Novel ecofriendly corrosion inhibition of mild steel in strong acid environment: Adsorption studies and thermal effects

T.A. Salman,[1] Q.A. Jawad,[2] M.A.M. Hussain,[3] A.A. Al-Amiery,[2]* L. Mohamed,[2] A.A.H. Kadhum[4] and M.S. Takriff[4]

[1]*Chemistry Department, College of Science, Al-Nahrain University, Baghdad, Iraq*
[2]*Energy and Renewable Energies Technology Center, University of Technology, Baghdad 10001, Iraq*
[3]*Al Rafidain University College, Department of Air-Conditioning and Refrigeration Engineering Technology, Iraq*
[4]*Department of Chemical and Process Engineering, University Kebangsaan Malaysia (UKM), Bangi, Selangor 43000, Malaysia*
E-mail: dr.ahmed1975@gmail.com

Abstract

A new ecofriendly coumarin derivative, namely 4-((4-amino-1*H*-1,2,4-triazole-5(4*H*)-thione-3-yl)methyl)coumarin (ATMC), was synthesized and the chemical structure was elucidated using Fourier Transform Infrared Spectroscopy (FT-IR), Nuclear Magnetic Resonance (NMR) and elemental analysis (CHN). ATMC was evaluated as a corrosion inhibitor and the concentrations were 0.1 mM to 0.5 mM for mild steel in 1 M hydrochloric acid in the temperature range of 303–333 K using gravimetric and surface analysis by means of scanning electron microscopy (SEM) techniques. The gravimetrical results show that ATMC inhibited the corrosion of mild steel in a strong acid solution with superior performance. It was found that the corrosion inhibition performance depends on the concentration of the studied inhibitor and the solution temperature. The inhibition efficiency increased with an increase in the concentration of the inhibitor and reached 96.5% at a concentration of 0.5 M and 303 K. Experimental and adsorption results are in good agreement.

1. Introduction

In general, corrosion is considered as a loss of metal due to the effect of corrosive agents [1]. However, in a broad sense, corrosion is the destructive result of the chemical reaction between a metal or metal alloy and its environment [2]. Hydrochloric acid is one of the most common acids, among the acidic solutions of the acid pickling process. It should be noted that the replacement of toxic inhibitors with environmentally friendly inhibitors to protect metals in a corrosive medium in the 2nd half of the 19th century [3]. The corrosion

mechanism in the atmospheric and aquatic environment shall always govern one aspect of electro-chemistry. Electrons shall flow from areas of the mild steel surface to other areas through an electrolyte capable of conducting ions. This stems from the stunning trend of metals to electrochemical interaction with water, oxygen and other substances in the aquatic environment. In the electrochemical corrosion process, the anode is the surface area of minerals being eroded by the loss of electrons while the cathode is the area that consumes the electrons resulting from the corrosion reaction.

Corrosion inhibitor is known as a chemical component that can reduce, prevent and combat corrosion when added in small amounts to the mineral environment. Corrosion inhibitors are the first line of defense against the corrosion of the oil and chemical industry [4]. Corrosion inhibitors are sought after temporary protection of metals during transport and storage as well as topical protection to prevent corrosion that may have resulted from the accumulation of small amounts of aggressive phase. An effective corrosion inhibitor should be cost-effective, compatible with the corrosive medium, and produce the desired effect when present in small concentrations [5]. Corrosion inhibitors work by (1) forming a film that is condensed on the metal surface, (2) producing corrosion products, for example, iron sulphide which acts as an inert separator, and (3) producing sediments that can eliminate or disable aggressive component [6]. Organic inhibitors work by forming a film on the surface of metals and can act as anodic, cathodic or mixed inhibitors. The formation of this protective film occurs with the help of strong reactions, such as orbital adsorption, chemical absorption, and electrostatic absorption that prevent corroded species from attacking the metal surface [7]. This absorption is usually one thick molecular layer and does not penetrate the bulk of the metal itself [8].

Corrosion inhibitors are widely used to protect metals and equipment, and must be acceptable, non-toxic and environmentally friendly due to environmental concerns. The cost and adverse effect associated with commercial and inorganic inhibitors has raised considerable awareness in the area of corrosion mitigation. Thus, corrosion scientists and engineers tend to influence inexpensive, readily available, environmentally friendly and environmentally acceptable green corrosion inhibitors [9]. Recently, interest in the development and use of low-cost and environmentally friendly compounds as corrosion inhibitors has increased [10–15]. Following up of the investigations for efficient corrosion inhibitors for mild steel in acidic solution [15–30], the present investigation is to study the inhibition action of the green corrosion inhibitor derivative of coumarin which is 4-((4-amino-1*H*-1,2,4-triazole-5(4*H*)-thione-3-yl)methyl)coumarin (ATMC), on the corrosion of mild steel in hydrochloric acid. The chemical formula of the novel ecofriendly corrosion inhibitor was elucidating according to spectroscopic techniques (FTIR, NMR) and CHN analysis. The effect of ATMC inhibition was investigated by weight lost calculations, as well as by surface analysis using scanning electron microscopy (SEM) with a different concentration of ATMC as corrosion inhibitor. The potential mechanism for ATMC absorption has been explored on the mild steel surface.

