PROGRESS IN COLOR, COLORANTS AND COATINGS

available online @ www.pccc.icrc.ac.ir

Progress in Color Colorants Coating 16 (2023), 347-359

Ministry of Science, Research and Technology
Institute for Color Science & Technology

Investigation of the Corrosion Inhibition Properties of 4-Cyclohexyl-3-Thiosemicarbazide on Mild Steel in 1 M HCl Solution

A. Mohammed[1], A. Y. I. Rubaye[2], W. K. Al-Azzawi[3], A. Alamiery[4]*

[1.] Department of Electromechanical Engineering, University of Technology-Iraq, P.O. Box: 10001, Baghdad, Iraq

[2.] Chemical and Petrochemical Techniques Engineering Department, Basra Engineering Technical College, Southren Technical University, P.O. Box: 102, Basra, Iraq

[3.] Department of Medical Instruments Engineering Techniques, Al-Farahidi University, P.O. Box:10001, Baghdad, Iraq

[4.] Department of Chemical and Process Engineering, Faculty of Engineering and Build Environment, Universiti Kebangsaan Malaysia, P.O. Box: 43600, Bangi, Selangor, Malaysia.

ARTICLE INFO

Article history:
Received: 08 Apr 2023
Final Revised: 10 May 2023
Accepted: 14 May 2023
Available online: 27 Aug 2023

Keywords:
4-Cyclohexyl-3-thiosemicarbazide
Corrosion inhibitor
DFT
LUMO.

ABSTRACT

The study investigated the effectiveness of 4-cyclohexyl-3-thiosemicarbazide (4C3T) as a corrosion inhibitor for mild steel in 1 M HCl solution using the weight loss method. Various concentrations of 4C3T, temperatures, and immersion times were used to determine the inhibitory efficiency. The results showed that increasing the concentration of 4C3T resulted in higher inhibition efficiency while increasing the temperature decreased it. The optimal conditions were found to be a concentration of 0.5 mM at 303 K, which resulted in a 95 % inhibition efficiency. The mechanism of inhibition involved the adsorption of 4C3T onto the mild steel surface, which prevented corrosion. The adsorption followed the Langmuir adsorption isotherm, where physical and chemical adsorption coexisted. Quantum chemical calculations were used to support the findings. Overall, the study highlights the potential of 4C3T as a corrosion inhibitor for mild steel in HCl solution and offers insights into the underlying inhibitory process. Prog. Color Colorants Coat. 16 (2023), 347-359© Institute for Color Science and Technology.

1. Introduction

Corrosion is a major problem in various industries and can result in significant economic costs due to damage and loss of productivity. The direct and indirect costs associated with corrosion can be substantial, and therefore, preventing corrosion is of utmost importance [1]. Corrosion protection of metallic structures is a crucial concern in many industries due to the significant financial and safety losses from corrosion [2, 3]. Mild steel is widely used in various applications due to its low cost and excellent physical and mechanical properties [4, 5]. However, mild steel is highly susceptible to corrosion, particularly in acidic environments [6]. Therefore, it is necessary to discover effective methods to protect mild steel from corrosion [7]. Several methods are used to prevent corrosion, including protective coatings, cathodic protection, and corrosion inhibitors. Corrosion inhibitors are chemicals that can be added to a corrosive environment to reduce or prevent a material's corrosion. Corrosion inhibitors work by adsorbing onto the metal surface, forming a protective barrier, and reducing the corrosion rate [8].

*Corresponding author: * dr.ahmed1975@ukm.edu.my
dr.ahmed1975@gmail.com

Doi: 10.30509/pccc.2023.167126.1212

Corrosion inhibitors are widely accepted for preventing corrosion in various industries, including oil and gas, chemical processing, and transportation [9]. Corrosion inhibitors offer several advantages over other methods, such as ease of application, cost-effectiveness, and compatibility with other corrosion prevention methods [10]. One approach to reducing corrosion in acidic solutions is using organic compounds as corrosion inhibitors. Heterocyclic compounds containing N, S, and O-atoms, π-bonds, and aromatic systems have been effective inhibitors by adsorbing onto the mild steel surface and reducing corrosion [11-14]. The corrosion inhibitor 4C3T has been chosen for this study due to its highly functionalized structure, which includes -NH, NH_2, and C=S functional groups and three N and one S atoms. These features allow easy attachment to the mild steel surface and effective corrosion reduction [15, 16].

Additionally, 4C3T can be synthesized using green chemistry principles through multicomponent one-pot reactions with good yields. The corrosion inhibition efficiency (IE) of 4C3T has been investigated using density functional theory (DFT). This cost-effective and time-saving method provides detailed information about the mechanism of corrosion inhibition. Molecular properties such as EHOMO, ELUMO, ΔE, GS, GH, χ, and ΔN have been estimated using DFT, which helps simulate the experimental results obtained. This study explores the use of thiosemicarbazide derivatives as corrosion inhibitors in acidic media, focusing on the inhibitive performance of 4-cyclohexyl-3-thiosemicarbazide (4C3T) on mild steel corrosion in 1 M HCl, using weight loss techniques. The impact of varying immersion times and acidic inhibitor solutions was examined, and various thermodynamic parameters were determined. The experimental results were compared to theoretical data obtained using density functional theory (DFT) to understand the effective coordination mechanism between the inhibitor and the mild steel surface. The chemical structure of the tested inhibitor is demonstrated in Figure 1.

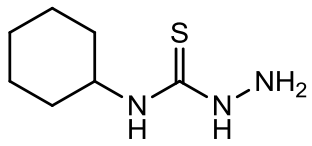


Figure 1: Chemical structure of 4C3T.

2. Experimental

2.1. Mild steel samples

The mild steel samples used in this study were obtained from a metal samples company, and their dimensions were 4.0×2.5×0.1 cm. Gravimetric measurements were carried out using samples with dimensions of 1.0 ×1.0 ×0.1 cm. These samples contained C (0.21), S (0.05), Mn (0.05), Si (0.38), P (0.09), Al (0.01), and Fe (the remainder) in weight percent. The samples were cleaned following conventional G1-03/ASTM [17]. Prior to testing, the mild steel samples were pre-treated by grinding with emery paper, washing with double-distilled water, degreasing with ethanol, and drying at room temperature to remove any surface impurities.

2.2. HCl solution

To create the corrosive environment, 1 M HCl was used, diluted from a 37 % analytical hydrochloric acid obtained from Merck-Malaysia using deionized water. The inhibitor 4C3T was added to the solution at concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 mM.

2.3. Weight loss analysis

Gravimetric measurements were performed to determine the corrosion inhibition properties of 4C3T on mild steel. The experiments involved immersing the mild steel samples in 1 M HCl solution with various concentrations of the inhibitor for different exposure times (1, 5, 10, 24, and 48 hours) at 303 K. After removal from the solution, the samples were cleaned with deionized water and acetone, dried, and weighed. The corrosion rate was then calculated by averaging the weight loss of three test specimens using equation 1 [18]. Tests were conducted using various concentrations of 4C3T for a 5-hour exposure period to evaluate the impact of temperature.

$$C_R(g.m^{-2}.h^{-1})=\frac{\Delta w}{st} \quad (1)$$

The weight loss of the structural steel was determined by measuring Δw in grams. The area of the specimen was denoted as s in units of square meters, while the immersion time was recorded in hours as t. equations 2 and 3:

$$\theta=\frac{IE(\%)}{100} \quad (2)$$

$$IE(\%)=\frac{C_{R(0)}-C_{R(i)}}{C_{R(0)}} \quad (3)$$

Where $C_{R(0)}$ is the corrosion rate in an untreated environment, $C_{R(i)}$ is the corrosion rate in a treated.

