

Terephthalohydrazide and isophthalohydrazide as new corrosion inhibitors for mild steel in hydrochloric acid: Experimental and theoretical approaches

Shaimaa B. Al-Baghdadi¹, Ahmed A. Al-Amiery¹, Tayser S. Gaaz², Abdul Amir H. Kadhum^{3,4}

¹ University of Technology (UOT), Baghdad, Iraq

² Technical College Al-Musaib, Al-Furat Al-Awsat Technical University, Al-Musaib, Babil, Iraq

³ Al-Ameed University, Karbalaa, Iraq

⁴ Department of Chemical & Process Engineering, Universiti Kebangsaan Malaysia (UKM),
Bangi, Selangor, Malaysia

E-mail: dr.ahmed1975@ukm.edu.my

Most organic corrosion inhibitors have polar groups through which the molecule can be adsorbed strongly or specifically on the metal surface. In this investigation, terephthalohydrazide and isophthalohydrazide were synthesized as corrosion inhibitors, and their corrosion-inhibiting properties on mild steel were evaluated in a corrosive environment by weight loss measurements. The results of corrosion experiments revealed that terephthalohydrazide and isophthalohydrazide as inhibitors controlled or reduced corrosion through adsorption mechanism and showed inhibitive efficiencies of 96.4 % and 97.2 %, respectively, at the optimum concentration of 0.5 mM. The surface morphology of the metal was evaluated by scanning electron microscopy. The terephthalohydrazide or isophthalohydrazide molecules were adsorbed on the mild steel surface, and the process of adsorption follows chemical adsorption. Quantum chemical calculations of the tested corrosion inhibitors were consistent with the experimental observations.

INTRODUCTION

Mild steel has attracted wide attention because of its low price and remarkable mechanical characteristics. It is one of the most considerable structural materials exposed to external conditions, particularly in corrosive environment [1], where corrosion on metal surfaces is potent and severe. Acidic solutions can dissolve metals; thus, corrosion inhibitors are utilized to decrease the corrosive attack of acidic solutions on metals [2-4]. Suitable inhibitor derived from organic compounds [5-8] is the common choice for a particular medium and mineral of considerable importance. However, the inhibition efficiencies of organic compounds are imputed by their steric hindrance, functional sites, unshared electron pairs, and the pi-bonds that determine the type of interaction between organic molecules and metal surface [9,10]. Several studies showed that the inhibitor blocks the site

of corrosion and increases the adsorption process even in small amounts; thus, it increases the life of metals. A literature review showed that the usage of organic molecules as corrosion inhibitors for mild steel in hydrochloric acid solution has been known for a long time. A huge number of organic molecules, especially those that contain heteroatoms, such as phosphorous, sulfur, oxygen, and nitrogen, in addition to pi-bonds, have been used as corrosion inhibitors to control the corrosion of mild steel surface [11,12]. The inhibition process occurs by inhibitor adsorption, and the inhibition efficiency is highly dependent on the structure and chemical properties under certain methodological conditions [13-16]. A large number of organic compounds, such as thioureas [17], thiophenes [18], oxazoles [19], sulfonamides [20], trizinate [21], pyridines [22], quinolones [23], hydrazones [24], triazoles [25], and hydrazides [26], have been used as corrosion inhibitors for mild steel in acidic solutions. The present study complements our previous researches on the synthesis of new corrosion inhibitors [26-37]. Herein, we synthesized and fully characterized new interface inhibitors, namely, terephthalohydrazide and isophthalohydrazide, and studied the application of these inhibitors for the corrosion inhibition of mild steel specimens in 1 M hydrochloric acid solution through weight loss techniques. Surface investigations of mild steel specimens in the absence and presence of terephthalohydrazide and isophthalohydrazide were achieved to characterize the inhibitor film, which protects the mild steel surface. Density functional theory (DFT) was also performed to study the relationship between practical results and calculate quantitative values. The chemical structures of terephthalohydrazide and isophthalohydrazide are shown in Figure 1. We believe that this study is the first to synthesize these chemical compounds,

study the ability of the inhibitors to control corrosion, and provide insight for further investigations within the framework of this research topic to measure inhibition efficiency.

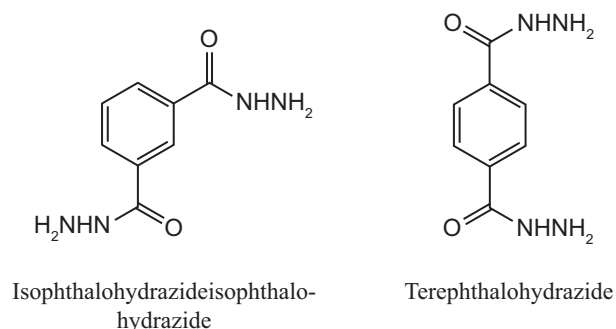


Fig. 1. Structure schemes of terephthalohydrazide and isophthalohydrazide

EXPERIMENTAL SECTION

Materials and methods

Mild steel specimens (4.5 cm) were used as primary substrates for weight loss techniques. The specimens have the following composition: carbon, 0.210; manganese, 0.050; silicon, 0.380; aluminum, 0.010; sulfur, 0.050; phosphorus, 0.090; and iron, balance. The mild steel specimens were polished using various emery paper grades, washed with water and then acetone, and dried. Hydrochloric acid (1 M) was prepared by diluting of 37 % HCl (analytical grade) with double distilled water.

Corrosion inhibitors

The two corrosion inhibitors, terephthalohydrazide and isophthalohydrazide, were synthesized by reacting 20 mmol hydrazine hydrate (I) with 5 mmol benzene-1,4-diformylchloride (or benzene-1,3-diformylchloride) in 200 mL of ethanol under reflux conditions for 10 h. The product was filtered and recrystallized from ethanol. Figure 2 demonstrates the chemical synthesis of the target compounds. The chemical structures of terephthalohydrazide and isophthalohydrazide are shown in Figure 1. The purity of the synthesized corrosion inhibitors was confirmed by thin-layer chromatography. The products were characterized by Fourier transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^1H NMR), carbon nuclear magnetic resonance (^{13}C NMR), and elemental analysis method (CHN). Characterization of terephthalohydrazide: yield, 77 %; melting point (M.P.), 300 °C; FT-IR (cm^{-1}): 3291.7 and 3201.8 (N–H, amine), 3056.1 (C–H, aromatic), and 1709.4 (C=O); ^1H NMR, DMSO_d^6 , δ (ppm): 3.94 (2H, amine), 7.85 (2H, s, aromatic), and 8.98 (2H, s, amine); ^{13}C NMR, DMSO_d^6 , δ : 128.1 (H–C, aromatic), 134.7 (C–C, aromatic), and 167.2 (O=C, carbonyl); che-

mical formula: $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$; CHN (found/calculated): 49.48/49.73 (C), 5.19/5.11 (H), and 28.85/29.01 (N). Characterization of isophthalohydrazide (2b): yield, 74%; M.P., 233 °C; FT-IR (cm^{-1}): 3276.8 and 3199.1 (N–H, amine), 3046.0 (C–H, aromatic), and 1688.5 (C=O); ^1H NMR, DMSO_d^6 , δ (ppm): 7.67–7.71 (1H, t, aromatic), 8.26 (2H, d, aromatic), and 9.03 (1H, d, amine); ^{13}C NMR, DMSO_d^6 , δ : 128.3 (H–C, aromatic), 130.1 (H–C, aromatic), 131.6 (C–C, aromatic), 132.9 (H–C, aromatic), and 168.6 (O=C, carbonyl); CHN (found/calculated): 49.48/49.26 (C), 5.19/5.12 (H), and 28.85/28.35 (N).

