# Corrosion Inhibition of Reinforced Steel in 3.5% Sodium Chloride using Expired Pentoxifylline Drug: A Mass Loss Study

**\*Aisha Al-abbasi[1], Zainab Abu Alqasim[2], Fadwa Rahuma[1], Mona Hamel[1]**

[1]Chemistry Department, Faculty of Science/Sabha, Sebha University, Libya
[2]Chemistry Department, College of Education/Ghat, Sebha University, Libya

\* Corresponding author: ais.alabbasi@sebhau.edu.ly
ORCIDs: Aisha Al-Abbasi: https://orcid.org/0000-0002-6082-9246

## Abstract

Corrosion is a major issue affecting the durability and performance of various metallic materials, leading to substantial economic losses and safety hazards. The corrosion of reinforced steel in sodium chloride environment poses a significant concern for various industrial applications. This study aims to investigate the corrosion inhibition properties of expired pentoxifylline drug on reinforced steel in a 3.5% NaCl solution. The mass loss method was utilized to quantify the corrosion rate and assess the efficiency of the expired pentoxifylline drug as a potential corrosion inhibitor. The results indicate that the corrosion rate of steel in the 3.5% NaCl solution decreased significantly in the presence of expired drug. Higher concentrations of expired drugs have shown a greater impact on corrosion inhibition. Investigation of the effects of temperature on corrosion inhibition efficacy. The inhibition efficiency increased with increasing concentrations of the inhibitor and decreased with increasing immersion time. The experimental data were tested according to the Langmuir adsorption isotherm, through which the equilibrium adsorption constant ($K_{ads}$) was calculated and found to

be 4.38 litres mol$^{-1}$ as the maximum value when immersed for one day. The standard free energy of adsorption ($\Delta G_{ads}^o$) ranged from 45 to 30.5 kJ mol$^{-1}$.

**Keywords:** Reinforced steel, sodium chloride medium, inhibition, expired drugs, pentoxifylline

# تثبيط التآكل للصلب المقوى في كلوريد الصوديوم بنسبة 3.5 % باستخدام عقار بنتوكسيفيلين منتهي الصلاحية: دراسة فقدان الكتلة

**عائشة العباسي[1]\*، زينب أبو القاسم[2]، فدوى رحومة[1]، منى هامل[1]**

1قسم الكيمياء، كلية العلوم/سبها، جامعة سبها، ليبيا

2قسم الكيمياء، كلية التربية/غات، جامعة سبها، ليبيا

**الملخص**

يعد التآكل مشكلة رئيسية تؤثر على متانة وأداء المواد المعدنية المختلفة، مما يؤدي إلى خسائر اقتصادية كبيرة ومخاطر تتعلق بالسلامة. يشكل تآكل الفولاذ المقوى في وسط كلوريد الصوديوم مصدر قلق كبير للعديد من التطبيقات الصناعية. تهدف هذه الدراسة إلى دراسة خصائص تثبيط التآكل لدواء البنتوكسيفيلين منتهية الصلاحية على الفولاذ المقوى في محلول كلوريد الصوديوم 3.5%. تم استخدام طريقة فقدان الكتلة لقياس معدل التآكل وتقييم كفاءة دواء البنتوكسيفيلين منتهي الصلاحية كمثبط محتمل للتآكل. تشير النتائج إلى أن معدل تآكل الفولاذ في محلول كلوريد الصوديوم 3.5% انخفض بشكل ملحوظ في وجود دواء البنتوكسيفيلين منتهية الصلاحية. أظهرت التركيزات الأعلى من الأدوية منتهية الصلاحية تأثيرًا أكبر على تثبيط التآكل. زادت كفاءة التثبيط مع زيادة تركيزات المثبط وانخفضت مع زيادة زمن الغمر. تم اختبار البيانات التجريبية وفقًا لمقياس امتزاز لانجمير، والذي من خلاله تم حساب ثابت الامتزاز المتوازن (K$_{ads}$) ووجد أنه 4.38 لتر مول$^{-1}$ كقيمة قصوى عند الغمر لمدة يوم واحد. تراوحت طاقة الادمصاص الحرة القياسية من 45 إلى 30.5 كيلوجول/مول.

