

Experimental and Theoretical Investigation on the Corrosion Inhibitor Potential of N-MEH for Mild Steel in HCl

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ABSTRACT

There are significant losses at high costs for long periods due to the corrosion and damage it causes in most industrial processes, especially the oil and gas industries. The corrosion inhibition ability of N-methyl-2-(1-(5-methyl thiophene-2-yl) ethylidene) hydrazine carbothioamide (N-MEH) was examined. It was tested on mild steel in a 1 M hydrochloric acid solution. Gravimetric measurements and scanning electron microscopy (SEM) were used to confirm the effort compound as a corrosion inhibitor. The experimental results showed that the maximum inhibition efficacy of 95.3 % was performed at an optimal inhibitory concentration of 0.005 M and 303 K using weight loss techniques. SEM indicates that N-MEH molecules are absorbed onto the surface of mild steel. As a complementary technique, density functional theory (DFT) was used to look at the interactions between N-MEH molecules and mild steel surfaces. N-MEH molecules' adsorption on the surface of mild steel follows the processes of chemical and physical absorptions and obeys the Langmuir isothermal adsorption model. Prog. Color Colorants Coat. 15 (2022), 111-122© Institute for Color Science and Technology.

1. Introduction

The dissolution of metals is generally mitigated by corrosion inhibitors, especially in aqueous solutions [1]. Hydrochloric acid is commonly used in the metallurgical industry in various processes, such as scale removal of metals, deactivation of equipment in atomic power plants, chemical or electrochemical processes in oil refineries, rocket fuel components in rocket technology [2, 3]. It is believed that organic compounds containing atoms of nitrogen, oxygen, and

sulfur have a defensive action against corrosion of various metals and alloys [4]. Many synthetic compounds have shown strong anticorrosive efficacy, but both human beings and the atmosphere are very toxic to some of these compounds. The use of natural, synthetic products as alternative corrosion prevention agents, which are harmless and environmentally friendly, has given prominence to the toxicity, protection, and environmental concerns of corrosion inhibitors. The production of non-toxic, safe, and

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efficient inhibitors, known as eco-friendly or green corrosion inhibitors, has become increasingly desirable from the standpoint of safety [5-9]. Studies have concentrated on applying non-toxic inhibitors labeled green or eco-friendly environmental inhibitors over the past couple of decades. In keeping the environment healthier, safer, and under pollution control, organic compounds from natural plants can play a major role. In their corrosion inhibition studies, several writers have used different nitrogen-containing compounds. These compounds included quaternary ammonium salts [10], polyamino-benzoquinone polymers [11], azoles [12], aniline-N-salicylidene substitute [13], amides [14], heterocyclic compounds [15], and cationic surfactants [16]. Other authors focused on inhibitors containing sulfur [17]. Some ions' effect on the inhibition efficiency of some organic compounds included in other studies. Chromium [18], iodide [19], and chloride [20] were found in these ions. Also studied was the structural effect of organic compounds as corrosion inhibitors [21]. In all these tests, the compounds' nitrogen atoms demonstrated that they could absorb very well on the metal's surface and form a protective layer, which improved corrosion inhibition with an increase in inhibitor concentration, reaching 99% inhibition in some cases [22]. No investigations were published on the uses of N-methyl-2-(1-(5-methylthiophen-2-yl) ethylidene) hydrazinecarbothioamide (N-MEH) as a corrosion inhibitor.

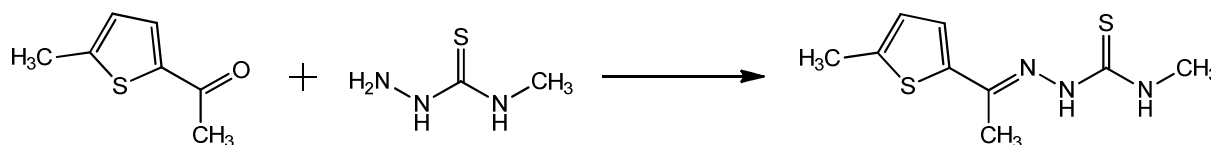
The current research investigates the impact of temperature on mild steel surfaces' corrosion inhibition in a 1 M hydrochloric acid environment. In our study, mild steel was chosen because high-temperature hydrochloric acid is commonly used in the mild and low alloy steel industries. N-MEH was prepared through a synthesis that provided a high percentage yield of this pure compound in this work. This research aims to study the effect of temperature on the corrosion inhibition of mild steel in 1 M HCl solution by N-

