

Experimental and Theoretical Chemical Studies of Linalool and Caffeine as Corrosion Inhibitors for Mild Steel in Sulfuric Acid Solutions

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Abstract: This study used potentiodynamic polarization curve measurements, electrochemical impedance spectroscopy (EIS), and quantum chemical calculations to examine the inhibitory and adsorption properties of linalool and caffeine on the corrosion of mild steel in sulfuric acid (H₂SO₄) solutions. The obtained results revealed that linalool is more effective than caffeine as a corrosion inhibitor for mild steel in 0.5 M H₂SO₄ solutions. Potentiodynamic polarization curves indicated that linalool acts as a mixed-type inhibitor, whereas caffeine is an anodic-type inhibitor for mild steel in 0.5 M H₂SO₄ solutions. According to the impedance measurements, the corrosion mechanism occurs under activation control. Theoretical fitting was also used to assess various adsorption isotherms, including Langmuir, Flory-Huggins, and kinetic-thermodynamic models. Both inhibitors act through a physical adsorption mechanism on the mild steel surface. However, their adsorption process is a non-ideal one. Quantum chemical parameters were calculated and explained.

Keywords: mild steel; linalool; caffeine; H₂SO₄; corrosion.

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1. Introduction

Despite having numerous technological applications, the limited corrosion resistance of mild steel, particularly in acidic media used for pickling and cleaning, restricts its use.

[1-8]. Thus, preventing mild steel corrosion is a priority concern for both corrosion scientists and material technologists. Despite the availability of various approaches, such as surface modifications, anodic and cathodic protection, and metal coatings, the use of inhibitors has been proved to be a simple and cost-effective method of protecting metals from corrosion [8-13]. Numerous inhibitors are organic molecules with nitrogen, oxygen, sulphur, phosphorus, and aromatic rings that may attach to the metal's surface [4, 8–23]. The ability of an organic inhibitor molecule to adhere to the metal surface typically influences its ability to reduce corrosion rates. Adsorbed organic compounds block active sites and create impediments between the metallic surface and the aggressive medium by shaping a deterrent layer on the metallic surface, thereby reducing the metal dissolution [19, 24].

Linalool (3,7-dimethyl-1,6-octadien-3-ol), which is present in numerous flowers and spice plants, is a natural fragrance compound that has various commercial uses, mainly due to its pleasing odour [25]. Caffeine (1,3,7-trimethylxanthine) is a naturally occurring chemical that

is mostly present in food and is considered non-toxic. [26]. Both organic compounds have different structures and present some expected characteristics for a potential corrosion inhibitor, as seen in Figures 1 and 2. Thus it is worth finding out how the structures of these two organic compounds affect their inhibitory performance against the corrosion of mild steel in sulfuric acid solutions.

In this context, the present study compares the influence of Linalool and Caffeine on the corrosion behavior of mild steel in sulfuric acid solutions. The inhibition performance is examined using electrochemical measurements as well as theoretical quantum chemical calculations.

2. Materials and Methods

2.1. Solution preparation.

The test solutions of 0.5 M sulfuric acid (H_2SO_4) were diluted from 80 % analytical grade (Scharlau chemical industries) concentrated acid with distilled water. High-purity (99 %, Aldrich Chem. Co.) linalool and caffeine, shown in Figures 1 and 2, were used as organic inhibitors in the concentration range from 3×10^{-4} M to 9×10^{-3} M.

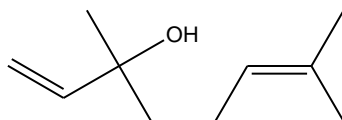


Figure 1. The chemical structure of linalool.

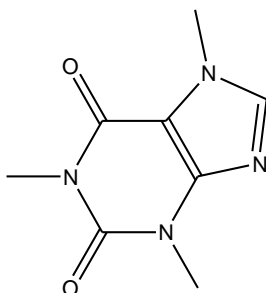


Figure 2. The chemical structure of caffeine.

2.2. Electrochemical studies.

Electrochemical studies (electrochemical impedance (EIS) and polarization measurement) were performed by connecting the Gill AC transfer function analyzer ACM instrument (UK) to a three-electrode electrochemical cell setup. A detailed description of electrochemical techniques was previously stated [4, 27, 28].

