



Electrochemical studies of novel corrosion inhibitor for mild steel in 1 M hydrochloric acid

Ahmed A. Al-Amiery^{a,*}, Mohammed H. Othman Ahmed^b, Thamer Adnan Abdullah^c,
Taysir Sumer Gaaz^{d,*}, Abdul Amir H. Kadhum^b

^a Energy and Renewable Energies Technology Center, University of Technology, Baghdad, Iraq

^b Department of Chemical & Process Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Bangi, Selangor 43600, Malaysia

^c Branch of Applied Chemistry, Applied Science Department, University of Technology, Baghdad, Iraq

^d Department of Machinery Equipment Engineering Techniques, Technical College Al-Musaib, Al-Furat Al-Awsat Technical University, Al-Musaib, Babil 51009, Iraq

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ABSTRACT

The electrochemical performance of a novel organic corrosion inhibitor 6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3], for mild steel in 1 M hydrochloric acid is evaluated by potentiodynamic curves. The experimental results show that the investigated inhibitor [HT3], which can effectively retard the corrosion process that occurs to mild steel with a hydrochloric acid solution by providing a protective coating for the mild steel that, can be weakened by increasing the temperature. Furthermore, the inhibition efficiency of [HT3] increased with increasing the concentrations of the inhibitors and decreased with increasing temperature.

Introduction

The use of organic compounds containing these atoms, especially nitrogen, to reduce corrosion attack on steel has been studied in some detail [1]. The availability of non-bonded (lone pair) and p-electrons in inhibitor molecules facilitates electron transfer from the inhibitor to the metal. A coordinate covalent bond, involving transfer of electrons from inhibitor to the metal surface, may be formed. The strength of the chemisorption bond depends upon the electron density of the donor atom in the functional group and also the polarizability of the group [2]. The electron density in the metal at the point of attachment changes, resulting in retardation of the cathodic or anodic reactions [3]. The effectiveness of the organic inhibitors depends on their adsorption rates and covering capabilities on metal surfaces. Many sources have determined that adsorption depends on the molecular structure and surface charge of the metal and type of electrolyte. Inhibitors adsorbed by a metal surface immersed in an aqueous phase replace water molecules adsorbed by the surface. Electrostatic interactions between inhibitor molecules and a metal are prominent during this inhibition action [4]. The adsorption of inhibitors on the metal/solution interface is influenced by: (i) the nature and surface charge of the metal; (ii) the type of aggressive electrolyte; and (iii) the chemical structure of the inhibitors [5]. Inhibitors act through a process of surface adsorption, so the efficiency of a given inhibitor depends on the characteristics of the

environment in which it acts, the nature of the metal surface and electrochemical potential at the interface [6,7]. Inhibition efficiency is attributed to a combination of a moderation of film pH, reduction of chloride activity and concomitant release of inhibitor anions [8–10]. Acid solutions are widely used in industrial applications, such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. As a result of the general aggressiveness of acid solutions, inhibitors are commonly used to reduce corrosive attack on metallic materials [11]. Continuation of previous researches [12–21], we investigate a new organic inhibitor namely 6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3], which was successfully employed as a corrosion inhibitor for mild steel in 1 M hydrochloric acid. The inhibitory effect was investigated using potentiodynamic polarization. The inhibition efficiency of [HT3], (74%) and could be considered an effective corrosion inhibitor to conserve metal surface from atmospheric corrosion.

Materials and methods

All chemicals used in this synthesis were of reagent grade (supplied by Sigma-Aldrich, Selangor, Malaysia) and were used as received without further purification. The purity of the compounds was checked by thin-layer chromatography (TLC) on silica gel G plates with benzene, ethyl acetate, methanol 40:30:30 (v/v) or toluene: acetone 75:25 (v/v)

* Corresponding authors.