MEH, using weight loss measurements, and find that it is a very effective corrosion inhibitor. Therefore, this study's performance is intended to be the building block or nucleus for a new family or group of thiophene derivatives in all corrosion inhibitor studies. Density Function Theory (DFT) was used to examine the interactions between N-MEH molecules and the mild steel surface as a complementary technique. Besides, some practical, theoretical density calculations (DFT) are performed to identify the actual sites where adsorption of inhibitors occurs on the surface of mild steel. The N-MEH molecules adsorb during the processes of chemisorption and physisorption on the mild steel surface. The isothermal adsorption model follows Langmuir.

2. Experimental

2.1. Synthesis of N-MEH

An ethanolic solution of equimolar quantities of 1-(5-methylthiophen-2-yl) ethenone and methylthiosemicarbazide, was refluxed for 2 hours. Few drops of acetic acid were added with continually refluxing for another 3 hours (Scheme 1). N-MEH's purity was confirmed by thin-layer chromatography (TLC) and filtered, washed with ethanol, and dried, yielding 54 %, M.P. 175-177 °C. The product was characterized by spectroscopic (FT-IR, ¹H-NMR, and ¹³C-NMR) and CHN elemental analysis techniques. 3342.84 and 3265.17, for N-H; 2941.52, for C-H aliphatic; 1570.4 for C=N and 1001.63 for C=S. ¹H-NMR, DMSO-d₆, δ: 2.31 ppm (3H, s, CH₃); 2.54 ppm (3H, s, CH₃); 2.97 ppm (3H, s, CH₃), 6.83 ppm (1H, m, thiophene ring); 7.19 ppm (1H, d, thiophene ring); 7.31 ppm (1H, d, NH) and 9.49 ppm (1H, d, NH). ¹³C-NMR, DMSO-d₆, δ: 14.8; 15.1; 32.2; 121.9; 126.4; 127.5; 142.9; 151.3 and 177.9. CHN-micro elemental analysis (Calculated/Found): C, 47.55/47.90; H, 5.76/5.59; N, 18.48/18.13.



Scheme 1: Synthetic route of N-MEH.

2.2. Composition of material samples

The mild steel coupons (2.0 cm × 2.5 cm × 0.1 cm) having a composition, 0.21 wt % carbon, 0.09 wt % phosphorus, 0.05 wt % manganese, 0.038 wt % silicon, 0.01 wt % aluminum, 0.050 wt % sulfur, and iron (balance) have been utilized in the current investigation. The specimen surface was mechanically polished with various emery papers to prepare the samples for before each test. After that, the specimens were rinsed with double-distilled water, then degreased with acetone, and finally dried with a desiccator. Hydrochloric acid solution (1 M) was freshly prepared by diluting an appropriate volume of analytical grade 37 % hydrochloric acid with distilled water.

2.3. Weight loss measurements

The measurements were conducted in aerated, non-stirred, freshly prepared hydrochloric acid solution. Gravimetric techniques were evaluated by subtracting the weight in the N-MEH's absence and presence as a new corrosion inhibitor in a 1 M hydrochloric acid environment. different concentrations of N-MEH i.e., 0.001, 0.002, 0.003, 0.004 and 0.005 (M) in corrosive environments were utilized as electrolytes for gravimetric techniques. The period of immersion times 1, 2, 5, 10, and 24 h were used for weight loss measurements. During experiments, each electrolyte's temperature was held constant using a thermostatically regulated water bath, and coupons were immersed in the electrolytes mentioned above at 303, 313, 323, and 333 K for five h. All tests were conducted in triplicate, and the average values of weight loss were calculated to gain reproducibility. From the gravimetric data, the corrosion rate (C_R) surface coverage (θ) and inhibition efficiency (IE) were calculated according to the ASTM standards and by using Equations 1-3 [23, 24].

