A new synthesized coumarin-derived Schiff base as a corrosion inhibitor of mild steel surface in HCl medium: gravimetric and DFT studies

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Abstract

The inhibition efficiency of a new coumarin derivative, namely 2-(6-methylcoumarin-4-yl)-*N′*-(3-nitrobenzylidene)acetohydrazide (MCNAH), in controlling corrosion of mild steel in 1 M hydrochloric acid solution was investigated by gravimetric techniques at various temperatures (303, 313, 323 and 333 K). The impact of immersion time and temperature on inhibition performance of MCNAH was also studied. MCNAH was synthesized and the chemical structure was elucidated by magnetic resonance spectroscopy (MRS) and Fourier-transform infrared spectroscopy (FT-IR). The experimental results suggested that MCNAH is an excellent corrosion inhibitor for mild steel in 1 M hydrochloric acid environment. The synthesized inhibitor (MCNAH) has the ability to impede the corrosion of mild steel in 1 M hydrochloric acid environment at low and high concentrations. The inhibitive efficiency was found to increase with increasing concentration of MCNAH and decrease with increasing time and temperature. The thermodynamic parameters were estimated and discussed. The adsorption of the synthesized inhibitor on the surface of the tested mild steel in the presence of HCl obeyed the Langmuir adsorption isotherm. The relationship between the structure of the new synthesized inhibitor and its inhibitive effects was investigated using theoretical calculations. The experimental and density functional theory (DFT) calculation results are in good agreement. The results clearly show that the inhibition mechanism involves a blocking mechanism of action of the inhibitor.

Keywords: *MCNAH, corrosion inhibitor, coumarin, DFT, surface adsorption.*

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1. Introduction

Mild steel, as a major building material, is widely used in various engineering applications such as transportation, energy production, shipbuilding, water and oil desalination, and also in the electrochemical and other industries. These applications are due to its low cost and important mechanical properties in addition to availability [1, 2]. With these unique properties of mild steel, it is liable to corrosion when exposed to various corrosive media, especially acidic ones [3]. The use of acidic environments is widespread in industry, especially in descaling, cleaning, acidification, and petrochemical branches [4], making mild steels more vulnerable to corrosion. There are many important ways to protect and control corrosion, the most important of which being the use of corrosion inhibitors, as it is the most practical method that is economically feasible and environmentally friendly, in addition to many other important advantages [5]. The majority of known inhibitors are natural products or synthetic organic compounds that contain multiple bonds and heterogeneous atoms such as phosphorous, sulfur, oxygen and nitrogen that have the ability to give a pair of electrons not shared and create coordination bonds with the metal (iron) and thus form a layer on the surface of metal works to inhibit the corrosion of mild steel [6]. These inhibitors work against metallic corrosion in acidic and basic environments. Cyclic and non-cyclic nitrogen compounds are effective inhibitors against corrosion of mild steel in acidic solutions [7]. Absorption of free electronic pairs of heteroatoms atoms on the surface of the metal increases the inhibition efficiency and reduces the corrosion rate [8]. The degree of corrosion inhibition due to absorption depends on the geometry of the particles and their size in addition to the vacuum impediment, and the thermal stability of the inhibitor molecules [9]. Following up on the investigations for active corrosive inhibitors for steel alloy in acidic media [10–33], the present study declares the corrosion inhibitive effectiveness of a new synthesized coumarin, namely 2-(6-methylcoumarin-4-yl)-*N′*-(3-nitrobenzylidene)acetohydrazide (MCNAH). The gravimetric technique was applied to examine the enhanced corrosion inhibition. The electronic parameters such as HOMO, LUMO, atomic charges and dipole moment were computed to understand the performance of the synthesized inhibitor against the corrosive environment.

2. Experimental

2.1. Materials

Weight loss measurements for corrosion investigations were performed on coupons of mild steel with the composition: carbon = 0.066%, manganese = 0.050%, phosphorous = 0.090%, silicon = 0.380%, aluminum = 0.010%, sulfur = 0.05% and remainder iron. Previously to all experiments, the MS (Mild steel) coupons were washed and cleaned according to ASTM standard guidelines G1-03 [34]. The test environment (1 M hydrochloric acid) was prepared from analytical reagent grade hydrochloric acid and distilled water.

