Corrosion Inhibition Effect of Expired Levothyroxine Drug on Stainless Steel 304L in 0.5 M H$_2$SO$_4$ Solution

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The inhibition of Stainless Steel 304L (SS (304L)) in 0.5 M H$_2$SO$_4$ was study by use expired levothyroxine drug as eco-friendly inhibitor. There are many techniques ((Mass loss (ML), potentiodynamic polarization (PP) tests and electrochemical impedance spectroscopy (EIS)) utilized in this study to explain the protection process. The corrosion inhibition (%IE) rise with improving doses of the expired levothyroxine drug and reduction by temperature raising. The activation and adsorption parameters were calculated and discussed. %IE of SS (304L) occurs by the adsorption process, and this SS (304L) is subject to the adsorption of Langmuir. From the EIS examination, we notice the reduction of the double layer by raising the concentration of expired levothyroxine drug, on the other hand, the charge transfer resistance is increased. The surface morphology of SS (304L) metal was examined by employing various techniques such as AFM, FTIR, SEM and EDX. Results were of all techniques used are in excellent coherence.

Keywords: Expired levothyroxine, SS (304L), H$_2$SO$_4$, SEM, EDX, AFM.

1. INTRODUCTION

SS as a construction material has many uses in altered fields such as in the pharmaceutical manufacturing, petrochemical manufacturing, buildings and chemical vessels. SS alloys have a high corrosion hindrance degree due to good mechanical characters, and the attendance of alloying element Cr, which forms a surface passive layer film of Cr-rich oxide [1]. Metal corrosion occur as a result of oxidation - reduction reactions found in the environment surround the metal [2]. The distinguished acidic inhibitors are pharmaceutical composite and organic composite that include N (N-heterocyclic), Oxygen, long carbon series and aromatic composite. The advantages of organic inhibitors such as great % IE, cheap, environment eco-friendly and effortlessly to ready but sometimes toxic. Recently, some chemical drugs are studied as eco-friendly organic corrosion inhibitors of metals in aqueous media [3].
The aimed to utilized eco-friendly materials as inhibitors of SS (304L) dissolution in a 0.5 M H₂SO₄ solution and the selected was to utilize expired levothyroxine due to its properties: it includes N (N-heterocyclic), Oxygen and aromatic composite that utilized in the process of protecting the SS (304L) as well as cheapness and availability. In this research, numerous tests have been utilized to investigate the hindrance behavior, containing electrochemical and mass loss studies, in addition to studying the metal surface by several tests.

2. MATERIALS AND METHODS

2.1. Metal sample

This investigation has been performed utilizing SS (304L) contains the next composition as weight percent: 0.024 C, 0.061 V, 0.087 Mo, 0.2 Co, 5.699 Ni, 14.293 Cr and balance Fe.

2.2. Chemicals

Expired levothyroxine drug is an organic composite, which have the chemical formula C₁₅H₁₁I₄NO₄ and purchased from Sandozinc and Pfizer inc companies was utilized here as inhibitor (S)-2-Amino-3-[4-(4-hydroxy-3,5-diiodophenoxy)-3,5-diiodophenyl]propanoic acid Mol. Wt. =776.8 g/mol

2.3. Solutions

The corrosive medium (0.5M H₂SO₄) was prepared from 96% sulfuric acid using double distilled water, without or by addition altered dose of Expired levothyroxine drug ranging from 25 to 150 ppm, by dilution from the stock solution (1000 ppm).

2.4. Techniques used for corrosion measurements

2.4.1 ML technique

For mass loss (ML) estimations, coins have the area surface (2 cm x 2 cm) x 2 that existence to the aggressive solution that utilized. The samples are cut and sanded as before, then we wash the samples
with double distilled water, dried, and weighed, and put them in solutions prepared from altered dose of
of Expired levothyroxine drug from 25 ppm to 150 ppm. This occurs in the presence of 0.5M H_2SO_4 to
compare with a sample that was placed in a solution of 0.5 M sulfuric acid without any additives.
Samples are left for half an hour in solutions. Then collected and dried, the samples are weighed, and
then placed again in their solutions. Experiments are repeated three times and average values are
measured to get the most accurate data. The temperature ranges from 25-45 °C. The % IE and surface
degree coverage (θ) of Expired levothyroxine drug for the dissolution of SS (304L) were determinate
from the following balance [4]:

\[ \text{IE}\% = \theta \times 100 = [1 - \frac{(W)}{(W^o)}] \times 100 \]  

Where, W^o and W are the MLs uninhibited and with altered doses of Expired levothyroxine drug,
correspondingly.