$$C_R(mmpy) = \frac{87.6W}{dat} \quad (1)$$

W is the weight loss, d is the density a is the surface area, and t is the immersion time.

$$IE\% = \frac{C_{R(without\ inh)} - C_{R(with\ inh)}}{C_{R(without\ inh)}} \times 100 \quad (2)$$

$$\theta = \frac{C_{R(without\ inh)} - C_{R(with\ inh)}}{C_{R(without\ inh)}} \quad (3)$$

2.4. Surface analysis

The mild steel surface was first abraded using various emery paper grades and washed with double distilled water before exposure the coupons for five h in corrosive solution without and with the addition of the synthesized inhibitor (0.005 M). After the exposure period, the coupons were washed with double distilled water and dried. The mild steel surface was investigated using a scanning electron microscope (SEM, TM1000 Hitachi Tabletop Microscope).

2.5. Computational study

A computational quantum chemical modeling technique was conducted using density-functional theory (DFT) to measure the N-MEH molecule's electronic structure. The physical properties of N-MEH molecule were performed using DFT/B3LYP with a 6-31G basis package, and the geometry optimization of N-MEH molecule was obtained. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) as frontier molecular orbitals were used to estimate important parameters, such as energy gap (ΔE), global hardness (η), softness (σ), absolute electronegativity (χ), and the number of transferred electrons (ΔN) according to Equations 4-8, [25, 26]:

$$\Delta E = E_{HOMO} - E_{LUMO} \quad (4)$$

$$\eta = -\frac{E_{HOMO} - E_{LUMO}}{2} \quad (5)$$

$$\sigma = \frac{1}{\eta} \quad (6)$$

$$\chi = -\frac{E_{HOMO} + E_{LUMO}}{2} \quad (7)$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{in}}{2(\eta_{Fe} + \eta_{in})} \quad (8)$$

where χ_{Fe} and η_{Fe} were 7 and 0 eV mol⁻¹, respectively.

3. Results and Discussion

3.1. Synthesis and structure elucidation of the synthesized inhibitor

The refluxation of 1-(5-methylthiophen-2-yl) ethanone with methylthiosemicarbazide in ethanolic solution yield N-methyl-2-(1-(5-methylthiophen-2-yl) ethylidene) hydrazinecarbothioamide (N-MEH). FT-IR, proton and carbon NMR, and CHN-analysis were

used to characterize N-MEH as a corrosion inhibitor. The FTIR spectrum of N-MEH as corrosion inhibitor exhibited stretching frequency band for the $\nu(\text{C}=\text{N})$ at 1570.4 cm^{-1} and for $\nu(\text{C}-\text{S})$ at 1001.63 cm^{-1} . The carbonyl stretching frequency $\nu(\text{C}=\text{O})$ band around 1700 cm^{-1} disappears, and the $\text{C}=\text{N}$ stretching frequency in the spectrum of FTIR for the N-MEH appears to confirm that the double bond between carbon and nitrogen ($\text{C}=\text{N}$) formed, and N-MEH was indeed synthesized through the condensation reaction. The new corrosion inhibitor's proton NMR spectrum displayed a signal related to the H-imino proton ($\text{C}=\text{N}$), demonstrating the target compound's formation.

3.2. Weight loss measurements

The C.R. of mild steel was determined by weight loss measurement in 1 M HCl at 303, 313, 323, and 333 K in the presence of N-MEH. The quantitative information is presented in Figure 1. The appreciable decrease in weight loss was observed with the increase in N-MEH concentration at each temperature from these results. For example, the mild steel C_R was 6.73 mmpy in the acidic solution with a low inhibitor concentration. It decreased to the optimum N-MEH concentration of 2.0 mmpy at 303 K. The weight loss experimental findings for mild steel coupons in hydrochloric acid solution in the absence and presence

N-MEH are shown in Figure 1. Weight loss techniques are a dependable method utilized to optimize the concentrations of investigated inhibitors on the rate of corrosion and inhibition efficiency at different exposure periods [27]. The weight loss experimental findings revealed that the addition of N-MEH to the tested medium prevents coupon corrosion, reduces the rate of corrosion, and increases the inhibition efficiency with the increase in the concentration of rate (Figure 1). N-MEH had significant inhibition efficiency (95.3 %) at 0.005 M for five h of exposure. Also, because of nitrogen and sulfur heteroatoms in the inhibitor molecules, the excellent inhibitive behavior is due to N-MEH molecules' reaction with the surface of mild steel. Moreover, the resonance effect and N-MEH molecules' stability may be related to N-MEH's significant inhibition efficiency.

