



Electrochemical and Thermodynamic Study of Septrin and Flagyl as Corrosion Inhibitors for Mild Steel in Acidic Media

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Abstract

Corrosion of mild steel in acidic media is a significant issue in industrial applications, leading to material degradation and increased maintenance costs. This study investigates the corrosion inhibition properties of Septrin (Co-trimoxazole) and Flagyl (Metronidazole) for mild steel in 2 M HCl, with the aim of finding alternative, cost-effective inhibitors. These drugs were selected due to their potential anticorrosion properties, with limited research available on their inhibitory efficiency in acidic environments. The study was conducted over a temperature range of 303 K to 363 K, with inhibitor concentrations varying from 25 g/L to 75 g/L. Both drugs exhibited promising corrosion inhibition, with Flagyl showing superior performance. The adsorption of both inhibitors followed the Langmuir and Freundlich isotherms, indicating a physisorption mechanism. Gibbs free energy calculations confirmed the spontaneity and stability of the adsorption process, with Septrin showing ΔG_{ads} values of -19.13 kJ/mol at 303 K and -22.91 kJ/mol at 363 K, while Flagyl showed -16.46 kJ/mol at 303 K and -19.72 kJ/mol at 363 K. Electrochemical tests revealed that Flagyl reduced the corrosion rate from 149.35 mm/year to 60.02 mm/year at a concentration of 75 g/L, while Septrin reduced it to 78.53 mm/year, resulting in inhibition efficiencies of 59.8% and 47.4%, respectively. Thermodynamic analyses indicated an increase in activation energy in the presence of both inhibitors. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analyses showed that both inhibitors improved the surface conditions of mild steel, with Flagyl being the more effective inhibitor. Future research should focus on evaluating the long-term stability of these inhibitors in corrosive environments.

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1.0 Introduction

Corrosion, a significant challenge in many industrial processes, especially those involving acidic environments, affects applications such as oil well acidizing, acid cleaning, pickling, and descaling [1, 2]. Corrosion of metals, particularly mild steel in acidic environments such as hydrochloric acid (HCl), is a significant challenge in various industrial sectors, including the oil, gas, and chemical industries. Mild steel, valued for its low cost and excellent mechanical properties,

including strength and rigidity, is commonly used in industries for constructing petroleum refineries, petrochemical plant equipment, chemical reactors, heat exchangers, boilers, storage tanks, and oil and gas pipelines [2,4]. However, mild steel is prone to corrosion, particularly in aggressive environments, necessitating the use of corrosion inhibitors [5]. Traditional corrosion inhibitors, such as inorganic compounds are widely used to mitigate this issue. However, many of these inhibitors are expensive, toxic, or environmentally harmful, prompting the search for more sustainable and cost-effective alternatives. Septrin and Flagyl offer a cost effective and a greener alternative to traditional inhibitors like benzotriazole and imidazole derivatives. While commercial inhibitors often achieve higher efficiency, they pose environmental and health risks due to their synthetic nature and toxicity. In contrast, Septrin and Flagyl provide moderate inhibition through electrostatic interactions and π -electron bonding while being biodegradable and eco-friendly. Their non-toxicity makes them a sustainable choice for corrosion control, aligning with the growing demand for green inhibitors.

In recent years, attention has shifted toward utilizing pharmaceutical compounds as corrosion inhibitors, due to their low cost, widespread availability, and biocompatibility [6-9]. While several pharmaceutical agents have shown promise in inhibiting corrosion, the potential of widely used drugs like Septrin (Co-trimoxazole) and Flagyl (Metronidazole) remains underexplored. These drugs are commonly prescribed antibiotics with known antimicrobial properties, but their efficacy as corrosion inhibitors in acidic media, particularly for mild steel, has not been thoroughly studied. This gap in the literature motivated the present study, which aims to evaluate the corrosion inhibition properties of Septrin and Flagyl in 2 M HCl and understand the underlying mechanisms that make these drugs effective in this context. The selection of Septrin and Flagyl for this study is based on their molecular structures, which contain functional groups known for their ability to interact with metal surfaces. Septrin (Co-trimoxazole) consists of a combination of sulfamethoxazole and trimethoprim, both of which have nitrogen and oxygen atoms in their molecular structures, capable of donating electron pairs to the metal surface. These interactions are critical for the adsorption process that leads to the formation of a protective barrier on the metal. Flagyl (Metronidazole), on the other hand, contains a nitroimidazole ring, which is rich in nitrogen and oxygen atoms that can similarly interact with the surface of mild steel. The presence of these functional groups enhances the drug's ability to adsorb onto the metal surface and reduce corrosion rates by disrupting the electrochemical reactions that occur in acidic environments.

Recent studies have used Density Functional Theory (DFT) and Molecular Dynamics (MD) simulations to understand the adsorption behavior of drug-based corrosion inhibitors. While this study did not conduct such simulations, existing research supports the experimental findings. Asefi et al. [48] showed that Metronidazole (Flagyl) strongly adsorbs onto mild steel due to charge transfer via nitrogen and oxygen atoms. Similarly, Adejoro et al. [49] confirmed through MD simulations that sulfamethoxazole (a component of Septrin) interacts with the steel surface via van der Waals forces and coordinate bonding. These findings align with the observed superior inhibition efficiency of Flagyl over Septrin. Future studies incorporating molecular modeling could further validate the adsorption mechanisms.

This study addresses the need for alternative corrosion inhibitors by investigating the effectiveness of Septrin and Flagyl in mitigating corrosion of mild steel in 2 M HCl. The research fills an important gap in the literature by exploring the potential of these pharmaceutical compounds as corrosion inhibitors and providing insights into how their molecular structures contribute to their inhibitory action. Understanding the corrosion inhibition mechanism and the thermodynamic and electrochemical behavior of these drugs can pave the way for their potential industrial applications, offering a more sustainable and cost-effective solution to corrosion problems. The Molecular structure is illustrated in Figure 1.

2. Materials and Methods

2.1. Materials and preparations

Septrin (C₂₄H₂₉N₇O₆S, molecular weight 543.6) and Flagyl (C₆H₉N₃O₃, molecular weight 171.15) were obtained from Unique Pharmaceutical Ltd. Ikeja Lagos State, Nigeria and Vinco Pharmaceutical Nigeria Ltd Sango-Ota Ogun State, Nigeria respectively. A commercially available grade of mild steel, A36Cr, containing 0.03% P, 0.01% Mn, 0.26% C, 0.03% S, 0.3% Cr, 0.4% Si, with the remainder being iron, was purchased locally and mechanically press-cut into coupons with dimensions of 2 cm × 1.5 cm × 0.3 cm, giving a total surface area of 8.05 cm². A small 5 mm diameter hole near the upper edge of each coupon was made to facilitate suspension in the corrosive medium. The exposed surface of the steel plates was abraded with sandpaper to remove any scale, oxide layers, and surface contaminants. Following this, the plates were thoroughly washed with double-distilled water to eliminate dust and rinsed with ethanol to remove grease. The mild steel plates were then dipped in acetone and stored in desiccators to protect them from moisture. For electrochemical tests, the working electrode (WE) was the mild steel coupon, providing an exposed surface area of 8.05 cm². The reference electrode used was silver/silver chloride (Ag/AgCl), and the counter electrode was also designed to provide an exposed surface area of 8.05 cm². The test solution was prepared by diluting 7% HCl (analytical reagent grade) to achieve a 2 M HCl solution using double-distilled water.

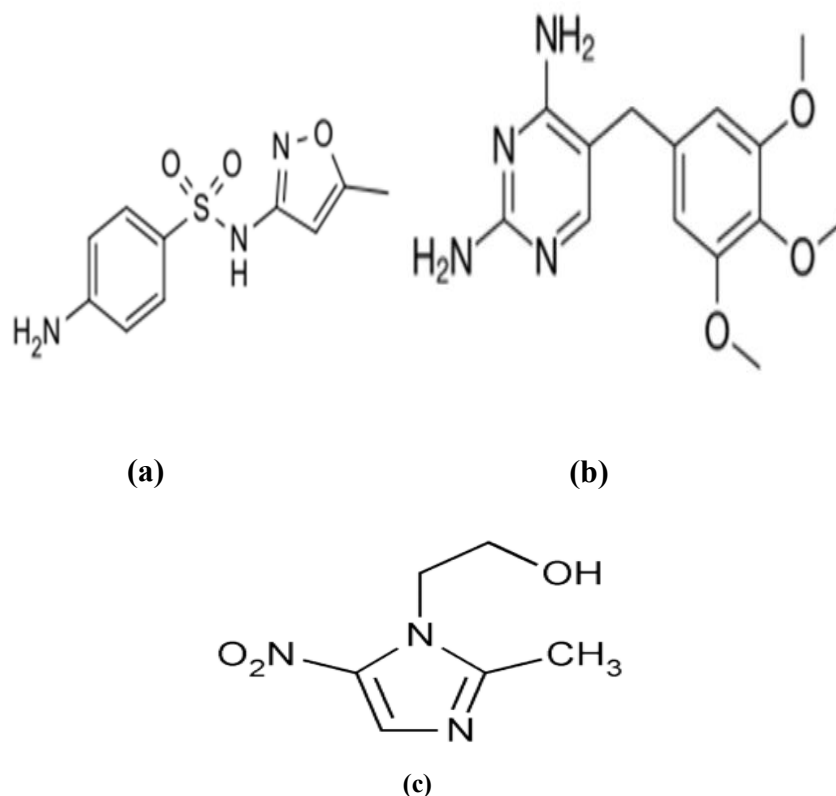


Fig.1. Molecular structure (a) sulfamethoxazole (b) Trimethoprim (c) metronidazole (1-Hydroxyethyl-2-methyl-5-nitroimidazole; CAS: 443-48-1)

2.0 Methods

The study utilized a range of methods, including electrochemical measurement, adsorption modeling, and thermodynamic evaluation. Characterization techniques were also employed, such as Fourier Transform Infrared (FTIR) spectroscopy, Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDX). These methods were integral to investigating the corrosion inhibition efficiency and providing insights into the interaction mechanisms at both the surface and molecular levels.

2.1 Electrochemical Measurements

Electrochemical measurements were carried out using a standard three-electrode cell setup, where the working electrode was a mild steel specimen (Fe) with dimensions of 2 cm x 2 cm, polished with a series of emery papers (320 to 1200 grit) and rinsed with distilled water before each measurement. The reference electrode was a saturated Ag/AgCl electrode, and the counter electrode was a platinum (Pt) sheet with an exposed surface area of 1 cm². Prior to the electrochemical tests, the working electrode was immersed in the electrolyte solution (2 M HCl) for 30 minutes to ensure the stabilization of the open-circuit potential (OCP).

Linear Sweep Voltammetry (LSV) was performed over a potential range of -1.5 V to 0.0 V versus the OCP, with a scan rate of 10 mV/s. The measurements were carried out in both the absence and presence of various concentrations (25 g/L, 50 g/L, and 75 g/L) of Septrin (Co-trimoxazole) and Flagyl (Metronidazole) drug inhibitors. The electrochemical tests were conducted at room temperature (303 K), with the solutions maintained in a static condition to simulate typical corrosion environments. No stirring was applied during the tests to avoid the influence of solution movement on the results. The inhibition efficiency was calculated by comparing the corrosion rates in the presence and absence of the inhibitors. The corrosion rate was obtained from the corrosion current density (I_{corr}) values derived from the Tafel extrapolation method. All measurements were repeated three times to ensure the reproducibility of the results. This work follows the procedure of Nnanna and Owate,[14].

$$\text{IE}(\%) = 100 \left(1 - \frac{I_{\text{corr inhibitor}}}{I_{\text{corr uninhibitor}}} \right) \quad (1)$$

$I_{\text{corr inhibitor}}$ and $I_{\text{corr uninhibitor}}$ are corrosion current densities with the presence and absence of inhibitor respectively.

