Corrosion Inhibition Efficiency of Expired Nitazoxanide Drug on Carbon Steel in Hydrochloric Acid Solution

M. M. Motawea

Department of Chemistry, College of Science, University of Bisha, Bisha, Kingdom of Saudi Arabia and Delta Higher Institute of Engineering & Technology Mansoura, Egypt
E-mail: dr_mmm_2018@yahoo.com

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The corrosion inhibition of the expired Nitazoxanide drug was investigated in inhibiting the carbon steel (CS) corrosion in 1M HCl using chemical method (weight loss (WL)), two electrochemical test (potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) techniques) combined with surface analysis. The results show that the expired Nitazoxanide drug are effective and attain their action as mixed type corrosion inhibitors, and their corrosion inhibition affinities were increase with the rising of their concentration and lower temperature. The adsorption of the expired Nitazoxanide drug on the CS surface was obeyed Langmuir isotherm. The adsorption thermodynamic parameters calculated show that the adsorption was a spontaneous, endothermic process accompanied by an increase in the entropy. The maximum data of the inhibition approached to 90% within the presence of 300 ppm expired Nitazoxanide drug using potentiodynamic polarization process. The results of surface analysis and the electrochemical technique were in a great agreement

Keywords: Acid corrosion, C-steel, SEM, AFM, FTIR, Adsorption, Nitazoxanide drug

1. INTRODUCTION

Carbon steel is one of the iron alloys that greatly use in the manufacture of industrial products because it shows excellent, low-temperature toughness, hydrogen -induced crack and fracture resistances and a good weldability [1]. C-steel corrosion causes short shelf life, self-discharge, safety issues (evolution hydrogen gas evolution) and lower of valuable capacity, to decrease these undesirable manner, corrosion of C-steel must be controlled [2]. Numerous inhibitors in used are either produced from cheap raw material or selected from composite having hetero atoms in their long-chain carbon or aromatic system [3-4]. The studies show that the inhibition effect of these organic compound occurring by its adsorption on surface of C-steel. Organic heterocyclic compound have used for the corrosion inhibition of C-steel [5-10], copper [11], aluminum [12-14], and other metals [15] in different aqueous
solution. The drug adsorbed assisted to protect the metal surface [16]. The select of some medication for inhibitor of corrosion is taking due to contain active centers, ecofriendly environmentally and simply purified and formed [17]. In current years, the drugs utilize as corrosion hindrance for altered metals result to their nontoxic environment [18-19]. Adsorption of the drug molecules on the surface of metal facilitates its protection [20-31].

The target of this paper is to examine the inhibitive effect of Nitazoxanide towards the corrosion of C-steel in 1M HCl using electrochemical and non-electrochemical techniques. The surface analysis of the C-steel samples was also tested.

2. MATERIALS AND METHODS

2.1. Metal sample

This investigation has been performed using carbon steel contains the next composition as weight percent: 0.350 Mn, 0.200 C, 0.024 P, 0.003 S, and balance Fe.

2.2. Chemicals

Inhibitor – expired Nitazoxanide is the investigated drug which has been used as inhibitor. Absolute ethanol (EtOH, 99%) were supplied from Gomhoria Company and used for the preparation of ethanolic-aqueous mixtures with bi-distilled water.

![Chemical structure of Nitazoxanide](image)

[2-[(5-nitro-1,3-thiazol-2-yl) carbamoyl] phenyl] ethanoate $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_5\text{S}$

$M.Wt = 309.283 \text{ g/mol}$

2.3. Solutions

The aggressive solution, 1M HCl has been prepared from a reagent bottle of the company name (Scharlau) containing concentration HCl (37%) with bi-distilled water, it was standardized using already
prepared standard 1M (Na$_2$CO$_3$) solution. The range of the concentration of inhibitor utilized was 50-300 ppm

2.4. Weight loss (WL) Method

For weight loss method, square samples of area surface (2.6 x 2.8 cm which exposed to the corrosive medium that applied. The samples have abraded with emery papers grit sizes (250,600 and 2000) and clean with acetone and finally dried by filter papers. The WL methods have taken in glass beaker (100 ml) employed in a water thermostat. The samples were then directly dipped in the test solution presence and absence different concentration of the investigated drug. The average weight loss for C-steel samples will achieve. The inhibition efficiency (%IE) and the degree of surface coverage ($\theta$) of Nitazoxanide for the corrosion of C-steel were measured as next [32]:

$$\% \text{IE} = 0 \times 100 = [1 - \left( \frac{W}{W^0} \right)] \times 100$$

(1)

Where, $W^0$ and $W$ are the WL presence and absence addition different concentration of Nitazoxanide, respectively.