3.3. Effect of immersion time

When elucidating the impact of corrosion inhibitor, time is a significant parameter. N-MEH's film stability and adsorption rate have been investigated at various exposure times (1, 5, 10, and 24 h). The results from the effect of immersion time on the corrosion rate and the synthesized corrosion inhibitor's inhibition efficiency are examined and shown in Figure 1.

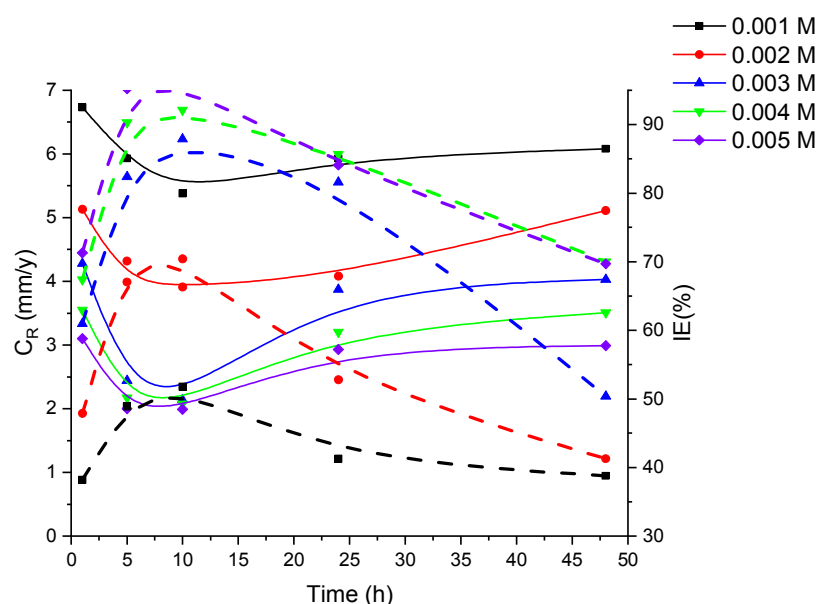


Figure 1: Variation of corrosion rate and inhibition efficiency with concentration of inhibitor for various immersion time at room temperature in 1M HCl.

At an immersion time of 5 h, the highest inhibition activity of the tested inhibitor was achieved. The high-speed adsorption of the N-MEH molecules on the coupon surface may be due to this result. Rapid adsorption of the N-MEH molecules on the mild steel surface was due to the active functional groups in the molecular structures of N-MEH molecules. At 24 h of immersion, inhibition efficiency for the tested inhibitor becomes decreased. The drop in inhibition efficiency was due to the desorption of N-MEH molecules from the testing coupon surface. Moreover, the rate of corrosion increased surprisingly with a more extended immersion period. The desorption of N-MEH molecules from the coupon surface may be due to these findings.

3.4. Effect of temperature

The effect of temperature on the corrosion rate and inhibitive activity of the N-MEH studied. The corrosion rate decreased with N-MEH's addition due to the N-MEH molecules' potential interactions with the coupon surface, which form a protective layer by the adsorbed N-MEH molecules on the coupon surface. It separated the coupon surface from the hydrochloric

acid solution. Weight loss measurements have studied the variation in corrosion rate at various solution temperatures (303, 313, 323, and 333 K). The change in the corrosion rate versus temperature shown in Figure 2 calculated by utilizing the Arrhenius plot according to Eq. 9:

$$\ln C_R = \ln A - \frac{E_a}{RT} \quad (9)$$

The activation energy value in N-MEH molecules' presence suggests that the inhibitor molecules were adsorbed on the coupon surface by chemisorption mechanism. The weight loss calculations results are exhibit in Figure 3. The IE % of N-MEH decreased with increasing temperatures. In the current investigation, N-MEH's inhibition efficiency was 95.3 % at 303 K but became 79.8 % at 333 K. At a higher temperature of the tested solution, the considered mechanism is exothermic. N-MEH has an excellent inhibition efficiency in the HCl medium with room temperature but has a low inhibitive performance at 333 k. Figure 3 shows that the inhibition efficiency of the N-MEH dropped when the temperature rises.

