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Investigating the Adsorption Mechanism of Expired Esomeprazole as a Corrosion Inhibitor on Carbon Steel in Desalination Water

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ABSTRACT

The impact of expired esomeprazole ($C_{17}H_{19}N_3O_3S$) as an inhibitor on the corrosion behaviour of carbon steel in desalination water was investigated using the weight loss technique. It was discovered that the corrosion rate of the carbon steel specimens decreased with increasing inhibitor concentrations. Based on the results obtained in the Jepril & Bakari (2022) study, isotherm models were utilized to investigate the adsorption mechanism of expired esomeprazole on the surface of carbon steel in the current work. Thermodynamic parameters were also considered. With a correlation coefficient (R^2) better than 0.9, the results showed that the inhibitor's adsorption on the surface followed the Langmuir, Freundlich, Adejo-Ekwenchi, and El-Awady adsorption isotherms. Physisorption was identified as the mechanism of adsorption.

دراسة آلية أمتزاز مثبط التآكل (الأيزوميبرازول المنتهي الصلاحية) على سطح الصلب الكربوني في مياه التحلية

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الكلمات المفتاحية:
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الملخص

تم دراسة تأثير الإيزوميبرازول منتهي الصلاحية (C17-H19-N3-O3S) كمثبط على سلوك تآكل الفولاذ الكربوني في مياه الشرب باستخدام تقنية فقدان الوزن. وقد وجدوا أن معدل التآكل لعينات الفولاذ الكربوني ينخفض مع زيادة تركيزات المثبط. بناءً على النتائج التي تم الحصول عليها في دراسة جبريل وبكاري 2022، في هذا البحث تم استخدام نماذج الأيسوثرم لدراسة آلية امتزاز مثبط الأيسوميبرازول منتهي الصلاحية على سطح الفولاذ الكربوني في مياه التحلية. وقد أخذت أيضاً معاملات الديناميكا الحرارية. أظهرت النتائج أن امتزاز المانع على السطح يتبع كلاً من النموذج الأيزوثرمي: لانجميور وفروندليتش وأديجو إكوينشي وكذلك العوضي. تبين أن قيمة معامل الارتباط والذي يحدد مدى إمتزاز المثبط على السطح أعلى من 0.9. وتبين أيضاً أن آلية الأمتزاز تكون فيزيائية.

1.Introduction:

Referring to the study conducted by A. Gebril and I. Bakari in 2022 [1], which evaluated the effect of expired esomeprazole as an inhibitor on the corrosion behavior of carbon steel in desalination water (drinking water), it was found that these carbon steel specimens, in the presence of the inhibitor, demonstrated that as the weight of the inhibitor increased, the rate of weight loss and corrosion decreased. Specifically, when the weight of the inhibitor was 2.0055 g, its maximum weight, the minimum corrosion rate was 0.0046 cm/year, and the maximum efficiency was discovered to be 52.08%. The goal of the inhibitor is to bind either at the cathodic phase or the anodic part of the corrosion process because corrosion can be either cathodic or anodic. This binding reduces, if not entirely prevents, the metal's electrons or protons from reacting with the environment, such as water. Inhibitors frequently cling to the surface of the metal through chemical or physical adsorption to stop or slow down corrosion. Consequently, the ability of an inhibitor to bind to the surface of a metal determines how well it inhibits corrosion. The relationship between the inhibitor and the solution as the mechanism of corrosion inhibition can be represented by the equation below [2]:

$$[\text{Inhibitor}]_{soln} + [nH_2O]_{adsorbed} \rightarrow [\text{Inhibitor}]_{adsorbed} + [nH_2O]_{soln}$$

Organic substances like amino acids, alcohols, and amines are found in organic corrosion inhibitors. These inhibitors function by adhering to the surface of the metal and creating a shield between it and the corrosive environment. Consequently, industrial

