The Proton Pump Inhibitor (Lansoprazole Drug) As a Corrosion Inhibitor for High Carbon Steel in Hydrochloric Acid Solution

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The proton pump inhibitor (Lansoprazole Drug) as a Corrosion Inhibitor for High Carbon Steel in Hydrochloric Acid Solution

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ABSTRACT
The proton pump inhibitor lansoprazole (PPIL) drug is examined as corrosion inhibitor for high carbon steel (HCS) dipped in 1.0M HCl. The study was conducted utilizing ac impedance spectroscopy (EIS), Mass loss (MI), polarization tests, and surface checks were utilized to illustrate the importance of this PPIL extract to the prevent corrosion process for HCS. The influence of temperature and concentration of PPIL on the efficiency of inhibition were tested. The corrosion mechanism occurs, when the PPIL extract molecules block the active center in the electrode surface. The inhibition efficiency (%IF) of HCS occurs by the adsorption procedure and HCS is subject to the adsorption of Langmuir. Polarization curves showed that PPIL drug is a mixed-type inhibitor that retards the dissolution of HCS. IF % was deliberated with altering in the concentration of PPIL various temperature of the medium. From the outcome data we get that the good agreement in the all methods.

INTRODUCTION
In modified manufacturing processes, acidic medium is used to remove undesired measure and corrosion product [1]. In the pickling of metal alloys, HCl and H2SO4 are commonly used. The inhibitors used are one of the most effective methods for preventing metal reduction in acidic solutions by preventing decomposition[2, 3]. The organic composites utilized including hetero atoms, (N, S and O) were utilized to diminution the steel dissolution [4–7]. The attendance of π- electrons and lone pairs in molecules of inhibitor qualify electron movement from an inhibitor to the metal superficial, producing a covalent bond. The utilized compounds inclosing non-toxic and natural composites have utilized as inhibitors due to they're eco-friendly environmental [8–13]. In the current years, pharmaceutical compounds have utilized as corrosion hindrance. The drugs have utilized as protection dissolution of metals and alloys has some benefits over the utilized of organic/inorganic inhibitors due to their environmental atmospheres [14]. Drugs are non-hazardous, low-cost, unimportant negative impact on the environment, so it's suggested substituting the traditional toxic corrosion protection [15-16]. Experimental efforts have been ready recently on utilize of drugs as inhibitors for prevent dissolution of metals in altered media [17]. Gece [18] literature survey utilizes of many types of drugs as corrosion protection of several metals. Ampicillin, Ampiclox, tetracycline, cloxacillin, penicillin G, methocarbamol, azithromycin, orphenadrine [19]. Flucloxacillin, amoxicillin has tested for prevent dissolution of Al [20]. Cefalexin, cefadroxil, and cefazolin have been used as iron corrosion inhibitors in acidic solutions [21]. The PPIL drug was chosen as a corrosion inhibitor because of the following: i The active site of the PPIL molecule is constituted of (O, N, S) atoms. ii) This drug appears to be environmentally friendly and useful in biological research [22], and iii) PPIL medicine can be easily synthesized and purified [23]. PPIL was tested as a corrosion inhibitor for HSC in an acidic environment and demonstrated a high %IE

EXPERIMENTAL
The HCS samples composition HCS is an alloy with a conformation of “0.55 – 0.93 % C, 0.3- 0.9 % Mn” and the rest iron
Solutions Analytical reagent grade, 37 percent HCl was dissolved in bi-distilled water to create the aggressive conditions. The required doses were prepared by liquefaction with bi-distilled water using the standard stock inhibitors (1000 ppm) of the PPIL medication. The PPIL dose applied was (100-150-200-250-300) ppm. The structure of PPIL is shown below:
Mass loss (ML) tests Six specimens of HCS had utilized with area $20 \times 20 \times 2$ mm, were scratched by papers emery till 2000 grit size. All the destructive environments were exposed to air. The IE % and the surface coating ($\theta$), of PPIL were calculated from next balance (1):

$$\% \text{IE} = \theta \times 100 = [1 - (\text{CR}_{\text{inh}}/ \text{CR}_{\text{free}})] \times 100$$

Where $\text{CR}_{\text{free}}$ and $\text{CR}_{\text{inh}}$ are the corrosion rate absence and existence of PPIL drug, correspondingly.

