition comparison Using Extract onliness [9] , Similar synergistic behaviour between plant extracts and iodide ions has been reported for Benincasa hispida peel extract in 1 M HCl, where the synergy coefficients exceeded 1 [10], for Medicago sativa extract [11], and for bamboo leaf extract in phosphoric acid [12]. The role of iodide is generally explained by its specific adsorption on the metal surface, which facilitates the adsorption of the organic inhibitor species [13]. A synergistic effect between *Punica granatum* extract and KI on S355 steel has also been reported [14].

From District Other, maybe For some ions Minerals that Affect on behavior surface metal or ingredients The class Protective The formed in presence inhibitor organic. in the

study Current, It was completed to choose ions Zinc(Zn^{+3}) and ions Cerium(Ce^{+3}) As additions For comparison with KI With the aim evaluation Its impact when Merge it with extract peel pomegranate under same circumstances empiricism , Synergism between metal cations and organic inhibitors has also been reported, for example between Zn^{2+} and Azadirachta indica gum on mild steel in 1 M HCl [15] and between Ce^{3+} and an amino acid on carbon steel in NaCl solution [16].

Based on to that, focus the study Current on comparison impact addition Zn^{2+} and Ce^{3+} and KI to extract peel pomegranate in inhibition corrosion steel The soft in acid hydrochloric. It depends the study on road loss the weight and measurements Electrochemical In what in that Dynamic electrochemical polarization (PDP) and spectrum impedance Electrochemical (EIS), to side Technologies analysis The surface, With the aim evaluation an average Erosion and efficiency inhibition, and verification from impact Extract And additions on behavior surface steel.

It aims the study to evaluation bezel to improve efficiency inhibition corrosion steel The soft when to merge extract peel pomegranate with Zn^{2+} , Ce^{3+} and KI and comparison performance Systems The different ones, and determining any system he The most effectiveness in inhibition Erosion in solution acid hydrochloric Based on to results loss the weight and measurements Electrochemical Analysis surface.

2. Materials and Method

2.1 Materials and reagents(Materials and Reagents)

In This is amazing the study, It was completed Use Samples from steel The soft In dimensions ($2.0 \times 2.0 \times 0.2$ cm) poison. It was completed to prepare surfaces Samples mechanically Using paper emery from carbide silicone (SiC) with granules ranges between 400 and 1200, then It was completed wash Samples With water distillate and drying it before Test [17].

It was completed to prepare solution acid hydrochloric 1M from acid hydrochloric Center (37%) Using Water distillate or Removed ions. as It was completed to prepare solutions Additives chloride Zinc ($ZnCl_2$), chloride Cerium ($CeCl_3 \cdot 7H_2O$), and iodide Potassium (KI) when Concentrations Required According to Design The experiment.

It was completed to prepare extract peel pomegranate (PPE) from Shells pomegranate Dried, Which Dried in shadow then It was ground To obtain on powder homogeneous. It was completed Extraction the components active Using 70% methanol when $60^\circ C$ For the duration 4 hours , then It was completed nomination Extract And it evaporated solvent under pressure low To obtain on Extract Center. after that, It was completed to prepare solution stock from Extract With focus 1000 ppm For its use in Experiments The suffix.

It was completed Use extract peel pomegranate In concentrations different in Experiments Primary To determine the focus The most effectiveness in to forbid corrosion steel The soft one, then It was completed Use the focus optimum Study impact Addition Joint for ions Zn^{2+} , Ce^{3+} and KI .

2.2 Preparation of mild steel samples and surface treatment

It was completed cutting Samples steel The soft mechanically to to cut In dimensions Equal ($2.0 \times 2.0 \times 0.2$ cm) To unify conditions to prepare Samples and reduce Contrast superficial between Experiments. It was completed to equip surfaces mechanically Using paper emery carbide silicone (SiC) Size grains It ranges from 400 to 1200 To achieve surface homogeneous and reduce impact scratches And the flaws superficiality on results a test Erosion [17].

After Sandpaper, It was completed wash Samples With water distillate then With alcohol ethyl To remove remains Sandpaper and impurities Superficial, then It was completed drying it and its weight Using balance My analysis accurately ± 0.1 mg . It was completed storage Samples in dryer until It is Using it in Tests Erosion.

Untreated samples were used as a control group. (Blank) While the other samples were exposed to a hydrochloric acid solution containing pomegranate peel extract alone or in combination with Zn^{2+} , Ce^{3+} and KI According to the specified experimental conditions.

Table 1. Materials, reagents, tools and equipment used in the study

No	Materials used	Tools and equipment and their quality
1	Mild steel with dimensions of 2.0 x 2.0 x 0.2cm	Analytical balance, accuracy 0.0001g
2	hydrochloric acid HCl at a concentration of 1 M	glass immersion vessels
3	pomegranate peel extract (PPE), at concentrations of 200, 400, and 600 ppm	Rotary evaporator (Rotary Evaporator)
4	Zinc chloride ZnCl_2 at a concentration of 1 mM	Water bath/heater with temperature control
5	Cerium chloride $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ at a concentration of 1 mM	device Potentiostat/Galvanostat
6	Potassium iodide KI at a concentration of 2 mM	Electrochemical Impedance Spectroscopy Unit EIS
7	methanol 70%	three-electrode electrochemical cell
8	ethanol	Reference pole Ag/AgCl or SCE
9	distilled water	Platinum auxiliary electrode Pt
10	sandpaper SiC at temperatures of 400–1200	Scanning electron microscope SEM
11	—	Atomic Force Microscope AFM
12	—	Fourier transform infrared spectrometer FTIR

2.3 Middle Test Design Experiments

Weight loss and electrochemical corrosion experiments were performed using a 1% hydrochloric acid solution. As an acidic reference medium for comparing experimental systems, a comparative experimental design was used to study the effect of pomegranate peel extract alone, and then its effect when combined with Zn^{2+} , Ce^{3+} and KI. Maintaining a constant temperature, immersion time, and number of repetitions for each stage of the study, in accordance with the principles of laboratory immersion tests [18].

It is clear Table(1) Matrix Experiments Used in the study, Which It includes Systems empiricism and concentrations extract Shells pomegranate And additions, In addition to degree the heat and duration Immersion and number Copying empiricism.

It included the study on solution HCl With focus 1M As a group officer (Blank), And three Concentrations from extract Shells pomegranate: 200, 400, and 600 ppm. And after that She was there Systems The vehicle Which It included the focus The Chosen One from extract Shells pomegranate with 1 milli mall from Zn^{2+} , and 1 milli mall from Ce^{3+} , and 2 milli mall from KI.

