

Inhibition of C38 Steel Corrosion by *Anethum graveolens* Essential Oil in Acidic Medium: Gravimetric and Theoretical Studies

Malick Bathily^{1,2,*}, Khaly Cissé¹, Baba Ngom³, Mohamed Znini², Diadioly Gassama¹

¹Department of Physics and Chemistry, UFR Sciences and Technologies, Iba Der Thiam University of Thiès, Thiès, Senegal

²Laboratory of Natural Substances & Synthesis and Molecular Modeling, Faculty of Sciences and Techniques, Moulay Ismail University of Meknes, BP 509 Boutalamine, Errachidia 52003, Morocco

³Laboratory of Water and Environmental Sciences and Technologies (LaSTEE), Polytechnic School of Thiès, Thiès, Senegal

*Corresponding author: malickbathily@gmail.com

Received June 23, 2025; Revised July 25, 2025; Accepted August 01, 2025

Abstract This work aims to highlight the value of an aromatic and medicinal plant from the Errachidia region, *Anethum graveolens*. This study evaluates the inhibitory effect of essential oil extracted from the seeds of this plant on the corrosion of C38 steel in 1M HCl medium. The essential oil was extracted from seeds using a Clevenger apparatus, achieving an average yield of 3.5% via hydrodistillation. Characterization by chromatography (GC/FID and GC/MS) identified 12 constituents representing 98% of the oil's global composition, with carvone (43.5%), dillapiol (26.7%), and limonene (15.4%) being the main components. Gravimetric tests revealed a remarkable inhibitory effect on steel corrosion, with increased concentration and temperature achieving an inhibition efficiency of 82.54% at 0.5 g/L and 338 K. Thermodynamic parameters determined show that the inhibitor's adsorption on the metallic surface follows the Langmuir model. The results indicate a mixed adsorption behavior of this essential oil. DFT calculations correlate the inhibitory activity with the electronic properties of the main constituents of the essential oil.

Keywords: Essential oil, *Anethum graveolens*, 1M HCl, Inhibitor, Corrosion, Gravimetric measurements, Langmuir

Cite This Article: Malick Bathily, Khaly Cissé, Baba Ngom, Mohamed Znini, and Diadioly Gassama, "Inhibition of C38 Steel Corrosion by *Anethum graveolens* Essential Oil in Acidic Medium: Gravimetric and Theoretical Studies." *Chemical Engineering and Science*, vol. 10, no. 1 (2025): 8-17. doi: 10.12691/ces-10-1-2.

1. Introduction

Corrosion, a natural phenomenon that degrades metallic materials, is a major challenge for industry [1]. Steel, a material widely used in numerous sectors, is particularly sensitive to acidic corrosion, especially in hydrochloric acid environments. To mitigate the economic and environmental impacts of this phenomenon, corrosion inhibitors are commonly employed. While synthetic inhibitors are known for their effectiveness [2,3,4,5,6,7], their environmental and health impacts drive the search for more sustainable alternatives. Natural products, such as plant extracts, show great potential as corrosion inhibitors due to their low toxicity and biodegradability.

Numerous studies have highlighted the potential of natural substances as alternatives to synthetic corrosion inhibitors. Previous research conducted within our research team has already demonstrated the efficacy of these natural substances. For instance, studies by Cissé *et al.* [8,9] revealed that Arabic gum effectively protects S235 steel in corrosive environments. Their results demonstrated 83% efficiency at an optimal concentration

of 0.3% in a 1M HCl medium and 88% inhibition in a 1M perchloric acid (HClO₄) solution. Similarly, Gassama *et al.* [10,11] explored the inhibitory properties of clay materials for E400 reinforcing steel. Their studies showed optimal inhibitory efficiencies of up to 70% for volcanic clay tuffs and 62% for montmorillonite.

