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Corrosion Inhibition Effect of Expired Levothyroxine Drug on Stainless Steel 304L in 0.5 M H_2SO_4 Solution

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The inhibition of Stainless Steel 304L (SS (304L)) in 0.5 M H_2SO_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_2SO_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 H_2SO_4 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.

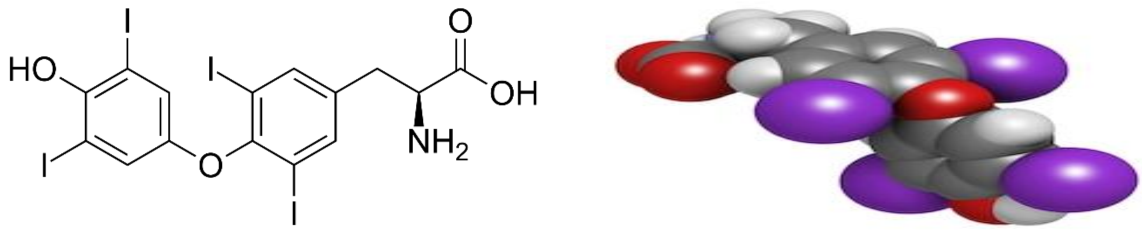
2. MATERIALS AND METHODS

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 $C_{15}H_{11}I_4NO_4$ 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 H_2SO_4) 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 ^{0}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]:

$$IE\% = \theta x100 = [1-(W/W^o)] \text{ x } 100 \qquad (1)$$

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]:

$$\% \text{ IE} = \Theta \text{ x } 100 = [1- (i_{corr(inh)}/ i_{corr(free)}] \text{x } 100 \qquad (2)$$

Where, $i_{corr(free)}$ and $i_{corr(inh)}$ 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]:

$$C_{dl} = 1/(2\pi f_{max}R_p) \qquad (3)$$

Where, f_{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:

$$\% \text{ IE} = \Theta \text{ x } 100 = [1- (R°_{ct}/ R_{ct}] \text{x } 100 \qquad (4)$$

Where, $R°_p$ 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 ^{0}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 π-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.

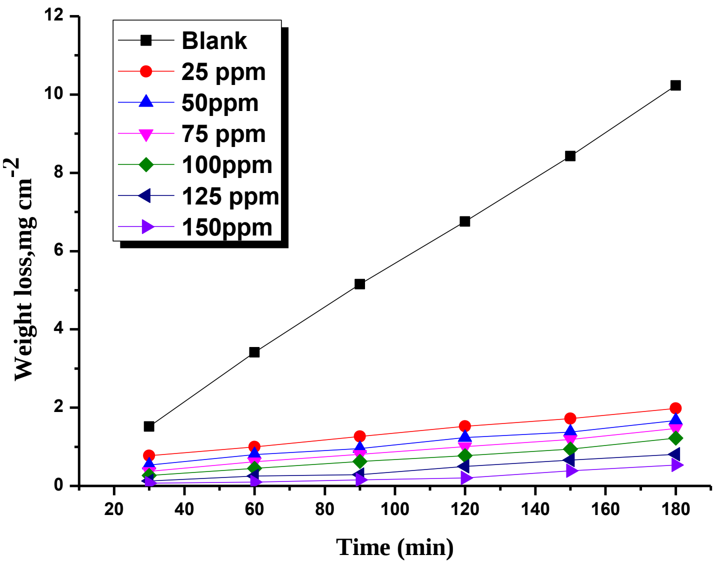


Figure 1. Time- ML bends for dissolution of SS (304L) attendance and lack altered doses Expired levothyroxine drug.

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

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

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.