**الكلمات المفتاحية:** الفولاذ الصلد، وسط كلوريد الصوديوم، التثبيط، الأدوية منتهية الصلاحية، البنتوكسيفيلين

## 1. Introduction

Corrosion is a complex electrochemical process that promotes the deterioration of metallic structures through electrochemical reactions with the environment (Arya & Joseph, 2021; Siddaiah et al., 2021). Steel is produced from iron by adding a small percentage of other elements, such as carbon, chromium, copper, phosphorous, silicon, and sulfur (Javaherdashti et al., 2016). Steel has many industrial applications and thus making it vulnerable to multiple corrosion attacks. The steel is dissolved by the chemicals surrounding it through a chemical, electrochemical or biochemical reaction on the surface of the metal (Javaherdashti et al., 2016). This causes a severe damage to the structures, resulting in a massive corrosion; thus, we need to protect the steel against corrosion attack (Al-Moubaraki & Obot, 2021). Numerous studies have been conducted to develop the corrosion resistance of steels in various chemical environments, especially in acidic and saline media (Al-abbasi, 2021; Al-Abbasi, 2023; Al-abbasi et al., 2020; AL-abbasi, 2018; Bahrami et al., 2010; Goulart et al., 2012; Khaled & Hackerman, 2003; M. Suliman, A Al-abbasi, A., 2007; M. S. Suliman, Al-abbasi A., 2007; Yadav et al., 2015). The use of corrosion inhibitors is a widely recognized method to mitigate corrosion by altering the electrochemical corrosion process. However, many conventional inhibitors pose environmental concerns or are costly to produce (Al-abbasi & Kassim, 2011; Al-abbasi et al., 2022; Al-abbasi et al., 2010; Al-abbasi et al., 2012). Expired drugs, which are otherwise discarded, could potentially serve as alternative corrosion inhibitors due to their chemical composition and accessibility (Gece, 2011; Raja, 2016). Most drug inhibitors are organic compounds that contain sulfur, oxygen and nitrogen. Drugs have been presented as corrosion inhibitors for toxic organic inhibitors (Baari & Sabandar, 2021; Khalifa, 2018; N. A. Belkher, 2019 ). Medicines have nontoxic, inexpensive, and safe effects on the environment, and they can be manufactured from

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natural products, so it was suggested to replace traditional toxic corrosion inhibitors with medicines (Njoku et al., 2023). Many researchers agree that these drugs are inhibitors that can compete favourably with corrosion inhibitors(Gece, 2011; Karthikeyan, 2016).
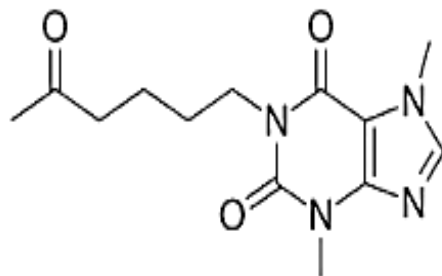


Figure 1: Chemical structure of pentoxifylline

This research aims to investigate the potential of expired pentoxifylline as a corrosion inhibitor for reinforced steel in a 3.5% NaCl solution by the mass loss method, which simulates corrosive conditions in marine environments (L.P. Xuan, 2019). The mass loss method was utilized to quantify the corrosion rate and assess the efficacy of the expired drugs as potential corrosion inhibitors. Pentoxifylline (Fig. 1) has a chemical formula of $C_{13}H_{17}N_4O_3$ and a molecular weight of 277.164 gm/mol. A comprehensive experimental setup was conducted to evaluate the inhibitory effects of expired pentoxifylline on corrosion through corrosion testing. Additionally, the effects of temperature on corrosion inhibition efficacy were investigated.

## 2. Experimental Section
## 1.2 Chemicals and Instrumentation
The chemicals used were all of a high degree of purity and were produced by the well-known companies sodium chloride (BDH Chemicals Ltd.), tin chloride (BDH Chemicals Ltd.), and antimony trioxide (BDH Chemicals Ltd.). The pentoxifylline expired drug 400 ppm (Snofi/Turkey) was obtained from a local pharmacy. digital balance (Kern), water bath (Grant Instruments

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Ltd/Cambridge), and VU-Visible Spectrophotometer (Thermo-Electron Corporation).

## 2.2 Samples

The samples were brought from the Misurata Iron and Steel Factory/in Libya, and they are steel bars consisting of iron with the addition of some elements (C, Si, Mn, P, S) in different proportions according to Table (1). The samples were prepared by cutting reinforcing bars with a diameter of 10 mm into small pieces of approximately 4 cm in length, and they were previously cleaned before immersion in the aforementioned solutions. The surface of the sample was treated with sandpaper (300-1200), washed with distilled water and placed in a desiccator at room temperature until use. The amount of loss was calculated by weight (mg) for each sample by recording the weights after immersion time, as they were cleaned after being removed from the solution by Clark's solution as recommended by ASTM-G1.

**Table 1: The chemical composition of alloy steel**

| Element | Fe | S | P | Mn | Si | C |
| --- | --- | --- | --- | --- | --- | --- |
| the weight% | 98,606 | 0.0004 | 0.011 | 0.57 | 0.23 | 0.30 |

## 2.3 Standard solution preparation

A stock solution of sodium chloride with a concentration of 17.5% (g/L) was prepared. A 3.5% NaCl solution was prepared by dissolving the needed amount of NaCl in deionized water. One litre of a drug solution with a concentration of 400 ppm was prepared by dissolving one tablet (400 mg) in distilled water. A concentration range of 50-200 ppm of pentoxifylline was prepared and used in this study.

