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Study of expired drug Phenazopyridine hydrochloride as a novel corrosion inhibitor for carbon steel in 1 M Hcl solution

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Abstract

This study is designed to evaluate the effectiveness of expired drug such as phenazopyridine hydrochloride (PPH) as a novel corrosion inhibitor for carbon steel (CS-metal) in HCl solution (1 M). The recycling of expired drugs is considered an environmentally friendly and sustainable way to save on economic cost. The drug PPH was examined using FTIR spectroscopy to identify active groups likely to be associated with the metallic surface in order to form a protective coating to inhibit the corrosion. A number of weight loss and electrochemical studies were performed at different inhibitor concentrations for different periods of immersion of 1, 3, 6, 9, and 24 hours at 298 K. The results show that inhibition efficacy was concentration dependent, with inhibited efficiencies of 53 %, 58 %, 75 %, and 75 % achieved for inhibitions at 50, 100, 200, 300, and 400 ppm concentrations, respectively, according to standard immersion time. It was noted at optimum concentration of 300 ppm, the efficiency of inhibition was 75% after 9 hours of exposure. The study revealed that there is an agreement between measurements of weight lost and dynamic voltage polarization. The study also involves the application of scanning election microscopy (SEM) in assessing the alterations on the metal surface upon immersion in an acidic environment. The adsorption of PPH drug on the metallic surface follows Langmuir Isotherm whereby the process of inhibition shows a clear connection between physical and chemical adsorption mechanism. The experimental results were supported by a theoretical study through calculating a set of quantum mechanical parameters which provided a deep understanding of the inhibition mechanism.

Keywords: Acetic media, Carbon steel, Corrosion inhibitor, Expired drug (PPH), Langmuir equation and DFT studies, SEM, Tafel curves, Weight loss measurements.

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1. Introduction

CS-metal plays an essential role in various industries, where it is used widely as a structural material in industrial applications like petroleum. It is also the main component in manufacturing geometrical alloys and the production of steel due to their good mechanical properties and low cost. However it's still highly exposed to corrosion in harsh environments, especially in acidic mediums due to its high chemical reactivity [1, 2]. The corrosion of metals creates huge losses in material supplies and it is one of the main challenges which confront industries [3]. Thus, the prevention of corrosion and finding effective ways to delay the process in acidic environments is of great importance to extend the lifespan of metal equipment which contributes as well to protecting the environment and decreasing the cost of repair [4]. Corrosion occurs in many instances because of the extensive use of hydrochloric acid in the process of pickling, rescaling, petrochemical, marine, chemical industries [5]. Corrosion inhibition is considered the main strategy for protecting metals long-term. Corrosion inhibitors are chemicals used in a corrosion-causing environment in small concentrations to minimize corrosion rate by mostly lowering rate of reaction between the metal and its environment through formation of a shielding layer on the metal surface [6]. The use of inhibitors represents one of the simplest and most effective ways to protect CS-metal while undergoing treatment processes. A number of scientists have become interested because of the many benefits that come with using corrosion inhibitors for protecting metal [7]. The interest of scientists is focused on designing inhibitors of high efficiency, low cost, and minimal environmental impact. This design majorly depends on the chemical composition of the inhibitor, containing active groups that are electron-rich due to the presence of heteroatoms (N, O, S, or P). Their chemical structure also has double bonds, aromatic rings with π electrons, and unsaturation bonds, which are active in the adsorption process [8-10]. These inhibitors may be adsorbed on a surface physically or chemically or a mixture of both through interaction that creates a layer to resist corrosion in corrosive environments and assist to displace water at a broad temperature range [11-13]. The adsorption mechanism is described as the interaction between the LUMO (lowest unoccupied molecular electron orbital) of the metal and the HOMO (highest occupied molecular orbital) of the heterogenous atoms [14]. The performance of an organic compound as a corrosion inhibitor is largely dependent on adsorption on the surface of the metal including displacing a water molecule at a corroding interface. This is due to the electronic configuration of the inhibitor, steric factor, aromaticity, electron-donor density, functional groups like CHO-, N=N-, R-OH, surface area of the active part of the molecule and the molecular weight of the inhibitors [15-17]. The physical absorption is because of the attractive electrostatic forces existing between the metal surface which is electrically charged and the inhibiting organic ions or dipoles. The chemical absorption is to the reaction between lone electron pairs or P electrons of the adsorbate with the metal forming a coordinate type of bond. This may happen in a heteroatom (O, N, S, Se, P) with lone pairs of electrons and/or in the adsorbed molecule with aromatic rings [18, 19]. The proposed mechanism is the decrease in one or both of the anode and cathode reactions through adsorption of the inhibitor onto their respective active sites [20, 21]. It is known that a number of organic compounds are used as corrosion inhibitors for carbon steel. However, only a small number of non-toxic and environmentally friendly chemicals have been studied as corrosion inhibitors. Nonetheless with increasing environmental awareness, most of the traditional organic inhibitors are no longer applicable because of their harmful effects to the environment and living organisms. Hence, the increasing demand for safe and sustainable inhibitors has pushed researches to develop environmentally friendly corrosion inhibitors. In this regard, studies have been done on natural extracts of plants and fruits [22] ionic liquids [23, 24] drugs [25-27] and organic polymers [28, 29] as effective inhibitors for green corrosion to prevent acidic corrosion of metals. Nevertheless, these inhibitors remain limited in practical applications due to the time-consuming and expensive manufacturing steps or the limited usability period. Considering the natural origin of these drugs and their non-toxicity and environmental compatibility seem to make them a perfect candidate for replacing traditional corrosion inhibitors [30-32]. Several drugs have been reported to inhibit corrosion of carbon steel in acidic solutions [33-37]. Nevertheless, since most of drugs are very expensive than organic inhibitors being used presently in various industries, the use of new drugs as inhibitors is not economical which limits the application of drug as corrosion inhibitors. It is reported that medicines keep about 90% of their original effectiveness after their expiration for a long period [38]. So instead, these expired pharmaceuticals can be used as corrosion inhibitors as they are more effective economically and more convenient for situational industrial. This will reduce the high cost of removing expired medicines as well as the pollution caused by the decomposition of medicines, which is uncontrollable when these medicines meet sunlight as well as moisture. Some of these have been documented as expired drugs that aid as corrosion inhibitors in acidic solutions [39-43]. The drug PPH is used to reduce the symptoms of urinary tract inflammation like the sensation of pain, burning, and the chronic need for urination. This drug does not treat the cause of inflammation, rather, it only helps in relieving the symptoms while other treatment methods are used [44]. The scientific name for the drug PPH according to IUPAC nomenclature is 2,6-Diamino-3-(phenylazo)pyridine hydrochloride. It has a molecular weight is 249.70 g/mol and molecular formula of ($C_{11}H_{12}ClN_5$). The structural formula for PPH has been given in Figure 1. In this study, the drug PPH has been selected due to no previous study has reported the efficacy of this drug as a corrosion inhibitor. Its chemical composition as a dye is suitable as a corrosion inhibitor.

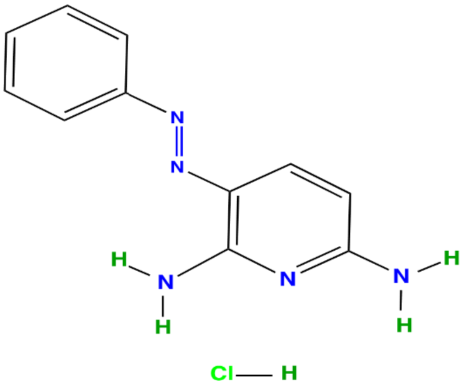

Figure 1.
The molecular structure of phenazopyridine hydrochloride (PPH).

