The Inhibition Effect of Aerial Part of *Daucus carota* L Essential Oil on the Corrosion Performance of Mild Steel in HCl Medium

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Abstract: The aim of the present work is to investigate the inhibitory effect of the aerial part of *Daucus carota* L essential oil (EO) on mild steel in a 1.0M HCl solution. The electrochemical study is performed using potentiodynamic polarization (PDP) curves, and electrochemical impedance spectroscopy (EIS) measurements in the presence of various concentrations of the examined *Daucus carota* L essential oil (EO). PDP results show that the studied EO behaved as a mixed-type inhibitor. EIS measurements indicated that the EO could inhibit the corrosion of mild steel by the formation of a protective film on the surface of mild steel. The experimental results showed an efficiency of 96.5% for a concentration of 2 g/l. In addition, The DFT results proved that the major components, especially α-pinene (23.5%), β-Bisabolene (3.96%), and Pseudo limonene (7.20%) having a high electron-accepting ability and interact actively with the iron surface, which may be responsible for the inhibition ability of the investigated EO. Furthermore, the computational complies with the experimental data.

Keywords: *Daucus carota* L; inhibition; adsorption; mild steel; HCl; DFT.

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1. Introduction

Corrosion represents a more common phenomenon in most industries, and it accounts for a significant portion of maintenance revenues due to corrosion damage [1,2]. In numerous cases, corrosion damage has resulted in attendant environmental problems due to leakage of degraded metallic components, plant shut down, and structures collapse [3,4]. Literature reveals that mild steel has drawn significant attention among all the metals due to its high mechanical strength and exceptionally low cost [5,6]. Mild steel is one of the most important iron alloys used in various industries, especially in petroleum production units [7]. As a result, they deteriorate rapidly in the presence of corrosive species (SO$_4^{2-}$, Cl$^-$ etc.). Due to the use of several industrial processes, acidic solutions (specifically HCl, H$_2$SO$_4$, HNO$_3$, etc.) are widely employed in numerous techniques such as cleaning of boilers, pickling of metals or steels, acid descaling, processing of ores, acidizing of oil wells, recovery of ion exchangers [8,9]. The use of natural products, including essential oils, purified substances, and plant extracts, as barriers
against the spread of harmful synthetic chemicals has become an ecological necessity attracting great interest worldwide [10]. Several researchers have shown that natural products are the most appropriate in terms of their safe impact on the environment. They are rich in effective organic compounds that have strong corrosion-inhibiting properties against corrosion of metals [11,12]. The low cost, ecological character, biodegradability, availability of these eco-friendly” or "green" inhibitors have made them one of the most commonly used corrosion inhibitors. Most of these products contain different constituents with high electron density such as nitrogen, phosphorus, oxygen, and sulfur or polar groups, π bonds in their structures that facilitate their adsorption on the metal surface.

Many essential oils (EO) have been studied as environmentally friendly corrosion inhibitors [13,14].

The aim of this work is to study the effect of the essential oil (EO) of the aerial part of Daucus carota L on the corrosion of mild steel in 1.0 M HCl using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Density functional theory (DFT) based computations in the gaseous as well as in the aqueous phase were performed to investigate the dependence between the quantum chemical descriptors of three major components of the examined EO and their experimental inhibition efficiency.

2. Materials and Methods

2.1. Materials and sample preparation.

The mild steel involved in this work to realize all the corrosion experiments was composed as follows (in wt%): 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S, and the remainder Fe. The evaluated samples were pre-treated by polishing the surface with 120-2000 abrasive paper, rinsed with distilled water, degreased with acetone, and dried before each experiment. The corrosive media was obtained by diluting 37% analytical-grade HCl with distilled water. EO (Daucus carota L) inhibitor with a concentration in the range of 0.5 g/l to 2.0 g/l was utilized.

2.2. Electrochemical measurements.

The electrochemical setup is composed of three electrodes layout in a glass cell, with a Pt as a counter electrode and an Electrode (Ag/AgCl) as reference electrode "RE". The experiments were conducted in a 50 ml volume cell at 298 ± 2 K using a temperature control water bath. All electrochemical measurements were carried out with Volta Lab PGZ 100.