## 2.4 Weight loss method for measuring corrosion rate

Sample preparation and immersion corrosion testing were based on ASTM (American Society for Testing and Materials) procedures (ASTM, G1-90 and G31-72). The steel samples were initially cleaned in an acetone solution. This method is summarized by weighing the samples to calculate their corrosion before exposure to the corrosion environment and then exposure

to the corrosion environment for a period of time (Figure 2). Then, some products are taken and removed from the corrosion by some chemical methods and then weighed again, and the difference in weight reflects the weight lost due to corrosion.
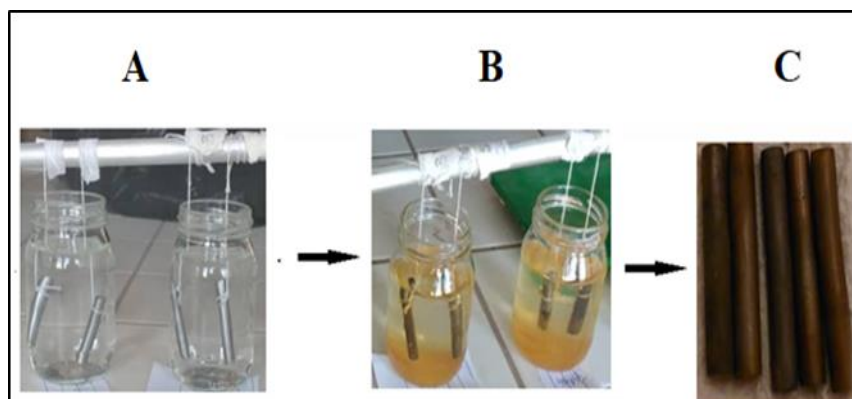


Figure 2: The weight loss method used where (a) the samples were first immersed, (b) before removing the samples from the medium, and (d) after the end of the experiment

A series of experiments are performed using the mass loss method. Steel samples are immersed in a 3.5% NaCl solution containing various concentrations of expired drugs, which serve as corrosion inhibitors. The corrosion rate can be calculated using the following equation:

$$R = \frac{8.76 \times 10^4 W}{AtD} \tag{1}$$

where R = corrosion rate, W = weight lost (g), A = surface area $cm^{-2}$, and t = time (h). The corrosion rates of steel samples in the presence of expired drugs at different concentrations were compared to assess their corrosion inhibition efficacy. The inhibition efficiency was calculated using the following relationship:

$$lnh\% = \left(1 - \frac{R_{lnh}}{R_0}\right) \times 100 \tag{2}$$

where $R_{lnh}$ is the rate of corrosion in the presence of the inhibitor drug and $R_0$ is the rate of corrosion in the absence of the drug.

## 3. Results and discussion

To understand the inhibitory effect of pentoxifylline, the chemical weight loss method at room temperature was applied. The obtained data were collected in Table (2) to evaluate the corrosion inhibition properties of steel in 3.5% NaCl salt media. Moreover, corrosion was measured at different temperatures.

### 1.3 Inhibitory properties of pentoxifylline in 3.5% NaCl

Iron dissolution rates were determined chemically by weight loss at room temperature (30°C). The data obtained for the corrosion rate of steel in 3.5% NaCl solution in the absence and presence of pentoxifylline (PXF) are listed in Table (2). In addition, Figure (3) shows the change in the weight loss of steel as a function of the concentration of the inhibitory drug, as corrosion was recorded in a saline medium of 3.5% NaCl in the absence and presence of different concentrations of pentoxifylline. We notice from Figure (3) that the weight loss increases with increasing time, and in general, the weight loss decreases with increasing inhibitor concentration, and there is a significant decrease in weight when the concentration is increased from 40 to 80 ppm. After that, weight loss is almost consistent when the concentration is raised from 80 to 200 ppm. This could be explained by the adsorbed molecules retching equilibrium, where the quantity of molecules adsorbed and desorbed is equal. The inhibition efficiency values for steel iron in 3.5% sodium chloride media with different concentrations are listed in Table (2).

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**Table 2: Results obtained from studying the effect of pentoxifylline on corrosion of steel**