2.5. Electrochemical techniques

Potentiodynamic polarization (PP) method was taken in a typical three compartments glass cell [33]. The potential range was (-800 to +200 mV vs. saturated calomel electrode (SCE)) at open circuit potential (OCP) with a scan rate 1 mVs$^{-1}$. All measurements were obtain with C-steel electrode in 1 M HCl with and without various concentrations (50 – 300 ppm) of the expired Nitazoxanide at 25°C.

Then corrosion current densities ($i_{\text{corr}}$) was calculated for the measurements and was used to calculate the $\% \text{IE}$ and the $\theta$ from equation (2) as next:

$$\% \text{IE}_{\text{PP}} = 0 \times 100$$

(2)

$$\theta = 1 - \left( \frac{i_{\text{corr(inh)}}}{i_{\text{corr(free)}}} \right)$$

(3)

Where $i_{\text{corr(free)}}$ and $i_{\text{corr(inh)}}$ are the corrosion current in the presence and absence of Nitazoxanide, correspondingly.

Impedance (EIS) tests were done by AC signs of 5 mV peak-to-peak amplitude and at a range of frequency of $10^7$ Hz to 0.1Hz [34-35]. The capacity of double layer ($C_{\text{dl}}$), $\% \text{IE}$ and $\theta$ were obtained from Eq. (3) and (4) which are given as:

$$C_{\text{dl}} = \frac{1}{(2 \pi f_{\text{max}} R_{\text{ct}})}$$

(4)

Where $f_{\text{max}}$ is the maximum frequency, $R_{\text{ct}}$ are the charge transfer resistances.

$$\text{IE} \% = [1 - \left( \frac{R_{\text{ct}}}{R_{\text{ct}}} \right)] \times 100$$

(5)

Where $R_{\text{ct}}$ and $R_{\text{ct}}$ are the charge transfer resistances without and with Nitazoxanide, respectively.

All electrochemical measurements were achieve utilized Potentiostat /Galvanostat / Zra analyzer (Gamry PCI4-G750). A personal computer with DC105 software for potentiodynamic, EIS300 software for EIS; the computer has used for summation value. Echem Analyst 5.5 Software had applied for drawing and fitting data.
2.8. Surface Analysis:

The C-steel samples used for analysis of morphology surface were ready in 1M HCl (blank) and presence of 300 ppm of expired Nitazoxanide at 25°C for 24 hours after abraded mechanically used different emery papers up to 4000 grit size. Then, after this dipping time, the examination was approved by utilizing (SEM) tests, (AFM) and (FTIR).

3. RESULTS AND DISCUSSION

3.1. Weight loss (WL) method

WL of C-steel, in mg cm\(^{-2}\) of the surface area, was measured at different time periods in the presence and absence of different concentration (50 -300 ppm) of the expired Nitazoxanide. The curves attained with different concentration of drug fall considerably below that of free acid as shown in Figure 1. The inhibition efficiency (% IE) are record in Table 1. In all cases, the inhibition efficiency of the drug increase with raising concentration of the expired Nitazoxanide and the corrosion rate was lowered. These results show that, the expired Nitazoxanide under study are good efficient as inhibited CS dissolution in solution of 1M HCl. A maximum %IE of 90.1 % was noted at 300 ppm concentration at 2hours. This performance could be recognized to rise of the number of adsorbed molecules at the surface of C-steel \([36]\). The adsorption process is made possible due to the existence of heteroatoms such as nitrogen and oxygen atoms, which are regarded as centers of adsorption \([37]\).