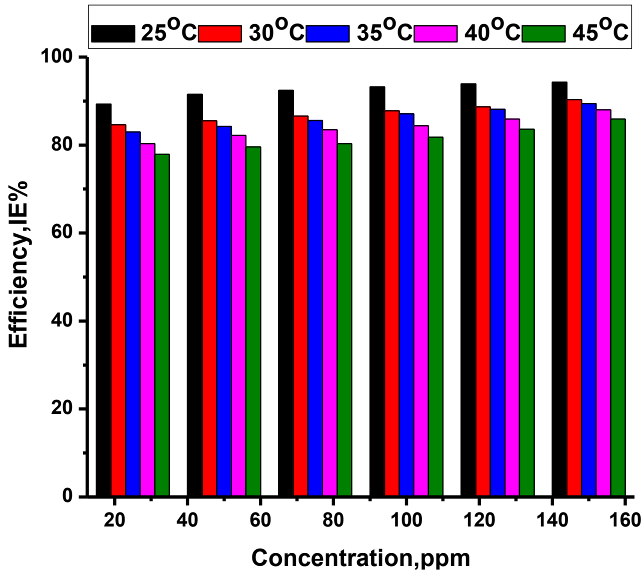


Figure 2. Effect of different concentrations (ppm) on the %IE of expired levothyroxine at altered temperature.

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

k_{corr} = A exp-E^*_a/RT (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.

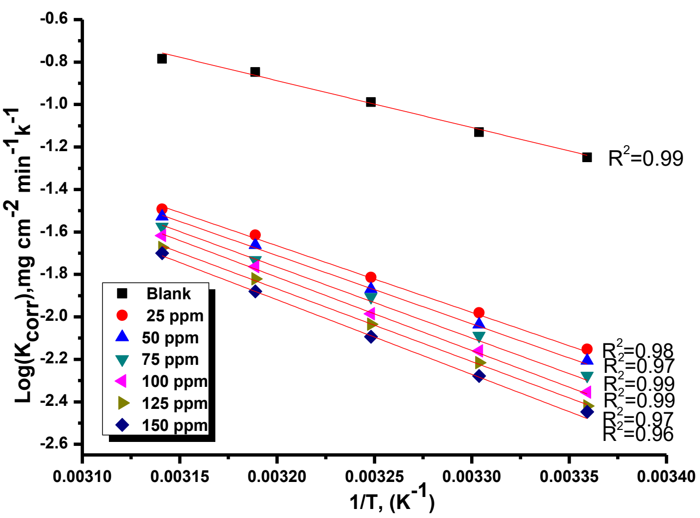


Figure 3. log k_{corr} vs. 1/ T for dissolution of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug

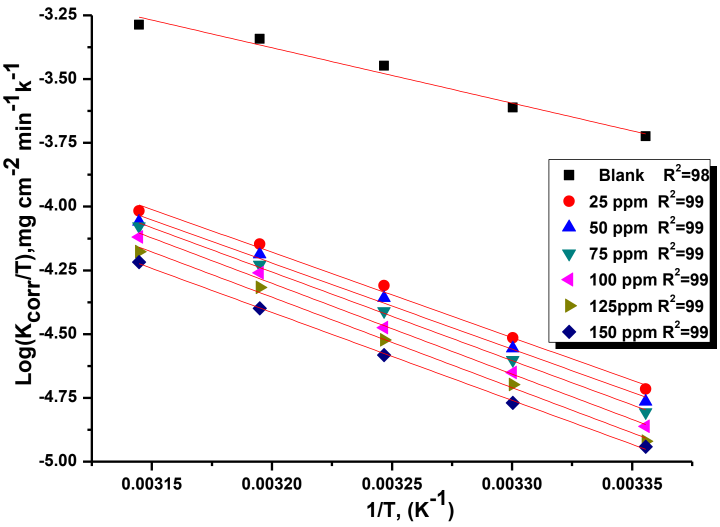


Figure 4. log k_{corr} / T vs. (1/ T) for dissolution of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug

Table 2. E^*_a, ΔH^* and ΔS^*data for liquefaction of SS (304L) in 0.5 M sulfuric acid without and with change of Expired levothyroxine drug

Conc. ppm	E^*_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}
Blank	49.3	46.6	118.2
25	68.2	67.4	66.2
50	69.4	69.8	63.4
75	71.5	72.2	52.5
100	74.8	75.5	48.8
125	75.6	76.2	46.3
150	76.3	77.1	45.4