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sectors like oil and gas, petrochemicals, and marine applications frequently use organic inhibitors [3]. The type of interaction at play can be determined by examining the adsorption kinetics, the heat of adsorption, and the reversibility and specificity of the bond formed [4].
Physically adsorbed species interact quickly with the electrode due to electrostatic or Van der Waals forces; however, they can be easily removed from the surface, for example, by dipping the metal into an inhibitor-free solution. In contrast, during the chemisorption process, charge sharing or charge transfer happens more slowly and with greater adsorption heat. This type of adsorption affects only a few metals and is only partially reversible [5, 6].
It is evident from a comparison of these qualities that chemisorption, which can range from straightforward adsorption to the construction of actual physical barriers, is often necessary for effective inhibitory action [6, 7]. Many authors have presented a variety of general hypotheses for how inhibitors function, such as an increase in the proton discharge process's overvoltage, which creates the partial cathodic reaction of the corrosion process, an increase in ohmic resistance because a film of an inhibitor is present at the metal-solution interface, or nonspecific adsorption phenomena [4-7].
These concepts have been expanded upon and clarified through research into the connections between molecular structure and inhibitory characteristics. Furthermore, a thorough investigation of the electrochemical behavior of metallic materials in the presence of inhibitors, a more detailed evaluation of the potential dependence of the adsorption phenomena, and a better understanding of the energy parameters involved in the interaction between inhibitors and metallic materials have significantly improved our understanding of the phenomenon [4].
The purpose of this research is to examine the adsorption mechanisms of expired esomeprazole, which was recognized in Ref. [1] as an efficient corrosion inhibitor on carbon steel surfaces. To achieve this, thermodynamic parameters and five different isotherm models (Equations 1–8) were utilized to analyze the adsorption of the aforementioned inhibitor. Notably, Ref. [1] contains detailed information on the samples' dimensions, weight loss experimental method, corrosion rate, and efficiency results.

2. Experimental Work Material

2.1. Carbon Steel

Because it is widely utilized in many buildings, carbon steel was the material employed in this investigation and was acquired from the local market. The chemical composition of this substance is displayed in Table 1, which complies with the requirements of the Muisrata (Libya) steel industry. As shown in Fig. 1, the specimens were cut from bars with a cross-sectional area of 10 mm by 10 mm and a length of roughly 65 mm. They were then thoroughly cleaned and polished using emery sheets (400 and 1200).

Table 1: Chemical Composition of Carbon Steel [1].

Component	C	Si	Mn	S	P	e
Wt. %	0.153	0.046	0.424	0.048	0.012	Balance

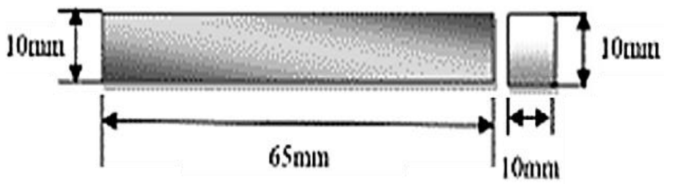

Figure 1: Dimensions of Low Carbon Steel Specimens.

2.2 Esomeprazole Inhibitor

Esomeprazole inhibitor (C17 H19 N3 O3S), molar mass 345.42 g/mol [8] was used as an expired medicine. It is mixed with water in the beakers.
The chemical structure of expired esomeprazole is shown in Fig. 2. [8]
Esomeprazole is a medicine that lowers stomach acid [8]. It is marketed under several trade names, including Nexium (or Neksium) [9]. It is used to treat Zollinger-Ellison syndrome, peptic ulcer disease, and gastroesophageal reflux disease. [10].

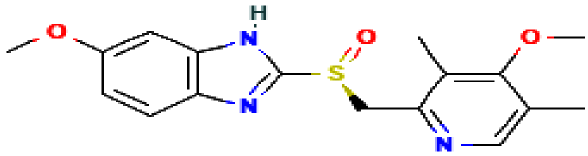

Figure 2: Chemical Structure of Expired Esomeprazole [8].

2.3 Desalination Water

The test solution used in this study was desalination water (drinking water) samples, and a number of 600-ml beakers were used and filled with water. Table 2 shows the chemical analysis of the used desalination water done at the laboratories of the Faculty of Science, Sebha University, Libya.