This manuscript presents the capabilities of PPH drug as an effective corrosion inhibitor because it contains a phenyl group, an azo group, a pyridine moiety, and two amine groups. These factors contribute to the reaction between PPH molecule and the carbon steel. Additionally, this drug has a large size (molecular weight = 249.70 g/mol) and plane geometric structure which allows it to cover a larger surface area on the carbon steel surface due to adsorption. The study included weight loss measurements, potentiodynamic polarization and scanning electron microscopy (SEM) to evaluate the surface changes on the carbon steel subjected to an acidic environment with and without the inhibitor in different concentrations for different immersion times. Moreover, DFT analysis has been performed, predicting then structure of neutral and protonated forms of PPH upon corrosion inhibition.

2. Experimental

2.1. Materials and Chemicals

Expired PPH drug was obtained in tablet form (500 mg) which expires in may 2023 from a local pharmacy. All materials used come from Merck company in high purity. Water has been distilled twice was used to ensure its purity in preparing aqueous solutions. Standard samples of carbon steel (CS-metal) have been used of the type (Alloy: C1010) with the code (ZDP) and the number (Part #: L9000) with a mass of 11.4011g, they were obtained from the laboratories of Al-Shuaiba refinery in Basrah - Iraq. The chemical composition of the utilized carbon steel (Alloy: C1010) sample Cr 0.098 %, Mn 0.46 %, Si 0.164 %, C 0.124 %, Fe 98.7 %, Sn 0.0084 %, Pb 0.0128 %, Co 0.0288 %, Al 0.030 %, Ni 0.094 %, Cu 0.149 %, Mo 0.051 %. All the steel samples were polished using sandpaper (grain 400,1200, and 2000) to achieve a smooth, clean, and level surface. Metal samples were washed with ethanol solvent and dried well before any tests were made. These samples were then used in weight loss tests and other electrochemical studies. A solution of (1 M) hydrochloric acid has been prepared by serial dilution of 37% HCl. Expired PPH tablets used as inhibitors were crushed and dissolved in 1 M hydrochloric acid in order to prepare the desired concentrations of the inhibitor solution for corrosion testing.

2.2. Infrared Spectra Analysis

The infrared spectrum of the expired drug (PPH) was recorded using an FT-IR spectrophotometer (German BRUKER FT-IR - ALPHA II) in the range of 400 – 4000 cm^{-1} at Chemistry Department, College of Science, Basrah University.

2.3. Gravimetric Measurements

Weight loss experiments are one of the simplest ways of testing for corrosion, with data of great value. These tests are useful in establishing the optimum inhibitor concentration and understanding the adsorption mechanism of inhibitor molecules at given temperatures. Accordingly, experiments are carried out at an immersion temperature of 298K. CS-metal samples have dimensions of 68mm x 12.5mm x 1.5mm, which are polished with sandpaper, cleaned followed by aqueous ethanol washes, drying, and weighing in accordance reference [45]. The steel samples were immersed in 250 ml of hydrochloric acid (1 M) with and without several concentrations of PPH drug at 50 ppm, 100 ppm, 200 ppm, 300 ppm, and 400 ppm, for different time durations: 1, 3, 6, 9, and 24 hours at 25 °C. After the specified period, the samples were retrieved and immersed in Clark solution for a few minutes to isolate corrosion products adherent to the surface. They were then cleaned thoroughly with soap and water, followed by washing with acetone and then distilled water, dried, and ultimately weighed [46, 47]. The corrosion rate (CR) for carbon steel samples, surface coverage of inhibitor on metal surface (θ), and the inhibition efficiency (IE %) have been recorded using Equations 1, 2, 3 and 4 in 1 M hydrochloric acid with the inhibitor and without an inhibitor [48-52]:

$$C_{R_o} = \frac{W}{a\,.\,d\,.\,t} \qquad (1)$$

$$C_{R_{(i)}} = \frac{W}{a\,.\,d\,.\,t} \qquad (2)$$

$$\theta = \left(1 - \frac{C_{R_{(i)}}}{C_{R_{(0)}}}\right) \qquad (3)$$

$$IE\ \% = \left(1 - \frac{C_{R_{(i)}}}{C_{R_{(0)}}}\right) \times 100 \qquad (4)$$

W is the weight lost (mg), **a** is the surface area of the sample (cm^2), **t** is the immersion time (hr), **d** is the density of the carbon steel (g/cm^3), $\boldsymbol{C_{R_o}}$ and $\boldsymbol{C_{R_{(i)}}}$ are the corrosion rates in the absence and presence of the inhibitor, respectively.

2.4. Electrochemical Measurements

Electrochemical tests were performed in a three-electrode cell using a Potentiostat/Galvanostat G300-45050 (Gamry Instruments Inc., USA). The data was then analyzed using Echem Analyst 5.0 software. The three-electrode system consists of a working electrode (1 cm^2 exposed surface area of carbon steel), counter electrode (platinum), and saturated calomel electrode (SCE) reference electrode. SCE was used as reference electrode to measure all potentials. Tafel curves were recorded with potential switching over from - 0.25 to 0.25 V vs. open circuit potential and with a scanning rate of 1.0 mVs^{-1} [53] Experiments were conducted after an immersion period of 9 h in hydrochloric acid (1 M) with and without various concentration of the inhibitors. The removal of dissolved oxygen from the solution was given special attention so as to guarantee the measurement and eliminate any possible secondary reactions occurring on the surface of the electrode. The low voltages (LVs) were then measured after an hour of conditioning in OCP, where the electrode/electrolyte solution had come into a state of near equilibrium. The corrosion current density (I_{corr}), surface coverage (θ), and inhibitor efficiency (IE %) were esteemed by Equations 5 and 6 respectively These are some parameters used in the determination of corrosion inhibitors efficiency [54, 55].

$$\theta = \frac{I_{corr}^{(0)} - I_{corr}^{(i)}}{I_{corr}^{(0)}} \qquad (5)$$

$$IE\ \% = \frac{I_{corr}^{(0)} - I_{corr}^{(i)}}{I_{corr}^{(0)}} \times 100 \qquad (6)$$

Where $I_{corr}^{(i)}$ and $I_{corr}^{(o)}$ are the current density, respectively, with and without the inhibitor. This drug was used for testing as an inhibitor, and it will allow to be estimated the potentials of the corrosion inhibition based on the linear polarization method and highlights the effect of this drug in protecting carbon steel from corrosion and providing innovative solutions to combat corrosion challenges in various industries.

2.5. Surface Analysis

The surface morphology of CS - coupons was investigated using a model scanning electron microscope (SEM) model (TM1000 Hitachi Tabletop Microscope). This study was conducted to understand the changes that may occur in the shape of steel samples in view of different protective effects of inhibitor applied on the surface immersed in acidic solution (1 M) for up to 9 h at a temperature of 298 K with and without the addition of 300 ppm of corrosion inhibitor.