Electrochemical tests A three electrode set up was engaged for electrochemical tests. They were arranged in a glass cell, platinum foil as auxiliary electrode, (SCE) saturated calomel electrode coupled to fine luggin capillary as a reference electrode, a and HCS as a working electrode (WE). The WE was prepared of square coins of HCS with area 1 cm$^2$. The electrode surface was treated in the similar manner as in the ML test. All tests were achieved at temperature (25 °C). Before starting the tests, the potential of electrode was studied for 25 min. Measurements were performed by Gamry apparatus (PCI4/750) with Gamry classification depends on the ESA 400 and computer frame works software DC 105 for PP tests, software EFM140 for EFM and software EIS 300 for EIS.

Potentiodynamic polarization (PP) tests PP scan used to obtain Tafel curves by sweeping the working potential from -600 to 400 mV at scan rate 1 mVs$^{-1}$. $i_{\text{corr}}$ was calculated by extrapolation of cathodic and anodic Tafel lines to gives log $i_{\text{corr}}$ and $E_{\text{corr}}$ for HCl and in existence of PPIL drug. Then $i_{\text{corr}}$ was utilized to compute the %IE and $\theta$ as bellow Eq. (2):

$$\% \text{IE} = 100 \times \theta = 100 \times [1-(i_{\text{corr}}/i_{\text{corr}}^{\circ})]$$

Where $i_{\text{corr}}(\text{inh})$ and $i_{\text{corr}}(\text{free})$ are current obtained from corrosion attendance and lack of PPIL drug, individually.

Electrochemical impedance spectroscopy test (EIS) EIS tests were directed in frequency medium (100 x10$^3$ Hz to 10 Hz). From the study of Nyquist digrams, one can measured $R_{\text{ct}}$ and $C_{\text{dl}}$. The % IE and $\theta$ were calculated utilizing the next Eq. (3):

$$\% \text{IE} = 100 \times \theta = [1-(R_{\text{ct}}/R_{\text{corr}}^{\circ})] \times 100$$

Where $R^{\circ}$ and $R_{\text{ct}}$ are the resistances the uninhibited and inhibited PPIL drug, respectively.

Electrochemical frequency modulation test (EFM) The EFM results were obtained by connecting the sign of a potential perturbation with an amplitude of 10 mV to two frequencies of 2.5 Hz. The (CF-2 and CF-3) causality factors, ($i_{\text{corr}}$) and $\beta$, and $\beta_c$ were calculated by using the highest peeks.

SEM Studies After sinking the samples in solutions attendance and lack of 300 ppm PPIL after one day, the surface characteristics (20 x 20 x 4 mm) of HCS were examined. For this experiment, JEOL JSM-5500 was used.
**FT-IR tests**

FTIR analysis was performed using an “IR (Perkin-Elmer) spectrophotometer at the central Lab, Faculty of Pharmacy, Mansoura University, Egypt, to determine the functional groups existence in PPIL drug after adding 300 ppm in a solution of 1.0 M HCl without dipping the HCS metal coins and with a similar dose in 1.0 M HCl” after dipping the HCS three hours.

**AFM tests**

AFM gives the morphological properties of the HCS metal surface were planned. This exam happens in 1 M of HCl without PPIL drug inhibitor and in the case of the highest dose of PPIL (300 ppm). AFM was carried out in contact mode utilizing (Park systems, XE-100 model).

**Computational chemical approaches**

**Quantum chemical calculations**

Theoretical simulations were carried out using the DMol3 module built in Materials Studio version 7.0 software to investigate the relationship between the molecular structure and the reactivity of the PPIL molecule.

**Monte Carlo (MC) Simulation**

The Materials Studio programme version 7.0 was used to run MC simulations in a simulation box with periodic boundary conditions (Accelrys Inc., San Diego, CA, USA). “The pure CS crystal was used, and it was cleaved along with the most stable (lower energy) plane (1 1 0), resulting in a 30 vacuum slab. The plane CS surface of (1 1 0) was relaxed by lowering its energy, and then the surface of CS (1 1 0) was extended to a supercell (10/10). The simulation analysis has been carried out in a test box containing the simulated corrosive species and inhibitor molecule”, with the high-quality force field known as COMPASS being assigned to combine organic parameters and inorganic substances.

**Results and discussion**

**Mass loss (ML) tests**

ML was approved for HCS in 1.0 M HCl and attendance of altered doses of PPIL and is known in Fig. 1. “% IE value measured are documented in Tables 1 and 2, it is illustrious that the % IE rises with improving the PPIL dose and break down with improving the temperature from 30-50°C”.