Table 2: Analysis of Desalination Water [1].

	Parameter	Desalination Water
1	pH	008.77
2	Conductivity (µs/cm)	103.70
3	Salinity (ppt)	000.10
4	TDS (mg/L)	051.00
5	Total Alkalinity (mg/L)	025.00
6	Hardness Ca^{++} (mg/L)	022.00
7	Hardness Mg^{++} (mg/L)	013.00
8	SO4 (mg/L)	000.50
9	K^{+} (mg/L)	009.50
10	Na^{+} (mg/L)	025.00
11	Cl^{-} (mg/L)	003.90
12	Total Hardness (mg/L)	038.00

3. Results and Discussion

According to the research results of Jepril and Bakari, (2022) [1],

Table 3 presents the findings of the corrosion tests conducted on carbon steel specimens in desalination water. Using several adsorption isotherm models (equations 1–8), these findings have been used to analyze the adsorption of the Expired Esomeprazole inhibitor on the samples of carbon steel surfaces.

3.1. Thermodynamic Parameters of Adsorption of Expired Esomeprazole in Aqueous Medium

To grasp the inhibitive mechanism, one must grasp thermodynamic parameters. The following equation was used to determine the free energy of adsorption, which can describe the interaction between adsorbed molecules and metal surfaces [11]:

$$\Delta G°_{ads} = -\,R\,T\,\ln\left(55.5 \times K_{ads}\right). \qquad (1)$$

Where K_{ads} is the adsorption equilibrium constant, R² is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature in Kelvin, and the value of 55.5 is the concentration of water in solution expressed in mol/L [12]. The free energy of adsorption is related to the equilibrium constant K_{ads} of adsorption, which can be calculated using the equation:

$$K_{ads} = \frac{\left(\frac{\theta}{1-\theta}\right)}{I_{inh}}. \qquad (2)$$

In Table 4, a thermodynamic parameter for the adsorption of expired esomeprazole in water is provided. The stability of the absorbed layer on the electrode surface is ensured by the negative value of. In general, values up to -20 KJ/mol are constant with the electrostatic interaction between charged molecules and charged metal (physisorption), whereas negative values higher than - 40 KJ/mol involve the sharing or transfer of electrons from the inhibitors to the metal surface to form a co-ordinate type of bond (Chemisorption) [11].
Based on the experimental data presented in Table 4, the calculated value of $\Delta G°_{ads}$ was found to be negative and less than 40 kJ/mol. The values for expired esomeprazole extract are in the range of -6.526405 kJ/mol to -8.508811 kJ/mol. This indicates that phytoconstituents are adsorbed on the metal surface by a physical adsorption process. The relatively high and negative free energy value indicates strong and spontaneous adsorption of the expired esomeprazole components on the metal surface, which explains its potential corrosion IE. Thus, the mechanism to be proposed for the expired esomeprazole inhibitor system is most probably based on

physical adsorption. In general, the presence of heteroatoms in inhibitor molecules, such as nitrogen (N), oxygen (O), and sulfur (S) atoms with a lone pair of electrons, can increase the adsorption, causing the inhibitor molecules to form insoluble stable films and reducing metal dissolution [11].

3.2. Adsorption Isotherm Models

The inhibitor adsorption is influenced by their structural makeup, and it is believed that is closely related to the electrochemical reaction taking place on the metal surface [11, 13]. The process of an organic compound in the aqueous phase $Org_{(aq)}$ adsorbing inhibitor molecules to the electrode surface can be thought of as a quasi-substitution between the water molecules and the organic compound.

$$Org_{(sol)} + XH_2O_{(aq)} = Org_{(aq)} + H_2O_{(sol)}. \quad (3)\ [13]$$

Where X is the number of the number of water molecules in the inhibitor, the kind, quantity, charge density, molecule size, interactions between the inhibitor and the metal, and formation of metallic complexes are all factors that influence how effective the inhibition is.