Plots of log k_{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 (ΔS^*, ΔH^*) determined from the theory of transition state by applied the next balance [8]:

k_{corr} = RT/Nh exp (ΔS^*/R) exp ($-\Delta H^*$/RT) (6)

A plot of log (k_{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 (($-\Delta H^*_a$/2.303R), and $\Delta S^*$is calculated utilizing intersections of the lines [log(R/Nh) +ΔS^*_a/2.303R]. The data of these parameters ($\Delta H^*$and ΔS^*) are verified in Table 2. The measured ΔH^* reflected endothermic procedure [9]. The ΔS^* 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].

$$C/\theta = 1/K_{ads} + C \qquad (7)$$

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 ($1/K_{asd}$), the adsorption constant give result to the ΔG^o_{ads} by next:

$$\Delta G^o_{ads} = -RT \ln (55.5\, K_{ads}) \qquad (8)$$

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

$$\log K_{ads} = -\Delta H^o_{ads}/2.303RT + \text{constant} \qquad (9)$$

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

$$\Delta G^o_{ads} = \Delta H^o_{ads.} - T\Delta S^o_{ads.} \qquad (10)$$

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

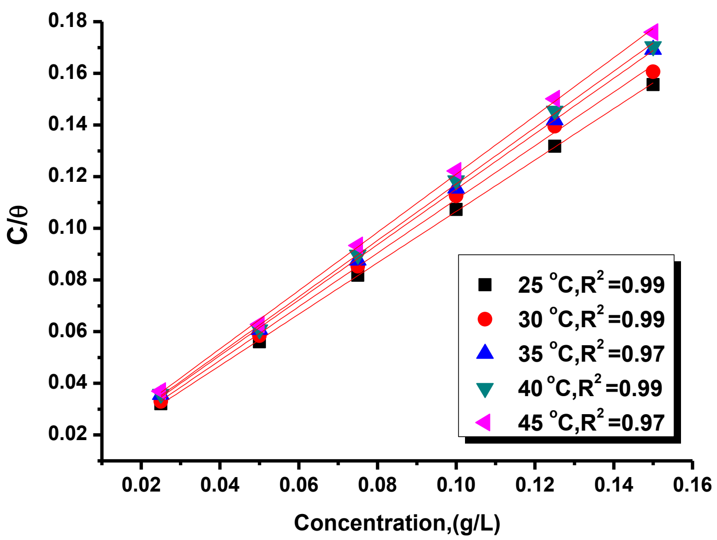


Figure 5. Langmuir isotherm for Expired levothyroxine adsorption on SS (304L) surface in solution from 0.5 M sulfuric acid at altered temperatures

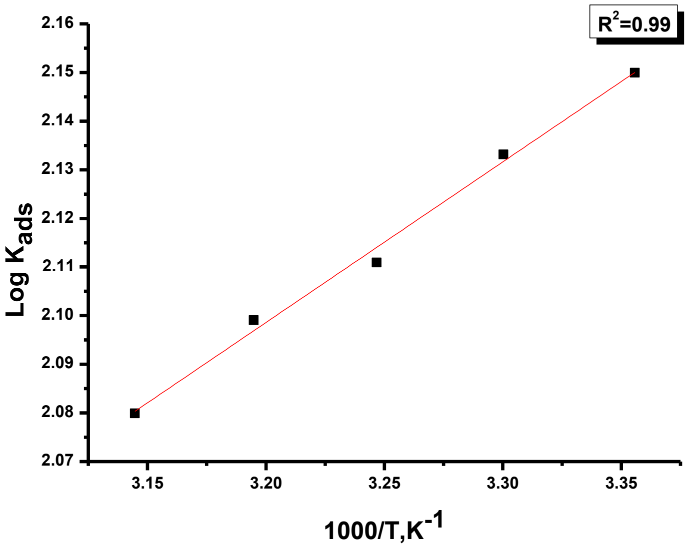


Figure 6. (log K_{ads}) vs. (1000/T) for the dissolution of SS (304L) in 0.5 M H_2SO_4 in the existence of Expired levothyroxine drug at altered temperatures