2.4.2 Electrochemical tests

The SS (304L) utilized for electrochemical tests (potentiodynamic polarization (PP) and AC
impedance (EIS) tests), a cylindrical rod welding in araldite with area of 1.0 cm^2 was employed. Prior
to each investigate the surface of SS (304L) coins were mechanically scratched with altered grades of
emery papers, and rinsed by bidistilled water.

PP technique was utilized through a cell involving of three classic electrodes, which is the
working electrode that is studied. This electrode consists of SS (304L) metal, where the test of
preparation was explained earlier, and the surface area exposed in it is 1 cm^2, the second electrode is
the reference electrode and the third electrode is the auxiliary electrode. Before each electrochemical
measurement, the SS (304L) electrode was left 30 min in the solution to give the chance to the open
circuit potential to attain a steady state. Polarization bends were verified at a steady scan rate of 0.2 mVs^{-1}
initially from -0.5 V to 0.5 V (SCE). In this technique, the current density is a function of the
calculation. Experiments are repeated three times to confirm them. The % IE enabled for Expired
levothyroxine drug is as follows [5]:

\[ \% \text{ IE} = \Omega \times 100 = [1 - \frac{\text{i}_{\text{corr(inh)}}}{\text{i}_{\text{corr(free)}}}] \times 100 \]  

Where, \text{i}_{\text{corr(free)}} and \text{i}_{\text{corr(inh)}} are the uninhibited and inhibited current density data,
correspondingly.

In this technique, we utilized the same cell previously utilized in PP test. We performed the
experiment by utilizing AC signals ranging from (1x10^5 Hz to x 0.1 Hz), with an amplitude of peaks
10mV at OCP. The double layer capacitance (C_{dl}) was measured by [6-7]:

\[ C_{dl} = \frac{1}{(2\pi f_{\text{max}} R_{p})} \]  

Where, \text{f}_{\text{max}} is the maximum frequency.

All the results of impedance were compatible with the appropriate equivalent circuit using the
Gamry Echem program, and by using the charge transfer resistance as a function of knowing the quality
of protection. The % IE and the (θ) from the impedance tests were obtained by:

\[ \% \text{ IE} = \Omega \times 100 = [1 - \left(\frac{R_{\text{ct}}}{R_{\text{ct}}}\right)] \times 100 \]
Where, $R^\circ_p$ and $R_p$ are the resistances unprotected and protected Expired levothyroxine drug, individually.

Electrochemical techniques were carried out by using Potentiostate/ Galvanostate (PCI4-G750) with software DC 105, EIS 300 for calculations, connected to a computer for data record and store. Each experiment was performed on a newly abraded electrode using a freshly prepared electrolyte. All electrochemical studies were applied at $25^\circ$C.

2.5. Surface Examinations:

The morphological properties of the SS (304L) metal surface were studied. This exam happens in 0.5 M of sulfuric acid in the absence of a corrosion inhibitor (Expired levothyroxine drug) and in the case of the highest dose of Expired levothyroxine drug (150 ppm). Then, the coins were dipped in destructive environments at one day, the specimens were prepared quietly with bidistilled water, dried and mounted into the achieved examined test utilizing scanning electron microscopy (SEM), X-ray dispersive energy (EDX), Fourier transform infrared (FT-IR) spectroscopy and atomic force microscope (AFM).

3. RESULTS AND DISCUSSION

3.1. Mass loss (ML) tests

The ML of SS (304L) at different time periods with and without altered doses of the Expired levothyroxine was displayed in Fig. 1. Show the results obtained in a time of 120 minutes as an example of the study. The diagrams in the existence of Expired levothyroxine lie under the curve of free destructive environments (Fig.1). The % IE and the corrosion rate ($k_{corr}$) are documented in Table 1. In all cases, the improve inhibition of corrosion with higher dose of Expired levothyroxine drug can be attributed to the formation of a layer of the drug on the SS (304L) surface by adsorption. This film is formed by the pairs of free electrons existence on the Nitrogen atoms in the levothyroxine drug molecules as well as the $\pi$-electrons of the aromatic rings. These results designated that, the Expired levothyroxine under test are good substance that hinder dissolution of SS (304L) in destructive environments.
Figure 1. Time- ML bends for dissolution of SS (304L) attendance and lack altered doses Expired levothyroxine drug.