2.4. DFT

The Gaussian 09 software [19] was used for quantum chemical calculations. Optimizing the inhibitor structure in the gaseous phase was conducted using the B3LYP method and the "6-31G^{++}" (d,p) basis set. Koopmans theory [20] was applied to determine the ionization potential (I) and electron affinity (A), which are related to E_{HOMO} and E_{LUMO}, respectively. Equations 4 and 5 were utilized for this purpose.

$$I=-E_{HOMO} \quad (4)$$

$$A=-E_{LOMO} \quad (5)$$

To evaluate the electronegativity (χ), softness (σ), and hardness (η), using the equations 6-8:

$$\chi=\frac{I+A}{2} \quad (6)$$

$$\eta=\frac{I-A}{2} \quad (7)$$

$$\sigma=\eta^{-1} \quad (8)$$

To determine the transported electrons number (ΔN), [21] used equation 9:

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

The electronegativity and hardness values for iron were equal to 7 eV and zero eV, respectively; hence these results lead to equation 10:

$$\Delta N=\frac{7-\chi_{inh}}{2(\eta_{inh})} \quad (10)$$

3. Results and Discussion

3.1. Weight loss measurements

The weight loss method, which was used to determine the corrosion rates and inhibition efficiencies of the mild steel coupons, has some limitations that could affect the results' accuracy. One major limitation of the weight loss method is that it is prone to errors and uncertainties due to the difficulty of accurately measuring the weight of the corroded samples. Even slight variations in the measurement process, such as the duration of washing and drying, could lead to significant errors in the results. Additionally, the weight loss method does not provide information on the nature and morphology of the corrosion products, which can be important in understanding the underlying mechanisms of corrosion inhibition. Furthermore, the weight loss method assumes that the corrosion rate is constant over time, which may not always be true. Corrosion rates may change over time due to variations in the concentration of the corrosive solution or the inhibitor and changes in temperature and other environmental factors, which could result in inaccurate corrosion rate measurements and affect the calculation of inhibition efficiencies.

To mitigate these limitations, it is important to carefully control experimental conditions and measure the weight of the samples with high precision to minimize errors.

3.1.1. Effect of concentration

Figure 2 depicts the outcomes of weight loss tests on mild steel subjected to untreated and treated 1 M HCl solutions. The impact of varying concentrations of 4C3T on the corrosion rate was analyzed. Since HCl is a potent acid, the untreated solution resulted in rapid corrosion. However, an increase in the concentration of 4C3T led to a notable decline in the corrosion rate. Thus, 4C3T acts as an effective protector of mild steel against the harmful impact of HCl. The highest inhibition efficacy was observed at 0.5 mM, with 95 % for 4C3T. 4C3T contains a large molecular structure with hetero-elements such as sulphur and nitrogen atoms that help them adhere to the mild steel surface and create a protective coating. As the concentration of 4C3T increased to 0.5 mM, their effectiveness as corrosion inhibitors also increased. However, at concentrations approaching 1.0 mM, the inhibition efficacy remained nearly constant due to 4C3T particle adsorption on the metal substrate. Additionally, the varied functional groups in 4C3T enhance its ability to prevent corrosion by elevating the electron density of the active sites on the metal surface.

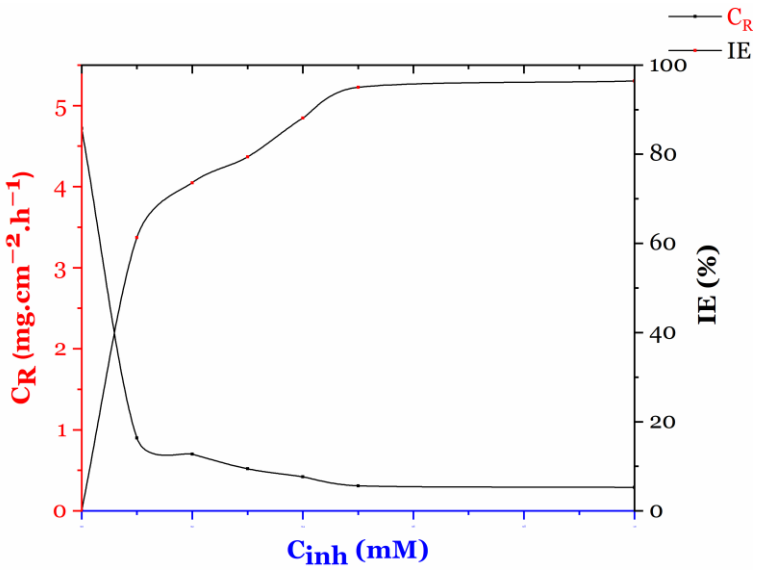


Figure 2: The impact of 4C3T concentration on the corrosion rate and inhibition efficacy of mild steel exposed to 1 M HCl for 5 hours at 303 K.

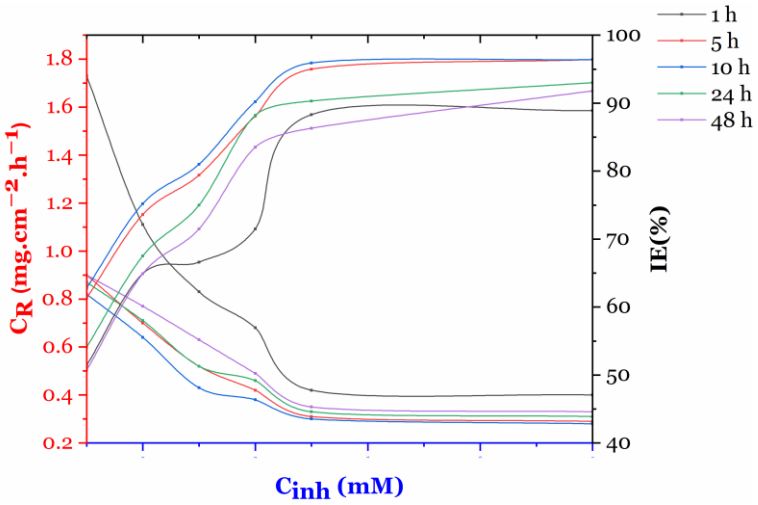


Figure 3: The impact of 4C3T concentration and immersion time on the corrosion rate and inhibition efficacy of mild steel exposed to 1 M HCl at 303 K.

3.1.2. Effect of immersion time

To examine the impact of immersion time on the inhibitory efficacy of 4C3T in reducing corrosion on mild steel, 1 M HCl was treated with varying doses of 4C3T (0.1 to 1.0 mM) for exposure periods ranging from 1 to 48 hours at 303 K. Figure 3 illustrates the findings of the study. During the first 10 hours of immersion, there was a rapid increase in inhibitory efficacy. It remained stable between 10 and 24 hours before gradually decreasing from 24 to 48 hours. Longer exposure times resulted in increased inhibitory effectiveness due to higher concentrations of 4C3T particles adsorbed onto the mild steel surface. As more particles were adsorbed onto the metallic surface, the adsorption density of 4C3T particles also significantly increased. This allowed for physisorption and chemisorption, which are interactions between inhibitor molecules and iron atoms on metallic surfaces. If a few inhibitor molecules leave the surface, the effective area covered by the inhibitor and its inhibitory activity might decrease. The high inhibitory efficacy observed over a long exposure period highlights the stability of the 4C3T particles layer adsorbed in an acidic medium.