![Figure 1. WL-time diagrams for the CS in 1M HCl without and with various expired Nitazoxanide concentrations at 25 °C.](image)

<table>
<thead>
<tr>
<th>Conc., ppm</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>81.1</td>
<td>71.2</td>
<td>68.6</td>
<td>59.6</td>
<td>52.8</td>
</tr>
</tbody>
</table>
3.2. Adsorption isotherm

The common adsorption isotherms fitting were used to analyze the data are Langmuir, Freundlich, Flory–Huggins and Frumkin [38]. In the present study, the data of our experiment, revealed that the best fit for Langmuir isotherm. Figure 2 show the drawing of (C /θ vs. C) at 25°C for expired Nitazoxanide. This curve gave straight lines representative that the adsorption of expired Nitazoxanide on surface of CS follow Langmuir isotherm:

\[
\frac{C}{\theta} = \frac{1}{k_{ads}} + C
\]  

(6)

Where C is the expired Nitazoxanide concentration in the bulk electrolyte, and \(k_{ads}\) is the adsorption equilibrium constant of the expired Nitazoxanide adsorption (\(K_{ads} = 1/\) intercept). \(\Delta G^o_{ads}\) was measured from the next equation:

\[
\log k_{ads} = \log(1/55.5) - (\Delta G^o_{ads}/2.303R)(1/T)
\]  

(7)

where 55.5 is the concentration of water in solution in mol l\(^{-1}\) and T is the temperature absolute. Adsorption enthalpy change (\(\Delta H^o_{ads}\)) was obtained from plotting log \(k_{ads}\) against 1/T (Figure 3) using the next equation:

\[
\log k_{ads} = (-\Delta H^o_{ads}/2.303RT) + \text{constant}
\]  

(8)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>C/θ (mol/l)</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
<th>45°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>82.9</td>
<td>74.7</td>
<td>69.1</td>
<td>61.3</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>84.8</td>
<td>77.5</td>
<td>72.5</td>
<td>64.8</td>
<td>60.2</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>85.3</td>
<td>77.5</td>
<td>74.6</td>
<td>69.5</td>
<td>64.3</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>87.2</td>
<td>84.8</td>
<td>77.8</td>
<td>72.6</td>
<td>68.5</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>90.1</td>
<td>86.2</td>
<td>80.8</td>
<td>74.9</td>
<td>72.8</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. Langmuir curves of expired Nitazoxanide on CS in HCl at altered temperatures
Table 2. Adsorption thermodynamic parameters obtain from Langmuir plots of Nitazoxanide on CS surface in HCl at various temperatures

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>$K_{ads}$ M$^{-1}$</th>
<th>$-\Delta G^o_{ads}$, kJ mol$^{-1}$</th>
<th>$-\Delta H^o_{ads}$, kJ mol$^{-1}$</th>
<th>$\Delta S^o_{ads}$ J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>165</td>
<td>18.2</td>
<td>32</td>
<td>70.7</td>
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<tr>
<td>35</td>
<td>150</td>
<td>18.9</td>
<td></td>
<td>68.4</td>
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<tr>
<td>45</td>
<td>132</td>
<td>19.1</td>
<td></td>
<td>67.1</td>
</tr>
<tr>
<td>55</td>
<td>122</td>
<td>19.6</td>
<td></td>
<td>63.2</td>
</tr>
<tr>
<td>65</td>
<td>95</td>
<td>20.1</td>
<td></td>
<td>60.4</td>
</tr>
</tbody>
</table>

Figure 3. log $k_{ads}$ against $1/T$ for CS in corrosive solution with expired Nitazoxanide.

The standard activation entropy ($\Delta S^o_{ads}$) can be measured utilized Vant’t Hoff equation (9):

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

$\Delta G^o_{ads}$ was calculated using Eq. (3) where one molecule of water is replaced by one molecule of inhibitor [39]. The values of $\Delta G^o_{ads}$ and K are given in Table (2). The negative sign of $\Delta G^o_{ads}$ designates that the adsorption of expired Nitazoxanide on the CS surface is a spontaneous process. Mostly, the $\Delta G^o_{ads}$ value around -20 kJ mol$^{-1}$ or less negative specifies electrostatic interaction among inhibitor and the charged metal surface (i.e. physisorption). Those around -40 kJ mol$^{-1}$ or more negative suggestive of charge sharing or transferring from the inhibitor molecules to the surface of C-steel to form a coordinate type of bond (i.e. chemisorptions) [40-41]. In the current work, the measured data of free energy of Nitazoxanide Table (2) are – 20.1 kJ mol$^{-1}$ or less: which designated that adsorption takes place via physisorption. Small data of $K_{ads}$, however, reveal that such interactions among adsorbing Nitazoxanide molecules and the surface of C-steel are weaker, demonstrating that the Nitazoxanide molecules are easily removable by the solvent molecules from the surface of C-steel [42].
3.3. Temperature effect