Table 3. Parameters of Langmuir adsorption of Expired levothyroxine on the SS (304L) surface at change temperatures

Temp. °C	**$-\Delta G^o_{ads}$ kJ mol^{-1}**	**$-\Delta H^o_{ads}$ kJ mol^{-1}**	**ΔS^o_{ads} J mol^{-1}K^{-1}**
25	23.1		77.6
30	22.5		74.4
35	21.3	33	69.1
40	21.1		67.9
45	20.4		64.2

The data of the table approve the spontaneous adsorption of Expired levothyroxine drug on the SS (304L) surface, through the negative data gotten from ΔG^0_{ads}, whose negative value lowered with higher temperature, which confirms that the adsorbed layer is more stable at little temperatures. The ΔG^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. ΔH^o_{ads} data less than 40 kJ/mol refer to the physisorption process [13]. The ΔS^o_{ads} values are positive due to the rise of disorder becease desorption of water molecules from the surface of SS (304L) [14].

3.2. Potiotdynamic 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 (β_c & β_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.

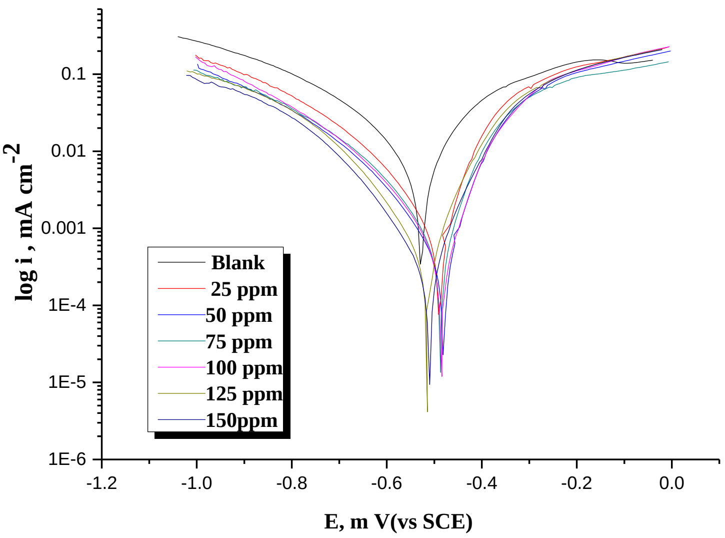


Figure 7. The PP diagrams for the dissolution of SS (304L) in 0.5 M H_2SO_4 existence and lack altered doses of Expired levothyroxine drug

Table 4. The effect of doses of Expired levothyroxine drug on the E_{corr}, i_{corr}, Tafel slopes (β_a& β_c), % IE, and Θ for the corrosion of SS (304L) in 0.5 M H_2SO_4

[inh.] ppm	- E_{corr}, mV (vs.SCE)	i_{corr}, µA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	CR mpy	Θ	% IE
0	523	4341	138	96	1985	----	----
25	489	722	120	62	329	0.834	83.4
50	483	508	118	59	232	0.883	88.3
75	486	396	112	65	180	0.909	90.9
100	488	359	121	72	152	0.917	91.7
125	512	310	109	62	133	0.929	92.9
150	516	296	116	71	121	0.932	93.2