In this same vein, a growing interest in the use of vegetable and essential oils as corrosion inhibitors has been observed in the literature. Numerous studies have investigated various essential oils, such as those from *Eucalyptus camaldulensis*, *Cyperus rotundus*, chamomile, *Mentha spicata* L., clove, fennel (*Foeniculum vulgare*), *Aaronsohnia pubescens*, *Santolina pectinata*, tea-tree, and *Carum carvi* L. [12,13,14,15,16,17,18,19]. An exhaustive review of the literature conducted by our team confirmed the increasing interest in these natural substances as eco-friendly alternatives to conventional corrosion inhibitors [20].

Our previous works align with this trend. Notably, we evaluated the inhibitory action of *Eucalyptus globulus* essential oil and clove essential oil using electrochemical methods on C24 steel in a 1M HCl medium. We also studied the inhibitory efficacy of *Eucalyptus globulus* essential oil on carbon steel XC38 in a 1M HCl medium

using gravimetric methods, obtaining highly encouraging results [21,22,23]. These studies revealed inhibition efficiencies exceeding 80% for both essential oils, thereby confirming their potential to replace more polluting synthetic inhibitors.

The present study aims to evaluate the efficacy of essential oil extracted from *A. graveolens* seeds as a corrosion inhibitor for C38 steel in a hydrochloric acid medium. By combining experimental gravimetric measurements and theoretical quantum chemistry calculations, we seek to establish a correlation between the molecular structure of the main components of the essential oil and their corrosion inhibition capacity. This interdisciplinary approach will provide a better understanding of the action mechanism of this natural inhibitor and identify the most active compounds.

2. Materials and Methods

2.1. Essential Oil Extraction Method

The plant material used for extracting our inhibitor comes from *A. graveolens* seeds, harvested in the wild in the Errachidia region, southeastern Morocco. The botanical identification was confirmed by the Biology Department of the Faculty of Sciences and Techniques of Errachidia, where a reference sample is preserved. After harvest, the seeds were cleaned, sorted, and dried for ten days away from light to preserve their aromatic compounds. Once dried, the seeds were ground using a mill and prepared for the extraction step.

The essential oil was extracted via hydrodistillation using a Clevenger-type apparatus, following the method described in the European Pharmacopoeia [24]. The dried and ground plant material was subjected to steam distillation, allowing the volatilization of aromatic compounds. These volatile compounds were then condensed and collected. A distillation duration of three hours was chosen to optimize the essential oil yield.

2.2. Characterization of the Essential Oil

To determine the precise composition of the essential oil extracted from *A. graveolens* seeds, detailed chromatographic analysis was conducted. Two complementary techniques were employed: gas chromatography (GC) and gas chromatography coupled with mass spectrometry (GC/MS).

The GC analysis, performed on a PerkinElmer Autosystem GC XL chromatograph equipped with polar (Rtx-Wax) and nonpolar (Rtx-1) columns, allowed the separation and identification of various compounds based on their polarity. The operating conditions, optimized for effective separation, were strictly controlled. The parameters were as follows:

- Injector and detector temperatures: 280 °C
- Oven program: Temperature ramp from 60 °C to 230°C at 2°C/min, followed by an isothermal phase at 230°C for 35 minutes.
- Carrier gas: Helium at a flow rate of 1 mL/min.
- Injection mode: Split (1:50), with an injection volume of 0.2 µL.

Polar (Ir p) and nonpolar (Ir a) retention indices of the compounds were calculated by referencing a series of n-alkanes using the Total Chrom Navigator software. These indices were then compared with literature data for compound identification.

To confirm identifications and obtain additional structural information, samples were analyzed via GC/MS using the same capillary columns. Operating conditions were similar to GC, with the addition of a PerkinElmer TurboMass mass detector. Mass spectra obtained by electron impact covered a mass range of 35 to 350 Da. These spectra were compared with reference databases, enabling precise identification of the compounds present in the essential oil.

The identification of compounds was achieved by comparing retention indices obtained on both capillary columns with those referenced or reported in the literature [25]. Moreover, the mass spectra were cross-referenced with commercial and personal libraries available [26] and a reference manual [27].