For potentiodynamic polarization experiments, open circuit potential (OCP) of the system after immersion for 30 minutes until a stable open circuit potential (Eocp) was obtained. Then, the polarization plot was plotted by sweeping the applied potential from -900 mV/Ag/AgCl to -100 mV/Ag/AgCl with respect to OCP with a constant sweep rate of 1 mVs⁻¹. The inhibition efficiency (ηPDP%) is calculated according to the following equation [15]:

\[
\eta_{\text{PDP}} \% = \left( \frac{i^0_{\text{corr}} - i_{\text{corr}}}{i^0_{\text{corr}}} \right) \times 100
\] 

(1)

where \(i^0_{\text{corr}}\) and \(i_{\text{corr}}\) are the corrosion current densities in the absence and presence of the inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) measurements were conducted out using a transfer function analyzer (VoltaLab PGZ 100), with a small amplitude a.c. signal (10
mVrms) in the frequency range of 100 kHz to 100 mHz. The EIS diagrams have been achieved in the Nyquist representation. Subsequently, the results were analyzed in an equivalent electrical circuit using the Bouckamp program [16]. The inhibiting efficiency derived from EIS ($\eta_{EIS}$) can be computed using the following equation:

$$\eta_{imp \ %} = \left( \frac{R_{ct} - R_{ct}^0}{R_{ct}} \right) \times 100$$

(2)

$$\theta = \left( \frac{R_{ct} - R_{ct}^0}{R_{ct}} \right)$$

(3)

where $R_{ct}^0$ and $R_{ct}$ are the charge transfer resistance in the absence and presence of the inhibitor, respectively. $\theta$ correspond to the recovery rate.

2.3. DFT methodology.

The electronic quantum chemistry utilizing the DFT method was undertaken to investigate the electronic structure of molecules. The FMOs and DFT descriptors were determined utilizing Gaussian 09 [17]. In this regard, the effect of solvents (water) was included in all DFT computations employing the using integral equation formalism variant of the Polarizable Continuum Model (IEFPCM) [18]. Gaussian View 5 is utilized to visualize the frontier molecular orbitals and MEP. $\alpha$-pinene, $\beta$-Bisabolene, and Pseudolimonene were geometrically optimized by DFT modeling. This modeling was conducted with the B3LYP function, 6-31G (d,p) basis set.

The molecular electrostatic potential (MEP) and Fukui indices are useful predictors of reactive sites for nucleophilic and electrophilic attacks [19].

A variety of DFT descriptors (e.g., HOMO and LUMO energies, gap energy ($\Delta E_g$), global softness ($\sigma$), global hardness ($\eta$), back donation energy ($\Delta E_{b-d}$), chemical electronegativity ($\chi$) and the fraction of electrons transferred ($\Delta N$)) were evaluated.

These quantum descriptors were calculated according to the following equations (4-7) [20]:

$$\Delta E_{gap} = E_{LUMO} - E_{HOMO}$$

(4)

$$\eta = \frac{\Delta E_{gap}}{2} = \frac{E_{LUMO} - E_{HOMO}}{2}$$

(5)

$$\sigma = \frac{1}{\eta} = \frac{2}{E_{LUMO} - E_{HOMO}}$$

(6)

$$\Delta E_{b-d} = -\frac{\eta}{4}$$

(7)

The fraction of the transferred electrons ($\Delta N_{110}$) is determined using the work function ($\varphi_{Fe}=4.82$ eV) as follows [21]:

$$\Delta N = \frac{\Phi - \chi_{inh}}{2(\eta_{Fe_{inh}} + \eta_{inh})}$$

The Fukui index reveals the available location in the inhibitors where either the nucleophilic or electrophilic attacks occur. The Fukui index for both the nucleophilic ($f_k^+$) and electrophilic ($f_k^-$) attack may be given by employing Mulliken Population Analysis (NPA) as shown in the following expressions:
\[ f_k^+ = P_k(N+1) - P_k(N) \]
\[ f_k^- = P_k(N) - P_k(N-1) \]
where, \( P_k \) is the population of \( k \) atom, while \( P_k(N+1), P_k(N-1) \) represent the anionic, neutral, and cationic species, respectively.