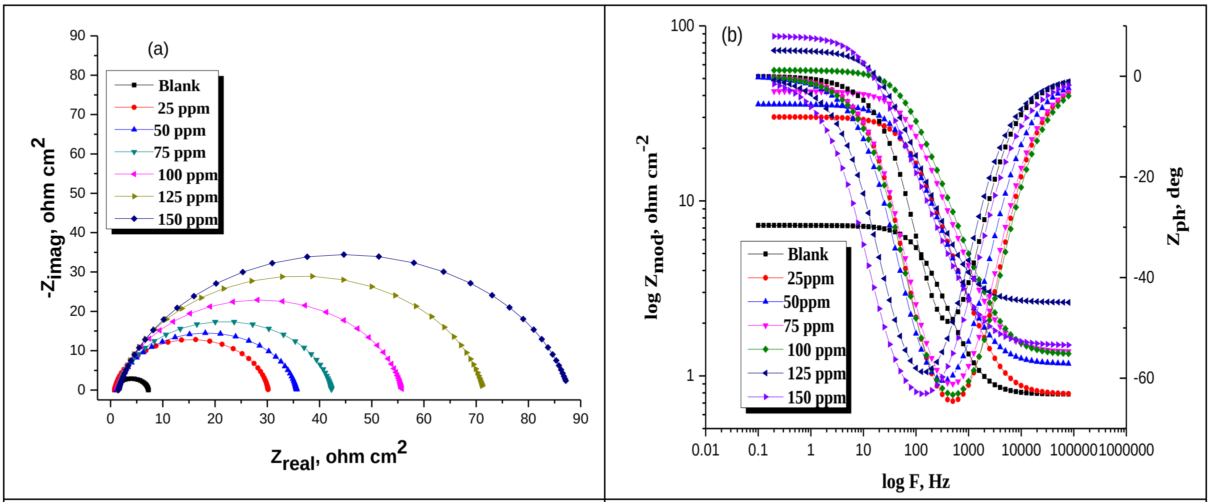
The slight change in β_c and β_c values evidences that no change occurred in the inhibition mechanism in the absence and attendance of the Expired levothyroxine drug [15]. As seen from Table (4) the shift in (E_{corr}) value after addition of the Expired levothyroxine drug is less than 85 mV which again 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 increases. 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:

$$\mathbf{C_{dl} = Y_0\,(\omega_{max})^{n-1}} \qquad (11)$$

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 %.



(a) Nyquist	(b) Bode

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

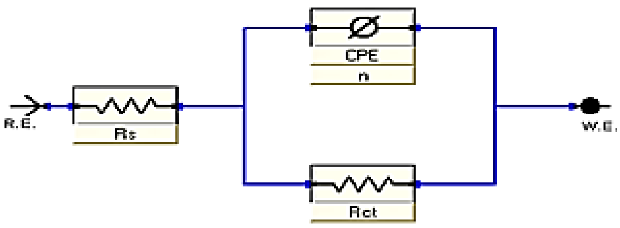


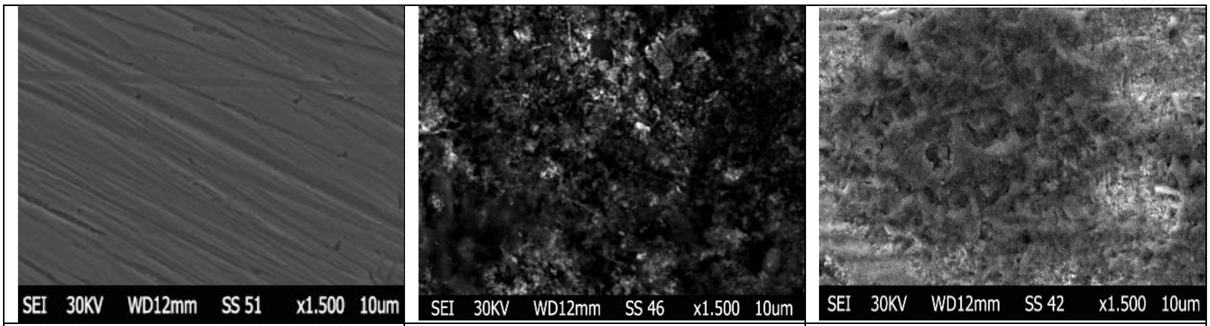
Figure 9. Simple circuit utilized to fit the EIS outcomes

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

[inh] ppm	Y_o, ($\mu\ \Omega^{-1}\ s^n\ cm^{-2}$) x$10^{-6}$	n	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}	Θ	% IE
0.0	313	0.931	7	198	--	--
25	225	0.914	30	79	0.761	76.1
50	210	0.896	36	63	0.798	79.8
75	196	0.890	42	54	0.830	83.0
100	183	0.889	55	47	0.869	86.9
125	174	0.880	71	32	0.899	89.9
150	168	0.857	87	23	0.917	91.7

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].

