# Adsorption, temperature and corrosion inhibition studies of a coumarin derivatives corrosion inhibitor for mild steel in acidic medium: gravimetric and theoretical investigations

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### Abstract

The corrosion inhibition features of a new eco-friendly coumarin derivative, namely, 4-((4-((4-hydroxy-3-methoxybenzylidene)amino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)-methyl)coumarin (HATC), for corrosion of the mild steel surface in an acidic environment was studied using gravimetric techniques and quantum chemical calculations. It was concluded that the tested coumarin derivative is an excellent corrosion inhibitor with high inhibition efficiency. The inhibition performance increases with increasing concentration of the investigated coumarin (HATC) and decreases with increasing temperature. The mechanism of adsorption includes a physical adsorption mechanism. Theoretical studies done on the new coumarin molecule using the density functional theory (DFT) have shown that the most likely entities in coumarin molecules to bond to the metal surface are nitrogen, sulfur and oxygen atoms.

*Keywords:* corrosion inhibition, HATC, coumarin, quantum chemical calculation, adsorption.

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## 1. Introduction

Mild steel is one of the most important engineering alloys because it has significant mechanical characteristics, which made it widespread in addition to cheapness and strength. Corrosion intensity increases when a mild steel surface is exposed to external conditions in

an acidic environment [1]. Corrosion inhibitors are generally used in acid environments and therefore inhibitors are used to combat corrosion [2, 3]. The process of selecting an appropriate corrosion inhibitor is one of the most important issues to consider when working in an acid environment, and therefore the use of organic compounds is of great importance [4-8]. The efficiency of organic compounds in corrosive solutions is attributed to several factors, the most important of which are the presence of functional groups and electron pairs in the phosphorus, sulfur, oxygen and nitrogen atoms, in addition to the double and triple bonds, as well as aromatic rings. Small amounts of corrosion inhibitors have the ability to block the corrosion sites and improve the adsorption process on the mild steel surface, thus protecting the mild steel surface and increasing its life time [9, 10]. Previous studies demonstrate the possibility of employing organic molecules as anti-corrosion agents for mild steel in corrosive environment that were utilized for years. The literature shows that the inhibition of corrosion of a metal surface induces a mechanism of anti-corrosion adsorption on the metal surface and the inhibition efficiency depends in particular on the chemical composition of the corrosion inhibitor molecule and its chemical properties under certain experimental conditions. A large number of synthesized and natural organic compounds whose chemical structures contained nitrogen, oxygen and/or sulfur have been used as corrosion inhibitors in order to reduce the corrosion of steel in an acidic environment [11, 12]. The electronic frontier is often used as an index of relative reactivity or stability of inhibitor molecule [13–16]. In light of previous studies [17–42], the present study reports the synthesis and characterization of a new eco-friendly coumarin compound, namely 4-((4-((4hydroxy-3-methoxybenzylidene)amino)-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)methyl)coumarin (HATC), as well as a study of its behavior as a corrosion inhibitor and adsorption mechanism on the surface of mild steel in 1.0 molar hydrochloric acid using weight loss technique and a surface study technique. The effect of temperature on the dissolution of mild steel in acidic environment was studied in presence of HATC. The mechanism of inhibition was imputed based on density functional theory (DFT) calculations.

### 2. Experimental

### 2.1 Chemistry

Chemicals and solvents were purchased from Sigma-Aldrich, Kuala Lumpur, Malaysia. Chemicals were used without further purification. Spectroscopic techniques were used to characterize the chemical formula of HATC as a synthesized corrosion inhibitor. Fourier Transform Infrared (FT-IR) spectroscopy was used to record the spectrum of HATC for the purpose of identifying and characterizing the functional groups present in HATC. FT-IR spectra were recorded using a Nicolate 6700 Scientific Thermal Spectrophotometer for analysis. A preliminary analyzer Carlo Erba 5500 was used to determine the percentages of carbon, hydrogen and nitrogen in the HATC molecule. Nuclear magnetic resonance (NMR) spectra were recorded using AVANCE III 600 MHz.