| Inhibitor conc. (ppm) | ΔW (g) | A (cm²) | t (day) | Temp. | C.R | Inh% |
|---|---|---|---|---|---|---|
| 0 | 0.007 | 8.158976 | 2 | 30 °C | 0.398 | |
| 40 | 0.0031 | 8.031021 | 1 | 30 °C | 0.179 | 55.009 |
| 80 | 0.0023 | 7.327033 | 1 | 30 °C | 0.146 | 63.412 |
| 120 | 0.0016 | 7.539768 | 1 | 30 °C | 0.098 | 75.266 |
| 160 | 0.0015 | 7.885796 | 1 | 30 °C | 0.088 | 77.829 |
| 200 | 0.0015 | 7.7401 | 1 | 30 °C | 0.09 | 77.412 |
| 0 | 0.0107 | 7.975443 | 2 | 30 °C | 0.311 | / |
| 40 | 0.0052 | 7.940432 | 2 | 30 °C | 0.152 | 51.188 |
| 80 | 0.0036 | 7.12152 | 2 | 30 °C | 0.117 | 62.321 |
| 120 | 0.0033 | 7.365027 | 2 | 30 °C | 0.104 | 66.603 |
| 160 | 0.0033 | 7.722987 | 2 | 30 °C | 0.099 | 68.151 |
| 200 | 0.0035 | 8.413944 | 2 | 30 °C | 0.096 | 68.994 |
| 0 | 0.0126 | 7.576192 | 3 | 30 °C | 0.257 | / |
| 40 | 0.0072 | 8.512697 | 3 | 30 °C | 0.131 | 49.144 |
| 80 | 0.005 | 7.866171 | 3 | 30 °C | 0.098 | 61.780 |
| 120 | 0.0046 | 7.940432 | 3 | 30 °C | 0.09 | 65.167 |
| 160 | 0.005 | 8.37752 | 3 | 30 °C | 0.092 | 64.113 |
| 200 | 0.0047 | 7.567871 | 3 | 30 °C | 0.096 | 62.657 |
| 0 | 0.0155 | 7.794579 | 4 | 30 °C | 0.231 | / |
| 40 | 0.0079 | 7.586397 | 4 | 30 °C | 0.121 | 47.634 |
| 80 | 0.0065 | 8.188335 | 4 | 30 °C | 0.092 | 60.081 |
| 120 | 0.0062 | 8.341096 | 4 | 30 °C | 0.086 | 62.621 |
| 160 | 0.0056 | 7.904008 | 4 | 30 °C | 0.082 | 64.371 |
| 200 | 0.0061 | 8.359308 | 4 | 30 °C | 0.085 | 63.304 |
| 0 | 0.0192 | 7.904008 | 5 | 30 °C | 0.225 | / |
| 40 | 0.0097 | 7.92222 | 5 | 30 °C | 0.114 | 49.595 |
| 80 | 0.0083 | 8.158976 | 5 | 30 °C | 0.094 | 58.122 |
| 120 | 0.0078 | 7.867584 | 5 | 30 °C | 0.092 | 59.187 |
| 160 | 0.0073 | 7.776681 | 5 | 30 °C | 0.087 | 61.357 |
| 200 | 0.0075 | 7.758312 | 5 | 30 °C | 0.09 | 60.204 |
| 0 | 0.0216 | 7.864287 | 6 | 30 °C | 0.212 | / |
| 40 | 0.0125 | 7.901339 | 6 | 30 °C | 0.122 | 42.401 |
| 80 | 0.009 | 7.394072 | 6 | 30 °C | 0.094 | 55.684 |
| 120 | 0.0083 | 7.12152 | 6 | 30 °C | 0.090 | 57.566 |
| 160 | 0.0086 | 7.311333 | 6 | 30 °C | 0.091 | 57.174 |
| 200 | 0.0098 | 8.213612 | 6 | 30 °C | 0.092 | 56.54 |
| 0 | 0.0236 | 7.666624 | 7 | 30 °C | 0.204 | / |
| 40 | 0.018 | 8.586801 | 7 | 30 °C | 0.139 | 31.902 |
| 80 | 0.0162 | 8.37752 | 7 | 30 °C | 0.128 | 37.181 |
| 120 | 0.015 | 8.12004 | 7 | 30 °C | 0.122 | 39.99 |
| 160 | 0.0122 | 6.774393 | 7 | 30 °C | 0.119 | 41.497 |

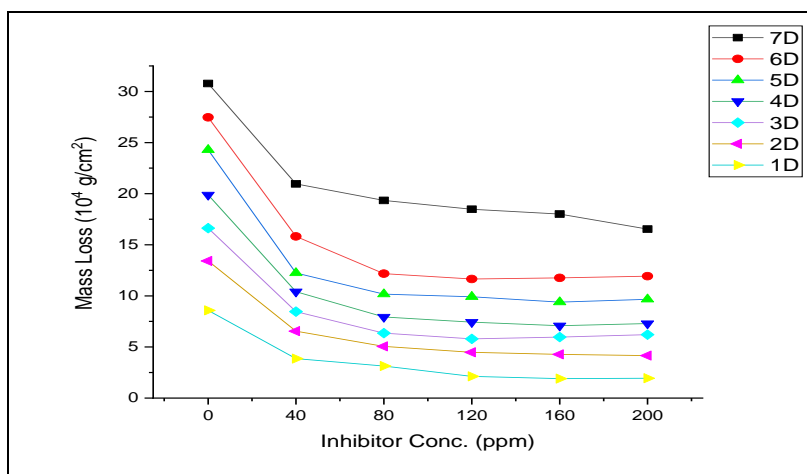| 200 | 0.0128 | 7.7401 | 7 | 30 °C | 0.11 | 46.278 |
|---|---|---|---|---|---|---|
| 160 | 0.002 | 7.886 | 1 | 40 °C | 0.088 | 58.102 |
| 160 | 0.003 | 7.938 | 1 | 50 °C | 0.146 | 47.557 |
| 160 | 0.003 | 7.864 | 1 | 70 °C | 0.183 | 12.157 |