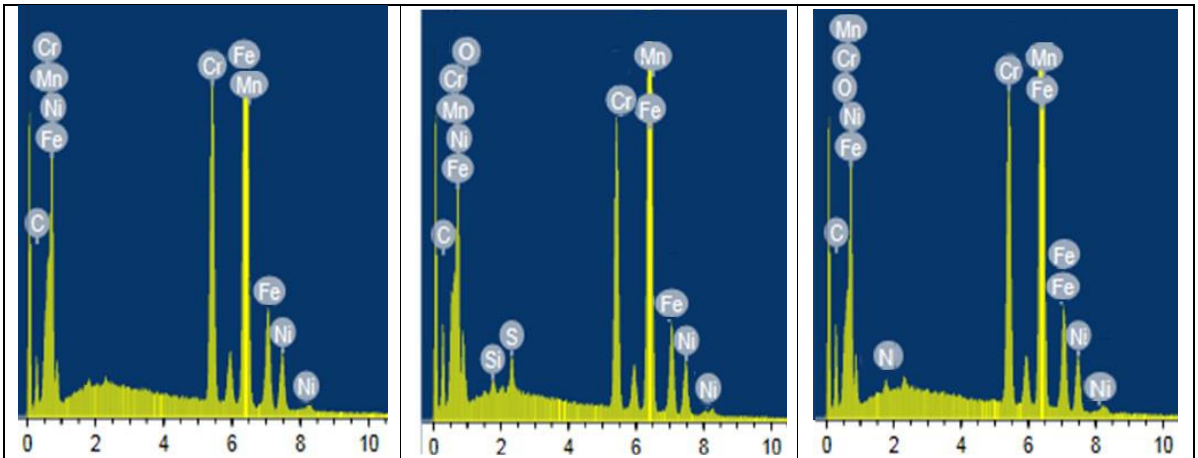


(a) Basic sample	(b) Blank (H_2SO_4 only)	(c) In 0.5 M H_2SO_4 with 150 ppm Expired levothyroxine

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).



SS (304L) only	SS (304L) in 0.5 M HCl (Blank)	In attendance of 150 ppm of Expired levothyroxine drug

Figure 11. EDX examination of SS (304L) without and with 150 ppm Expired levothyroxine drug for 1-day immersion

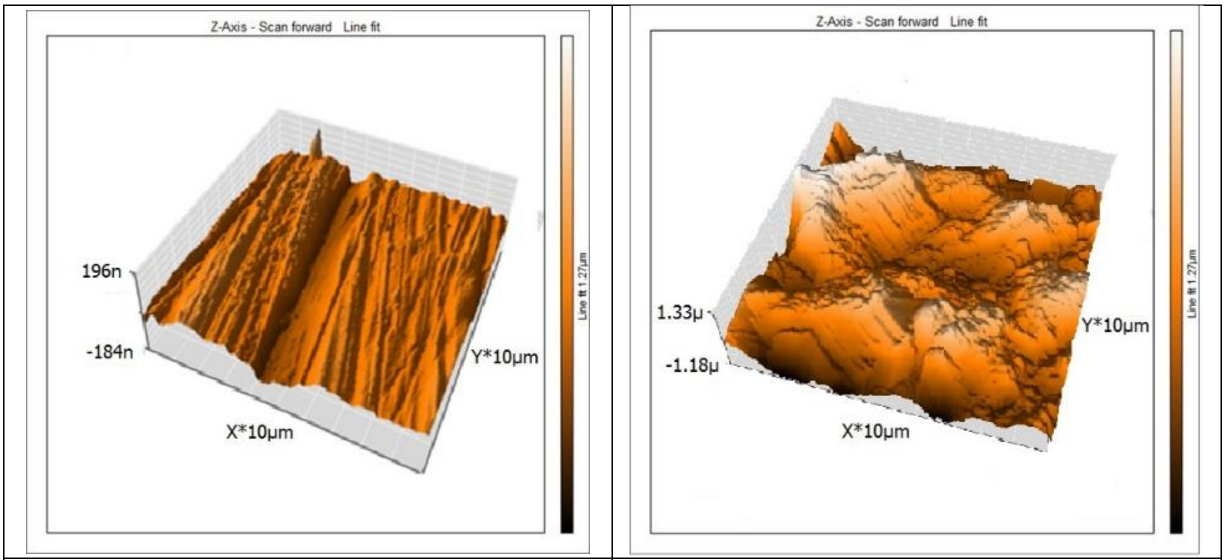
This information exhibits that the C, N and O atoms secured the SS (304L) surface. The C and O elements were measure by EDX study and displayed that protective film including the chemical Expired levothyroxine inhibitor formula adsorbed on the surface of SS (304L) [26].