3.1.3. Effect of temperature

The study investigated the effects of temperature on the inhibition of mild steel corrosion in acidic solutions treated with 4C3T at concentrations ranging from 0.1 to

1.0 mM. Figure 4 illustrates that as the temperature increased from 303 K to 333 K, the corrosion rate of 4C3T increased, and its inhibition efficiency decreased. The inhibitory effect of 4C3T decreased with increasing temperature, indicating physical adsorption. At high temperatures, 4C3T particles were removed from the metal surface due to adsorption.

At 303 K, the maximum inhibition efficiency for 4C3T was observed at a concentration of 0.5 mM, with 95 % efficiency. However, as the temperature increased, the inhibition efficiency decreased. The inhibitor was less effective at higher temperatures at the highest concentration of 4C3T (1.0 mM) due to physical absorption processes and van der Waals interactions between the 4C3T particles and the mild steel surface.

In the oil and gas production process, the temperature at the bottom of the well is high. Therefore, a suitable corrosion inhibitor should maintain its effectiveness in corrosive media at high temperatures. Figure 4 clearly shows that as the temperature increases, the corrosion rate slightly increases, and the effectiveness of the inhibiting is little affected. This changes is due to the excellent performance of the corrosion inhibitor, which has been specially formulated to maintain its effectiveness even at high temperatures. The importance of an effective corrosion inhibitor in oil and gas production cannot be overstated. Corrosion can cause significant damage to equipment, resulting in costly repairs and downtime. Therefore, it is essential to use a corrosion inhibitor that can withstand the harsh conditions encountered in the production process, including high temperatures and corrosive media. The results shown in Figure 4 provide strong evidence that the corrosion inhibitor used in the production process is highly effective, even at elevated temperatures. It demonstrates the quality of the inhibitor and the expertise of the team that selected and implemented it. The findings of this study underscore the importance of carefully selecting an appropriate corrosion inhibitor for a given production process and ensuring ongoing monitoring and evaluation to ensure continued effectiveness, as highlighted in previous research [22]. Additionally, the study found that increasing the concentration of the inhibitor led to a reduction in corrosion rates at the same temperature, indicating that the concentration of the inhibitor plays a crucial role in enhancing surface coverage of inhibitor chemicals and effectively separating the metallic surface from the corrosive environment [23].

Comparing the inhibitory efficiencies of 4C3T in this study with previously published inhibitors, Figure 5 shows that these inhibitors are suitable for HCl solutions. The results indicate that in the presence of 0.5 mM of 4C3T, the inhibition efficiency reached 96 % at 303 K in a 1 M HCl environment, which surpasses the performance of some previously studied inhibitors [24-53].

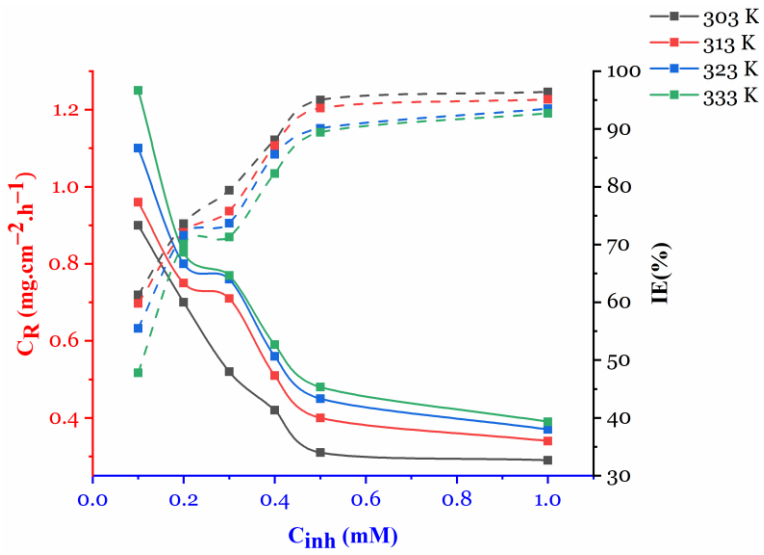


Figure 4: The impact of 4C3T concentration and different temperatures on the corrosion rate and inhibition efficacy of mild steel exposed to 1 M HCl for 5 h.

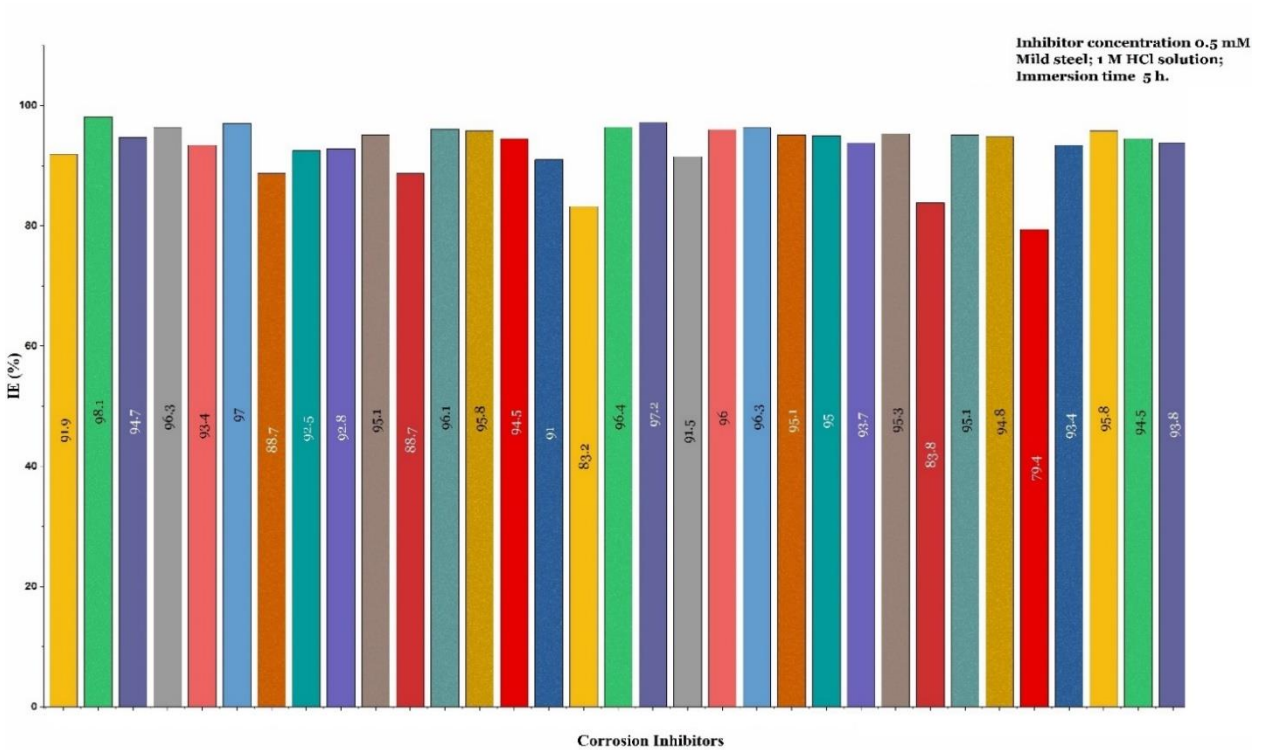


Figure 5: The comparison of tested inhibitors with previously reported inhibitors for corrosion of mild steel in HCl solution.

