Protection of mild steel in H₂SO₄ solution with 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)indolin-2-one

S.S. Al-Taweel,^{1*} T.S. Gaaz,^{2*} L.M. Shaker³ and A. Al-Amiery³

¹College of Science, University of Al-Qadisiyah, Al-Diwaniyah, 58002, Iraq

²Al-Mussaib Technical College, Al-Furat Al-Awsat Technical University, 51006, Babylon, Iraq

³University of Technology, Baghdad 10001, Iraq

*E-mail: taysersumer@atu.edu.iq, saja.al-taweel@qu.edu.iq

Abstract

The use of a natural or synthesized corrosion inhibitor is an important method for the protection of surfaces of metals and alloys from corrosion. The inhibitor molecules adsorbed on a metal surface block the contact between the corrosive solution and the metal surface. In this work, a new indoline derivative, namely, 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)-indolin-2-one (HTTI), was synthesized by condensation of equimolar quantities of 2,3-dioxindoline and 4-amino-5-thioxo-3-(2-hydroxyphenyl)-1,2,4-triazole in methanol. The molecular structure of HTTI was characterized by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (¹H NMR) spectroscopies along with micro-elemental analysis that was utilized to determine the elemental concentrations of carbon, hydrogen and nitrogen atoms in the synthesized compound. The corrosion inhibition efficiency of HTTI was investigated for mild steel in 0.5 M sulfuric acid solution by using the weight loss method to determine the concentration, time and temperature effects. The new synthesized inhibitor shows a high inhibition activity of 93.4% at 500 ppm. The results indicate that HTTI slows down the corrosion reaction in the corrosive environment and the inhibitor efficiency increases with increasing inhibitor concentration and decreases with an increase in time and temperature. Moreover, the inhibition efficiency increases with immersion time till 10 hours and decreases after 24 hours. The adsorption of the new synthesized corrosion inhibitor on mild steel surface obeys the Langmuir adsorption isotherm.

Keywords: hydroxyphenyl, HTTI, sulfuric acid, corrosion, indoline.

Received: July 1, 2020. Published: August 12, 2020

doi: [10.17675/2305-6894-2020-9-3-14](https://doi.org/10.17675/2305-6894-2020-9-3-14)

1. Introduction

In general, the use of inhibitors is considered as a practical methodology to prevent metals from corroding in an acidic medium [1–3]. The most prominent organic inhibitors contain nitrogen, oxygen and sulfur atoms [4–6]. Chemical substances comprising functional groups and π -electrons are preferred as inhibitors for preventing metal corrosion. From the findings

of previous studies, it is found that the majority of organic inhibitors act by adsorption on metal surfaces [7–9]. The corrosive electrolyte type, the surface charge, the nature of the metal and the inhibitor chemical structure are the parameters that affect the adsorption process. Excellent inhibition is given by the compounds that contain both nitrogen and sulfur than that earned by compounds that contain one of these elements [10–12]. On the other hand, triazole and triazole-type compounds containing nitrogen, sulfur and a heterocycle attract much attention due to the high quality of corrosion protection they provide [13–15]. Studies are ongoing with chemically manufactured triazole derivatives as inhibitors of mineral corrosion in acid environments [16–18]. As an example, an oxadiazole-triazole derivative proved its effectiveness as a corrosion inhibitor of mild steel in a sulfuric acid solution, its efficiency at 298 K was more than 97.6%. As yet another example for efficient inhibitors, azole derivatives worked as inhibitors for 304L stainless steel corrosion in HCl [19–21]. We are synthesizing new organic compounds with multiple functional groups and heteroatoms such as phosphorous, sulfur, oxygen and/or nitrogen in order to study the effectiveness of these organic compounds as anti-corrosive substances in acid environments [22–28]. This work demonstrates the appraisal of the inhibition performance of 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)indolin-2-one on mild steel corrosion in 0.5 M sulfuric acid environment by gravimetric techniques.