E-mail addresses: dr.ahmed1975@gmail.com (A.A. Al-Amiery), taysirsumer@gmail.com (T.S. Gaaz).

as the mobile phase; the spots were located under UV light at 254 and 365 nm. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Scientific Nicolet 6700 FT-IR Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). Nuclear magnetic resonance (NMR) spectra were recorded using an AVANCE III 600 MHz spectrometer (Bruker, Billerica, MA, USA). The Synthesis of corrosion inhibitor 6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3] was done according to this method. A mixture of 4-formylphenol (1.22 g, 10 mmol) and 4-amino-5-hydrazinyl-3-mercapto-1,2,4-triazole (1.46 g, 10 mmol) with ferric ammonium sulfate (5.0 g, 10 mmol) in water (50 mL) was reacted under reflux condition. After 6 h, a solution of ferric ammonium sulfate (20 mmol, 10 g) in water (50 mL) was added to the mixture of reaction. The reaction continued for 4 h, TLC, using ethyl acetate, monitored the progress of the reaction: n-hexane (1:1). The mixture of the reaction was cold; the precipitate was filtered, washed with water, dried and recrystallized by ethanol. IR: 3305.1 and 3278.8 cm^{-1} (NH), 3155 cm^{-1} (O–H), 3082.5 cm^{-1} (C–H; aromatic group), and 16132.9 cm^{-1} (C=N). ^1H NMR (δ 2.053 for Acetone as a solvent): δ s, 2.935 NH; s, 3.298 NH; 5.1 OH; dd 6.990 and 7.004 for CH aromatic; dd 7.775 and 7.790 for CH aromatic; 9.837 for SH. ^{13}C NMR (Acetone solvent has δ 29.45 and 206.31): 116.45C–H for OH–C=C–H; 125.25 = C–C; (127.39, 129.24, 130.43, 132.79 Aromatic carbons), 146.41C=N, 159.89C–OH; 161.71C=N; 163.99 N=C–SH.

Electrochemical measurement

Mild steel specimens were obtained from Gamry Instruments Inc. and were used as working electrodes throughout this study, each with an active surface area of 4.5 cm^2 . The composition (wt.%) of the mild steel was as follows: Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; and Al, 0.01. The specimens were cleaned according to ASTM standard procedure G1-03 [22]. Measurements were conducted in aerated, non-stirred 1.0 M HCl solutions containing different concentrations of the inhibitor. Electrochemical measurement was performed at the steady-state corrosion potential using a Gamry eurocell. The measurements were performed using the Gamry Instrument Potentiostat/Galvanostat/ZRA (REF 600) model (Gamry, Warminster, PA, USA). The potentiodynamic polarization curves were swept from -0.2 to $+0.2$ V SCE over the corrosion potential at a scan rate of $0.5 \text{ mV}\cdot\text{s}^{-1}$. The electrochemical measurements began to be collected approximately 30 min after the working electrode was immersed in the solution to allow the steady state potential to stabilize. Each measurement was repeated five times, and only the average values were reported to verify reproducibility of the experiments.

Results and discussion

To synthesize 6-(4-hydroxyphenyl)-3-mercapto-7,8-dihydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine [HT3] as a corrosion inhibitor, the reaction sequence outlined in Fig. 1 was followed, starting from commercially available 4-formylphenol and (4-amino-5-hydrazinyl-3-mercapto-1,2,4-triazole).

The synthesis was carried out by refluxing 4-amino-5-hydrazinyl-3-mercapto-1,2,4-triazole with 4-formylphenol in the presence of with ferric ammonium sulfate. The molecular weight of the synthesized corrosion inhibitor was 248 g/mol which was calculated based on the molecular formula ($\text{C}_9\text{H}_8\text{N}_6\text{OS}$) and supported via mass spectrometry.

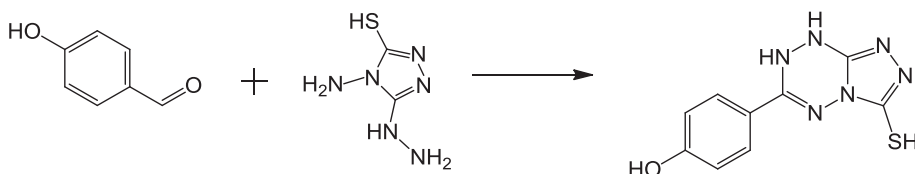


Fig. 1. Chemical synthesis of inhibitor.