2.2. Synthesis of the inhibitor

The starting materials, solvents and catalysts were purchased from Sigma/Aldrich and were used without further treatment. The melting points were physically measured using a melting point device. The technique utilized to get the infrared absorption spectra was performed on a Fourier-transform infrared spectroscopy (FT-IR) Shimadzu/8300 spectrometer. Magnetic resonance spectroscopy (MRS), a spectroscopic technique to observe local magnetic fields around atomic nuclei for the synthesized inhibitors, was performed on Bruker/Spectrospin-300 MHz with tetramethylsilane as internal standard.

2.3. Synthesis of 6-metheyl-coumarin-4-acetohydrazide

A mixture of equimolar quantities of ethyl 6-metheyl-coumarin-4-acetate and hydrazine hydrate was refluxed for 6 h, and thin layer chromatography was used as an analytical technique to observe the completion of the reaction. The mixture was poured onto ice and filtered. The filtered cake was recrystallized from ethanol and used for the next step.

2.4. Synthesis of N′-[(1)-ethylidene]-2-(6-methyl-2-oxo-2H-chromen-4-yl)acetohydrazide (MCNAH) corrosion inhibitor

A mixture of equimolar quantities of 6-metheyl-coumarin-4-acetohydrazide and *meta*-nitrobenzaldehyde in ethanol was refluxed for 8 h. The mixture was poured onto ice, dried and washed with water and alcohol, yield 71%. m.p. 215°C. FT-IR, cm^{-1}: amino group (3338.5 and 3236.4), benzene ring (3066.8 and 3051.7), methyl group (2864.2), carbonyl group (1701.9), azomethine group (1649.6); ^1H NMR with DMSO-d_6, δ: 2.31 (s, 3H, $–CH_3$), 3.17 (s, 2H, $–CH_2$), 6.11 (d, 1H, –C=CH), 7.29–7.40 (1H, aromatic rings); 8.18 (s, 1H, –N=CH), ^{13}C NMR with DMSO-d_6: 142.1 ($C–NO_2$), 129.1, 126.9, 125.2, 118, 117.3 (benzene ring), 167.6 (C=O), 141.6 (C=N), 33.2 (CH_2), 146.4, 111.2, 159.8, (lactone ring), 154.2, 113.7, 132.8, 133.9, 121.7, 115.9 (benzene of coumarin).

2.5. Weight loss measurements

Gravimetric investigations were performed by immersion of mild steel test coupons in hydrochloric acid solution (1 M) in the absence and presence of 1/100, 2/100, 3/100, 4/100 and 5/100 of the tested inhibitor at 303 K. A coupon after 5 hours of immersion was rinsed with distilled water and washed with acetone. The coupons were re-weighed after drying to calculate the weight loss by the ASTM procedure [34]. Duplicated parallel experiments were performed and the corrosion rate was calculated from the average value using Equation 1.

$$C_{\mathrm{R}} = \left(W(\text{average weight loss})\right) / \left(a(\text{area}) \cdot t(5\ \text{h})\right) \quad (1)$$

The inhibition efficiency (*IE*%) and surface coverage θ were measured using Equations 2 and 3:

$$IE\% = \left(CR - CR_{(\mathrm{i})}\right) / CR \times 100 \tag{2}$$

$$\theta = \left(CR - CR_{(\mathrm{i})}\right) / CR \tag{3}$$

Where *CR* is the corrosion rate in blank solution and $CR_{(\mathrm{i})}$ is the corrosion rate in the presence of the synthesized inhibitor. The corrosion rates are expressed in $\mathrm{mg/cm^2 \times h}$.