2.3. Quantum Chemical Calculations.

Quantum chemical calculations using the semi-empirical method PM3 within "Molecular Orbital Package" (MOPAC) program were performed through ChemOffice 2004, CHEM 3D Ultra-Molecular modeling, and Analysis-Cambridge soft-version 8.

3. Results and Discussion

3.1. Potentiodynamic polarization data measurements.

The potentiodynamic polarization curves of mild steel depicted in Figure 3 indicate that linalool acts as a mixed-type inhibitor retarding the anodic metal dissolution and the cathodic hydrogen evolution reactions. Conversely, caffeine act as an anodic type inhibitor suppressing the anodic mild steel dissolution.

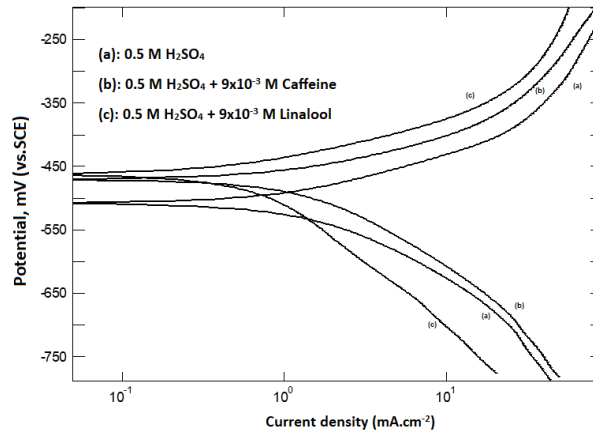


Figure 3. Potentiodynamic polarization curves for mild steel in 0.5 M H₂SO₄ solution in the absence and presence of Linalool and Caffeine at 30°C.

3.2. Electrochemical impedance spectroscopy results.

Figure 4 depicts Nyquist impedance plots of depressed capacitive semicircles in the high-frequency (HF) range and a small inductive loop in the low-frequency (LF) range. The capacitive semicircle reveals that the mild steel dissolution occurs under activation control and can be credited to the charge transfer reaction and the time constant of the electric double layer [4,16]. The presence of an inductive loop elucidates the occurrence of a Faradic process on free electrode sites that can be attributed to the relaxation of intermediates controlling the anodic process resulting from adsorption species such as FeSO₄ [29] or inhibitor species [30, 31] on the metal electrode surface. Increasing the size of these capacitive semicircles with linalool and caffeine concentrations denotes an increase in the corrosion resistance and forming a protective layer on the metal surface.

The bode impedance plots given in Figure 5a show that the modulus impedance increases with adding linalool and caffeine. Besides, Figure 5b reveals the presence of inhomogeneities in the system, as shown by the low phase angle values [32-34].

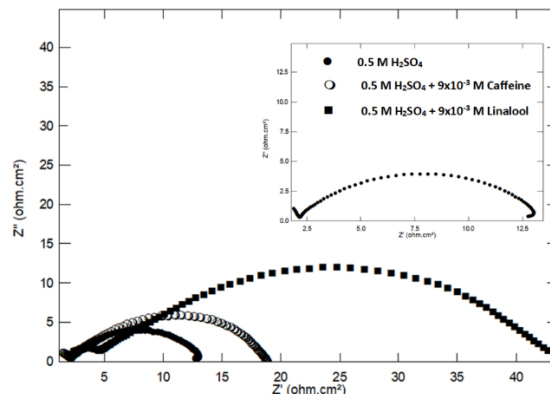


Figure 4. Nyquist impedance plots for mild steel in 0.5 M H₂SO₄ in the absence and presence of linalool and caffeine at 30°C.