It was completed procedure all Systems The seven when degree heat 25°C For the duration immersion 24 hour, with three Samples Independent ($n = 3$) per system in Tests loss the weight.

Table 2. Matrix of experimental concentrations and times

The symbol	Experimental system	Concentration PPE	Ion concentration	Temperature	Time of immersion	Number of duplicates
B	HCl only (1 M)	0	0	25 °C	24 hours	3
P1	HCl + PPE	200 ppm	0	25 °C	24 hours	3
P2	HCl + PPE	400 ppm	0	25 °C	24 hours	3
P3	HCl + PPE	600 ppm	0	25 °C	24 hours	3
P+Zn	HCl + PPE optimum Zn ²⁺	optimum	1 mM	25 °C	24 hours	3
P+Ce	HCl + PPE optimum Ce ³⁺	optimum	1 mM	25 °C	24 hours	3
P+KI	HCl + PPE optimum KI+	optimum	2 mM	25 °C	24 hours	3

2.4 Weight Loss Measurement Test

A weight loss experiment was conducted to evaluate the corrosion behavior of mild steel and the inhibitory efficacy of pomegranate peel extract (PPE) in a 1 M hydrochloric acid solution. Mild steel samples were cut to dimensions of 2.0 × 2.0 × 0.2 cm, then progressively polished using silicon carbide sheets with grain sizes ranging from 400 to 1200. They were washed with distilled water and then ethanol, dried, and accurately weighed using an analytical balance [17]. Subsequently, the samples were immersed in 100 mL of the test solution for 24 hours at 25°C, with three independent replicates for each system. After immersion, the samples were removed, washed, dried, and weighed again. The weight loss (ΔW) was calculated from the difference between the weight before and after immersion according to the equation:

$$\Delta W = W_0 - W$$

Where W_0 represents the weight of the sample before soaking, and W is its weight after soaking.

The corrosion rate was calculated (CR) in mm/y according to the equation:

$$CR = \frac{87.6 \times \Delta W}{\rho \times A \times t}$$

Where it represents ΔW loss the weight (mg), the density of the mild steel (g/cm³), the surface area exposed to the solution (cm²), and the immersion time (h). Since all surfaces of the mild steel sample were exposed to the solution, the total surface area of the cm-sized sample was calculated using the following relationship: $\rho A t$ 2.0 × 2.0 × 0.2

$$A = 2(2.0 \times 2.0) + 4(2.0 \times 0.2) = 9.6 \text{ cm}^2$$

Corrosion inhibition efficiency was also calculated (IE%) using the equation [17]:

$$IE(\%) = \frac{\Delta W_{blank} - \Delta W_{inh}}{\Delta W_{blank}} \times 100$$

The weight ΔW_{blank} loss of the sample in the inhibitor-free solution was represented by the weight ΔW_{inh} loss in the presence of the inhibitor. All measurements were performed in three independent replicates, and the results are presented as mean ± standard deviation. (Mean ± SD).

2.5 Electrochemical measurements(Electrochemical Measurements)

Electrochemical measurements were performed using a three-electrode electrochemical cell, which included a sample of mild steel as the working electrode and a reference electrode. Ag/AgCl, and a platinum electrode as an auxiliary electrode. After immersing the working electrode in the test solution, the system was left for 30 minutes to

monitor the change in open-circuit voltage and to reach a semi-steady state before conducting subsequent electrochemical measurements [19,20].

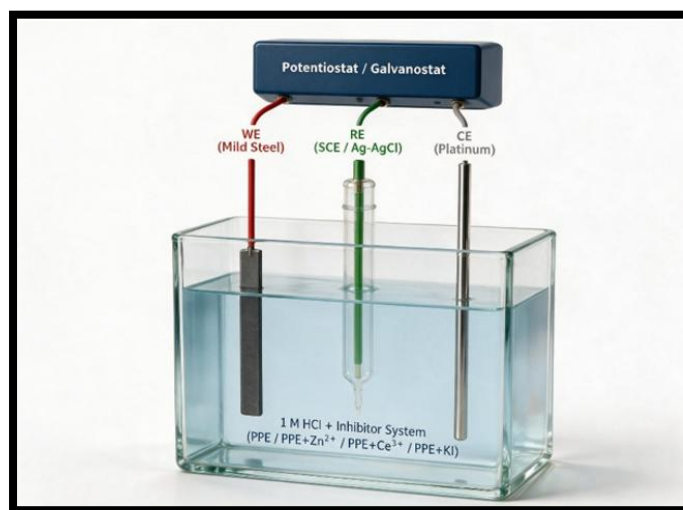


Figure 1. An illustration of Three-electrode electrochemical cell used in measurements

2.5.1 Open circuit voltage (OCP)

The open circuit voltage was recorded (OCP) for 30 minutes after immersing the soft steel electrode in the test solutions at 25°C. Measurements were used OCP to monitor changes in electrode surface potential over time and to assess the attainment of a semi-steady state before performing potentiodynamic polarization measurements and electrical resistivity spectroscopy.

2.5.2 Dynamic potential polarization (PDP)

After reaching a near-steady state of open-circuit voltage, dynamic potential polarization measurements were performed within the range of ± 250 mV around the corrosion potential (E_{corr}), with a scan rate of 1 mV/s. Polarization curves were used to determine the corrosion potential (E_{corr}), corrosion current density (I_{corr}), and the anodic (β_a) and cathodic (β_c) Tafel slope, and then the corrosion inhibition efficiency was calculated based on the corrosion current density values [19,20].

2.5.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy measurements were performed (EIS) on a frequency range of 100 kHz up to 10 mHz Using a 10-strength disturbance mV. Regarding the open-circuit voltage, impedance data were used to determine the charge transfer resistance (R_{ct}) and the electrical capacitance of the double layer (C_{dl}), as well as the resistance of the solution (R_s), by matching the data using the equivalent circuit model used in the analysis. [20]

Corrosion inhibition efficiency was calculated from the data EIS using the relationship :

$$IE_{EIS} \% = \left(\frac{R_{ct,inh} - R_{ct,blank}}{R_{ct,inh}} \right) \times 100$$

Where $R_{ct,inh}$ represents the charge transfer resistance in the presence of the inhibitor, while $R_{ct,blank}$ represents the charge transfer resistance in the uninhibited solution [20].