2.6. Quantum chemical calculations

DFT calculations were performed by utilizing Gaussian 03 software. The geometrical structure was optimized utilizing the B3LYP hybrid functional at 6-31G (d, p). The calculated parameters such as HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), ΔE (energy gap), μ (dipole moment), χ (electronegativity), η (hardness), σ (softness) and ΔN (fraction of electrons transferred) were estimated for the synthesized corrosion inhibitor. ΔN from the tested inhibitor to the surface of coupons were estimated using the electronegativity and hardness values. These parameters were calculated according to equations 4–8 [35, 36]:

$$\Delta E = E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}} \tag{4}$$

$$\eta = -\frac{1}{2}\left(E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}\right) \tag{5}$$

$$\sigma = \frac{1}{\eta} \tag{6}$$

$$\chi = -\frac{1}{2}\left(E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}\right) \tag{7}$$

$$\Delta N = \frac{\chi_{\mathrm{Fe}} - \chi_{\mathrm{inh}}}{2\left(\eta_{\mathrm{Fe}} + \eta_{\mathrm{inh}}\right)} \tag{8}$$

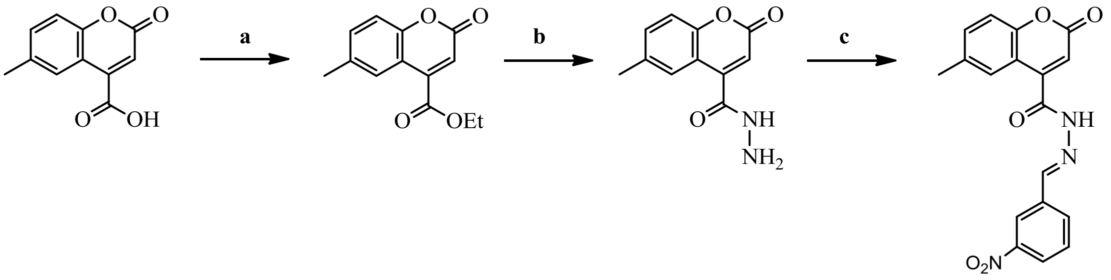
3. Results and discussion

3.1. Chemistry

The reaction sequences for the synthesis of the new corrosion inhibitor starting from 6-metheyl-coumarin-4-carboxylic acid are outlined in Scheme 1.

Ethyl 6-metheyl-coumarin-4-acetate was obtained by refluxing 6-metheyl-coumarin-4-carboxylic acid with ethyl alcohol in the presence of concentrated sulfuric acid to afford ethyl 6-metheyl-coumarin-4-acetate in good yield. The reaction of ethyl 6-metheyl-coumarin-4-acetate with hydrazine yielded 6-metheyl-coumarin-4-acetohydrazide. The reaction of 6-metheyl-coumarin-4-acetohydrazide with 3-nitrobenzaldehyde afforded the target compound, namely *N´*-[(1)-ethylidene]-2-(6-methyl-2-oxo-2H-chromen-4-yl)aceto-hydrazide (MCNAH).

The FT-IR spectrum of MCNAH demonstrated absorption bands at (3338.5 and 3236.4) cm^{-1} for (3338.5 and 3236.4) and (3066.8 and 3051.7) cm^{-1} for aromatic ring. A methyl group was located at 2864.2 cm^{-1}, in addition the carbonyl and azomethine groups were located at 1701.9 and 1649.6 cm^{-1} respectively. The ^1H NMR spectrum exhibited a singlet for 3H at 2.31 ppm and a singlet at 3.17 ppm due to the methyl and methylene groups, respectively. A specific doublet band was located at δ 6.11 ppm due to the vinyl group proton. The other significant band was located at δ 8.18 ppm due to the single proton of the azomethine group.



Scheme 1. Synthesis of MCNAH.