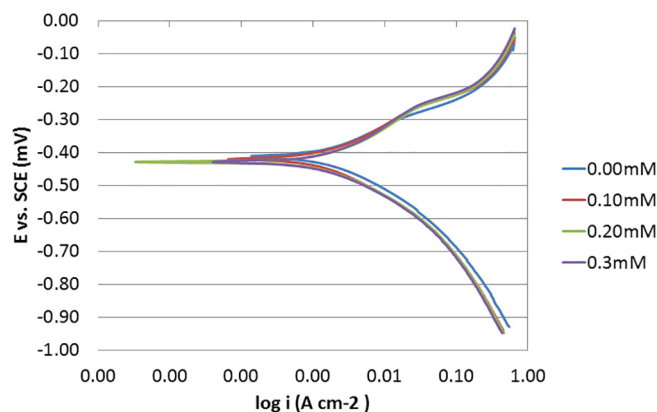


Fig. 2. Potentiodynamic polarization curves for mild steel in 1.0 M HCl with various concentrations of the inhibitor at 30 °C.

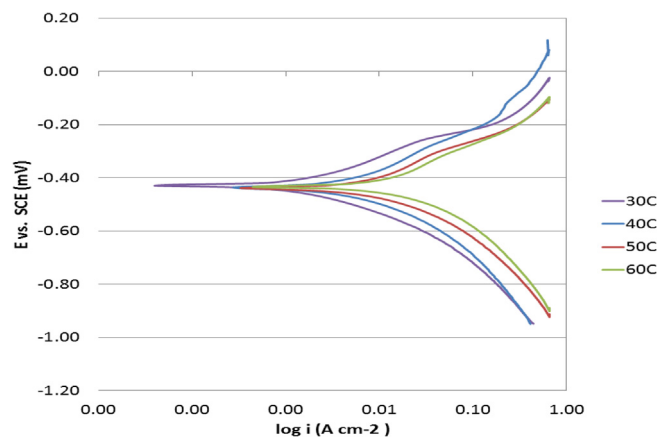


Fig. 3. Potentiodynamic polarization curves for mild steel in 1.0 M HCl with 0.5 mM HT3, at different temperatures.

HT3 can be dissolved in acetone, dichloromethane, dimethylformamide, dimethylsulfoxide, ethanol or methanol solutions. A proton-NMR spectrum for the corrosion inhibitor show the absorption bands at 3305.1 and 3278.8 cm^{-1} for amine NH and azomethane (C=N) and stretching at 16132.9 cm^{-1} can be seen. The bands at 3155 and 3082.5 cm^{-1} are from O–H and C–H aromatic respectively. The ^1H NMR spectrum exhibits two singlet signals at δ 2.935 ppm and 3.298 ppm due to the N–H protons groups respectively, δ 5.100 (s, 1H, for OH), and δ 6.990 (d, ^1H), 7.004 (s, ^1H), 7.775 (d, ^1H) and 7.790 (s, ^1H) for aromatic ring, also at δ 9.837 (s, ^1H , for –SH).

^{13}C NMR, spectrum for the corrosion inhibitor illustrates a signal appears at 163.99 ppm due to the N=C–SH group also 159.89 ppm and 146.41 ppm are from hydroxyl and azomethane groups respectively. Bands at 127.39, 129.24, 130.43 and 132.79 ppm are from carbon atoms in the aromatic ring.

Electrochemical

Polarization measurements

Potentiodynamic polarization method was conducted to obtain the curves shown in Figs. 2 and 3. Fig. 2 shows the Potentiodynamic

Table 1

Polarization parameters for mild steel in 1.0 M HCl with various concentrations of corrosion inhibitor.