3. Results and Discussion

3.1. Electrochemical studies.

3.1.1. Polarization studies.

The polarization plots of mild steel in 1.0 M HCl at 298 K without and with adding the investigated Essential Oil (EO) were obtained after 30 min of immersion time. Figure 1 displays the overall behavior of the steel/acid / EO system, while Table 1 summarizes the values of the corrosion current densities (\( i_{corr} \)), the corrosion potential (\( E_{corr} \)), the anodic (\( \beta_a \)) and cathodic (\( \beta_c \)) Tafel slopes as well as the effectiveness of inhibition (\( \eta_{PP\%} \)) for various inhibitor concentrations in 1.0 M HCl.

![Figure 1. Polarization curves for mild steel obtained at 298 K in 1.0 M HCl solution containing different concentrations of EO.](image)

From Figure 1 we can observe that the presence of essential oil leads to a decrease in the cathodic and anodic current densities. This decrease is due to the increase in the concentration of essential oil. The cathodic polarization curves form quasi-parallel straight lines, and this indicates that the existence of essential oil in the HCl 1.0 M medium does not affect the mechanism of the proton reduction at the surface of mild steel is mainly done by a charge transfer mechanism (pure activation mechanism) according to the following reaction [22].

\[ 2H^+ + 2e^- \rightarrow H_2 \]

According to Table 1, it can be observed that the value of \( i_{corr} \) decreases significantly with increasing inhibitor concentration, reaching a minimum value of 34 \( \mu A.cm^{-2} \) at the optimal concentration of 2.0 g/l. On the other hand, the inhibition effectiveness increases with inhibitor concentration to reach a maximum value of 96.5%. As can be seen too in Figure 1 and Table 1, the addition of the studied EO in the corrosive medium cause a small shift in the corrosion
potential "Ecorr". This finding implies that the addition of the EO reduces the anodic dissolution of mild steel and cathodic reaction. Moreover, it can be concluded that the essential oil act as a mixed-type inhibitor. In fact, according to the literature, when the displacement in the E_corr values between the inhibited and uninhibited systems is less than 85 mV with that of the blank solution, the inhibitor can be classified as a mixed-type [23,24].

Table 1. Electrochemical parameters and inhibition efficiency of steel corrosion in 1.0 M HCl before and after adding various concentrations of the examined EO at 298 K.

| Medium | Conc. g/l | -E_corr mV/Ag/AgCl | E_corr mV | i_corr μA cm⁻² | βc mV dec⁻¹ | βa mV dec⁻¹ | ηPP % |
|--------|-----------|---------------------|-----------|---------------|-------------|-------------|-------|
| HCl 1.0 M | -- | 498 | 983 | 140 | 150 | - |
| EO | 0.5 | 489 | 85 | 129 | 132 | 91.3 |
| | 1.0 | 495 | 58 | 133 | 135 | 94.1 |
| | 1.5 | 507 | 52 | 134 | 140 | 94.7 |
| | 2.0 | 500 | 34 | 136 | 134 | 96.5 |

3.1.2. EIS studies.

The stationary techniques are an excellent technique that has been used in understanding the mechanism of corrosion and passivation phenomena of metals and alloys in their surrounding environments. The application of electrochemical impedance spectroscopy (EIS) is then indispensable [25]. The Nyquist and Bode plots of submerged mild steel in an acidic medium without and with the essential oil of various concentrations at 298 K after 30 min of open circuit immersion are presented in Figure 2.

![Figure 2. Nyquist and Bode's plots obtained for mild steel in 1.0 M HCl solution without and with different concentrations of EO at 298 K.](image-url)
The fitted Nyquist plots display a single capacitive loop in both the without and with of the essential oil. This finding indicates that the corrosion reaction in 1.0 M HCl is mainly controlled by the charge transfer process [26]. In addition, these spectra exhibit a similar shape for all utilized concentrations, demonstrating that there is almost no change in the corrosion mechanism [27].

The increased concentration of essential oil led to an increase in the diameter of the semi-circle, which can be attributed to the increase of the surface coverage with inhibitor concentration [20]. In the Bode diagrams, a single peak appears in both compounds and the blank sample, confirming the model of the equivalent circuit used to adjust the impedance spectra. The increase of log Z at low frequencies in the Bode diagram confirms better protection with increased essential oil (EO) concentration [28,29]. Based on the examination of the phase angle diagrams, the increase in the inhibitor concentration leads to more negative values of the phase angle, reflecting the adsorption of the studied essential oil species onto the mild steel surface [30].