Gravimetric measurements

Weight loss techniques were performed using mild steel coupons in 1 M hydrochloric acid environment in the absence and the presence of terephthalohydrazide or isophthalohydrazide at the concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 mM. The mild steel coupons were initially ground, cleaned, and weighed.

The mild steel coupons were immersed in corrosive solution and allowed to react for 1, 5, 10, and 24 h at various temperatures (303, 313, 323, and 333 K). The mild steel coupons were removed after the specified immersion time, cleaned with distilled water and then acetone, and dried. Each experiment was performed in triplicate, and the mean was calculated. Weight loss was determined by the difference in the weight of mild steel coupons before and after exposure to HCl with or without inhibitor. Corrosion rate (C_R), inhibition efficiency (IE%), and surface coverage (θ) were determined according to Equations 1–3:

$$C_R (\text{mg cm}^{-2} \text{ h}^{-1}) = \frac{W}{at}, \quad (1)$$

$$\theta = \frac{C_{R_0} - C_{R_i}}{C_{R_0}}, \quad (2)$$

$$\text{IE (\%)} = \frac{C_{R_0} - C_{R_i}}{C_{R_0}} \times 100, \quad (3)$$

where W is the weight loss of mild steel coupon (mg), a is the exposed coupon area (cm^2), t is the immersion time (h), and C_{R_0} and C_{R_i} are the corrosion rates without and with terephthalohydrazide (or isophthalohydrazide), respectively.

Surface characterization

The surface of the mild steel coupons was characterized by scanning electron microscopy (SEM; Hitachi TM1000 tabletop microscope). The mild steel coupons were immersed for 5 h in HCl with or without terephthalohydrazide or isophthalohydrazide. The coupons were removed, rinsed with acetone, dried, and used for measurements.

DFT Calculations

Quantum calculations for terephthalohydrazide and isophthalohydrazide molecules were performed in neutral mode using DFT with B3LYP function [38–39]. All computations were carried out through the Gaussian 03 software using the 6-31G(d,p) basis set [40]. 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 number of transferred electrons (ΔN) according to Equations 4–8, [41,42]:

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

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

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

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

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

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

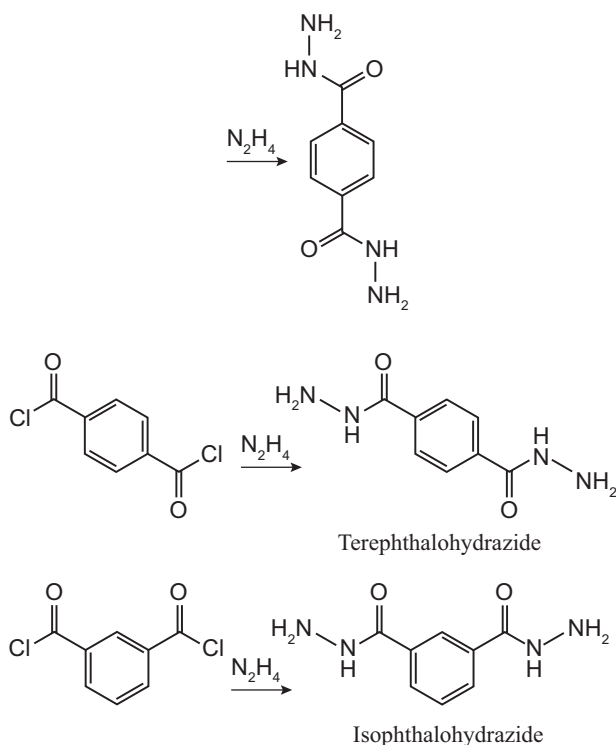


Fig. 2. Synthetic route for the terephthalohydrazide and isophthalohydrazide

RESULTS AND DISCUSSION

Chemistry

The synthesis of the corrosion inhibitors terephthalohydrazide and isophthalohydrazide was achieved through the reaction of acid chloride with hydrazine. The schematic reactions for the preparation of the corrosion inhibitors are shown in Figure 2. The chemical structures of the isolated compounds were confirmed through spectroscopic techniques as described in the experimental section.

Weight loss measurements

The results of the weight loss experiment for mild steel specimens in corrosive environment with and without terephthalohydrazide or isophthalohydrazide are demonstrated in Figures 3 and 4. Weight loss experiment is a dependable technique used to optimize the effect of the concentrations of the tested inhibitor on corrosion rate and inhibition efficiency at various immersion times [29]. The obtained results revealed that the presence of

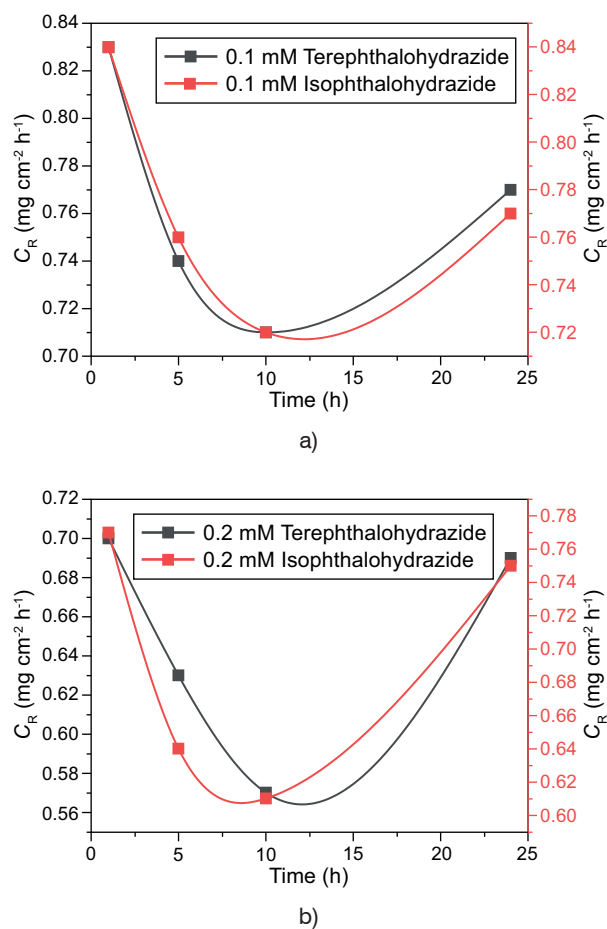


Fig. 3. Effect of various concentrations of terephthalohydrazide and isophthalohydrazide on the corrosion rates in mg cm² h⁻¹ for mild steel in 1 M HCl at various immersion times (Continue on next page)