2. Experimental

2.1. Chemistry and materials

Solvents and primary chemicals were supplied from Sigma-Aldrich, KL, Malaysia, and were used as supplied without further purification. The Fourier-transform infrared spectroscopy (FT-IR) spectrum was recorded using a Thermo Scientific Model Nicolate 6700 Spectrophotometer. CHN analysis were done using Carlo Erba 5500 CHN elemental analyzer. Nuclear magnetic resonance (NMR) spectra were recorded on an AVANCE III 600 MHz spectrometer.

2.2. Synthesis of corrosion inhibitor

A mixture of equimolar quantities of 2-(2-oxo-2*H*-chromen-4-yl)acetic acid (0.03 mol) and 4-aminothiosemicarbazide (0.03 mol) was stirred and allowed to cool (0–5°C) and phosphorus oxychloride (15 g) had been added. The mixture was refluxed for then the excess of phosphorus oxychloride was removed under reduced pressure. Add dry pyridine (5 ml). The mixture was poured onto ice. The precipitated was filtered and recrystallized from ethanol. The yield of brown powder was 57%. Melting point: 258°C. The chemical structure of the synthesized inhibitor was demonstrated in Scheme 1. The inhibitor molecule was characterized *via* spectroscopically techniques, namely FTIR, NMR and CHN analysis. CHN, analytical calculation/found for the synthesized inhibitor with the chemical formula $C_{12}H_{10}N_4O_2S$: C, 52.54/52.31; H, 3.67/3.29; N, 20.43/20.17. FT-IR (cm^{-1}): 3287.5, 3172.7 and 3161.3 (amino groups), 2911.6 (methylene group), 1713.8 (carbonyl group). ^{1}H-NMR in DMSO-d6 (ppm): d, 1H, 7.31, J=7.84, 1.34; d, 1H, 7.39, J=8.33, 1.28; d, 1H, 7.67, J=8.33, 7.32; d, 1H, 7.51, J=784, 1.32 (protons of aromatic ring). s, 1H, 5.93 (=C–H of coumarin), s, 5.16 (NH$_2$), s, 4.01 2H (CH$_2$). ^{13}C-NMR in DMSO-d6 (ppm): 39.4, 109.5, 115.3, 118.9, 121.9, 127.3, 132.8, 150, 153.6, 159.4, 176.2.
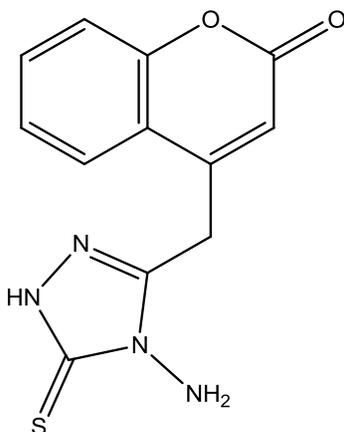
Scheme 1. Chemical structure of the synthesized inhibitor.

2.3. Electrode and electrolytes

Coupons of mild steel which have the chemical composition of Fe, 99.21; C, 0.21; Si, 0.38; P, 0.09; S, 0.05; Mn, 0.05; and Al, 0.01; and it had an effective surface area of 4.5 cm^2 were used for gravimetric and surface analysis. Initially the coupons were polished then washed with distilled water, acetone and dry at room temperature [31–33]. Hydrochloric acid solutions of 1 M were used and the concentrations of inhibitor were varied from 0.1 mM to 0.5 mM.

2.4. Weight loss method

Mild steel coupons were immersed in corrosive solution without and with various concentrations [34] of ATMC. The influence of immersion time was carried out for the period (1, 5, 10, 24, 48 and 72) 24 hours; the experiments were performed at room temperature. Water bath had been utilized to change the temperatures from 303 K to 333 K. The immersion coupons in corrosive environment were weighed. The obtained data were used to calculate corrosion rate (*CR*) in mmpy, inhibition efficiency (*IE*), and surface coverage (θ) from equations 1–3.

$$CR = \frac{87.6w}{tad} \tag{1}$$

$$IE\% = \frac{CR_0 - CR_{in}}{CR_0} \times 100 \tag{2}$$

$$\theta = \frac{CR_0 - CR_{in}}{CR_0} \tag{3}$$

where *w* is the weight loss of coupons, *a* is the area of coupons, *d* is the density, and *t* is the immersion time. The same process was repeated for temperature studies with the immersion period of 5 hours.
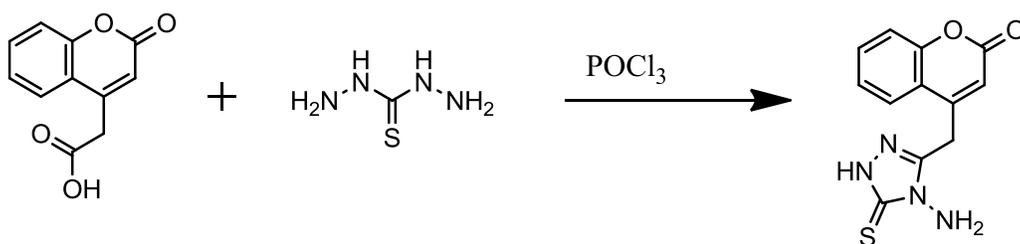
2.5 Surface analysis

The scanning electron microscope was used to investigate the coupon surface in absence and presence the corrosion inhibitor in the corrosive environment.