Table 1. Variation of % IE of Expired levothyroxine with various doses from ML testing at 120 min immersed in 0.5 M sulfuric acid

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>Corrosion rate (C.R) x 10^{-2} mg. cm^{-2} min^{-1}</th>
<th>θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>5.2</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>25</td>
<td>0.556</td>
<td>0.893</td>
<td>89.3</td>
</tr>
<tr>
<td>50</td>
<td>0.442</td>
<td>0.915</td>
<td>91.5</td>
</tr>
<tr>
<td>75</td>
<td>0.395</td>
<td>0.924</td>
<td>92.4</td>
</tr>
<tr>
<td>100</td>
<td>0.353</td>
<td>0.932</td>
<td>93.2</td>
</tr>
<tr>
<td>125</td>
<td>0.317</td>
<td>0.939</td>
<td>93.9</td>
</tr>
<tr>
<td>150</td>
<td>0.296</td>
<td>0.943</td>
<td>94.3</td>
</tr>
</tbody>
</table>

3.1.1. Temperature effect

Study the impact of temperature on the dissolution of SS (304L) pieces utilized in the investigation and dipped in 0.5 M of sulfuric acid was studied in the existence and lack of different doses of Expired levothyroxine. It has been found that by raising the dose from 25 ppm to 150 ppm, the rate of protection rises in contrast to the C.R, which lowers with increasing concentrations of Expired levothyroxine drug. By temperature increasing of the aggressive environment the %IE will be lowers, while there is a direct parallel with C.R and temperature. On the other hand, %IE of Expired levothyroxine decreased with raising temperature Fig. 2. This suggests possible desorption of some of the adsorbed levothyroxine drug molecules from the metal surface at higher temperatures.
Figure 2. Effect of different concentrations (ppm) on the %IE of expired levothyroxine at altered temperature.

By applied Arrhenius equation and the activation energy can be estimated:

\[ k_{\text{corr}} = A \exp\left(-\frac{E_a^*}{RT}\right) \]  

(5)

Where, \( E_a^* \) is the activation of energy of SS (304L) in aggressive environment existence and nonexistence Expired levothyroxine drug, and \( A \) is was utilized for the term exponential factor of Arrhenius.

Figure 3. \( \log k_{\text{corr}} \) vs. \( 1/ T \) for dissolution of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug
Figure 4. log $k_{\text{corr}} / T$ vs. $(1/T)$ for dissolution of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug

Table 2. $E_a^*$, $\Delta H^*$ and $\Delta S^*$ data for liquefaction of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug

<table>
<thead>
<tr>
<th>Conc. 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>Blank</td>
<td>49.3</td>
<td>46.6</td>
<td>118.2</td>
</tr>
<tr>
<td>25</td>
<td>68.2</td>
<td>67.4</td>
<td>66.2</td>
</tr>
<tr>
<td>50</td>
<td>69.4</td>
<td>69.8</td>
<td>63.4</td>
</tr>
<tr>
<td>75</td>
<td>71.5</td>
<td>72.2</td>
<td>52.5</td>
</tr>
<tr>
<td>100</td>
<td>74.8</td>
<td>75.5</td>
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<tr>
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<td>75.6</td>
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<td>46.3</td>
</tr>
<tr>
<td>150</td>
<td>76.3</td>
<td>77.1</td>
<td>45.4</td>
</tr>
</tbody>
</table>

Plots of log $k_{\text{corr}}$ versus $(1/T)$ for SS (304L) in 0.5 M sulfuric acid existence and nonexistence various doses of Expired levothyroxine drug is display graphically in Fig. 3 the calculated values of $E_a^*$ from are documented in Table 2. It obvious that $E_a^*$ improve with raising doses of Expired levothyroxine drug representative that, the energy barrier for the corrosion reaction raised, also demonstrating that adsorption of Expired levothyroxine molecules on SS (304L) surface is physical. The $(\Delta S^*, \Delta H^*)$ determined from the theory of transition state by applied the next balance [8]:

$$k_{\text{corr}} = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{2.303R} \right) \exp \left( \frac{-\Delta H^*}{RT} \right)$$  \hspace{1cm} (6)

