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N-Methyl-2-(1-(5-methylthiophen-2-yl)ethylidene) hydrazinecarbothioamide as Corrosion Inhibitor for Mild Steel in HCl Solution: Weight Loss and DFT Investigations

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ABSTRACT

For This study investigated the corrosion inhibition performance of N-methyl-2-(1-(5-methylthiophen-2yl)ethylidene)hydrazinecarbothioamide (MTET) on mild steel in hydrochloric acid (HCl) solution using weight loss and density functional theory (DFT) methods. The effects of temperature were also studied at the range of 303 to 333 K. The corrosion inhibition efficiency of MTET increased with increasing concentration and exposure time, while it decreased with increasing temperature. At the highest concentration of 0.0005 M, the inhibition efficiency reached 95.5% after 5 hours of immersion time. The Langmuir adsorption isotherm was found to describe the adsorption behavior of MTET on the mild steel surface, and the free energy value indicated that the inhibition process was both chemical and physical in nature. DFT calculations showed that the adsorption of MTET on the mild steel surface involved the formation of chemical bonds between the nitrogen and sulfur atoms of MTET and the iron atoms of mild steel. Overall, the results suggest that MTET is an effective inhibitor for mild steel corrosion in HCl solution, and the DFT calculations provide valuable insights into the underlying mechanisms of the inhibition process.

1. INTRODUCTION

Iron and its alloys are extensively used in industrial construction due to their excellent mechanical durability, easy processing, and low production cost [1,2]. However, steel is often exposed to corrosive environments, such as acidic solutions during etching, acid pickling, acid descaling, acid cleaning, and oil-well acidification [3]. Steel alloys are highly susceptible to corrosion in acidic conditions, resulting in significant economic losses. Therefore, there is a significant need for effective corrosion-control technologies. Mild steel is a widely used material in engineering and has significant industrial importance, especially in construction, petroleum, metal-processing, chemical processing, and marine industries [4,5]. However, it is highly susceptible to corrosion in aggressive environments such as acidic and chloride solutions, which limits its usefulness [6]. To address this issue, the development of cost-effective and eco-friendly corrosion inhibitors is in high demand. Many inhibitors have been reported to date that interact with the metal surface to reduce its vulnerability to corrosive agents by decreasing the current density and halting its dissolution [7,8]. Organic compounds containing heteroatoms such as O, N, and S, or a π-bond, are reported to have high corrosion inhibition efficiencies [9-11]. These inhibitors are usually synthetic compounds formed by condensation of amino, hydroxyl, or carbonyl functionalities. They can interact with metals via a lone pair of electrons present on the heteroatom or the pi electronic cloud and adsorb on the surface [12]. However, such inhibitors may have toxicity issues during synthesis or utility, leading to the need for eco-friendly corrosion inhibitors [13-15]. Consequently, scientists are turning their focus toward natural substances such as plant extracts [16,17] and amino acids [18-20]. We focused on synthesizing a novel Schiff base for acid corrosion inhibition of mild steel that can serve as a multifunctional protective agent. The compound was derived from the reaction between N-methyl-2-(1-(5-methylthiophen-2-yl)ethylidene)hydrazinecarbothioamide (MTET), a thiophen derivative, and a thiosemicarbazide derivative (as shown in Figure 1). The results of our study demonstrate that this inhibitor has potential as a novel corrosion inhibitor. We investigated the inhibition efficiency of MTET on mild steel corrosion in an HCl solution using a weight-loss technique and correlated the experimental results with quantum chemical calculations employing density functional theory (DFT). These calculations were used to explain how the inhibitor interacts with the mild steel surface to effectively coordinate with it.

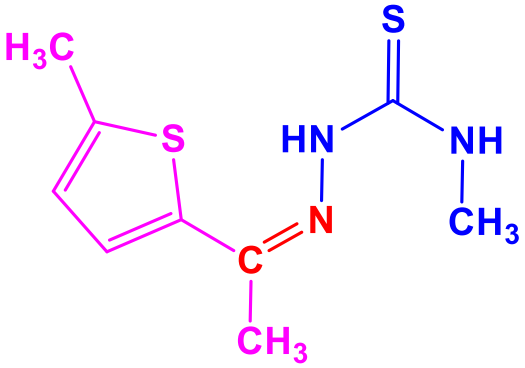

Fig. 1. MTET chemical structure.