**Table 1.** CR, θ and %IE obtain from ML tests for HCS attendance and lack altered doses of PPIL at 30°C and 120 min.

| Conc., ppm | CR., x10² mg cm⁻² min⁻¹ | θ     | % IE     |
|------------|--------------------------|-------|----------|
| Blank      | 93.4 ±0.0173             | ---   | ---      |
| 100        | 6.8 ±0.0145              | 0.805 | 80.5     |
| 150        | 5.8 ±0.0230              | 0.850 | 85.0     |
| 200        | 5.2 ±0.0155              | 0.884 | 88.5     |
| 250        | 4.6 ±0.0239              | 0.902 | 90.2     |
| 300        | 4.1 ±0.0153              | 0.912 | 91.2     |

**Figure 1.** Time -ML bends for the HCS dissolution in 1.0 M HCl and in attendance of altered doses of PPIL
drug at 30°C

The PPIL molecules are adsorbed on surface of HCS by designed adsorbed layer PPIL drug molecules which reduced the dissolution of HCS. By rising the dose of PPIL, CR lowered and increased %IE [24] as displayed in Table 2.

**Table 2.** Impact of temperature on $k_{corr}$, $\theta$, and %IE of HCS attendance and lack of altered doses of PPIL drug.

| Conc., ppm | Temp., °C | $k_{corr}$, x10$^{-2}$ mg cm$^{-2}$min$^{-1}$ | $\theta$ | % IE |
|------------|-----------|-----------------------------------------------|--------|------|
| 100        | 30        | 6.8 ± 0.0203                                  | 0.805  | 80.5 |
|            | 35        | 8.8 ± 0.0014                                  | 0.758  | 75.8 |
|            | 35        | 10.0 ± 0.0015                                 | 0.757  | 75.7 |
|            | 45        | 13.2 ± 0.0023                                 | 0.714  | 71.4 |
|            | 50        | 18.1 ± 0.0015                                 | 0.616  | 61.6 |
| 150        | 30        | 5.8 ± 0.0023                                  | 0.850  | 85.0 |
|            | 35        | 6.6 ± 0.0015                                  | 0.840  | 84.0 |
|            | 35        | 8.0 ± 0.0014                                  | 0.791  | 79.1 |
|            | 45        | 9.8 ± 0.0012                                  | 0.790  | 79.0 |
|            | 50        | 14.0 ± 0.0017                                 | 0.686  | 68.6 |
| 200        | 30        | 5.2 ± 0.0011                                  | 0.885  | 88.5 |
|            | 35        | 6.0 ± 0.0016                                  | 0.849  | 84.9 |
|            | 35        | 6.5 ± 0.0010                                  | 0.842  | 84.2 |
|            | 45        | 7.0 ± 0.0230                                  | 0.818  | 81.8 |
|            | 50        | 10.7 ± 0.0225                                 | 0.781  | 78.1 |
| 250        | 30        | 4.6 ± 0.0222                                  | 0.902  | 90.2 |
|            | 35        | 5.9 ± 0.0145                                  | 0.856  | 85.6 |
|            | 35        | 6.2 ± 0.0173                                  | 0.853  | 85.3 |
|            | 45        | 6.8 ± 0.0162                                  | 0.851  | 85.1 |
|            | 50        | 9.2 ± 0.0123                                  | 0.790  | 79.0 |
| 300        | 30        | 4.1 ± 0.0114                                  | 0.912  | 91.2 |
|            | 35        | 4.7 ± 0.0152                                  | 0.884  | 88.4 |
|            | 35        | 5.1 ± 0.0203                                  | 0.860  | 86.0 |
|            | 45        | 5.6 ± 0.0221                                  | 0.854  | 85.4 |
|            | 50        | 6.5 ± 0.0208                                  | 0.820  | 82.0 |

**Kinetic-thermodynamic parameters** Using Arrhenius equation, the energy of activation “(E$\alpha$)” for disintegration of the HCS was calculated from the slope of log $k_{corr}$ against 1/T of planned” (Fig.2):

$$Log k_{corr} = log A - E^*/aR \cdot 2.303RT$$  \hspace{1cm} (5)

Where $A$ is Arrhenius pre-exponential element. $E^*$ rise in the existence of the PPIL drug. The investigation of the results was documented in Table (3), there is an rise in the activation energy by improving the dose of PPIL drug, led to the rise of the thickness of the barrier layer designed on HCS surface. This increase is due to the adsorption nature of PPIL on the HCS surface, and corresponds to the physical adsorption. Transitional state equation, the changes in entropy and enthalpy were calculated.