Nyquist and Bode spectra could be assimilated, by analogy, to electrical impedance. The different process that occurs at the electrode/electrolyte interface can be modeled using an equivalent electrical circuit which is depicted in Figure 3 [31].

![Figure 3](https://doi.org/10.33263/BRIAC125.64876503)

**Figure 3.** Equivalent circuit compatible with experimental impedance data.

In which, Rs is the solution resistance, Rct stands for the charge transfer resistance, and CPE represents a constant phase element. The CPE is shown in the circuit instead of the double-layer capacitor to give a more accurate fit because the double layer in the interface does not act as a perfect capacitor.

The CPE impedance is defined by two values, Q and n, and it is described by the equation [32]:

\[ Z_{\text{CPE}} = Q^{-1}(j\omega)^n \]

where, Q is the CPE constant, \( \omega \) is the angular frequency (rad. s\(^{-1} \)), j is an imaginary number defined by \( j^2 = -1 \), and n is a CPE exponent, which can be used as a heterogeneity indicator or the surface roughness [33,34]. The double-layer capacity values were calculated using the following equation:

\[ C_{dl} = (Q \cdot R_{ct}^{n-1})^{1/n} \]

The values of essential oil's electrochemical parameters such as Rs, Rct, Cdl, Q, ndl, and \( \eta_{EIS}(\%) \) were determined and listed in Table 2. This indicates that Rct values increase with increasing inhibitor concentration, and the Cdl values decrease. The increase in Rct values is attributed to forming a protective inhibitor film on the mild steel surface. Also, a diminution in Cdl may be due to a reduction of the local dielectric constant and/or a rise in the electrical double layer's thickness which implies that EO acts by adsorption at the interface mild steel/1M HCl. The corrosion inhibition efficiencies of the mild steel increase with increasing EO concentration to reach a maximum value of 96.0% in the concentration of 2.0 g/l. However, the slight deviation of the value of ndl from the unity can be related to the deviation of CPE from the ideal capacitive behavior due to inhomogeneity on the mild steel surface resulting from porous layer formation [35,36].

https://biointerfaceresearch.com/
Table 2. EIS parameters for the uninhibited and inhibited solution in the presence of different concentrations of EO at 298 K.

| Conc. (g/l) | E (%) | Rs (Ω cm²) | Rct (Ω cm²) | Cdl (µF cm⁻²) | ndl | Q (µF.S⁻¹) | Θ | ηimp % |
|------------|-------|------------|-------------|---------------|------|------------|---|--------|
| HCl 1M     |       | 1.12       | 34.7        | 121.0         | 0.773| 419        |   | -      |
| EO 0.5     | 2.2   | 388.6      | 79.3        | 0.810         | 153  | 0.911      | 91.1|
| 1.0        | 2.4   | 551.5      | 65.8        | 0.789         | 132  | 0.937      | 93.7|
| 1.5        | 2.3   | 590.2      | 41.8        | 0.850         | 73   | 0.941      | 94.1|
| 2.0        | 2.8   | 871.8      | 28.3        | 0.784         | 69   | 0.960      | 96.0|

3.1.3. Adsorption isotherm and effect of temperature.

The inhibition mechanism in the aggressive medium can be examined by various adsorption isotherms. For this purpose, many different adsorption models are available to fit the adsorption data in order to describe the adsorption process, but Langmuir, Frumkin, Freundlich, El Awady as well as Flory-Huggins models are the most commonly used isotherm models [37]. The linearized form of this isotherm equation is as follows (equations 8-13):

- **Langmuir [38]**
  \[ K_{ads} C_{inh} = \frac{\theta}{1-\theta} \]  
  \[ (8) \]
- **Temkin [39]**
  \[ e^{-2f\theta} = K_{ads} C_{inh} \]  
  \[ (9) \]
- **Freundlich [40]**
  \[ \theta = K_{ads}^{n} C_{inh}^{n} \]  
  \[ (10) \]
- **Frumkin [41]**
  \[ \frac{\theta}{1-\theta} e^{-2f\theta} = K_{ads} C_{inh} \]  
  \[ (11) \]
- **Flory-Huggins [42]**
  \[ \frac{\theta}{C_{inh}} = K_{ads} (1-\theta)^{a} \]  
  \[ (12) \]
- **El-Awady [43]**
  \[ \left( \frac{\theta}{1-\theta} \right)^{1/y} = K_{ads} C_{inh} \]  
  \[ (13) \]

where \( K_{ads}, C_{inh} \) and \( \theta \) represent adsorption-desorption constant.