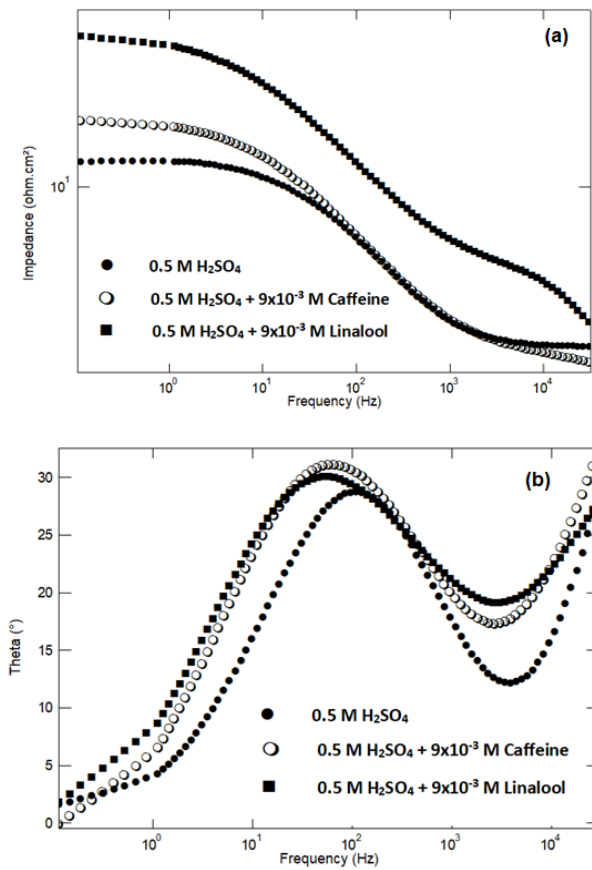


Figure 5. (a) Bode impedance and (b) Bode Theta of mild steel in 0.5 M H₂SO₄ in the absence and presence of linalool and caffeine at 30°C.

The experimental and computer fit results of the Nyquist and impedance plots with the corresponding equivalent circuit model of 0.5 M H₂SO₄ containing 9x10⁻³ M Linalool are given in Figure 6. The equivalent circuit used, inserted in Figure 6, contains the solution resistance (R_s), film resistance (R_f), and charge transfer resistance (R_{ct}). It also contains an inductive element (L), constant phase elements of the film (CPE_f), and none ideal and none ideal constant phase elements (CPE₁) that are connected in parallel to R_{ct}. The CPE consists of the non-ideal capacitance (Q) and a constant (n).

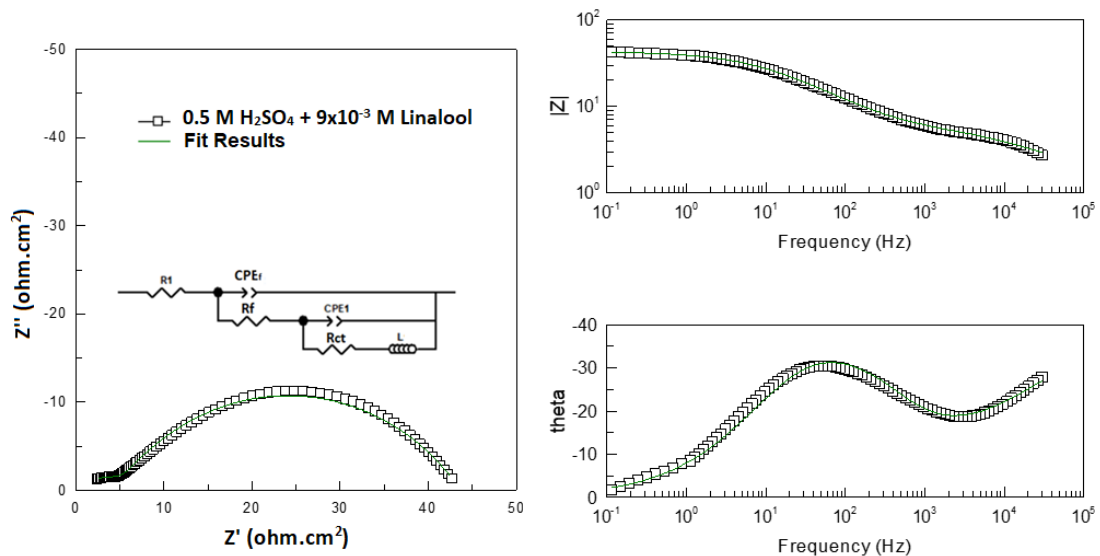


Figure 6. The experimental and computer fit results of Nyquist and impedance plots of 0.5 M H₂SO₄ containing 9x10⁻³ M linalool.