2. Materials and Methods

2.1. Synthesis of the corrosion inhibitor

The 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)indolin-2-one inhibitor (HTTI) was synthesized and its chemical structure is demonstrated in Figure 1. The synthesized inhibitor is typically formed by condensation of equimolar quantities of a 2,3-dioxindoline (50.0 mmol) and 4-amino-5-thioxo-3-(2-hydroxyphenyl)-1,2,4-triazole (50.0 mmol) in methanol as a solvent in the presence of a few drops of hydrochloric acid for 6 hours. The precipitate was filtered off and recrystallized from ethyl alcohol. The yield was 51% and the melting point of the inhibitor was m.p. 180°C; FT-IR: 3199.3 and 3173.8 cm^{-1} for amino groups, 1731.8 cm^{-1} for carbonyl, 1618.4 cm^{-1} for imine, and 1111.5 cm^{-1} for thiol group. ^1H NMR (DMSO- d_6): 11.93 ppm (d, amino proton), 11.09 ppm (d, amino proton), 7.03–7.81 (multiplet, aromatic protons). CHN analysis Calculated/Found (%) for $\text{C}_{16}\text{H}_{11}\text{N}_5\text{O}_2\text{S}$; C: 56.96/57.08, H: 3.29/3.26, N: 20.76/20.43.

Figure 1. Structure of HTTI.

2.2. Mild steel coupons

The experiments were carried out on mild steel coupons with the composition %: silicon 0.38; carbon 0.21; aluminum 0.01; manganese 0.05; phosphorus 0.09; sulfur 0.05 and the remainder iron. The coupons to be tested were made in 4.5 cm × 2.0 cm × 0.1 cm dimensions and suspended in the sulfuric acid environment with fishing thread passing through a hole drilled on top of these coupons. Emery papers were used to polish and degrease the mild steel coupons to be tested, then cleaned and washed with double distilled water and acetone.

2.3. Solutions

The corrosive solution with a concentration of 0.5 M was prepared by dropwise addition of concentrated sulfuric acid to distilled water.

2.4. Weight Loss Measurements

Weight loss measurements were performed on mild steel coupons prepared as described above. The experiments were carried out at temperature of 303–333 K. The weighed cleaned mild steel coupons were immersed in the corrosive environment, each experiment was conducted in triplicate in aerated solutions and the mean value was taken. To evaluate the weight loss (for exposure periods of 1, 5, 10 and 24 h), the mild steel coupons were removed from corrosive media.

The weight losses (in the absence and in the presence of HTTI at concentrations of 100, 200, 300, 400 and 500 ppm) were determined. The corrosion rates (CR) of mild steel coupons in the corrosive environment were calculated by Equation 1.

$$C_R \text{ (mm/y)} = \left[\frac{87.6 \Delta W}{\rho A t} \right] \quad (1)$$

where ΔW is the weight loss (g); ρ is the density of tested coupons ($\text{g}\cdot\text{cm}^{-3}$); A is the surface area of the tested coupons (cm^2) and t is the exposure time (h).

The inhibition efficiency of mild steel in H_2SO_4 solution was determined according to Equation 2.

$$IE(\%) = \left[\frac{W_0 - W_{\text{inh}}}{W_0} \right] \times 100 \quad (2)$$

The degree of surface coverage can be calculated according to Equation 3.

$$\theta = \frac{IE}{100} \quad (3)$$

3. Results and Discussion

3.1. Synthesis of HTTI

The condensation reaction between 2,3-dioxindoline and 4-amino-5-thioxo-3-(2-hydroxyphenyl)-1,2,4-triazole was carried out as shown in Figure 2, and the final product was characterized by spectroscopic techniques.

Figure 2. The condensation reaction between 2,3-dioxindoline and an 4-amino-5-thioxo-3-(2-hydroxyphenyl)-1,2,4-triazole.