3.2. Adsorption isotherm

Adsorption isotherms were employed in this study to investigate the mechanism of interaction between 4C3T and the metal surface. Surface coverage (θ) values were determined through gravimetric testing and used to evaluate the most appropriate isotherm model. The Langmuir, Temkin, and Freundlich isotherms were used to analyze the adsorption process, as described in Table 1. Physical or chemical adsorption may have caused the 4C3T particles to adhere to the metal surfaces. Results indicated that the Langmuir adsorption isotherm model was the most suitable for 4C3T with a regression coefficient (R2) of 0.998 at 303 K. The Langmuir isotherm plots between C_{inh}/θ and C_{inh} are represented in Figure 6, and the slope and intercept values for 4C3T were estimated and are presented in Table 1. Equation 11 was used to calculate the adsorption parameters.

$$C_{inh}/\theta=(K_{ads})^{-1}+C \quad (11)$$

Where C_{inh} is the inhibitor concentration, θ is the area of the tested surface, and K_{ads} is a constant. ΔG_{ads}^{o} and K_{ads} were calculated according to the plot between C/θ and C.

Equation 12 was used to calculate the adsorption parameters ΔG_{ads}^{o} and K_{ads}.

$$\Delta G^{o}_{ads}=-RT\ \ln(55.5K_{ads}) \quad (12)$$

Where 55.5 is the molar concentration of water, R is the gas constant, and T is Temperature.

The chemisorption mechanism is influenced by the value of ΔG_{ads}^{o}, which should be highly negative, ideally below -40 $kJmol^{-1}$. In contrast, a ΔG_{ads}^{o} value around -20 $kJmol^{-1}$ or less negative indicates physisorption [54-58]. The value of ΔG_{ads}^{o} for 4C3T was determined to be -27.56 $kJmol^{-1}$, indicating that both chemisorption and physisorption mechanisms may be present.

Table 1: The thermodynamic parameters for the 4C3T.

Parameter	303 K	313 K	323 K	333 K
Intercept	0.072	0.078	0.085	0.104
Slope	0.957	0.965	0.978	0.965
R2	0.998	0.998	0.998	0.998

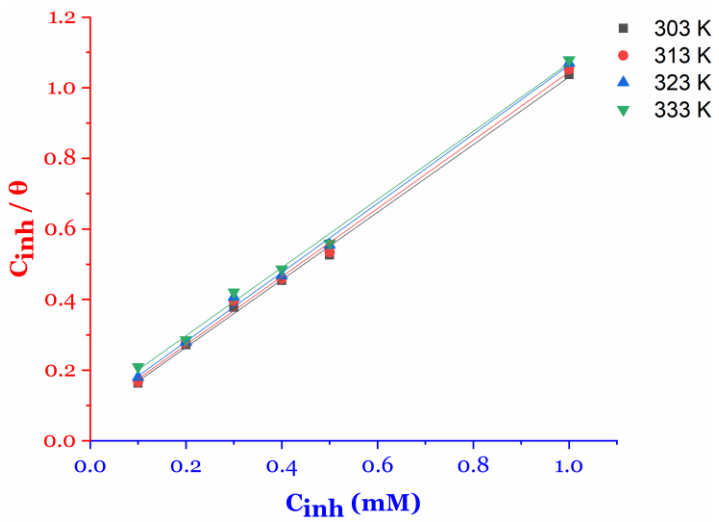
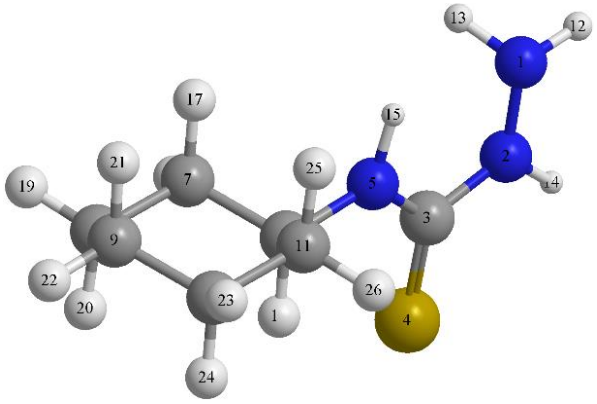


Figure 6: Langmuir isotherm of 4C3T plot for mild steel in HCl.

3.3. Quantum Computations

In general, quantum chemical calculations can provide valuable insights into the mechanism of corrosion inhibition and can help predict potential inhibitors' effectiveness. These calculations typically involve using a computational model to simulate the behavior of the inhibitor molecule in solution and at the metal surface. The choice of basis set and functional for quantum chemical calculations can significantly impact the accuracy and reliability of the results. Commonly used basis sets for quantum chemical calculations include the 6-31G, 6-31G(d), and 6-31+G(d) basis sets, among others. The choice of function, which describes the relationship between electron density and energy, can also significantly affect the accuracy of the results. Common functionals used for corrosion inhibition studies include B3LYP, M06, and PBE. To support the study's findings, we used quantum chemical calculations to investigate the adsorption mechanism of the inhibitor molecule on the mild steel surface and to predict the corrosion inhibition efficiency. The structural properties of 4C3T molecules can be analyzed using the quantum chemical technique, and various thermodynamic parameters can be determined based on the structural parameters of 4C3T at B3LYP/6-311G(d,p) [59, 60]. The Mulliken charges (Table 2) are utilized to identify the inhibitor's adsorption sites [61]. The study outcomes indicate that the negatively charged oxygen and nitrogen atoms are the most favored locations for the inhibitor's adsorption through a donor-acceptor relationship [61]. The benzene ring present in 4C3T molecules supports the formation of complexations between the adsorbate and surface coordination bonds [61]. The highest occupied molecular orbital (HOMO) of 4C3T identifies the molecule's site for electron donation, predominantly observed in the S and N atoms [62]. According to previous studies, the nitrogen, sulfur, and carbon atoms in the molecule are mainly responsible for the molecule's ability to accept electrons, as shown by the shape of the lowest unoccupied molecular orbital (LUMO) [63, 64]. Figure 7 illustrates the equivalent reception sites of 4C3T based on the LUMO shape.

Table 2: The Mulliken charges of 4C3T molecules in the gas phase.



Atom	Charge	Atom	Charge
[N(1)]	-0.161	[C(7)]	-0.074
[N(2)]	0.220	[C(8)]	-0.058
[C(3)]	0.186	[C(9)]	-0.057
[S(4)]	-0.730	[C(10)]	-0.059
[N(5)]	0.028	[C(11)]	-0.068
[C(6)]	0.077	[H(12)]	0.112

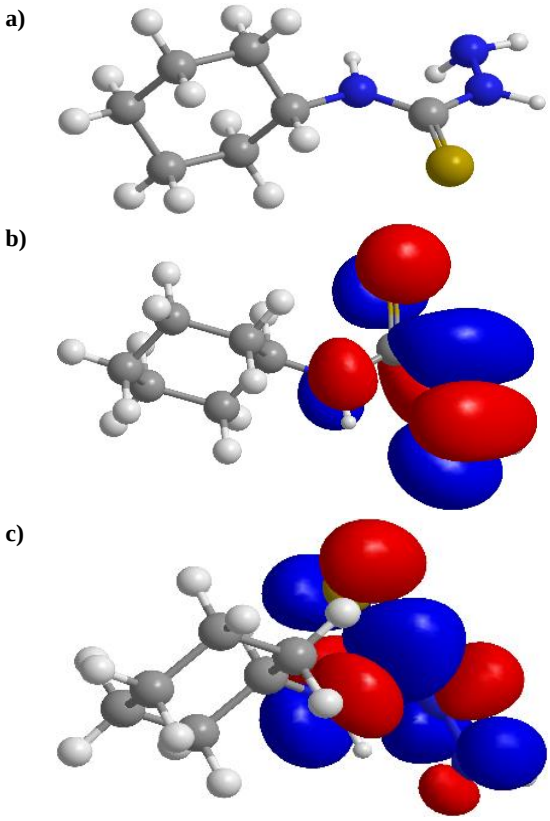


Figure 7: The (a) optimized structure, (b) EHOMO, and (c) ELUMO of 4C3T molecules.