3.2. Effect of concentration and immersion time

The effects of various concentrations of tested inhibitor on the mild steel corrosion inhibition in corrosive solution are demonstrated in Figure 1. It may be observed that on increasing the concentration of MCANH in the acidic solution, the corrosion rates (*CR*s) decreased significantly. On the other hand, the inhibition efficiencies increase with addition of MCANH due to the adsorption of additional inhibitor molecules on the mild steel surface. However, above the 0.5 mM concentration of MCANH, the inhibition efficiency was almost constant, indicating that 0.5 mM concentration of MCNAH is the optimum concentration for the inhibition of mild steel corrosion in the corrosive solution. MCNAH displays the highest inhibition efficiency of 95.1% at 0.5 mM. The *IE* of MCANH can be explained on the basis of various active sites in the molecular structure of MCANH molecules, the presence of various heteroatoms, substituent groups and aromatic rings. The MCANH molecules have five oxygen atoms and two nitrogen atoms, as well as substituent groups: –C=N–, –NH, carbonyls, lactone and nitro group at the 3-position of the benzene ring and a $-CH_3$ group at the 6-position of coumarin. These heteroatoms and substituent functional groups have free electrons pairs that increase the electron density and enhance the inhibition efficiency. The resonance effect also increases the stability of the inhibitor molecule that enhances the inhibition efficiency.

To evaluate the variation of the inhibitor film stability on the surface of mild steel in acidic environment with immersion time, weight loss tests were performed at 303±2 K for 1, 5, 10 and 24 h in 1 M hydrochloric acid at various inhibitor concentrations of (0.1, 0.2, 0.3, 0.4 and 0.5) mM.

Figures 1 and 2 display that the corrosion rate decreases with immersion time until 10 h. After 10 hours, the *CR* increases. On the other hand, the *IE* increases with an increase in the immersion time until 10 h.

After 10 hours, the *IE* decreases due to denaturation of adsorbed layer of tested inhibitor on the surface of mild steel.

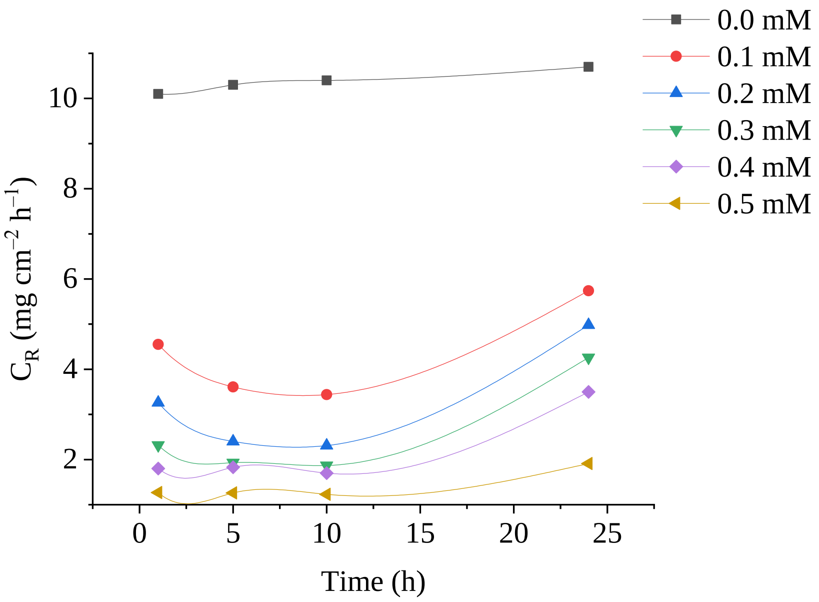


Figure 1. Variation of corrosion rate with concentration and immersion time.