3.2. Corrosion Rates

The mild steel corrosion rate in sulfuric acid environment can be evaluated by the weight loss method. The dissolution mechanism of iron in sulfuric acid environment obeys Equations 4–6.

First of all, we assume a blocking mechanism of action of the synthesized inhibitor. As a result of the above reactions with a significant solubility of the corrosion products, mild steel loses weight in the corrosive acid environment. The results on the metal weight loss expressed as the corrosion rate as a function of time and concentration of the new synthesized inhibitor are shown in Figure 3.

These findings demonstrate that the corrosion rate of the tested coupon metal in sulfuric acid solution decreases with increasing immersion time in the absence and in the presence of various concentration of the tested inhibitor. The effect of inhibitor concentration on the corrosion rate in the acidic environment for 1, 5, 10 and 24 hours immersion times is demonstrated in Figure 3. HTTI as a corrosion inhibitor is seen to decrease the C_R at the tested concentrations, indicating that it slows down the corrosion reaction. These effects become clearer with increasing the inhibitor concentration, indicating that the inhibition significantly depends on the inhibitor concentration.

Figure 3. The corrosion rate of mild steel in 0.5 M H₂SO₄ in the absence and presence of HTTI.

3.3 Inhibition efficiency

The inhibitive performance of HTTI was determined by gravimetric techniques after exposure times of 1, 5, 10 and 24 hours at 303 K. These data are in Figure 4 from which it is obvious that the inhibitive efficiency increases as the concentration of HTTI increases. The highest inhibitive efficiency was 93.4% at the inhibitor concentration of 500 ppm and the immersion time of 5.0 h. No significant impact on the inhibitive performance was observed upon increasing the inhibitor concentration in the acidic environment. From Figure 4 it is obvious that the inhibition efficiency increases with increasing time. After exposure for 10 hours, the inhibition efficiency decreases due to the deterioration of bonds between the inhibitor molecules and mild steel.

3.4. Temperature

The corrosion rate and inhibition efficiency of mild steel coupons in 0.5 M H₂SO₄ solution in the presence of the tested inhibitor at various temperatures obtained by the gravimetric technique is demonstrated in Figure 5. As one can see from Figure 5, increasing the temperature increases the corrosion rate and decreases the inhibition efficiency. At the inhibitor concentrations tested, the corrosion rate was 8.9 mmpy at a solution temperature of 303 K and 12.63 mmpy at 333 K at the inhibitor concentration of 500 ppm. The inhibition efficiencies under these conditions were 93.4% and 66.94%, respectively. The significant inhibition efficiency of the inhibitor studied was attributed to the resonance effect and the presence of five nitrogen atoms and two oxygen and one sulfur atoms which have lone pairs of electrons, as well as the presence of aromatic rings which give planarity and resonance. All the above parameters facilitate the adsorption of inhibitor molecules on the mild steel surface.

Figure 4. The inhibition efficiency of mild steel in 0.5 M H_2SO_4 in the presence of HTTL.

Figure 5. The temperature effects on corrosion rate and inhibition efficiency.

Figure 5. The temperature effects on corrosion rate and inhibition efficiency (*continued*).

3.5. Adsorption

Adsorption depends on two major parameters, *i.e.*, the metal composition and the structure of the corrosion inhibitor, as well as minor parameters such as the inhibitor concentration, solution temperature and exposure time. The Langmuir adsorption isotherm was found to agree with the results of this work. Figure 6 demonstrates the plot of $^{\circ}C/\theta$ vs. concentration to be linear, which fits the Langmuir adsorption isotherm represented by Equation 7.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (7)$$

where C is the HTTI concentration and K_{ads} is the adsorption constant.

Figure 6. Langmuir adsorption isotherm for HTTI adsorption on the tested coupons in 0.5 M sulfuric acid solution.