2.2 Fourier transform infrared spectrophotometry (FTIR) Characterization

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the Seprtin and Flagyl drugs over a wavenumber range of 400 to 4000 cm^{-1} . This technique was applied to analyze the molecular structure and identify the functional groups present in these corrosion inhibitors [15][16].

2.3 Surface Characterization

The surface morphology of mild steel specimens was examined before and after exposure to 2 M HCl for 3 hours at room temperature. The specimens were first cleaned with distilled water to remove any residues and dried with a stream of air. The samples were then divided into two groups: one group was exposed to the corrosive solution without inhibitors (blank), while the second group was exposed to the same solution containing 75 g/L concentrations of Seprtin and Flagyl inhibitors. After exposure, the samples were carefully removed, rinsed with distilled water, and dried under ambient conditions. For SEM analysis, the specimens were mounted on aluminum stubs using conductive double-sided carbon tape to ensure proper electrical conductivity. The samples were examined using a JSM-7800F Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX) for elemental analysis. The SEM was operated at an accelerating voltage of 15 kV, with a high resolution of 3.0 nm. The EDX system was used to identify the elemental composition of the mild steel surface before and after exposure to the corrosion media and inhibitors. Both SEM and EDX analyses were performed to evaluate the effect of the inhibitors on the surface morphology and to investigate the elemental composition of the mild steel after exposure to the corrosive solution [17-19]

3.0 Results and Discussion

3.1 FTIR Characterization of the Seprtin and Flagyl drug

The FTIR analysis of Seprtin as a corrosion inhibitor, shown in Figure 2, identifies several functional groups responsible for its adsorption on mild steel, enhancing its inhibitory effectiveness. Key findings include O–H/N–H stretching at 3465.11 cm^{-1} and 3376.18 cm^{-1} , indicating hydroxyl and amine groups that facilitate hydrogen bonding and metal coordination. O–H stretching at 3297.17 cm^{-1} further supports hydroxyl involvement. Aromatic C–H stretching at 3142.92 cm^{-1} suggests π -electron interactions with the metal, while C–H stretching at 2917.46 cm^{-1} denotes hydrophobic alkyl chains. C=N stretching at 1618.41 cm^{-1} and C=C aromatic stretching at 1595.87 cm^{-1} reveal imine and aromatic systems enhancing adsorption through donor-acceptor interactions. N–O asymmetric stretching at 1501.25 cm^{-1} points to nitro groups engaging in electron transfer, and S=O stretching at 1381.67 cm^{-1} confirms sulfonyl groups' coordination with the metal. C–N stretching at 1302.99 cm^{-1} and C–O stretching at 1230.90 cm^{-1} highlight nitrogen- and oxygen-containing groups strengthening adsorption. C–O–C asymmetric stretching at 1188.21 cm^{-1} indicates ether groups contributing through lone pairs on oxygen. The out-of-plane aromatic C–H bending at 926.20 cm^{-1} and low-frequency peak at 572.92 cm^{-1} support aromatic π - π interactions and metal-sulfur bonding, respectively, while the metal-ligand bonding at 415.51 cm^{-1} confirms stable coordination with the steel surface [20,21].

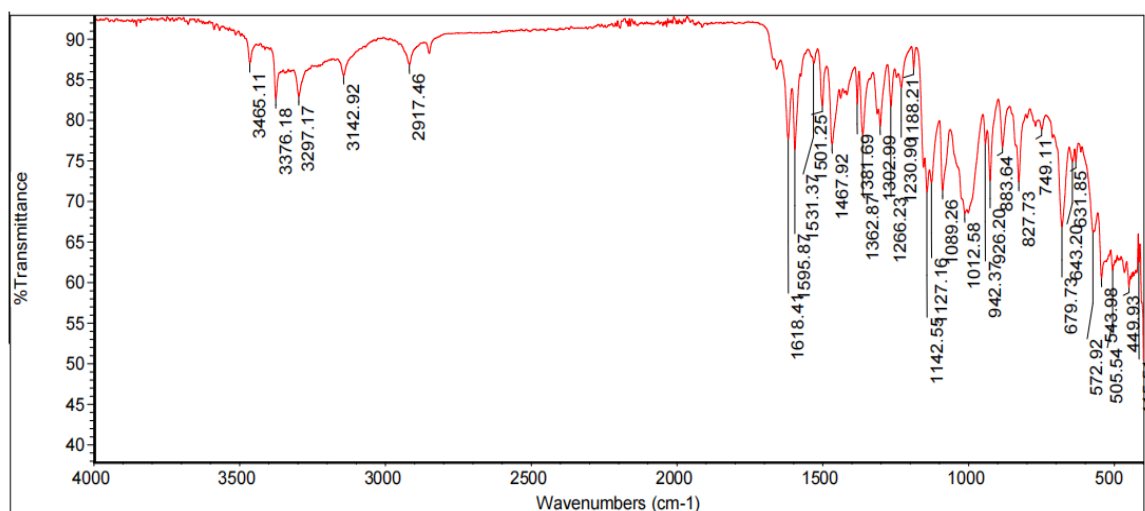


Fig. 2 FTIR Spectrum of Seprtin

The FTIR analysis of Flagyl as a corrosion inhibitor, shown in Figure 3, highlights the critical role of various functional groups in its adsorption on mild steel. The O–H/N–H stretching at 3210.35 cm^{-1} reveals hydroxyl and amine groups, which form hydrogen bonds or coordinate with metal atoms to enhance adsorption. Aromatic C–H stretching at 3099.57 cm^{-1} indicates aromatic rings facilitating π -electron interactions with the metal surface. Alkyl C–H stretching at 2916.35 cm^{-1} shows aliphatic chains creating a hydrophobic barrier on the steel. C=O stretching at 1646.81 cm^{-1} suggests

carbonyl groups engage in donor-acceptor interactions with the metal. The N–O asymmetric stretching at 1534.33 cm^{-1} and symmetric stretching at 1367.17 cm^{-1} imply nitro groups are involved in electron transfer, reinforcing the adsorption layer. Aromatic C=C stretching at 1471.95 cm^{-1} confirms aromatic systems contribute via π - π interactions. CH₂ bending vibrations at 1427.16 cm^{-1} point to alkyl groups enhancing hydrophobicity. C–N stretching at 1264.38 cm^{-1} and 1072.74 cm^{-1} reflects nitrogen-containing groups forming coordination bonds with metal atoms. C–O stretching at 1186.02 cm^{-1} and C–O–C asymmetric stretching at 1156.41 cm^{-1} denote interactions with alcohols, ethers, or esters. Out-of-plane aromatic C–H bending at 987.10 cm^{-1} and 906.97 cm^{-1} further support π - π stacking between aromatic rings and the metal surface. C–H deformation at 863.43 cm^{-1} indicates aliphatic groups' involvement, while C–Cl stretching at 825.01 cm^{-1} and 646.59 cm^{-1} suggests weak van der Waals interactions from halogen atoms. Low-frequency peaks at 520.33 cm^{-1} , 502.97 cm^{-1} , 464.75 cm^{-1} , 438.86 cm^{-1} , and 426.46 cm^{-1} indicate metal-ligand interactions, demonstrating Flagyl's stable coordination with the metal surface, enhancing corrosion protection[22,23].

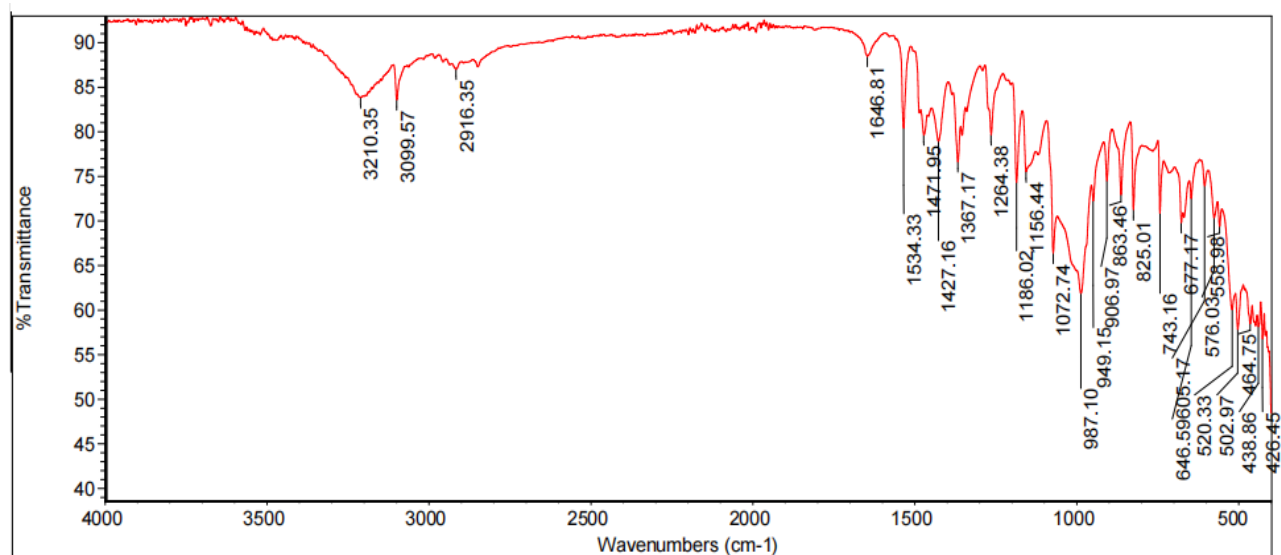


Fig. 3 FTIR Spectrum of Flagyl

3.2 Electrochemical measurement

3.2.1 Open Circuit Potential (OCP)

Figures 4 and 5 illustrate the open circuit potential (OCP) profiles showing the voltage between the working electrode (mild steel) and the reference electrode (Silver/Silver Chloride) in 2M HCl over time for the Septrin and Flagyl drugs as inhibitors. The Septrin inhibitor, as depicted in Figure 4, at its maximum concentration, the potential shifts from a lower value of -0.73 V to -0.66 V , indicating a reduction in the corrosion rate due to the increase in inhibitor concentration from 0.0 g/100 ml to 7.5 g/100 ml . Similarly, the potential increases progressively from -0.73 V to -0.70 V and -0.68 V when the inhibitor concentration rises to 2.5 g/100 ml and 5.0 g/100 ml , respectively. The nearly straight line in the graph indicates that the process reaches stability after the first two seconds and maintains stability for the remaining 12 seconds. These results demonstrate that the OCP values in the presence of Septrin inhibitor, at various concentrations, in 2M HCl are more anodic than in the absence of the drug, as confirmed by Kwolek et al. [22].

In contrast as shown in Figure 5, for the Flagyl inhibitor, the OCP behavior follows a different trend. At the lowest concentration (0.0 g/100 ml to 2.5 g/100 ml), the potential shifts from -0.75 V to -0.40 V . For the other concentrations (5.0 g/100 ml and 7.5 g/100 ml), the potentials shift to -0.60 V and -0.61 V , respectively, from the initial -0.75 V . This indicates that increasing the inhibitor concentration results in the corrosion potential shifting toward the cathodic direction, as shown in Figure 3. The OCP profile for Flagyl inhibitor achieves stability immediately at 0.0 seconds and remains stable throughout the 7.8 -second measurement period at various concentrations.