2. EXPERIMENTAL

2.1 Synthesis of MTET

The synthesis of the compound involved refluxing 1-(5-methylthiophen-2-yl)ethanone (0.1 mmol) in 100 mL ethyl alcohol with N-methylhydrazinecarbothioamide (0.1 mmol) and a few drops of glacial acetic acid for 8 hours. The resulting solid was recrystallized from ethyl alcohol, yielding a 61% yield. Various spectroscopic techniques were used to characterize the brown product. FTIR: 3321.5 and 3239.8 cm^{-1} (N–H, amines), 2938.5 cm^{-1} (C–H, aliphatic), 1549.3 cm^{-1} (C=N, imine), 1142.4 and 1057.2 cm^{-1} (C-O, sy and asy). ^{1}H-NMR ($CDCl_3$-600 MHz): δ 2.17 (3H, s, -C-CH3), 2.29 (3H, s, -C-CH_3), 2.66 (3H, s, N-CH_3),6.95 (1H, d, C-H thiophene, *J* = 8.1 Hz), and 7.27 (1H, d, C-H thiophene, *J* = 8.1 Hz). ^{13}C NMR: δ 14.1 (1C, s, CH_3), 15.8 (1C, s, CH_3), 28.9 (1C, s, CH_3), 127.1 (1C, s), 127.8 (1C, s), 140.1 (1C, s), 141.7 (1C, s), 156.1 (1C, s), 179.5 (1C, s).

2.2 Materials

Table 1 shows the elemental analysis of the mild steel sample used in the gravimeter measurements.

Table 1. Chemical composition (wt%) of mild steel samples.

C%	**Mn%**	**Si%**	**Al%**	**S%**	**P%**	**Fe**
0.21	0.05	0.38	0.01	0.05	0.09	balance

The solubility of PMBMH in a 1 M hydrochloric acid solution was determined by diluting 37% HCl (Merck-Malaysia) in double-distilled water. The experiment involved measuring the effect of different concentrations of PMBMH (0.0001, 0.0002, 0.0003, 0.0004, 0.0005, and 0.001 M) at various immersion times (1, 5, 10, 24, and 48 h) both with and without the inhibitor. The effect of temperature (303, 313, 323, and 333 K) was also studied for various inhibitor concentrations with an immersion time of 5 h.

2.3 Weight-loss techniques

The article outlines the methodology used for weight-loss measurements, which followed the procedures as described in references [21-23]. Mild-steel specimens were prepared by cleaning, polishing, and weighing, and then submerged in a 1 M HCl solution at temperatures ranging from 303 K to 333 K. The specimens were exposed to the solution for varying lengths of time (1, 5, 10, 24, and 48 hours) while being treated with different amounts of inhibitor. In order to ensure reproducibility, each measurement was performed three times, and only the average results were presented. The corrosion rate, inhibition efficiency and surface coverage area were subsequently calculated using Equations (1) to (3).

$$C_R = \frac{87600W}{atd} \tag{1}$$

$$IE\% = \frac{C_{R(o)} - C_{R(inh)}}{C_{R(o)}} \times 100 \tag{2}$$

$$\theta = \frac{C_{R(o)} - C_{R(inh)}}{C_{R(o)}} \tag{3}$$

The weight loss of the mild steel specimen (W, g), the surface area of the mild steel (a, cm2), and the exposure time (t, h) were used to calculate the rate of corrosion, taking into account the density of the mild steel (d, gcm^{-3}). $C_{R(o)}$ represents the corrosion rate in the absence of MTET, while $C_{R(inh)}$ represents the corrosion rate in the presence of MTET.