3. Results and discussion

3.1. Characterization of ATMC

The reaction sequences for the synthesis of ecofriendly coumarin derivative namely 4-((4-amino-1*H*-1,2,4-triazole-5(4*H*)-thione-3-yl)methyl)coumarin (ATMC) starting from 2-(2-oxo-2*H*-chromen-4-yl)acetic acid and 4-aminothiosemicarbazide are outlined in Scheme 2. ATMC was obtained by refluxing 2-(2-oxo-2*H*-chromen-4-yl)acetic with 4-aminothiosemicarbazide in the presence of phosphorus oxychloride.

FTIR is used to obtain infrared spectra of absorptions or emissions of solids, liquids or gases. The spectra of FTIR are used to qualitatively identified of organic functional groups. The data from FTIR spectrum of ATMC, exhibit the characteristic vibrations of amino, methylene, azomethine and carbonyl groups. The presence of these functional groups, especially an azomethine group within the ATMC confirms cyclization of 4-aminothiosemicarbazide with carboxyl group of coumarin derivative. The amino groups stretching bands were observed for ATMC, at 1712, 1628, and 3287, 3172 and 3161 cm^{-1}. C=N stretching band was observed at 1600 cm^{-1}. CH$_2$ vibration band is observed at 2911 cm^{-1}. NMR spectroscopy, has the ability to characterize any isotope except if the isotope has together even numbers of protons and neutrons. ^{1}H-NMR spectrum for a molecule provide data about the number of signals and each chemically various proton in a structure is also magnetically various. Position of signal with respect to an internal standard, namely tetramethylsilane (TMS), is often used as an internal standard since almost all proton signals appear downfield from the TMS signal. ^{1}H-NMR in DMSO-d6 (ppm): The aromatic ring has four proton doublet protons 7.31, 7.39, 7.67 and 7.51. Also the inhibitor molecule has singlet at 5.93 for one proton of vinyl group of coumarin molecule in addition to two singlet protons each for two hydrogens at and 4.01 for methylene group and 5.16 for amino group. Carbon-13 NMR is a significant tool elucidate the chemical structure of organic molecule. It is detects only the ^{13}C isotope of carbon. ^{13}C-NMR in DMSO-d6 (ppm): 39.4 for carbon of methylene group. 109.5, 115.3, 118.9, 121.9, 127.3, 132.8 for 150, 153.6, 159.4, 176.2

Scheme 2. The synthesize of corrosion inhibitor.

3.2, Gravimetric analysis

a. Effect of ATMC concentration

The dissolution of surface of mild steel in corrosive environment for considerable time were demonstrate as an electrochemical reaction and causes MS weight losses [35]. The inhibition efficiency of ATMC *versus* corrosion rate was studied by observing the MS mass losses. Corrosion rates, inhibition efficiencies and surface coverages were calculated according to equations 1, 2 and 3, respectively. The mass loss of mild steel was measured without and with addition of ATMC as corrosion inhibitor. Figure 1 demonstrates the deference's of ATMC concentration with corrosion rates at 303 K for the period 1, 5, 10, 24, 48 and 72 hours in hydrochloric acid environment. The corrosion rate

decreases with concentration increase whereas the inhibition efficiency increase with concentration of ATMC increase due to the presence of considerable number of adsorption sites which were brought through significant ATMC concentrations. Differences in corrosion rates (*CRs*) and inhibition efficiencies (*IEs*) based on variation concentrations of ATMC inhibitor molecules for immersion time of 1–72 hours in HCl solution at 303 K have been explain in Figures 1 and 2. At was 5 hours immersion time, the corrosion rate of ATMC reached the minimum value as in Figure 1 and the inhibition efficiency reached the maximum value of 93.84% as in Figure 2. The adsorption of ATMC molecules is a replacement reaction that involves elimination of H_2O molecules from the MS surface. The immersion time was varied from 1 to 72 hours. The molecules of ATMC were adsorbed chemically due to interactions of unshared electrons with the MS surface. The *CR* was observed to increase and *IE* decreased after 10 h of immersion and further decreased after the longest time of immersion that was 72 hours in this study. The increase in *CR* and decrease in *IE* was imputed to desorption of ATMC molecules from the MS surface.