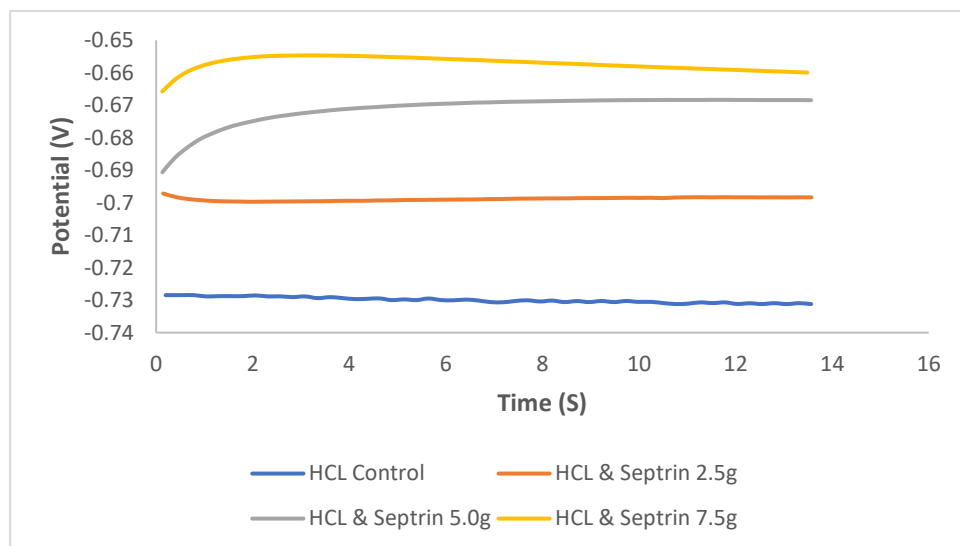


Fig 4. Open Circuit Potential for Septrin drug inhibitor in 2M HCl at 30⁰

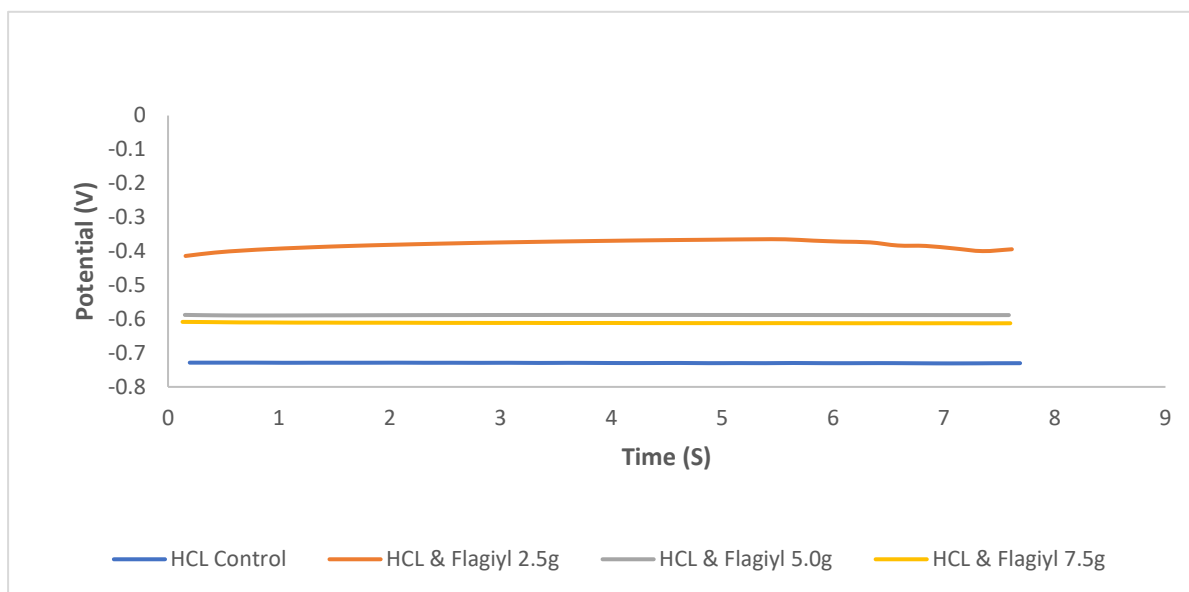


Figure 5. Open Circuit Potential for Flagyl drug inhibitor in 2M HCl at 30⁰

3.2.2 Linear Sweep Voltammetry (LSV)

Figures 6 and 7 present the Linear Sweep Voltammetry (LSV) results, illustrating the relationship between the potential of the reference electrode and the current density. It is important to recall that the corrosion rate is directly proportional to the current density. Both plots in Figures 6 and 7 reflect similar trends, demonstrating the effect of inhibitor concentration on reducing the current density. In both figures, the current density in the control environment is significantly reduced from approximately 0.1 A/cm² to nearly 0.0000001 A/cm² with the addition of varying inhibitor concentrations (2.5 g/100 ml, 5.0 g/100 ml, and 7.5 g/100 ml) at a potential of -0.5 V. This reduction in current density indicates an anodic rather than cathodic behavior. The inhibitor performance, as shown in the graphs, suggests that both Septrin and Flagyl influence the corrosion process at both the anodic and cathodic sites. This behavior classifies them as mixed inhibitors, consistent with the findings of Kwolek et al. [24] and Liangtian et al. [25].

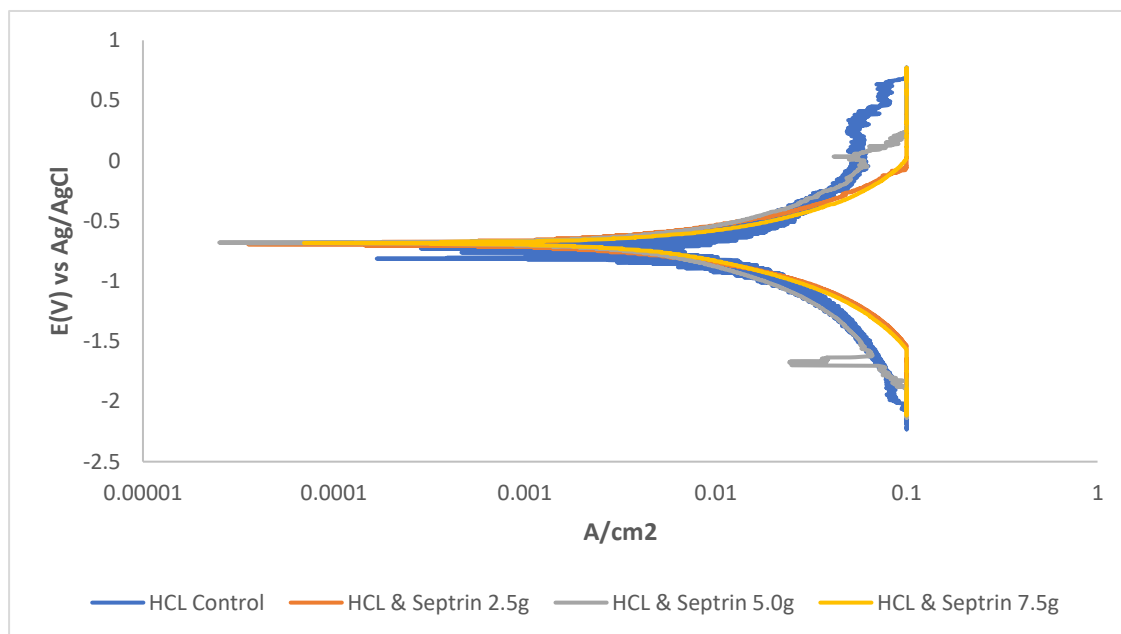


Fig. 6. Linear Sweep Voltammetry for Septrin drug inhibitor in 2M HCl

Table 1. Tafel plots Septrin for drugs inhibitors

Inhibitor	Inh conc.	CR	Jcorr	Ecorr	PR	$\eta(\%)$
(g/l)	(Mol/L)	(mm/yr)	(A/cm ²)10 ⁻³	(V)	{ Ω }	
Blank	0	149.35± 0.05	12.85± 0.16	0.79± 0.01	12.39± 0.01	
25	0.05	107.89± 0.12	9.47± 0.11	0.7± 0.06	13.4± 0.01	27.8± 0.01
50	0.09	80.94± 0.15	6.94± 0.14	0.69± 0.01	14.09± 0.01	45.8± 0.01
75	0.14	78.53± 0.15	6.76± 0.12	0.68± 0.01	18.01± 0.01	47.4± 0.01

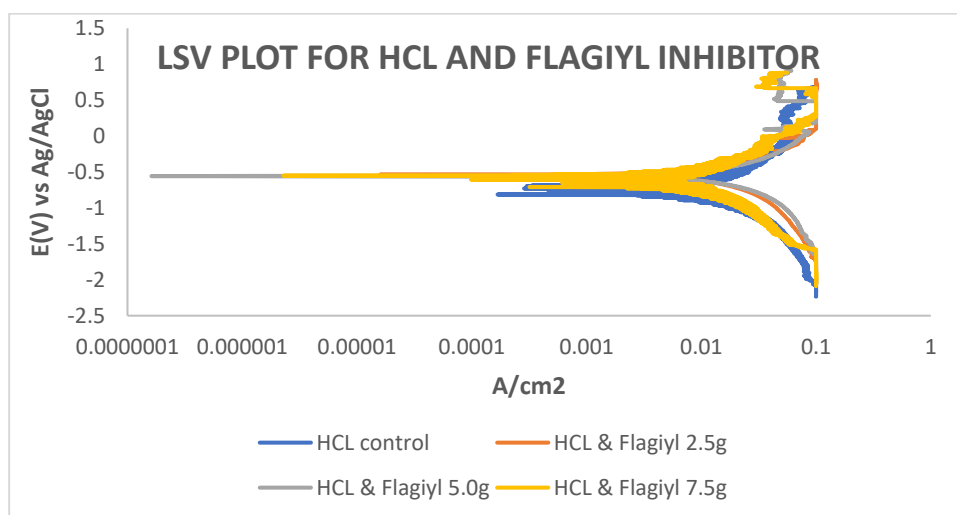


Fig 7. Linear Sweep Voltammetry for Flagyl drug inhibitor in 2M HCl

Table 2. Tafel plots flagyl for drugs inhibitors

Inhibitor	Inh conc.	CR	Jcorr	Ecorr	PR	η (%)
(g/l)	(Mol/L)	(mm/yr)	(A/cm ²)10 ⁻³	(V)	{ Ω }	
Blank	-	149.35± 0.05	12.85± 0.15	0.79± 0.05	12.39± 0.05	-
25	0.09	110.05± 0.05	9.47± 0.12	0.7± 0.05	7.28± 0.05	26.3± 0.01
50	0.18	70.62± 0.05	6.08± 0.15	0.56± 0.05	8.67± 0.05	52.7± 0.01
75	0.27	60.02± 0.05	5.17± 0.11	0.54± 0.05	16.65± 0.05	59.8± 0.01

3.3 Corrosion rate and Inhibitors Concentration

A detailed comparison of the graphs in Figures 8 and 9 reveals a clear trend where the corrosion rate (CR) decreases with increasing concentrations of inhibitors. Specifically, the performance of the Flagyl drug as a corrosion inhibitor shows a significant reduction in the corrosion rate. At a zero-inhibitor concentration (0.0 g/L), the corrosion rate is measured at 149.35 mm/year. However, as the concentration of Flagyl increases to 75 g/L, the corrosion rate drops dramatically to 60.024 mm/year. Similarly, the Septrin drug also demonstrates a notable reduction in the corrosion rate with increasing concentrations. At an initial concentration of 0.0 g/L, the corrosion rate is likewise measured at 149.35 mm/year. When the concentration of Septrin is raised to 75.0 g/L, the corrosion rate decreases to 78.53 mm/year.