2.4 DFT investigations

Recently, researchers have conducted conceptual computations to replicate experimental observations using ChemOffice software. Quantum chemical computations were carried out using the conventional theory of Becke's three-parameter hybrid functional (B3LYP) level with a Gaussian 03 version, taking the 6-31G set as the reference to analyze the chemical reactivity of the MTET molecule in the gas phase. Various quantum parameters such as energy gap (ΔE), fraction of electron transfer (ΔN), dipole moment (μ), ionization energy (I), electron affinity (A), absolute electronegativity (χ), hardness (η), and softness (σ) were produced using the investigated approach [24-30]. Equations (4)–(9) were used to compute quantum chemical parameters, including χ, η, σ, and ΔN.

$$I = -E_{HOMO} \tag{4}$$

$$A = -E_{LUMO} \tag{5}$$

$$\chi = \frac{I + A}{2} \tag{6}$$

$$\eta = \frac{I - A}{2} \tag{7}$$

$$\sigma = \frac{1}{\eta} \tag{8}$$

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} - \eta)} \tag{9}$$

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The corrosion rates and inhibition efficiency of the corrosion inhibitor were assessed at various concentrations (0.0001, 0.0002, 0.0003, 0.0004, 0.0005, and 0.0010 M) and temperatures (303-333 K) using weight-loss measurements, and the results are depicted in Figure 2 and Figure 3. The synthesized inhibitor, MTET, proved to be effective in reducing mild-steel corrosion. Figure 2 displays the effect of MTET concentration on the corrosion rate and inhibition efficiency. The results showed that increasing the inhibitor concentration led to a reduction in the corrosion rate and an improvement in inhibition, particularly at 303 K. This suggests that higher concentrations of inhibitor lead to a greater adsorption of inhibitor molecules onto the metal substrate, which leads to wider surface coverage, and hence limited contact between the metal and acid solution. The highest inhibition efficiency of MTET was observed at a concentration of 0.0005, with an inhibition effectiveness of 95.5% [31-36].

The impact of corrosion inhibitors at different concentrations on mild steel in 1 M HCl solution varies, and higher concentrations generally provide better protection against corrosion. However, optimal concentrations may depend on the inhibitor and other factors such as temperature and the presence of other ions in the solution. Additionally, some inhibitors may lose effectiveness or even become corrosive at high concentrations. Therefore, consulting relevant literature and specific studies is advisable for accurate information on the chosen inhibitor.

One study examined the performance of various organic corrosion inhibitors, including imidazole, benzotriazole, and 2-mercaptobenzothiazole, in 1 M HCl solution, showing that higher inhibitor concentrations led to lower corrosion rates, but the optimal concentration varied depending on the inhibitor type. Similarly, another study analyzed the effect of different concentrations of pomegranate peel extract as a natural inhibitor on mild steel corrosion in 1 M HCl solution, and found that the corrosion rate decreased with increasing inhibitor concentration, but the inhibition efficiency reached a maximum at a specific concentration. In another study, castor oil was used as a green inhibitor, and the researchers found that the corrosion rate decreased with increasing inhibitor concentration up to a certain point, after which the inhibition efficiency decreased. Overall, the effectiveness of different concentrations of corrosion inhibitors on mild steel corrosion in acid solutions is complicated and varies depending on various factors, including the inhibitor type, concentration, and solution conditions.

The effect of different concentrations and immersion periods of MTET on mild steel corrosion in 1 M HCl solution at 303 K was investigated (Figure 2). As shown in Figure 2, increasing the MTET concentration led to a significant reduction in the corrosion rate. For instance, at 0.001 M MTET concentration, the corrosion rate decreased by almost 70% compared to 0.0001 M. The immersion time also played a crucial role in the corrosion inhibition. Longer immersion times resulted in better corrosion protection. At 0.001 M MTET concentration, the corrosion rate was the lowest after 48 h of immersion, with a 69% decrease compared to the 1-hour immersion time. These findings suggest that MTET could be a potential alternative to conventional corrosion inhibitors for protecting metal surfaces.