2.6 Description superficial (Surface Characterization)

Study Changes Morphology And the spectrum that to speak on surface steel The soft after Expose him Middle acidic and systems Inhibitors, It was completed Use microscopes

Electronic Scanner (SEM) And microscopes power Atomic (AFM) Analysis X-rays under Al-Hamra Using Conversion Fourier (FTIR).

Include Comparison surface polished before Exposure, and the surface Exhibition For solutions HCl With focus 1M without inhibitor, and the surface Exhibition For the system PPE + HCl, and the surface Exhibition For the system The compound KI + PPE, With the aim comparison the condition Morphology For the surface under conditions different.

It was completed Use photo SEM For comparison Morphology public For the surface, while Used Measurements AFM To assess topography surface in condition HCl without inhibitor and the situation KI + PPE.as Conducted Measurements FTIR extract peel pomegranate before Immersion And for the surface after Exposure For the system KI + PPE Study Changes potential in Groups Functional.

3. Results and Discussion

3.1 The effect of pomegranate peel extract concentration on weight loss

A preliminary study was conducted to evaluate the effect of pomegranate peel extract concentration (PPE) Weight loss of soft steel in 1 M hydrochloric acid solution for 24 hours at 25°m The study included the solution without the inhibitor and concentrations of 200, 400, and 600. ppm from PPE Using three independent iterations for each system, as shown in Table (3).

Table 3. Effect of pomegranate peel extract concentration on mild steel weight loss and inhibition efficiency in 1M HCl at 25 °C for 24 hours.

the system	Sample	weight before(mg)	weight after(mg)	weight loss(mg)	average
HCl only	B1	6278.4	6212.0	66.4	66.6
	B2	6310.2	6243.5	66.7	
	B3	6288.6	6221.9	66.7	
PPE 200 ppm	P200-1	6254.1	6202.9	51.2	51.3
	P200-2	6291.7	6240.5	51.2	
	P200-3	6276.3	6224.8	51.5	
PPE 400 ppm	P400-1	6302.4	6248.2	49.0	49.2
	P400-2	6268.9	6215.1	49.2	
	P400-3	6295.6	6241.8	49.4	
PPE 600 ppm	P600-1	6284.7	6238.1	46.6	46.6
	P600-2	6315.2	6268.7	46.5	
	P600-3	6273.8	6227.1	46.7	

It is clear Table(3) that middle loss the weight For steel The soft in solution Empty from damper He was 66.6 mg , while It decreased to 51.3 and 49.2 and 46.6 mg when Use extract peel pomegranate In concentrations 200 and 400 and 600 ppm on Succession .And it reached efficiency inhibition 22.97% and 26.13% and 30.03% on Succession.

Show the focus 600 ppm less loss For weight and higher efficiency To inhibit between Concentrations The laboratory, So It was completed to choose this the focus For studies Additional on Systems vehicle.

maybe that It is related decrease loss the weight With the presence ingredients membership in extract peel pomegranate that may react with surface steel or absorb attic,

Which may Helps in reduction Interaction between surface The middle acid.He suggests this Interpretation As a reason possible For results [22,21].

3.2 Study of Synergistic Systems

After selecting a concentration of 600 ppm The effect of combining pomegranate peel extract with Zn^{2+} At a concentration of 1 mmol, and Ce^{3+} With focus 1mM , and KI With a concentration of 2 mM At 25 °C For 24 hours, with the aim of comparing the performance of the integrated systems with the performance of the extract alone.

Table 4. The effect of ionic additives on the efficiency of inhibiting the corrosion of mild steel.

The symbol	Experimental system	PPE (ppm)	Zn^{2+} (mM)	Ce^{3+} (mM)	KI (mM)	Repeated 1(mg)	Repeated 2(mg)	Repeated 3(mg)	Average weight loss(mg)	IE%
B	Only HCl (1 M)	0	0	0	0	66.4	66.7	66.7	66.60 ± 0.17	0.00
P	HCl + PPE	600	0	0	0	46.6	46.5	46.7	46.60 ± 0.10	30.03
P+Zn	HCl + PPE + Zn^{2+}	600	1	0	0	29.8	29.9	30.1	29.93 ± 0.15	55.06
P+Ce	HCl + PPE + Ce^{3+}	600	0	1	0	24.9	25.1	25.0	25.00 ± 0.10	62.46
P+KI	HCl + PPE + KI	600	0	0	2	16.55	16.80	17.05	16.80 ± 0.25	74.77

It is clear Table (4) that middle loss the weight He was 66.60 ± 0.17 mg For the solution The officer, Which It decreased to 46.60 ± 0.10 mg when Use PPE With focus ppm 600 , with efficiency inhibition It reached 30.03%. when addition Zn^{2+} I t decreased middle loss the weight to 29.93 ± 0.15 mg, with efficiency inhibition It reached 55.06%.

in system PPE + Ce^{3+} , He was middle loss the weight 25.00 ± 0.10 mg, with efficiency inhibition It reached 62.46%. And in the time same, register system PPE + KI less middle loss weight, when 16.80 ± 0.25 mg, with higher efficiency inhibition It reached 74.77%.

Based on these results, the ranking of inhibition efficiency was:

$$PPE + KI > PPE + Ce^{3+} > PPE + Zn^{2+} > PPE > Blank$$

The marked increase in inhibition efficiency when personal protective equipment is combined with the additives suggests a possible synergistic effect between the extract components and the studied additives, particularly in the system . PPE + KI This is consistent with what previous studies have indicated about the synergistic effect between plant extracts and iodine ions in inhibiting steel corrosion in acidic environments [9].

As for explaining the mechanism of influence Zn^{2+} , Ce^{3+} , and I^- cannot be definitively determined from the results of weight loss alone, and the increase in inhibition efficiency may be related to changes in the interfacial interaction between the steel surface and the components of the medium and the extract , Earlier studies attribute the role of iodide to its specific adsorption on the steel surface [13], whereas synergism between cations and organic inhibitors has been reported for Zn^{2+} [15] and, through complex formation with organic molecules, for Ce^{3+} [16].

3.3 Temperature effect

After determining the system PPE + KI As the most efficient of the integrated systems, the effect of temperature on the damper's performance was studied during a constant immersion period of 24 hours. Experiments were conducted at temperatures of 25, 35, and

55 °C . Using a solution HCl With a concentration of 1M As a control solution at each temperature.

Table (5-a). Weight loss of mild steel in the control solution at different temperatures.