The choice of a suitable model depends on the value of the correlation coefficient \( R^2 \). Thus, the isotherm, having the highest value of \( R^2 \), can be chosen to explain the changes in the adsorption performance of the inhibitors.

The plot of \( \ln (C_{inh}/\theta) \) versus \( \ln C_{inh} \) gave a straight line, as shown in Figure 4. The linear regression coefficient \( s( R^2) \) is almost equal to 1, confirming that the adsorption of studied essential oil in 1.0 M HCl solution follows Langmuir's adsorption isotherm.

![Figure 4. Langmuir adsorption isotherm.](https://biointerfaceresearch.com/)
The values of the adsorption parameters and the estimated coefficients of the essential oil studied in 1.0M HCl are grouped in Table 3. Determining thermodynamic parameters, including free enthalpy of absorption $\Delta G_{ads}$ and equilibrium constant $K_{ads}$, will allow us to know the type and mechanism of adsorption. The $\Delta G_{ads}$ values (free energy of adsorption) were calculated using the following relationship [44]:

$$\Delta G_{ads} = -RT \ln \left( \frac{C_{solvent}}{K_{ads}} \right)$$

where, R is the universal gas constant, and the absolute temperature is denoted by T, and the $C_{solvent}$ is the concentration of water in solution equal 1000 g/L [33]. Generally, values of $\Delta G_{ads}$ around or below -20 kJ mol/l suggest that the process of adsorption is linked to the electrostatic interaction between the charged inhibitor molecules and the charged metal surface, called "physisorption" [45]. In contrast, values of $\Delta G_{ads}$ around or greater than -40 kJ mol/l are related to charge transfer of the inhibitor molecules toward the metal surface, forming a coordinated type of metal bonding called "chemisorption" [46]. The computed $\Delta G_{ads}$ values for essential oil in the present investigation were observed equal $-25$ kJ mol$^{-1}$, suggesting that the EO's adsorption on mild steel surface is physical-type adsorption.

### Table 3. Isotherms parameters of adsorption of essential oil by mild steel.

| Inhibitor | $K_{ads}$ (L/g) | $\Delta G_{ads}$ (KJ/mol) | $R^2$ | Slope |
|-----------|----------------|--------------------------|-------|-------|
| EO        | 24.5           | -25.0                    | 0.99988 | 1.02  |

3.1.4. Temperature effect and activation parameters.

The effect of temperature on the inhibitory efficacy of the essential oil was also investigated potentiometrically. The polarization curves obtained in 1.0 M HCl before and after adding 2.0 g/l of the inhibitor at 298K-328K are shown in Figure 5 as examples; the curves have the same appearance.

![Figure 5. Effect of temperature on the cathodic and anodic polarization plots of steel in 1.0M HCl medium without and with the addition of 2.0 g/l of essential oil.](image)

The values of $i_{corr}$, corrosion potentials ($E_{corr}$), anodic and cathodic tafel slopes ($\beta_a, \beta_c$) and inhibitory efficiencies are displayed in Table 4.

### Table 4. Influence of temperature on electrochemical parameters of mild steel in 1.0M HCl without and with the addition of 2.0 g/l of essential oil.

| Compounds | Temperature K | $-E_{corr}$ mV/Ag/AgCl | $i_{corr}$ $\mu$A cm$^{-2}$ | $-\beta_c$ mV dec$^{-1}$ | $\beta_a$ mV dec$^{-1}$ | $\eta_{PP}$ % |
|-----------|---------------|-------------------------|-----------------------------|--------------------------|--------------------------|----------------|
| Blank     | 298           | 498                     | 983                         | 140                      | 150                      | -              |
|           | 308           | 477                     | 1200                        | 184                      | 112                      | -              |
### Compounds