#### 2.2 Synthesis of corrosion inhibitor

A mixture of equimolar quantities of 4-coumarinacetic acid (0.03 mole) and 4-aminothiosemicarbazide (0.03 mole) was stirred and allowed to cool (0-5°C) and phosphorus oxychloride (15 g) was then added. The mixture was then refluxed under reduced pressure to remove excess phosphorus oxychloride. Dry pyridine (5 ml) was added. The mixture was poured onto ice. The precipitate was filtered off and recrystallized from ethanol. The yield of brown powder was 57%. Melting point: 258°C. The chemical structure is demonstrated in Scheme 1. 4-((4-Amino-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)methyl)coumarin (ATMC) was characterized by spectroscopic techniques, namely FTIR, NMR and CHN analysis. CHN, analytical calculated/found values 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<sup>-1</sup>): 3287.5, 3172.7 and 3161.3 (amino groups), 2911.6 (methylene group), 1713.8 (carbonyl group). <sup>1</sup>H-NMR in DMSO-d<sub>6</sub> (ppm): d, 1H, 7.31, J=7.84, 1.34; d, 1*H*, 7.39, J=8.33, 1.28; d, 1H, 7.67, *J* = 8.33, 7.32; d, 1H, 7.51, *J* = 7.84, 1.32 (protons of aromatic ring); s, 1H, 5.93 (=C-H of coumarin), s, 5.16 (NH<sub>2</sub>), s, 4.01 2H (CH<sub>2</sub>).<sup>13</sup>C-NMR in DMSO-d<sub>6</sub> (ppm): 39.4, 109.5, 115.3, 118.9, 121.9, 127.3, 132.8, 150, 153.6, 159.4, 176.2. Finally the new corrosion inhibitor HATC was synthesized by refluxing a mixture of ATMC (0.03 mmol) and 4-hydroxy-3-methoxybenzaldehyde (0.03 mmol) in alcohol (100 mL) for 1 hours, then a few drops of acetic acid were added and the reflux was continued for another 7 hours. The mixture was cooled, filtered and dried. The precipitate was recrystallized from a mixture of DMF and EtOH to afford HATC as a new corrosion inhibitor. The yield of vellow powder was 77%. Melting point: 243°C. The chemical structure of the synthesized inhibitor was demonstrated in Scheme 1. CHN, analytical calculation/found values for the synthesized inhibitor with the chemical formula  $C_{20}H_{16}N_4O_2S$ : C, 58.81/59.27; H, 3.95/3.78; N, 13.72/14.05. FT-IR (cm<sup>-1</sup>): 3314.8 for amino group, 3199.3 for hydroxy group, 3071.1 for benzene ring, 2932.8 for methyl group, 1719.6 for carbonyl group and 1637.9 for azomethine group. <sup>1</sup>H NMR: δ 3.74 (s, 2H, CH<sub>2</sub>), 3.94 (s, 3H, OCH<sub>3</sub>), 6.07 (s, 1H, C–H), 6.90-7.18 (m, 1H, aromatic-H), 7.27 (dd, 1H), 7.30 (1H, d, coumarin-H), 7.97 (s, 1H, OH) and 8.75 (s, 1H, NH). <sup>13</sup>C NMR: δ 174.94 (C=O), 160.28 (C=S), 153.77, 159.02, 149.79, 147.55, 146.23, 145.71, 131.88, 127.03, 126.12, 124.11, 122.89, 117.66, 115.87, 114.73, 114.26, 110.82, 56.48 and 30.72.



*a=hydrazinecarbothiohydrazide, Phosphorusoxychloride; b= 4-hydroxy-3-methoxybenzaldehyde* 

Scheme 1. Chemical structure of the synthesized inhibitor.

#### 2.3 Materials and corrosion tests

A sample of mild steel with the following composition (% by weight) was used: 99.21% Fe; 0.21% C; 0.38% Si; 0.09% P; 0.05% S; 0.05% Mn and 0.01% Al. Mild steel was mechanically cut and grounded by emery papers. The mild steel coupons were washed in acetone and distilled water, then dried and used. The acidic environment was prepared at a concentration of 1.5 M HCl by diluting concentrated hydrochloric acid (37%) with distilled water. The corrosion inhibitor was used in different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 mM).