Temperature (°C)	Immersion time (hours)	Repeated 1(mg)	Repeated 2(mg)	Repeated 3(mg)	Average weight loss± SD (mg)
25	24	66.4	66.7	66.7	66.60 ± 0.17
35	24	80.1	79.8	79.8	79.90 ± 0.17
55	24	113.5	112.9	112.8	113.07 ± 0.38

Standard solutions showed an increase in average weight loss with rising temperature, rising from 66.60 ± 0.17 mg At 25 °C To 79.90 ± 0.17 mg At 35 °C Then to 113.07 ± 0.38 mg At 55 °C This indicates an increase in the corrosion rate in an acidic environment with rising temperature under the studied conditions. Table (5-b) shows this Effect of temperature on weight loss and inhibition efficiency of the system PPE + KI This includes weight loss results and inhibition efficiency at the three temperatures.

Table (5-b). The effect of temperature on weight loss and the effectiveness of the inhibition system PPE + KI.

Temperature (°C)	Immersion time (hours)	Repeated 1(mg)	Repeated 2(mg)	Repeated 3(mg)	Average weight loss± SD (mg)	IE (%)
25	24	16.55	16.80	17.05	16.80 ± 0.25	74.77
35	24	24.9	24.8	25.1	24.93 ± 0.15	68.79
55	24	34.4	34.2	35.0	34.53 ± 0.42	69.46

The average weight loss for the diet was PPE + KI amounts to 16.80 ± 0.25 mg at 25 °C , 24.93 ± 0.15 mg at 35 °C, and 34.53 ± 0.42 mg at 55 °C. The inhibition efficiency was 74.77%, 68.79%, and 69.46% at the same temperatures, respectively.

The damping system recorded its highest damping efficiency at 25 °C, and also exhibited the lowest absolute weight loss at this temperature. Therefore, 25 °C was considered the optimal temperature among those studied and was used to investigate the effect of subsequent immersion time.

It can be observed that the inhibition efficiency did not change linearly with increasing temperature; it decreased from 74.77% at 25°C to 68.79% at 35 °C. Then it rose slightly to 69.46% at 55°C. These results alone do not allow us to prove a specific mechanism for this change, so changes in the behavior of the interface layer or in the degree of absorption of the extract components can be considered as possible explanations, without confirming a specific mechanism , The influence of temperature on synergistic systems of natural inhibitors with iodide or metal cations in HCl has also been examined previously [14,15].

3.4 Immersion time effect

After setting the temperature to 25°C, the effect of immersion time on the system's performance was studied. PPE + KI At three times: 6, 24, and 72 hours, using a solution HCl His focus M1. Use the control solution each time. Table (6-a) shows the weight loss of mild steel in the solution. HCl M 1 At different immersion times.

Table (6-a). Weight loss of mild steel in solution 1M HCl at different immersion times.

Temperature (°C)	Immersion time (hours)	Repeated 1(mg)	Repeated 2(mg)	Repeated 3(mg)	Average weight loss± SD (mg)
25	6	25.5	25.6	25.1	25.40 ± 0.26
25	24	66.4	66.7	66.7	66.60 ± 0.17
25	72	95.1	95.6	95.4	95.37 ± 0.25

The control solution showed a consistent increase in average weight loss with increasing immersion time, rising from 25.40 ± 0.26 mg After 6 hours to 66.60 ± 0.17 mg after 24 hours , then to 95.37 ± 0.25 mg After 72 hours, indicating that the corrosion process continues with increased exposure time to the acidic environment.

Table (6-b). Effect of immersion time on weight loss and inhibitory system efficiency PPE + KI.

Temperature (°C)	Immersion time (hours)	Repeated 1(mg)	Repeated 2(mg)	Repeated 3(mg)	Average weight loss± SD (mg)	IE (%)
25	6	17.7	17.3	17.9	17.63 ± 0.31	30.59
25	24	16.55	16.80	17.05	16.80 ± 0.25	74.77
25	72	30.0	29.5	29.8	29.77 ± 0.25	68.78

The average weight loss for the diet was PPE + KI amounts to 17.63 ± 0.31 mg after 6 hours, 16.80 ± 0.25 mg after 24 hours, and 29.77 ± 0.25 mg after 72 hours, while the inhibition efficiency was 30.59%, 74.77%, and 68.78%, respectively.

Showed Results that efficiency inhibition Increased from 30.59 % after 6 hours To reach to Its peak when 74.77% after 24 hour, then It decreased to 68.78% after 72 hour .despite that loss The whole For weight shadow less in order damper comparison With the solution The officer, unless that The decrease in efficiency inhibition when 72 hour It indicates to that more time Exposure no Leads necessarily to more ongoing in efficiency Protection.

Based on to Results, It was completed to choose a period Soaking For the duration 24 hour As the best time between periods The studied one, where I registered higher efficiency inhibition In proportion 74.77% , And it was Use This is amazing Duration in Tests Next.

3.5 Measurements And the results Electrochemical

3.5.1 An effort The circle Open (OCP)

After immersing the mild steel electrode in the test solutions, the open-circuit voltage was recorded (OCP) for 30 minutes at 25 °C for all studied systems, namely HCl at a concentration of 1 M , PPE at a concentration of 600 ppm, and the combined systems PPE + Zn^{2+} , PPE + Ce^{3+} , and PPE + KI.

Table 7. Change in open circuit voltage (OCP) The effect of mild steel on time in the studied systems

Time(min)	HCl only	HCl + PPE 600 ppm	PPE + Zn ²⁺	PPE + Ce ³⁺	PPE + KI
0	-485	-479	-477	-474	-471
2	-483	-477	-475	-472	-469
4	-481	-475	-473	-470	-467
6	-480	-474	-472	-469	-466
8	-479	-473	-471	-468	-465
10	-478	-472	-470	-467	-464
12	-477	-471	-469	-466	-463
14	-476	-470	-468	-465	-462
16	-475	-469	-467	-464	-461
18	-474	-469	-466	-463	-460
20	-474	-468	-466	-463	-460
22	-473	-468	-465	-462	-459
24	-473	-467	-465	-462	-459
26	-473	-467	-464	-461	-458
28	-473	-466	-464	-461	-458
30	-472	-466	-463	-460	-457