Table 3: Data Related to Ref. [1].

Sample No.	Weight Before Immersion (g)	Weight After Immersion (g)	Weight Loss (W) (g)	Area (cm²)	Corrosion Rate (cm/year)	Inhibitor (Concentration) (I_{inh}) (g)	Efficiency of Inhibitor (IE) (%)
1	34.4200	34.2800	0.1400	19.9238	0.0088	0.2500	08.30
2	34.8095	34.6777	0.1813	20.1178	0.0082	0.5000	14.60
3	34.8930	34.7650	0.1280	20.4232	0.0079	0.7509	17.70
4	34.9711	34.8462	0.1249	20.7368	0.0076	1.0077	20.80
5	34.7919	34.6894	0.1023	20.7200	0.0062	1.2538	35.40
6	34.6666	34.5700	0.0966	21.2400	0.0057	1.5000	40.60
7	34.7571	34.6682	0.0889	20.2664	0.0055	1.7541	42.70
8	34.6813	34.6062	0.0751	20.3448	0.0046	2.0055	52.80
9	34.2367	34.0789	0.1578	20.6192	0.0096	0.0000	-
10	34.3039	34.1618	0.1421	20.0704	0.0089	0.0000	-
11	34.9062	33.7603	0.1459	20.8744	0.0092	0.0000	-
12	34.3799	34.2279	0.1520	20.1488	0.0095	0.0000	-

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions; the most frequently used are those of Langmuir, Temkin, Frumkin, Frendlich, Adejo Ekwenchi, and El-Awady. All these isotherms are of the general form:

$$f(\theta, x)\ \exp(-2a\ \theta) = K_{ads}\ I_{inh} \quad (4)\ [13]$$

Where f (θ, x) is the configuration factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm, θ is the degree of the surface coverage, is the inhibitor concentration in the electrolyte, x is the size ratio indicating the number of water molecules displaced by one molecule of organic inhibitor, (a) is the molecular interaction parameter, and (K) is the equilibrium constant for the adsorption. Corrosion is generally assumed to be prevented through the development and maintenance of a protective coating on the metal surface [13]. To calculate the surface coverage θ, it was assumed that the inhibitor efficiency is due mainly to the blocking effect of the adsorbed species, and hence IE% = 100 [13]. To calculate the surface coverage θ, it was assumed that the inhibitor efficiency is due mainly to the blocking effect of the adsorbed species, and hence IE% = 100 [13].

To gain insight into the process of inhibitor adsorption on the carbon steel surface, the surface coverage numbers were theoretically fitted into a variety of adsorption isotherms. The correlation coefficient (R^2) values were then used to determine which isotherm was the best fit [14].

3.2.1. Langmuir Adsorption Isotherm

The Langmuir isotherm compares and measures the adsorptive capacities of various adsorbents and defines gas-solid phase adsorption [14]. The link between a material's inhibitory concentration and surface coverage is described by the Langmuir isotherm, which is expressed as follows:

$$\frac{I_{inh}}{\theta} = \frac{1}{K_{ads}} + I_{inh}. \quad (5)\ [15]$$

Plotting log against log gave a linear relationship, as shown in Figure 3. The parameters of the Langmuir isotherm are presented in Table 4. The R^2 value of 0.9219 indicated a strong adherence to the Langmuir adsorption isotherm [15]. The use of the Langmuir isotherm to study the adsorption of expired esomeprazole on the surface of mild steel revealed that the adsorbate and adsorbent interact well [16].