The temperature influence on the corrosion parameters of C-steel with the addition of Expired Nitazoxanide was calculated utilizing WL. A major advantage of WL is its relative simplicity and availability. The outcome data of C-steel corrosion behaviour in HCl including altered concentrations of Expired Nitazoxanide for 120 min in temperature range 25-45°C were existence in Table (1). Assessment of this Table make known that the rate of C-steel corrosion improved with raised temperature [43-46]. On the other hand, the %IE of Expired Nitazoxanide lowered with higher temperature. This proposes possible desperation of some of the adsorbed Nitazoxanide molecules from the surface of C-steel at maximum temperatures. Such manner displays that the additives were physically adsorbed on the C-steel [47-49].

3.4. Kinetic–thermodynamic corrosion parameter

The influence of temperature (25 – 45°C) on the %IE of the expired Nitazoxanide was measured without and with of altered concentrations (50 - 300 ppm) of expired Nitazoxanide. Arrhenius Eq. (4) was used Arrhenius – type plot:

\[
\log k_{\text{corr}} = \log A - \frac{E^*}{2.303R} \left(\frac{1}{T}\right)
\]

where \( E^* \) is the apparent activation energy, \( A \) is the frequency factor, \( R \) equal 8.314 joule/K.mol, and \( T \) = Kelvin temperature[50-53]. Plots of \( \log k_{\text{corr}} \) and \( 1000/T \) were shown in Figure 4. Enthalpy of activation for corrosion process (\( \Delta H^* \)) and entropy of activation for corrosion process (\( \Delta S^* \)) were determined by plotting \( \log k_{\text{corr}}/T \) vs. 1/T (Figure 5), according to transition state- type equation:

\[
\log \frac{k_{\text{corr}}}{T} = \log \left(\frac{R}{Nh} + \frac{\Delta S^*}{2.303R}\right) + \frac{(-\Delta H^*/2.303R)}{(1/T)}
\]

where \( h \) = constant and \( N \) = Avogadro number.

![Figure 4](image-url)

**Figure 4.** (\( \log k_{\text{corr}}/T \)) against (1000/T) in 1M HCl presence and absence of different concentrations of expired Nitazoxanide.
The results of Table (3) revealed that, the attendance of expired Nitazoxanide improved the $E^*_{a}$ of CS signifying strong adsorption of the Nitazoxanide molecules on C-steel and these additives makes energy barrier rises with raising the concentrations of Nitazoxanide. The $E^*_{a}$ data rise with Nitazoxanide concentration is often deduced by physical adsorption [54]. $\Delta H^*$ data of are positive. This designates that the corrosion process is an endothermic one. The $\Delta S^*$ is large and negative. This suggests that the activated complex signifies association rather than dissociation step, demonstrating that a lowered in disorder occurred, from reactants to the activated complex [55].

**Figure 5.** Log ($k_{corr}/T$) vs (1000/T) curves for CS immersion in HCl presence and absence of different concentrations of expired Nitazoxanide.

**Table 3.** Activation parameters for CS in corrosive solution presence and absence of altered concentrations of expired Nitazoxanide.

<table>
<thead>
<tr>
<th>C inh. ppm</th>
<th>$E^*_{a}$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$-\Delta S^*$ (J mol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M HCl</td>
<td>47.2</td>
<td>46.5</td>
<td>117</td>
</tr>
<tr>
<td>50</td>
<td>63.7</td>
<td>60.8</td>
<td>78.8</td>
</tr>
<tr>
<td>100</td>
<td>65.1</td>
<td>63.3</td>
<td>74.4</td>
</tr>
<tr>
<td>150</td>
<td>67.9</td>
<td>64.6</td>
<td>73.5</td>
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<tr>
<td>200</td>
<td>68.6</td>
<td>65.8</td>
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<tr>
<td>250</td>
<td>69.5</td>
<td>66.8</td>
<td>67.1</td>
</tr>
<tr>
<td>300</td>
<td>70.9</td>
<td>68.9</td>
<td>64.5</td>
</tr>
</tbody>
</table>