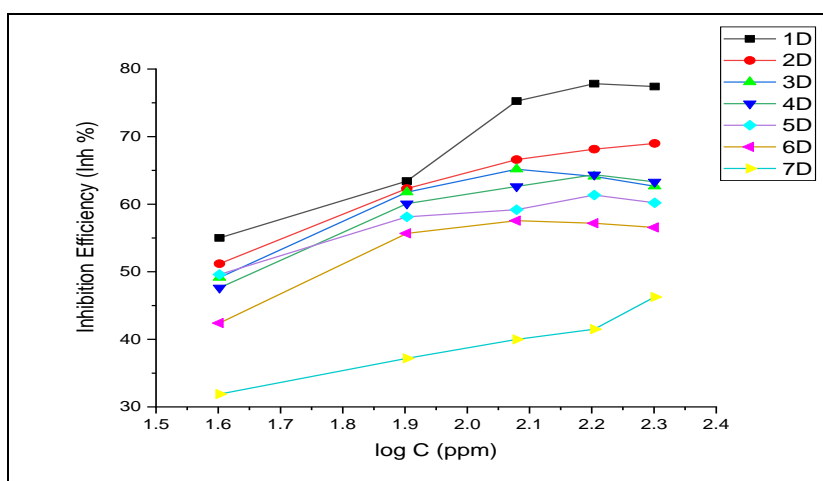Figure 3: Corrosion rate in the absence and presence of pentoxifylline (PXF) at 30°C



Figure 4: Variation in the Inhibition Efficiency (Inh%) of Pentoxifylline for Steel Corrosion in 3.5% NaCl

It is clear that the inhibition efficiency increases with increasing concentrations of inhibitors. From Figure (4) above, we notice that the inhibition efficiency is high when the sample is immersed for one day, but the efficiency decreases with increasing time. We also note that the inhibition efficiency at a concentration of 40 ppm is low, but it increases as the concentration increases, i.e., from 80 to 200 ppm.

## 2.3 Adsorption isotherms

Adsorption is an important step in corrosion inhibition. Four types of adsorption processes can occur: I) electrostatic attraction between a charged metal and charged molecules, II) interaction between the metal surface and unshared electrons in inhibitor molecules, II) electron transport through π-bond electrons or aromatic rings, and IV) a combination of the above mechanisms.

Experimental data of the coverage surface (θ) were fitted to the Langmuir adsorption isotherm to calculate the adsorption constant (K) and the free energy of adsorption. The Langmuir relation for adsorption is given by the following equation:

The adsorption isotherm can be used to calculate the adsorption constant, where

$$\frac{[I]}{\theta} = \frac{1}{k_{ads}} + [I] \tag{3}$$

The equation proposed by Villamil (Villamil et al., 1999) was used, taking into account the attraction between the molecules of the inhibitor as follows:

$$\frac{C}{\theta} = \frac{n}{k_{ads}} + nC \tag{4}$$

where $K_{ads}$ is the adsorption constant, θ is the surface fraction covered by pure iron, and C is the inhibitor concentration. The graph representing the change in the covered part θ in terms of C at different temperatures (303.15, 323.15 & 343.15 K) can be plotted. Where the slope represents the $K_{ads}$ equilibrium constant, and n is a

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constant associated with the attraction between molecules, as shown in Figure (5).
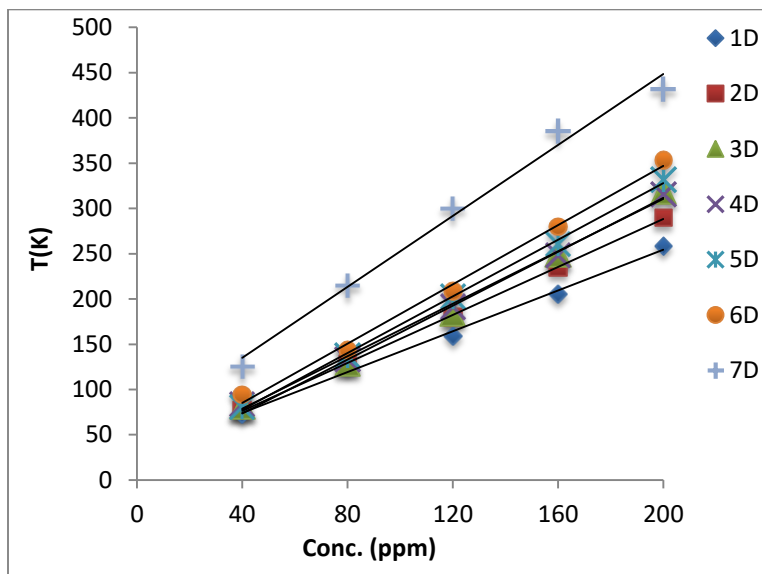


Figure 5: Curve fitted to the Langmuir isotherm

From the intersections of straight lines on the Y axis, Kads values were calculated and are presented in Table (3). We note that the values of $R^2$ ($R^2$ is straight line fit) were higher than 0.99, which indicates the applicability of the results obtained from the Langmuir equation. Positive n values indicate a weak attraction force between the molecules in the solution, while the $K_{ads}$ values are less than the correct one, which indicates that the process of escaping molecules after their adsorption on the surface is the most common, and for this reason, it gave this drug a low efficiency with increasing time. It was noted that the free energy of gypsum for the adsorption process has negative values, which indicates that the adsorption process on the iron surface is spontaneous.