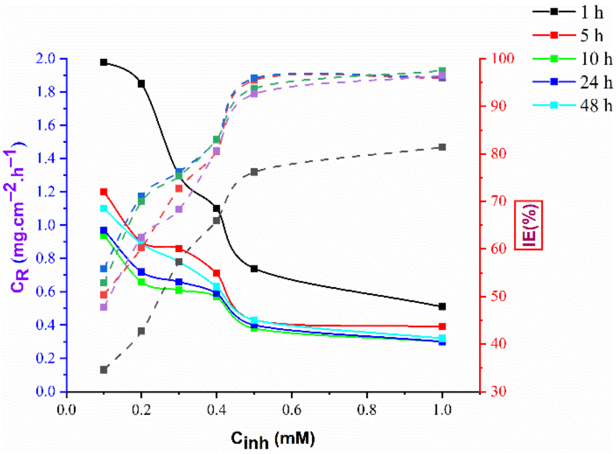

Fig. 2. Investigating the impact of different concentrations of MTET on metallic coupons' corrosion rate and inhibition effectiveness when immersed in 1 M HCl for varying time intervals at a temperature of 303 K.

The inhibitory effect of MTET at various concentrations (0.1000–0.001 M) on metallic substrate corrosion was analyzed using the mass reduction technique. The metallic samples were immersed in a corrosive solution for 5 hours at different temperatures ranging from 303 to 333 K. The results depicted in Figure 3 illustrate that the corrosion rate increased while the inhibition efficiency decreased as the temperature increased from 303 to 333 K for the same concentration of MTET. This suggests that temperature has a significant impact on the effectiveness of MTET as a corrosion inhibitor. As the temperature rises, the activity of the corrosive species in the solution increases, thereby diminishing the corrosion inhibition effect of MTET. Additionally, the reduction in inhibition efficiency at elevated temperatures can be attributed to the thermodynamic instability of MTET. At higher temperatures, the chemical compound breaks down, rendering it less effective in inhibiting corrosion [37].

Moreover, a rise in temperature could accelerate the reaction between MTET and the metallic substrate, causing the inhibitor to be consumed and reducing its inhibition efficiency. Therefore, temperature is a critical factor in determining the effectiveness of MTET as a corrosion inhibitor. The efficiency of MTET was highest at 303 K, and a decline in inhibitory potency was observed at higher temperatures for all doses, indicating physisorption. At high temperatures, MTET molecules were lost from the metallic surface due to desorption [38].

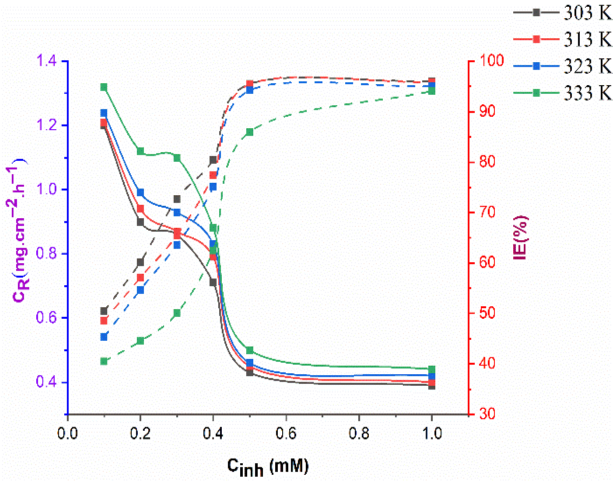

Fig. 3. The impact of MTET concentration on the rate of corrosion and inhibition efficiency of metallic coupons in 1 M HCl was studied for a period of 5 hours at various temperatures.