$$Log (k_{corr}/T) = [log(R/Nh) + \Delta S^*/aR \cdot 2.303RT] \cdot -\Delta H^*/aR \cdot 2.303RT$$  \hspace{1cm} (6)

where (h) give Planck's constant .Figure (3), shows straight lines resulting from a plotting log ($k_{corr}/T)$ against 1000/T, where this figure shows the transitional state of the PPIL drug. Slopes given from the bends are utilized to measured enthalpy ($-\Delta H^*/aR \cdot 2.303RT)$, and the activation entropy measured utilizing intercept of the lines [log(R/Nh) + $\Delta S^*/aR \cdot 2.303RT]$ .The entropy data are negative symbol in the existence of PPIL and these negative data demonstration that display that activated complex in the rate determining
step favors an coagulation rather than a separate on solution, so the lowering in disorder happened throughout the sequence from reactant to the started complex. [27]. The $\Delta H^*$ has a negative sign indicates that the corrosion process is exothermic”.

### Figure 2. Log $k_{corr}$ – $1/T$ bends for HCS existence and nonexistence of altered doses of PPIL drug

### Figure 3. Log $k_{corr}/T$ – $1/T$ diagrams for HCS existence and nonexistence of altered doses of PPIL drug

### Table 3. Activation parameters for HCS dissolution existence and nonexistence of altered doses of PPIL drug

| Conc. ppm | $E_a^*$, kJ mol$^{-1}$ | $-\Delta H^*$, kJ mol$^{-1}$ | $-\Delta S^*$, J mol$^{-1}$K$^{-1}$ |
|-----------|-------------------------|-------------------------------|----------------------------------|
| Blank     | 25.7±0.2309             | 9.2±0.1453                    | 218.3±0.1453                     |
| 100       | 26.1±0.2028             | 10.2±0.2404                   | 212.0±0.2729                     |
| 150       | 28.3±0.1732             | 11.1±0.2028                   | 204.0±0.1764                     |
| 200       | 32.8±0.2333             | 13.1±0.2333                   | 188.0±0.1528                     |
| 250       | 38.8±0.2646             | 15.7±0.2309                   | 167.2±0.1732                     |
| 300       | 38.8±0.1528             | 15.7±0.2603                   | 167.2±0.1764                     |

**Adsorption isotherms** Numerous isotherms had utilized to fit data [25], but the excellent fit was succeeded to obey Langmuir adsorption isotherm which was exposed in Figure (4) for the PPIL drug. Langmuir measured from the next eqn. [26]:

$$
\text{log } k_{corr} = -\frac{E_a^*}{R} \left( \frac{1}{T} \right) + \log \frac{k_0}{R} - \frac{\Delta H^*}{RT}
$$
\[ C/ \theta = 1/K_{ads} + C \]  \hspace{1cm} (6)

Where C is concentrations of PPIL drug, \( K_{ads} \) is the adsorption equilibrium constant, and can be calculated from Figure (4), the difference among \( C/ \theta \) and C where \( \theta \) is the surface coverage, = \( 1E/100 \). The \( \Delta G^o_{ads} \) and \( K_{ads} \) data are in Table (4). The \( \Delta G^o_{ads} \) founded by:

\[ \Delta G^o_{ads} = -RT \ln (55.5 K_{ads}) \]  \hspace{1cm} (7)

The PPIL adsorption is spontaneous and this is proven by the \( \Delta G^o_{ads} \) negative sign. From the data of \( \Delta G^o_{ads} \) (around to -20 kJ mol\(^{-1}\)), proven that the PPIL adsorption is physisorption. Vant’t Hoff equation can be used to measure \( \Delta H^o_{ads} \) and \( \Delta S^o_{ads} \) expressed by:

\[ \ln K_{ads} = \frac{-\Delta H^o_{ads}}{RT} + \text{const} \]  \hspace{1cm} (8)

and eq. (9):

\[ \Delta G^o_{ads} = \Delta H^o_{ads} - T \Delta S^o_{ads} \]  \hspace{1cm} (9)

Figure 5 demonstrates the relation among \( \Delta G^o_{ads} \) and T. A negative symbol of \( \Delta S^o_{ads} \) proved that the disorder of corrosion procedure is lowered by utilizing PPIL drug (Table 4).