Table 3 shows the results of quantum chemical computations for several parameters such as EHOMO, ELUMO, ΔE, electronegativity (χ), softness (σ), hardness (η), and the number of electrons transported (ΔN) for the inhibitor molecules studied. A higher EHOMO value indicates a better ability of a molecule to donate electrons, which can be transferred from an acceptor molecule with a lower energy empty molecular orbital. For 4C3T, the EHOMO value (-6.139 eV) is consistent with the reported results in Table 2. ELUMO represents a molecule's ability to accept electrons; smaller EHOMO values facilitate this process. Hardness (η) measures the potential chemical change over the total number of atoms, and an increase in η enhances molecule stability. Softness (σ) is a measure of electron cloud polarization, and lower values of ΔE and higher σ are desirable for good corrosion inhibition. The values calculated for 4C3T in Table 2 show that it is a potent corrosion inhibitor with a high ΔN value, indicating better electron exchangeability. These quantitative parameters (EHOMO, ELUMO, ΔE, η, σ, and ΔN) agree well with the test results. The metal's back donation establishes contact between the inhibitor and metal surfaces [65, 66].

Table 3: DFT variables for 4C3T molecules in the gas phase.

Parameter	Value
$I\ eV$	6.139 eV
$A\ eV$	7.927 eV
$E_{HOMO}\ eV$	-6.139 eV
$E_{LUMO}\ eV$	7.927 eV
$\Delta E\ eV$	14.066
$\chi\ eV$	0.89
$\eta\ eV$	-7.033
$\sigma\ eV^{-1}$	-0.14
ΔN	0.5

3.4. Mechanism of inhibition

Organic inhibitors act by adsorbing onto the metal surface, replacing other corrosive species and water molecules [67]. Factors affecting this process include the organic molecule's state in a corrosive environment and the metal surface's charge [68]. In HCl solution, the steel surface is positively charged, attracting chloride ions and leading to the adsorption of cationic species [69].

4C3T, when protonated in 1 M HCl solution, can be electrostatically adsorbed onto the metal surface through physisorption. Nitrogen heteroatoms are released from 4C3T on the surface, forming coordination and back-donating bonds through donor-acceptor interactions (chemisorption) [70-72]. Figure 8 depicts the suggested inhibitory mechanism for 4C3T as a potential inhibitor of mild steel corrosion in 1 M HCl solutions. The coating of 4C3T on the mild steel surface protects the surface from corrosive ions' penetration. The protective coating is believed to form through the interaction of heteroatoms with the metal surface. The mild steel surface's physical adsorption of inhibitor molecules is aided by the electrostatic interaction between the protonated 4C3T molecules and pre-absorbed Cl- ions and the interaction between the inhibitor molecules' electron pairs and the iron's vacant d-orbital [73].

3.5. Potential applications of 4C3T

The findings of this study have important practical implications for industries that rely on mild steel equipment and structures. Using 4C3T as a corrosion inhibitor can provide a cost-effective and environmentally

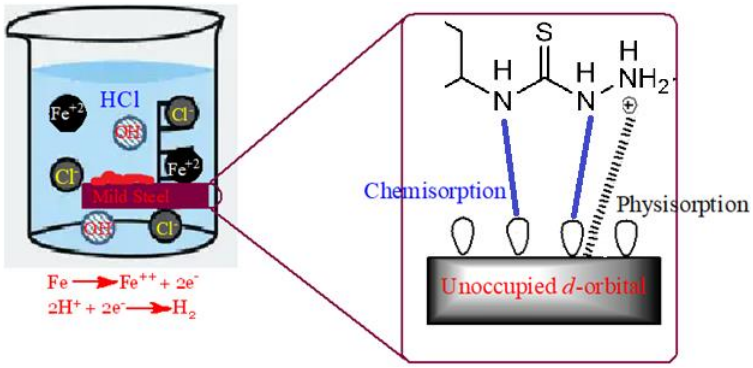


Figure 8: Postulated inhibited mechanism of 4C3T.

friendly method of reducing corrosion in mild steel. The results indicate that a maximal inhibitive efficacy of up to 96 % can be achieved at the optimal concentration of 0.5 mM for a 5-hour immersion period at 303 K. To apply these findings in real-world applications, industries can consider using 4C3T as a corrosion inhibitor in the design and maintenance of mild steel equipment and structures. The optimal concentration and immersion time can be adjusted based on the specific needs and conditions of the application. The Langmuir adsorption isotherms can also be utilized to understand the relationship between the concentration of the inhibitor and the surface coverage of the mild steel, allowing for more accurate and efficient use of the inhibitor.

Additionally, the findings of the quantum chemistry computations can be used to guide the design and development of new and improved corrosion inhibitors. The energies of frontier molecular orbitals (EHOMO & ELUMO) and the energy gap can provide insight into the protection performance of potential inhibitors, allowing for more targeted and effective inhibitor development. Overall, the practical implications of this study suggest that using 4C3T as a corrosion inhibitor can potentially reduce the economic and environmental costs of mild steel corrosion in various industries.

4. Conclusion

In conclusion, the study has demonstrated that 4C3T is an effective inhibitor of mild steel corrosion in 1 M HCl solution. The optimal concentration for inhibitive efficacy was 0.5 mM for a 5-hour immersion period at 303 K, with a maximum inhibitive efficacy of up to 96 %. The study has also shown that the protection performance of 4C3T against mild steel corrosion increases with concentration but decreases slightly with increased immersion time and temperature. The Langmuir adsorption isotherms suggest that 4C3T molecules adsorb onto the metal substrate surface, and both physical and chemical adsorptions are involved in the adsorption mechanism. The observed activation energy values suggest that the chemical adsorption of 4C3T molecules on a mild steel surface is spontaneous. The findings of the quantum chemistry computations also support the weight loss test results, with energies of frontier molecular orbitals and energy gap being consistent with the protection performance. These results have significant implications for future research and practical applications in corrosion inhibition. The study has provided valuable insights into the adsorption mechanism of 4C3T molecules on mild steel surfaces, which could inform the design of more effective corrosion inhibitors. Additionally, the findings highlight the importance of considering immersion time and temperature when assessing the performance of corrosion inhibitors, as well as the need for more environmentally friendly options. Overall, the study provides a promising avenue for developing cost-effective and environmentally friendly corrosion inhibitors for various industries.