Conc. (mM)	Polarization parameters Potentiodynamic (PD)					
	β_a (Vdec ⁻¹)	β_c (Vdec ⁻¹)	I_{corr} (μAcm^{-2})	$-E_{corr}$ (mV vs. SCE)	Corrosion Rate (mpy)	IE (%)
Blank	0.15	0.21	3180	462	1212	0.00
0.3	0.15	0.20	1720	437	656.3	45.91
0.4	0.15	0.20	1490	436	566	53.14
0.5	0.13	0.15	826	429	315.6	74.03

Table 2

Polarization parameters for mild steel in 1.0 M HCl with 0.5 mM corrosion inhibitor at different temperatures.

Temp °C	Conc. mM	Polarization parameters Potentiodynamic (PD)					
		β_a (Vdec ⁻¹)	β_c (Vdec ⁻¹)	I_{corr} (μAcm^{-2})	$-E_{corr}$ (mV vs. SCE)	C_R mpy	IE %
30	Blank	0.15	0.21	3180	462	1212	0.00
30	0.5	0.13	0.15	826	429	315.6	74.03
40	Blank	0.15	0.23	4740	450	1806	0.00
40	0.5	0.12	0.59	2320	426	883.4	51.05
50	Blank	0.18	0.24	12,100	432	4611	0.00
50	0.5	0.16	0.2	4310	421	1643	64.38
60	Blank	0.20	0.25	19,600	491	7462	0.00
60	0.5	0.16	0.22	11,500	431	4378	41.32

polarization curves for mild steel in the solution of 1 M HCl at different concentrations of the corrosion inhibitor at 30 °C, while Fig. 3 shows the Potentiodynamic polarization curves for mild steel in the solution of 1 M HCl with 0.5 mM of the inhibitor at different temperatures.

Fig. 2 illustrates the effect of a range of inhibitor concentrations from 0.10 to 0.3 mM on mild steel in 1 M HCl using potentiodynamic polarization. Fig. 2 reveals that the anodic and cathodic processes change with the addition of various concentrations of HT3. A compound can be classified as an anodic- or cathodic-type inhibitor when the change in ECORR is greater than 85 mV [23]. Because its largest displacement is 429 mV at 30 °C (Table 1), so, the HT3, act as a mixed-type inhibitor, which mean that the addition of HT3, to acidic solution reduces the anodic dissolution of mild steel and retards cathodic hydrogen.

Fig. 3 illustrates the effect of a range of concentrations from 0.10 to 0.3 mM on mild steel in 1 M HCl. Table 2 shows that i_{corr} raise with rising temperatures of the solution, whilst i_{corr} diminution with the addition of HT3, to the corrosive solution throughout the examined temperature domain. Such attitude may be demonstrated as follows: HT3 adsorbs on the metal surface, and an increase in temperature effects in the desorption of several adsorbed molecules, exhibit more metal surface to the corrosive solution, consequently increasing the metal dissolution average and decreasing inhibition efficiency [24]. The increase of inhibitor molecules reason the estimated ECORR value to shift toward positively values, that reason the inhibitory effect of HT3, on the corrosion of mild steel at 30 °C; while, this value diminution with temperature of solution, that suggest a decrease in the level of protection of inhibitor [24–28]. The numerical values of the variations of corrosion current density (i_{corr}), corrosion potential (E_{CORR}), anodic Tafel slope (β_a) and cathodic Tafel slope (β_c) with various concentrations of the inhibitor and at various solution temperatures were obtained from polarization profiles and are presented in Tables 1 and 2.

These values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at E_{CORR} . The inhibition efficiency (IE) was calculated using the Eq. (1):

$$IE (\%) = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities in the absence and presence of the inhibitor, respectively.

Based on Table 1, we can see that the current density values (I_{corr}) decreases when the concentration of HT3, increases. Table 2 illustrates that, I_{corr} increases with the temperature of the tested solution. In addition, the anodic tafel slope (β_a) and the cathodic tafel slope (β_c) had changed with the addition of the HT3. This shows that the HT3, influences the anodic and cathodic reactions [29]. In addition, the transition of values of E_{corr} to more positive values were detected in different HT3 concentrations, which reflects the inhibitory effect on the corrosion of mild steel at 30 °C. However, for the E_{corr} values those are decreased with the increment of the solution temperature, which indicates a decrease in the level of protection of the inhibitor. This also confirms that a protective layer on mild steel samples has been generated as a result of the absorption of HT3, molecules to the surface of mild steel [30]. The inhibition efficiencies (IE) illustrated in Table 1 and 2 were calculated by applying the Eq. (1). The efficiencies increased with the concentration of the inhibitor, but decreased with increasing the temperature. By increasing both the temperature of the HCl solution and the corrosion inhibitors, efficiencies will decrease.