The percent inhibition efficiency (%P) was calculated using the equation:

$$\%P = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100$$

where R_{ct0} and R_{ct} are the values of the charge transfer resistance ($\Omega \text{ cm}^2$) in the absence and the presence of linalool and caffeine, respectively.

It is noticed, from Table 1, that n values are less than one, which is quite an indication that the circles are depressed in nature. Such phenomenon is commonly known as frequency dispersion which could be ascribed to different physical phenomena, including roughness and inhomogeneities of the solid surfaces [4, 27, 28]. Moreover, R_{ct} and %P values increase while the non-ideal double-layer capacitance (Q_{dl}) values decrease with the addition of Linalool and Caffeine. The latter is due to the adsorption of Linalool and Caffeine on a mild steel surface [27, 28].

Table 1. The electrochemical impedance parameters for the corrosion of mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of linalool and caffeine at 30°C.

Inhibitor	Conc., mol. L ⁻¹	Q _r μF/cm ²	N	R _r Ω.cm ²	R _{ct} Ω.cm ²	Q _{dl} μF/cm ²	n	L Henri.cm ²	%P
Linalool	Blank	160	0.58	2.49	10.85	1380	0.79	0.0034	-
	4.0x10 ⁻³	735	0.52	4.86	16.02	1282	0.70	0.0035	32.27
	5.0x10 ⁻³	729	0.51	5.33	22.8	1236	0.68	0.0085	52.41
	7.0x10 ⁻³	730	0.59	5.26	27.21	1223	0.68	0.0101	60.12
	8.0x10 ⁻³	728	0.60	4.50	29.94	1193	0.68	0.0098	63.76
	9.0x10 ⁻³	580	0.48	6.70	37.05	1182	0.69	0.0162	70.71
Caffeine	0.2x10 ⁻³	318	0.58	2.51	12.00	1379	0.78	0.00346	9.58
	0.4x10 ⁻³	320	0.58	2.83	13.11	1378	0.75	0.0041	17.23
	1.0x10 ⁻³	317	0.58	2.70	13.96	1356	0.76	0.0055	22.27
	7.0x10 ⁻³	316	0.57	2.77	14.34	1515	0.76	0.0057	24.33
	9.0x10 ⁻³	318	0.57	2.66	16.45	2608	0.72	0.0059	34.04

3.3. Adsorption isotherms.

Theoretical fitting of Langmuir, kinetic-thermodynamic model, and Flory Huggins isotherms was recognized on the obtained degrees of surface coverage values from AC impedance measurements using the equation ($\theta = \% P/100$) to illustrate the mechanism of linalool and caffeine adsorption on mild steel surface [2, 4, 27, 28]. The obtained adsorption parameters are listed in Table 2.

Table 2. Linear fitting parameters of linalool and caffeine according to the mentioned models in 0.5 M H_2SO_4 at 30°C.

Inhibitors	Kinetic-Thermodynamic Model			Flory-Huggins Model		
	K	1/y	R ²	K	x	R ²
Linalool	182	0.566	0.90	-	-	-
Caffeine	9.05	3.193	0.76	154	9.34	0.62

It was noticed that caffeine experimental data fitted all applied adsorption isotherms except the Langmuir isotherm. However, the linalool result fitted only the kinetic-thermodynamic model. This assures the non-ideal behavior of both inhibitors on the corrosion inhibition of mild steel in 0.5 M H_2SO_4 . The number of active sites occupied by a single inhibitor molecule, denoted as 1/y, and the size parameter x, which provides insight into the

number of adsorbed water molecules replaced by the inhibitor molecule, is greater than unity for caffeine, indicating that caffeine molecules are bulky molecules that occupy more than one active site. On the other hand, $1/y$ of linalool shows that its molecules are tiny molecules [4, 35]. The numerical values of the binding constant K approve the experimental data in which linalool is more efficient as a corrosion inhibitor for mild steel in 0.5 M H_2SO_4 than caffeine molecules [4, 27, 28].

Moreover, the binding constant is linked to the standard free energy of adsorption (ΔG_{ads}), as reported previously. The calculated ΔG_{ads} from K values of the kinetic-thermodynamics model were -29.77 and $-15.66 \text{ kJ.mol}^{-1}$ for linalool and caffeine, respectively. Such negative values are an indication of the spontaneity and stability of the physical adsorption processes of both inhibitors [4, 27, 28].