### 2.4 Weight loss measurements

Weight loss tests were conducted using the method described in the literature [43, 44]. Weight loss calculations were carried out at 303, 313, 323 and 333 K for 1, 3, 5, 10 and 24 hours, by immersing mild steel specimens in an acidic environment without and with different concentrations of the inhibitor. Specimens were ejected, washed, dried and weighed accurately. The corrosion rate (*CR*) in mpy, inhibition efficiency (*IE*%) and surface coverage ( $\theta$ ) were calculated by 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. (Note: Eq. 3 is only valid for inhibitors with blocking action).

#### 2.5 Quantum Chemical Calculations

The quantum chemical calculations of the new inhibitor molecules were made using the density functional theory (DFT), which includes the three hybrid functions of Becke parameters with the Lee-Yang-Parr functional binding function (B3LYP) [45]. The base group 6-31G(d,p) was used for all calculations. The calculations were made without parity restrictions using Gaussian 03, version E.01 [46]. The parameters such as the energy of the highest occupied molecular orbital ( $E_{HOMO}$ ), lowest unoccupied molecular orbital ( $E_{LUMO}$ ), energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), global softness ( $\sigma$ ), global hardness ( $\eta$ ), electrophilicity ( $\omega$ ), fraction of electrons transferred ( $\Delta N$ ), and electronegativity ( $\chi$ ) were calculated [42].

Parameter	Definition	Calculation method
$\Delta E$	Energy gap	$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$
χ	Electronegativity $(\chi)$ is a chemical property that describes the tendency of an atom to attract a shared pair of electrons (or electron density) towards itself.	$\chi = -1/2 \cdot (E_{\rm HOMO} + E_{\rm LUMO})$
η	Global hardness is the resistance of an atom to a charge transfer	$\eta = -1/2 \cdot (E_{\rm HOMO} - E_{\rm LUMO})$
ω	Global electrophilicity index	$\omega = \chi^2/2\eta$
σ	Global softness is capacity of an atom (or atoms) to receive electrons	$\sigma = 1/\eta = -2/(E_{\rm HOMO} - E_{\rm LUMO})$
$\Delta N$	The fraction of electrons transferred [59] from the inhibitor to the Fe atom	$\Delta N = \frac{\chi_{\rm Fe} - \chi_{\rm inh}}{2(\eta_{\rm Fe} + \eta_{\rm inh})}$

**Table 1** shows how these parameters are calculated.

The  $\chi_{Fe}$  was equated to 7 eV/mol and  $\eta_{Fe}$  was equated to 0 eV/mol.

To detect the atomic active sites of HATC molecules, Fukui functions  $(f(\mathbf{r}))$  were effectively utilized [47, 48]. The  $(f(\mathbf{r}))$  refer to the variation in the *N*-electron density system of an electron which is added  $(f^+(\mathbf{r}))$  or removed  $(f^-(\mathbf{r}))$  [49]. Equations 4 and 5 were used to calculate the Fukui indices condensed  $(f^+k \text{ and } f^-k)$  on atom *k*.

$$f^{+}k = \rho k(N+1)(r) - \rho k(N)(r)$$
(4)

$$f^{-}k = \rho k(N)(r) - \rho k(N-1)(r)$$
(5)

Where  $\rho k_{(N+1)}$  is the electron densities of (N+1), and  $\rho k_{(N-1)}$  is the electron density of (N-1).

### 3. Results and Discussion

#### 3.1 Characterization of ATMC and HATC

The chemical structures of ATMC and HATC were elucidated by FTIR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR and CHN techniques. The FTIR (cm<sup>-1</sup>) spectrum of ATMC shows significant bands corresponding to  $\nu$ (N–H, asym),  $\nu$ (N–H, sym),  $\nu$ (C–H) and  $\nu$ (C=O) at 3287.5, 3172.7 3161.3, 2911.6, 1713.8 cm<sup>-1</sup>, respectively. The <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm) of ATMC shows significant bands: a singlet at 4.01 ppm from two protons of methylene group, another singlet signal at 5.93 ppm due to the single proton of the pyronering (=C–H of coumarin). The singlet signal at 5.16 ppm was from the two protons of the amino group. Finally, the aromatic ring has doublet signals of one proton at 7.31, 7.39, 7.67 and 7.521. <sup>13</sup>C-NMR bands in DMSO-d<sub>6</sub> (ppm) were found at 39.4, 109.5, 115.3, 118.9, 121.9, 127.3,