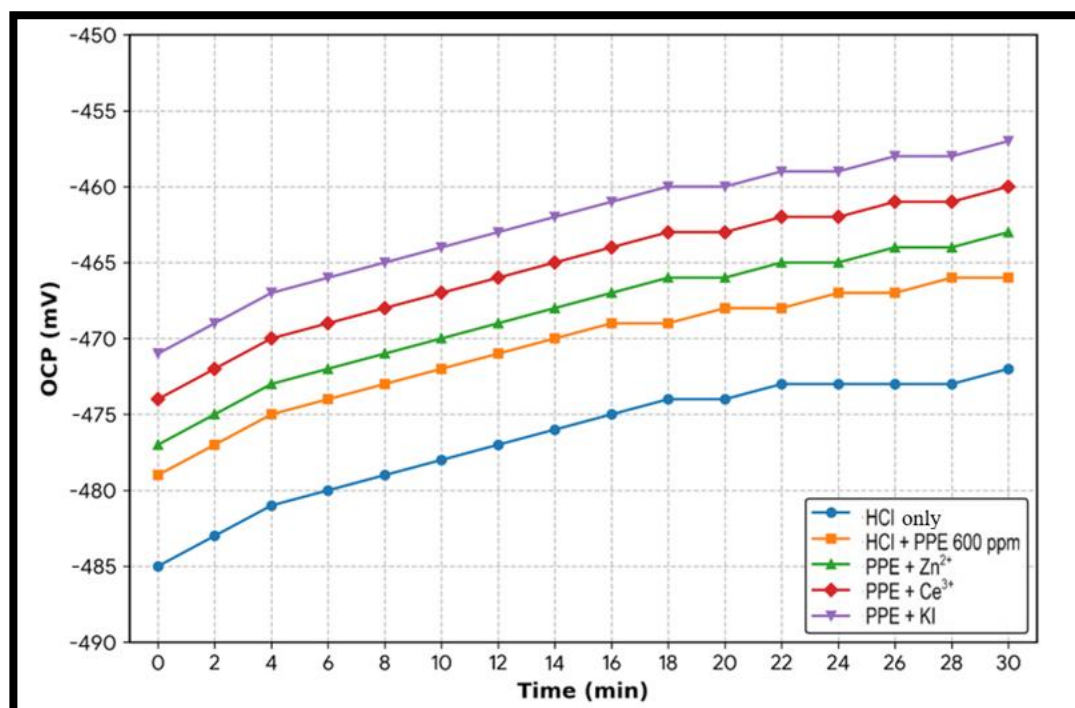


Figure 2. Change in open circuit voltage (OCP) Over time, mild steel in the studied systems

Figure (2) illustrates the change in open circuit voltage (OCP) During the measurement period, all systems showed a gradual shift towards less negative values during the first few minutes, then moved towards a more stable state over time. The open-circuit potential of the inhibitor-free solution was approximately -485 mV at the beginning of the measurement and stabilized at approximately -472 mV after 30 minutes, while the

value shifted in the presence of PPE From -479 to -466 mV The final values reached approximately -463 , -460 , and -457 mV In systems PPE+ Zn^{2+} and PPE+ Ce^{3+} and PPE+KI Consequently, this is the same order that will later be reflected in the results of weight loss and polarization in terms of inhibition efficiency ($PPE+KI > PPE+Ce^{3+} > PPE+Zn^{2+} > PPE$).

3.5.2 Potential polarization curves

After reaching a semi-stable open-circuit voltage state (OCP) Potential polarization measurements of mild steel were performed in a 1 M HCl solution, and in the studied inhibitor systems, namely PPE at a concentration of 600 ppm, PPE + Zn^{2+} , PPE + Ce^{3+} , and PPE + KI. The polarization curves were used to determine the corrosion potential (E_{corr}), corrosion current density (I_{corr}), and the anodic (β_a) and cathodic (β_c) Tafel slope, and then to evaluate the corrosion inhibition efficiency of the studied systems.

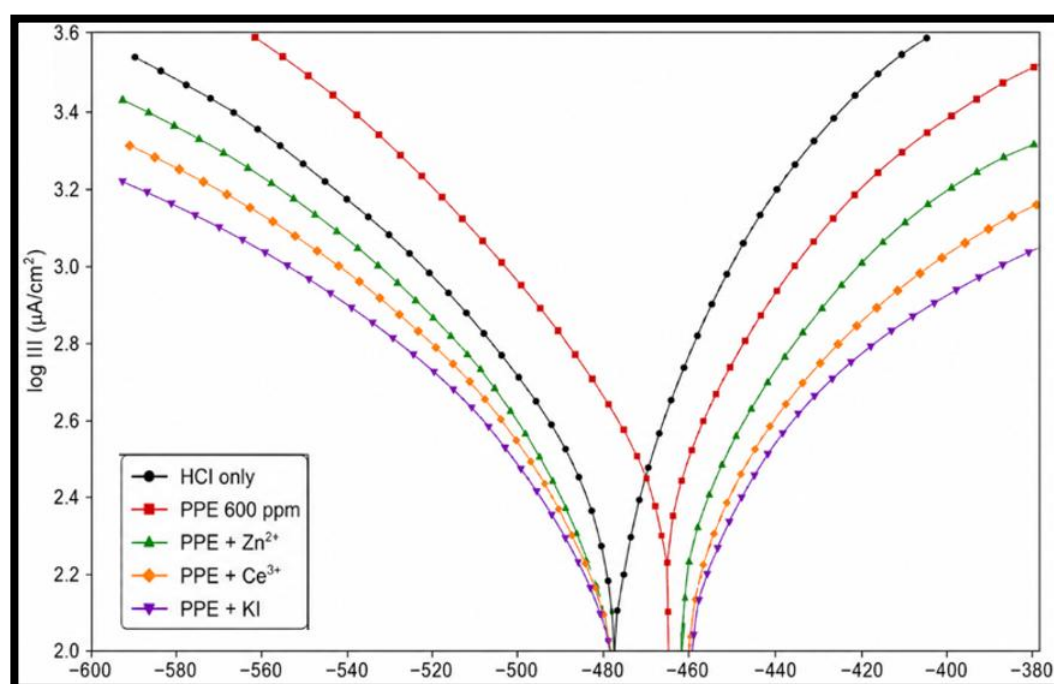


Figure 3. Potential polarization curves of mild steel in 1 M HCl solution and in the presence of different inhibitory regimes at 25 °C.

The polarization curves showed a clear decrease in the corrosion current density upon addition. PPE and combined systems compared to the inhibitor-free solution, with the reduction being more pronounced in the PPE + KI system.

The potential polarization parameters and corrosion inhibition efficiency values for the studied systems are shown in the table (8).