5. References

1. N. K. Gupta, M. A. Quraishi, C. Verma, A. K. Mukherjee, Green Schiff's bases as corrosion inhibitors for mild steel in 1 M HCl solution: experimental and theoretical approach, *RSC Adv.*, 6(2016), 102076-102087.
2. K. Wan, P. Feng, B. Hou, Y. Li, Enhanced corrosion inhibition properties of carboxymethyl hydroxypropyl chitosan for mild steel in 1.0 M HCl solution, *RSC Adv.*, 6(2016), 77515-77524.
3. M. Bobina, A. Kellenberger, J.-P. Millet, C. Muntean, N. Vaszilcsin, Corrosion resistance of carbon steel in weak acid solutions in the presence of l-histidine as corrosion inhibitor, *Corros. Sci.*, 69(2013), 389-395.
4. K. R. Ansari, M. A. Quraishi, Experimental and quantum chemical evaluation of Schiff bases of isatin as a new and green corrosion inhibitors for mild steel in 20% H_2SO_4, *J. Taiwan Inst. Chem. Eng.*, 54(2015), 145-154.
5. A. A. Farag, M. A. Hegazy, Synergistic inhibition effect of potassium iodide and novel Schiff bases on X65 steel corrosion in 0.5 M H_2SO_4, *Corros. Sci.,74(* 2013), 168-177.
6. Sudheer, M. A. Quraishi, 2-Amino-3,5-dicarbonitrile-6-thio-pyridines: new and effective corrosion inhibitors for mild steel in 1 M HCl, *Ind. Eng. Chem. Res.*, 53(2014), 2851-2859.
7. B. Xu, Y. Ji, X. Zhang, X. Jin, W. Yang, Y. Chen, Experimental and theoretical studies on the corrosion inhibition performance of 4-amino-N,N-di-(2-pyridylmethyl)- aniline on mild steel in hydrochloric acid, *RSC Adv.*, 5(2015), 56049-56059.
8. Y. Ji, B. Xu, W. Gong, X. Zhang, X. Jin, W. Ning, Y. Meng, W. Yang, Y. Chen, Corrosion inhibition of a new Schiff base derivative with two pyridine rings on Q235 mild steel in 1.0 M HCl, *J. Taiwan Inst. Chem. Eng.*, 66(2016), 301-312.
9. L. O. Olasunkanmi, I. B. Obot, E. E. Ebenso, Adsorption and corrosion inhibition properties of N-{n-[1-R-5-(quinoxalin-6-yl)-4,5-dihydropyrazol-3-yl]phenyl} methanesulfonamides on mild steel in 1 M HCl: experimental and theoretical studies, *RSC Adv.*, 6(2016), 86782-86797.
10. S. Junaedi, A. A. H. Kadhum, A. Al-Amiery, A.B. Mohamad, M. S. Takriff, Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino-5- Oleyl 1,3,4-Thiadiazol (AOT), *Int. J. Electrochem. Sci.*, 7(2012), 3543-3554.
11. H.S. Aljibori, A.H. Alwazir, S. Abdulhadi, W.K. Al-Azzawi, A. A. H. Kadhum, L. M. Shaker, A. A. Al-Amiery, H.Sh. Majdi, The use of a Schiff base derivative to inhibit mild steel corrosion in 1 M HCl solution: a comparison of practical and theoretical findings, *Int. J. Corros. Scale Inhib.*, 11(2022), 1435-1455.
12. W. K. Al-Azzawi, S. M. Salih, A. F. Hamood, R. K. Al-Azzawi, M. H. Kzar, H. N. Jawoosh, L. M. Shakier, A. Al-Amiery, A. A. H. Kadhum, W. N. R. W. Isahak, M.S. Takriff, Adsorption and theoretical investigations of a Schiff base for corrosion inhibition of mild steel in an acidic environment, *Int. J. Corros. Scale Inhib.*, 11(2022), 1063-1082.
13. D. M. Jamil, A. Al-Okbi, M. Hanon, K.S. Rida, A. Alkaim, A. Al-Amiery, A. Kadhum, A.A.H. Kadhum, Carbethoxythiazole corrosion inhibitor: as an experimentally model and DFT theory, *J. Eng. Appl. Sci.*, 13(2018), 3952-3959.
14. A. Alobaidy, A. Kadhum, S. Al-Baghdadi, A. Al-Amiery, A. Kadhum, E. Yousif, A.B. Mohamad, Eco-friendly corrosion inhibitor: experimental studies on the corrosion inhibition performance of creatinine for mild steel in HCl complemented with quantum chemical calculations, *Int. J. Electrochem. Sci.*, 10(2015), 3961-3972.
15. S. Subhashini, A. Sabirneeza, Gravimetric and electrochemical investigation of water soluble poly(vinyl alcohol-threonine) as corrosion inhibitor for mild steel. In: Proceedings of WCECS, San Francisco, USA, II(2011), 657-662.
16. S. Umoren, M. Solomon, S. Ali, H. Dafalla, Synthesis, Characterization, and utilization of a diallylmethylamine-based cyclopolymer for corrosion mitigation in simulated acidizing environment, *Mater. Sci. Eng.*, 100(2019), 897-914.
17. ASTM, G. G 31-72 American Society for Testing and Materials 1990 Philadelphia.
18. NACE Standard TM 0169/G31-12a. Standard Guide for Laboratory Immersion Corrosion Testing of Metals, (2012).
19. Gaussian 09, Revision D.01, Frisch, M.J.; Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H.,Vreven, T., Montgomery, Jr., J.A., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S.; Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski, J., Fox, D.J. Gaussian, Inc., Wallingford CT, (2013).
20. Koopmans, T. Ordering of wave functions and eigenenergy's to the individual electrons of an atom. *Physica*, 1(1933), 104-113.
21. S. Al-Bghdadi, M. Hanoon, J. Odah, L. Shaker, A. Al-Amiery, A.A. Benzylidene as Efficient Corrosion

Inhibition of Mild Steel in Acidic Solution. *Proceedings*, 41(2019), 27. https://doi.org/10.3390/ecsoc-23-06472