2.6. Quantum Chemical Computation

The DFT theoretical simulations were calculated by Schrodinger material science through B3LYP using (6-31 G++ basis set) [56-58]. Build mode for molecule was used to achieve the optimized 2D and 3D structures with specified LUMO and HOMO levels. The various factors such as electrophilicity, nucleophilicity, ionization potential, global hardness and softness, electron transfer fraction and electronegativity were calculated [59-63]. The chemical hardness (η) and softness (σ) values have been calculated based on ionization potential value (I) and electron affinity value (A) according to Koopman's theorem in relation to molecular orbital energies, as shown in Equations 7, 8, 9 and 10.

$$-E_{(HOMO)} = I \qquad (7)$$

$$-E_{(LUMO)} = A \qquad (8)$$

$$\eta = \frac{(I - A)}{2} \qquad (9)$$

$$\sigma = \frac{1}{\eta} \qquad (10)$$

The values for electronegativity (χ), the electrophilicity index (ω), and the electron transfer fraction (ΔN) were calculated with Equations 11,12 and 13.

$$\chi = \frac{I + A}{2} \qquad (11)$$

$$\omega = \frac{\chi^2}{4\eta} = \frac{1}{\varepsilon} \qquad (12)$$

$$\Delta N = \frac{\emptyset_{Fe} - \chi_{inh}}{2\eta_{inh}} \qquad (13)$$

Where $\emptyset_{Fe}$ is the work function for an iron atom Fe (110) and is equal to 4.82 eV.

3. Results and Discussion

3.1. Characterization Studies

The infrared spectrum (FT-IR) for the expired drug PPH Figure 2 revealed a weak band at 3067cm^{-1} belonging to the stretching of aromatic C-H bonds while showing multiple bands with different intensities in the range of 514 – 840 cm^{-1} which could belong to the bending bands of the same bonds. On the other hand, the spectrum exhibited strong bands at 1416 and 1596 cm^{-1} for symmetric and asymmetric stretching of the aromatic C=C bond respectively. Two more strong bands can be seen near 3471 and 3340 cm^{-1} attributed to the asymmetric and symmetric stretching of N-H bond for the primary amine -NH_2, while a medium intensity band for C-N is found at 1248 cm^{-1}. It's also worth noting that the spectrum showed medium intensity bands for the Azo group N=N at 1510 and 1449 cm^{-1} for asymmetric and symmetric stretching vibrations.

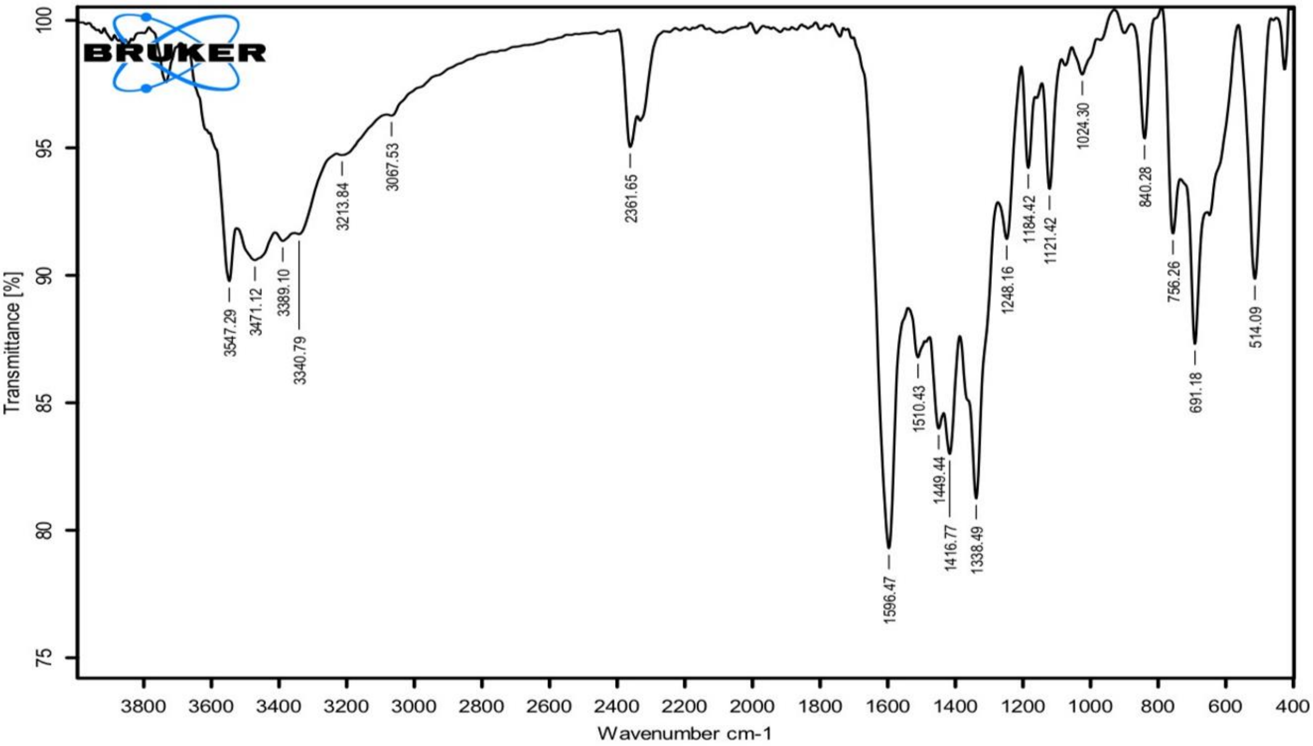

Figure 2.
Infrared spectrum (FT-IR) of the expired drug PPH.

3.2. Weight Loss Measurements

Weight loss measurements were performed to assess the corrosion behavior of CS – samples exposed to aggressive media. The experiments were conducted at 298 K with multiple durations of immersion to observe the effect of time on the efficacy of the inhibiting layer. The samples were immersed into hydrochloric acid (1 M) solutions for 1, 3, 6, 9, and 24 hours with and without the presence of different concentrations of the inhibitor 50, 100, 200, 300, and 400 ppm. Diverse concentrations were used to assess the effect of increasing the concentration of the inhibitor on their efficiency. The results of the experiments are summarized in Table 1. Table 1 displays the values of surface coverage (θ), inhibitor efficiency (IE %), and corrosion rate (CR) obtained, respectively, from the equations 1, 2, 3 and 4. It can be seen from the table that the corrosion rate (CR) for the metal increased with increasing immersion time in the absence of the inhibitor. On the other hand, while the inhibitor is present, with increasing concentration of inhibitor as well as immersion duration, the surface coverage (θ) increases and the corrosion rate (CR) decreases while the efficiency of the inhibitor showed an increase. Figure 3 establishes with Table 1 that an increase in inhibitor concentration yielded further enhanced inhibition effectiveness (IE %), indicating that it was attributed to the increased surface coverage by the inhibitory layer of the inhibitor molecules, thus indicating an enhancement in the quality of the protective layer with time [42, 64-66].

Table 1.
Weight loss measurements in 1 M solution of HCL with and without different PPH concentrations in different immersion periods at 25 °C.