Table 8. Potential polarization parameters and corrosion inhibition efficiency of mild steel in the studied systems

order	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	β_a (mV/dec)	β_c (mV/dec)	IE (%)
HCl only	-484	821	93	119	0.00
PPE 600 ppm	-465	574	97	120	30.09
PPE + Zn^{2+}	-462	371	102	125	54.81
PPE + Ce^{3+}	-461	304	105	128	62.97

PPE + KI	-456	249	107	131	69.67
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Maybe note from Table (8) that addition PPE led to decrease value I_{corr} from 821 $\mu\text{A}/\text{cm}^2$ in solution HCl to 574 $\mu\text{A}/\text{cm}^2$, Detective efficiency inhibition In proportion 30.09%. And it increased efficiency inhibition when to merge PPE with Additions Other, where It reached 54.81% in system PPE + Zn^{2+} , and 62.97% in system PPE + Ce^{3+} , while register system PPE + KI higher efficiency inhibition In proportion 69.67%. A similar decrease in I_{corr} for the extract/KI combination relative to the extract alone was reported for Benincasa hispida peel extract in 1 M HCl [10].

as Transformed Values E_{corr} gradually about Values Positivity more, from -484 mV in solution Empty from damper to -456 mV in system PPE + KI Change It is estimated about 28 mV, This shift is smaller than 85 mV, the limit commonly used to classify an inhibitor as mixed-type [10].

Values showed β_a and β_c A gradual change occurred with the addition of inhibitory systems; as they increased β_a increased from 93 to 107 mV/dec, while β_c rose from 119 to 131 mV/dec. These changes indicate that the electrochemical reactions on the steel surface are affected by the presence of inhibitory systems, coinciding with the marked decrease in I_{corr} .

The ranking of inhibition efficiency was as follows:

$$\text{PPE} + \text{KI} > \text{PPE} + \text{Ce}^{3+} > \text{PPE} + \text{Zn}^{2+} > \text{PPE}$$

These results indicate the superiority of the combined system PPE + KI in the protection of mild steel within the studied systems, with the possibility of a synergistic effect between the components of pomegranate peel extract and iodide ions.

3.5.3 Spectroscopy Resistance Electrochemical (EIS)

Electrolytic resistance measurements were performed EIS To evaluate the surface behavior of soft iron in solution HCl With a concentration of 1M To study the impact PPE and the systems combined with Zn^{2+} , Ce^{3+} and KI On the resistance to charge transfer. Table (9) shows the electrolysis parameters of resistance and corrosion inhibition efficiency of mild iron in the studied systems, with values R_s and R_{ct} and C_{dl} And the calculated inhibition efficiency from the data EIS.

Table 9. Electrochemical impedance parameters and corrosion inhibition efficiency of mild steel in the studied systems.

the system	R_s ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE (%)
HCl only	1.61	33.00	186	0.00
PPE 600 ppm	1.67	46.65	152	29.26
PPE + Zn^{2+}	1.70	71.92	123	54.12
PPE + Ce^{3+}	1.73	86.79	114	61.98
PPE + KI	1.76	107.20	102	69.22

It is clear from the table (9) That adding PPE to HCl solution resulted in an increase in R_{ct} from 33.00 to 46.65 $\Omega \cdot \text{cm}^2$, with a decrease in C_{dl} from 186 to 152 $\mu\text{F}/\text{cm}^2$, and the calculated inhibition efficiency from EIS was 29.26%.

And when merging With PPE additives, R_{ct} increased to 71.92, 86.79 and 107.20 $\Omega \cdot \text{cm}^2$ in PPE + Zn^{2+} , PPE + Ce^{3+} and PPE + KI systems, respectively, while C_{dl} decreased to 123, 114 and 102 $\mu\text{F}/\text{cm}^2$, respectively.

The calculated inhibition efficiency from the data also reached EIS values are 54.12%, 61.98%, and 69.22 % in systems combined with Zn^{2+} , Ce^{3+} and KI, respectively. The PPE + KI system recorded the highest R_{ct} and the highest inhibition efficiency among the systems studied.

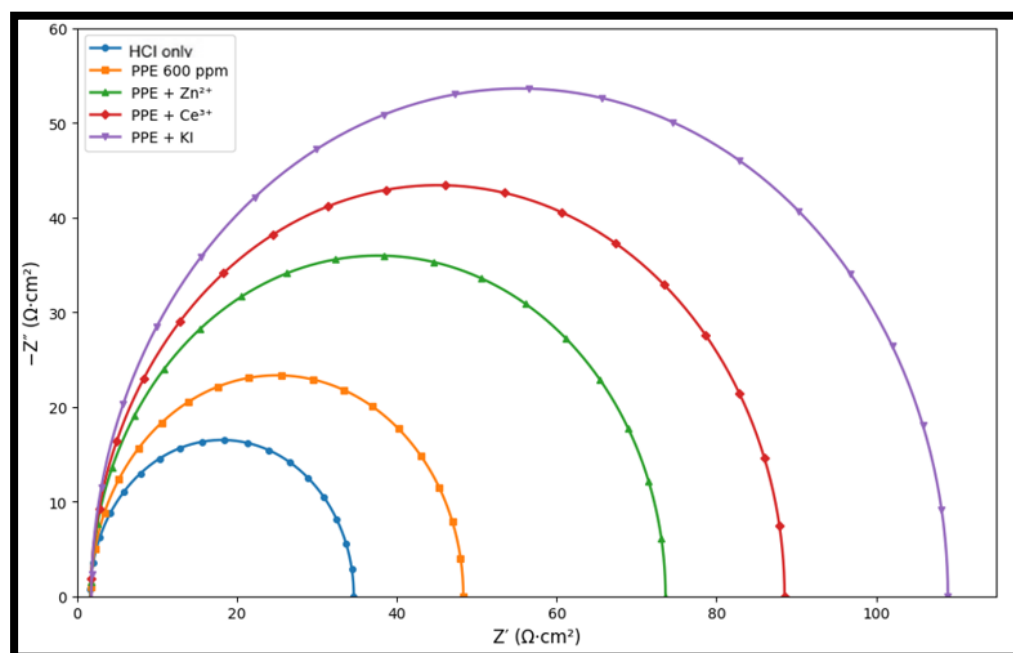


Figure 4. DiagramsNyquist for mild steel in a 1 M HCl solution in the absence and presence of PPE and combined systems at 25 °C.