This comparative analysis highlights that both Flagyl and Septrin exhibit strong corrosion inhibition properties, with Flagyl proving slightly more effective at higher concentrations in reducing the corrosion rate. The observed decrease in corrosion rate with increasing inhibitor concentration indicates that both drugs play a significant role in mitigating the corrosion process in the tested environment. These results align with the general understanding that the effectiveness of corrosion inhibitors typically improves with higher concentrations, as they form more substantial protective layers on the surface of the material, thereby slowing down the corrosion reaction [26].

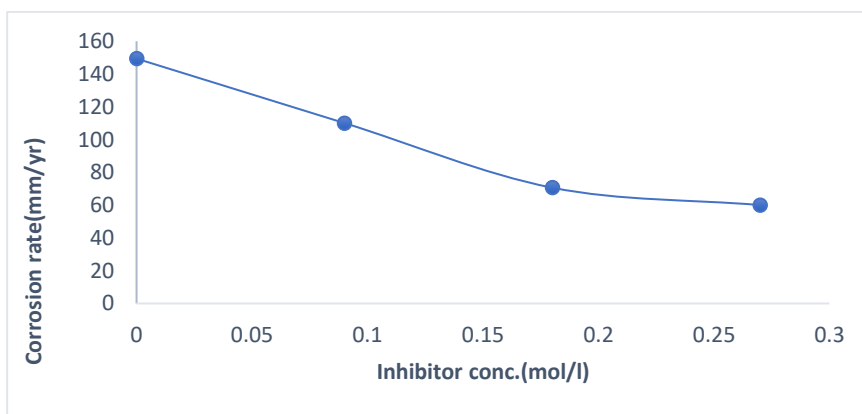


Fig. 8. Graph of Corrosion rate against Inhibitor Concentration for Septrin Drug inhibitor in 2M HCl

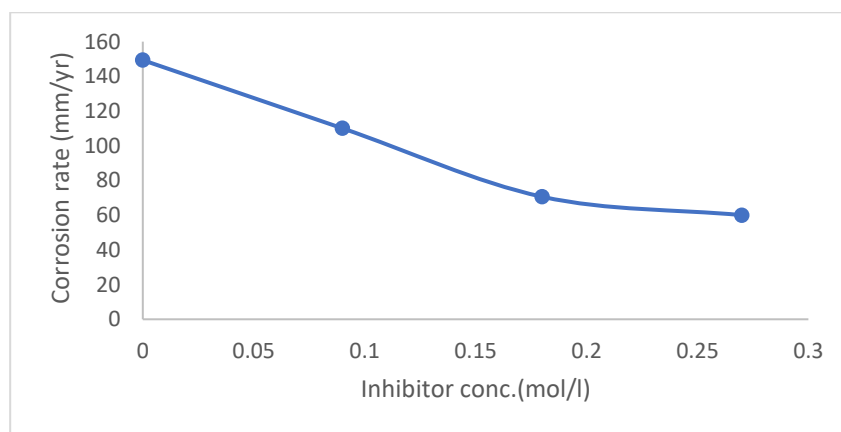


Fig.9 Graph of Corrosion rate against inhibitor Concentration for Flagyl drug in 2M HCl

3.4. Corrosion Inhibition Efficiency and Inhibitors Concentration

A detailed comparison of the graphs in Figures 10 and 11 indicates a clear relationship between the increasing inhibitor concentration and the corresponding enhancement in inhibitor efficiency. As the concentration of the inhibitors rises from 0.0 g/L to 75.0 g/L, the efficiency of the inhibitors in mitigating corrosion significantly improves. For the Flagyl drug, the inhibitor efficiency increases from 0.0% at 0.0 g/L to 59.8% at the highest tested concentration of 75.0 g/L. Similarly, the Septrin drug exhibits an increase in inhibitor efficiency, rising from 0.0% at 0.0 g/L to 47.4% at 75.0 g/L. This outcome suggests that as the concentration of the inhibitors is increased, the extent of surface coverage of these inhibitors on the metal surface also increases. The enhanced surface coverage likely results in the formation of more robust and uniform protective films, which effectively block active corrosion sites and reduce the overall corrosion rate. Consequently, the inhibition efficiencies of both Flagyl and Septrin drugs improve as their concentrations increase, as shown by the upward trend in the graphs [27]. The observed increase in inhibitor efficiency with increasing concentration is consistent with the general principles of corrosion inhibition, where higher concentrations of inhibitors lead to greater adsorption onto the metal surface, enhancing the protective effect. This relationship underscores the effectiveness of both Flagyl and Septrin as corrosion inhibitors and highlights the importance of optimizing inhibitor concentrations to achieve maximum protection in corrosive environments.

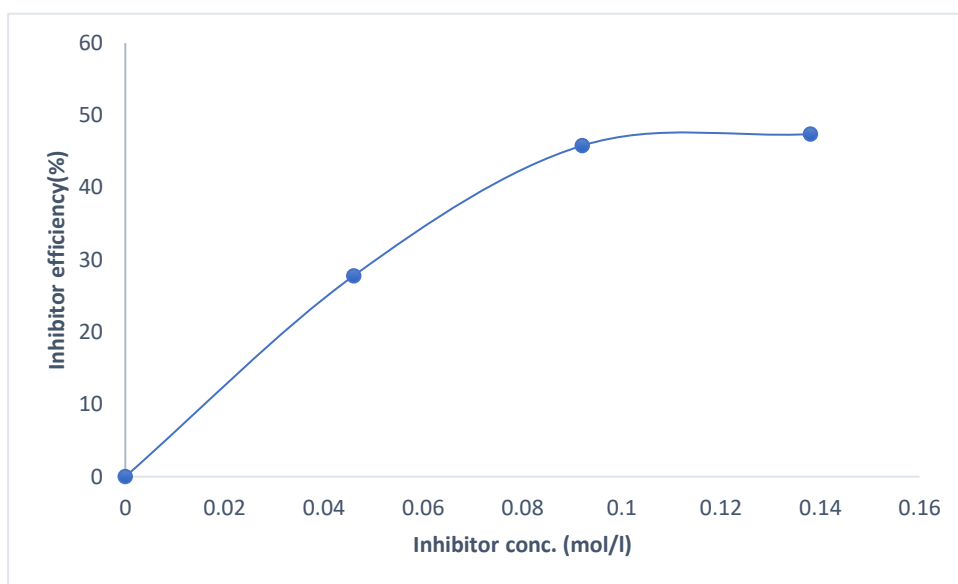


Fig. 10. The graph of Inhibition Efficiency against Inhibition Concentration for Septrin drug inhibitor in 2M HCl

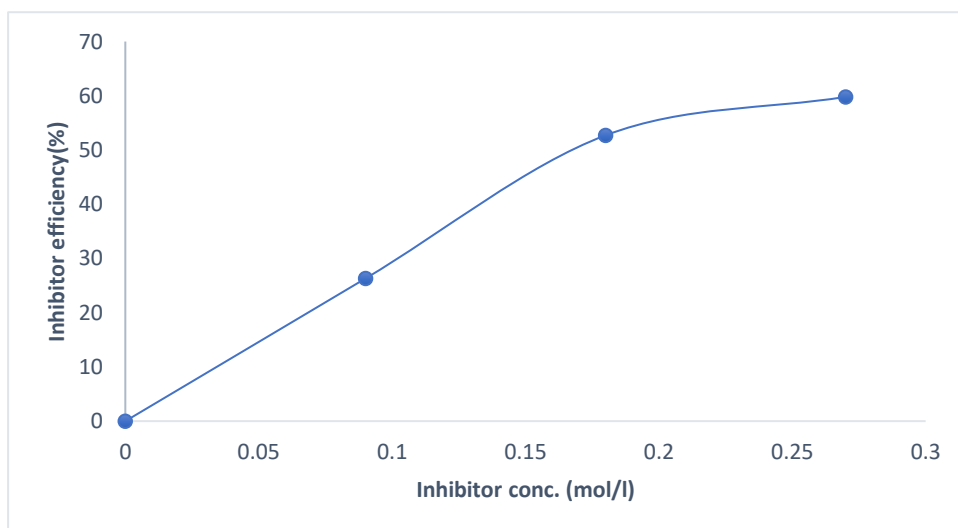


Fig.11. The graph of Inhibition Efficiency against Inhibitor concentration for Flagyl drug in 2M HCl

3.5. Thermodynamic studies

The mechanism of corrosion inhibition can be understood based on the adsorption behavior of the inhibitors on the metal surface, as outlined by various studies [29]. In this research, several adsorption isotherms were evaluated to describe the adsorption characteristics of the Flagyl and Septrin drugs on mild steel in a 2M HCl solution. Among the tested models, the Langmuir and Freundlich adsorption isotherms provided the best fit for the experimental data, indicating their suitability in describing the adsorption process.

This investigation aimed to assess the effectiveness of these drugs as corrosion inhibitors using four distinct adsorption isotherm models, which are detailed in Figures 12 through 15. From these figures, the adsorption mechanisms of Flagyl and Septrin on the mild steel surface in 2M HCl were elucidated. Additionally, the spontaneity of the adsorption process was determined, providing insights into the thermodynamic feasibility of the inhibition mechanism.

The data used to generate these graphs were derived from Table 3, which provided the foundation for plotting the adsorption behavior of the drugs across different concentrations. The results of this analysis, including the key parameters and coefficients of the adsorption models, are summarized in Tables 4 and 5. These tables highlight the critical outcomes from the eight adsorption plots, showcasing the adsorption efficiency and thermodynamic properties of the inhibitor molecules [28].

The successful application of the Langmuir and Freundlich isotherms suggests that the adsorption of these drugs onto the mild steel surface follows a monolayer adsorption process with heterogeneous surface interactions [29]. This finding supports the conclusion that both Flagyl and Septrin form protective layers on the metal surface, reducing corrosion by limiting the interaction between the corrosive medium and the mild steel [30].

$$\text{LANGMUIR} \quad \frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

$$\text{TEMKIN} \quad \theta = \ln C + \ln K \quad (3)$$

$$\text{FREDNULICH} \quad \ln \theta = \ln K + \ln C \quad (4)$$

$$\text{EL-AWADY} \quad \log \frac{\theta}{1-\theta} = \log K + \log C \quad (5)$$

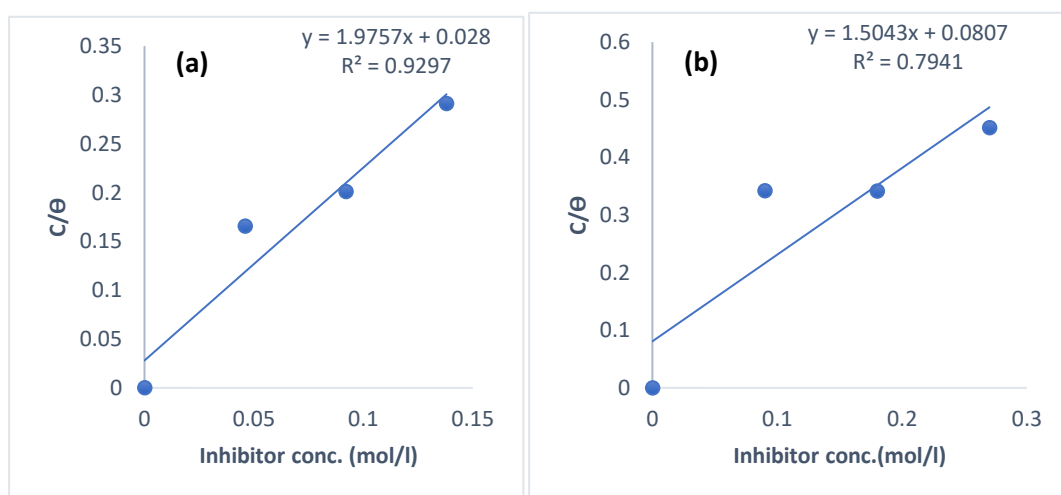


Fig. 12. Langmuir Adsorption Isotherm for (a) Septrin and (b) Flagyl drugs as corrosion inhibitor in 2M HCl

Table 4 provides valuable insights into the adsorption behavior of Septrin and Flagyl as corrosion inhibitors on mild steel surfaces in 2M HCl, evaluated through the Langmuir and Freundlich adsorption isotherms. The data for Septrin indicate that it closely follows both the Langmuir and Freundlich adsorption isotherms, with regression values of 0.9297 and 0.9231, respectively. Furthermore, the Gibbs free energy of adsorption (ΔG_{ads}) for Septrin shows spontaneity, with values of -19.92 kJ/mol and -10.335 kJ/mol for the two isotherms. Given that ΔG_{ads} values are less than -20 kJ/mol, but not exceeding -40 kJ/mol, the adsorption mechanism can be classified as physical adsorption [31].