Table 4: Adsorption Parameters for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

Sample No.	Surface Coverage (θ)	$\frac{\theta}{1-\theta}$	Adsorption Constant (K_{ads}) (g^{-1})	Adsorption Energy ($\Delta G°_{ads}$) (kJ/mol)
1	0.08300	0.090512	0.362048	- 7.437460
2	0.14600	0.170960	0.341920	- 7.295672
3	0.17700	0.215067	0.286412	- 6.85656
4	0.20800	0.252626	0.250696	- 6.526405
5	0.35400	0.547988	0.437062	- 7.904217
6	0.40600	0.683502	0.455668	- 8.007558
7	0.42700	0.745201	0.424834	- 7.833877
8	0.52800	1.118644	0.557788	- 8.508811

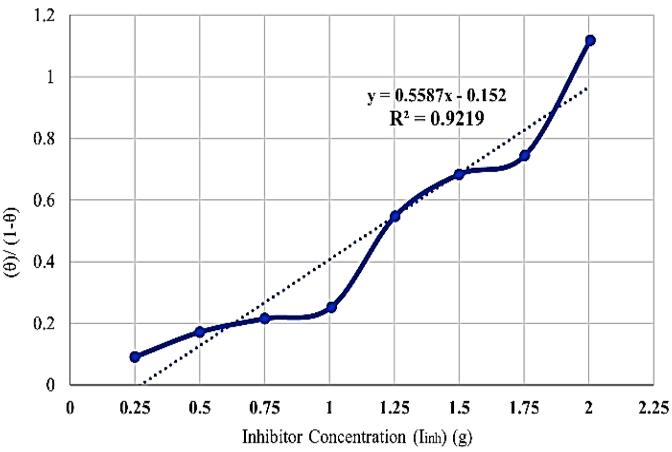

Figure 3: Langmuir Isotherm for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

3.2.2. Temkin Adsorption Isotherm

For the Temkin adsorption isotherm, the degree of surface coverage (θ) is related to inhibitor concentration (I_{inh}) as per equation [17-19]:

$$Exp.\ (-2\ a\ \theta) = K_{ads}\ I_{inh} \quad (6)\ [19]$$

Plots of (θ) against log (I_{inh}), as presented in Figure (2). The R^2 value is 0.9629. Since the value of R^2 0.9 indicates that the experimental data is not well fitted into the Temkin adsorption isotherm [20, 21], The Temkin model is more obeying as compared with the Langmuir isotherm.

Table 5: Freundlich Parameters for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

Sample No.	Logarithm Surface Coverage (θ) log (θ)	Logarithm Inhibitor (Concentration) log (I_{inh}) (g)
1	- 1.080922	- 0.602060
2	- 0.835647	- 0.301030
3	- 0.752027	- 0.124418
4	- 0.681937	0.003331
5	- 0.450997	0.098228
6	- 0.391474	0.176091
7	- 0.369572	0.244054
8	- 0.277366	0.302222

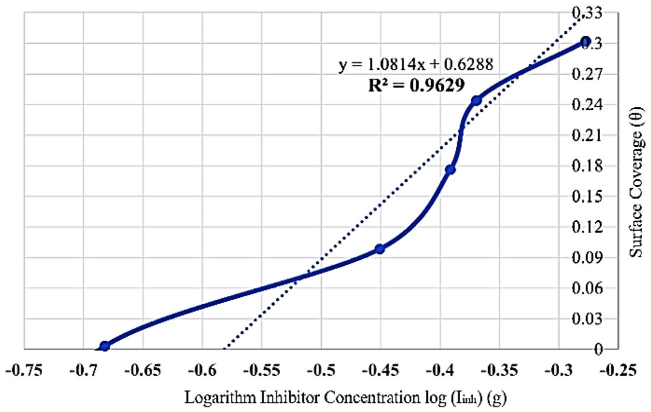

Figure 4: Temkin Isotherm for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

3.2.3. Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm model has been chosen thirdly to evaluate the adsorption potential of the absorbent solution. The Freundlich isotherm is given by the equation [22]:

$$\log \theta + \log K_{ads} + n \log I_{inh} \qquad (7)\ [22]$$

Where n is the interaction parameter. The parameters of the Freundlich isotherm are shown in Table 6. A plot of log θ vs. log (I_{inh}) is shown in Figure (5), which gives a linear relation with R^2 value of 0.9629, which indicates that the adsorption of expired esomeprazole on the carbon steel surface obeys the Freundlich isotherm model.