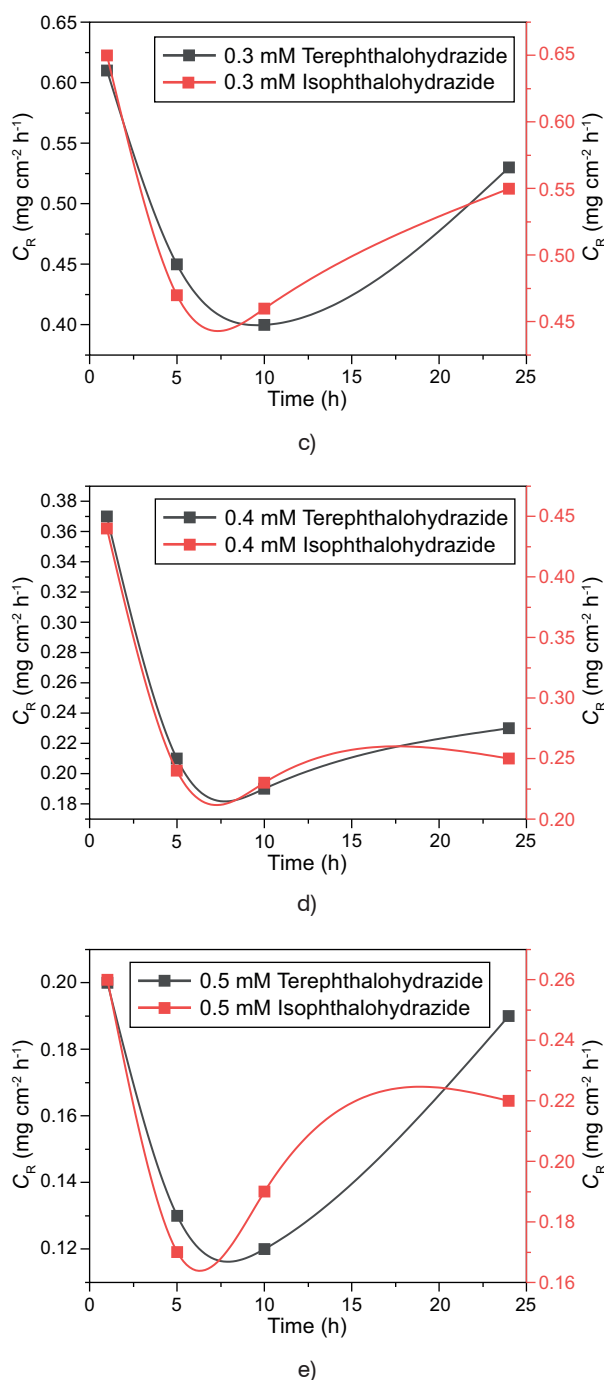


Fig. 3. Effect of various concentrations of terephthalohydrazide and isophthalohydrazide on the corrosion rates in $\text{mg cm}^{-2} \text{h}^{-1}$ for mild steel in 1 M HCl at various immersion times

terephthalohydrazide or isophthalohydrazide in acidic solution prevents the corrosion of mild steel, reduces the corrosion rate, and increases the inhibition efficiency with the increase in the concentration of the tested corrosion inhibitors (Figs. 3 and 4). Terephthalohydrazide had higher inhibition efficiency (97.02 %) than isophthalohydrazide (96.4%) at 0.5 mM for 5 h of immer-

sion. Moreover, the excellent inhibitive activity is imputed to the reaction of terephthalohydrazide or isophthalohydrazide molecules with the surface of mild steel because of the existence of nitrogen and oxygen heteroatoms in the inhibitor. Besides, the differences in the inhibition efficiencies between terephthalohydrazide and isophthalohydrazide may be related to the position of the substituent group and the steric hindrance of the molecule. The terephthalohydrazide molecule has less steric hindrance. Steric hindrance increases the reaction of inhibitor molecules with the mild steel surface.

Effect of immersion time

Time is an important parameter when elucidating the effect of corrosion inhibitors. The film stability and adsorption rate of the synthesized inhibitors were investigated at different exposure periods (1, 5, 10, and 24 h). Figures 3 and 4 represent the results of the effect of exposure time effect on the corrosion rates and inhibition efficiencies of the synthesized corrosion inhibitors.

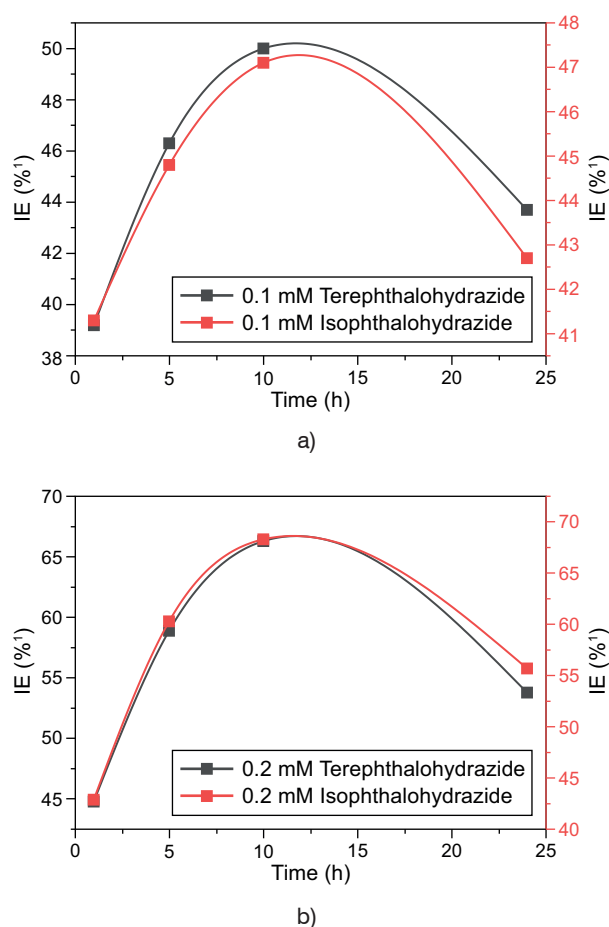


Fig. 4. Effect of various concentrations of terephthalohydrazide and isophthalohydrazide on the inhibition efficiencies for mild steel in 1 M HCl at various immersion times (Continue on next page)