A plot of log ($k_{\text{corr}}/T$) versus $(1/T)$ also gave straight lines as appeared in Fig. 4, for SS (304L) dissolution in 0.5 M of sulfuric acid in the existence and lack of altered doses of Expired levothyroxine drug. Slopes from the shape are used to calculate enthalpy ($(-\Delta H^* / 2.303R)$, and $\Delta S^*$ is calculated utilizing intersections of the lines $[\log(R/Nh) + \Delta S^* / 2.303R]$. The data of these parameters ($\Delta H^*$ and $\Delta S^*$) are verified in Table 2. The measured $\Delta H^*$ reflected endothermic procedure [9]. The $\Delta S^*$ attendance and
lack of Expired levothyroxine drug are large and negative; this indicates that the activated complex in the rate-determining step replaces the dissociation step with the association step [10].

3.1.2. Adsorption isotherms

Expired levothyroxine drug adsorbed on the SS (304L) surface and the data of (θ) for change doses of Expired levothyroxine in 0.5 M sulfuric acid were determined from ML data utilizing the follows equation (1). By utilizing these data and for applying altered adsorption isotherms, Langmuir adsorption isotherm was recognized to be the best explanation of the inhibitor adsorption behavior studied on the surface of SS (304L) Expired levothyroxine drug [11].

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

(7)

Where, C, K_{ads} express on the dose and equilibrium constant of adsorption procedure respectively. Drawing (C) vs. (C/θ) of Expired levothyroxine drug at change temperatures was presented in Fig. 5 The intercept equal to (1/K_{ads}), the adsorption constant give result to the \( \Delta G_{ads}^{o} \) by next:

\[
\Delta G_{ads}^{o} = -RT \ln (55.5 K_{ads})
\]  

(8)

The \( \Delta G_{ads}^{o} \) data at all temperatures are recognized in Table 3. The (\( \Delta H_{ads}^{o} \)) was measure agreeing to the Van't Hoff eqn. [12].

\[
\log K_{ads} = -\Delta H_{ads}^{o}/2.303RT + \text{constant}
\]  

(9)

Plotting (\( \log K_{ads} \)) vs. (1/T) give straight line as displayed in Fig. 6, the slope = (-\( \Delta H_{ads}^{o} \)/2.303R), from this slope; the \( \Delta H_{ads}^{o} \) data was calculated and is recorded in Table 3. Then by applying the next balance:

\[
\Delta G_{ads}^{o} = \Delta H_{ads}^{o} - T\Delta S_{ads}^{o}
\]  

(10)

Table (3) shows the adsorption parameters for the obtained Expired levothyroxine drug.

Figure 5. Langmuir isotherm for Expired levothyroxine adsorption on SS (304L) surface in solution from 0.5 M sulfuric acid at altered temperatures
The data of the table approve the spontaneous adsorption of Expired levothyroxine drug on the SS (304L) surface, through the negative data gotten from $\Delta G^o_{ads}$, whose negative value lowered with higher temperature, which confirms that the adsorbed layer is more stable at little temperatures. The $\Delta G^o_{ads}$ data was around 20 kJ mol$^{-1}$ indicated the attendance of physical adsorption reaction. Fig. (5). Results, we note that the value of enthalpy is negative, which means that adsorption molecules of drug are exothermic. The exothermic procedure can refer to physical or chemical adsorption, but the value governs the kind of adsorption. $\Delta H^o_{ads}$ data less than 40 kJ/mol refer to the physisorption process [13]. The $\Delta S^o_{ads}$ values are positive due to the rise of disorder because desorption of water molecules from the surface of SS (304L) [14].
3.2. Potentiodynamic Polarization (PP) technique

Polarization tests is carrying out in 0.5 M sulfuric medium attendance and lack altered doses of Expired levothyroxine drug at 25°C. The outcome data are collected in Table (4) and drowning in Fig. 7. The corrosion parameters from PP measurements were tabulated in Table (4). It is clear that the cathodic and anodic Tafel slopes ($\beta_c$ & $\beta_a$) have a little shift compared to the blank corrosive medium, means that that Expired levothyroxine drug has the ability to influence both cathodic and anodic reactions by forming a protective film on the SS (304L) surface.