The diagrams showed Nyquist Increase in the diameter of the semicircle when added PPE Then, when combined with the studied additives, noting the largest diameter in the system PPE + KI This corresponds to a high charge transfer resistance of $33.00.\Omega\cdot\text{cm}^2$ in HCl Alone to $107.20 \ \Omega\cdot\text{cm}^2$ In the system PPE + KI This indicates an increased resistance to charge transfer in the presence of the damper system. The trends from the results are consistent EIS With the results of weight loss and open-circuit polarization, the system appears PPE + KI The highest efficiency among integrated systems. These results support a clear improvement in protection performance when integrated.PPEWith the additives studied, although a detailed explanation of the mechanism still requires further surface and spectral evidence , A comparable increase in the capacitive arc radius after adding iodide to a plant extract was reported for *Benincasa hispida* peel extract [10].

3.6 Surface description

3.6.1 Morphological description of the surface (SEM and AFM)

The morphological characterization of the mild steel surfaces was performed using a scanning electron microscope (SEM) and the atomic force microscope (AFM) The study aimed to compare the surface condition before and after exposure to an acidic medium and inhibitor systems. The comparison included the polished surface before exposure and the surface exposed to the solution . HCl With a concentration of 1M Without a depressant, the surface exposed to the system PPE + HCl The surface exposed to the embedded system PPE + KI.

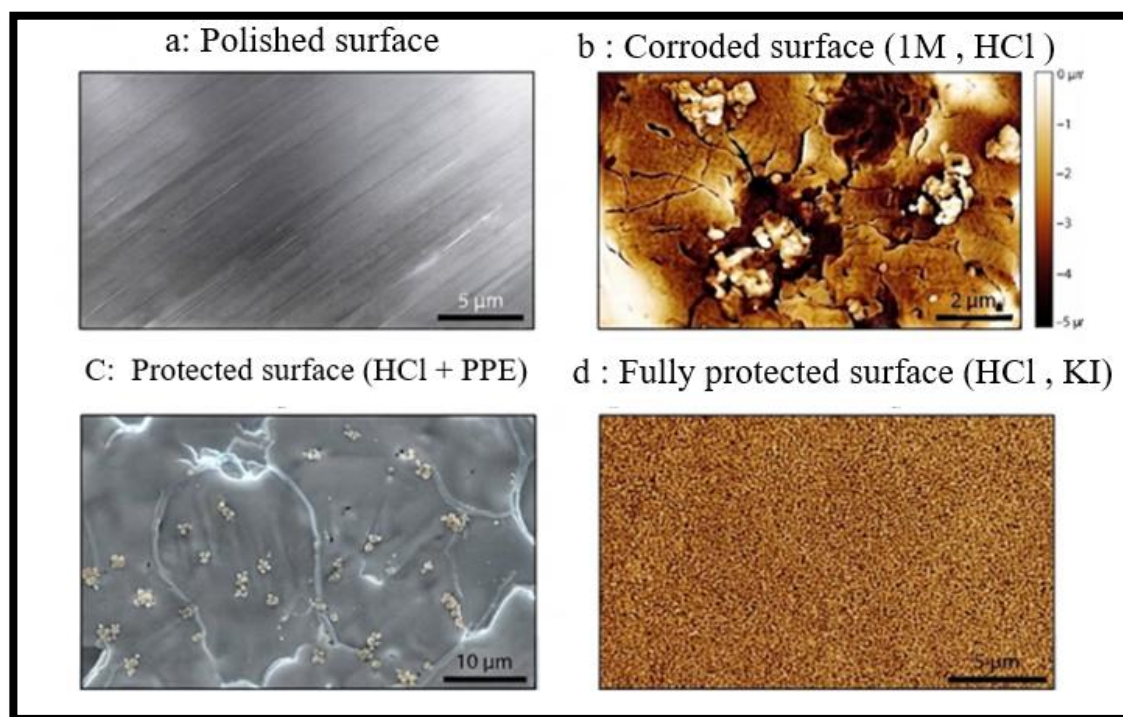


Figure 5. Morphological images of the mild steel surface: (a) Polished surface before exposure, (b) Surface exposed to solution (c) Surface exposed to the HCl + PPE system , (d) Surface exposed to the PPE + KI system.

The polished surface in Figure (5-a) showed a relatively homogeneous appearance with traces of polishing resulting from sample preparation, representing the reference state of the surface before exposure to the acidic medium..

In contrast, the surface exposed to the solution showed HCl alone, as shown in Figure (5-b) using AFM, caused a clear change in surface texture and heterogeneity, with the appearance of pits and cracks as seen in the image and color scale. These features indicate significant erosion resulting from exposure to the acidic environment in the absence of an inhibitor. The depth of the pits, as shown in the image scale, is approximately 5 μm according to the data in the file.

surface Exhibition For the system HCl + PPE , as he Explained in Figure (5-C) Using microscope electronic Scanner (SEM) , It appeared more homogeneity comparison on the surface Exhibition For the acid alone, with some Changes and deposits Local.maybe that be This is amazing Features Related With the presence ingredients Extract on surface.

As for with regards For the surface Exhibition For the system PPE + KI, as he Explained in Figure (5-d) Using microscope power Atomic (AFM) , Lost Show fabric more homogeneity And less roughness comparison on the surface Exhibition For the acid alone, with decrease marked in Features surface Related by erosion.

The general morphological observations are consistent with the trend shown by the weight loss results and EIS; the PPE + KI system recorded the highest inhibition efficiency in weight loss and polarization tests, and also recorded the highest charge transfer resistance R_{ct} value of 107.20 $\Omega\cdot\text{cm}^2$. These results together support the improvement in the surface condition of steel in the presence of the combined system, without considering the morphological images alone as conclusive evidence of the inhibition mechanism.

3.6.2 Infrared spectroscopy (FTIR)

Infrared spectroscopy was used for spectroscopic analysis (FTIR) To identify some of the functional groups present in pomegranate peel extract (PPE) To compare the spectrum of the extract before immersion with the spectrum recorded on the iron surface after exposure to the system PPE + KI The aim of the comparison was to observe changes

in the positions of some absorption bands that may be related to changes in the chemical environment of the extract components when they are on the surface of iron.