| Compounds | Temperature K | $-E_{corr}$ mV/Ag/AgCl | $i_{corr}$ µA cm$^{-2}$ | $-\beta_c$ mV dec$^{-1}$ | $\beta_a$ mV dec$^{-1}$ | $\eta_{pp}$ % |
|-----------|---------------|-------------------------|--------------------------|--------------------------|--------------------------|----------------|
| EO        | 318           | 487                     | 1450                     | 171                      | 124                      | -              |
|           | 328           | 493                     | 2200                     | 161                      | 118                      | -              |
|           | 298           | 500                     | 34                       | 136                      | 134                      | 96.5           |
|           | 308           | 514                     | 72                       | 147                      | 135                      | 94.0           |
|           | 318           | 502                     | 130                      | 154                      | 131                      | 91.0           |
|           | 328           | 521                     | 260                      | 159                      | 129                      | 88.2           |

Results in Table 4 reveal that current densities ($i_{corr}$) increase with increasing temperature from 298 K to 328 K. Also, the cathodic part is parallel, indicating that the reduction of H+ protons on the mild steel surface follows the same pure activation mechanism over the entire temperature range. Generally, the rise in temperature leads to an elevation of the values of $i_{corr}$. The variation in the $i_{corr}$ values for the blank solution exhibits a regular and fast increase, indicating an increasing metallic dissolution with temperature elevation. The rise of $i_{corr}$ values with temperature in the essential oil is much smaller than the blank solution.

Thanks to the temperature effect, several activation and adsorption parameters can be drawn.

The activation energy ($E_a$), the entropy of activation ($\Delta S_a$), and enthalpy of activation ($\Delta H_a$) for corrosion reaction of mild steel in 1M HCl without and with the addition of the essential oil tested at concentration 2.0 g/l were calculated from Arrhenius and transition state plot.

Different activation and thermodynamic parameters can be calculated as follows [47,48]:

$$i_{corr} = Ae^{\left(\frac{E_a}{RT}\right)}$$

$$\ln \left(\frac{i_{corr}}{T}\right) = \ln \left(\frac{R}{hN_a}\right) + \left(\frac{\Delta S_a}{R}\right) - \frac{\Delta H_a}{RT}$$

where, $E_a$, $h$, $N$, $A$, $T$, and $R$ and are activation energy, Plank constant, Avogadro number, pre-exponential factor, absolute temperature, and gas constant, respectively.

![Figure 6](https://biointerfaceresearch.com/6495)

**Figure 6.** Arrhenius plots for mild steel corrosion in 1M HCl in the absence and in presence of 2.0 g/l of essential oil.

From the Arrhenius Plots, $\ln(i_{corr})$ vs. $1000/T$ at an optimum concentration of the three quinoxaline compounds tested display in Figure 6. Figure 6 shows a straight-line curve having
a slope equal to \(-\frac{E_a}{RT}\), from which \(E_a\) was calculated. Another plot of \(\ln \left(\frac{i_{corr}}{T}\right)\) vs. \(1000/T\) shows a straight-line curve presented in Figure 6 with a slope and intercept equal to \(-\frac{\Delta H_a}{R}\) and \(\ln \left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{R}\), respectively. The values of the thermodynamic parameters relating to this inhibitor are given in Table 5.

From the results in Table 5, we find that \(E_a\) values in the presence of the essential oil are higher than in the solution without inhibitor. This increase in \(E_a\) indicates that the energy barrier of corrosion reaction increases in the presence of inhibitor without changing the mechanism of dissolution [49,50]. However, the adsorption phenomenon of an organic molecule is not considered only as a chemical or physical adsorption product, but a wide range of conditions, ranging from the dominance of chemisorption or the electrostatic effects may occur due to the nature of the complex of the inhibition of corrosion process [51].

The positive signs of the enthalpies \(\Delta H_a\) reflected the endothermic nature of the steel dissolution process [15,52]. The values of activation entropies \(\Delta S_a\) increase and are negative in the presence of the essential oil, meaning a decrease in the disorder during the transformation of the reagents into activated complex [53,55].