Conclusions

In this manuscript, we presented for the synthesis of organic inhibitor which was tested and the changes in potentiodynamic polarization measurements were utilized to study the corrosion inhibition of mild steel in 1.0 M HCl solutions at 30, 40, 50 and 60 °C, with the use of the inhibitor. This inhibitor exhibited a good inhibition performance as an organic inhibitor. This inhibitor has heteroatoms, O, and N that are found to have higher basicity and electron density and thus act as corrosion inhibitor. The acidic corrosion of mild steel was reduced by addition of appropriate novel inhibitor concentrations. The inhibition efficiencies increased with inhibitor concentration but were reduced proportionally with temperature. The inhibitor acts as an efficient corrosion inhibitor on a mild steel surface with a maximum inhibition efficiency of 74%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.rinp.2018.04.004>.

References

- [1] Ahamad I, Gupta C, Prasad R, Quraishi M. An experimental and theoretical investigation of adsorption characteristics of a Schiff base compound as corrosion inhibitor at mild steel/hydrochloric acid interface. *J Appl Electrochem* 2010;40:2171–83.
- [2] Abiola O, Oforka N, Ebenso E, Nwinuka N. Eco-friendly corrosion inhibitors: the inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media. *Anti-Corros Methods Mater* 2007;54:219–24.
- [3] Yıldırım A, Cetin M. Synthesis and evaluation of new long alkyl side chain acetamide, isoxazolidine and isoxazoline derivatives as corrosion inhibitors. *Corros Sci* 2008;50:155–65.
- [4] Emregül K, Hayvalı M. Studies on the effect of vanillin and protocatechualdehyde on the corrosion of steel in hydrochloric acid. *Mater Chem Phys* 2004;83:209–16.
- [5] Okafor PC, Zheng Y. Synergistic inhibition behaviour of methylbenzyl quaternary imidazole derivative and iodide ions on mild steel in H₂SO₄ solutions. *Corros Sci* 2009;51:850–9.
- [6] Al-Obaidy A, Kadhum A, Al-Baghdadi S, Al-Amiery A, Kadhum A, Yousif E, et al. 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;10:3961–12972.
- [7] Zheludkevich M, Poznyak S, Rodrigues L, Raps D, Hack T, Dick L, et al. Active protection coatings with layered double hydroxide nanocontainers of corrosion inhibitor. *Corros Sci* 2010;52:602–11.
- [8] Tedim J, Poznyak S, Kuznetsova A, Raps D, Hack T, Zheludkevich M, et al. Enhancement of active corrosion protection via combination of inhibitor-loaded nanocontainers. *ACS Appl Mater Interfaces* 2010;2:1528–35.
- [9] Yousif E, Win Y, Al-Hamadani A, Al-Amiery A, Kadhum A, Mohamad A. Furosemide as an environmental-friendly inhibitor of corrosion of zinc metal in acid medium: experimental and theoretical studies. *Int J Electrochem Sci* 2015;10:1708–18.
- [10] Schneider G, Clément-Chomienne O, Hilfiger L, Schneider P, Kirsch S, Böhm HJ, et al. Virtual screening for bioactive molecules by evolutionary de novo design. *Angewandte Chem Int Ed* 2000;39:4130–3.
- [11] Fayyad E, Almaadeed M, Jones A, Abdullah A. Evaluation techniques for the corrosion resistance of self-healing coatings. *Int J Electrochem Sci* 2014;9:4989–5011.
- [12] Al-Amiery A, Kadhum A, Mohamad A, Junaedi S. Novel hydrazinecarbothioamide as a potential corrosion inhibitor for mild steel in HCl. *Materials* 2013;6:1420–31.