Conclusions

The 3-((3-(2-hydroxyphenyl)-5-thioxo-1,2,4-triazol-4-yl)imino)indolin-2-one compound (HTTI) was synthesized and fully characterized. HTTI was found to have a significant inhibition efficiency for mild steel coupons in 0.5 M sulfuric acid environment. The inhibitive performance increased with increasing inhibitor concentration and decreased with increasing exposure time and solution temperature. The adsorption of HTTI molecules on mild steel surface obeys the Langmuir adsorption isotherm.

Conflict of Interests

The authors declare there is no conflict of interests.

Acknowledgments

The authors are grateful to the University of Technology Baghdad-Iraq for support.

References

1. H.-L. 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, *Corros. Sci.*, 2004, **46**, no. 10, 2455–2466. doi: [10.1016/j.corsci.2004.01.023](https://doi.org/10.1016/j.corsci.2004.01.023)
2. T.A. Salman, D.S. Zinad, S.H. Jaber, M. Al-Ghezi, A. Mahal, M.S. Takriff and A.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. Bio Tribo Corros.*, 2019, **5**, 1–11. doi: [10.1007/s40735-019-0243-7](https://doi.org/10.1007/s40735-019-0243-7)
3. H.J. Habeeb, H.M. Luaibi, R.M. Dakhil, A.A.H. Kadhum, A.A. Al-Amiery and T.S. Gaaz, Development of new corrosion inhibitor tested on mild steel supported by electrochemical study, *Results Phys.*, 2018, **8**, 1260–1267. doi: [10.1016/j.rinp.2018.02.015](https://doi.org/10.1016/j.rinp.2018.02.015)
4. A. Al-Amiery, A. Kadhum, A. Mohamad, A. Musa and C. Li, Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hydrochloric acid, *Mater.*, 2013, **6**, no. 12, 5466–5477. doi: [10.3390/ma6125466](https://doi.org/10.3390/ma6125466)
5. S. Junaedi, A. Kadhum, A. Al-Amiery, A. Mohamad and M. Takriff, Synthesis and characterization of novel corrosion inhibitor derived from oleic acid: 2-Amino5-Oleyl1,3,4-Thiadiazol (AOT), *Int. J. Electrochem. Sci.*, 2012, **7**, 3543–3554.
6. A. Kadhim, A. Al-Okbi, D.M. Jamil, A. Qussay, A.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**, 4013–4019. doi: [10.1016/j.rinp.2017.10.027](https://doi.org/10.1016/j.rinp.2017.10.027)
7. K.F. Al-Azawi, I.M. Mohammed, S.B. Al-Baghdadi, T.A. Salman, H.A. Issa, A.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**, 278–283. doi: [10.1016/j.rinp.2018.02.055](https://doi.org/10.1016/j.rinp.2018.02.055)
8. S.B. Al-Baghdadi, F.G. Hashim, A.Q. Salam, T.K. Abed, T.S. Gaaz, A.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**, 1178–1184. doi: [10.1016/j.rinp.2018.02.007](https://doi.org/10.1016/j.rinp.2018.02.007)
 9. T.A. Salman, Q.A. Jawad, M.A. Hussain, A. Al-Amiery, L. Shaker, A.A.H. Kadhum, and M.S. Takriff, Novel ecofriendly corrosion inhibition of mild steel in strong acid environment: Adsorption studies and thermal effects, *Int. J. Corros. Scale Inhib.*, 2019, **8**, no. 4, 1123–1137. doi: [10.17675/2305-6894-2019-8-4-19](https://doi.org/10.17675/2305-6894-2019-8-4-19).
 10. S.S. Al-Taweel, K.W.S. Al-Janabi, H.M. Luaibi, A.A. Al-Amiery and T.S. Gaaz, Evaluation and characterization of the 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**, no. 4, 1149–1169. doi: [10.17675/2305-6894-2019-8-4-21](https://doi.org/10.17675/2305-6894-2019-8-4-21)
 11. D.S. Zinad, Q.A. Jawad, M.A.M. Hussain, A. Mahal, L. Mohamed and A.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**, no. 1, 134–151. doi: [10.17675/2305-6894-2020-9-1-8](https://doi.org/10.17675/2305-6894-2020-9-1-8)
 12. 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**, 3961–3972.
 13. A.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, *Mater.*, 2013, **6**, 1420–1431. doi: [10.3390/ma6041420](https://doi.org/10.3390/ma6041420)
 14. M.H.O. Ahmed, A.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**, 728–733. doi: [10.1016/j.rinp.2017.12.039](https://doi.org/10.1016/j.rinp.2017.12.039)
 15. T.A. Salman, A. Al-Amiery, L. Shaker, A.A.H. 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**, no. 4, 1035–1059. doi: [10.17675/2305-6894-2019-8-4-14](https://doi.org/10.17675/2305-6894-2019-8-4-14)
 16. A.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, *Mol.*, 2015, **20**, 366–383. doi: [10.3390/molecules20010366](https://doi.org/10.3390/molecules20010366)