132.8, 150, 153.6, 159.4 and 176.2. These bands confirm the structure of the ATMC molecule and this is another confirmation of the synthesis of ATMC as a precursor for HATC. The FTIR (cm<sup>-1</sup>) spectrum of HATC shows significant bands corresponding to  $\nu$ (N–H),  $\nu$ (O–H),  $\nu$ (C–H, aromatic),  $\nu$ (C–H aliphatic),  $\nu$ (C=O) and  $\nu$ (C=N) at 3314.8, 3199.3, 3071.1, 2932.8, 1719.6 and 1637.9 cm<sup>-1</sup>, respectively.

The <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm) of HATC shows significant bands: a singlet at 3.74 ppm from two protons of the methylene group and 3.94 ppm from three protons of the methoxide group, other singlet signals at 7.97 and 8.75 ppm due to single protons of the hydroxy group and amino group, 7.30 ppm from the single proton of the pyrone ring (=C–H of coumarin). Finally, the aromatic ring has singlet, multiplet and doublet signals from one proton at 6.07, 6.90–7.18, 7.27 ppm respectively. <sup>13</sup>C-NMR bands in DMSO-d<sub>6</sub> (ppm) were found at  $\delta$  174.94 (C=O), 160.28 (C=S), 153.77, 159.02, 149.79, 147.55, 146.23, 145.71, 131.88, 127.03, 126.12, 124.11, 122.89, 117.66, 115.87, 114.73, 114.26, 110.82, 56.48 and 30.72. These bands confirm that the number of carbon atoms was twenty and this is another confirmation that HATC was synthesized.

### 3.2 Gravimetric method

Weight loss measurements were performed on mild steel submerged in 1.0 M HCl for (1, 5, 10 and 24) hours in the absence of different concentrations of HATC. Experiments were conducted at different temperatures.

### 3.3 Effect of the inhibitor concentration, immersion time and temperature

Figure 1 demonstrates the effect of HATC concentration on the 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 due to the presence of a considerable number of adsorption sites which were brought through significant HATC concentrations. The differences in corrosion rates (CRs) at various concentrations of HATC inhibitor molecules for immersion time of 1-24 hours in HCl solution at 303 K are shown in Figure 1.



Figure 1. Effect of HATC concentration and time on the corrosion rate of mild steel.

The percentage inhibition efficiency (IE%) of HATC as a corrosion inhibitor was calculated at different concentrations (1.0, 2.0, 3.0, 4.0 and 5.0) mM, immersion times (1, 5, 10 and 24) h and temperatures (303, 313, 323 and 333) K. Plots of *CR* and *IE% versus* HATC concentrations at different times are shown in Figures 1 and 2. The plots of *IE% versus* HATC concentrations at different temperatures are shown in Figure 3. The results demonstrate that *IE%* increases with increasing concentration and decreases with increasing time (after 10 hours). Also, *IE%* decreases with increasing temperature.



**Figure 2.** Effect of MS immersion time in the corrosive environment at various concentrations of HATC.

One characteristic shown in Figure 2 is the variation in the direction of the IE% of the corrosion inhibitor studied at high and low concentrations. For example, at a time of immersion for a period of 5 and 10 hours approximately the same values of IE% at concentrations of 0.4 and 0.5 mM at the same temperature (at 303 K) were found, but the inhibition efficiencies varied at the other concentration and in all cases the inhibition efficiencies decrease after 24 hours.



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

As demonstrated in Figure 3, the effect of temperature on the surface of mild steel in a corrosive environment in the presence of the corrosion inhibitor is quite complex due to the fact that with increase in temperature, etching and desorption of inhibitor occur, as a consequence of that additional metal surface is coming into contact with the acidic environment which increases the *CR*. The dissolution of the mild steel surface may hinder the corrosion rate and thus decompose the layer that protects the surface.