- [13] Rubaye A, Abdulwahid A, Al-Baghdadi SB, Al-Amiery A, Kadhum AH, Mohamad A. Cheery sticks plant extract as a green corrosion inhibitor complemented with LC-EIS/ MS spectroscopy. *Int J Electrochem Sci* 2015;10:8200–9.
- [14] Al-Amiery A, Al-Majedy YK, Kadhum A, Mohamad A. New coumarin derivative as an eco-friendly inhibitor of corrosion of mild steel in acid medium. *Molecules* 2015;20:366–83.
- [15] Kadhum A, Mohamad A, Hamed L, Al-Amiery A, San N. Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. *Materials* 2014;7:4335–48.
- [16] Mohamad A, Kadhum A, Al-Amiery A, Ying L, Musa A. Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0M H₂SO₄. *Met Mater Int* 2014;20:459–67.
- [17] Al-Amiery A, Kadhum A, Alobaidy A, Mohamad A, Hoon P. Novel corrosion inhibitor for mild steel in HCl. *Materials* 2014;7:662–72.
- [18] Al-Amiery A, Kadhum A, Mohamad A, Musa A, Li C. Electrochemical study on newly synthesized chlorocoumarin as an inhibitor for mild steel corrosion in hydrochloric acid. *Materials* 2013;6:5466–547.
- [19] Junaedi S, Kadhum A, Al-Amiery A, Mohamad A, Takriff M. 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;7:3543–54.
- [20] Mohamad. Furosemide as an environmental-friendly inhibitor of corrosion of zinc metal in acid medium: experimental and theoretical studies. *Int J Electrochem Sci* 2015;10:1708–15.
- [21] Al-Azawi K, Mohammed I, Al-Baghdadi S, Salman T, Issa H, Al-Amiery A, et al. 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;9:278–83.
- [22] Standard A. “G1-03,” Standard Practice for preparing, cleaning, and evaluating corrosion test specimens, *Annual Book of ASTM Standards*, 2003;3:17-25.
- [23] Al-Amiery AA, Kassim FAB, Kadhum AAH, Mohamad AB. Synthesis and characterization of a novel eco-friendly corrosion inhibition for mild steel in 1 M hydrochloric acid. *Scientific Reports* 2016;6.
- [24] Ashassi-Sorkhabi H, Asghari E, Ejbari P. Electrochemical studies of adsorption and inhibitive performance of basic yellow 28 dye on mild steel corrosion in acid solutions. *Acta Chim Slov* 2011;58:270–7.
- [25] Ahmed MHO, Al-Amiery AA, Al-Majedy YK, Kadhum AAH, Mohamad AB, Gaaz TS. Synthesis and characterization of a novel organic corrosion inhibitor for mild steel in 1M hydrochloric acid. *Results Phys* 2018.
- [26] Kadhim A, Al-Okbi AK, Jamil DM, Qussay A, Al-Amiery AA, Gaaz TS, et al. Experimental and theoretical studies of benzoxazines corrosion inhibitors. *Results Phys* 2017;7:4013–9.
- [27] Jamil DM, Al-Okbi AK, Al-Baghdadi SB, Al-Amiery AA, Kadhim A, Gaaz TS, et al. Experimental and theoretical studies of Schiff bases as corrosion inhibitors. *Chem Cent J* 2018;12:7.
- [28] Habeeb H, Luaibi H, Abdullah T, Dakhil R, Kadhum A, Al-Amiery A. Case study on thermal impact of novel corrosion inhibitor on mild steel. *Case Stud Therm Eng* 2018;12:64–8.
- [29] Saliyan VR, Adhikari AV. Quinolin-5-ylmethylene-3-([8-(trifluoromethyl)quinolin-4-yl]thio)propanohydrazide as an effective inhibitor of mild steel corrosion in HCl solution. *Corros Sci* 2008;50:55–61.
- [30] Amin MA, Ibrahim MM. Corrosion and corrosion control of mild steel in concentrated H₂SO₄ solutions by a newly synthesized glycine derivative. *Corros Sci* 2011;53:873–85.