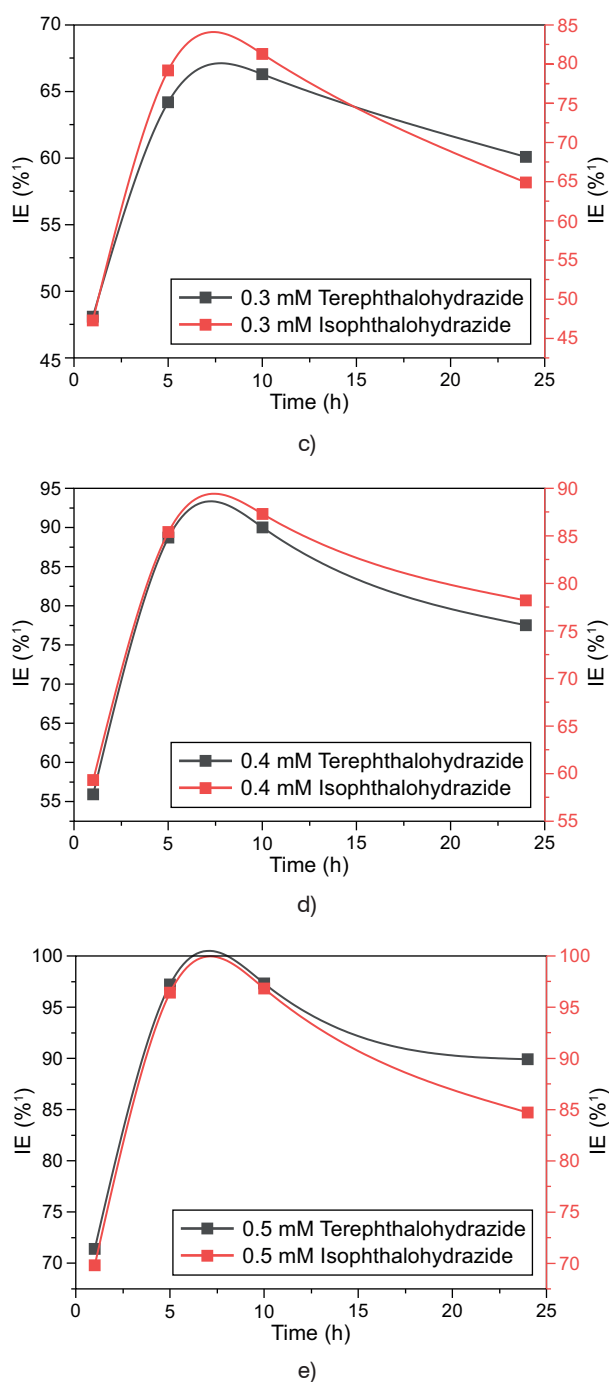


Fig. 4. Effect of various concentrations of terephthalohydrazide and isophthalohydrazide on the inhibition efficiencies for mild steel in 1 M HCl at various immersion times

The highest inhibition efficiencies for both examined inhibitors were attained at the exposure time of 5 h. This outcome may be ascribed to the high-speed adsorption of the inhibitor molecules on the surface of the testing coupons. The active functional groups in the molecular structures of these inhibitors were responsible for the quick adsorption of the molecules. The inhibition efficiencies for the two tested inhibitors decreased at 24

h of exposure. The reduction in inhibition efficiencies was imputed to the desorption of the inhibitor molecules from the mild steel surface. Furthermore, the corrosion rates remarkably increased with longer exposure time. This observation can be attributed to the desorption of inhibitor molecules from the mild steel surface. The uncovered coupon was exposed to HCl environment, which resulted in the dissolution of mild steel. In addition, the increase in corrosion rates with long exposure period can be attributed to the decrease in the number of inhibitory molecules in the HCl medium.

Effect of temperature

The effect of temperature on the corrosion rate and inhibitor efficiency of the synthesized corrosion inhibitors was investigated. Corrosion rate decreased in the presence of terephthalohydrazide or isophthalohydrazide because the strong interaction of the tested inhibitor molecules with the surface of mild steel produced a protective film through the adsorbed inhibitor molecules on the mild steel surface, which isolated the mild steel from the HCl environment. The variation in corrosion rate at different solution temperatures (303, 313, 323, and 333 K) was investigated by gravimetric techniques. The change in corrosion rate versus temperature demonstrated in Figure 5 was calculated by utilizing the Arrhenius plot according to Equation 9:

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

The values of activation energies in the presence of terephthalohydrazide or isophthalohydrazide molecules propose that the molecules of the corrosion inhibitors were adsorbed on the mild steel surface through chemisorption.

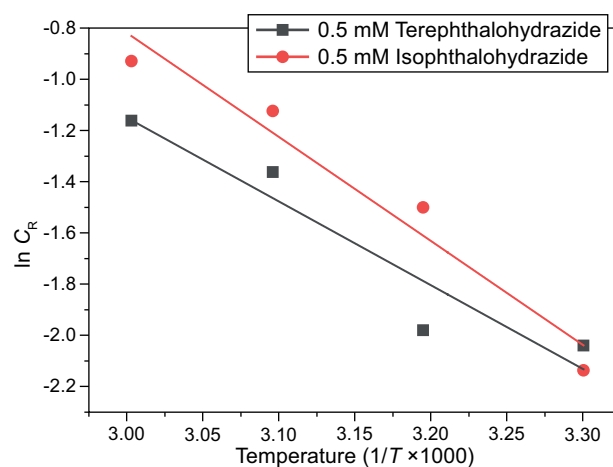


Fig. 5. The Arrhenius plots for corrosion of mild steel in corrosive environment in the presence of the tested inhibitors (0.5 mM) at different temperature

The results of weight loss measurements are demonstrated in Figure 6. The inhibition efficiencies of the corrosion inhibitors decreased with increasing temperatures. In this study, the inhibition efficiency of terephthalohydrazide was 97.2% at 303 K but became 84.4 % at 333 K. Similarly, the inhibition efficiency of isophthalohydrazide was 96.4 % at 303 K and 83.1 % at 333 K.

The thermodynamic mechanism is considered an exothermic mechanism and results in weak adsorption or desorption (reversed adsorption) at high temperatures.

Terephthalohydrazide and isophthalohydrazide have excellent inhibition efficiencies in hydrochloric acid solutions with low temperature but have weak inhibition performance at a higher temperature. Figure 6 demonstrates that the inhibition efficiencies of the tested inhibitors decreased when the temperature increased.

Adsorption isotherms

The surface coverage (θ) obtained by weight loss technique for terephthalohydrazide and isophthalohydrazide was utilized to determine the adsorption isotherm model. The study of adsorption isotherms is very important to understand the nature of interactions between the inhibitor molecules and the mild steel surface. These molecules can adsorb on the coupon surface through physical or chemical reactions. The phenomenon of adsorption isotherm could be understood according to various adsorption isotherms, including Langmuir,