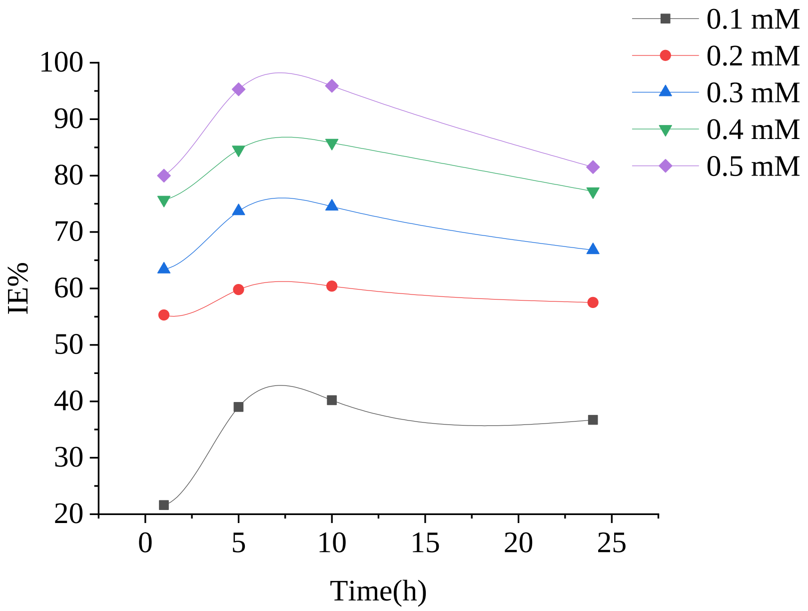


Figure 2. Variation of inhibition efficiency with concentration and immersion time.

3.3. Effect of temperature

To demonstrate the corrosion inhibition mechanism and to evaluate the thermodynamic factors of the corrosion process, gravimetrical techniques were used at 303, 313, 323 and 333 K. The effect of temperature on the inhibition process of mild steel in the presence of MCANH as a corrosion inhibitor is demonstrated in Figure 3. The efficiency of corrosion inhibition of mild steel slightly decreased with increasing temperature. The decrease in *IE* was imputed to the denaturation of inhibitor molecules that adsorbed on the mild steel surface.

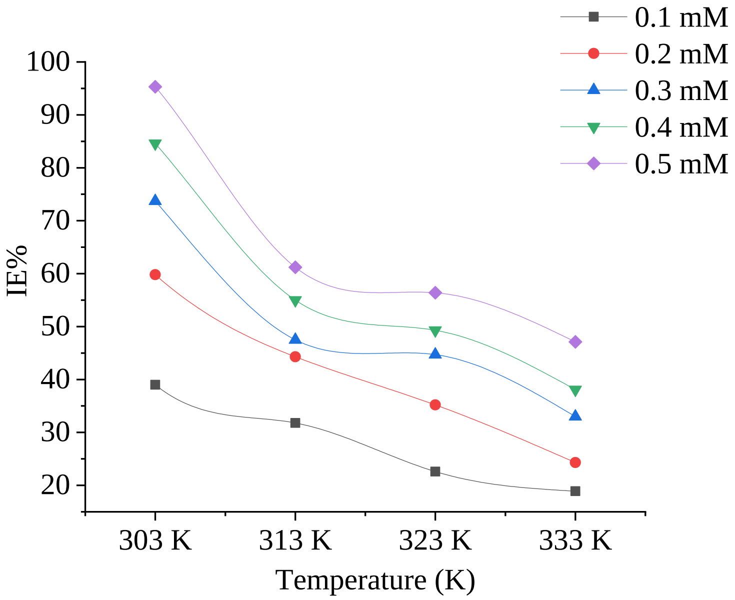


Figure 3. Variation of inhibition efficiency with temperature.

The temperature effect on the corrosion properties without and with addition of the tested corrosion inhibitor may be evaluated through differentiation E_a that was derived according to Arrhenius Equation 9.

$$\log C_R = \log A - \frac{E_a}{2.303RT} \tag{9}$$

Where *A* is a constant, *T* is the absolute temperature, and *R* is the universal gas constant.

The E_a was evaluated from the slope value from the Arrhenius plot without and with the tested inhibitor as in Figure 4. The activation energy without the tested corrosion inhibitor was 33.15 kJ/mol, and it was 57.83 kJ/mol with the inhibitor. The higher value of E_a with addition of the investigated corrosion inhibitor suggests that the inhibitor molecules form a film covering the surface of mild steel in the hydrochloric acid medium.