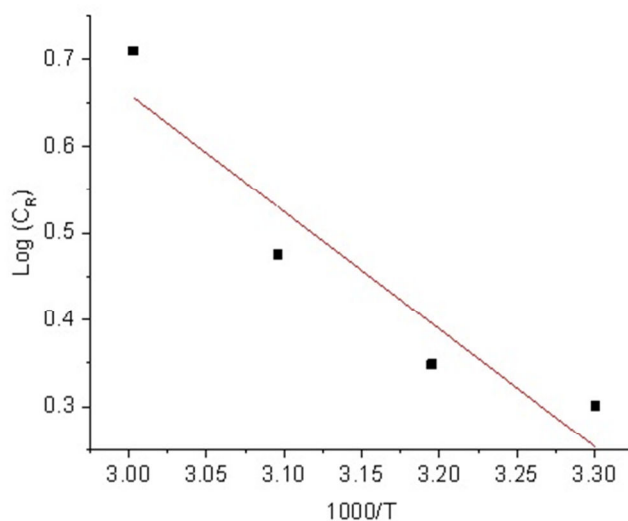


Figure 2: The Arrhenius plot for mild steel corrosion in acidic solution in the presence of N-MEH (0.005 M) at various temperatures.

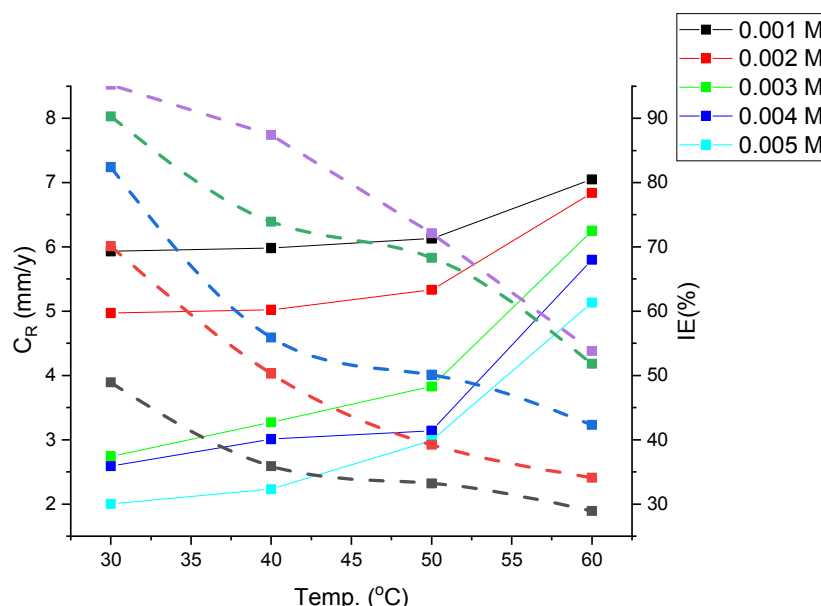


Figure 3: Variation of corrosion rate and inhibition efficiency with a concentration of inhibitor for various temperature in 1M HCl.

Table 1: Adsorption characters on tested coupon surface by N-MEH from Langmuir, Temkin, and Freundlich adsorption models.

Inhibitor	Adsorption Isotherms		
	Langmuir (R ²)	Temkin (R ²)	Freundlich (R ²)
N-MEH	0.993	0.955	0.939

3.5. Adsorption isotherms

Generally, in acid corrosion, it is believed that inhibitor molecules work on the metal surface via an adsorption mechanism. The structural charge of a double layer can be calculated by the inhibitor molecules' adsorption, thereby reducing the rate of partial electrochemical reactions. Furthermore, adsorption, which occurs mainly at the metal surface's active sites, can impede the metal reactivity during the dissolution process. Besides, if the inhibitor molecules' reduction obeys the absorption, the solid film may form a barrier. Anyway, knowledge of the inhibitor molecules' adsorption behavior is significant to determine its mechanism of action. An adsorption isotherm shows the relationship between the adsorbate molecules' interface coverage and the material's solution concentration.