Table 5. Values of the activation parameters \(E_a\), \(\Delta H_a\), and \(\Delta S_a\) for mild steel in 1.0 M HCl without and with the addition of 2.0 g/l of essential oil.

| Medium   | Conc | \(E_a\) (KJ/mol) | \(\Delta H_a\) (KJ/mol) | \(\Delta S_a\) (J/mol K) |
|----------|------|------------------|-------------------------|--------------------------|
| 1M HCl   | Blank| 21.0             | 18.5                    | -126.0                   |
|          | EO   | 54.4             | 51.8                    | -25.0                    |

3.2. Theoretical investigations.

3.2.1. DFT optimization.

Theoretical investigations provide valuable insight into the chemical activity of inhibitory molecules by using electronic descriptors that describe the characteristics of these species and, subsequently, the corrosion inhibition mechanisms [56,57]. To explore the structural effect on the inhibition efficiency obtained experimentally, only three major constituents present in studied EO were considered, namely alpha-pinene (23.5%), bisabolene (3.96%), and pseudo limonene (7.20%). The highest \(E_{HOMO}\) value shows an enhancement in electron donor, and this signifies a stronger corrosion inhibition performance with increasing adsorption of the inhibitory molecule onto the mild surface. Besides, the smallest \(E_{LUMO}\) value denotes the capacity to accept electrons from the metal surface [58]. In addition, the lower value of the gap energy \(\Delta E_{gap}\) is represented by the maximum interaction of the metal/inhibitor and hence high protection effectiveness. The chemical structure and optimized structure of \(\alpha\)-pinene, \(\beta\)-Bisabolene, and Pseudo-limonene in the aqueous phase are given in Figure 7.
The FMOs (HOMOs/ LUMOs) orbitals of the various molecules are presented in Figure 8. According to the resulting plots, it is observed that in the chosen molecules, the HOMO orbital for the α-pinene and Pseudolimonene located over the entire molecules and mainly on the aromatic doublets and the methyl groups. This finding suggests the high electrophilic and nucleophilic nature of α-pinene and Pseudolimonene.

Further, these FMOs are delocalized on methyl-cyclohexene moiety and −C=C− bonds for β-Bisabolene, which are the responsible sites for donating and/or accepting electrons from the metal surface. In addition, it can be noticed from Figure 8 that the red regions in the molecular electrostatic potential (MEP) refer to the negative electrostatic potential and have been intensified around −C=C− bonds.

**Figure 7.** Chemical structure and optimized structure of α-pinene, β-Bisabolene and Pseudo-limonene at B3LYP/6-31G(d, p) level of theory in the aqueous phase.

|          | α-pinene | β-Bisabolene | Pseudolimonene |
|----------|----------|--------------|----------------|
| **HOMO** | ![HOMO](image1) | ![HOMO](image2) | ![HOMO](image3) |
| **LUMO** | ![LUMO](image4) | ![LUMO](image5) | ![LUMO](image6) |
| **MEP**  | ![MEP](image7) | ![MEP](image8) | ![MEP](image9) |

**Figure 8.** FMOs (i.e., HOMO and LUMO) and electrostatic potential (MEP) structures for α-pinene, β-Bisabolene and Pseudolimonene at DFT/6-311G(d,p) in the aqueous phase.
Different quantum chemical descriptors including gap energy (ΔE\textsubscript{gap}), global softness (σ), global hardness (η), back donation energy (ΔE\textsubscript{back-d}), chemical electronegativity (χ), and the fraction of electrons transferred (ΔN) in the aqueous phase were also determined and listed in Table 6. Based on Table 6, the HOMO of the three basic components of Daucus carota L. essential oil in both phases are as follows: α-pinene > β-Bisabolene > Pseudolimonene, which reflects that α-pinene have good electron-donating properties towards the metal surface.

As seen also in Table 6, the theoretical order of gap energy (ΔE\textsubscript{g}) and hardness (η) in the gaseous and aqueous phases is α-pinene < β-Bisabolene < Pseudolimonene, suggesting that α-pinene and β-Bisabolene have good electron-donating properties on the surface [59,60].