**Figure 4.** Langmuir bends for HCS in 1 M HCl and in attendance of altered dose of PPIL at altered temperatures

**Figure 5.** Plots \( \Delta G^o_{ads} \) vs T for PPIL adsorption in 1.0M HCl solution

**Table 4.** Langmuir data for HCS without and utilizing changed PPIL contents at (30°C- 50°C)

| Temp., K | \( K_{ads} \times 10^3 \) M\(^{-1} \) | \( -\Delta G^o_{ads} \) kJ mol\(^{-1} \) | \( -\Delta H^o_{ads} \) kJ mol\(^{-1} \) | \( -\Delta S^o_{ads} \) J mol K\(^{-1} \) |
|---------|------------------|-----------------|-----------------|-----------------|
| 303     | 24.6             | 8.0±0.0028      |                 |                 |
| 308     | 25.1             | 8.4±0.0128      |                 |                 |
| 313     | 30.1             | 13.3±0.0528     | 154±0.2528      | 534±0.1351      |
| 318     | 32.8             | 15.9±0.0321     |                 |                 |
| 323     | 35.7             | 18.4±0.0428     |                 |                 |
**Potentiodynamic polarization (PP) tests** Figure 6 displays PP diagrams for HCS attendance and absence of altered doses of PPIL drug at 25°C. With an addition of the dose of PPIL drug the data of $i_{corr}$ lowered, which lead to reducing in the CR. Table 5 documented the parameters of PP, $i_{corr}$, $E_{corr}$, Tafel slopes ($\beta_a$, $\beta_c$), (CR), ($\theta$) and (%IE). The anodic and cathodic slopes were lightly varied with the improving the dose of PPIL drug and $E_{corr}$ was a little changed (about 41 mV), demonstrative that PPIL acts as a mixed–kind inhibitor” [28]. The parallel Tafel lines indicate that there no mechanism change with and without PPIL.

Table 5. PP results of HCS dissolution with and without altered dose of PPIL at 25°C

| Conc., ppm | $i_{corr}$, $\mu$A cm$^{-2}$ | $-E_{corr}$, mV vs SCE | $\beta_a$, mVdec$^{-1}$ | $\beta_c$, mVdec$^{-1}$ | CR, mm y$^{-1}$ | $\theta$ | %IE |
|------------|-----------------|--------------------------|------------------|------------------|----------------|---------|-----|
| HCL        | 583.0±0.1155    | 517±0.2333               | 85.6±0.1453      | 144.3±0.2028     | 266.4          | --      | --  |
| 100        | 159.0±0.1732    | 477±0.1453               | 122.7±0.1653     | 839.5±0.3528     | 72.57          | 0.727   | 72.7|
| 150        | 107.7±0.2028    | 478±0.14313              | 81.7±0.1553      | 247.1±0.1453     | 48.87          | 0.816   | 81.6|
| 200        | 74.6±0.2603     | 476±0.1732               | 78.6±0.2309      | 212.6±0.2906     | 34.10          | 0.872   | 87.2|
| 250        | 51.4±0.1764     | 480±0.1453               | 58.1±0.2309      | 120.6±0.1732     | 23.47          | 0.912   | 91.2|
| 300        | 40.0±0.2028     | 477±0.1323               | 61.9±0.1553      | 121.6±0.2028     | 18.29          | 0.931   | 93.1|

**Figure 6.** PP diagrams for the HCS dissolution attendance and lack of altered dose of PPIL drug at 25°C

**EIS tests** Figure 7, 8 demonstrations the Nyquist and Bode diagram, given at OCP both existence and nonexistence of altered dose of PPIL at 25°C, respectively. The rise of the capacitive loop diameters with the addition of PPIL drug was owing to improve in the thickness of the adsorbed layer designed on the surface of HCS. EIS data for “PPIL drug were calculated utilizing the excellent equivalent circuit in Fig. 9, which indicates a distinct charge transfer and fits well with the given results. The CPE is put in the circuit in its place of a pure double layer capacitor to obtain a maximum precise fit” [29-30]. $C_{dl}$, was determined utilizing balance (10) and (11):