The weight loss technique obtained the surface coverage (θ) for N-MEH. It was used to evaluate the adsorption isotherm model. It is essential to research adsorption isotherms to understand the essence of the

interactions between the inhibitor molecules and the mild steel surface. These molecules can be adsorbed by physical or chemical reactions on the coupon surface. According to different adsorption isotherms, like Langmuir, Temkin, and Freundlich isotherms, the adsorption isotherm phenomenon can be understood. The adsorption parameters of the Langmuir, Temkin, and Freundlich isotherms for tested inhibitors are described in Table 1.

The adsorbent type of inhibitor's performance can be understanding by fitting the data into one of the known isotherms of adsorption represented in Figure 4. The adsorption of N-MEH molecules on the surface of mild steel obeys the Langmuir isothermal adsorption model. The Langmuir isotherm for N-MEH matches well with the regression coefficient value (R^2). Both values of slope and intercept obtained for the Langmuir model are 0.1796 and 0.7642, respectively [28, 29]. The plot between C/θ and C of the Langmuir model is shown in Figure 4. K_{ads} was evaluated by Eq. 10:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (10)$$

The Langmuir model plot gives a straight line which is quite significant to determine the free energy (ΔG_{ads}). The relation between ΔG_{ads} and K_{ads} may be determined according to Eq. 11 [30, 31]:

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}}) \quad (11)$$

where 55.5 is water concentration, R is gaseous constant, and T is the absolute temperature.

The importance of ΔG_{ads} appeared in evaluating the interaction nature and relation between N-MEH molecules and the coupon surface. It was proved in literature reviews [32, 33] that if $\Delta G_{\text{ads}} \leq -20 \text{ kJ mol}^{-1}$ refers, the interaction of adsorption is physical adsorption, and if $\Delta G_{\text{ads}} \geq -40 \text{ kJ mol}^{-1}$ indicates that the interaction is chemical adsorption. The ΔG_{ads} value N-MEH $40.02 \text{ kJ mol}^{-1}$. This value proposed that the interactive nature of N-MEH molecules on the tested coupon surface is chemisorption. Thus, the adsorption isotherms of N-MEH molecules as a corrosion inhibitor on a mild steel surface might be initially a process of physical adsorption. But, the adsorption-dominant model was suggested by ΔG_{ads} value can be

categorized as chemical adsorption.

3.6. SEM studies

Figure 5 describes the images of mild steel surface coupons in the absence and presence of 0.005 M of N-MEH after five h exposure to 1 M hydrochloric acid solution. In the lack of N-MEH, the mild steel surface is represented in Figure 5a, with an extreme corrosion attack in the case of immersion in 1 M hydrochloric acid solution for 5 h. It is evident that the mild steel surface suffered a significant shift from the previous one when the N-MEH was added to the test solution, and the surface of coupon was generally smoother, as shown in Figure 5b. It is presumed that creating a protective layer is randomly distributed on the entire surface of the mild steel. This may be due to the adsorption at the coupon surface and the formation of an N-MEH molecule protective layer that blocks the active sites present on the coupon's surface. Moreover, the interaction of N-MEH molecules with the active sites on the coupon surface, causing a reduce in the contact between coupon surface and the hydrochloric acid environment and sequentially showing significant corrosion inhibition characteristics.