Table 6: Freundlich Parameters for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

Sample No.	Logarithm Surface Coverage (θ) log (θ)	Logarithm Inhibitor Concentration (I_{inh}) (g)
1	- 1.080922	- 0.602060
2	- 0.835647	- 0.301030
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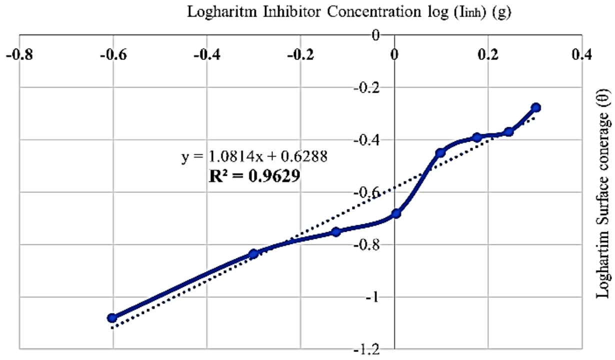

Figure 5: Freundlich Isotherm for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

3.2.4. Adejo Ekwenchi Adsorption Isotherm

The Adejo Ekwenchi isotherm establishes an inverse relationship between the amount of adsorbate uptake from the bulk concentration and the difference between the total amount of surface area on the adsorbent surface and the fraction that is covered by the adsorbate at a specific temperature, prior to reaching the maximum value of surface cover [23]. It is given by the equation:

$$\log (1/1-\theta) = \log K_{ads} + b \log I_{inh}. \qquad (8)\ [23]$$

Where the b parameter is used to determine the mode of adsorption of an inhibitor on the metal surface. The parameters of the Adejo Ekwenchi isotherm are shown in Table 7. A plot of log (1/1- θ) vs. log (I_{inh}) as shown in Figure (6) gives a linear relation with R^2 value of 0.9417, which indicates that the adsorption of expired esomeprazole on the carbon steel surface obeys the Adejo Ekwenchi isotherm model.

Table 7: Adejo Ekwenchi Parameters for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

Sample No.	$\frac{1}{1-\theta}$	$\log(\frac{1}{1-\theta})$	Logarithm Inhibitor Concentration (I_{inh}) (g)
1	0.480556	- 0.318256	- 0.602060
2	0.544767	- 0.263789	- 0.301030
3	0.570767	- 0.243541	- 0.124418
4	0.594552	- 0.225810	0.003331
5	0.689181	- 0.161667	0.098228
6	0.718662	- 0.143475	0.176091
7	0.730155	- 0.136585	0.244054
8	0.782861	- 0.106315	0.302222

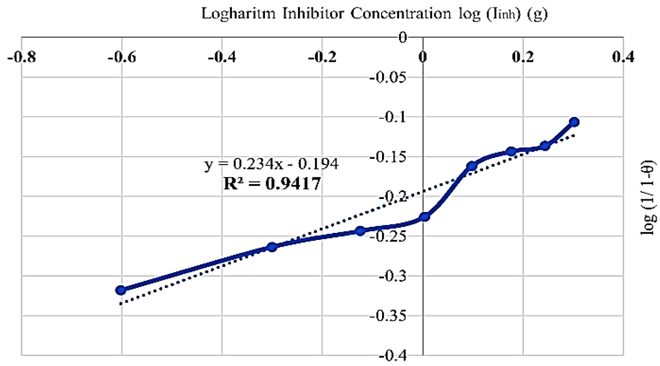

Figure 6: Adejo Ekwenchi Isotherm for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

3.2.5. El-Awady Adsorption Isotherm

The experimental data were fitted into the El-Awady isotherm model. The characteristic of the model is expressed by the equation [24]:

$$\text{Log}\ (\theta /1-\theta) = \log K_{ads} + y \log I_{inh}. \qquad (9)\ [24]$$

Where, y represents the number of active sites. Table 7 presents the El-Awady isotherm's parameters. A plot of log (θ /1- θ) vs. log (I_{inh}), as on Figure (6), yields a linear relation with an R^2 value of 0.9321, indicating that the isotherm is following the El-Awady isotherm model for the adsorption of expired esomeprazole on the surface of carbon steel. Figure 8 shows comparison between the correlation coefficients of the adsorption isotherm models.