Generally, the *CR* and *IE* of ATMC molecules depend on the ability of adsorption on the MS. The highest inhibition efficiency of 96.5% have been achieved at the concentration of 0.5 mM attributed to the availability of heterogeneous atoms in the chemical structure of ATMC molecules that participates as active functional groups and electrostatic bonds between ATMC with surface of MS. Nitrogen, sulfur and oxygen atoms interact with the mild steel surface through adsorption and that increase the inhibition efficiency. The active centers in the ATMC molecule that are amine, thionyl, lactone and carbonyl groups interact with the mild steel surface via electron donation to the empty d-orbital of iron thereby enabling the adsorption of the ATMC molecule to the surface of mild steel.
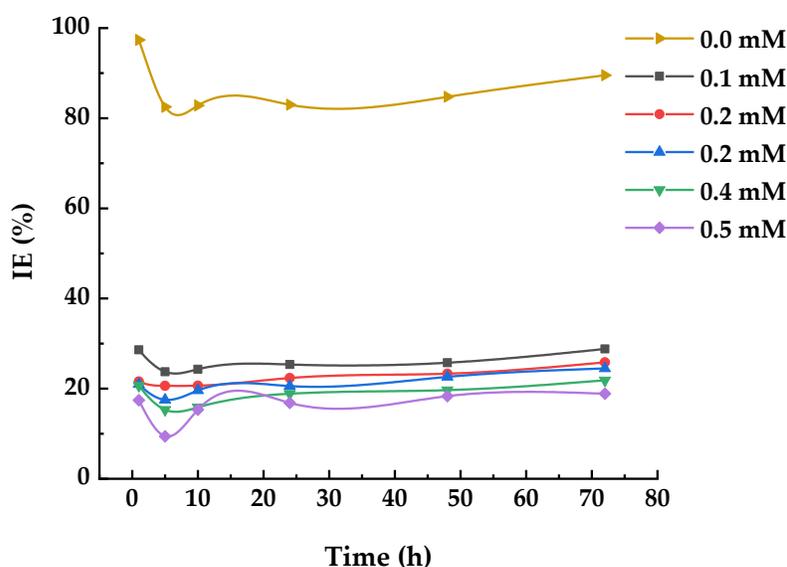

Figure 1. Effect of immersion time on corrosion rate of MS in corrosive environment with various concentrations of ATMC.
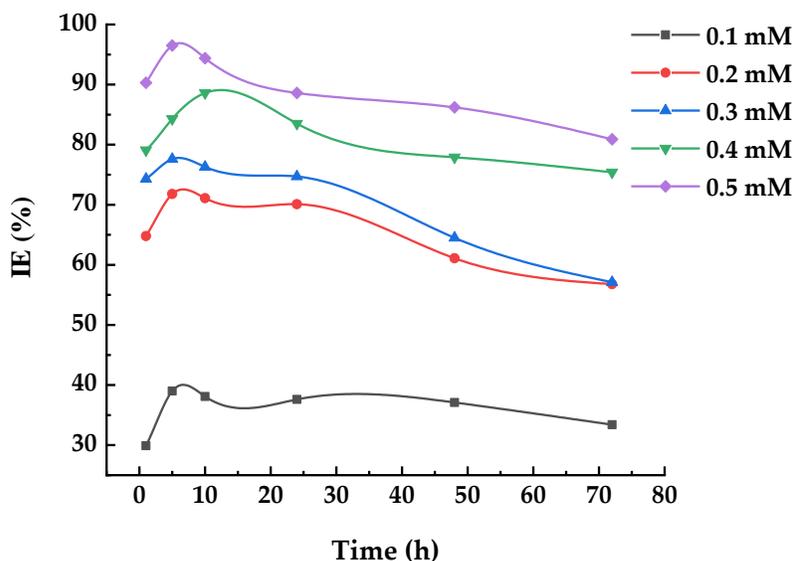
Figure 2. Effect of immersion time on inhibition efficiency of MS in corrosive environment with various concentrations of ATMC.

b. Temperature effect

Corrosion rate and inhibition efficiency were used to investigate the effect of temperature. The corrosion rate increase with increasing temperature [36], as shown in Figure 3. *IEs* were decreased with the increase of temperature, and this attributed to instability of ATMC molecules when subjected to higher temperatures. In addition, the solution viscosity was decrease which progress to more diffusion, which permit increased transport of reactants and product on the surface of MS. The *CR* in absence of ATMC molecules is four times that with ATMC molecules, because the inhibitor isolates the metal from the environment.
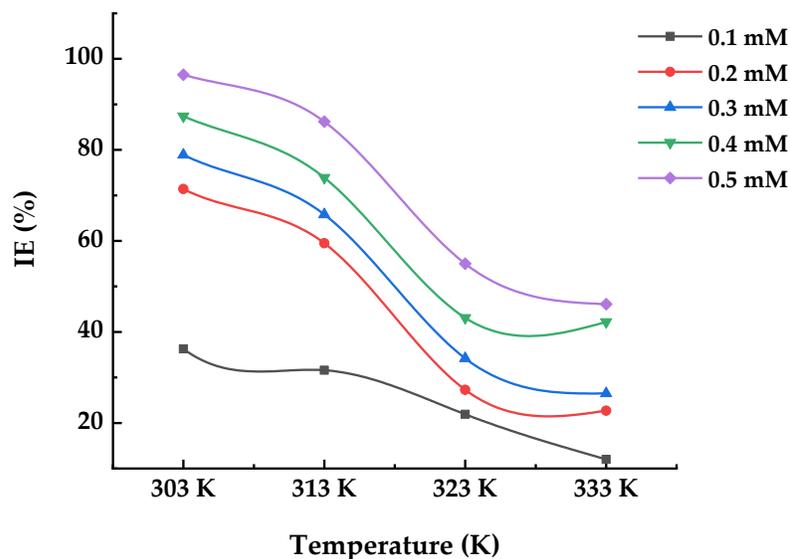

Figure 3. Effect of temperature mild steel on *IE* in 1 M HCl.