To calculate the number of inhibitor molecules adsorbed from each active site on the surface of pure iron, the thermodynamic adsorption

isotherm was used, which is represented by the following relationship:

$$\log \frac{\theta}{1-\theta} = \log K^{\sim} + y \log C \qquad (5)$$

Where $k^{\sim}$ is the equilibrium constant, $\theta$ is the covered area of the iron surface, C is the concentration of the inhibitor, and y represents the number of inhibitor molecules adsorbed from one active site on the surface of the pure iron.

The free energy of adsorption ($\Delta G_{ads}^{o}$) was also calculated from the equation

$$\Delta G_{ads}^{o} = -R \, ln(55.5 \, K_{ads}) \qquad (6)$$

The constant $K^{\sim}$ can be expressed in terms of $K_{ads}$ using the equation $K_{ads} = (K^{\sim})^{(1/y)}$. All these coefficients have been calculated and placed in Table (4). Plotting the relationship between log ($\theta/(1-\theta)$) against log C will give a slope of a straight line equal to y and an intercept equal to $\log k^{\sim}$ at 303 K, as shown in Figure (6). The straight lines had acceptable correlation coefficients $R^{2}$, as shown in Table (4), indicating the validity of this model for the inhibitor. $1/y$ is the number of surface active sites occupied by one inhibitor molecule. If the values are greater than unity, this indicates that each inhibitor molecule will occupy more than one active site. We note that the values calculated in this study are greater than one and range from 1 to 4, which indicates that each inhibitor molecule occupies from 1 to 4 active sites, as it is in a ratio of 1:1 when immersed for one day and increases until it reaches 4 molecules when immersed for four days. Then, it begins to decrease again to be three active sites for each inhibitor molecule when immersed for seven days.
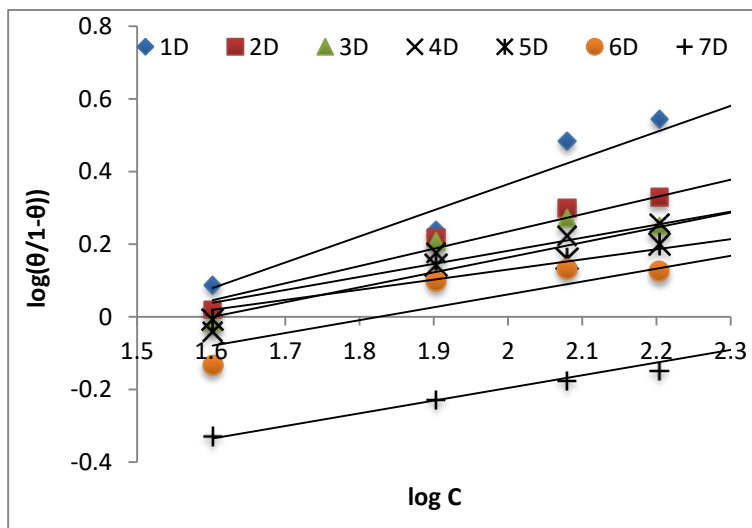
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Figure 6: Curve fitted to the Al-Awady adsorption isotherm

**Table 3: Calculated values of (n, Kads, $\Delta G^*_{ads}$) from the Langmuir equation**

| Time (day) | n | $k_{ads}$ | $\Delta G_{ads}$ KJmol$^{-1}$ | $R^2$ |
|---|---|---|---|---|
| 1 | 1.127 | 0.039 | -6.312 | 0.995 |
| 2 | 1.325 | 0.057 | -9.545 | 0.9996 |
| 3 | 1.489 | 0.106 | -14.725 | 0.994 |
| 4 | 1.448 | 0.069 | -11.211 | 0.997 |
| 5 | 1.566 | 0.105 | -14.638 | 0.999 |
| 6 | 1.637 | 0.084 | -12.757 | 0.995 |
| 7 | 1.96 | 0.035 | -5.448 | 0.989 |

Larger values of $K_{ads}$ mean favourable adsorption and thus better inhibitory activity, i.e., strong interaction between the bilayer present at the super-phase boundary, including the removal of adsorbed molecules from the surface with difficulty, which is consistent with immersion for 1 day since the recorded values were 4; for this, it was found that, a better n efficiency was recorded when immersed for one day.