The inhibition efficiency of MTET was evaluated at various temperatures (303, 313, 323, and 333 K) and concentrations (0.0005 M and 0.001 M). The results depicted in Figure 4 demonstrate that MTET exhibited significant inhibition efficiency at 0.0005 M, with inhibitive performance of 95.5% at 303 K, 95.4% at 313 K, 94.2% at 323 K, and 80% at 333 K. Similarly, at 0.001 M, the inhibition efficiencies were 96% at 303 K, 95.8% at 313 K, 95% at 323 K, and 94.1% at 333 K. As the temperature increased, the inhibition efficiency of MTET slightly decreased, especially at the highest inhibitor concentration (0.001 M). These results can be explained by referring to both chemisorption and physisorption mechanisms. The interaction between MTET molecules and the iron atoms on the mild steel surface, forming coordination bonds through the transfer of ion pairs of heteroatoms from the inhibitor molecules to Fe-orbitals, is an example of chemical adsorption. In contrast, the interactions between the mild steel surface and MTET molecules due to van der Waals forces are an example of physical adsorption. Thus, the inhibition efficiency of MTET primarily depends on the environmental temperature. The reduction in inhibitive performance at elevated temperatures can be attributed to both chemical and physical adsorption mechanisms. These findings can help optimize the conditions for utilizing MTET as a corrosion inhibitor for mild steel.

3.2 Adsorption isotherm

Understanding the interaction mechanism between the inhibitor particles and the mild steel surface is facilitated by the adsorption isotherm. Gravimetric tests were performed to gather surface coverage (θ) values for the inhibitor, and three different isotherm models - Temkin, Freundlich, and Langmuir - were used to analyze the adsorption mechanism. The Langmuir isotherm model was found to best describe the adsorption process, indicating a monolayer adsorption where metal ions were adsorbed onto the adsorbent surface at a fixed maximum capacity. The Temkin isotherm model suggested that the adsorption process was controlled by the heat of adsorption, indicating physisorption. On the other hand, the Freundlich isotherm model indicated that the adsorption process was controlled by the heterogeneity of the adsorbent surface, and that the adsorption was a multi-layer process. These results indicate that the adsorption of metal ions onto the adsorbent was a combination of physisorption and chemisorption, with physisorption being the dominant mechanism. The Langmuir isotherm model is a useful tool for determining the maximum capacity of the adsorbent and the metal ion uptake under different conditions. The Temkin and Freundlich isotherms provide insight into the nature of the adsorption process and the role of heat and surface heterogeneity, respectively. These findings lay a foundation for the design and optimization of adsorption processes for removing metal ions from aqueous solutions. The inhibitor molecules attached to the metallic substrate can be physically or chemically adsorbed. The computed slope and intercept values for the Langmuir isotherm were 0.904 ± 0.046 and 1.238E-4 ± 2.35E-5, respectively, indicating that the Langmuir adsorption isotherms fit the data well, as shown by the regression coefficient (R2) of 0.9896 for MTET. Figure 4 depicts the adsorption isotherm plot of Langmuir between C_{inh}/θ and C_{inh} . Using Equation (10), the adsorption parameters can be determined:

$$C_{inh}/\theta = (K_{ads})^{-1} + C \qquad (10)$$

where C_{inh} is the concentration of MTET and K_{ads} is the constant.

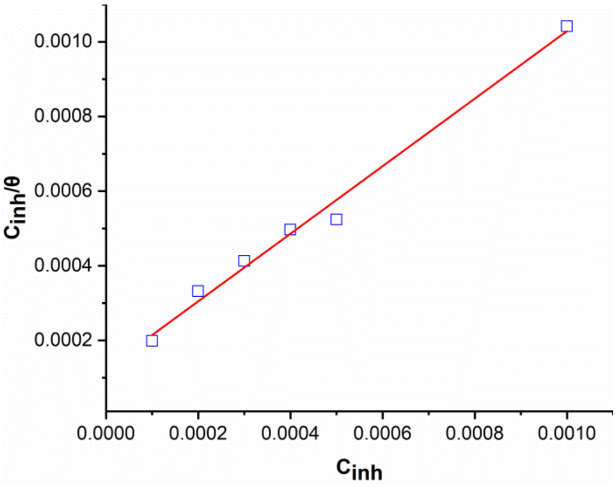

Fig. 4. Langmuir isotherm for metallic coupon in inhibited acidic solution.

To determine the adsorption free energy ΔG^{o}_{ads} and K_{ads}, the plot between C/θ and C was evaluated. Equation (11) was used to calculate these parameters, which involves the molar concentration of water (represented by 55.5), the universal gas constant (denoted by R), and the absolute temperature (denoted by T).