Table 6. Electronic properties of α-pinene, β-Bisabolene, and Pseudolimonene in gas and aqueous phases.

| Descriptor     | E\textsubscript{HOMO} (eV) | E\textsubscript{LUMO} (eV) | ΔE\textsubscript{g} (eV) | η (eV) | σ (eV\textsuperscript{-1}) | χ (eV) | ΔN (eV) | ΔE\textsubscript{back-d} (eV) |
|----------------|-----------------------------|-----------------------------|---------------------------|--------|-----------------------------|--------|---------|---------------------------|
| **Gaseous phase** |                             |                             |                           |        |                             |        |         |                           |
| α-pinene       | -5.941                      | 0.803                       | 6.745                     | 3.372  | 0.296                       | 2.568  | 0.333   | -0.843                    |
| β-Bisabolene   | -6.150                      | 0.830                       | 6.980                     | 3.490  | 0.286                       | 2.660  | 0.309   | -0.872                    |
| Pseudolimonene | -6.492                      | 0.653                       | 7.146                     | 3.573  | 0.279                       | 2.919  | 0.265   | -0.893                    |
| **Aqueous phase** |                             |                             |                           |        |                             |        |         |                           |
| α-pinene       | -5.975                      | 0.768                       | 6.743                     | 3.371  | 0.296                       | 2.603  | 0.328   | -0.842                    |
| β-Bisabolene   | -6.210                      | 0.727                       | 6.938                     | 3.469  | 0.288                       | 2.741  | 0.299   | -0.867                    |
| Pseudolimonene | -6.561                      | 0.591                       | 7.152                     | 3.576  | 0.279                       | 2.984  | 0.256   | -0.894                    |

In addition, the interaction energy will increase with the rinsing softness of the organic species. Moreover, the electron transferred (ΔN) and back-donation (ΔE\textsubscript{back-d}) was also calculated (Table 6). It can be noted that the inhibition efficiency increases by increasing the electron-donating ability of these inhibitors to donate electrons to the metal surface. Thus, the highest fraction of electrons transferred contributes to the most efficient adsorption of the different components onto the steel surface, leading to the highest protection and inhibition. The calculated ΔE\textsubscript{back-d} values for the three molecules (ΔE\textsubscript{back-d} < 0) reveal that back donation is more favored for all studied molecules (Table 6). The fraction of electrons (ΔN) quantifies the transfer of electrons from molecule to the metal if ΔN > 0 and from metal to molecule if ΔN < 0 [48,61]. The positive values obtained for the three molecules confirm the great impact of these molecules on steel corrosion. According to the literature, some researchers indicated that high dipole moment values can improve corrosion inhibition efficiency.

3.2.2. Locally reactive site analysis.

The local reactive sites contained in the inhibitors were identified via the condensed Fukui index (FI) analysis. By extension, the activity of the examined Daucus carota L. essential oil was also explored by determining the nucleophilic and electrophilic characteristics of the three major constituents. Therefore, the objective of this part is to predict the best adsorption sites of each molecule. In this concept, the computed Fukui indices were determined and plotted in Figure 9 in the aqueous phase at B3LYP/6-31G (d,p).

From the results in Figure 9 it can be observed that the C1, C3, and C10 atoms in α-pinene present the highest positive values of both Fukui indices (f\textsuperscript{+}, f\textsuperscript{-}), indicating that these centers contribute highly to the success of the adsorption process to mild steel.
In addition, all other atoms that constitute the double bonds in β-Bisabolene (C4, C6, C8, and C10) Pseudolimonene (C2, C5, C7, C9, C12, and C13) are one of the active sites for adsorption. These results reveal that these atomic sites are responsible for nucleophilic and electrophilic attack characters [62,63]. In terms of comparison with the observed distribution of HOMO and LUMO electron densities and the computed electronic descriptors, it can be seen that there is a good agreement.

4. Conclusions

In the present study, the essential oil of the aerial part of Daucus carota L. was evaluated as an inhibitor for mild steel in 1 M HCl. It is shown in this paper from the experimental results that the EO act as an effective inhibitor for mild steel in acidic solution, and their effectiveness increases with their concentration. The polarization plots indicate that the investigated EO inhibits the evolution reaction of the cathodic and anodic. The EIS measurements showed that charge transfer resistance (Rct) increases and double-layer capacitance (Cdl) decreases in the presence of inhibitor. Moreover, the studied EO inhibits the corrosion process by adsorbing on the mild steel surface, and their adsorption mode followed Langmuir adsorption isotherm. The theoretical study predicts that α-pinene and β-Bisabolene provide better inhibition efficiency than Pseudolimonene.
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**Conflicts of Interest**

The authors declare no conflict of interest.

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