Time immersion (hr)	Concentration (ppm)	Weight loss (gm)	$C_{R_{(i)}}$ (cm/hr)	Surface coverage (θ)	IE %
1 h	0	0.0113	78.53×10^{-6}	….	….
	50	0.0083	54.95×10^{-6}	0.37	37
	100	0.0070	45.55×10^{-6}	0.41	41
	200	0.0055	39.69×10^{-6}	0.50	50
	300	0.0048	30.84×10^{-6}	0.57	57
	400	0.0040	24.74×10^{-6}	0.60	60
3 h	0	0.0264	93.48×10^{-6}	….	….
	50	0.0131	55.67×10^{-6}	0.41	41
	100	0.0113	40.83×10^{-6}	0.47	47
	200	0.0102	33.41×10^{-6}	0.55	55
	300	0.0085	29.38×10^{-6}	0.62	62
	400	0.0080	22.23×10^{-6}	0.65	65
6 h	0	0.0772	96.07×10^{-6}	….	….
	50	0.0432	37.65×10^{-6}	0.47	47
	100	0.0321	33.41×10^{-6}	0.53	53
	200	0.0225	28.30×10^{-6}	0.60	60
	300	0.0192	22.04×10^{-6}	0.65	65
	400	0.0176	27.01×10^{-6}	0.68	68
9 h	0	0.1782	126.34×10^{-6}	….	….
	50	0.1035	46.11×10^{-6}	0.53	53
	100	0.0753	31.87×10^{-6}	0.58	58
	200	0.0477	26.27×10^{-6}	0.65	65
	300	0.0306	22.36×10^{-6}	0.75	75
	400	0.0289	21.46×10^{-6}	0.75	75
24 h	0	0.6278	187.52×10^{-6}	….	….
	50	0.430	75.01×10^{-6}	0.55	55
	100	0.236	32.61×10^{-6}	0.60	60
	200	0.1629	26.32×10^{-6}	0.65	65
	300	0.1173	22.46×10^{-6}	0.74	74
	400	0.0943	20.21×10^{-6}	0.75	75

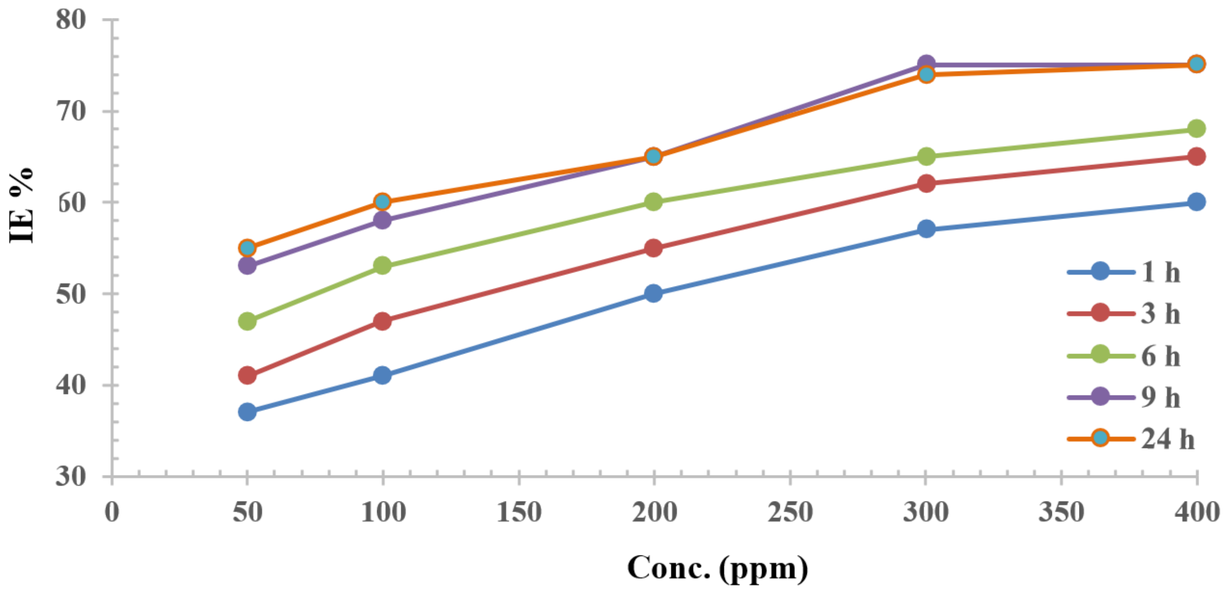

Figure 3.
Shows the change in inhibition efficiency (IE%) with and without different concentrations of PPH in different immersion periods in 1 Molarity hydrochloric acid at 25 °C.

3.3. Potentiodynamic Polarization Measurements (PDP)

The PDP study was conducted to comprehend the mechanism of corrosion CS-metal on the anode with hydrogen gas generation on the cathode in both absence and presence of several concentrations of PPH drug at 298 K. Tafel plots that show the relationship between the corrosion current (I_{corr}) and the corrosion potential (E_{corr}) and through it the corrosion process of carbon steel in hydrochloric acid (1 M) can be characterized Figure 4. Electrochemical parameters such as the corrosion voltage (E_{corr}), cathodic slope (βc), anodic slope (βa), corrosion current (I_{corr}), and inhibitor efficiency (IE%) obtained from the Figure 4 and inserted in Table 2. When the inhibitor is placed in an acidic medium, the anode and cathode reactions decrease, which enforces the inhibition effect of the drug [67]. It can be seen from Figure 4 that the Tafel curves shift to lower current values with increasing concentration. The parallel lines in the cathode curves, indicating that the corrosion mechanism is not influenced by the addition of the inhibitor, while the slope of the anodic part indicates the inhibitor influence [68, 69].