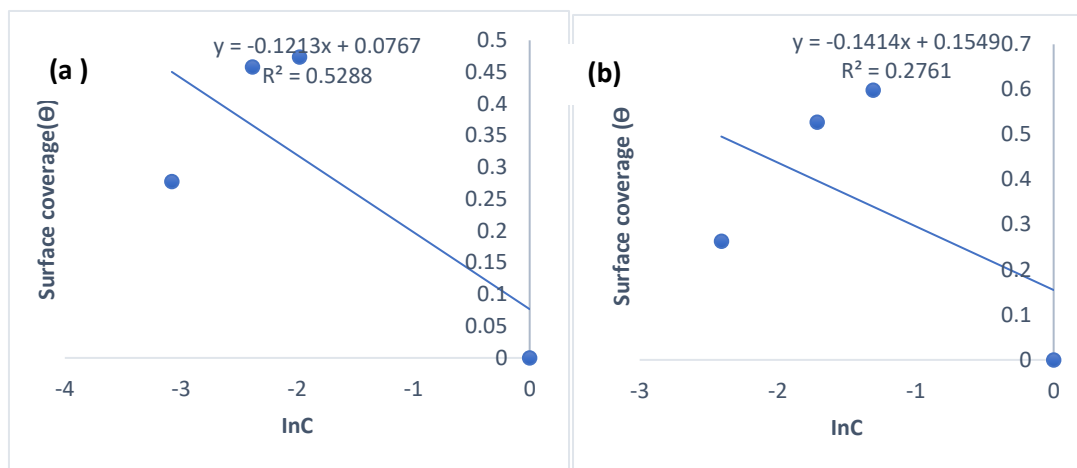


Fig. 13. Temkin Adsorption Isotherm for (a) Septrin and (b) Flagyl drugs as corrosion inhibitor in 2M HCl

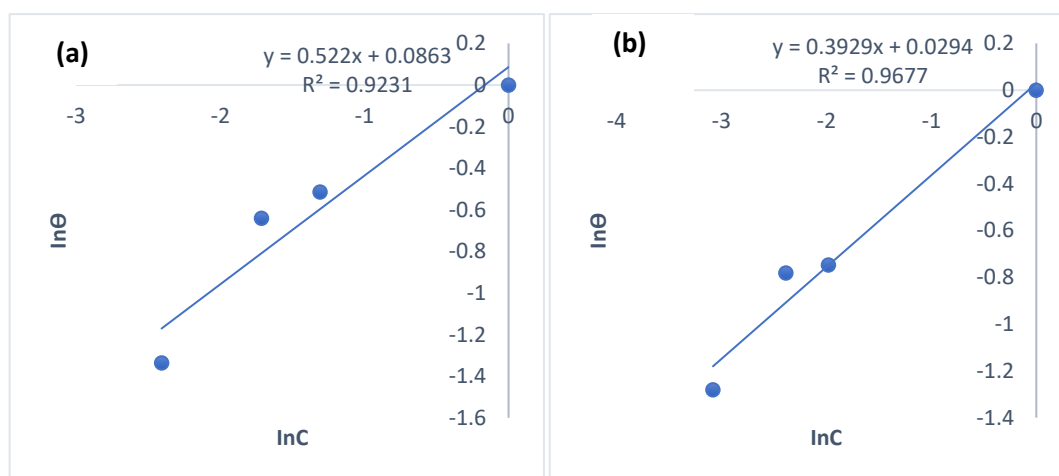


Fig. 14. Frednulich Adsorption Isotherm for (a) Septrin and (b) Flagyl drugs as corrosion inhibitor in 2M HCl

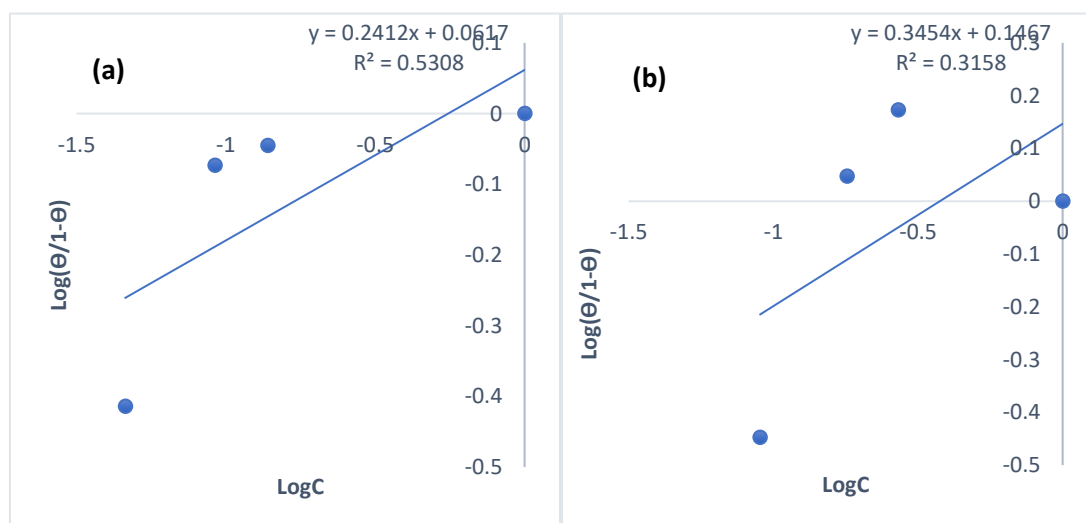
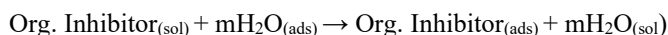


Fig. 15. EL-Awady Adsorption Isotherm for (a) Septrin and (b) Flagyl drugs as corrosion inhibitor in 2M HCl

Similarly, Table 4 shows that Flagyl follows the Freundlich adsorption isotherm more closely, with a regression value of 0.9677. The Gibbs free energy of adsorption for Flagyl is -10.192 kJ/mol, indicating a spontaneous and physical adsorption process. Although the Langmuir isotherm is not as closely followed by Flagyl, with a regression value of 0.7941, the Gibbs free energy value of -16.458 kJ/mol still points to a spontaneous adsorption process driven by physical interactions [31].

The adsorption process for both drugs is governed by the physical adsorption mechanism due to the relatively low Gibbs free energy values, suggesting weak interactions between the inhibitor molecules and the metal surface. The adsorption of these inhibitors is influenced by factors such as the molecular structure of the inhibitors, the composition of the metal surface, temperature, and electrochemical potential at the metal/solution interface, as supported by the work of Coulibaly et al. [32] and Zeino et al.[33].It is important to note that metallic corrosion inhibition involves the adsorption of inhibitor molecules onto the metal surface, displacing pre-adsorbed solvent molecules, such as water (H₂O). The adsorption process for Flagyl and Septrin in the aqueous solution can be understood as a quasi-substitution mechanism, in which the inhibitor molecules replace water molecules adsorbed at the electrode surface. This process can be represented as follows:



This quasi-substitution mechanism emphasizes the competitive adsorption between the inhibitor molecules and water molecules at the metal/solution interface, which is crucial for effective corrosion inhibition. The results confirm that both Flagyl and Septrin exhibit strong adsorption behaviors, making them effective corrosion inhibitors under the tested conditions.

Table 3. Table of Values for Septrin and Flagyl Adsorption Mechanism in 2M HCl on Mild Steel at 30°C

Septrin	Isotherm	Adsorption K _{ad}	Regression R ²	Gibbs Energy ΔG _{ad}
	Langmuir	35.7143	0.9297	-19.92
	Frenudlich	1.0901	0.9231	-10.335
	Temkin	1.0797	0.5288	-10.31
	EL-Awardy	1.1527	0.5308	-10.47
Flagyl				
		12.3916	0.7941	-16.458
	Frenudlich	1.0298	0.9677	-10.192
	Temkin	1.1675	0.2761	-10.507
	EL-Awardy	1.4018	0.3158	-10.967

3.6. Corrosion and Temperature

3.6.1 Effect of Temperature

During the course of this study, as illustrated in Figure 16(a-b), it was observed that the corrosion rate (CR) in mm/year increased with rising temperature, both in the absence and presence of a 75 g/L inhibitor concentration for the two drugs. Without these inhibitors, the corrosion rate increased significantly from 149.35 mm/year to 224.09 mm/year (approximately 50%) when the temperature was raised from 302 K to 363 K. In the presence of 75 g/L Septrin, the corrosion rate rose from 78.53 mm/year to 205.95 mm/year (around 62%), while for Flagyl at the same concentration, it increased from 60.024 mm/year to 171.96 mm/year (approximately 87%) over the same temperature range. This data indicates that Flagyl exhibits a steeper gradient than Septrin under these temperature conditions [34].

Fig.16 Corrosion against Temperature for maximum and minimum Inhibition concentration for (a) Septrin and (b) Flagyl drug as corrosion inhibitor.

3.6.2 Arrhenius Analysis

Figures 17(a-b) present the plots of the natural logarithm of the corrosion rate (CR) versus the reciprocal of temperature multiplied by one thousand (1000/T) for Septrin and Flagyl drugs. These plots yield straight lines, with the slope corresponding to $-E_a/2.302R$ and the intercept representing $\ln A$ from the Arrhenius equation. The corrosion rate (CR) was determined using this equation, which highlights its dependence on temperature (T) and the pre-exponential factor (A), as shown below.

$$\text{Log CR} = \text{Log A} - (E_a)/RT \quad (6)$$

In this context, E_a represents the activation energy for the corrosion of mild steel in 2 M HCl, while $\log A$ is the pre-exponential factor. R is the gas constant, A is the Arrhenius pre-exponential factor, and T is the absolute temperature. As observed in Table 7, the activation energy E_a for the HCl solution is 17.32 kJ/mol. However, in the presence of a 75.0 g/L concentration of the drugs, E_a increases to 33.45 kJ/mol for Septrin and 38.13 kJ/mol for Flagyl. This increase

indicates a retardation of the corrosion reaction, as the reaction can only proceed if energy greater than E_a is applied. The significant change in E_a values may be attributed to either precipitation on the electrode surface or a change in the potential difference at the metal-solution interface due to adsorption, as suggested by Okewale & Adesina. [35], as shown in Figures 17(a-b). The data in Table 4 further indicates that the thermodynamic activation energy (E_a) for corrosion in mild steel in 2 M HCl solution is higher in the presence of Septrin and Flagyl compared to the free acid solution. This suggests that Septrin and Flagyl reduce inhibition efficiency at higher temperatures, as also collaborated [36,37].