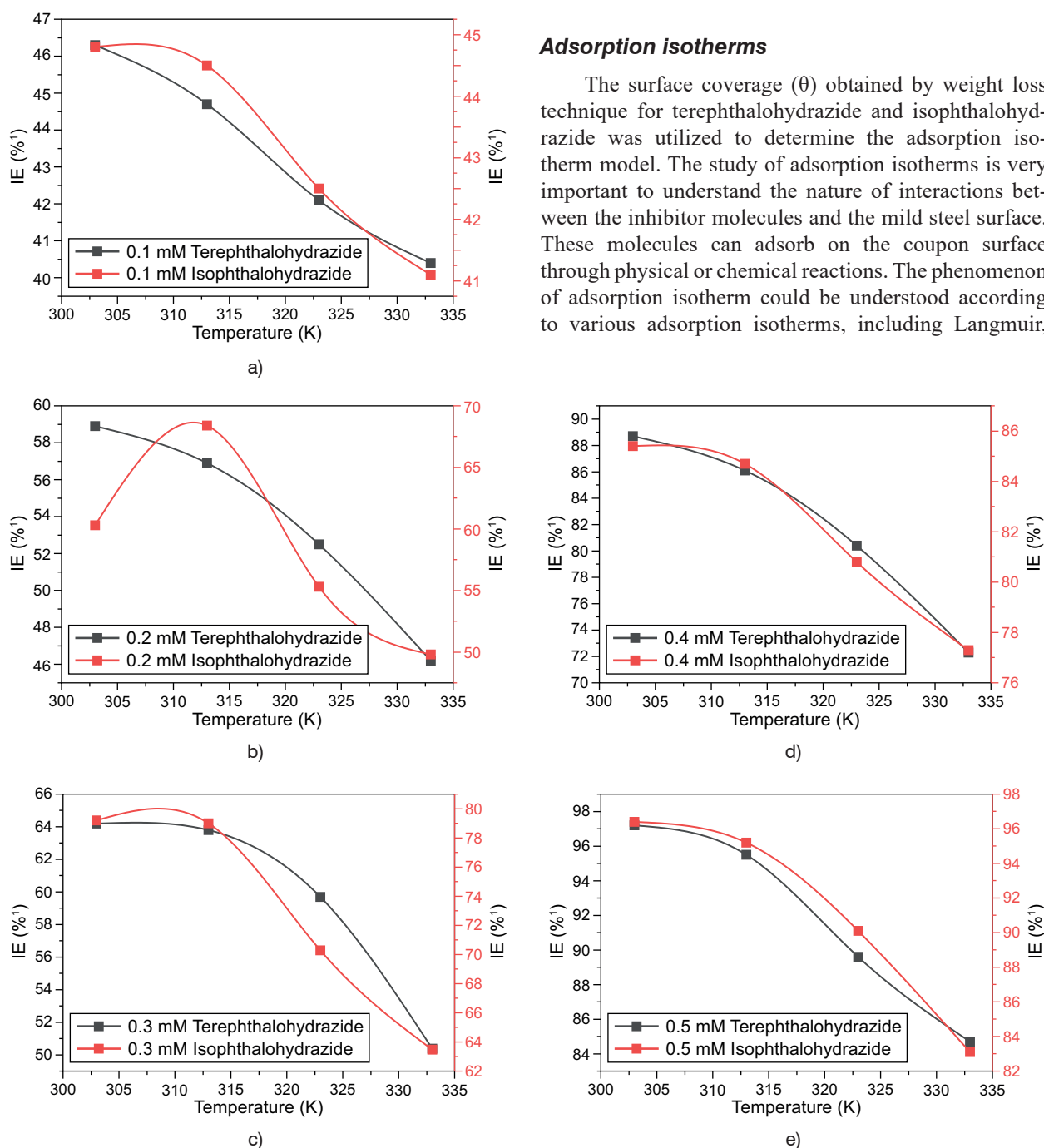


Fig. 6. Effect of various concentrations of terephthalohydrazide and isophthalohydrazide on the inhibition efficiencies for mild steel in 1 M HCl at various temperature

Temkin, and Freundlich isotherms. Table 1 represents the adsorption parameters of Langmuir, Temkin, and Freundlich isotherms for both inhibitors.

Tab. 1. Chemical properties of AA1100

Inhibitor	Adsorption Isotherms		
	Langmuir (R^2)	Temkin (R^2)	Freundlich (R^2)
Terephthalohydrazide	0.997	0.986	0.952
Isophthalohydrazide	0.993	0.979	0.927

Langmuir isotherm quite fit with the values of the regression coefficients (R^2) for terephthalohydrazide and isophthalohydrazide molecules. The slope and intercept values obtained for the Langmuir adsorption isotherms are 0.7984 and 0.18506 for terephthalohydrazide and 0.15683 and 0.7275 for isophthalohydrazide, respectively [29,30]. The Langmuir isotherm plot (C/θ versus C) is demonstrated in Figure 7. K_{ads} was determined according to Equation 10:

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

Straight lines were obtained from the plot between C/θ and C . This plot was important to calculate the free energy (ΔG_{ads}). ΔG_{ads} and K_{ads} have a relationship as shown in Equation 11 [31,33]:

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

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

ΔG_{ads} has great importance in determining the nature of the interaction between inhibitor molecules and the metal surface. $\Delta G_{\text{ads}} \leq -20 \text{ kJ mol}^{-1}$ indicates that the adsorption interaction is physisorption, and $\Delta G_{\text{ads}} \geq -40 \text{ kJ mol}^{-1}$ implies that the adsorption interaction is chemisorption [44]. The ΔG_{ads} values for terephthalohydrazide and isophthalohydrazide were 40.38 and

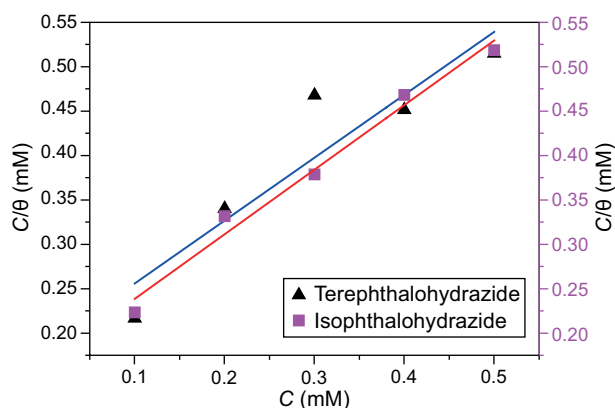
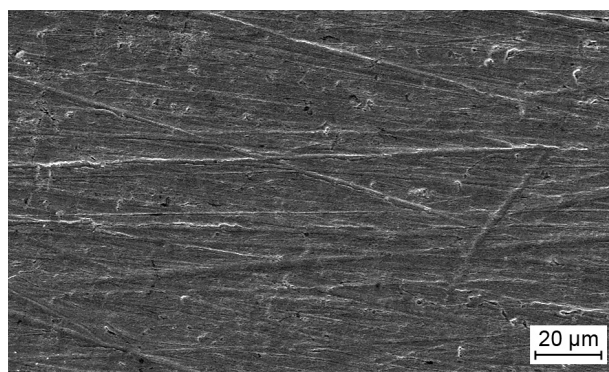


Fig. 7. Langmuir adsorption isotherms for mild steel in the presence of terephthalohydrazide or isophthalohydrazide

39.91 kJ mol^{-1} , respectively. These values suggest that the nature of adsorption interaction of terephthalohydrazide as corrosion inhibitor on mild steel surface is chemisorption, whereas that of isophthalohydrazide is chemisorption. The chemical interactions between the inhibitor and metal surface are initiated by the decomposition reaction. Thus, the adsorption isotherms of terephthalohydrazide as a corrosion inhibitor on mild steel surface might be initially a physisorption process, but the adsorption-dominant model proposed by the value of ΔG_{ads} can be categorized as chemisorption [45].



a)



b)



c)

Fig. 8. SEM micrographs of: a) in 1 M HCl, b) in the presence of 0.5 mM terephthalohydrazide, and c) in the presence of 0.5 mM isophthalohydrazide

Surface characterization after immersion

The surface morphology of the mild steel was observed in the presence and absence of terephthalohydrazide (or isophthalohydrazide) at an optimal concentration (0.5 mM) by SEM. The micrographs are shown in Figure 8. Figure 8a shows a high corrosion rate in 1 M HCl environment with severe damage on the mild steel surface. The corrosion rate was decreased by the presence of terephthalohydrazide (Fig. 8b) or isophthalohydrazide (Fig. 8c). The protective layer formed was observed by contrasting mild steel coupons in the presence of an inhibitor to mild steel coupons without an inhibitor (Fig. 8a). The morphology of mild steel coupons exposed to hydrochloric acid solution with an inhibitor was almost free from defect; therefore, terephthalohydrazide and isophthalohydrazide have anti-corrosion effect in HCl environment.