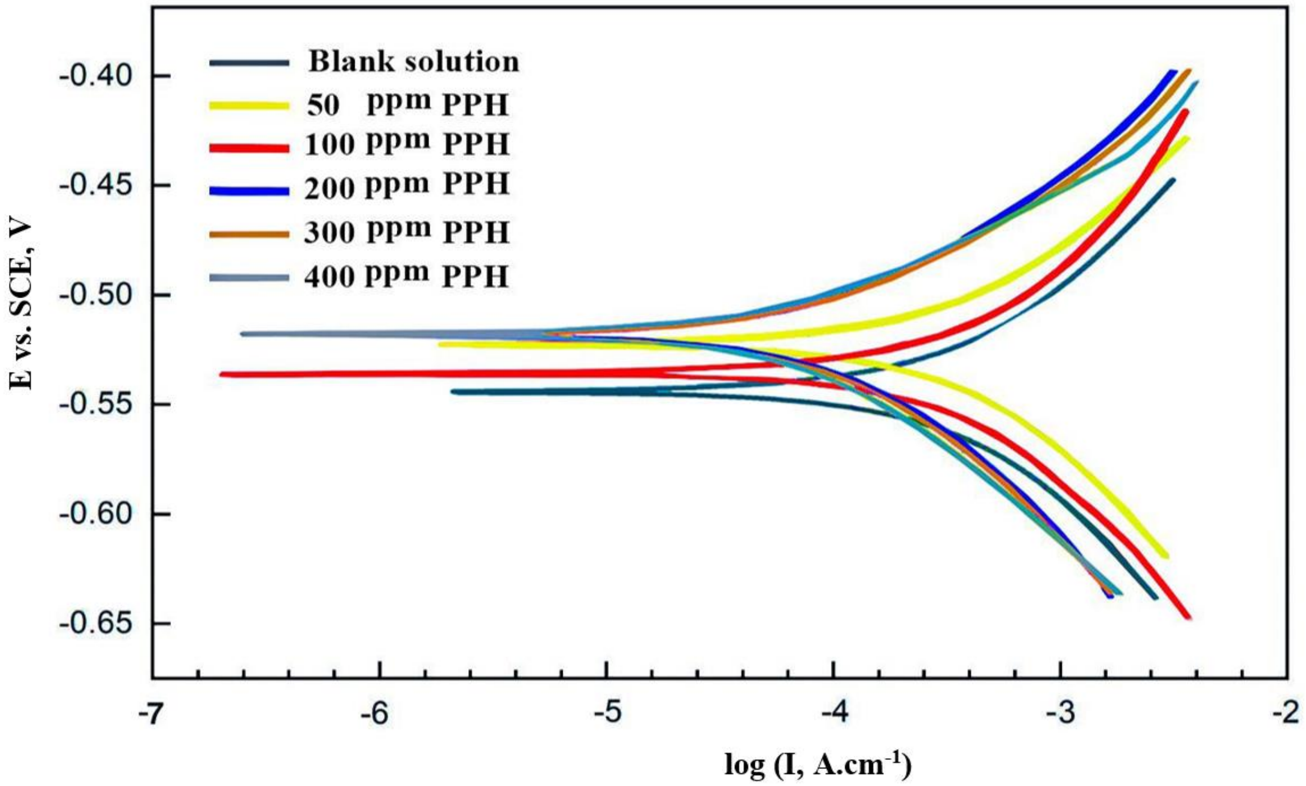

Figure 4.
Tafel polarization curves for a sample of CS-metal in 1 M HCl at 298 K with different PPH concentrations.

Table 2.
Electrochemical polarization factors for studying corrosion inhibitors on CS-steel coupons in 1 M HCl with and without different inhibitor concentrations.

Conc. (ppm)	**Anodic slope, $\beta_a\ (mV/dec)$**	**Cathodic slope, $-\beta_c\ (mV/dec)$**	**Corrosion Potential, E_{corr} (mV versus SCE)**	I_{corr} $(\mu A/cm^2)$	**θ**	**IE %**
0	125	137	−539	730		….
50	105	148	−541	328	0.55	55
100	100	157	−543	292	0.60	60
200	94	165	−537	234	0.68	68
300	90	177	−535	175	0.76	76
400	92	178	−533	175	0.76	76

It can be noticed that the corrosion current density deceased to 175 µA/cm^2 and 328 µA/cm^2 in the presence of 50 and 300 ppm of the inhibitor respectively, compared to 730 µA/cm^2 when no inhibitor was present. However, this indicates a protective layer formation on the metal surface, which in turn protects it against corrosion of the carbon steel substrate by impeding the contact of the corrosive molecules through surface of the metal [70]. The other observations are that the shape of the Tafel curves remained unaltered for different inhibitor concentrations. This revealed that the βc and βa values have negligible variations, meaning that the mechanism of corrosion has not changed and the drug used inhibits both anodic and cathodic electrochemical reactions [71]. Inhibitive efficiency increases from low to high concentrations, up to 76%. This occurs due to the ability of inhibitor molecules adsorbed by the metal system to prevent the reaction with corrosive media by shielding the anode and cathode sites on the surface through adsorption molecules of inhibitor and lowering corrosion rate of CS-metal [72, 73]. The shift in the Ecorr value was less than 6 mV, thus confirming that PPH is a mixed-type inhibitor. This means that it inhibits either anodic or cathodic electrochemical reactions in acidic solutions [74, 75]. The above results reveal that adsorption of inhibitor molecules on the carbon steel surface can provide excellent protection from its acid corrosion. The obtained results of inhibition efficiency were coherent and consistent between weight loss measurements and potentiodynamic polarization measurements.

3.4. Evaluation of Surface Morphology

The differences in the surface morphology of the polished sample and the sample previously subjected to a hydrochloric acid immersion for nine hours with and without PPH were observed using a scanning electron microscope (SEM), and the relevant images are represented in Figure 5. The polished uncorroded CS - samples are represented in Figure 5-a with a smooth surface. Conversely, the surface of the CS - metal treated with HCl (1 M) is very rough, exhibiting unsightly holes from the chloride ions attack (Figure 5-b). The inhibited sample exhibited a reduction of both large-sized and small-sized holes (Figure 5-c) suggesting that a protective inhibiting layer has formed shielding the direct interaction of chloride ions with the metal surface.

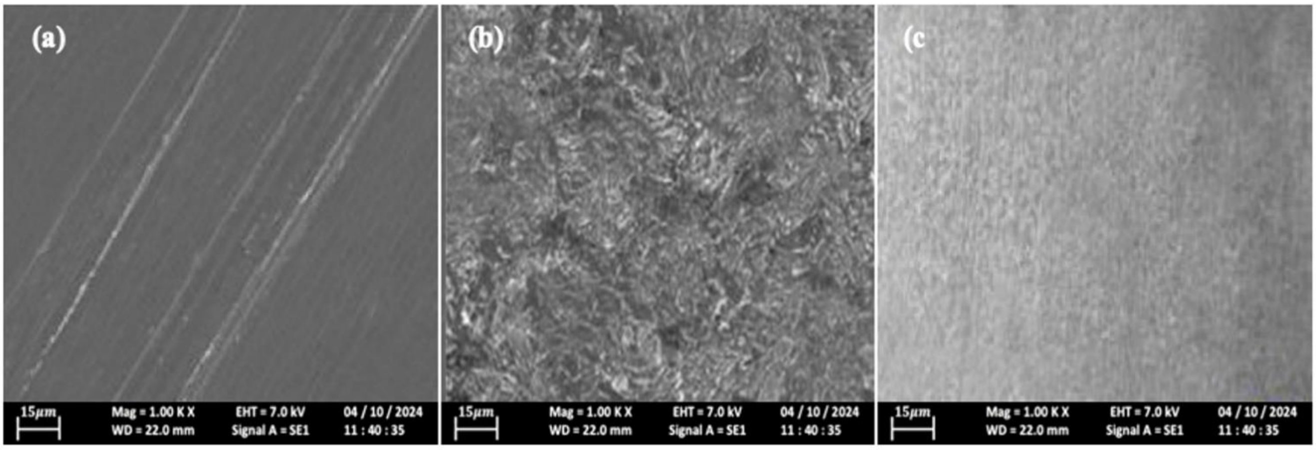

Figure 5.
SEM images of the carbon-steel surface (C1010) treated with 1 M HCl for 9 hr at 298 K. (a) Polished (C1010), (b) Before inhibition, (c) Inhibition with 300 ppm of PPH.

3.5. The Adsorption Isotherms That Control the Inhibition Process

The inhibition of corrosion is considered to occur mainly from the adsorption of the inhibitors on metal surfaces. In this context, the metal surface shielded with inhibitor molecules is resistant to corrosion, while the exposed surface is susceptible to corrosion. Thus, the surface coverage (θ) can be used to observation on the adsorption behavior of inhibiting molecules, which may be quantitatively expressed using adsorption isotherm models like Langmuir, Freundlich, Temkin, and Frumkin[76]. Consequently, these calculations of the adsorption isotherms become important to define the type of interaction between organic molecules and the metal surface. These calculations of surface coverage (θ) which is derived from the inhibition efficiency value (θ = EI (%)/100) at various concentrations of the drug in acidic environments of 1 M hydrochloric acid at 298 K, determined through weight loss and potentiodynamic polarization measurements (see Table 1 and 2). The results indicated a strong agreement with the Langmuir isotherm equation providing the most accurate fit for the data. This equation can be generally represented as follows in Equation 14.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad 14$$

K_{ads} refers to the adsorption-desorption equilibrium constant. The value for K_{ads} can be calculated by plotting C/θ against C (Figure. 6), where the linear correlation's R-squared value was determined to be 0.952 and 0.979, tending towards one and suggesting that the absorption of PPH molecules onto a metallic surface is in agreement with Langmuir isotherm equation.