#### 3.4 Thermodynamic and Activation Parameters

Adsorption is an important process in inhibiting the corrosion of mild steel surface because corrosion inhibition is often carried out using organic compounds. The mechanism of inhibition can be identified by determining inhibitor behavior through studying and understanding the thermodynamics of the adsorption process. Corrosion rate depends on temperature as it can be demonstrated by Arrhenius equation (Equation 6):

$$\log CR = \log A - \frac{E_a}{2.303RT} \tag{6}$$

Where CR (g·cm<sup>-2</sup>·h<sup>-1</sup>) is the corrosion rate, A is a constant,  $E_a$  is the activation energy, R (8.314 J·K<sup>-1</sup>mol<sup>-1</sup>) is the gas constant and T is the absolute temperature.

The activation enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ) values were calculated from the transition state as in Equation 7:

$$\log\left(\frac{CR}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^*}{2.303R}\right)\right] + \left(-\frac{\Delta H^*}{2.303R}\right)\left(\frac{1}{T}\right)$$
(7)

where *h* is Planck's constant and *N* is Avogadro number.

Figure 4 demonstrates the activation energy and it was calculated from the Arrhenius equation and slope value, in the presence and absence of HATC. The value of activation energy for hydrochloric acid solution without HATC is 32 kJ/mol, while in the presence of

HATC as a corrosion inhibitor it is 61.73 kJ/mol. The high value of activation energy of HATC implies that the HATC molecules form a layer that protects the surface of mild steel from the corrosive solution.

Conc. mM	$\frac{E_a}{(\text{kJ} \cdot \text{mol}^{-1})}$	$\Delta H_a$ (kJ·mol <sup>-1</sup> )	$\frac{\Delta S_a}{(\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})}$
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

Table 2. Kinetic parameters for MS in 1.0 M HCl in the presence and absence of HATC.



Figure 4. Arrhenius plot for mild steel in 1 M HCl in the presence and absence of HATC.

In Table 2,  $\Delta H$  with a positive value refers to an endothermic dissolution process for surface of mild steel at room temperature in the presence of HATC molecules.  $\Delta H$  increased with a temperature increase, which supports the endothermic nature of MS surface dissolution and the decrease of the inhibition performance of HATC molecules. The entropy activation values at room temperature were negative and became positive with increasing temperature. In the absence of HATC molecules, the entropy activation values were positive and tended to be negative at higher concentrations of HATC. A negative activation entropy value indicated that, at room temperatures and the maximum concentration of HATC studied, the MS surface was protected by the HATC molecules.

Langmuir, Temkin, and Frumkin absorption isotherms were used to realize the adsorption nature of HATC molecules as inhibitor for the corrosion of mild steel (MS)

surface. Figure 4 agrees with the Langmuir isotherm with a slope coefficient value less than one. The Langmuir adsorption isotherm is represented by Equation 8.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \tag{8}$$

Figure 5 demonstrates the slope of straight line for the value concentration/surface coverage *versus* concentration. The intercept value represents the adsorption equilibrium constant that indicates a high absorption rate of HATC molecules on the MS surface [47].



Figure 5. Langmuir adsorption isotherm plot for HATC in acidic environment on MS surface.

The  $K_{ads}$  [48, 49] is correlated with the free energy of adsorption ( $\Delta G_{ads}^0$ ) as in Equation 9.

$$\Delta G_{\rm ads}^0 = -RT \ln(1000K_{\rm ads}) \tag{9}$$

In the present study, the  $\Delta G_{ads}^0$  value of HATC was -32.85 kJ/mol. This value elucidates that HATC is adsorbed on the MS surface spontaneously and approaches a mixed adsorption type.