22. M.M. Solomon, S.A. Umoren, M.A. Quraishi, D. Tripathi, E.J. Abai, Effect of Alkyl Chain Length, Flow, and temperature on the Corrosion Inhibition of Carbon Steel in a Simulated Acidizing Environment by an Imidazoline-Based Inhibitor, *J. Pet. Sci. Eng.*, 187(2020), 106801.
23. B.S. Mahdi, H.S.S. Aljibori, M.K. Abbass, W.K. Al-Azzawi, A.H. Kadhum, M.M. Hanoon, W.N.R.W. Isahak, A.A. Al-Amiery, H.Sh. Majdi, Gravimetric analysis and quantum chemical assessment of 4-aminoantipyrine derivatives as corrosion inhibitors, *Int. J. Corros. Scale Inhib.*,3(202), 1191–1213.
24. A.A. Alamiery, Study of corrosion behavior of N'-(2-(2-oxomethylpyrrol-1-yl) ethyl) piperidine for mild steel in the acid environment, *Biointerface Res. Appl. Chem.*, 12(2022), 3638-3646.
25. A. Alamiery, A. Mohamad, A. Kadhum, M. Takriff, Comparative data on corrosion protection of mild steel in HCl using two new thiazoles, *Data Brief*, 40(2022), 107838.
26. A.M. Mustafa, F.F. Sayyid, N. Betti, L.M. Shaker, M.M. Hanoon, A.A. Alamiery, A.A.H. Kadhum, M.S. Takriff, Inhibition of mild steel corrosion in hydrochloric acid environment by 1-amino-2-mercapto-5-(4-(pyrrol-1-yl)phenyl)-1,3,4-triazole, S. *Afr. J. Chem. Eng.*, 39(2022), 42-51.
27. A.A. Alamiery, Investigations on corrosion inhibitory effect of newly quinoline derivative on mild steel in HCl solution complemented with antibacterial studies, *Biointerface Rese. Appl. Chem.*, 12(2022), 12, 1561-1568.
28. I. A. Alkadir Aziz, I.A. Annon, M.H. Abdulkareem, M.M. Hanoon, M.H. Alkaabi, L.M. Shaker, A.A. Alamiery, W.N.R. Wan Isahak, M.S. Takriff, Insights into corrosion inhibition behavior of a 5-mercapto-1,2,4-triazole derivative for mild steel in hydrochloric acid solution: experimental and DFT studies, *Lubricants*, 9(2021), 122.
29. A. Alamiery, Short report of mild steel corrosion in 0.5 M H_2SO_4 by 4-ethyl-1-(4-oxo4-phenylbutanoyl)thiosemicarbazide, *Tribologi*, 30(2021), 90-99.
30. A.A. Alamiery, W.N.R.W. Isahak, M.S. Takriff, Inhibition of mild steel corrosion by 4-benzyl-1-(4-oxo-4-phenylbutanoyl)thiosemicarbazide: Gravimetrical, adsorption and theoretical studies, *Lubricants*, 9(2021), 93.
31. M.A. Dawood, Z.M.K. Alasady, M.S. Abdulazeez, D.S. Ahmed, G.M. Sulaiman, A.A.H. Kadhum, L.M. Shaker, A.A. Alamiery, The corrosion inhibition effect of a pyridine derivative for low carbon steel in 1 M HCl medium: Complemented with antibacterial studies, *Int. J. Corros. Scale Inhib.*, 10(2021), 1766-1782.
32. A. Alamiery, Corrosion inhibition effect of 2-N-phenylamino-5-(3-phenyl-3-oxo-1- propyl)-1,3,4-oxadiazole on mild steel in 1 M hydrochloric acid medium: Insight from gravimetric and DFT investigations, *Mater. Sci. Energy Technol.*, 4(2021), 398–-406.
33. Alamiery, Anticorrosion effect of thiosemicarbazide derivative on mild steel in 1 M hydrochloric acid and 0.5 M sulfuric Acid: Gravimetrical and theoretical studies, *Mater. Sci. Energy Technol.*, 4(2021), 263–273.
34. Alamiery, W.N.R.W. Isahak, H. Aljibori, H. Al-Asadi, A. Kadhum, Effect of the structure, immersion time and temperature on the corrosion inhibition of 4-pyrrol-1-yln-(2,5-dimethyl-pyrrol-1-yl)benzoylamine in 1.0 m HCl solution, *Int. J. Corros. Scale Inhib.*, 10(2021), 700-713.
35. Alamiery, E. Mahmoudi, T. Allami, Corrosion inhibition of low-carbon steel in hydrochloric acid environment using a Schiff base derived from pyrrole: gravimetric and computational studies, *Int. J. Corros. Scale Inhib.*, 10(2021), 749-765.
36. A.J.M. Eltmimi, A. Alamiery, A.J. Allami, R.M. Yusop, A.H. Kadhum, T. Allami, Inhibitive effects of a novel efficient Schiff base on mild steel in hydrochloric acid environment, *Int. J. Corros. Scale Inhib.*, 10(2021), 634-648.
37. A. Alamiery, L.M. Shaker, T. Allami, A.H. Kadhum, M.S. Takriff, A study of acidic corrosion behavior of Furan-derived Schiff base for mild steel in hydrochloric acid environment: Experimental, and surface investigation, *Mater. Today: Proc.*, 44(2021), 2337-2341.
38. S. Al-Baghdadi, A. Al-Amiery, T. Gaaz, A. Kadhum, Terephthalohydrazide and isophthalo-hydrazide as new corrosion inhibitors for mild steel in hydrochloric acid: Experimental and theoretical approaches, *Koroze Ochr. Mater.*, 65(2021), 12-22.
39. M.M. Hanoon, A.M. Resen, L.M., Shaker, A. Kadhum, A. Al-Amiery, Corrosion investigation of mild steel in aqueous hydrochloric acid environment using n- (Naphthalen-1yl)-1-(4-pyridinyl)methanimine complemented with antibacterial studies, *Biointerface Res. Appl. Chem.*, 11(2021), 9735–-9743.
40. S. Al-Baghdadi, T.S. Gaaz, A. Al-Adili, A. Al-Amiery, M. Takriff, Experimental studies on corrosion inhibition performance of acetylthiophene thiosemicarbazone for mild steel in HCl complemented with DFT investigation, *Int. J. Low-Carbon Technol.*, 16(2021), 181-188.
41. A. Al-Amiery, Anti-corrosion performance of 2-isonicotinoyl-nphenylhydrazinecarbothioamide for mild steel hydrochloric acid solution: Insights from experimental measurements and quantum chemical calculations, *Surf. Rev. Lett.*, 28(2021), 2050058.
42. M.S. Abdulazeez, Z.S. Abdullahe, M.A. Dawood, Z.K. Handel, R.I. Mahmood, S. Osamah, A.H. Kadhum, L.M. Shaker, A.A. Al-Amiery, Corrosion inhibition of low carbon steel in HCl medium using a thiadiazole derivative: weight loss, DFT studies and

antibacterial studies, *Int. J. Corros. Scale Inhib.*, 10(2021), 1812-1828.