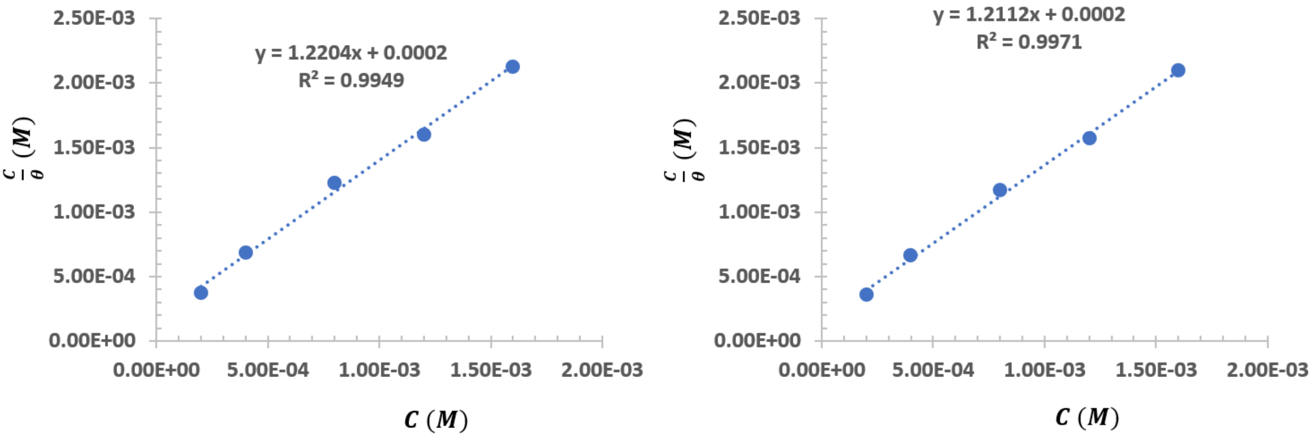

Figure 6.
Linear form of the Langmuir adsorption isotherm for PPH drug established on weight loss and potentiodynamic polarization (PDP) measurements at room temperature.

Through knowing the value of K_{ads}, the standard free energy of adsorption (ΔG^o_{ads}) was determined from Equation 15 [24, 77, 78]:

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^o_{ads}}{RT}\right) \qquad 15$$

Molar concentration of water is (55.5). These values are further presented in Table 3 where all the calculated ΔG^o_{ads} values were negative, indicating that the adsorption processes of the inhibitor onto the carbon steel surface were spontaneous upon immersion for a duration of 9 hours at 25 °C.

Table 3.
Langmuir isotherm adsorption factors for PPH on the metal surface.

Technique	Slope	R^2	K_{ads} ($L.mol^{-1}$)	ΔG^o_{ads} ($kJmol^{-1}$)
Weight loss	1.2204	0.9949	5000	− 31.052
PDP	1.2112	0.9971	5000	− 31.052

Interaction nature of drug molecules adsorbed to the metal surface can be attributed to electron sharing with surface metal atoms which causes physisorption adsorption of the PPH molecules [79, 80]. The mechanism of inhibition depends on the formation of a single protective layer on the metal surface [81]. Meaning that the overlap between the inhibiting molecule and the sample metal is a mix between electrostatic interactions and chemical adsorption [82]. The inhibition mechanism presumes the formation of a monomolecular film chemisorbed on the metal surface. This means; interaction is of a mixed electrostatic type adsorption with chemical adsorption. The mechanism here is that the inhibiting molecule can adhere on the metal surface through the interaction between the active groups such as the heterogeneous atoms and iron ions.

3.6. Theoretical Studies

Computer- based theoretical studies are important to materials science applications in addition to corrosion studies. Generalized electronic parameters, which directly correlate with the adsorption capacity of the inhibiting molecule and inhibition efficiency, provide greater insight into the further study of corrosion systems [58, 67, 83]. The simulation was carried out using the DFT program, which obtained the best stable structure for the inhibitor molecule under conditions that exist in vacuum, in turn obtaining the distribution of electron density in the energy levels. The optimized molecular structure for the drugs can be observed in Figure 7.

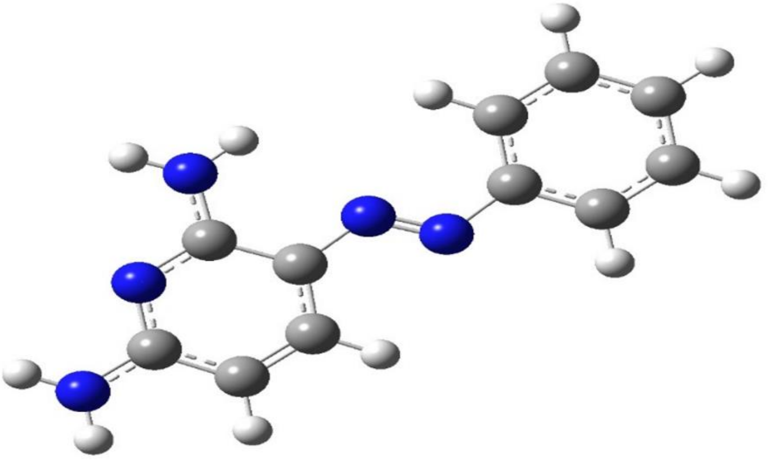

Figure 7.
The optimized molecular structure for the PPH molecule.

The essential quantum chemical parameters include E_{HOMO}, E_{LUMO}, energy gap (ΔE), electronegativity (χ), global chemical softness (σ), global chemical hardness (η), and fractions of electrons transferred (ΔN) (see Table 4), additionally, the charges of the atoms in the inhibitor molecule were computed. All these factors as a whole contribute to revealing the stability and interactions of the molecule [84].

Table 4.
Calculated quantum chemical parameters for PPH.

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η (eV)	σ (eV)	χ (eV)	ω (eV)	ΔN
PPH	-7.959	-3.489	$4.470\ eV$	2.235	0.447	5.724	3.664	0.285

These metals have a low LUMO (lowest unoccupied molecular orbital) which tend to attract lone pair electrons or π electrons of the electron – donating inhibitor molecules. Conversely, metal could donate electrons from the highest occupied molecular orbital (HOMO) or, the occupied π orbital electrons to the antibonding orbitals of the inhibitor molecule (LUMO) (π*) resulting in back-bonding. The bonding of the donor-acceptor nature of this interaction is between the inhibitor molecule and the empty d orbitals in the metal which is the primary reason for the adsorption of the inhibitor on the metal surface. In studies liberated previous, it showed a clear connection between the inhibitor efficiency and the molecular orbital energy [85]. It can be concluded that the tendency for the inhibitor to decrease corrosion is related to E_{HOMO}, E_{LUMO}, and the energy gap between them (ΔE) (Figure 8). The electron density in the energy levels E_{HOMO} and E_{LUMO} returns mainly to the bonding orbitals (π) which is located inside nitrogen atoms, Azo group, and the aromatic ring in the inhibitor molecule.