The equation is as follows:

$$\Delta G^{o}_{ads} = -RT\, ln(55.5K_{ads}) \qquad (11)$$

The type of adsorption mechanism can be determined by the adsorption free energy ΔG^{o}_{ads}, with values around -40 $kJ.mol^{-1}$ indicating a chemisorption mechanism, while values around -20 $kJ.mol^{-1}$ suggest a physisorption mechanism [39,40]. The ΔG^{o}_{ads} value for METE was found to be -33.36 $kJ.mol^{-1}$, indicating a combination of both chemisorption and physisorption mechanisms. This suggests that the adsorption of MTET on the surface is a result of both chemical and physical interactions. The negative value of ΔG^{o}_{ads} indicates that the adsorption process is exothermic and spontaneous, and the magnitude of the ΔG^{o}_{ads}value suggests that the adsorption process is primarily dominated by chemisorption, with MTET molecules forming stable and irreversible chemical bonds with the surface. However, the value's proximity to -20 $kJ.mol^{-1}$ suggests that some level of physical interaction also contributes to the adsorption process, which is typical of many real-world systems where both chemical and physical interactions occur.

3.3 Computational investigations

Various kinetic parameters of MTET can be obtained from Gaussian records by using the quantum chemical approach to analyze its structural features (Figure 5) at B3LYP/6-311G(d,p) [41,42]. Mulliken charges are used to determine the adsorption centers of the inhibitor, and the results in Table 2 show that the sulfur and nitrogen atoms in MTET with the highest negative charges are the most preferred sites for adsorption on the metal substrate via donor-acceptor interactions. The benzene ring in MTET promotes the development of the adsorbate-surface coordination bond complexations [43,44]. The highest occupied molecular orbital (HOMO) of MTET (Figure 5) indicates that the S and N atoms can primarily transfer electrons to the metal substrate, while the lowest unoccupied molecular orbital (LUMO) reveals that the N, O, and C atoms in MTET are particularly reactive as electron acceptors [45,46]. Various quantum chemical parameters such as EHOMO, ELUMO, ΔE, χ, η, σ, and ΔN are computed and presented in Table 3. The EHOMO value of MTET is low (-5.474 eV), indicating its electron-donating capability, while the ELUMO value indicates its ability to accept electrons [46,47]. The values of ΔE, η, and σ provide information about the molecule's polarity, stability, and electron cloud polarization, respectively [48,49]. A highly effective corrosion inhibitor should have low values for ΔE and η but a high value for σ. The computed quantum chemical parameters of MTET are in excellent accordance with the experimental results, suggesting that the metal shares electrons with the inhibitor (back-donation) [50,51].

Table 2. Atomic charges of MTET in gas phase.

Atom	Atom Type	Charge
C(1)	5-RING C, a TO N, O, OR S	-0.14
C(2)	5-RING C, b TO N, O, OR S	-0.15
C(3)	5-RING C, b TO N, O, OR S	-0.15
C(4)	5-RING C, a TO N, O, OR S	-0.04
S(5)	5-RING SULFUR WITH p LONE PAIR	-0.08
C(6)	ALKYL CARBON, SP3	0.18
C(7)	SP2 CARBON IN C=N	0.47
N(8)	IMINE NITROGEN	-0.51
C(9)	ALKYL CARBON, SP3	0.06
N(10)	NITROGEN IN N-N=C MOIETY	-0.36
C(11)	THIOAMIDE CARBON, DOUBLY BONDED	0.50
S(12)	SULPHUR IN THIOAMIDE	-0.38
N(13)	THIOAMIDE NITROGEN	-0.73