Quantum chemical studies

Quantum chemistry calculations are quite important in obtaining additional information on the inhibition phenomenon. The inhibitive efficiency is related with some quantum parameters, namely, the energy of HOMO

(E_{HOMO}), the energy of LUMO (E_{LUMO}), ΔE , σ , η , χ , and ΔN , in addition to atomic charges (Mulliken charges). These factors are shown in the optimization of the investigated inhibitive molecules [46]. These factors are quite useful in predicting the interactions between the metal surface and inhibitor molecules and the mechanism of inhibition. Table 2 represents the quantum chemical parameters calculated by DFT for the synthesized inhibitors.

The optimized structures of terephthalohydrazide and isophthalohydrazide are displayed in Figure 9. Theoretical chemical calculations were used to study the interactions between inhibitor molecules and metallic surface. HOMO value indicates the ability of a molecule to donate electrons to the low energy of the unoccupied d-orbitals of metal, whereas the LUMO value infers the ability to accept electrons from metal atoms. A low E_{LUMO} indicates that an inhibitor molecule can accept electrons from metals through the back-donation mechanism. A high ΔE value represents good inhibition activity. η and σ are important parameters that provide information about molecular stability and reactivity [47]. A hard molecule has considerably high ΔE , whereas a soft molecule has low ΔE . Thus, a molecule with high σ and low η values has a remarkable inhibition performance [48].

Tab. 2. Quantum parameters for terephthalohydrazide and isophthalohydrazide

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	η	σ	χ (eV)	ΔN
Terephthalohydrazide	-10.942	-9.197	9.531	4.7655	0.2098	6.1765	1.4
Isophthalohydrazide	-1.411	-3.829	5.35	2.675	0.3738	6.513	2.3

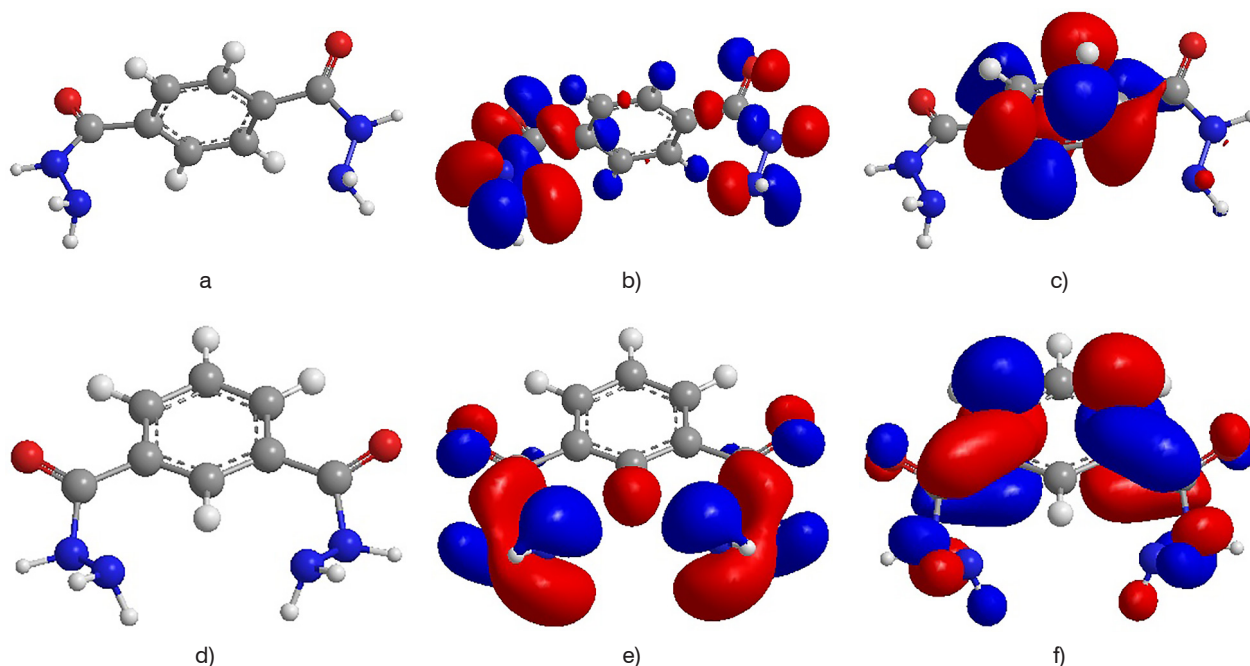


Fig. 9. Optimized structures, HOMO, and LUMO of terephthalohydrazide and isophthalohydrazide molecules

As shown in Table 3, the ΔE for terephthalohydrazide and isophthalohydrazide were 9.531 and 5.35 eV, respectively. This result is comparable to the experimental observation. The σ and ΔN for terephthalohydrazide were greater than those for isophthalohydrazide. Moreover, the η for terephthalohydrazide was less than that for isophthalohydrazide. This result supports the experimental findings. The η and σ values of the studied inhibitors are important parameters to evaluate the stability and reactivity of molecules. Chemical hardness indicates the resistance of the electron cloud of molecules to deformation or polarization. A hard molecule has large ΔE , whereas a soft molecule has small ΔE . Molecules with higher σ value will easily adsorb on the metal surface. Thus, an inhibitor with higher σ value and lower η value has better performance as corrosion inhibitor [49]. The value of HOMO for terephthalohydrazide is bigger than that for isophthalohydrazide. This result quite fits with the methodological results. Mulliken charges are important to determine the adsorption sites of the tested inhibitors. Inhibitor molecules with more negative charges have better ability to be adsorbed on the mild steel surface [50]. Table 3 shows that nitrogen and oxygen atoms possess the highest negative charge. Thus, these atoms coordinate with the metal surface. The results suggest that terephthalohydrazide forms strong coordination bonds with the mild steel surface and demonstrates better inhibition performance (97.2 %) than isophthalohydrazide (96.4 %).