Negative $\Delta G^*_{ads}$ values greater than 40 kJ/mol indicate that the adsorption process is spontaneous and is characterized as a chemical adsorption process. When comparing the free energy calculated from both the Langmuir equation and the Awadhi equation, it can be said that the adsorption process is physical with weak chemical adsorption.

**Table 4: Calculated values from the Alawadi equation for (y, $K_{ads}$, $\Delta G^*_{ads}$)**

| Time (day) | K | y | $1/y$ | $k_{ads}$ | $\Delta G^*_{ads}$ KJmol$^{-1}$ | $R^2$ |
|---|---|---|---|---|---|---|
| 1 | 0.342 | 0.718 | 1.28 | 4.381 | -45.673 | 0.938 |
| 2 | 0.49 | 0.475 | 2.107 | 1.032 | -33.65 | 0.956 |
| 3 | 0.483 | 0.359 | 2.783 | 1.345 | -35.854 | 0.727 |
| 4 | 0.421 | 0.411 | 2.431 | 1.023 | -33.58 | 0.866 |
| 5 | 0.421 | 0.278 | 3.595 | 1.513 | -36.834 | 0.865 |
| 6 | 0.473 | 0.354 | 2.825 | 1.354 | -35.909 | 0.749 |
| 7 | 0.381 | 0.348 | 2.870 | 1.094 | -34.141 | 0.964 |

## 3.3 Effect of temperature on the inhibition of iron corrosion in sulfuric acid

The effect of temperature on the corrosion rate of pure iron was studied in a medium of 3.5% NaCl in the presence and absence of the inhibitor (160 ppm) at different temperatures (30, 40, 50 and 70°C). All the experimental results were taken after 24 hours of immersion in the prepared solutions, and the results are collected in the corresponding Figure (7). It is clear from the figure that the corrosion is high in the absence of the inhibitor at temperatures 30 and 40, and the corrosion decreases when the temperature is raised to 70 degrees Celsius. The main reason beyond corrosion decreasing when the temperature is raised to 70 degrees is that at higher temperatures, the dissolved oxygen in the water (which is an oxidizing agent) is released from water which causes the corrosion to decrease. However, the corrosion in the presence of the inhibitor is low at a certain temperature, after which the corrosion increases with increasing temperature, i.e., from 40 to 70 degrees Celsius.
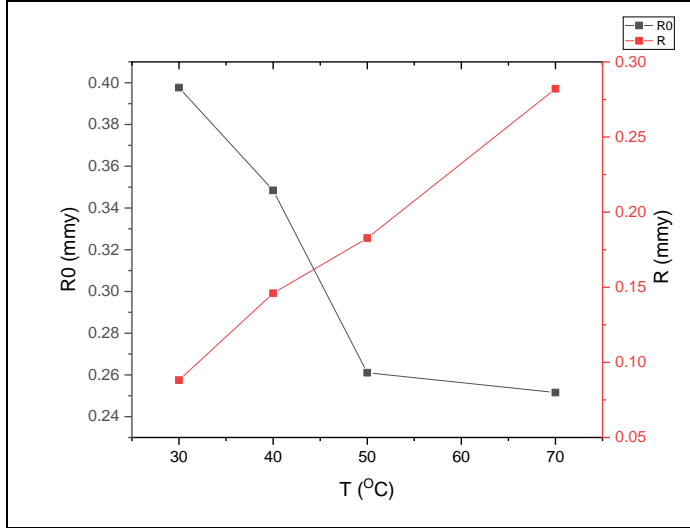
Figure 7: Corrosion rate at different temperatures in the absence and presence of 160 ppm of inhibitor in 3.5% NaCl

The activation energy was determined for the corrosion of iron amid 3.5% sodium chloride using the corrosion rate at different temperatures, namely, 30°C, 40°C, and 70°C, and substituting it into the Arrhenius equation as in Figure (8):

$$k = A \cdot e^{-\Delta E_a^*/RT} \qquad (7)$$

where
$$Slope = \frac{-\Delta E^*}{R}.............(R = 8.314 J/mol.K)$$

Additionally, the activation entropy $\Delta S^*$ and activation enthalpy $\Delta H^*$ were calculated from the transition state equation.

$$K = \left(\frac{RT}{Nh}\right) e^{\Delta S^*/R} e^{-\Delta H^*/RT} \qquad (8)$$