-
17. 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**, 8200–8209.
 18. A.A.H. Kadhum, A.B. Mohamad, L.A. Hammed, A.A. Al-Amiery, N.H. San and A.Y. Musa, Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin, *Mater.*, 2014, **7**, 4335–4348. doi: [10.3390/ma7064335](https://doi.org/10.3390/ma7064335)
 19. D.S. Zinad, M. Hanoon, R.D. Salim, S.I. Ibrahim, A.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**, no. 1, 228–243. doi: [10.17675/2305-6894-2020-9-1-14](https://doi.org/10.17675/2305-6894-2020-9-1-14)
 20. 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**, 459–467. doi: [10.1007/s12540-014-3008-3](https://doi.org/10.1007/s12540-014-3008-3)
 21. Q.A. Jawad, D.S. Zinad, R.D. Salim, A.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**, no. 11, 729. doi: [10.3390/coatings9110729](https://doi.org/10.3390/coatings9110729)
 22. D.M. Jamil, A.K. Al-Okbi, S.B. Al-Baghdadi, A.A. Al-Amiery, A. Kadhim and T.S. Gaaz, Experimental and theoretical studies of Schiff bases as corrosion inhibitors, *Chem. Cent. J.*, 2018, **12**, 1–7. doi: [10.1186/s13065-018-0376-7](https://doi.org/10.1186/s13065-018-0376-7)
 23. 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**, 1708–1718.
 24. 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**, no. 2, 502–518. doi: [10.17675/2305-6894-2020-9-2-6](https://doi.org/10.17675/2305-6894-2020-9-2-6)
 25. R.D. Salim, Q.A. Jawad, K.S. Ridah, L.M. Shaker, A.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**, no. 2, 550–561. doi: [10.17675/2305-6894-2020-9-2-10](https://doi.org/10.17675/2305-6894-2020-9-2-10)
 26. A.A. Al-Amiery, L.M. Shaker, A.A.H. Kadhum and 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**, no. 1, 89–101. doi: [10.24874/ti.2020.42.01.09](https://doi.org/10.24874/ti.2020.42.01.09)
 27. A. Al-Amiery, T.A. Salman, K.F. Alazawi, L.M. Shaker, A.H. Kadhum and M.S. Takrif, Quantum chemical elucidation on corrosion inhibition efficiency of Schiff base: DFT investigations supported by weight loss and SEM techniques, *Int. J. Low-Carbon Technol.*, 2020, **15**, 202–209. doi: [10.1093/ijlct/ctz074](https://doi.org/10.1093/ijlct/ctz074)

-
28. A. Al-Amiery, L.M. Shaker, A.H. Kadhum and M.S. Takrif, Synthesis, characterization and gravimetric studies of novel triazole-based compound, *Int. J. Low-Carbon Technol.*, 2020, **15**, 164–170. doi: [10.1093/ijlct/ctz067](https://doi.org/10.1093/ijlct/ctz067)