![Figure 7. The PP diagrams for the dissolution of SS (304L) in 0.5 M H$_2$SO$_4$ existence and lack altered doses of Expired levothyroxine drug](image)

**Table 4.** The effect of doses of Expired levothyroxine drug on the $E_{corr}$, $i_{corr}$, Tafel slopes ($\beta_a$& $\beta_c$), % IE, and $\Theta$ for the corrosion of SS (304L) in 0.5 M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>[inh.] ppm</th>
<th>$E_{corr}$, mV (vs.SCE)</th>
<th>$i_{corr}$, $\mu$A cm$^{-2}$</th>
<th>$\beta_c$, mV dec$^{-1}$</th>
<th>$\beta_a$, mV dec$^{-1}$</th>
<th>CR mpy</th>
<th>$\Theta$</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>523</td>
<td>4341</td>
<td>138</td>
<td>96</td>
<td>1985</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>25</td>
<td>489</td>
<td>722</td>
<td>120</td>
<td>62</td>
<td>329</td>
<td>0.834</td>
<td>83.4</td>
</tr>
<tr>
<td>50</td>
<td>483</td>
<td>508</td>
<td>118</td>
<td>59</td>
<td>232</td>
<td>0.883</td>
<td>88.3</td>
</tr>
<tr>
<td>75</td>
<td>486</td>
<td>396</td>
<td>112</td>
<td>65</td>
<td>180</td>
<td>0.909</td>
<td>90.9</td>
</tr>
<tr>
<td>100</td>
<td>488</td>
<td>359</td>
<td>121</td>
<td>72</td>
<td>152</td>
<td>0.917</td>
<td>91.7</td>
</tr>
<tr>
<td>125</td>
<td>512</td>
<td>310</td>
<td>109</td>
<td>62</td>
<td>133</td>
<td>0.929</td>
<td>92.9</td>
</tr>
<tr>
<td>150</td>
<td>516</td>
<td>296</td>
<td>116</td>
<td>71</td>
<td>121</td>
<td>0.932</td>
<td>93.2</td>
</tr>
</tbody>
</table>
The slight change in $\beta_c$ and $\beta_a$ values evidences that no change occurred in the inhibition mechanism in the absence and attendance of the Expired levothyroxine drug [15]. As seen from Table (4) the shift in (E$_{corr}$) value after addition of the Expired levothyroxine drug is less than 85 mV which again proves mixed type inhibition [16]. Table (4) indicates that values of ($i_{corr}$) are lower for inhibited solutions than uninhibited one, and the improving with the rise in the Expired levothyroxine drug concentration, indicating that Expired levothyroxine drug is excellent inhibitor for SS (304L) corrosion in sulfuric acid.

3.3. Electrochemical Impedance Spectroscopy (EIS) tests

Nyquist bends gotten from the SS (304L) at potentials after 30 min dipping in 1.0 M sulfuric acid in the addition and non-addition of different dose of Expired levothyroxine drug. The achieved Nyquist and Bode that are drowning in diagrams for Expired levothyroxine drug are displayed in Fig. 8(a,b). Nyquist diagrams are designated by a semicircle loop. These establish that a charge transfer procedure refers to the dissolution of SS (304L) metal [17]. The matching circuit that define for SS (304L) and electrolyte are establish in Fig. 9. EIS parameters and % IE were obtain and recorded in Table (5). The results gained in the impedance coefficients for SS (304L) in 0.5 M sulfuric acid in the attendance and lack of altered dose of Expired levothyroxine drug. Fig. 8(a,b) shows the region of low frequency, and in the existence of Expired levothyroxine drug, the impedance values rise compared to the absence of the Expired levothyroxine drug, the radius of the circle rises when the concentration of the Expired levothyroxine drug rises and hence, the charge transfer resistance in corrosion reactions increase. From all the above, there is high resistance recognized as the result of adsorption of the Expired levothyroxine drug at the interface SS (304L) /solution [18-20]. The interfacial capacitance $C_{dl}$ data can be estimated from CPE parameter ($Y_0$ and $n$) is defined in next balance:

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

(11)