$$C_{dl} = \frac{Y_0}{\omega_{max}^{n-1}} \quad (10)$$

$$\omega_{max} = 2\pi f_{max} \quad (11)$$

Where $Y_0$ = the CPE degree and $f_{max}$ is the frequency at which the imaginary constituent of the EIS is highest. The obtained diagrams are very parallel for all samples existence and lack of altered dose of PPIL drug, display that no change in the mechanism of corrosion [31]. Table 6 demonstrations the impedance data which established the data of $R_{ct}$ increase with raising the dose of the PPIL drug and this pointed to the rise in % IF. This might be because of the rise of the thickness of the adsorbed layer by raising the PPIL drug concentrations. The lowering in CPE/$C_{dl}$ value owing to a dimension in local dielectric constant, suggesting that PPIL protect the dissolution of HCS by metal/acid adsorbed [32, 33].
Table 6. EIS data for HCS dissolution without and with altered dose of PPIL drug at 25°C

| Conc., M | $R_S$, Ωcm² | $Y_0$, µΩ⁻¹ s⁰ cm⁻² | n | $R_{ct}$, Ω cm² | $C_{dl}$, µFcm⁻² | θ | IE% |
|---------|-------------|---------------------|---|---------------|-----------------|---|-----|
| Blank   | 1.846±0.0173| 532                 | 0.895 | 28.1±0.1453  | 437.0±0.2333     | ---- | ---- |
| 100     | 1.757±0.0203| 75                  | 0.865 | 191.2±0.1623 | 58.9±0.1202      | 0.853 | 85.3 |
| 150     | 1.835±0.0155| 71                  | 0.897 | 216.9±0.1403 | 55.52±0.2309     | 0.870 | 87.0 |
| 200     | 2.333±0.0145| 60                  | 0.798 | 265.2±0.2028 | 42.5±0.1553      | 0.894 | 89.4 |
| 250     | 1.827±0.0172| 58                  | 0.829 | 300.2±0.2309 | 38.9±0.1651      | 0.906 | 90.6 |
| 300     | 1.935±0.0203| 72                  | 0.839 | 372.0±0.1233 | 48.9±0.1732      | 0.924 | 92.4 |

Figure 7. Nyquist diagrams for HCS dissolution attendance and lack of altered dose of PPIL drug at 25°C

Figure 8. Bode diagrams for dissolution of HSC existence and nonexistence of altered dose of PPIL drug at 25°C
EFM Test The EFM bends for HCS in the existence and lack of (100 – 300 ppm) PPIL were verified and displayed in Fig. 10, by increasing the PPIL dose, \( i_{\text{corr}} \) has decrease to a lesser data. Table 7 exhibited that the PPIL has verified the shift of corrosion potential lesser than 85 mV in altered dose of the uninhibited solution. So, the PPIL drug sets as a mixed type inhibitor. The highest peak has utilized to determine \( (i_{\text{corr}}) \), causality factors (CF-2 and CF-3) and the Tafel slopes \( (\beta_c \text{ and } \beta_a) \) [34]. %IE increase by raising the study dose of PPIL drug and was determine by Eq.(2).

Table 7. EFM parameters for HCS existence and nonexistence altered dose of the PPIL at 25°C

| [inh], ppm | \( i_{\text{corr}} \), \( \mu \text{A Cm}^{-2} \) | CR mpy | CF-2 | CF-3 | \( \theta \) | %IE |
|-----------|-----------------|--------|------|------|--------|-----|
| Blank     | 539± 0.2028     | 246±0.1453 | 1.6  | 2.5  | --     | --  |
| 100       | 91 ± 0.1553     | 42±0.1732  | 1.9  | 2.3  | 0.830  | 83.0|
| 150       | 85±0.1453       | 38±0.2309  | 1.8  | 3.1  | 0.840  | 84.0|
| 200       | 75±0.2431       | 34±0.2102  | 1.5  | 2.6  | 0.860  | 86.0|
| 250       | 73±0.2055       | 33±0.1732  | 1.5  | 3.3  | 0.865  | 86.5|
| 300       | 58±0.1742       | 26±0.2423  | 1.9  | 2.7  | 0.892  | 89.2|

FTIR Analysis The FTIR spectrum examination based on analyzing the coating film create on the HCS surface [35] Fig.(11a) demonstrates the FTIR band of the pure PPIL The -C-F stretching frequency of the alkyl halide group achieves at 1280 cm\(^{-1}\) with a strong band. The – O–C frequency appears as three strong bands at 1019, 1040 and 1078 cm\(^{-1}\) which representative three ether bonds in pure PPIL. The –
OH frequency of the alcohol group appears at 3281 cm\(^{-1}\) which has strong and broad intensity [36]. The –CN stretching frequency achieves at 1205 cm\(^{-1}\). The –C=C– frequency looks as multiple bands among (1400-1600) cm\(^{-1}\) which representative the multiple double bonds in the in pure PPIL drug. The data in Fig (11b) presented that – C –F extending frequency has shift from 1280 cm\(^{-1}\) to 1313 cm\(^{-1}\). The – O –C frequency has moved to make from three bands to one weak band at 1068 cm\(^{-1}\). The – OH extending frequency has moved from 3281 to 3420 cm\(^{-1}\). The –CN has moved from 1205 cm\(^{-1}\) to 1230 cm\(^{-1}\). This statement recommends that PPIL has coordinated with Fe\(^{2+}\), given the creation of the Fe\(^{2+}\)– PPIL complex at surface of HCS [37].