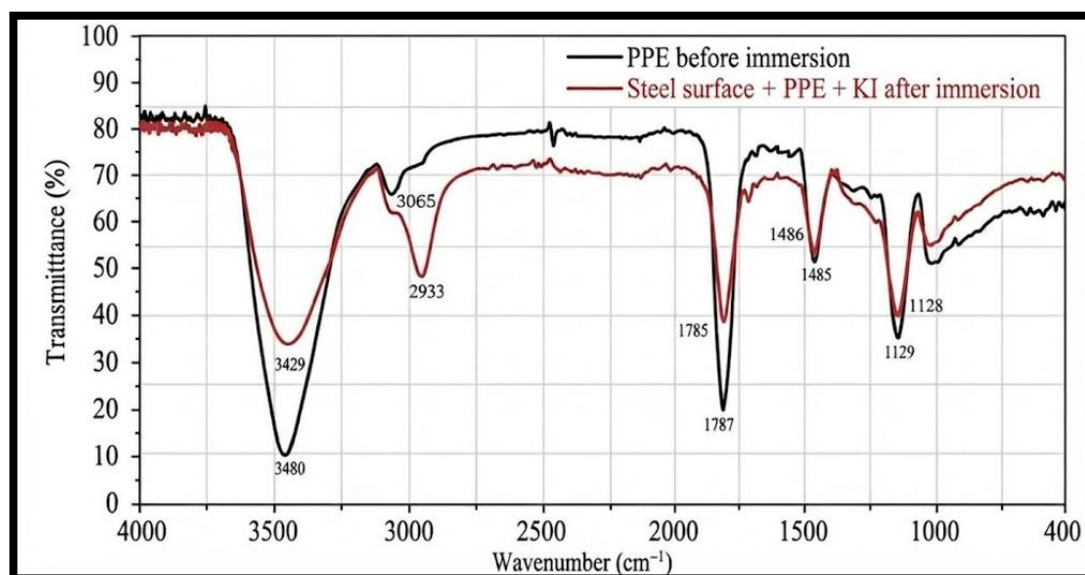


Figure 6. FTIR spectra of pomegranate peel extract (PPE) before immersion and of the mild steel surface after immersion in the PPE + KI system.

Spectrum showedThe PPE beam appeared at 3480 cm^{-1} before immersion, while it appeared at 3429 cm^{-1} after exposure to the damping system. This region can generally be attributed to O–H group vibrations. A beam also appeared at 3065 cm^{-1} . In the spectrum of the extract before immersion, and the package at 2933 cm^{-1} after immersion, and this region is associated with link vibrations C–H , especially aliphatic vibrations at lower values [23]

A package also appeared when 1787 cm^{-1} in the PPE spectrum before immersion and moved to 1785 cm^{-1} after immersion. Since the precise assignment of this region to a specific carbonyl group depends on the chemical composition of the sample and the environment surrounding the functional group, it has been described in general terms in this study within the vibrational region of carbonyl-containing groups [23].

As for the two bundles at 1486 and 1485 cm^{-1} , these bands fall within a region where several organic bond vibrations can overlap; therefore, it is preferable not to assign them to a specific functional group based solely on FTIR. The two bands that appeared at 1129 and 1128 cm^{-1} can generally be associated with bond vibrations C–O [23].

Table 10. FTIR beams for pomegranate peel extract before immersion and for the steel surface after immersion in the PPE + KI system.

Functional group/vibration type	PPE before immersion (cm^{-1})	steel surface + PPE + KI after immersion (cm^{-1})
O–H	3480	3429
C–H	3065	2933
C=O	1787	1785
Vibrations of organic bonds/structure	1486	1485
C–O	1129	1128

The table data shows (10) A change in the positions of some absorption bands after exposure to the inhibitory system, particularly the band transfer associated with the group O–H from 3480 to 3429 cm^{-1} , along with minor changes in other bands. These changes may reflect alterations in the chemical environment of some functional groups present in the extract components due to their surface location or interaction with the interfacial environment; however, FTIR alone is insufficient to definitively establish the nature of the bond or determine the adsorption mechanism.

These spectral observations are generally consistent with the results of weight loss and EIS Which showed an improvement in system performance PPE + KI The combined results support the possibility that some organic components in pomegranate peel extract contribute to the formation of a protective layer on the surface of steel, which is consistent with what previous studies have indicated about the role of organic compounds in pomegranate peel extract in inhibiting the corrosion of soft steel in acidic environments [5,6].

4. Conclusion

Pomegranate peel extract showed (PPEClear ability to prevent corrosion of soft steel in solutionHClWith a concentration of 1M, and a concentration of 600 PPM was chosen as the best concentration in the initial study, as it achieved an inhibition efficiency of 30.03%, The merger led PPE with carefully considered additives to improve inhibition efficiency, and the PPE + KI (2 mM) system recorded The highest efficiency reached74.77%, followed by PPE + Ce^{3+} (1 mM) at 62.46 % , then PPE + Zn^{2+} (1 mM) at 1% 55.06% , He was 25°C and 24 hours is the best study conditions for the system PPE + KI, as these conditions recorded the least weight loss and the highest inhibition efficiency of 74.77%. Electrochemical measurements supported the weight loss findings, as the corrosion current density decreased and the charge transfer resistance increased in the presence of the inhibitor. The system recordedPPE + KI Highest value for R_{ct} It reached 107.20 $\Omega \cdot \text{cm}^2$, and the inhibition efficiency of EIS reached 69.22%. Measurements also showed (OCP) and polarization cause a change in the electrochemical behavior of the surface with improved protection. Images showed SEM and AFM showed improved surface condition of the steel in the presence of PPE, and the surface of the PPE + KI system was more homogeneous and exhibited less corrosion compared to the surface exposed to HCl without the inhibitor. FTIR results also showed changes in some functional groups, supporting the possibility that the PPE components contribute to the formation of a protective layer on the surface, although FTIR alone does not constitute conclusive evidence of the inhibition mechanism. In general, it wasPPE + KI The most efficient system among those studied. The results suggest a potential synergistic effect between the system components; however, quantitatively proving synergy requires testing each of the components. Zn^{2+} , Ce^{3+} and KI individually and under the same experimental conditions.

We recommend that future researchers carry out additional studies to assess the performance and stability of the PPE + KI system under a wider range of experimental conditions. Study impact Times immersion and degrees heat Additional To check from stability efficiency inhibition on bezel Longest. Procedure Tests Independent for Zn^{2+} , Ce^{3+} and KI , addition to Systems Joint, To conduct evaluation quantitative more accuracy To influence Synergy. Procedure studies superficial and electrochemical Additional To determine nature The class The formed on surface steel The soft and mechanism correlation or adsorption ingredients extract Shells pomegranate. Study possibility application extract Shells pomegranate with KI As an inhibitor green to erode steel The soft in environments Acidity, with evaluation His stability and its effectiveness under conditions employment different.

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