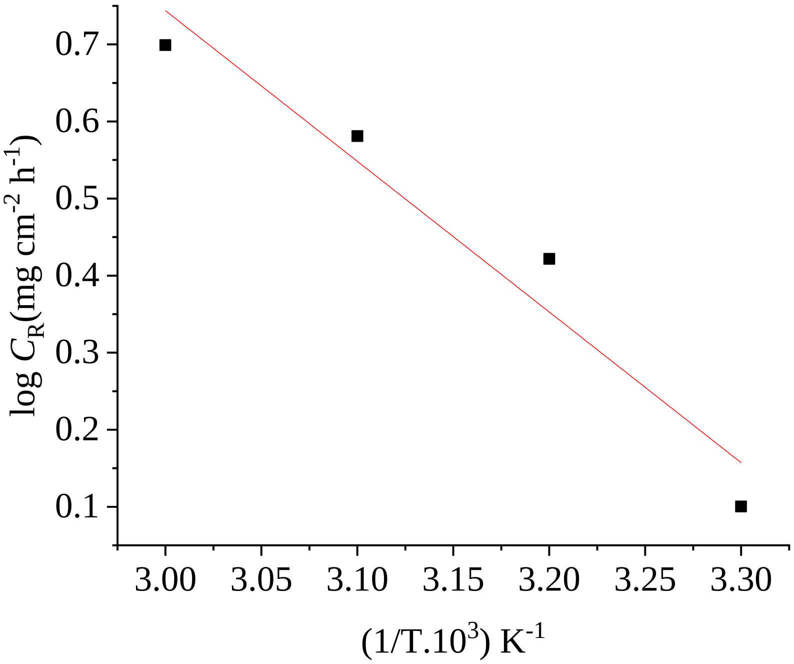


Figure 4. Arrhenius plot for the C_R *versus* the temperature in the corrosive medium.

3.4. Adsorption isotherm

To evaluate the adsorption attitude of the studied inhibitor on the surface of mild steel, various adsorption isotherms were investigated such as Langmuir isotherm, Temkin isotherm, and Frumkin isotherm [37]. The Langmuir isotherm was found to provide the best fit with the adsorption of the studied inhibitor on the surface of mild steel with a regression coefficient (R^2) value of *ca.* 1, as demonstrated in Figure 5. The Langmuir isotherm was represented by Equation 10.

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \tag{10}$$

Where C is the tested inhibitor concentration and θ is the surface coverage.

It can be obviously observed from Figure 5 that the plot of C/θ *vs.* C affords a straight line with a slope of 1. The K_{ads} (constant of adsorption equilibrium) acquired from the intercept was 184 L g^{-1} [38]. The adsorption equilibrium constant is related with ΔG^0_{ads} (adsorption free energy) through Equation 11 [39, 40].

$$\Delta G^0_{\text{ads}} = -RT \ln(1000 K_{\text{ads}}) \tag{10}$$

1000 is the concentration of water in hydrochloric acid media in g/L.

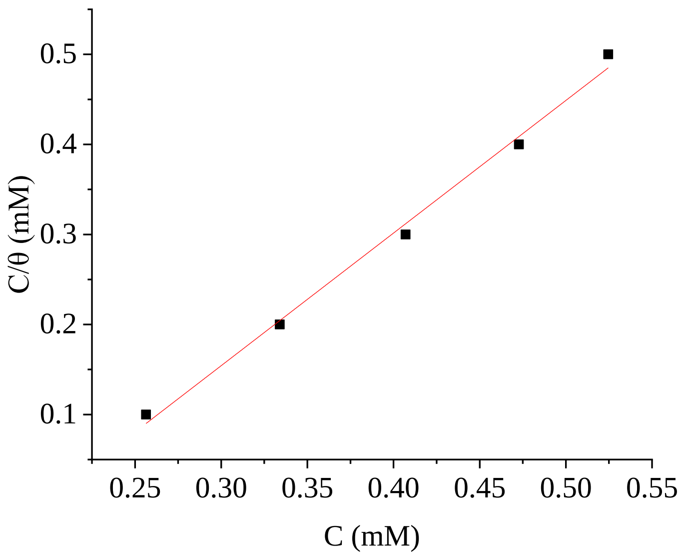


Figure 5. Langmuir isotherm plot for the inhibitor adsorption on the surface of mild steel in the corrosive medium.