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_2SO_4

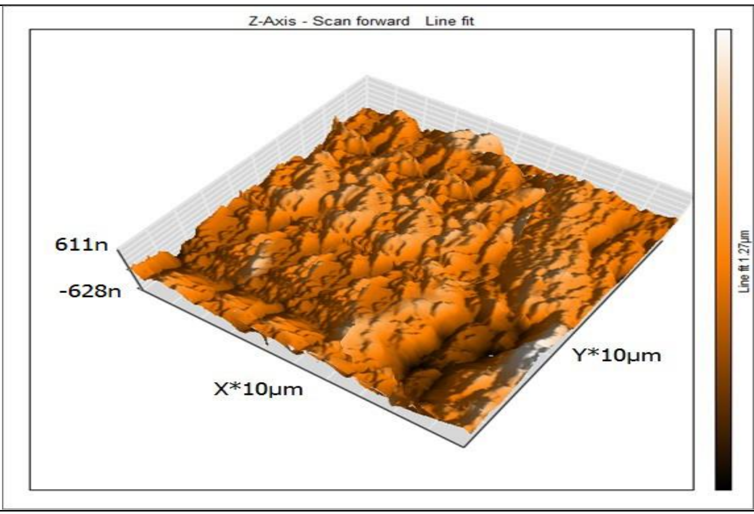
(Mass %)	Fe	Mn	C	O	Cr	S	N
Pure SS (304L)	66.72	1.10	9.81	----	16.58	----	----
Blank (0.5M H_2SO_4)	59.54	1.02	10.07	2.79	16.16	0.91	-----
Expired levothyroxine drug	53.87	0.76	9.43	3.84	12.99	----	6.03

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_2SO_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_2SO_4 and (c) SS (304L) in 0.5M H_2SO_4 with150 ppm Expired levothyroxine drug. The area and line roughness are recorded in Table (7). The roughness increased in attendance of destructive environment (H_2SO_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.



(a) polished SS (304L) | (b) SS (304L) in 0.5M H_2SO_4



(c) SS (304L)+ Expired levothyroxine drug

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 15h 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.

Parameters	Polished SS (304L)	SS (304L) in 0.5 M H_2SO_4	SS (304L) in 0.5 M H_2SO_4+150 ppm levothyroxine drug
The roughness average (Sa)	18	260	65
The mean value (Sm)	-10	-17	-12
The root mean square (Sq)	24	2150	115
The valley depth (Sv)	-83	-540	-423
The peak height (Sp)	152	1322	211
The peak-valley height (Sy)	245	1992	640

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 to3368 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.