Where, $Y_0$ is the CPE magnitude, and n is the variance CPE data of the: -1 ie n ie 1. Using equation 11. From Table (5) we note a lower in the values of $C_{dl}$ with an increase in the dose of Expired levothyroxine drug, and this can be explained by a decrease in the local dielectric constant and / or an increase in the thickness of the electrical double layer [21-23]. This due to the adsorption of Expired levothyroxine drug molecule on the SS(304L)/interface of solution and forming of a protective film on the interface of the SS (304L) solution. Table (5) lists the values of parameters like $R_{ct}$, by EIS fitting as well as the derived parameters Cdl and IE %.
Figure 8. The Nyquist (a) and Bode (b) diagram for dissolution of SS (304L) in 0.5 M sulfuric acid solution in in existence and nonexistence altered dose of Expired levothyroxine drug

Figure 9. Simple circuit utilized to fit the EIS outcomes

Table 5. Electrochemical kinetic parameters from EIS technique for corrosion of SS (304L) in 0.5 M \( H_2SO_4 \) without and with various doses of Expired levothyroxine drug

<table>
<thead>
<tr>
<th>[inh] ppm</th>
<th>( \gamma_0 ) (µΩ ( \cdot ) cm(^{-1} \cdot ) cm(^{2} \cdot ) s(^{1/6} ))</th>
<th>( n )</th>
<th>( R_{ct} ) ( \Omega ) cm(^2)</th>
<th>( C_{dl} ) ( \mu F ) cm(^2)</th>
<th>( \Theta )</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>313</td>
<td>0.931</td>
<td>7</td>
<td>198</td>
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<td>--</td>
</tr>
<tr>
<td>25</td>
<td>225</td>
<td>0.914</td>
<td>30</td>
<td>79</td>
<td>0.761</td>
<td>76.1</td>
</tr>
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<td>50</td>
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<td>75</td>
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<td>0.830</td>
<td>83.0</td>
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<td>100</td>
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<td>125</td>
<td>174</td>
<td>0.880</td>
<td>71</td>
<td>32</td>
<td>0.899</td>
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<td>150</td>
<td>168</td>
<td>0.857</td>
<td>87</td>
<td>23</td>
<td>0.917</td>
<td>91.7</td>
</tr>
</tbody>
</table>

3.4. Scanning electron microscopy analysis (SEM)

Fig. 10(a, b, c) refer to the micrograph or the topography that obtain on the SS (304L) specimen with and without 150 ppm of Expired levothyroxine drug after contact for one day submersion. It is very clear that polished SS (304L) surface suffer from huge damage in presence of the corrosive environment (sulfuric acid). This damage decreased in existence of Expired levothyroxine drug. This can be regarded
to formation of passive film through adsorption of the Expired levothyroxine drug on SS (304L) surface blocking the active center [24- 25].

![SEM images](image1)

**Figure 10.** SEM topography for SS (304L) free, existence and nonexistence 150 ppm of Expired levothyroxine drug after dipping for one day

3.5. *Energy Dispersive X-ray analysis (EDX)*

Determination the existence of elements, that adsorbed on SS (304L) surface by EDX spectrum after 1 day dipping in 0.5 M sulfuric with 150 ppm dose of Expired levothyroxine drug. Fig. 11 gives the EDX investigation of SS (304L) in 0.5 M sulfuric medium existence and lack 150 ppm of Expired levothyroxine inhibitor. EDX demonstrates extra lines, displaying the existence of C, N and O (attendance on structure of Expired levothyroxine drug).

![EDX spectra](image2)

**Figure 11.** EDX examination of SS (304L) without and with 150 ppm Expired levothyroxine drug for 1-day immersion
This information exhibits that the C, N and O atoms secured the SS (304L) surface. The C and O elements were measure by EDX study and displayed that protective film including the chemical Expired levothyroxine inhibitor formula adsorbed on the surface of SS (304L) [26].

Table 6. % weight of SS (304L) after one day of immersion with and without 150 ppm of Expired levothyroxine drug in 0.5 M H$_2$SO$_4$

<table>
<thead>
<tr>
<th>(Mass %)</th>
<th>Fe</th>
<th>Mn</th>
<th>C</th>
<th>O</th>
<th>Cr</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SS (304L)</td>
<td>66.72</td>
<td>1.10</td>
<td>9.81</td>
<td>----</td>
<td>16.58</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>Blank (0.5M H$_2$SO$_4$)</td>
<td>59.54</td>
<td>1.02</td>
<td>10.07</td>
<td>2.79</td>
<td>16.16</td>
<td>0.91</td>
<td>----</td>
</tr>
<tr>
<td>Expired levothyroxine drug</td>
<td>53.87</td>
<td>0.76</td>
<td>9.43</td>
<td>3.84</td>
<td>12.99</td>
<td>----</td>
<td>6.03</td>
</tr>
</tbody>
</table>