In this investigation, the evaluated value of ΔG^0_{ads} was –33.28 kJ/mol for the investigated corrosion inhibitor. This result indicates that the studied corrosion inhibitor is adsorbed spontaneously on the surface of mild steed and shows mixed mode adsorption [41].

3.5. DFT calculations

Generally, the HOMO is associated with the ability of a molecule to release an electron. The E_{HOMO} with high value indicate the nature of ability to donation electrons. On the other hand, low E_{HOMO} values are associated with the ability to accept electrons from molecules of a donor. An excellent inhibitor should have a high E_{HOMO} value in order to contribute its unshared electrons to the vacant d-orbital of iron (mild steel); moreover, a good inhibitor must have a low E_{LUMO} value in order to accept the unshared electrons transferred from the mild steel surface to the free orbitals of inhibitor molecules, and also the energy gap should be the smallest.

This investigation denotes that the new synthesized inhibitor has significant inhibition characteristics due to the low energy gap of 3.277 eV as shown in Table 1. The optimized geometrical structure, HOMO and LUMO are given in Figure 6. The dipole moment is another significant factor that has a considerable impact on the inhibitive characteristics of the inhibitor molecules on the mild steel surface. Generally, the dipole moment is related to the inhibitive performance. This inhibitor molecule under investigation has a dipole moment value of −4.52 indicating that this studied inhibitor has good inhibition efficiency. The 3-dimensional structure, HOMO and LUMO frontiers of MCNAH are demonstrated in

Figure 6. As shown in Figure 6, the HOMO distribution is on average around the isomethine group and the LUMO distribution in on average around the nitrobenzene ring.

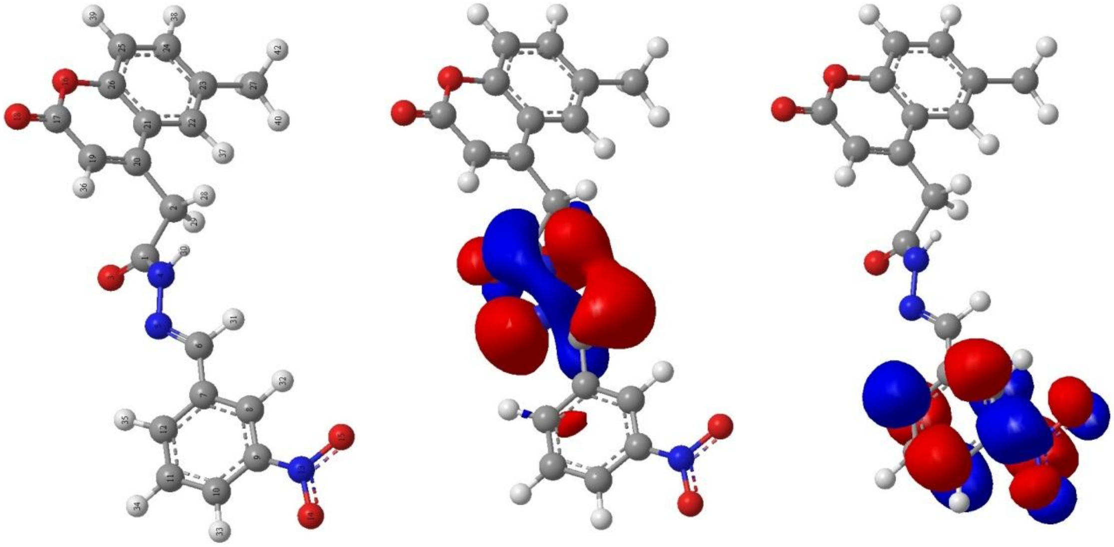


Figure 6. The 3-dimensional structure, HOMO and LUMO frontiers of MCNAH.

Table 1. Calculated quantum properties for the most stable conformation of MCNAH.