3.5. Electrochemical impedance spectroscopy (EIS) technique

EIS is a good method used for investigation the carbon steel corrosion in acid solution. EIS methods were done in 1M HCl solution without and with different concentrations of the Nitazoxanide. The diameter of a semicircle of the Nyquist plots (figure 6a) increases as a result of increasing the
concentration of Nitazoxanide; it indicates that the corrosion of Nitazoxanide is mainly controlled by a charge transfer process indicate the formation of a protective layer of the drug at the CS-solution interface. The Bode diagrams for the C-steel is displayed in Figure (6b) where the great frequency limit relates to electrolyte resistance $R_\Omega$. Several impedance parameter such as ($R_{ct}$), ($C_{dl}$) and (% IE) were measured and are record in Table (4). The data display that the ($R_{ct}$) data improve and ($C_{dl}$) capacitance double lowered with raising the Nitazoxanide concentration which attended with improving (% IE), due to the Nitazoxanide inhibitor adsorbed of this on the C-steel surface leading to formation of a film on Nitazoxanide surface. The Nyquist diagram obtained in most cases does not display perfect semicircle. Due to the heterogeneity of the C-steel surface [56-57].

![Figure 6a](image.png)

**Figure 6a.** Nyquist diagrams for the CS corrosion in HCl in the presence and absence of various concentrations of expired Nitazoxanide at $25{}^\circ$C

![Figure 6b](image.png)

**Figure 6b.** The Bode diagrams for the corrosion of C-steel in HCl in the presence and absence of expired Nitazoxanide concentrations of at $25{}^\circ$C
The results of EIS measurements were simulated utilizing the illustrated equivalent circuit (Figure 7), in which $R_{ct}$ is the resistance charge transfer and CPE is the constant phase element. Introduction of CPE instead of a pure double layer capacitor in the circuit gives a more accurate fit [58]. For calculated the $\%IE$, equation (3) is used, while equation (12) is used for calculated double layer capacitance ($C_{dl}$) [59].

$$C_{dl} = \frac{1}{2 \pi f_{max} R_{ct}}$$  \hspace{1cm} (12)

Where $f$ is the maximum frequency at the higher semicircle. The EIS data had report in (Table 4).

Figure 7. Equivalent circuit utilized for fitting EIS results

Table 4. EIS parameters in HCl in the presence and absence of expired Nitazoxanide concentrations.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Conc., ppm</th>
<th>$R_{ct}$, $\Omega$ cm$^2$</th>
<th>$C_{dl}$x10$^{-3}$ $\mu$Fcm$^{-2}$</th>
<th>$\theta$</th>
<th>$%IE$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1M HCl</td>
<td>0</td>
<td>53</td>
<td>220</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Nitazoxanide</td>
<td>50</td>
<td>210</td>
<td>171</td>
<td>0.747</td>
<td>74.7</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>311</td>
<td>135</td>
<td>0.829</td>
<td>82.9</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>400</td>
<td>122</td>
<td>0.867</td>
<td>86.7</td>
</tr>
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<td></td>
<td>200</td>
<td>428</td>
<td>110</td>
<td>0.876</td>
<td>87.6</td>
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<td></td>
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<td>456</td>
<td>95</td>
<td>0.883</td>
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<td></td>
<td>300</td>
<td>545</td>
<td>87</td>
<td>0.902</td>
<td>90.2</td>
</tr>
</tbody>
</table>

3.6. Potentiodynamic polarization (PP) measurements

Figure 8 shows Tafel plots at 25°C for CS in corrosive solution without and with various concentrations of expired Nitazoxanide. Linear extrapolation of anodic and cathodic branches of Tafel slopes give corrosion current densities, as indicated from the figure, increasing expired Nitazoxanide concentration leads to decrease cathodic "H$_2$ reduction" and anodic "metal dissolution" reactions. The ($\%IE$) and ($\theta$) were measured from equation (2,3). The PP parameters such as: ($E_{corr}$), ($I_{corr}$), ($\beta_a$) and ($\beta_c$) are existing in Table (5). From the Figure (8) and Table (5) one can see when the concentration of expired Nitazoxanide was raised, the corrosion current density gradually lowered and increased the protection efficiency. The closely steady data of ($E_{corr}$) and the lowered of corresponding partial cathodic
and anodic current densities, these data display that expired Nitazoxanide act as mixed kind inhibitor [60]. Addition of expired Nitazoxanide has insignificant effect on the data of $\beta_a$, $\beta_c$. Therefore, the addition of this antibiotic is simple site blocking of the electrode surface and lowering the surface area available for corrosion reaction [61]. Therefore the attendance of various concentration of expired Nitazoxanide concentration not change the corrosion mechanism.