3.3. Adsorption isotherms

The adsorption of ATMC molecules onto the surface of MS is the is the essential step of mechanism of adsorption. The most interested parameter in the adsorption process is the surface coverage (θ) that calculated from weight loss technique as in Equation 4.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + B \tag{4}$$

Organic molecules were adsorbed on the surface of mild steel when the interaction energies of MS surface and organic molecules were bigger than of MS surface and H_2O molecules [37]. Adsorption models namely, Langmuir, Frumkin, and Parsons–Temkin have been investigated and the one with the best fit would employee to measure the thermodynamic parameters. From the weight loss measurements, the surface coverage value increases with the increase of concentration of ATMC in corrosive environment; this was imputed to the protective layer formation of ATMC on surface of mild steel that diminishes its dissolution rate of surface of MS. The uses of Langmuir model was to study the mechanism of adsorption and Equation 4, was utilized to calculate the equilibrium constant parameter.

Figure 4 demonstrates the plot of Langmuir model for dissolution of surface of MS, which implied that the adsorption of the inhibitor molecules on to surface of MS assumed a one layer adsorption and the adsorption of the inhibitor molecules on the surface of MS obeyed Langmuir isotherm.
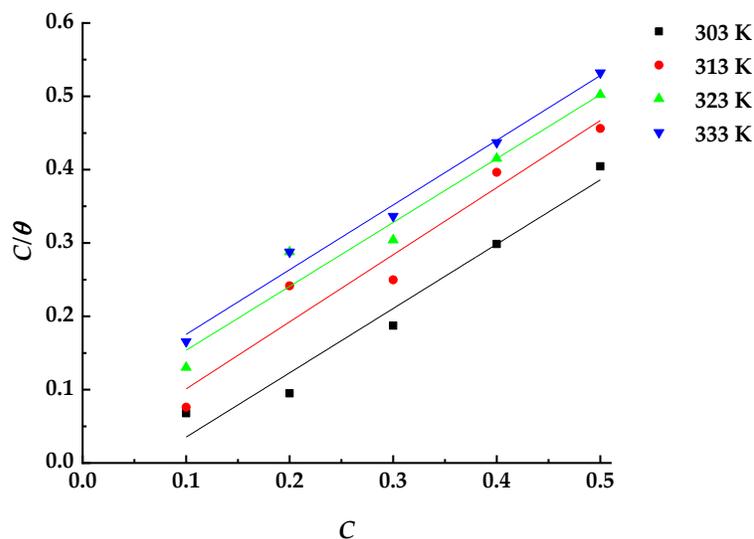

Figure 4. Langmuir plot for adsorption of ATMC on to mild steel surface.

3.4. Thermodynamic and kinetic parameters

Weigh loss measurement for various concentrations of ATMC as corrosion inhibitor and various temperatures were used to evaluate the kinetic parameters.

Arrhenius equation was used to evaluate the activation energy (E_a) of MS surface dissolution as described in Equation 5:

$$\log C_R = -\frac{E_a}{2.303RT} + \log a \tag{5}$$

where R was the molar gas constant, T was the absolute temperature and a was the frequency factor.

Figure 5 represents the plot of $\log CR$ *versus* $1/T$ at various concentrations (0.0 mM to 0.5 mM) of ATMC and the slope ($-E_a/2.303R$) was used to evaluate the activation energy. The E_a at the concentration of 0.0 mM was 55.9 kJmol^{-1} which was less than the E_a at 0.5 mM concentration, 90.2 kJmol^{-1}. Increasing of E_a results in the decreasing of *CR* of MS so, it can conclude a superior *IE* and these results due to the adsorption of ATMC molecules on the surface of MS that decrease the dissolution of available surface area of MS.

$$\frac{\log C_R}{T} = \log\left(\frac{R}{nh}\right) + \left(\frac{\Delta S_a}{2.303R}\right) - \left(\frac{\Delta H_a}{2.303T}\right) \tag{6}$$

Table 1. Kinetic parameters for MS in 1.0 M HCl in the presence and absence of ATMC.

Conc. mM	E_a (kJ·mol^{-1})	ΔH_a (kJ·mol^{-1})	ΔS_a (J·mol^{-1}·K^{-1})
0.0	55.9	51.0	−66.7
0.1	77.2	76.8	−155.1
0.3	83.4	82.5	−167.4
0.5	90.2	88.0	−178.4

The increase in E_a can be imputed to a considerable diminish in the adsorption of the ATMC molecules on the surface of MS with rising temperature and increasing in *CRs* due to a major area of MS surface was exposed to the corrosive solution.