Function	**Values**
E_{HOMO}	−8.755 eV
E_{LUMO}	−5.478 eV
$E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}}$	−3.277 eV
Dipole Moment (μ)	−4.52 Debye
$I=-E_{\mathrm{HOMO}}$ *(Hartree)*	8.755 eV
$A=-E_{\mathrm{LUMO}}$ *(Hartree)*	5.478 eV
$\eta=-0.5(E_{\mathrm{HOMO}}-E_{\mathrm{LUMO}})$	1.6385
$\sigma=1/\eta$	0.6103
$\chi=-0.5(E_{\mathrm{HOMO}}+E_{\mathrm{LUMO}})$	7.1165
$\Delta N=-\frac{\varnothing-\chi_{\mathrm{inh}}}{2(\eta_{\mathrm{Fe}}+\eta_{\mathrm{inh}})}$	0.2883

The ΔN value represented the association with adsorption of inhibitor molecules on the surface of mild steel. The values of ΔN demonstrate the inhibition impact resulting from donation of electrons that approbate with the study by Lukovits et al. If $\Delta N<3.6$, the inhibition efficiency increased with increasing electron-donating ability at the metal surface.

The χ_{Fe} is the electronegativity of iron whereas χ_{inh} is the electronegativity of the inhibitor. The η_{Fe} is the hardness of iron and the η_{inh} is the hardness of inhibitor molecules.

The Mulliken charges of MCNAH are displayed in Table 2. It can be shown that the highest atomic charges were found for O(3) −0.778201; O(14) −0.753294; O(15) −0.760271 and O(18) −0.755436. The relation between the corrosion inhibition mechanism and atomic charges of oxygen atoms may form adsorption active centers.

Table 2. The Mulliken charges of MCNAH molecule.

Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
C(1)	0.400895	C(8)	0.0076362	O(15)	−0.760271	C(22)	−0.05362
C(2)	−0.127506	C(9)	0.0923493	O(16)	−0.003368	C(23)	0.045831
O(3)	−0.778201	C(10)	−0.00203	C(17)	0.520338	C(24)	−0.028455
N(4)	0.441804	C(11)	−0.02986	O(18)	−0.755436	C(25)	−0.083927
N(5)	−0.067738	C(12)	−0.006098	C(19)	−0.173878	C(26)	0.265288
C(6)	0.0249598	N(13)	1.28579	C(20)	0.195672	C(27)	−0.143529
C(7)	0.03798	O(14)	−0.753294	C(21)	−0.01209	H(28)	0.0537125

3.5. Proposed Mechanism of Corrosion Inhibition

Inhibitor molecules were adsorbed on the surface of mild steel by displacing water molecules that were adsorbed on the surface of mild steel by inhibitor molecules. Generally, the electrostatic attraction between the charges of mild steel surface and molecules is called physisorption, on the other hand the transfer of electron pairs from the inhibitor molecules to the unoccupied d-orbital of mild steel surface that forms coordination bonds is called chemisorption. In the corrosive environment, the mild steel surface has negative charges which results of adsorbed chloride ion on the mild steel surface. The results clearly show that the inhibition mechanism involves a blocking mechanism of inhibitor action.

Since the adsorption energy of the inhibitor is 33.28 kJ/mol, we can conclude that the inhibitor is adsorbed on steel mainly electrostatically [42, 43].

4. Conclusions

1. MCNAH was synthesized, characterized and investigated as a corrosion inhibitor for mild steel in 1 M hydrochloric acid environment.
2. MCNAH is an excellent corrosion inhibitor for mild steel in the corrosive environment. Its inhibition efficiency increases with an increase in the inhibitor concentration. The maximum *IE*% is 95.1% at 0.5 mM.
3. The inhibition efficiency against corrosion of mild steel decreases with an increase in the temperature.

4. The inhibitor molecules are adsorbed on the mild steel surface following the Langmuir adsorption isotherm.
5. The results obtained from weight loss techniques and DFT calculations are in good agreement.

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Conflicts of interest

The authors declare no conflict of interest.

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