Tab. 3. Atomic charges of terephthalohydrazide and isophthalohydrazide

Inhibitors	Charges		
	O ₁	N ₂	N ₃
Terephthalohydrazide	−0.3532	−0.3552	−0.1918
Isophthalohydrazide	−0.382	−0.3530	−0.1902

CONCLUSIONS

Two new corrosion inhibitors, namely, terephthalohydrazide and isophthalohydrazide, were synthesized and fully characterized by FT-IR, ¹H NMR, and ¹³C NMR spectroscopic techniques and CHN analysis. The inhibition efficiencies were evaluated by weight loss methods. Terephthalohydrazide and isophthalohydrazide showed remarkable inhibition efficiencies of 97.2 % and 96.4 % at 0.5 mM, respectively. The experimental

results showed that increase in temperature increased the corrosion rates and decreased the inhibition efficiencies of the investigated corrosion inhibitors. The adsorption isotherm follows the Langmuir adsorption isotherm. The high negative value of ΔG_{ads} indicates that terephthalohydrazide and isophthalohydrazide can be adsorbed on the metal surface by chemical adsorption. SEM investigations confirmed the formation of a protective layer on the mild steel surface in 1 M hydrochloric acid environment. The theoretical and experimental findings were in good agreement.

REFERENCES

1. A.M. Fekry and R.R. Mohamed, Acetyl thiourea chitosan as an eco-friendly inhibitor for mild steel in sulphuric acid medium, *Electrochimica Acta* **2010**, 55, 1933.
2. H. Wang, R.-B. Liu, and J. Xin, Inhibiting effects of some mercapto-triazole derivatives on the corrosion of mild steel in 1.0 M HCl medium, *Corrosion Sci.* **2004**, 46, 2455.
3. T.A. Salman, D.S. Zinad, S.H. Jaber, M. Al-Ghezi, A. Mahal, M.S. Takriff and A. Al-Amiery, Effect of 1,3,4 Thiadiazole Scaffold on the Corrosion Inhibition of Mild Steel in Acidic Medium: An Experimental and Computational Study, *J. BioTribo-Corrosion* **2019**, 5, 1.
4. H.J. Habeeb, H.M. Luaibi, R.M. Dakhil, A.A.H. Kadhum, A. Al-Amiery and T.S. Gaaz, Development of new corrosion inhibitor tested on mild steel supported by electrochemical study, *Results Phys.* **2018**, 8, 1260.
5. A. Al-Amiery, A. Kadhim, A. Mohamad, A. Musa, and C. Li, Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hydrochloric acid, *Materials* **2013**, 6, 5466.
6. S. Junaedi, A. Kadhim, A. Al-Amiery, A. Mohamad and M. 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.* **2012**, 7, 3543.
7. A. Kadhim, A. Al-Okbi, D.M. Jamil, A. Qussay, A. Al-Amiery, T.S. Gaaz, A.A.H. Kadhum, A.B. Mohamad and M.H. Nassir, Experimental and theoretical studies of benzoxazines corrosion inhibitors, *Results Phys.* **2017**, 7, 4013.
8. S. A. Abd El-Maksoud, The effect of organic compounds on the electrochemical behaviour of steel in acidic media – a review, *Int. J. Electrochem. Sci.* **2008**, 3, 528–555.
9. M. A. Quraishi and R. Sardar, Corrosion inhibition of mild steel in acid solutions by some aromatic oxadiazoles, *Mater. Chem. Phys.* **2003**, 78, 425–431.
10. K.F., Al-Azawi, I.M. Mohammed, S.B. Al-Baghdadi, T.A. Salman, H.A. Issa, A. Al-Amiery, T.S. Gaaz, and A.A.H. Kadhum, Experimental and quantum chemical simulations on the corrosion inhibition of mild steel by 3-((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)imino) indolin-2-one, *Results Phys.* **2018**, 9, 278.
11. S.B. Al-Baghdadi, F.G. Hashim, A.Q. Salam, T.K. Abed, T.S. Gaaz, A. Al-Amiery, A.A.H. Kadhum, K.S. Reda and W.K. Ahmed, Synthesis and corrosion inhibition application of NATN on mild steel surface in acidic media complemented with DFT studies, *Results Phys.* **2018**, 8, 1178.