Table 1, ΔH with the positive value refer to endothermic dissolution process for surface of mild steel at room temperature in the presence of the ATMC molecules. The ΔH increased with a temperature increase, supporting the endothermic nature of surface dissolution of MS and decreasing of inhibition performance of ATMC molecules. The entropy activation values at room temperature were negative and become positive with increasing of temperature. In absence of ATMC molecules the entropy activation values were positive and tend to be negative at higher concentration of ATMC. Negative entropy

activation value indicated that, at room temperatures and maximum studied concentration of ATMC, the MS surface was protected by the ATMC molecules.
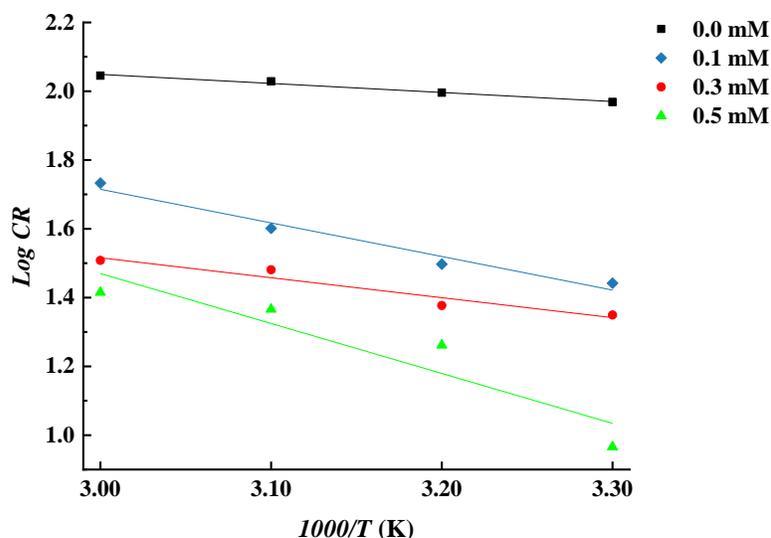

Figure 5. Arrhenius plot for mild steel in 1 M HCl in the presence and absence of ATMC.

3.5 Morphological studies

The mild steel surface was investigated with SEM in absence of ATMC molecules in corrosive environment and in presence of ATMC at the concentration of 0.5 mM for 5 hours as immersion time. Figure 6a, demonstrates the picture of surface of MS in the absence of ATMC molecules. It is clear that the surface of mild steel was corroded. On the other hand, Figure 6b, demonstrates the picture of surface of MS in presence of ATMC molecules and it was smooth and clear.
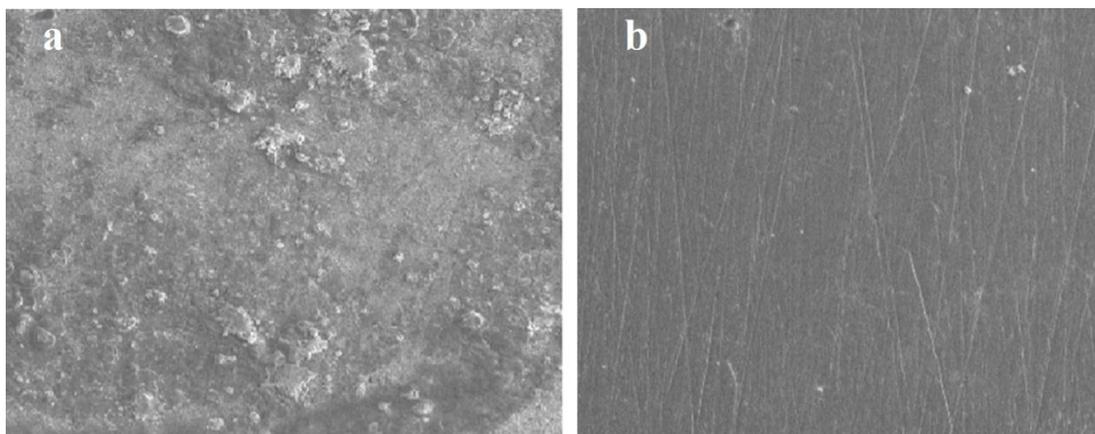

Figure 6. (a) SEM micrograph in absence of inhibitor, (b) SEM micrograph in presence of inhibitor. Both pictures refer to the mild steel in 1.0 M of HCl with concentration of inhibitor (0.5 mM) at 303 K immersed for 5 h.