![Figure 8](image_url)

**Figure 8.** Potentiodynamic polarization plots for CS in HCl in the presence and absence expired Nitazoxanide concentrations at 25°C

**Table 5.** Parameters for CS in the corrosive solution without and with expired Nitazoxanide concentrations at 25°C.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Conc. ppm</th>
<th>$i_{corr}$, $\mu A$ cm$^{-2}$</th>
<th>$-E_{corr}$, mV vs SCE</th>
<th>$\beta_a$, mV dec$^{-1}$</th>
<th>$\beta_c$, mV dec$^{-1}$</th>
<th>C.R mpy</th>
<th>$\Theta$</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.0</td>
<td>995</td>
<td>433</td>
<td>120.0</td>
<td>151</td>
<td>390</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nitazoxanide</td>
<td>50</td>
<td>240</td>
<td>420</td>
<td>118</td>
<td>144</td>
<td>261</td>
<td>0.759</td>
<td>75.9</td>
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<tr>
<td></td>
<td>100</td>
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<td>119</td>
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<td>0.834</td>
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<td>150</td>
<td>142</td>
<td>0.900</td>
<td>90.0</td>
</tr>
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</table>
3.7. Scanning Electron Microscopy (SEM) analysis

Figures 9(a-c) show different SEM micrographs of C-steel samples. Figure 9 (a) shows free C-steel. Figure 9(b) shows C-steel in corrosive solution. Figure 9(c) shows C-steel in corrosive solution + 300 ppm expired Nitazoxanide. The presence of C-steel in the acidic medium (Figure 9(b)) leads to genesis of pits, cracks, and corrosion produces on the surface. Presence of expired Nitazoxanide in the solution (Figure 9(c)) minimizes that pits, cracks and corrosion products and makes the surface smoother. This might be due to formation of a passive layer through expired Nitazoxanide adsorption on the CS surface that blocks the active center and minimizes metal contact with corrosive solution [62].

Figure 9. SEM micrographs for C-steel absence and presence of 300 ppm of expired Nitazoxanide after immersion for 1 day.

3.8. Atomic Force Microscopy (AFM) analysis

Figure 10. The 3D of optical images of AFM in blank (a) and expired Nitazoxanide inhibitor (b)
AFM is a remarkable analysis used for determining the surface roughness with high resolution [63]. Many details about C-steel surface morphology can be obtained from AFM measurements which help explaining the corrosion process. The 3D AFM images were represented in Figure (10).

The mean roughness is given (993 nm) for the blank which immersion in 1M HCl one day and examine. The observation of the C-steel surface which dipped in 1M HCl with of 300 ppm of expired Nitazoxanide given (121 nm) compared to the blank solution. The values showed that the roughness rises with adding HCl due to the corrosion occurs on the CS surface but decreased with adding the expired Nitazoxanide [64].

3.9. Fourier Transform Infrared Spectroscopy (FTIR) analysis

FTIR analysis of the Nitazoxanide was utilized to characterize the functional groups in it, while that of the corrosion product was utilized to check that the inhibition comes from the interaction between the metal and the Nitazoxanide. The FTIR spectra for Nitazoxanide, Nitazoxanide in 1M HCl solution are presented in Figure 11. The results obtained indicate that the interaction between the Nitazoxanide and the C-steel resulted in the inhibition process. The shifts in the spectra with the addition of the C-steel to Nitazoxanide in 1M HCl show in (Table 6) that there is an interaction between Nitazoxanide and the C-steel among the functional groups existence in the Nitazoxanide which resulted in inhibition [65-67].