Where N represents Avogadro's number, and h represents the Plank constant.
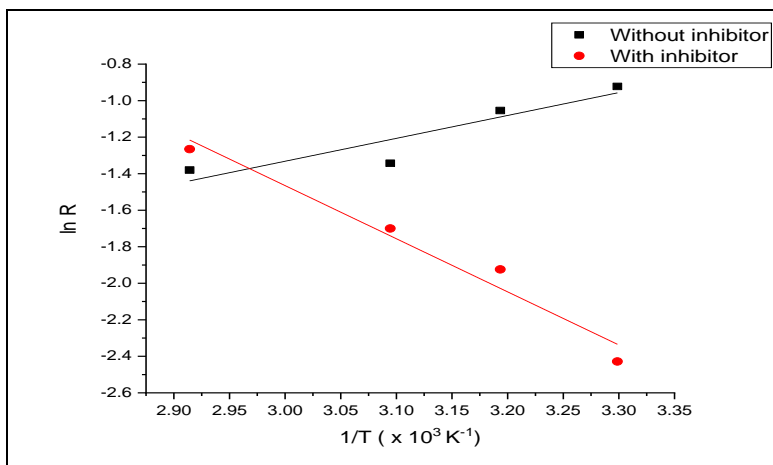
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Figure 8: Arrhenius plot for the activation energy calculation in the absence and presence of the inhibitor
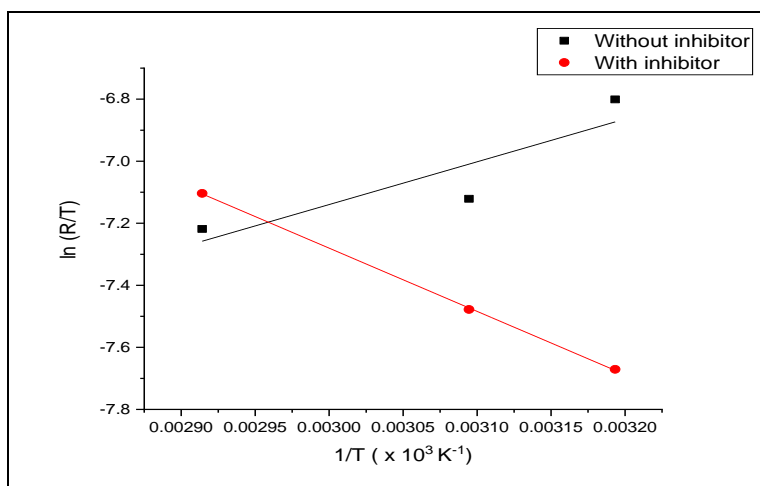


Figure 8: Transition state equation for enthalpy and entropy calculation in the absence and presence of the inhibitor

The thermodynamic activation functions were calculated at different concentrations of the inhibitory drug, as shown in Table (5).

**Table 5: Values of thermodynamic functions for corrosion of steel in 3.5% sodium chloride in the absence and presence of the drug**

| Inhibitors | $\Delta E_a^*$ (KJmol⁻¹) | $\Delta H_a^*$ (KJmol⁻¹) | $\Delta S_a^*$ (Jmol⁻¹ K⁻¹) |
|---|---|---|---|
| 3.5% NaCl | -10.42 | -13.107 | -295,469 |
| 3.5% NaCl +160 ppm | +24,188 | +21,504 | -193,495 |

From Table 5, we notice that the values of both the enthalpy and the activation energy are negative in the absence of the inhibitor, which indicates that the corrosion process is exothermic. In the presence of the inhibitor, we notice that both the enthalpy and the activation energy are positive, which indicates that the inhibition process is endothermic. While the entropy values are negative in the presence and absence of the inhibitor, they are more negative in the absence of the inhibitor, which indicates that the molecules are more random in the presence of the inhibitor compared to the absence of it, and therefore, the inhibitor molecules are more regular on the surface of iron than the sodium chloride molecules.

## 4. Conclusion

This research demonstrates that expired drugs have the potential to act as corrosion inhibitors for steel in 3.5% NaCl solutions. The corrosion rates of steel decrease with increasing concentrations of expired drugs. These findings highlight the possibility of utilizing expired drugs as eco-friendly corrosion inhibitors, contributing to the conservation of resources and cost reduction in industrial applications. Measurements of weight loss showed the following results:

i. In the presence of the inhibitor, the rate of weight loss decreased with increasing inhibitor concentration, while this rate increased with increasing number of immersion days for the tested samples.

ii. The inhibition efficiency increased with increasing concentrations of the inhibitor, reaching an average value of 77% at 160 ppm pentoxifylline. The efficiency decreased with increasing immersion time to the lowest value recorded when the sample was immersed for 7 days.

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iii.    The rate of weight loss in the absence of the inhibitor was found to decrease with increasing temperature due to the formation of a layer of ferrous oxide. In the presence of the inhibitor, it was found that the rate increases with increasing temperature.

iv.    The experimental data of the covered part of the sample were tested according to the Langmuir adsorption isotherm, through which the equilibrium adsorption constant ($K_{ads}$) was calculated and found to be 4.38 litres mol$^{-1}$ as the maximum value when immersed for one day.

v.    The standard free energy of adsorption ($\Delta G_{ads}^{o}$) was obtained and ranged from 45 -30.5 kJ mol$^{-1}$.

**5. Further research focus**: 1. Proposed potential mechanisms of corrosion inhibition by expired drugs based on electrochemical analysis. 2. Characterization of the surface morphology and composition of the inhibited steel samples.

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