Table 4. Arrhenius data for Septrin and Flagyl drugs as corrosion inhibitor.

Inhibitor	Slope	Intercept	R^2	E_a (KJ/mol)
Blank	-0.9046	7.9921	0.9999	17.3205
Septrin	-1.7472	10.1277	0.9992	33.4538
Flagyl	-1.9916	10.6746	0.9943	38.1335

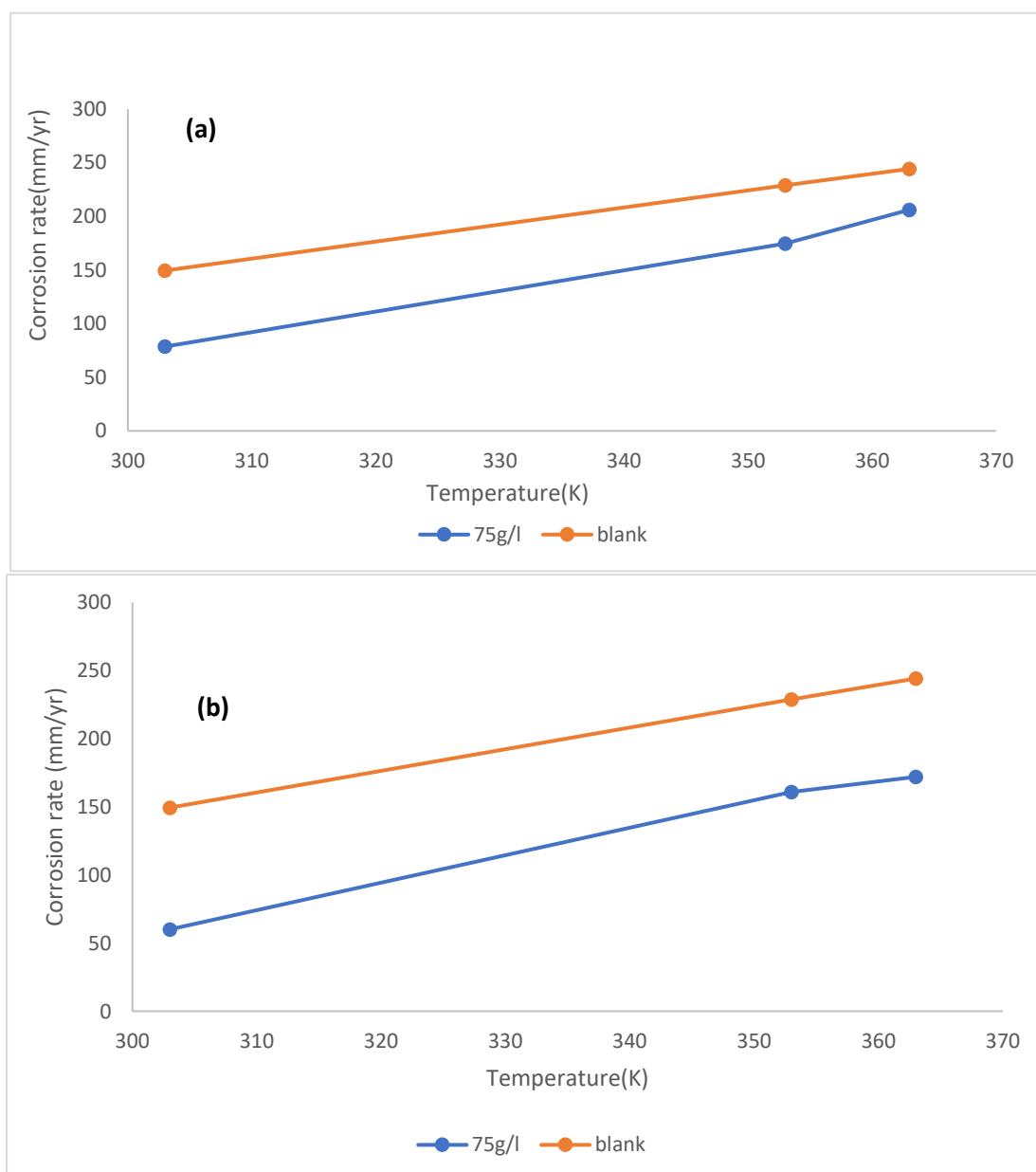
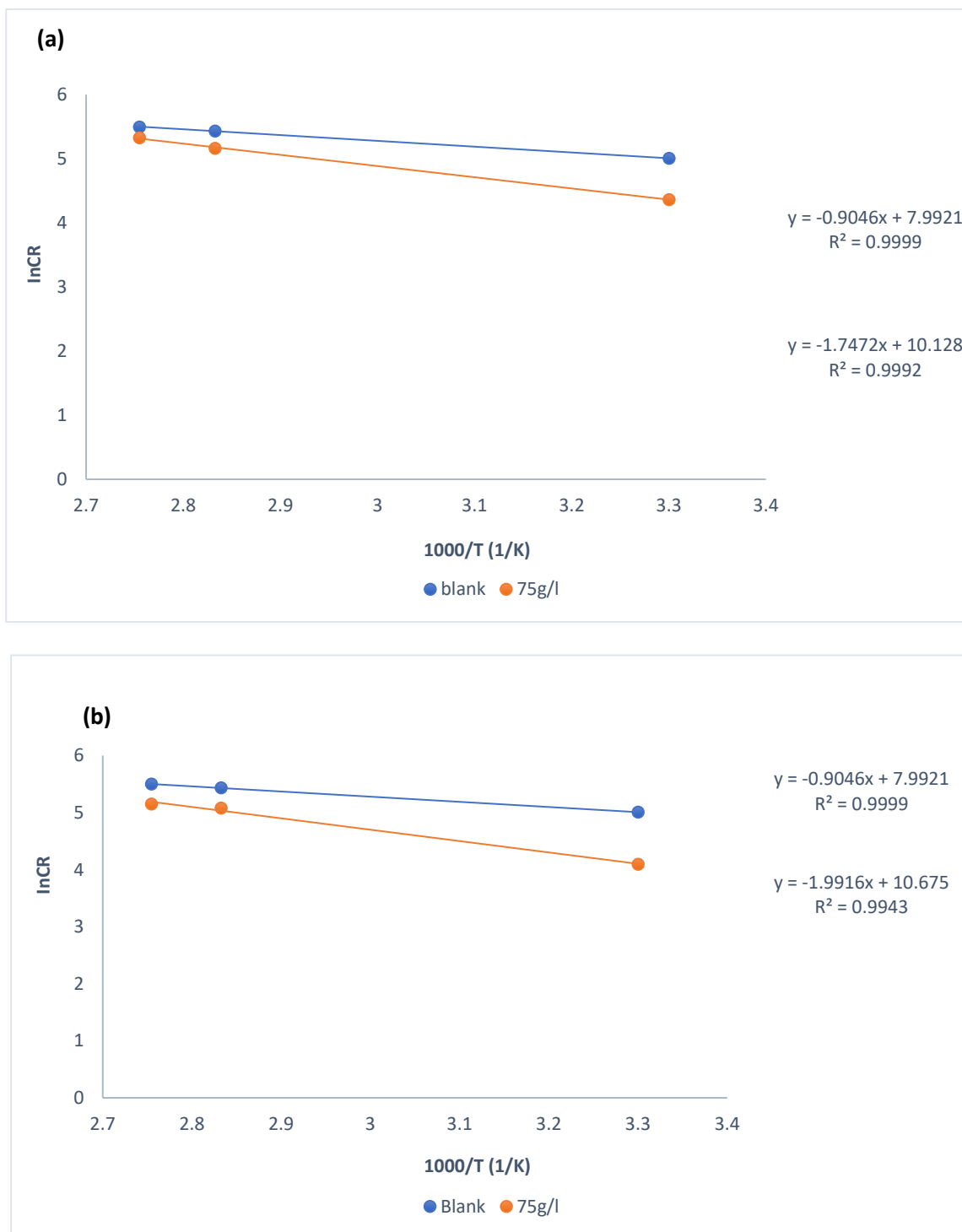


Fig.17.Arrhenius plots for (a) Septrin and (b) Flagyl drugs as corrosion inhibitor.



Figures 18(a-b): Transition state plots (CR/T vs. 1000/T)

These plots yield straight lines, where the slope corresponds to $-\Delta H/2.303R$ and the intercept to $\log(R/Nh) + \Delta S/2.303R$. From these, the values of ΔH and ΔS were calculated and are presented in Table 5. The positive ΔH values for both drugs indicate that the formation of the activated complex is endothermic. Meanwhile, the negative ΔS values suggest that the inhibitor molecules are adsorbed onto the mild steel surface in an orderly manner, leading to a decrease in entropy, as confirmed by Okewale & Adesina. [35]. The transition state equations are stated below.

$$CR = RT/Nh \cdot \exp(\Delta S/R) \cdot \exp(-\Delta H/RT) \quad (7)$$

$$\log(CR/T) = \log(R/Nh) + \Delta S/(2.303R) - \Delta H/(2.303R) \quad (8)$$

Studying of Table 4 reveals that the ΔH value for the dissolution of mild steel in 2M HCl in the presence of Flagyl is slightly higher (31.82 kJ mol⁻¹) compared to its absence (31.08 kJ mol⁻¹), but it is lower for Septrin (27.14 kJ mol⁻¹). The positive enthalpy values indicate the endothermic nature of the mild steel dissolution process, suggesting that dissolution is more difficult in the presence of Flagyl than without it, as supported by reference [33]. When comparing the entropy of activation (ΔS) values listed in Table 4, it is evident that the entropy of activation increases in the presence of Flagyl compared to the free acid solution or even the Septrin solution. This variation is related to the ordering and disordering of inhibitor molecules on the mild steel surface. The increased entropy of activation in the presence of Flagyl indicates that disorder increases as the system transitions from the reactant to the activated complex at the metal/solution interface [35]. Table 6 shows the Comparison of Thermodynamic Parameters with establish Literature Values