12. M. Bouklah, N. Benchat, A. Aouniti et al., Effect of the substitution of an oxygen atom by sulphur in a pyridazinic molecule towards inhibition of corrosion of steel in 0.5 M H₂SO₄ medium, *Progress in Organic Coatings* **2004**, 51, 118.
13. S. S. Al-Taweel, T. S. Gaaz, L. M. Shaker and A. Al-Amiery, Protection of mild steel in H₂SO₄ solution with 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)indolin-2-one, *Int. J. Corros. Scale Inhib.* **2020**, 9, 1014.
14. A.H.M.J. Al-Obaidy, A. Kadhum, S.B. Al-Baghdadi, A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad and E. Yousif, 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.* **2015**, 10, 3961.
15. A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad and S. Junaedi, A Novel Hydrazinecarbothioamide as a Potential Corrosion Inhibitor for Mild Steel in HCl, *Materials* **2013**, 6, 1420.
16. M.H.O. Ahmed, A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum, A.B. Mohamad and T.S. Gaaz, Synthesis and characterization of a novel organic corrosion inhibitor for mild steel in 1 M hydrochloric acid, *Results Phys.* **2018**, 8, 728.
17. S. D. Shetty, P. Shetty, and H. V. S. Nayak, The inhibition action of N-furfuryl-N'-phenyl thiourea on the corrosion of mild steel in acid media, *J. Serb. Chem. Society* **2006**, 71, 1073.
18. K. F. Khaled and N. A. Al-Mobarak, A predictive model for corrosion inhibition of mild steel by thiophene and its derivatives using artificial neural network, *Int. J. Electrochem. Sci.* **2012**, 7, 104.
19. M. Z. A. Rafiquee, N. Saxena, S. Khan, and M. A. Quraishi, Some fatty acid oxadiazoles for corrosion inhibition of mild steel in HCl, *Indian J. Chem. Technol.* **2007**, 14, 576.
20. E.E. Ebenso, T. Arslan, F. Kandemirli et al., Quantum chemical studies of some Rhodanineazosulpha drugs as corrosion inhibitors for mild steel in acidic medium, *Int. J. Quantum Chem.* **2010**, 110, 2614.
21. O.I. Sizaya and A.P. Andrushko, On the use of triazines as inhibitors of steel corrosion, *Prot. Met.* **2004**, 40, 164.
22. H. Ashassi-Sorkhabi, B. Shaabani, and D. Seifzadeh, Corrosion inhibition of mild steel by some schiff base compounds in hydrochloric acid, *Appl. Surf. Sci.* **2005**, 239, 154.
23. S. Acharya and S. N. Upadhyay, The inhibition of corrosion of mild steel by some fluoroquinolones in sodium chloride solution, *Trans. Indian Ins. Met.*, **2004**, 57, 297.
24. M. Abdallah, M. Al-Agez, and A. S. Fouda, Phenylhydrazones derivatives as corrosion inhibitors for α -brass in hydrochloric acid solutions, *Int. J. Electrochem. Sci.* **2009**, 4, 336.
25. M. A. Quraishi and D. Jamal, Fatty acid triazoles: novel corrosion inhibitors for oil well steel (N-80) and mild steel, *J. Am. Oil Chem. Soc.* **2000**, 77, 1107.
26. T. A. Salman, A. Al-Amiery, L. M. Shaker, A. Kadhum and M. S. Takriff, A study on the inhibition of mild steel corrosion in hydrochloric acid environment by 4-methyl-2-(pyridin-3-yl)thiazole-5-carbohydrazide. *Int. J. Corros. Scale Inhib.* **2019**, 8, 1035.
27. T. A. Salman, Q.A. Jawad, M. A. Hussain, A. Al-Amiery, L. M. Shaker, A. Kadhum and M. S. Takriff, Novel eco-friendly corrosion inhibition of mild steel in strong acid environment: Adsorption studies and thermal effects. *Int. J. Corros. Scale Inhib.* **2019**, 8, 1123.
28. S.S. Al-Taweel, K.W.S. Al-Janabi, H.M. Luaibi, A. Al-Amiery and T.S. Gaaz, Evaluation and characterization symbiotic effect of benzylidene derivative with titanium dioxide nanoparticles on the inhibition of the chemical corrosion of mild steel. *Int. J. Corros. Scale Inhib.* **2019**, 8, 1149.
29. D.S. Zinad, Q.A. Jawad, M.A.M. Hussain, A. Mahal, L. M. Shaker and A. Al-Amiery, Adsorption, temperature and corrosion inhibition studies of a coumarin derivatives corrosion inhibitor for mild steel in acidic medium: gravimetric and theoretical investigations, *Int. J. Corros. Scale Inhib.* **2020**, 9, 134.
30. S. Tu, X. H. Jiang, L. M. Zhou, M. Duan, H. Wang, X. M. Jiang, Synthesis of N-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides and their corrosion inhibition activities on X70 steel in 5 M HCl. *Corros. Sci.* **2012**, 65, 13–25.
31. M. A. Hegazy, A. M. Hasan, M. M. Emara, M. F. Bakr, A. H. Youssef, Evaluating four synthesized Schiff bases as corrosion inhibitors on the carbon steel in 1 M hydrochloric acid. *Corros. Sci.* **2012**, 65, 67–76.
32. L. R. Chauhan, G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium. *Corros. Sci.* **2007**, 49, 1143–1161.
33. A. Al-Amiery, Y.K. Al-Majedy, A.A.H. Kadhum and A.B. Mohamad, New Coumarin Derivative as an Eco-Friendly Inhibitor of Corrosion of Mild Steel in Acid Medium, *Molecules* **2015**, 20, 366.
34. A.Y.I. Rubaye, A.A. Abdulwahid, S.B. Al-Baghdadi, A. Al-Amiery, A.A.H. Kadhum and A.B. Mohamad, Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/MS spectroscopy, *Int. J. Electrochem. Sci.* **2015**, 10, 8200.
35. A. Kadhum, A. Mohamad, A.A.H. Kadhum, A.B. Mohamad, L.A. Hammed, A. Al-Amiery, N.H. San and A.Y. Musa, Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by New Coumarin, *Materials* **2014**, 7, 4335.
36. A. Mohamad, A. Kadhum, A. Al-Amiery, L. Ying and A. Musa, Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0 M H₂SO₄, *Met. Mater. Int.* **2014**, 20, 459.
37. D.S. Zinad, M. Hanoon, R.D. Salim, S.I. Ibrahim, A. Al-Amiery, M.S. Takriff and A.A.H. Kadhum, A new synthesized coumarin-derived Schiff base as a corrosion inhibitor of mild steel surface in HCl medium: gravimetric and DFT studies. *Int. J. Corros. Scale Inhib.* **2020**, 9, 228.
38. Q. A. Jawad, D. S. Zinad, R. D. Salim, A. Al-Amiery, T. S. Gaaz, M. S. Takriff and A. Kadhum, Synthesis, Characterization, and Corrosion Inhibition Potential of Novel Thiosemicarbazone on Mild Steel in Sulfuric Acid Environment, *Coatings* **2019**, 9, 729.
39. A. Al-Amiery, Antimicrobial and antioxidant activities of new metal complexes derived from (E)-3-((5-phenyl-1,3,4-oxadiazol-2-ylimino) methyl)naphthalen-2-ol, *Med. Chem. Res.* **2012**, 21, 3204.
40. D.M. Jamil, A.K. Al-Okbi, S.B. Al-Baghdadi, A. Al-Amiery, A. Kadhim and T.S. Gaaz, Experimental and theoretical studies of Schiff bases as corrosion inhibitors, *Chem. Cent. J.* **2018**, 12, 1.

41. E. Yousif, Y. Win, A. Al-Hamadani, A. Al-Amiery, A. Kadhum and A. Mohamad, Furosemi as an environmental friendly inhibitor of corrosion of zinc metal in acid medium experimental and theoretical studies, *Int. J. Electrochem Sci.* **2015**, 10, 1708.
42. J.A.A. Yamin, E. Ali Eh Sheet and A. Al-Amiery, Statistical analysis and optimization of the corrosion inhibition efficiency of a locally made corrosion inhibitor under different operating variables using RSM, *Int. J. Corros. Scale Inhib.* **2020**, 9, 502.
43. A. A. F. Sabirneeza, A novel water-soluble, conducting polymer composite for mild steel acid corrosion inhibition, *J. App. Poly. Sci.* **2016**, 127, 3084.
44. P. Singh, E. Ebenso, L. Olasunkanmi, I. Obot, M. Quraishi, Electrochemical, Theoretical, and Surface Morphological Studies of Corrosion Inhibition Effect of Green Naphthyridine Derivatives on Mild Steel in Hydrochloric Acid, *J. Phys. Chem. C* **2016**, 120, 3408
45. A. Mishra, C. Verma, H Lgaz, V. Srivastava, M. A. Quraishi, E. E. Ebenso, Synthesis, characterization and corrosion inhibition studies of N-phenyl-benzamides on the acidic corrosion of mild steel: Experimental and computational studies, *J. Mol. Liq.* **2018** 251, 317
46. A. Salim, Q. Jawad, K. Ridah, L.M. Shaker, A. Al-Amiery, A.A.H. Kadhum and M.S. Takriff, Corrosion inhibition of thiadiazole derivative for mild steel in hydrochloric acid solution, *Int. J. Corros. Scale Inhib.* **2020**, 9, 550.
47. A. Al-Amiery, L.M. Shaker, A.A.H. Kadhum, M.S. Takriff, Corrosion Inhibition of Mild Steel in Strong Acid Environment by 4-((5,5-dimethyl-3-oxocyclohex-1-en-1-yl)amino)benzenesulfonamide, *Tribol. Ind.* **2020**, 42, 89.
48. A. Braihi, A. Jawad, A. Kadhum, H. Aljibori, A. Al-Amiery, Chemical resistance of NR/SBR rubber blends for surfaces corrosion protection of metallic tanks in petrochemical industries, *Koroze a ochrana materiálu* **2020**, 64, 65.
49. E.Gad, E. Azzam, S. Halim, Theoretical approach for the performance of 4-mercapto-1-alkylpyridin-1-ium bromide as corrosion inhibitors using DFT, *Egypt. J. Petrol.* **2018**, 27, 695
50. A. A. Al-Amiery, L. S. Shaker, Corrosion inhibition of mild steel using novel pyridine derivative in 1 M hydrochloric acid, *Koroze a ochrana materiálu* **2020**, 64, 59.