3.6. Atomic force microscopy analysis (AFM)

From AFM analysis, it can be gained regarding the roughness on the surface [27-28]. The roughness shape data play a significant role in recognizing and report the efficiency of the inhibitor under study. The surface roughness of SS (304L) immersed in 0.5M H$_2$SO$_4$ in absence and presence of 150 ppm of Expired levothyroxine drug has evaluated by AFM. Fig. 12 (a) show polished SS (304L) where, (b) SS (304L) in 0.5M H$_2$SO$_4$ and (c) SS (304L) in 0.5M H$_2$SO$_4$ with 150 ppm Expired levothyroxine drug. The area and line roughness are recorded in Table (7). The roughness increased in attendance of destructive environment (H$_2$SO$_4$) because of the corrosion reaction but in the attendance of the Expired levothyroxine drug the roughness was decreased due to the adsorption of Expired levothyroxine drug on SS (304L)surface forming protective layer, indicating that the metal surface (SS (304L)) was became more smoothly and the corrosion rate was reduced.

![AFM images](image-url)
Figure 12. (a) 3D AFM image of SS (304L) free surface (b) 3D AFM image of SS (304L) after dipping in 0.5 M sulfuric acid for 24 h (c) 3D AFM after 15 h dipping 0.5 M sulfuric acid +150 ppm Expired levothyroxine drug.

Table 7. AFM parameters for SS (304L) in 0.5 M sulfuric acid absence and presence of 150 ppm of Expired levothyroxine drug.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Polished SS (304L)</th>
<th>SS (304L) in 0.5 M H₂SO₄</th>
<th>SS (304L) in 0.5 M H₂SO₄+150 ppm levothyroxine drug</th>
</tr>
</thead>
<tbody>
<tr>
<td>The roughness average (Sa)</td>
<td>18</td>
<td>260</td>
<td>65</td>
</tr>
<tr>
<td>The mean value (Sm)</td>
<td>-10</td>
<td>-17</td>
<td>-12</td>
</tr>
<tr>
<td>The root mean square (Sq)</td>
<td>24</td>
<td>2150</td>
<td>115</td>
</tr>
<tr>
<td>The valley depth (Sv)</td>
<td>-83</td>
<td>-540</td>
<td>-423</td>
</tr>
<tr>
<td>The peak height (Sp)</td>
<td>152</td>
<td>1322</td>
<td>211</td>
</tr>
<tr>
<td>The peak-valley height (Sy)</td>
<td>245</td>
<td>1992</td>
<td>640</td>
</tr>
</tbody>
</table>

3.7. Fourier transforms infrared spectroscopy (FT-IR)

The FT-IR spectrophotometer is an operational apparatus engaged for recognizing the function groups that attendance in the Expired levothyroxine drug and the type of interaction that occur among function group and SS (304L) surface [29]. Spectra of Expired levothyroxine drug and SS (304L) surface after soaking in 0.5 M sulfuric acid +150 ppm of Expired levothyroxine drug for 3 hours at 25°C is existing in Fig. 13. It is obviously clear that all bands of Expired levothyroxine drug observed on SS (304L) surface with low intensity and small shift. The peaks corresponding to OH stretch at 3360 cm⁻¹ shifted to 3368 cm⁻¹ and the peaks attributed to C-H stretch at 2931 cm⁻¹ shift to 2950 cm⁻¹, and the peaks of C=O stretch at 1740 cm⁻¹ showd shift at 1727 cm⁻¹, and the peaks of C-H bending at 1446 cm⁻¹ showd shift at 1438 cm⁻¹ which cross ponding to methyl group, and the peaks of aromatic C-H bending vibration at 1077 cm⁻¹ showd shift at 1088 cm⁻¹. This means that Expired levothyroxine drug is
completely adsorbed on SS (304L) surface. And the shifted peaks can be assigning to interaction of adsorbed inhibitor molecule with SS (304L) surface.

![FTIR fingerprint spectra](image)

**Figure 13.** FTIR fingerprint spectra of Expired levothyroxine drug stock solution and adsorbed layer of Expired levothyroxine drug on SS (304L) surface.