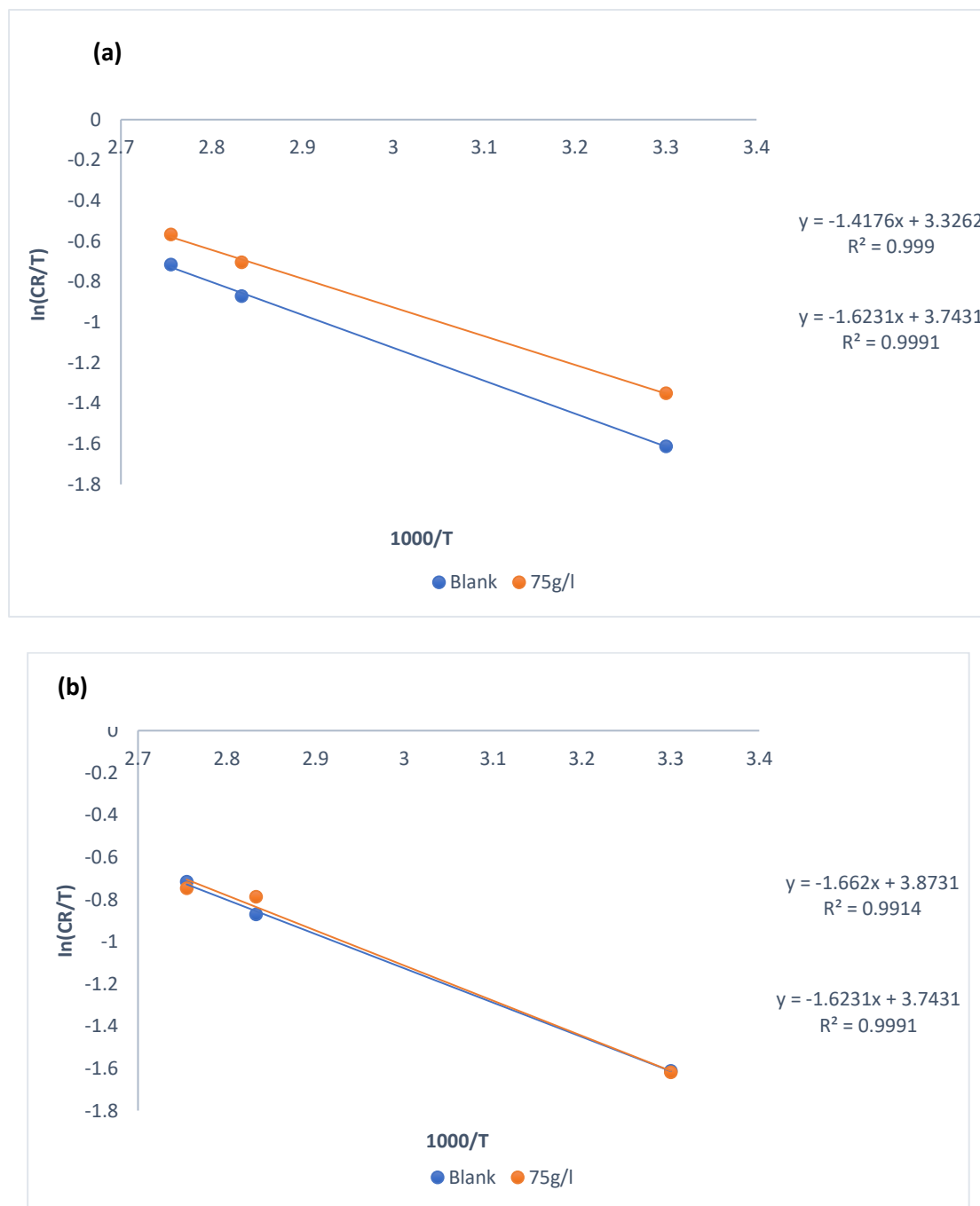


Fig.18 Graph of Log (CR/T) against 1000/T for maximum and minimum Inhibition concentration for (a) Septrin
(b) Flagyl drug as corrosion inhibitor in 2M HCl

Table 5 Activation Parameters of Septrin and Flagyl drug in 2M HCl at minimum and maximum inhibition.

Inhibitor	Slope	Intercept	R2	ΔH (KJ/mol)	ΔS° (J/mol/K)	ΔG° KJ/mol		
						303K	353K	363K
Blank	-1.6231	3.7431	0.9999	31.0758	-383.82	147.3733	166.564	170.403
Septrin	-14176	3.3326	0.9999	27.1429	-391.8	145.8583	165.448	169.366
Flagyl	-1.662	3.8731	0.9914	31.8225	-381.33	147.356	166.421	170.234

Table 6 Comparison of Thermodynamic Parameters with Literature Values

Inhibitor	Temperature (K)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)	Reference
Ampicillin	353	29.85	-375.2	163.5	[45]
Tetracycline	353	32.12	-368.7	167.11	[46]
Ciprofloxacin	353	28.65	-382.4	164.72	[47]
Septrin	353	27.1429	-391.8	165.448	This study
Flagyl	353	31.8225	-381.33	166.421	This study

3.7 Adsorption Studies

The Gibbs free energy (ΔG) change of the surroundings with respect to the reaction systems for free HCl solution, and HCl in the presence of Septrin and Flagyl at various temperatures, as shown in Table 8, are all positive. This indicates that the reactions are non-spontaneous in relation to the surroundings and are endothermic, favoring the reverse direction. This conclusion is derived from the relationship below.

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

For the free HCl solution, the Gibbs free energy increases from 147.37 to 170.40 kJ/mol, while for the HCl solution containing 75 g/L of Septrin, it increases from 145.86 to 169.37 kJ/mol. Similarly, the HCl solution with 75 g/L of Flagyl shows an increase from 147.36 to 170.23 kJ/mol. These values indicate that the free HCl solution is the most non-spontaneous compared to the HCl solutions containing Septrin and Flagyl. The standard free energy of adsorption at various temperatures was calculated using the following formula, as shown in Tables 9 and 10.

$$\Delta G^\circ_{\text{ads}} = -RT \ln (55.5K_{\text{ads}}) \quad (10)$$

In this context, the value 55.5 represents the molar concentration (M) of water in the solution [68]. The negative values of $\Delta G^\circ_{\text{ads}}$ confirm the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface. As illustrated in Tables 9 and 10, the Gibbs free energy of adsorption as shown from both models indicates a spontaneous process, characterized by a physisorption mechanism across various temperatures. Septrin, in particular, exhibits a higher degree of spontaneity compared to Flagyl. Generally, values around -20 kJ/mol or lower are indicative of physisorption, while values around -40 kJ/mol or higher suggest chemisorption [38,39].

3.7.1 Langmuir Adsorption

The Langmuir isotherm model for Gibbs free energy (ΔG) at different studied temperatures is depicted in Table 9 below.

Table 9. Standard Gibb Free Energy of Adsorption at the various temperature from Langmuir Isotherm

Inhibitor	303K	363K
	$\Delta G^\circ_{\text{ads}}$ KJ/mol	$\Delta G^\circ_{\text{ads}}$ KJ/mol
Blank	-	-
Septrin($K_{\text{ads}}=35.71, R^2=0.9297$)	-19.13	-22.91
Flagyl ($K_{\text{ads}}=12.39, R^2=0.7941$)	-16.46	-19.72

3.8 Frednulich Adsorption

The Frednulich isotherm model for Gibbs free energy (ΔG) at different studied temperatures is depicted in Table 10 below.

Table 10. Standard Gibb Free Energy of Adsorption at the various temperature from Frednulich Isotherm

Inhibitor	303K ΔG°_{ads} KJ/mol	363K ΔG°_{ads} KJ/mol
Blank	-	-
Seprtin($K_{ads}=1.0901, R2=0.9231$)	-10.34	-12.38
Flagyl($K_{ads}=1.0298, R2=0.9677$)	-10.19	-12.21

3.9 SEM study

The Scanning Electron Microscopy (SEM) micrographs presented in Figure 19(a-d) depict the surface morphology of mild steel coupons exposed to 2 M HCl at 363K, both in the absence of inhibitors and in the presence of Flagyl and Septrin inhibitors, respectively. Figure 19(a) reveals a severely damaged surface, characterized by a rough, dark appearance with evident cracks and pits, resulting from the aggressive acid attack at elevated temperatures. The absence of inhibitors has left the surface in a highly deteriorated state, making it the most critical among all temperature-activated conditions studied in this research. Notably, when compared to the mild steel surface exposed to ambient temperature (303K), the corrosion rate increased by 50% at 363K. The severity of the corrosion is starkly contrasted with the SEM micrograph of the unexposed mild steel, shown in Figure 19(d). The unexposed surface exhibits smooth, white, and colorless grains, with a well-ordered microstructure, highlighting the significant damage inflicted under high-temperature conditions without inhibition. Figures 19(c-d) show improved surface conditions compared to the uninhibited sample in Figure 19(a), with the mild steel surfaces protected by Flagyl and Septrin, respectively. In Figure 19(b), where Flagyl was used as the inhibitor, the micrograph reveals a surface with dispersed and clustered white films, along with areas of ash and black coloration. Similarly, in Figure 19(c), the presence of Septrin also results in a surface with white films, although these films appear more dispersed compared to those seen with Flagyl. The SEM analysis suggests that Flagyl provides better inhibition than Septrin, which aligns with the findings that Septrin loses about 67% of its efficiency at the elevated temperature of 363K, compared to ambient conditions, while Flagyl's efficiency decreases by 50%. This indicates that the surface morphology of mild steel is notably improved by the addition of either Septrin or Flagyl, with Flagyl offering slightly superior protection [40].

3.10 Energy Dispersive X-ray (EDX)

The surface analysis using Energy-Dispersive X-ray Spectroscopy (EDX) provided a detailed composition of the various elements present on the mild steel surface. These elements originate from different sources, including the mild steel substrate, the applied inhibitors, and the surrounding environment. The EDX spectra, depicted in Figures 20, 21, and 22, reveal the distinct atomic constituents, allowing for a comprehensive understanding of the surface chemistry under different conditions [41].

3.11 Mechanism of inhibition

The corrosion inhibition of mild steel in 2 M HCl by Septrin and Flagyl drugs can be explained through their molecular adsorption onto the steel surface. It is widely accepted that the primary inhibition mechanism involves the adsorption of drug molecules at the metal-solution interface, which reduces the active sites available for the corrosion process. The adsorption of these drugs onto the mild steel surface occurs through multiple interactions, including electrostatic interactions, π -electron interactions, charge transfer, and metal-ligand bonding [42].

Electrostatic interactions arise as the protonated species of Septrin and Flagyl in an acidic medium are attracted to negatively charged sites on the metal surface, leading to physisorption. Additionally, the aromatic rings present in the molecular structures of Septrin and Flagyl contain delocalized π -electrons, which facilitate π - π interactions with the vacant d-orbitals of iron atoms on the mild steel surface, strengthening the adsorption and enhancing inhibition efficiency. Furthermore, the presence of heteroatoms such as nitrogen, oxygen, and sulfur in the drug molecules allows for charge transfer via lone pair electrons, which coordinate with the vacant d-orbitals of Fe atoms to form metal-ligand bonds. This chemisorption process results in stronger adsorption and a more stable protective layer on the steel surface, further preventing corrosion [43].

The inhibition efficiency of these drugs is influenced by several factors, including their molecular structure, electron density distribution, the availability of adsorption sites, and their charge density. The molecular size and planarity of the inhibitors also play a role in their ability to cover the steel surface effectively. Additionally, the heat of hydrogenation and the formation of metallic complexes contribute to their protective performance. Based on the findings, Flagyl demonstrated superior corrosion inhibition compared to Septrin in a 2 M HCl solution containing mild steel. This higher efficiency can be attributed to its stronger adsorption potential, greater electron density, and enhanced metal-ligand interactions, which result in more effective surface coverage and protection against corrosive attack [44].