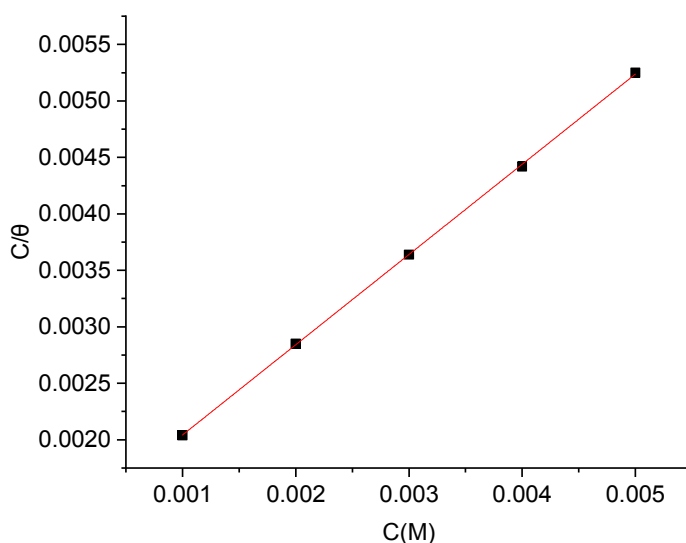


Figure 4: Langmuir adsorption model of N-MEH.

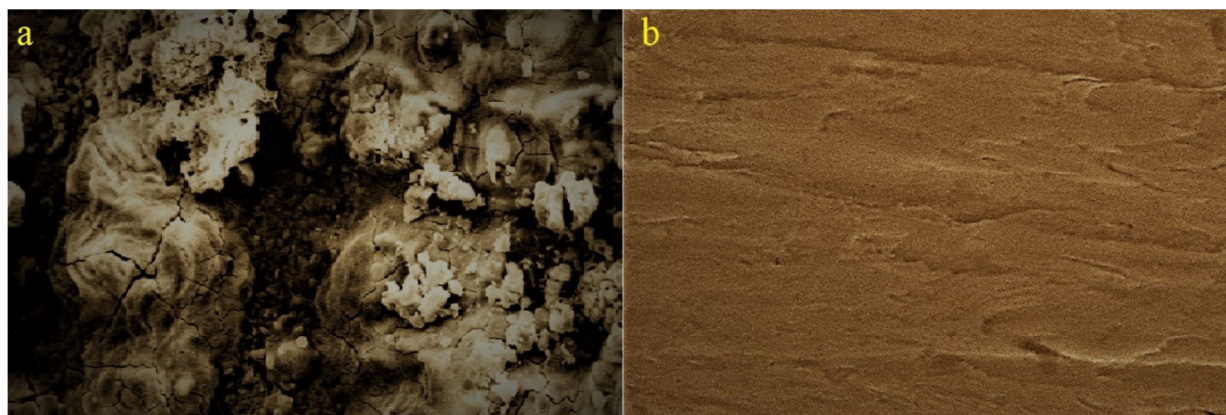


Figure 5: SEM micrographs of coupon surface, (a) in the absence of inhibitor, and (b) coupon surface in the absence of inhibitor at 0.005 M.

3.7. DFT analysis

DFT parameters are pretty valuable for predicting additional data on the inhibitive performance and inhibition mechanism. The inhibition activity is related with quantum chemical factors, namely, frontier M.O.s (Highest Occupied MO "HOMO" and Lowest Unoccupied MO "LUMO"), energy gap (ΔE), electronegativity (χ), global hardness (η), softness (σ), a fraction of transferred electrons (ΔN , and atomic charges. These parameters are demonstrated in the optimization of the studied inhibitor molecule [34]. Table 2 displayed the DFT parameters calculated by DFT for the N-MEH molecule.

The N-MEH optimized molecular structure is demonstrated in Figure 6. DFT studied were utilized to investigate interactions between N-MEH molecules and coupon surface. The Highest Occupied MO value refers to the inhibitor molecule's ability to give electrons to iron's vacant d-orbitals. The Lowest Unoccupied MO value indicates the N-MEH molecule's ability to accept electrons from iron. Unoccupied MO value's low value infers that an inhibitor molecule can get electrons from iron through a back-donation mechanism. The ΔE with a high value represents a significant inhibition efficiency. The other vital factors which provide essential data about molecular stability and reactivity were η and σ [35]. The complicated molecules have a high energy gap, and the soft molecules have a low energy gap. So, the molecules with a high value of softness and a low value of global hardness would have significant inhibitive efficiency [36].