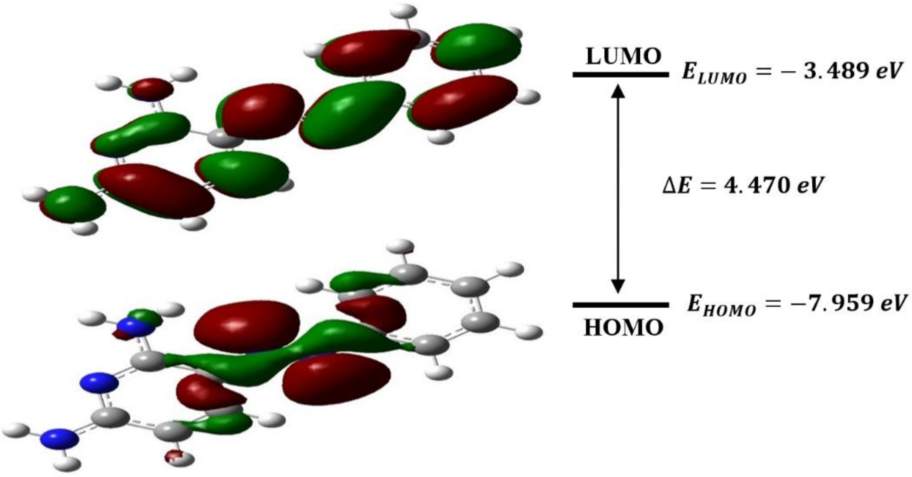

Figure 8.
The geometrical structure of LUMO and HOMO energy orbitals for PPH showing the energy difference between them.

An increase in E_{HOMO} $(-7.959\ eV)$ indications to the strong preference of the inhibitor molecule to donate electrons to the d orbitals of the iron atoms in carbon steel, while a decline in E_{LUMO} $(-3.489\ eV)$ provides further support for the tendency of the inhibitor molecules to accept electrons from the metal. Therefore, the molecular orbital electron surfaces reveal the ability of the inhibitor rings to donor and accept electrons under ideal conditions. The ability of the inhibitor molecule at the same time to accept and donate electrons is important in the process of interfering with the metal surface explains its adsorption on the metal surface. Thus, molecular orbital electron surfaces reveal that under ideal conditions, inhibitor rings can act as electron donors and electron acceptors. Inhibition of metal surface, depends on the ability of inhibitor molecule as able to simultaneously accept and donate electron [90]. The low energy gap of $(4.470\ eV)$ indicates that the inhibitor probably possesses rich chemical activities and kinetic stability, which help explain such high inhibition efficiencies along with the simple adsorbent onto the surface.

The inhibitor molecule is considered a soft molecule and according to this presented concept, it has a low ΔE value that can be absorbed onto the CS sample. Chemical hardness (η) and softness (σ) are two aimed at quantitative determinations that are assessed in describing selectivity and reactivity [86]. These have direct relations to the inhibition process and were often largely understood through Lewis acids and bases or Pearson's concept of hard and soft acids and bases [87]. The direction of corrosion inhibition reaction can be predicted by knowing the global reactivity index (ω) [88]. It can be guessed that the inhibitor molecule is a good electrophile if it has a high electrophilicity value and a good nucleophile if the electrophilicity value is low. The value of ΔN calculated for the molecule shows a value of 0.284 $(\Delta N > 0)$; this was an unequivocal indication of electron transfer from the inhibitor molecules to the metal surface [89]. In the previous studies, very interesting information was obtained from the value of ΔN where inhibition efficiency increased when ΔN (3.6) was less than this threshold and with the transferring capacity to the metal surface [90].

Furthermore, it is important to determine the part responsible for bonding and forming the protective covering. In general, atoms, and specifically heteroatoms, with negative Mullikan charges are of significance because they can donate electrons through electrostatic interactions [64]. Mullikan charges for the inhibitor are represented in Figure 9. It can be concluded easily that the heteroatoms have a high negative charge. Additionally, they also have the carbon atoms of an aromatic ring or that assist in dynamic spots in another way in adsorption of carbon steel surface by the inhibitor molecule in order to protect it from corrosion.

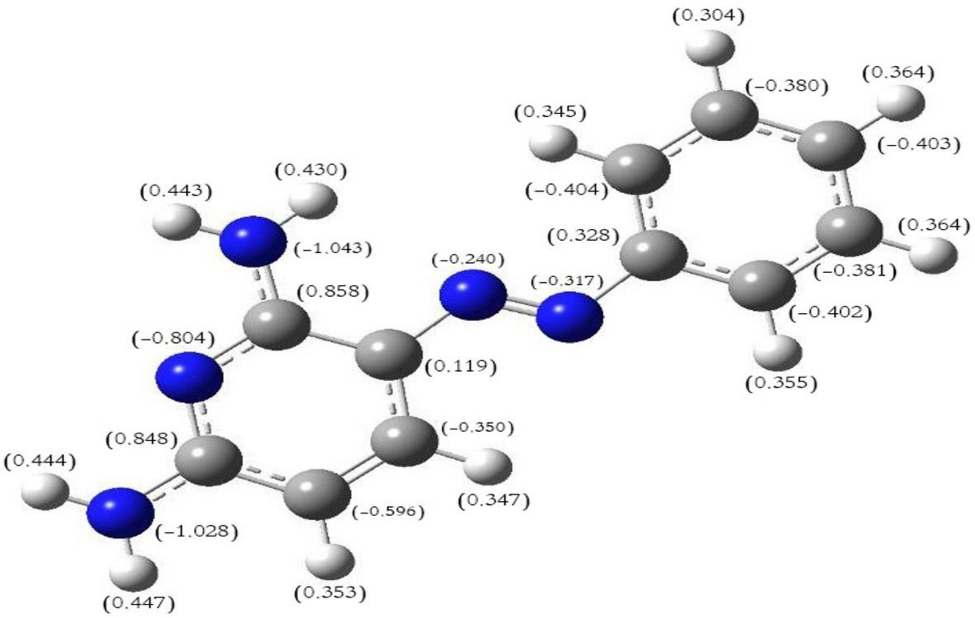

Figure 9.
Mulliken charges for PPH drug.

3.7. The Suggested Inhibition Mechanism

The mechanism of organic inhibitor molecules is affected by several factors, of which is the compound structure of the inhibitor and the charge allocation over its surface as well as the nature of the metallic surface and its charge. The effectiveness of organic inhibitors depends on their basic structural skeleton and the aggressiveness of the media that surround the substance, like air temperature and acids that assist the adsorption processes of the specific molecules onto the surface of the metal [91, 92]. Based on molecular adsorption, corrosion of carbon steel in 1 M HCl medium is inhibited by PPH which could mean the specific control of anodic and cathodic reactions is attained, resulting in corrosion inhibition. Figure 10 provides a schematic description of the proposed inhibition mechanism.