3.4. Activation parameters studies.

The potentiodynamic polarization curves of mild steel in 0.5 M H_2SO_4 in the presence of 3×10^{-3} M Linalool at different temperatures depicted in Figure 7 shows that raising the temperature speeds up both anodic metal dissolution and cathodic hydrogen evolution processes. Such behavior confirms the desorption of linalool from mild steel surfaces with increasing temperature. Similar observations were recorded for caffeine in 0.5 M H_2SO_4 solutions.

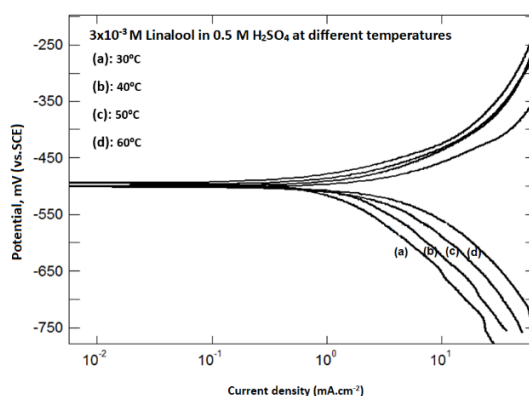


Figure 7. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 in the presence of linalool at different temperatures.

It has been noted that the calculation of the activation parameters is fundamentally important to illustrate the inhibition mechanism. This can be done through Arrhenius and transition state equations [15]:

$$\ln v = \ln A - \left(\frac{E_a}{RT} \right) \quad (1)$$

where v is the corrosion rate and is taken as reciprocal of the charge transfer resistance R_{ct} obtained from electrochemical impedance measurements, E_a is the apparent activation energy, A ; the pre-exponential factor and R is the universal gas constant:

$$v = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \quad (2)$$

where ΔH^* is the apparent enthalpy of activation, ΔS^* is the apparent entropy of activation, h is Planck's constant, and N is Avogadro's number, respectively. The activation parameters for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of 3×10^{-3} M Linalool and Caffeine are given in Table 3.

Table 3 shows that E_a and ΔH^* values increase in the presence of linalool and caffeine. The formation of the activated complex is an endothermic process due to the positive activation

enthalpy, ΔH^* . Negative values of ΔS^* suggests that the transition state is an association step [27, 28].

Table 3. Activation parameters of mild steel in 0.5 M H_2SO_4 solution as a function of different concentrations of Linalool and Caffeine at 30°C.

Inhibitors	E_a (KJ.mol ⁻¹)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .K ⁻¹)
-	28.37	25.73	-182
3x10 ⁻³ M Linalool	47.31	44.67	-122
3x10 ⁻³ M Caffeine	29.67	27.03	-175

3.5. Quantum chemical calculations.

Quantum structure-activity relationships have been applied to study the effect of molecular structure on the inhibition efficiencies of linalool and caffeine [36]. Structural Parameters such as E_{HOMO} (energy of highest occupied molecular orbital), E_{LUMO} (energy of lowest unoccupied molecular orbital), energy gap ΔE ($E_{LUMO}-E_{HOMO}$), absolute electronegativities(χ) and ionization potential (I), Electron Affinity(A), as well as the number of transferred electrons (ΔN), were calculated and presented in Table 4.

The value of ΔE provides a measure of the stability of the formed complex on the metal surface [37]. The higher HOMO–LUMO gap signifies a high molecular instability of linalool in chemical reactions, i.e., linalool has a physical adsorption character onto the metal surface. Thus, caffeine has more kinetic stability and less chemical reactivity than linalool [36].

Table 4. Quantum parameters of linalool and caffeine.

Inhibitors	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	I	A	H	χ	ΔN
Linalool	-9.49	1.00	10.49	9.49	-1.00	10.49	4.24	-0.13
Caffeine	-9.10	-0.27	8.83	9.10	0.27	8.83	4.68	-0.13

The number of transferred electrons (ΔN) was also calculated according to:

$$\Delta N = (\chi_{Fe} - \chi_{inhibitor}) / 2(\eta_{Fe} - \eta_{inhibitor})$$

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively. In order to calculate the fraction of electrons transferred, a theoretical value for the electronegativity of bulk iron was used $\chi_{Fe} = 7\text{eV}$, and a global hardness of $\eta = 0$, by assuming that for a metallic bulk [15].