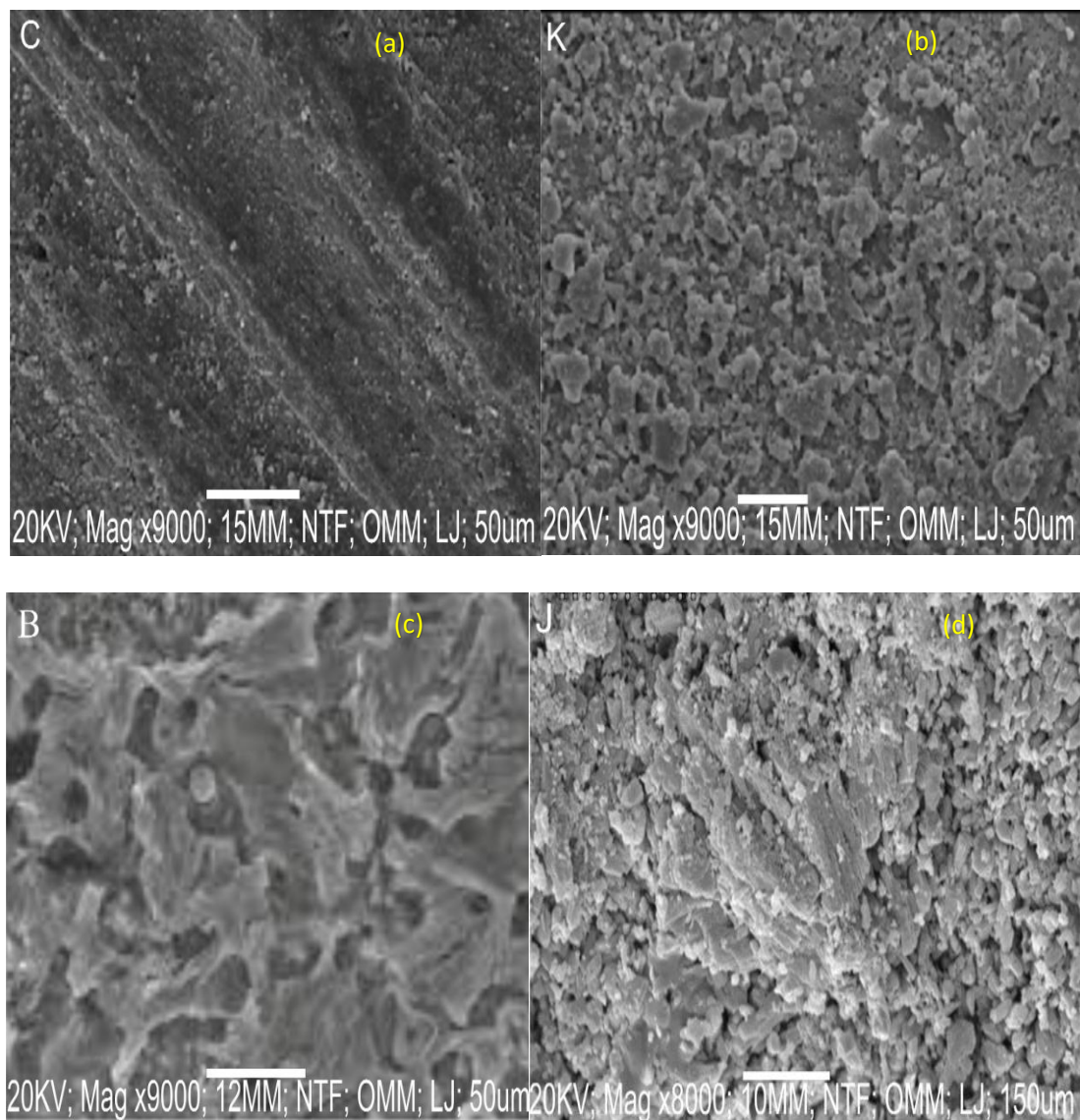


Fig.19. SEM image of (a) Mild Steel immersed in 2M HCL solution for 300s at 363K (b) Immersed in 2M HCL in the presence of 75.0g/l of Flagyl drug for 300s at 363K (c) Immersed in 2M HCL in the presence of 75.0g/l of Septrin drug for 300s at 363K (d) unexposed Mild Steel specimen(As received).

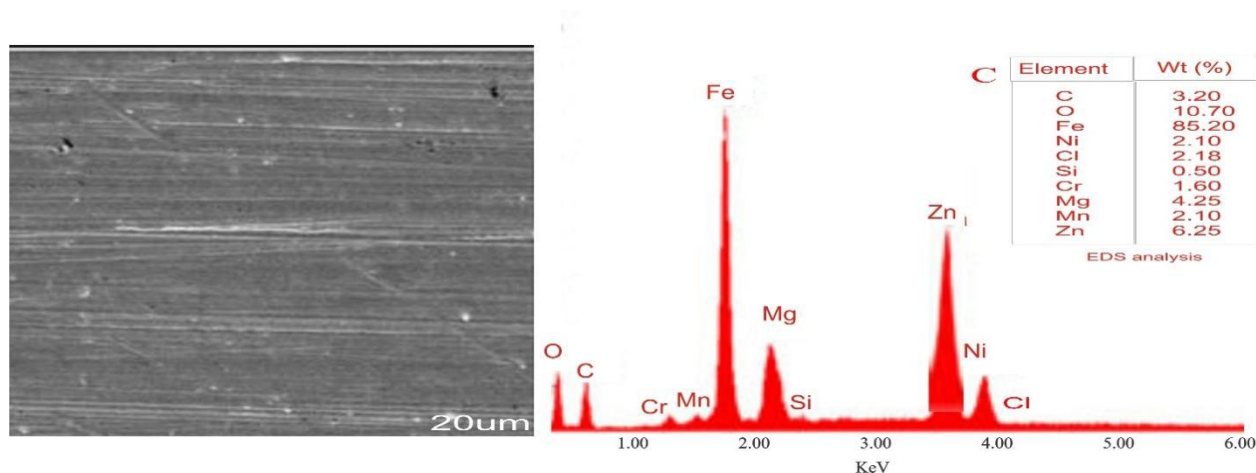


Fig.20 Energy Dispersive X-ray for Mild Steel dipped in 2M HCL for 300s at 363K

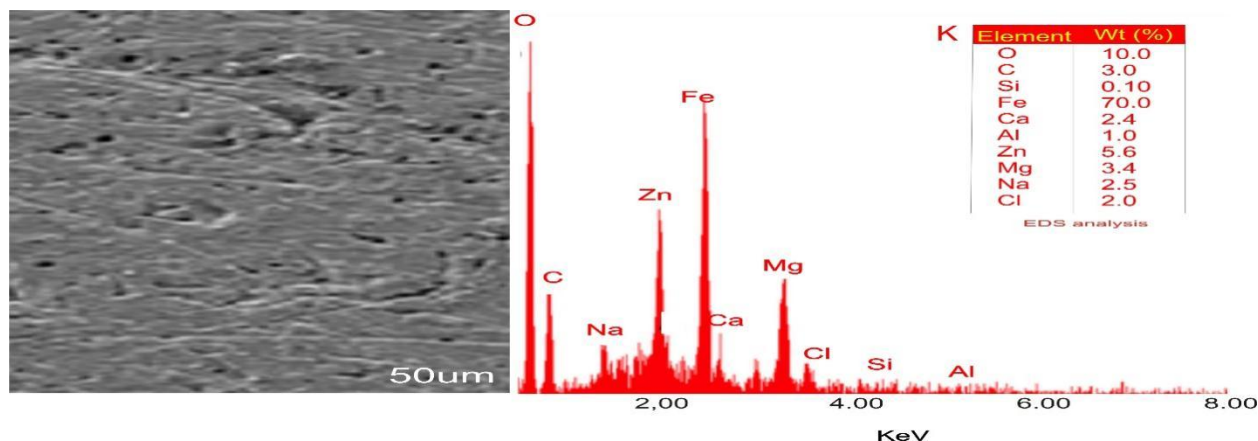


Fig.21 Energy Dispersive X-ray for Mild Steel exposed in 2M HCl in the presence of 75.0g/l of Flagyl drug for 300s at 363K

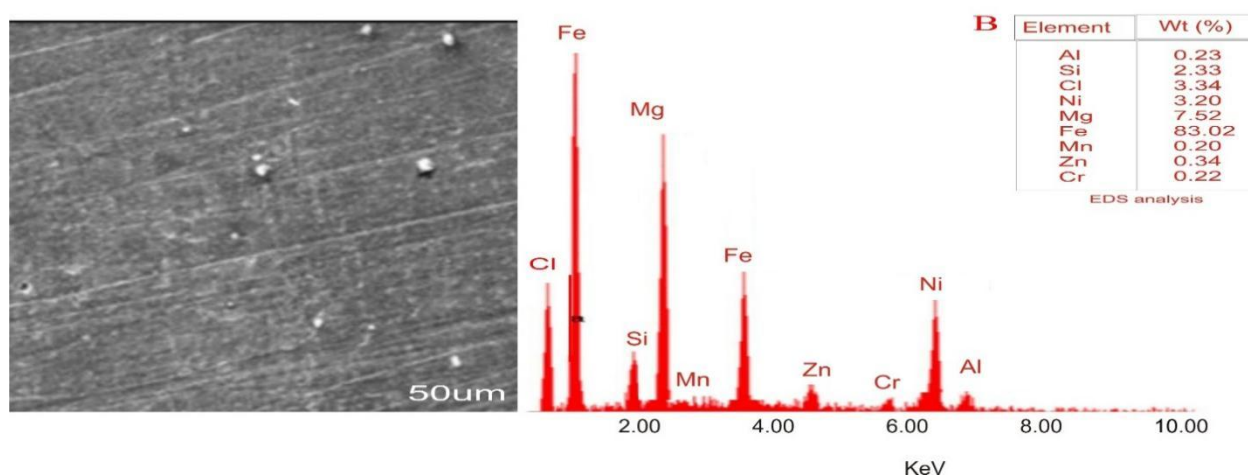


Fig.22. Energy Dispersive X-ray for Mild Steel dipped in 2M HCL in the presence of 75.0g/l of Septrin drug for 300s at 363K

4.0. Conclusion

This study thoroughly evaluated the corrosion inhibition properties of Septrin and Flagyl for mild steel in a 2 M HCl solution, employing electrochemical, thermodynamic, and adsorption analyses. The findings confirmed that both drugs act as effective corrosion inhibitors, with Flagyl demonstrating superior performance over Septrin. The adsorption behavior of these drugs on the mild steel surface was well described by the Langmuir and Freundlich isotherms, indicating a physisorption mechanism. The Gibbs free energy of adsorption (ΔG_{ads}) values were calculated, showing that Septrin had values of -19.13 kJ/mol at 303 K and -22.91 kJ/mol at 363 K, while Flagyl showed values of -16.46 kJ/mol at 303 K and -19.72 kJ/mol at 363 K. These results confirm the spontaneity and stability of the adsorption process, with both drugs forming a protective layer on the mild steel surface. Electrochemical measurements revealed a significant decrease in corrosion rates with increasing concentrations of both inhibitors. For Flagyl, the corrosion rate decreased from 149.35 mm/year (without inhibitor) to 60.02 mm/year at a concentration of 75 g/L, while Septrin reduced the corrosion rate from 149.35 mm/year to 78.53 mm/year at the same concentration. The inhibition efficiencies observed were 59.8% for Flagyl and 47.4% for Septrin at 75 g/L. The data clearly indicate that Flagyl is more effective in inhibiting corrosion compared to Septrin. Thermodynamic studies indicated that the activation energy (E_a) for the corrosion process increased in the presence of the inhibitors, with values rising from 17.32 kJ/mol for the free HCl solution to 38.13 kJ/mol for Flagyl and 33.45 kJ/mol for Septrin at a concentration of 75 g/L. Surface analysis using SEM and EDX confirmed the protective effect of these inhibitors. The SEM micrographs showed that in the absence of inhibitors, the mild steel surface was severely damaged, while the presence of Flagyl and Septrin significantly improved the surface condition. EDX analysis confirmed the presence of inhibitor elements on the steel surface, indicating successful adsorption and surface protection. In conclusion, this study demonstrates that both Septrin and Flagyl are effective corrosion inhibitors for mild steel in acidic environments, with Flagyl providing a higher inhibition efficiency. The results highlight the potential of these pharmaceutical compounds as cost-effective and environmentally friendly solutions for corrosion control in industrial applications, particularly in petrochemical plants. Future research should explore the long-term stability of these inhibitors and assess their performance under more complex corrosive

conditions. While Flagyl and Septrin show potential as eco-friendly corrosion inhibitors, their moderate efficiency suggests that further optimization, long-term stability studies, and industrial-scale testing are required before recommending their widespread use in industry. Future work should focus on real-world testing in industrial settings, exploring synergistic effects with other inhibitors, and conducting a cost-benefit analysis to assess the economic feasibility of Septrin and Flagyl as corrosion inhibitors.

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