![FTIR spectrum of inhibitor (Nitazoxanide) before and after adsorption on the CS surface](image-url)
Table 6. Observed wave numbers and the corresponding frequency assignment obtained from Nitazoxanide, and 300 ppm Nitazoxanide / HCl Solution after 24 of immersion

<table>
<thead>
<tr>
<th>Frequency Assignment</th>
<th>Observed wave numbers (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitazoxanide</td>
</tr>
<tr>
<td>O-H stretch</td>
<td>3419</td>
</tr>
<tr>
<td>N-H stretch</td>
<td>3331</td>
</tr>
<tr>
<td>(-\text{C} = \text{C} -) stretch</td>
<td>1640-1421</td>
</tr>
<tr>
<td>CN stretch</td>
<td>1310</td>
</tr>
</tbody>
</table>

3.10. Mechanism of corrosion inhibition

The mechanism includes the adsorption inhibitor on the C-steel surface immersion in HCl. Four natures of adsorption [68] may occurring contain Nitazoxanide drug at the interface between interface of CS–solution: 1) Electrostatic attraction among the charged metal and the charged molecules; 2) Interaction of unshared electron pairs in the molecule through the metal; 3) Interaction of π-electrons with the metal; 4) Summation of all the above. From the observations drawn from the various methods, corrosion protection of C-steel in 1M HCl solutions by Nitazoxanide as obtain from WL, PP and EIS tests were found be influenced by the concentration and the nature of the protection. Nitazoxanide molecule may protonated in the acid medium. So, there is difficult for these protonated molecules to adsorb on the positive C-steel surface [69]. Chloride ions get first adsorbed on surface of CS, the CS becomes negatively charged, and then the protonated Nitazoxanide molecules get adsorbed on the chloride layer as shown below forming physical adsorption mechanism:

A comparative study showing IE show of some of the drugs testified before in the literature is illustrated in Table 6. The present Nitazoxanide shows considerably important corrosion inhibition compared to some other drugs. The relatively high %IE of the Nitazoxanide can be qualified to the presence of phenyl ring as well as functional groups such as N, O and S atoms.
Table 6. A comparative chart listing the performance of some drugs as corrosion inhibitors drugs

<table>
<thead>
<tr>
<th>Inhibitor (drug)</th>
<th>Sample</th>
<th>Medium</th>
<th>IE %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penciilllin G</td>
<td>Mild steel</td>
<td>H₂SO₄</td>
<td>73.7</td>
<td>[70]</td>
</tr>
<tr>
<td>Penicillin V</td>
<td>Mild steel</td>
<td>H₂SO₄</td>
<td>63.3</td>
<td>[71]</td>
</tr>
<tr>
<td>Cefalexin</td>
<td>Mild steel</td>
<td>HCl</td>
<td>76.5</td>
<td>[72]</td>
</tr>
<tr>
<td>Ceftriaxone</td>
<td>Mild steel</td>
<td>HCl</td>
<td>90.0</td>
<td>[73]</td>
</tr>
<tr>
<td>Cefotaxime</td>
<td>Mild steel</td>
<td>HCl</td>
<td>90.0</td>
<td>[74]</td>
</tr>
<tr>
<td>Cefixime</td>
<td>Mild steel</td>
<td>HCl</td>
<td>90.0</td>
<td>[75]</td>
</tr>
<tr>
<td>Quinoline</td>
<td>Mild steel</td>
<td>HCl</td>
<td>88.7</td>
<td>[76]</td>
</tr>
<tr>
<td>Cetylpyridinium chloride</td>
<td>Carbon steel</td>
<td>HCl</td>
<td>81</td>
<td>[77]</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>Carbon steel</td>
<td>HCl</td>
<td>89</td>
<td>[78]</td>
</tr>
<tr>
<td>Etoricoxib</td>
<td>Carbon steel</td>
<td>H₃PO₄</td>
<td>80.6</td>
<td>[79]</td>
</tr>
<tr>
<td><strong>Nitazoxanide</strong></td>
<td>Carbon steel</td>
<td>HCl</td>
<td>90.2</td>
<td>Present work</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Nitazoxanide drug is establish to be excellent inhibitor for the C-steel corrosion in 1M HCl acid media. It is a physical adsorption. The %IE rises with the improving in the Nitazoxanide concentration and lowered temperature. The values of %IE show that the inhibitor is physical adsorbed on the C-steel surface in 1M HCl acid. The impedance results supplement the results obtained from PP studies. Rct value was found to be higher in the existence of the inhibitors. Higher value of (Rct), lead to increase the inhibition efficiency. The value of (Cdl) was found to be lower suggesting the inhibitors adsorb well on the C-steel surface even at low concentrations.

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