3.6 Inhibition mechanism

All the results of the used techniques (weight loss, absorption and morphology) in this study indicate that the new corrosion inhibitor ATMC has played a key role in inhibiting corrosion of mild steel in the acidic environment. It is possible to propose a schematic mechanism of inhibit the corrosion of the mild steel in the acidic environment by relying the study of the chemical structure and the electronic structure with the results of this study as shown in Figure 7. Since the ATMC molecules have many functional groups and heteroatoms in addition to electronic pairs as well as pi bonds and aromatic ring. The iron atoms have an unoccupied d-orbital, so the iron atoms have the ability to adsorbed the ATMC molecules un associated electrons and thus form strong bonds (coordination bonds) with the mild steel surface. The electrons of the ATMC molecules may accumulate in the atomic orbitals of the mild steel surface and may lead to electron repulsion on the surface of the mild steel and thus reverse transfer occurs. Electrons move from the atoms of the mild steel to the molecular orbitals of the new anti-corrosion molecules known as retrodonation. In this study, the corrosion of iron in an acidic environment produces a surface charged with positive charges, attracting negatively charged ions.
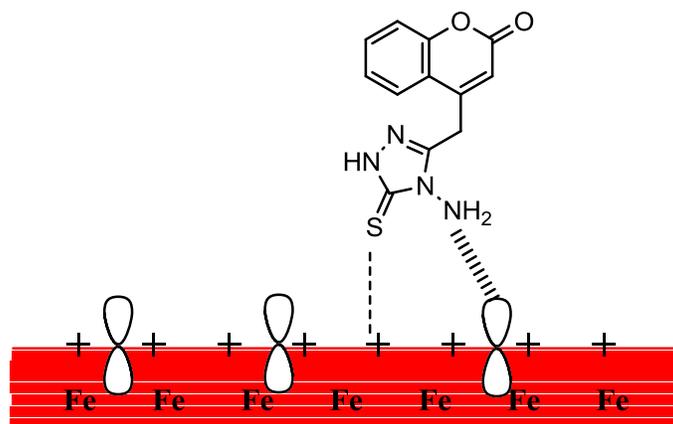
Figure 7. Interactions of ATMC on mild steel surface in acidic environment.

4. Conclusions

New ecofriendly corrosion inhibitor derived from coumarin namely 4-((4-amino-1*H*-1,2,4-triazole-5(4*H*)-thione-3-yl)methyl)coumarin (ATMC) was synthesized and the chemical structure was elucidate using spectroscopical and micro elemental techniques. The corrosion inhibition of mild steel had been investigated by weight loss and morphological studies. The new inhibitor has a superior inhibition efficiency due to the chemical structure of ATMC molecule has four nitrogen atoms, two oxygen atoms and one sulfur atom in addition to the aromatic ring. These atoms have act as active sites of adsorption. The adsorbed layer of ATMC on surface of mild steel was stable at 303 K. The absorption of ATMC obeys Langmuir isotherm. SEM confirmed the inhibition activity of the ATMC molecules as superior corrosion inhibitor.

Acknowledgement

Conflicts of interest

The authors declare no conflict of interest.

References

1. M.J. Schofield, Corrosion, *Plant Engineer's Reference Book, 2nd ed.*, Ed.: D.A. Snow, Oxford: Butterworth Heinemann, 2002, 961–986. doi: 10.1016/B978-075064452-5/50088-2

2. D. Jones, *Principles and Prevention of Corrosion, 2nd ed.*, New Jersey: Prentice Hall, 1996, 572 pp. ISBN: 0-13-359993-0

3. P. Arockiasamy, X.Q.R. Sheela, G. Thenmozhi, M. Franco, J.W. Sahayaraj and R.J. Santhi, Evaluation of Corrosion Inhibition of Mild Steel in 1 M Hydrochloric Acid Solution by Mollugo cerviana, *Int. J. Corros.*, 2014, **2014**, 1–7. doi: 10.1155/2014/679192

4. M. Taghavikish, N. Dutta and N. Choudhury, Emerging corrosion inhibitors for interfacial coating, *Coatings*, 2017, **7**, no. 12, 217–245. doi: 10.3390/coatings7120217

5. S. Papavinasam, Corrosion Inhibitors, *Uhlig's Corrosion Handbook, 3rd ed.*, Ed.: R.W. Revie, New York: Wiley, 2000, 1021–1033. doi: 10.1002/9780470872864.ch71

6. S. Umoren and U. Ekanem, Inhibition of mild steel corrosion in H_2SO_4 using exudate gum from pachylobus edulis and synergistic potassium halide additives, *Chem. Eng. Commun.*, 2010, **197**, 1339–1356. doi: 10.1080/00986441003626086

7. M. Kelland, Production chemicals for the oil and gas industry, *Chromatographia*, 2010, **72**, 199. doi: 10.1365/s10337-010-1557-2

8. D. Arthur, A. Jonathan, P. Ameh and C. Anya, A review on the assessment of polymeric materials used as corrosion inhibitor of metals and alloys, *Int. J. Ind. Chem.*, 2013, **4**, no. 2, 1–9. https://link.springer.com/article/10.1186/2228-5547-4-2

9. L.K.M.O. Goni and M.A.J. Mazumder, Green Corrosion Inhibitors, *Corrosion Inhibitors*, Ambrish Singh, IntechOpen, 2019. doi: 10.5772/intechopen.81376

10. A. Fouda, G. El-Ewady and A.H. Ali, Modazar as promising corrosion inhibitor of carbon steel in hydrochloric acid solution, *Green Chem. Lett. Rev.*, 2017, **10**, no. 2, 88–100. doi: 10.1080/17518253.2017.1299228

11. X. Li, H. Fu and S. Deng, Inhibition of the corrosion of steel in HCl, H_2SO_4 solutions by bamboo leaf extract, *Corros. Sci.*, 2012, **62**, 163–175. doi: 10.1016/j.corsci.2012.05.008

12. 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-Oleyl-1,3,4-Thiadiazol (AOT), *Int. J. Electrochem. Sci.*, 2012, **7**, 3543–3554.