3.8. Mechanism of corrosion inhibition

All result data prove that the Expired levothyroxine drug under study was inhibiting the dissolution of SS (304L) in 0.5 M sulfuric acid solution as a destructive environment. The results obtained indicate that the corrosion protection was caused by the Expired levothyroxine drug molecule tending to interact and adsorb on the SS (304L) / solution interface. It is known that the adsorption figure depends on several things, the most significant of which are: the chemical composition of the solution, the SS (304L) surface nature, and electrochemical potential at the SS (304L) / solution interface [30-31]. The corrosion protection is due to its physical adsorption of Expired levothyroxine drug molecules on the surface of SS (304L). The effect of Expired levothyroxine drug under study may be corresponding to the accumulation of the inhibitor molecule on the SS (304L), which prevent the direct contact of the SS (304L) surface with destructive environment. Generally, physisorption process needs existence of charged metal surface and charged molecules. At firstly, the anionic acid species were adsorbed on SS (304L) surface making the surface negative, the protonated Expired levothyroxine drug molecule (cationic) can then be adsorbed on the negatively charged SS (304L) surface by an electrostatic attraction. The protonated molecules could adsorb on specimen SS (304L) surface Fig. 14.
Figure 14. The Expired levothyroxine drug in 0.5 M H₂SO₄ solution are absorbed and inhibited corrosion of SS (304L).

The %IE of the expired investigated drug for SS (304L) in 0.5 M H₂SO₄ solution and some of the previously reported drugs are recorded in Table 8. As can be seen in this Table the %IE of the present expired levothyroxine drug is better than those of previously reported drugs.

Table 8. Comparison of corrosion efficiencies obtained for some drugs examined by other authors and in this study.

<table>
<thead>
<tr>
<th>Inhibitor (drug)</th>
<th>Sample</th>
<th>Medium</th>
<th>IE %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cefalexin (11x10⁻⁴M)</td>
<td>Mild steel</td>
<td>HCl</td>
<td>67.5</td>
<td>[32]</td>
</tr>
<tr>
<td>Penicillin V (15x10⁻⁴M)</td>
<td>Mild steel</td>
<td>H₂SO₄</td>
<td>63.3</td>
<td>[33]</td>
</tr>
<tr>
<td>Cefixime (8.8x10⁻⁴M)</td>
<td>Mild steel</td>
<td>HCl</td>
<td>62.0</td>
<td>[34]</td>
</tr>
<tr>
<td>Rhodanine azosulpha (1x10⁻³M)</td>
<td>Stainless Steel 304</td>
<td>HCl</td>
<td>70.1</td>
<td>[35]</td>
</tr>
<tr>
<td>Cefotaxime (1x10⁻³M)</td>
<td>Stainless Steel</td>
<td>H₂SO₄</td>
<td>71.7</td>
<td>[36]</td>
</tr>
<tr>
<td>Amifloxacin (50 ppm)</td>
<td>Mild steel</td>
<td>HCl</td>
<td>17.1</td>
<td>[37]</td>
</tr>
<tr>
<td>Enofloxacin (50 ppm)</td>
<td>Mild steel</td>
<td>HCl</td>
<td>18.3</td>
<td>[37]</td>
</tr>
<tr>
<td>Ceftobiprole (9.31x10⁻⁴M)</td>
<td>Mild steel</td>
<td>HCl</td>
<td>92.2</td>
<td>[38]</td>
</tr>
<tr>
<td>Expired levothyroxine</td>
<td>SS (304L)</td>
<td>H₂SO₄</td>
<td>94.3</td>
<td>This work</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

Inhibition of the dissolution of SS (304L) in 0.5 M sulfuric solution by Expired levothyroxine drug is determine by ML, PP and (EIS) tests. Levothyroxine drug was tested as green corrosion inhibitor for SS (304L) and give the best inhibition efficiency 94.3% at 150 ppm based on ML measurements. The adsorption of Expired levothyroxine drug on SS (304L) surface agreements with Langmuir
isotherm. The values of $\Delta G_{\text{ads}}$ and $\Delta H_{\text{ads}}$ assessed from Langmuir isotherm submit physisorption and exothermic process. Activation parameters were measured and debated. The SEM analysis indicated that a protective film of Expired levothyroxine drug is formed on SS (304L) surface that prevent the corrosion process. The PP data show that levothyroxine drug act as inhibitor of mixed for SS (304L). The electrochemical and non-electrochemical value are in excellent agreement.

References

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