Table 8: El-Awady Parameters for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

Sample No.	$\log(\frac{\theta}{1-\theta})$	Logarithm Inhibitor Concentration (I_{inh}) (g)
1	- 1.043294	- 0.602060
2	- 0.767105	- 0.301030
3	- 0.667426	- 0.124418
4	- 0.597522	0.003331
5	- 0.261229	0.098228
6	- 0.165260	0.176091
7	- 0.127726	0.244054
8	0.048691	0.302222

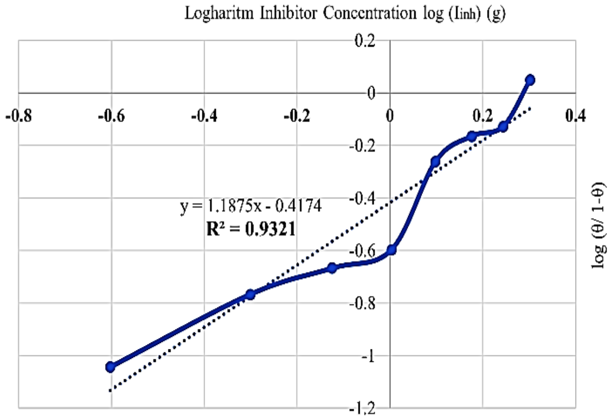

Figure 7: El-Awady Isotherm for Adsorption of Expired Esomeprazole on the Carbon Steel Surface.

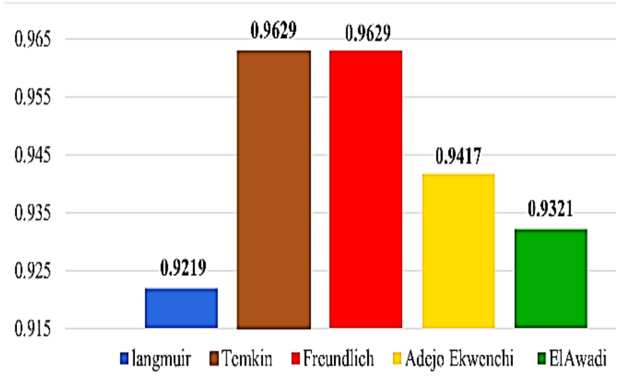

Figure 8: Comparison between the correlation Coefficients of the Adsorption Isotherm Models.

4. Conclusions

This study was conducted in response to a study by Jebril and Bakari (2022), which found that expired esomeprazole can be helpful in slowing down the rate at which carbon steel corrodes in desalinated water. The objective of this work was to determine the extent of inhibitor adsorption on the surface of carbon steel, assessed using a variety of adsorption isotherm models including Freundlich, Langmuir, Temkin, Adejo Ekwenchi, and El-Awady. Additionally, thermodynamic parameters such as adsorption energy and adsorption constant were considered to better understand the adsorption mechanism.

The findings from the analysis revealed the following:

1. The obtained correlation coefficients all exceeded 0.9, indicating effective adsorption of the inhibitor on the carbon steel surface. Notably, the Temkin and Freundlich isotherm models exhibited the highest correlation coefficients, with (R^2 = 0.9629).
2. Negative results indicated strong and spontaneous adsorption of the inhibitor on the metal surface, consistent with the physiosorption mechanism of adsorption for the expired esomeprazole inhibitor. Thus, it can be concluded that the expired esomeprazole inhibitors demonstrated good agreement with the experimental outcomes.
3. The findings corroborated the effectiveness of expired esomeprazole inhibitors in preventing carbon steel corrosion in desalinated water, as previously identified by Jebril and Bakari in their 2022 investigation. The strong adsorption of the inhibitor on the carbon steel surface further validated the potential of using expired esomeprazole inhibitor to protect carbon steel materials in desalination water systems.

5. References

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