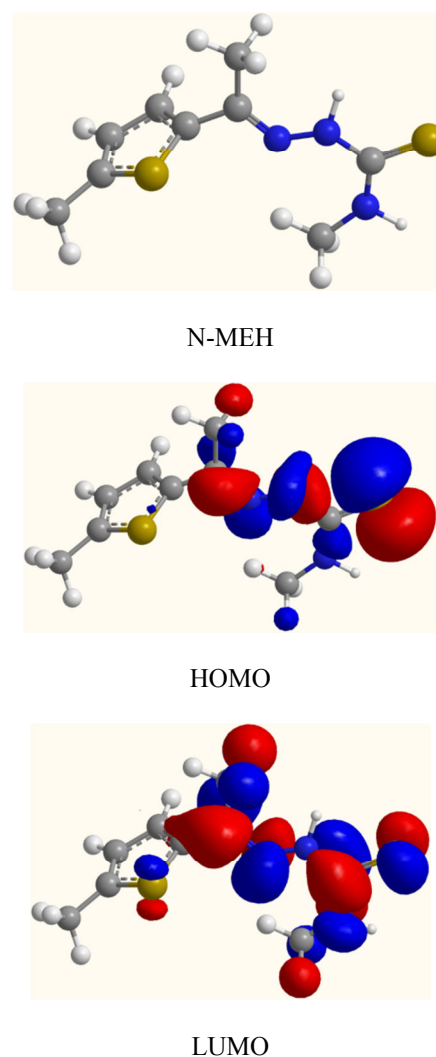
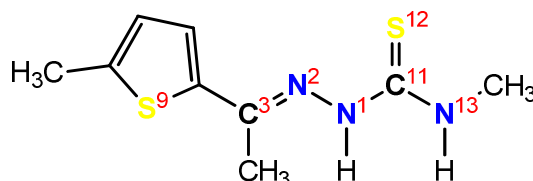


Figure 6: Optimized structure, Highest Occupied MO, and Lowest Unoccupied MO of N-MEH molecules.

Table 2: Quantum chemical parameters of N-MEH.

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η	σ	χ (eV)	ΔN
N-MEH	-8.883	-1.982	6.901	4.4415	0.225149	5.4325	1.9

Table 3: Atomic charges of N-MEH molecule.

Inhibitor	Charges						
	N ₁	N ₂	N ₁₃	S ₉	S ₁₂	C ₄	C ₅
N-MEH	-0.2679	-0.0522	-0.3022	-0.576	-0.3288	-0.2088	-0.3462

Molecules with a high value of σ will readily be adsorbed on the coupon surface [37]. The Highest Occupied MO value of the studied inhibitor is relatively high, which fits the experimental findings' results. Atomic charges of the inhibitor molecule are essential to evaluate the adsorption sites. Inhibitor molecules with high negative charges have good abilities to be adsorbed on the coupon surface [38]. Table 3 displayed that nitrogen and sulfur atoms possess the highest negative charge. So, the high negative atomic charges can coordinate with the d-orbital of Fe-atoms. The experimental findings proposed that N-MEH formed strong coordination bonds with the mild steel surface and showed significant inhibitive efficiency (95.3 %).

4. Conclusions

A new corrosion inhibitor, namely, N-methyl-2-(1-(5-methylthiophen-2-yl) ethylidene) hydrazine

carbothioamide (N-MEH), was synthesized. Its chemical structure was elucidated by spectroscopically techniques (FT-IR, ^1H -NMR, and ^{13}C -NMR) and CHN micro-elemental measurements. Gravimetric methods determined the inhibition efficiency. N-MEH exhibited considerable inhibition efficiency of 95.3 % at 0.005 M. The methodological findings revealed that raising temperature would increase the corrosion rate and reduce N-MEH inhibition efficiency as a tested corrosion inhibitor. The adsorption isotherm obeys the Langmuir isotherm model. The high negative value of ΔG_{ads} elucidates that N-MEH molecules can be adsorbed on the coupon surface through the chemisorption mechanism. SEM studies of N-MEH as a tested corrosion inhibitor for mild steel surface in 1 M hydrochloric acid solution confirmed the formation of a protective film on the coupon surface. The DFT calculations and methodological results were in good agreement.

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