43. A. Mustafa, F. Sayyid, N. Betti, M. Hanoon, A. Al-Amiery, A. Kadhum, M. Takriff, Inhibition evaluation of 5-(4-(1H-pyrrol-1-yl)phenyl)-2-mercapto-1,3,4-oxadiazole for the corrosion of mild steel in an acid environment: Thermodynamic and DFT Aspects, *Tribologia*, 38(2021), 39-47.
44. Y.M. Abdulsahib, A.J.M. Eltmimi, S.A. Alhabeeb, M.M. Hanoon, A.A. Al-Amiery, T. Allami, A.A.H. Kadhum, Experimental and theoretical investigations on the inhibition efficiency of N-(2,4-dihydroxytolueneylidene)-4-methylpyridin-2-amine for the corrosion of mild steel in hydrochloric acid, *Int. J. Corros. Scale Inhib.*, 10(2021), 885-899.
45. A.K. Khudhair, A.M. Mustafa, M.M. Hanoon, A. Al-Amiery, L.M. Shaker, T. Gazz, A.B. Mohamad, A.H. Kadhum, M.S. Takriff, Experimental and theoretical investigation on the corrosion inhibitor potential of N-MEH for mild steel in HCl, *Prog. Color, Colorant Coat.*, 15(2022), 111-122.
46. D.S. Zinad, R.D. Salim, N. Betti, L.M. Shaker, A.A. AL-Amiery, Comparative investigations of the corrosion inhibition efficiency of a 1-phenyl- 2-(1-phenylethylidene)hydrazine and its analog against mild steel corrosion in hydrochloric acid solution, *Prog. Color, Colorant Coat.*, 15(2022), 53-63.
47. R.D. Salim, N. Betti, M. Hanoon, A.A. Al-Amiery, 2-(2,4-Dimethoxybenzylidene)-N-phenylhydrazinecarbothioamide as an efficient corrosion inhibitor for mild steel in acidic environment, *Prog. Color, Colorant Coat.*, 15(2021), 45-52.
48. A.A. Al-Amiery, L.M. Shaker, A.H. Kadhum, M.S. Takriff, Exploration of furan derivative for application as corrosion inhibitor for mild steel in hydrochloric acid solution: Effect of immersion time and temperature on efficiency, *Mater. Today: Proc.*, 42(2021), 2968-2973.
49. A.M. Resen, M.M. Hanoon, W.K. Alani, A. Kadhim, A.A. Mohammed, T.S. Gaaz, A.A.H. Kadhum, A.A. Al-Amiery, M.S. Takriff, Exploration of 8-piperazine-1- ylmethylumbelliferone for application as a corrosion inhibitor for mild steel in hydrochloric acid solution, *Int. J. Corros. Scale Inhib.*, 10(2021), 368-387.
50. M.M. Hanoon, A.M. Resen, A.A. Al-Amiery, A.A.H. Kadhum, M.S. Takriff, Theoretical and experimental studies on the corrosion inhibition potentials of 2-((6-methyl-2-ketoquinolin-3-yl)methylene) hydrazinecarbothioamide for mild steel in 1 M HCl, *Prog. Color, Colorant Coat.*, 15(2021), 21-33.
51. F.G. Hashim, T.A. Salman, S.B. Al-Baghdadi, T. Gaaz, A.A. Al-Amiery, Inhibition effect of hydrazine-derived coumarin on a mild steel surface in hydrochloric acid, *Tribologia*, 37(2020), 45-53.
52. A.M. Resen, M. Hanoon, R.D. Salim, A.A. Al-Amiery, L.M. Shaker, A.A.H. Kadhum, Gravimetrical, theoretical, and surface morphological investigations of corrosion inhibition effect of 4-(benzoimidazole-2-yl) pyridine on mild steel in hydrochloric acid, *Koroze Ochr. Mater.*, 64(2020), 122-130.
53. A.Z. Salman, Q.A. Jawad, K.S. Ridah, L.M. Shaker, A.A. Al-Amiery, Selected BIS thiadiazole: synthesis and corrosion inhibition studies on mild steel in HCl environment, *Surf. Rev. Lett.*, 27(2020), 2050014.
54. S. Junaedi, A. Al-Amiery, A. Kadihum, A. Kadhum, A. Mohamad, Inhibitioneffects of a synthesized novel 4-aminoantipyrine derivative on the corrosion of mild steel in hydrochloric acid solution together with quantum chemicalstudies, *Int. J. Mol. Sci.*, 13(2013), 11915-11928.
55. A. Alamiery, W.N.R.W. Isahak, H.S.S. Aljibori, H.A. Al- Asadi, A.A.H. Kadhum, Effect of the structure, immersion time and temperature on the corrosion inhibition of 4- pyrrol-1-yl-n-(2,5-dimethyl-pyrrol-1-yl)benzoylamine in 1.0 M HCl solution, *Int. J. Corros. Scale Inhib., I10(*2021), 700-713.
56. S. Al-Baghdadi, F. Hashim, A. Salam, T. Abed, T. Gaaz, A. Al-Amiery, A.H. Kadhum, K. Reda, W. Ahmed, Synthesis and corrosion inhibition application of NATN on mild steel surface in acidic media complemented with DFT studies, *Results Phys.*, 8(2018), 1178-1184.
57. H.M. Abd El-Lateef, Corrosion inhibition characteristics of a novel salycilidene isatin hydrazine sodium sulfonate on carbon steel in HCl and a synergistic nickel ions additive: a combined experimental and theoretical perspective, *Appl. Surf. Sci.*, 501(2020), 144237.
58. I.B. Onyeachu, I.B. Obot, A.A. Sorour, M.I. Abdul-Rashid, Green corrosion inhibitor for oilfield application I: electrochemical assessment of 2-(2-Pyridyl) benzimidazole for API X60 steel under sweet environment in NACE brine ID196, *Corros. Sci.*, 150(2019), 183-193.
59. S.A. Umoren, M.M. Solomon, Protective polymeric films for industrial substrates: a critical review on past and recent applications with conducting polymers and polymer composites/nanocomposites, *Prog. Mater. Sci.*, 104(2019), 380-450.
60. W.K. Al-Azzawi, A.J. Al Adily, F.F. Sayyid, R.K. Al-Azzawi, M.H. Kzar, H.N. Jawoosh, A.A. Al-Amiery, A.A.H. Kadhum, W.N.R.W. Isahak, M.S. Takriff, Evaluation of corrosion inhibition characteristics of an N-propionanilide derivative for mild steel in 1 M HCl: Gravimetrical and computational studies, *Int. J. Corros. Scale Inhib.*, 11(2022), 1100-1114.
61. H. Ma, S. Chen, B. Yin, S. Zhao, X. Liu, Impedance spectroscopic study of corrosion inhibition of copper by surfactants in the acidic solutions, *Corros. Sci.*, 45(2003), 867-882.
62. G. Banerjee, S.N. Malhotra, Contribution to adsorption of aromatic amines on mild steel surface from HCl solutions by impedance, UV, and Raman spectroscopy, *Corrosion*, 48(1992), 10-15.

63. M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, Electrochemical and quantum chemical studies of new thiadiazole derivatives adsorption on mild steel in normal hydrochloric acid medium, *Corros. Sci.*, 47(2005), 485-505.
64. S. Deng, X. Li, Inhibition by Jasminum nudiflorum Lindl. leaves extract of the corrosion of aluminium in HCl solution, *Corros. Sci.*, 64(2012), 253-262.
65. G. Karthik, M. Sundaravadivelu, P. Rajkumar, Corrosion inhibition and adsorption properties of pharmaceutically active compound esomeprazole on mild steel in hydrochloric acid solution, *Res. Chem. Intermed.*, 41(2015), 1543-1558.
66. M. Farsak, H. Kelesand, M. Keles, A new corrosion inhibitor for protection of low carbon steel in HCl solution, *Corros. Sci.*, 98(2015), 223-232.
67. S.A. Umoren, M.M. Solomon, S.A. Ali, Dafalla, H.D.M. Synthesis, characterization, and utilization of a diallylmethylamine-based cyclopolymer for corrosion mitigation in simulated acidizing environment, *Mater. Sci. Eng. C*, 100(2019), 897-914.
68. H.M. Abd El-Lateef, Corrosion inhibition characteristics of a novel salycilidene isatin hydrazine sodium sulfonate on carbon steel in HCl and a synergistic nickel ions additive: a combined experimental and theoretical perspective, *Appl. Surf. Sci.*, 501(2020), 144237.
69. I.B. Onyeachu, I.B. Obot, A.A. Sorour, M.I. Abdul-Rashid, Green corrosion inhibitor for oilfield application I: electrochemical assessment of 2-(2-Pyridyl) benzimidazole for API X60 steel under sweet environment in NACE brine ID196, *Corros. Sci.*, 150(2019), 183-193.
70. S.A. Umoren, M.M. Solomon, Protective polymeric films for industrial substrates: a critical review on past and recent applications with conducting polymers and polymer composites/nanocomposites, *Prog. Mater. Sci.*, 104(2019), 380-450.
71. M.M. Solomon, S.A. Umoren, M.A. Quraishi, D. Tripathi, E.J. Abai, Effect of alkyl chain length, flow, and temperature on the corrosion inhibition of carbon steel in a simulated acidizing environment by an imidazoline-based inhibitor, *J. Pet. Sci. Eng.*, 187(2020), 106801.
72. R. Solmaz, G. Kardaş, M. Çulha, B. Yazici, M. Erbil, Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media, *Electrochim. Acta*, 53(2008), 5941-5952.
73. W.K. Al-Azzawi, A.J. Al Adily, F.F. Sayyid, R.K. Al-Azzawi, M.H. Kzar, H.N. Jawoosh, A.A. Al-Amiery, A.A.H. Kadhum, W.N.R.W. Isahak, M.S. Takriff , Evaluation of corrosion inhibition characteristics of an N-propionanilide derivative for mild steel in 1 M HCl: Gravimetrical and computational studies, *Int. J. Corros. Scale Inhib.*, 11(2022), 1100-1114.

How to cite this article:
A. Mohammed, A. Y. I. Rubaye, W. K. Al-Azzawi, A. Alamiery, Investigation of the Corrosion Inhibition Properties of 4-Cyclohexyl-3-Thiosemicarbazide on Mild Steel in 1 M HCl Solution. Prog. Color Colorants Coat., 16 (2023), 347-359.