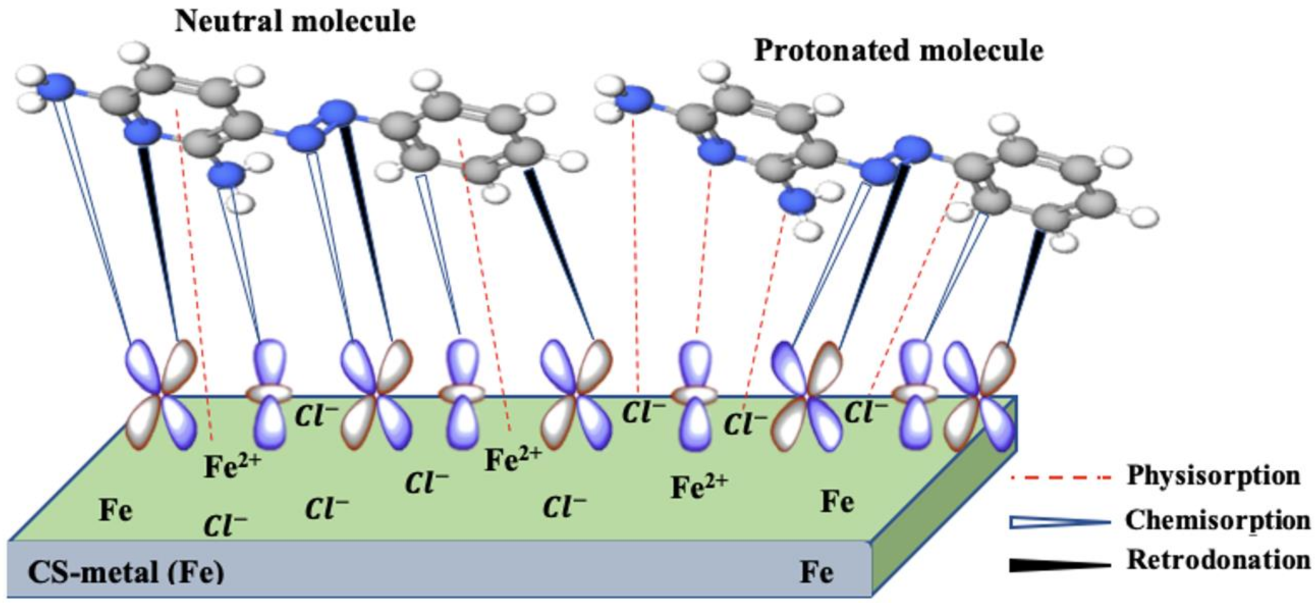

Figure 10.
Proposed adsorption mechanism for the PPH molecule on the carbon steel surface.

In acidic environment, molecules can be available in neutral or protonated molecules which means adsorption can occurs in different ways on the surface of a metal [93]. It can be deduced that the neutral inhibitory molecules exhibit mixed inhibition of chemisorption, physisorption and retro donation to metal surface with dominant cathodic inhibition effects. The chemisorption process takes place in the anode sites of the drug from heteroatoms in the drug (N: nitrogen atoms); this donor-acceptor interaction leads to the transfer of an electron pair from the drug to an empty d orbital of the metal, through a nitrogen atom in an azo group, a pyridine motif or an amino group, establishing a coordinate bond. This allows for the displacement of water molecules from the metallic surface and leads to sharing of electrons between the iron (Fe) atoms and heteroatoms. This reduces corrosion by increasing the number of inhibitory molecules that adhere to the metal/acid interface. In addition, the π electrons in the benzene ring are capable of forming a similar bond with the metal atoms. Physisorption depends on the electrostatic interactions regarding the charge of the inhibitor and the charged metal surface, where the drug contains pyridine and benzene ring in its structure that have high electron densities, interacting vigorously with the positive charges of iron ions in the carbon steel/solution interface to form ferrous ion complexes with the drug. They do act as a shield that is a barrier between the surface of steel and the destructive media. It is highly likely that the chloride ions (Cl^-), due to their low degree of hydration, produce by electrostatic forces additional negative charges on the adsorbed metals of the solution, thereby drawing in more cations [54]. On the other hand, the rerodonation (Pi backbonding) can be formed by the interaction between filled d-orbitals of metals with vacant π*- orbitals of unsaturated bond such as C=C, C=N and N=N bonds.

Metal surfaces in hydrochloric acid solution are commonly covered with a negative electronic charge (-Ve) as a result of the electrostatic adsorption of chloride ions (Cl^-) at the surface of the metal, forming ($FeCl^-$) complexes. While, the protonated species adsorb in the cathodic sites on carbon steel and reduce the release of hydrogen. Due to electrostatic interactions between protonated nitrogen atoms and the metal surface, the inhibition by PPH is established. The protonated form of the inhibitor would adsorb onto the metal surface through negatively charged chloride ions, which form a bridge between the charged metal surface and the protonated drug cations. As a result, an intense cover will procedure on the iron surface, reducing charge and mass transfers. Furthermore, the large size of the inhibitory molecule will increase the additional coverage of the surface where these molecules will prevent attacks by aggressive species.

4. Future Studies

This study has provided a solid foundation for future scientific investigations to achieve greater progress and more control over the corrosion process. The following are some areas for further research:

4.1. Optimization of Temperature

Further research could use a wider range of temperature to find an optimum temperature at which the inhibition efficiency is as high as possible, as well as possible higher temperatures could also be reached with lower inhibitor concentrations leading to a decrease in cost which is fundamental in practical applications.

4.2. The Ability to Modification the Inhibitor Molecule

The structure of PPH drug which contains terminal amine groups provide an opportunity to modify the molecule through Schiff bases reactions to increase the size and molecule weight and increase the number of functional groups in the molecule's structure. This will eventually lead to an increase in chemisorption and physisorption between the inhibitor molecule and iron surface. Thus increasing the thickness of the layer acting as film protection and increase in the efficiency of the inhibitor.

4.3. Synergistic Inhibition

Studying the possibility of combining phenazopyridine hydrochloride (PPH) and other organic or inorganic corrosion inhibitors has attractive synergy that could enhance the overall inhibition efficiency of preventing corrosion. Synergy studies may provide opportunities to create new combinations of inhibitors which will be multifunctional and extremely effective.

4.4. Use of Varying Acidic Environments

In order to improve scientific understanding and practical applications, various changes essential to be made. Some alterations to consider include using altered acidic circumstances such as sulfuric acid or hydrofluoric acid to estimate the performance of the inhibitor molecule. This provides a comprehensive evaluation of the inhibitor for its versatility and applicability in various industrial environments. As well as, recreating experiments using concentrations higher than 1 M from acidic environment to determine the resistance and efficiency of the inhibitor in harsh environments.

5. Conclusions

(1) By analyzing the infrared spectrum of the expired drug PPH, it shows that it keeps its chemical conformation, structure, and functional groups which indicates the continued presence of the main active ingredient in this medicine.
(2) This study clearly showed that expired PPH drug could be used as a corrosion inhibitor in acidic medium at 25 °C for carbon steel. It showed that it is possible to use PPH as an effective alternative to the toxic corrosion inhibitors in industrial applications, which assists in preventing environmental pollution by utilizing it instead of disposal.
(3) The weight loss measurements showed good performance against corrosion, where the inhibition effectiveness increased with increasing concentration, up to a value of 75 % at 300 ppm and 25 °C at an immersion period of 9 hours.
(4) PDP measurements indicated the drug is a mixed type inhibitor. The inhibition results suggested an acceptable agreement with the weight loss measurements.
(5) The mechanism of adsorption of the inhibitor followed Langmuir isotherm equation at 298 K, indicating that adsorption forms a monolayer in a spontaneous process.
(6) The metal's surface changes during corrosion were studied using scanning electron microscopy. The images showed an improvement in the texture of the surface after adding the inhibitor to the acidic solution, forming a smoother surface by the clear decrease in the number of holes from before the addition of the inhibitor.
(7) DFT-based theoretical calculations exceedingly matched experimentation results. Calculated geometrics and orbital energies produced an understanding of the adsorption mechanism of PPH drug on the carbon steel surface as well as a deeper look on the inhibition mechanism further.
(8) It can be concluded from the study that the proposed adsorption mechanism is a mixed mechanism between chemisorption and physisorption.

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