Figure 11a,b FTIR of pure PPIL and film found on the HCS after dipping in a solution inclosing PPIL

SEM test To examine the HCS surface changes after engagement in acidic solution existence and lack of PPIL drug. To evaluate the exchanges of the brass surface dipping in acid solution lack and attendance of inhibitor PPIL. The HCS surface was analyze by using SEM. The HCS surface is more degradation due to corrosion attack in the blank solution. Figure 12, suggests the micrograph given for HCS sheets in absence and utilizing 300 ppm of PPIL after dipping for only one day. The PPIL adsorption on the HCS surface, forming the shielding layer resulting in blocking the active areas so that the HCS become more smooth and inhibition”[38].

Figure 12. SEM appearance of HCS surface (a) before 1 M HCl dipping, (b) after 24 hours of 1 M HCl dipping, and (c) after 24 hours of 1 M HCl + 300ppm of PPIL dipping at 25°C

AFM test The AFM test produces images with atomic or near-atomic-resolution surface topography, allowing the measurement of surface roughness on an angstrom scale [39]. “The corrosive image of the HCS dipping in corrosive environment for 24 h in the existence and lack of the PPIL were detected by AFM (Fig.13), these pictures
of the HCS enclose a great amount of measurable data regarding the HCS surface alterations. Fig. 13a displays that the HCS before dipping had a surface adequately smooth to reflect light. Contrastingly, HCS dipping in solution test for 24 h (Fig. 13b) without of PPIL demonstrated a severely surface corroded. The HCS becomes more even in the existence of 300 ppm PPIL as displayed in Fig. 13c. The roughness of the free HCS was 20.6 nm. The maximum surface heterogeneity was detected on HCS exposed to corrosive solution nonexistence of PPIL as in Fig. 13b, the roughness raised to 694 nm, and the 3D observation displays great valleys and peaks. In difference, there is very lower corrosion destruction on the HCS on existence of 300 ppm of PPIL in 1.0 M HCl with only slight spikes as is shown in Fig. 13 c. The roughness reduced to 166 nm, respectively, which designated that inhibitive film is adsorbed on the HCS [40]. AFM measure the mean roughness (Sa), the average root mean (Sq) and the peak height (Sp). AFM data were documented in Table (8).

**Table 8.** AFM data for HCS surface nonexistence and existence of 300 ppm PPIL drug

| Sample       | Sa   | Sq   | Sp   |
|--------------|------|------|------|
| Free         | 20.63| 24.79| 60.26|
| Blank        | 694.90| 810.95| 1830.20|
| PPIL drug    | 166.87| 210.09| 765.75|

**Figure 13.** AFM Aafter dipping for 24 hours in the solution, HCS free (a), in 1 M HCl (b), and with 300 ppm PPIL medication (c).
Theoretical calculations

Quantum Chemical Parameters Some quantum chemical calculations can obtain to examine the impact of PPIL drug structure to study the productivity of inhibition mechanism. “Fig (14) demonstrations the optimized molecular structures of the PPIL. The data gained for investigating PPIL as: Highest occupied molecular orbital \( (\text{E}^\text{HOMO}) = -9.06 \text{ eV}, \) Lowest unoccupied molecular orbital \( (\text{E}^\text{LUMO}) = -0.87 \text{ eV}, \) Energy gap \( (\Delta \text{E}) = \text{E}^\text{LUMO} - \text{E}^\text{HOMO} = 8.91 \text{ eV}, \) Dipole moment \( (\mu) = 4.095 \text{ Debye}. \) The lesser the data of \( \text{E}^\text{LUMO}, \) is more appreciated to the molecule accept electron. The PPIL was better with the lesser negative \( \text{E}^\text{HOMO} \) energies and with lowering the value of \( \Delta \text{E} \) (energy gap) [41] and the stronger interaction among PPIL and HCS surface. Fig (14) shows high data of the HOMO density were found in the vicinity of sulfur and nitrogen atoms, pointing to the nucleophilic center is the sulfur and nitrogen atoms”.