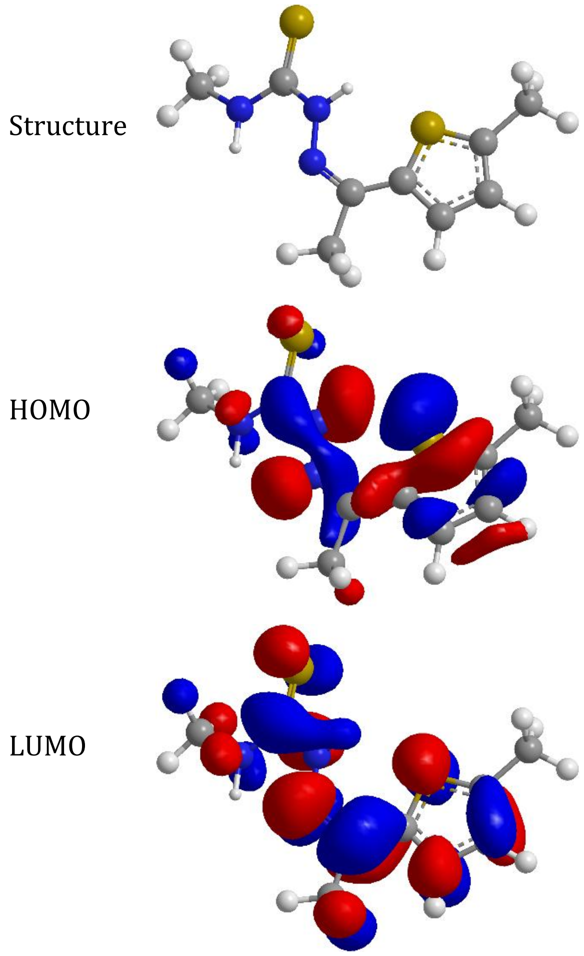

Fig. 5. Structure of MTET, as well as its HOMO and LUMO levels.

Table 3. The quantum chemical parameters of MTET molecules were analyzed in the gas phase using the B3LYP/6-311G(d,p) method.

I	A	E_{HOMO}	E_{LUMO}	ΔE	χ	η	σ	ΔN
5.47 eV	1.3 eV	-5.47 eV	1.30 eV	-6.77 eV	3.38 eV	2.08 eV	0.48 eV^{-1}	0.62 eV

4. SUGGESTED MECHANISM

The MTET molecules are protonated ions that are present in the corrosive media. They can be adsorbed on the mild steel interface where chloride ions have been previously adsorbed through electrostatic contact, which is a form of physical adsorption. Additionally, through chemical adsorption, MTET can be adsorbed on the metallic surface by donating lone pairs of electrons from nitrogen and oxygen atoms to the vacant orbital of iron atoms. The pi-electrons from the benzene ring and the unoccupied d-orbital of iron atoms interact as donors and acceptors [52].

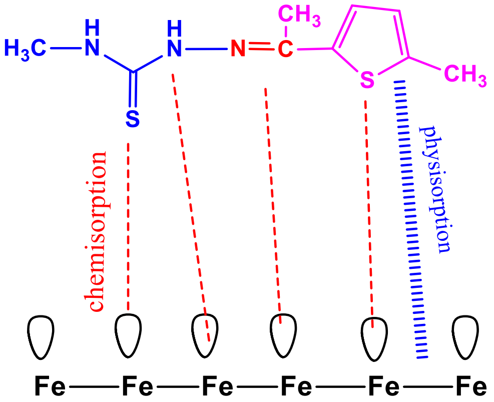

Fig. 6. Suggested inhibition mechanism of MTET molecules.

5. CONCLUSION

In conclusion, this research investigated the effectiveness of N-methyl-2-(1-(5-methylthiophen-2-yl)ethylidene)hydrazinecarbothioamide (MTET) as a corrosion inhibitor for mild steel in hydrochloric acid (HCl) solution. The study employed weight loss and density functional theory (DFT) methods to evaluate the inhibition performance of MTET at different concentrations, temperatures, and immersion times. The results showed that MTET was an efficient inhibitor, with inhibition efficiency increasing with concentration and exposure time but decreasing with temperature. The Langmuir adsorption isotherm and DFT calculations provided valuable insights into the adsorption behavior of MTET on the mild steel surface, showing that the inhibition process was both chemical and physical in nature. Therefore, MTET could be a potential candidate for corrosion inhibition in the petroleum industry and other sectors that require protection against mild steel corrosion in HCl solution.

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Sample availability

Samples of the compounds are available from the authors.

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