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, *Materials*, 2013, **6**, 1420–1431. doi: 10.3390/ma6041420

14. A.A. Al-Amiery, A.A.H. Kadhum, A.B. Mohamad, A.Y. Musa and C.J. Li, Electrochemical study on newly synthesized chlorocurcumin as an inhibitor for mild steel corrosion in hy-drochloric acid, *Materials*, 2013, **6**, 5466–5477. doi: 10.3390/ma6125466

15. 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, *Materials*, 2014, **7**, 4335–4348. doi: 10.3390/ma7064335

16. A.A. Al-Amiery, A.A.H. Kadhum, A. Kadihum, A.B. Mohamad, C.K. How and S. Junaedi, Inhibition of Mild Steel Corrosion in Sulfuric Acid Solution by New Schiff Base, *Materials*, 2014, **7**, 787–804. doi: 10.3390/ma7020787

17. A.A. Al-Amiery, A.A.H. Kadhum, A.H.M. Alobaidy, A.B. Mohamad and P.S. Hoon, Novel Corrosion Inhibitor for Mild Steel in HCl, *Materials*, 2014, **7**, 662–672. doi: 10.3390/ma7020662

18. A.B. Mohamad, A.A.H. Kadhum, A. Al-Amiery, L.C. Ying and A. Musa, Synergistic of a coumarin derivative with potassium iodide on the corrosion inhibition of aluminum alloy in 1.0 M H_2SO_4, *Met. Mater. Int.*, 2014, **20**, 459–467. doi: 10.1007/s12540-014-3008-3

19. H.R. Obayes, G.H. Alwan, A.H.MJ Alobaidy, A. Al-Amiery, A.A.H. Kadhum and A.B. Mohamad, Quantum chemical assessment of benzimidazole derivatives as corrosion Inhibitors, *Chem. Cent. J.*, 2014, **8**, no. 21, 1–8. doi: 10.1186/1752-153X-8-21

20. 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, *Molecules*, 2015, **20**, 366–383. doi: 10.3390/molecules20010366

21. E. Yousif, Y.-F. Win, A.H. Al-Hamadani, A. Al-Amiery, A.A.H. Kadhum and A.B. 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**, 1708–1718.

22. 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.

23. A.H.M.J Al-Obaidy, A.A.H. Kadhum, S.B. Al-baghdadi, A. Al-Amiery, A.B. Mohamad, A. Kadhum 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.

24. S.B. Al-Baghdadi, F.T.M. Noori, W.K. Ahmed and A.A. Al-Amiery, Thiadiazole as a Potential Corrosion Inhibitor for Mild Steel in 1 M HCl, *J. Adv. Electrochem.*, 2016, **2**, 67–69.

25. A.A. Al-Amiery, F.A.B. Kassim, A.A.H. Kadhum and A.B. Mohamad, Synthesis and characterization of a novel eco-friendly corrosion inhibition for mild steel in 1 M hydrochloric acid, *Sci. Rep.*, 2016, **6**. doi: 10.1038/srep19890

26. A. Kadhim, A.K. Al-Okbi, D.M. Jamil, A. Qussay, A.A. Al-Amiery, T.S. Gaas, 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

27. H.R. Obayes, A.A. Al-Amiery, G.H. Alwan, T.A. Abdullah, A.A.H. Kadhum and A.B. Mohamad, Sulphonamides as corrosion inhibitor: experimental and DFT studies, *J. Mol. Struct.*, 2017, **1138**, 27–34. doi: 10.1016/j.molstruc.2017.02.100

28. 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

29. 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

30. 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

31. ASTM G77-98, Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test, 1998.

32. 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

33. 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

34. T.A. Salman, D.S. Zinad, S.H. Jaber, M. Shayaa, A. Mahal, M.S. Takriff and A.A. Al-Amiery, Effect of 1,3,4 Thiadiazole Scafold on the Corrosion Inhibition of Mild Steel in Acidic Medium: An Experimental and Computational Study, *J. Bio-Tribo-Corros.*, 2019, **5**, no. **48**, 1–11. doi: 10.1007/s40735-019-0243-7

35. D. Mahmood, A.K. Al-Okbi, M.M. Hanon, K.S. Rida, A.F. Alkaim, A.A. Al-Amiery, A. Kadhum and A.A.H. Kadhum, Carbethoxythiazole corrosion inhibitor: As an experimentally model and DFT theory, *J. Eng. Appl. Sci.*, 2018, **13**, no. 11, 3952–3959. doi: 10.3923/jeasci.2018.3952.3959

36. A.Y.I. Rubaye, K.S. Rida, A.Q. Salam and A. Al-Amiery, Acetamidocoumarin as a based eco-friendly corrosion inhibitor, *Int. J. ChemTech Res.*, 2016, **9**, no. 11, 39–47.

37. H.J. Habeeb, H.M. Luaibi, T.A. Abdullah, R.M. Dakhil, A.A.H. Kadhum and A.A. Al-Amiery, Case study on thermal impact of novel corrosion inhibitor on mild steel, *Case Stud. Therm. Eng.*, 2018, **12**, 64–68. doi: 10.1016/j.csite.2018.03.005

♦ ♦ ♦