![Mulliken atomic charges of PPIL](image1)

![HOMO](image2)

![LUMO](image3)

**Figure 14.** Optimized orbital and Mullikan atomic of PPIL drug

Monte Carlo (MC) Simulation MC modeling is an excellent method for determining the most stable adsorption conformations of a pharmaceutical molecule in 1M HCl. “Figure 15 illustrates the simulation findings for the investigated pharmaceutical, which are described in Table 10. Figure 15 depicts the adsorbed molecule's most favorable confirmation on the Fe metal surface (110). Furthermore, the molecules stated are adsorbed on the metal surface from the motive, which is rich in inhibitory molecule electrons. The interactions between the occupied orbitals of the examined PPIL drug and the vacant orbitals of Fe (110), which are reflected by energy adsorption values \( (\text{E}_{\text{ads}}), \) of the rigid energy \( (\text{E}_{\text{rigid}}), \) of the deformation energy \( (\text{E}_{\text{def}}), \) and energy ratio values \( (\text{dE}_{\text{ads}}/dN_i) \) of the inhibitors, which is equivalent to the energy of substrate-adsorbate configurations where one of the adsorbate components has been removed are collected in Table 8. Adsorption energy values that are more negative indicate a highly stable and strong connection between adsorbed molecules and metal. When two materials are mixed during the adsorption process, an electron, ion, or molecule (adsorbent) is attached to the solid surface, adsorption energy is defined as declining energy [42]. As shown in Table 10, the greater adsorption energy of PPIL molecules on the hardened Fe surface predicts heavy adsorption of PPIL molecules, forming a stable adsorbed layer that protects the iron from decomposition”.

![Optimized geometry](image4)
Figure 15. The most suitable configuration for adsorption of the drug molecule on Fe (1 1 0) substrate obtained by adsorption locator module.

Table 10. Data and descriptors calculated by the Monte Carlo simulation for adsorption of drug molecule on Fe (1 1 0).

| Structures               | Total energy | Adsorption energy | Rigid adsorption energy | Deformation Energy | Compound dE\textsubscript{ad}/dN\textsubscript{i} | H\textsubscript{2}O dE\textsubscript{ad}/dN\textsubscript{i} |
|-------------------------|--------------|-------------------|-------------------------|-------------------|---------------------------------------------|---------------------------------------------|
| Fe (1 0 0)/PPIL /H\textsubscript{2}O | -3211.16     | -3960.653         | -4019.791               | -59.138           | -253.187                                    | -11.252                                    |

Mechanism of corrosion inhibition The hindrance of corrosion of PPIL drug on HCS in 1 M HCl environment established on the temperature, chemical structure and doses of PPIL. “By raising the dose of PPIL drug, one found some exchanges as; a lowering of ML, \( i_{corr} \), and \( C_{dl} \), an rise of \( R_{ct} \), \( (\theta) \) and \%IE. The mechanism of the protection procedures of organic assemblies is due to their adsorbed on the HCS surfaces and blocking the cathodic or anodic reactions or both. The PPIL has adsorbed on the HCS surface has prejudiced by some reasons as molecular size, the attendance of active sites on PPIL structure of inhibitor, charge density and abilities form complexes. The attendance of heteroatoms in the PPIL structure is liable for the adsorption procedure and the creation of coordinate bonds among the transfer of lone pairs of electron of heteroatoms to the Fe surface, these species can adsorb on the HCS [43]. Furthermore, PPIL may adsorb via the electrostatic interactions among protonated form of the PPIL and the negatively charged HCS surface. PPIL drug, on the other hand, is characterized by the presence of chelation sites that connect O and N atoms with lone pairs of electrons” (Fig. 16).
Conclusion
Adsorption inhibition of the PPIL against the dissolution of HCS in 1M HCl solution has been established. Raising the PPIL dose and lowering the temperature increased the percent IF. The creation of an insoluble adsorbed complex on the HCS surface is responsible for the PPIL drug’s percent IF, and the technique followed the Langmuir isotherm. The results of EIS testing were similar parallel to those of the PP test. The formation of a coating film on the HCS surface in 1M HCl solution is also demonstrated by SEM and AFM tests. All of the experiments and quantum chemistry computations came up with the best agreement.

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