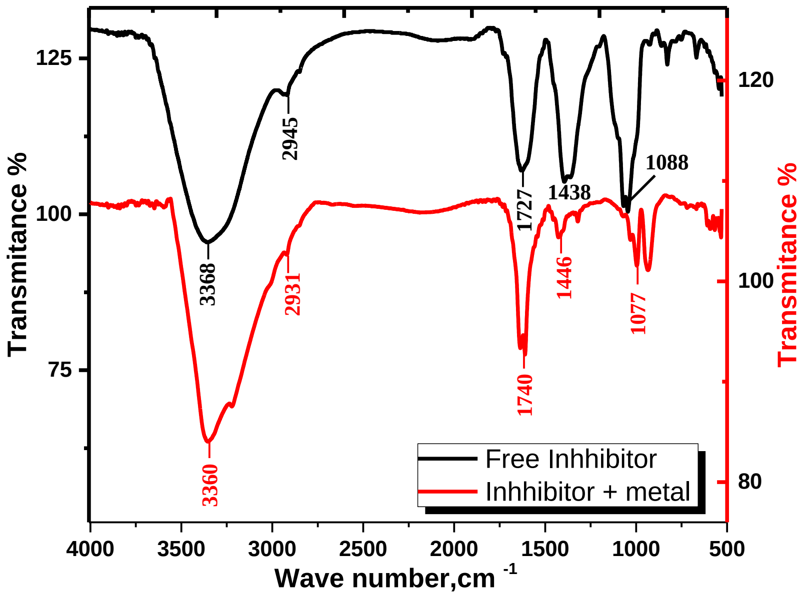


Figure 13. FTIR finger print spectra of Expired levothyroxine drug stock solution and adsorbed layer of Expired levothyroxine drug on SS (304L) surface.

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.

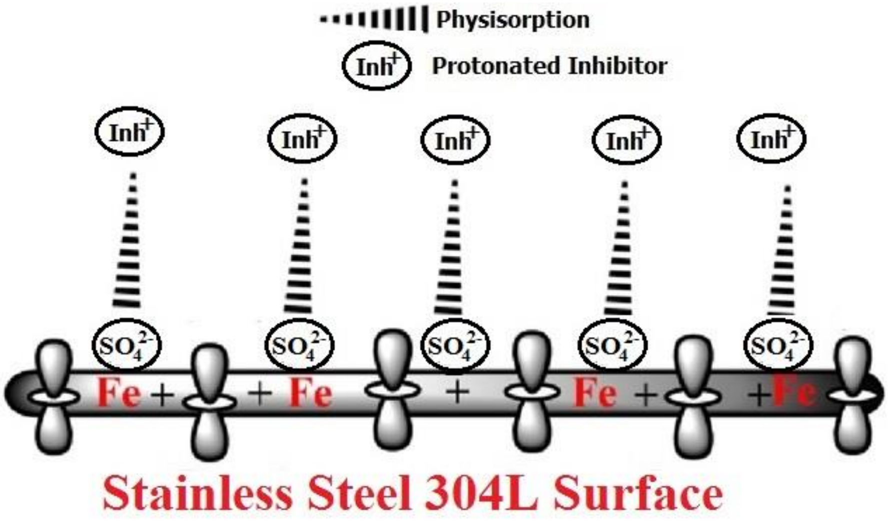


Figure 14. The Expired levothyroxine drug in 0.5 M H_2SO_4 solution are absorbed and inhibited corrosion of SS (304L).

The %IE of the expired investigated drug for SS (304L) in 0.5 M H_2SO_4 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.

Inhibitor (drug)	Sample	Medium	IE %	References
Cefalexin (11x10^{-4}M)	Mild steel	HCl	67.5	[32]
Penicillin V (15x10^{-4}M)	Mild steel	H_2SO_4	63.3	[33]
Cefixime (8.8x10^{-4}M)	Mild steel	HCl	62.0	[34]
Rhodanine azosulpha (1x10^{-3}M)	Stainless Steel 304	HCl	70.1	[35]
Cefotaxime (1x10^{-3}M)	Stainless Steel	H_2SO_4	71.7	[36]
Amifloxacin (50 ppm)	Mild steel	HCl	17.1	[37]
Enofloxacin (50 ppm)	Mild steel	HCl	18.3	[37]
Ceftobiprole (9.31x10^{-4}M)	Mild steel	HCl	92.2	[38]
Expired levothyroxine	SS (304L)	H_2SO_4	94.3	This work

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 ΔG_{ads} and ΔH_{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.

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