These quantities are related to an electron affinity (A) and ionization potential (I):

$$\chi = (I+A)/2 \tag{3}$$

$$\eta = (I-A)/2 \tag{4}$$

I and A are related in turn to E_{HOMO} and E_{LUMO}

$$I = -E_{HOMO} \tag{5}$$

$$A = -E_{LUMO} \tag{6}$$

According to other reports value of ΔN showed an inhibition effect resulting from electron donation. If $\Delta N < 3.6$, the inhibition efficiency increases by increasing the electron-donating ability of these inhibitors [13, 36]. This result supports the assertion that the adsorption of inhibitor on the metal surface can occur on the bases of donor-acceptor interactions between the π electrons of the compound and the vacant d-orbitals of the metal surface. Besides, the absolute electronegativities (χ) of Linalool and Caffeine are lower than that obtained from Lukovits's study for iron (7 eV). Thus, electrons transfer from linalool and

caffeine towards the mild steel surface until the equilibrium in chemical potential is attained. Such transfer aids the adsorption of the inhibitors on the electrode surface [15].

Besides, Mulliken charge distributions and the optimized molecular structures of linalool and caffeine using the semi-empirical method PM3 within the Molecular Orbital Package (MOPAC) program are depicted in Table 5. Mulliken population analysis is an extensively used method for predicting the adsorption centers of inhibitor molecules. Many researchers have supported that negatively charged heteroatoms increase the ability to adsorb on the metal surface by the donor-acceptor mechanism [4, 38, 39]. In view of this information, O₁₁ and almost C's atoms are the active centers in linalool, whereas O₁ and O₁₄ are the most electronegative atoms in caffeine. These atoms have the strongest ability to bond to the metal surface. Quite the reverse, C₁ in Linalool, C₂, N₃, N₇, and C₁₃ in caffeine, and the hydrogen atoms in both molecules carry positive charges, often sites where nucleophiles can attach. Accordingly, both inhibitors can accept electrons from Fe through these atoms. Such interaction with the metal surface with several active centers forms a protective layer on the mild steel surface.

Moreover, the OH electron-donating group in linalool increases its charge density more than caffeine, resulting in the highest inhibition efficiency.

3.6. Mechanism of inhibition.

The anodic dissolution of mild steel in acidic media has attracted much attention as a result of excessive exposure of mild steel to different acids in the pickling and descaling processes. Prajila *et al.* [40] reported the anodic dissolution of mild steel in sulfuric acid solutions. It was found that the sulfate ion (SO₄²⁻) is first adsorbed on the mild steel surface; a nonstable surface complex is formed that is directly desorbed:



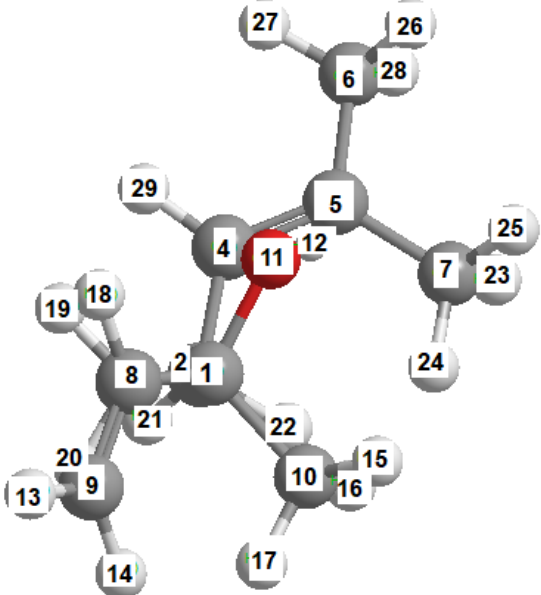
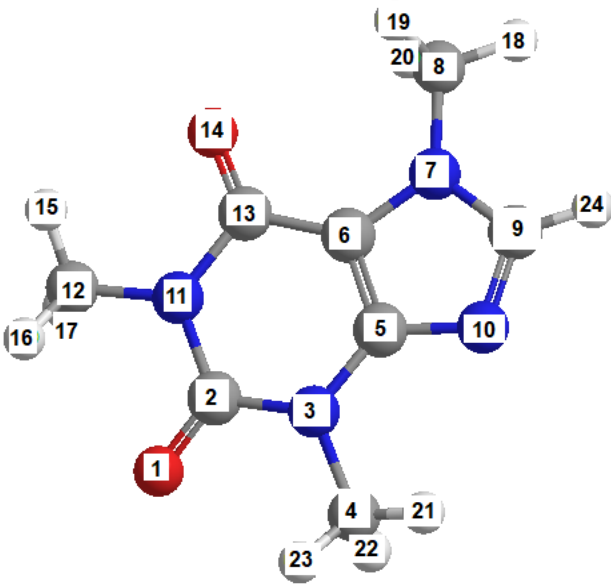
Caffeine inhibits the corrosion of mild steel by direct adsorption on the metal surface. However, without substitution, linalool adsorbs over the metal covered with a hydration sheath, which prevents its interaction with the metal surface. Yet, the high inhibition efficiency of linalool could be attributed to many factors, including the electric charge, orientation, shape, and size of the molecule [41]. The adsorption of moderate-size linalool (154.25 g/mol), an aliphatic inhibitor, is influenced by the electron density in the functional group, and since the OH group is electron-donating, thus the inhibitive efficiency increases as the electron density at the functional group increase [42]. Yet, caffeine (194.19g/mol), a large molecule, has an aromatic ring that may cause a steric hindrance on a mild steel surface, leading to difficulty in its adsorption process and reducing its inhibition efficiency [43, 44].

4. Conclusions

Linalool and caffeine are good corrosion inhibitors for mild steel in 0.5 M H₂SO₄ solutions. Their inhibitive action is attributed to their physical adsorption on the mild steel surface, forming an effective barrier that protects the surface from an aggressive acidic environment. Caffeine inhibits mild steel corrosion through direct adsorption on the steel

surface, whereas linalool adsorbs over the steel covered by a hydration sheath. Linalool inhibits mild steel corrosion more effectively than caffeine in 0.5 M H₂SO₄ solutions. The high inhibition efficiency of linalool could be attributed to various factors, including electric charge, orientation, shape, and size of the extracted molecules. Quantum chemical studies revealed that electrons transfer from linalool and caffeine to the mild steel surface. This transfer enhances inhibitor adsorption on the electrode surface. The results obtained from the experimental measurements and theoretical studies are in good agreement.

Table 5. Mulliken charge distribution of linalool and caffeine molecules.

Inhibitor	Atom Number	Type	Charge
 <p>Linalool</p>	1	C	0.13998
	2	C	-0.27553
	3	C	-0.20989
	4	C	-0.25033
	5	C	-0.13919
	6	C	-0.26556
	7	C	-0.27516
	8	C	-0.23550
	9	C	-0.33458
	10	C	-0.36206
	11	O	-0.32201
	12	H	0.22779
	13	H	0.17078
	14	H	0.16087
	15	H	0.13174
	16	H	0.10734
	17	H	0.11880
	18	H	0.20445
	19	H	0.14071
	20	H	0.13116
	21	H	0.13226
	22	H	0.12773
	23	H	0.11897
	24	H	0.10869
	25	H	0.11728
	26	H	0.11414
	27	H	0.11154
	28	H	0.11299
	29	H	0.19260
 <p>Caffeine</p>	1	O	-0.38737
	2	C	0.27324
	3	N	0.08519
	4	C	-0.28923
	5	C	-0.03334
	6	C	-0.44537
	7	N	0.34010
	8	C	-0.33836
	9	C	-0.27760
	10	N	-0.14244
	11	N	-0.07953
	12	C	-0.27057
	13	C	0.42245
	14	O	-0.38465
	15	H	0.14354
	16	H	0.1424
	17	H	0.11625
	18	H	0.13564
	19	H	0.15266
	20	H	0.15819
	21	H	0.15139
	22	H	0.11618
	23	H	0.14369
	24	H	0.26755

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Conflicts of Interest

The authors declare no conflict of interest.

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