### 3.5 Quantum Chemical Calculation

The quantum chemical parameters (QCPs) for the neutral form of the investigated inhibitor calculated by DFT/B3LYP with the 6-31+G(d) are listed in Table 3. Analysis of the data will be given in the following paragraphs. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and their effective part in chemical reactivity were also calculated [50]. Moreover  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , Hardness ( $\eta$ ),

Electrophilicity ( $\omega$ ), Ionization Potential (*I*), Dipole Momentum ( $\mu$ D), Atomic charges (*q*) and Proton affinities (*PA*) were considered as indicators of activity. Herein we utilized quantum chemistry to realize the relationship between inhibitor molecules and inhibition efficiency. The geometrical structure of the tested inhibitor was investigated, which confirmed the *IE* values obtained from experimental results.



Figure 6. Optimized structure, HOMO and LUMO for HATC.

The adsorption capability of the inhibitor molecules over a mild steel surface coupon is associated with HOMO and LUMO [41, 42]. HOMO is related to the capability of a molecule to contribute electrons, on the other hand, LUMO refers to the ability to accept electrons. From Figure 6, it is obvious that HOMO and LUMO electronic densities on the entire inhibitor molecule are completely steady because of Pi-electrons.

As in Figure 6, the analysis of frontier orbitals, HOMO and LUMO demonstrate that significant nucleophilic sites attack atoms of coumarin and triazole rings and these heteroatoms have the ability to interact with mild steel surface [51]. HOMO and LUMO are related with the abilities of donating and accepting electrons, respectively. A high value

of  $E_{\text{HOMO}}$  facilitates adsorption through influencing the donation process by the adsorbed film [52, 53].

An energy gap with low values is a significant indicator of excellent inhibition efficiency, due to low energy required to remove electrons from an occupied orbital [54]. The energy gap was also found to be 2.7 eV as in Table 3, which reveals that the synthesized corrosion inhibitor has a good inhibition efficiency. Hard molecules have big energy gaps, and hard molecules are less reactive than soft molecules [55, 56].

Another quantum parameter significant for corrosion inhibition efficiency was the dipole moment ( $\mu$ ). It is the related with the electrons distribution and bond polarity [57]. The hardness and softness can be related to the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  [58].

Parameter	Value
$\Delta E$	-2.704
НОМО	-8.194
LUMO	-5.490
Ι	8.194
A	5.490
μ	5.03
χ	5.842
η	1.352
ω	12.62
σ	0.739
$\Delta N$	0.82

**Table 3.** Computed parameters for HATC.

HATC is a new synthesized corrosion inhibitor with the smallest value of hardness 1.352 (eV). The corrosion inhibitor with a low hardness value is predicated to have an excellent inhibition efficiency [59]. For the easy electron transfer, adsorption occurs at the site of the molecule that has a high value of softness ( $\sigma$ ) [60]. HATC has a softness value of 0.739 eV, so this tested inhibitor has a superior inhibition efficiency.  $\Delta N$  was calculated according to Table 1 using theoretical values of  $\chi$  and  $\eta$  for iron that are 7 eV/mol and 0 eV/mol, respectively. The  $\Delta N$  value demonstrated the inhibition impact resulting from donation of electrons that agrees with Lukovits *et al.*'s investigation [40]. If the value of  $\Delta N$  is < 3.6, the *IE*% increases with the ability of electron donation at the surface of mild steel. The higher the value of  $\Delta N$ , the higher the IE% and hence the better the compound as inhibitor.

### 4. Conclusion

The results of the this study revaled that the new eco-friendly coumarin derivative, namely, 4-((4-((4-hydroxy-3-methoxybenzylidene)amino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)methyl)-coumarin (HATC), acted as a superior corrosion inhibitor for mild steel surface in corrosive acidic environment in a concentration-dependent technique. HATC has an excellent inhibition efficiency of 96% at a concentration of 0.5 mM, which decreases with an increase in temperature, which indicates physisorption. HATC molecules were adsorbed on mild surface surface obeying the Langmuir adsorption isotherm. The high inhibition efficiency of HATC molecules wasdue to the presence of nitrogen, sulphur and oxygen atoms in addition to benzene, lactone and triazole rings. The corrosion inhibition investigation of HATC molecules obviously implied its role in the protection of mild steel surface in hydrochloric acid solutions.

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## **Conflicts of Interest**

The authors declare no conflict of interest.

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