The relative percentages of the compounds were determined by calculating the areas of the chromatographic peaks obtained on the Rtx-1 and Rtx-Wax columns, without applying correction factors. These values were then compared with data from reference products, whether available in the laboratory or reported in the literature.

2.3. Corrosion Test

To study the inhibitory effect of *A. graveolens* essential oil, corrosion tests were conducted on C38 carbon steel samples. The chemical composition of this steel, excluding iron, is as follows:

Table 1.

Elément	P	Si	Al	Mn	C	S
Teneur en %	0.09	0.38	0.01	0.05	0.21	0.05

These samples were immersed in an aqueous 1M hydrochloric acid (HCl) solution, prepared by diluting a commercial concentrated solution. The commercial HCl has a density of 1.19, a molar mass of 36.46 g/mol, and a mass percentage of 37%, diluted with distilled water.

Before each test, the steel sample surfaces were carefully prepared by mechanical abrasion using sandpapers of decreasing grit size (400, 600, 1200) to obtain a clean and reproducible metal surface. The samples were then rinsed with double-distilled water, air-dried, and weighed precisely before immersion in 50 mL of corrosive solution. The tests were conducted both in the absence and presence of various essential oil concentrations (125 to 500 mg/L) at a temperature of 298 K. The immersion duration was set to 6 hours.

After each corrosion test, the steel plates were thoroughly washed with double-distilled water, degreased with ethanol, air-dried, and weighed again using a high-precision balance.

To evaluate the temperature effect on the inhibitory properties of *A. graveolens* essential oil, a gravimetric study was performed in a temperature range from 298 K to 338 K. The experimental conditions were similar to those

of the concentration tests: the plates followed the same preparation process before immersion in 50 mL of corrosive solution. The immersion duration for each temperature was maintained at 6 hours, and measurements were performed in the absence and presence of the essential oil.

2.4. Quantum Chemical Calculations Using the Density Functional Theory (DFT) Method

To deepen the understanding of the adsorption mechanism of the inhibitor on the steel surface at the molecular level, quantum chemical calculations were performed. These calculations analyze electronic parameters that provide crucial information about the inhibitor's propensity to interact with the metal. This capability largely depends on the electronic distribution of the inhibitor.

The Density Functional Theory (DFT) method was employed to establish a link between the molecular structure of the main constituents of the essential oil (EO) and their inhibitory efficacy. Calculations were carried out using **Gaussian 03** software.

The geometry of the molecules studied was optimized using the DFT method with the **B3LYP** functional (*Becke 3-parameter Lee-Yang-Parr*) and a 6-31G (d, p) basis set. This approach provides an accurate description of the electronic and structural properties, facilitating the interpretation of interactions between the EO compounds and the metallic surface.

3. Results and Discussions

3.1. Extraction Yields

The seeds of *A. graveolens* produced a colorless essential oil with a strong odor, yielding approximately 3.5% (v/m) relative to the dry plant material mass. This yield is significant and potentially profitable on an industrial scale. Compared to the literature, our yield aligns with results obtained for seeds collected in China (3.8%) [28] and Uzbekistan (4.2%) [29].

3.2. Chemical Composition of the Essential Oil of *Anethum graveolens*

The compounds in the essential oil (EO) from *A. graveolens* seeds were characterized using gas chromatography coupled with mass spectrometry (GC/MS) and flame ionization detection (GC/FID). Twelve compounds, representing 98% of the oil, were identified by comparing their mass spectra and retention indices with those of authentic standards (Table 2).

Compound numbering refers to the order of elution on the apolar column (Rtx-1).

Explanations of Retention Indices Used:

- **Ir**: Literature retention index on a nonpolar column (Rtx-1).
- **Ir_a**: Experimental retention index on a nonpolar column (Rtx-1).

- **Ir**: Experimental retention index on a polar column (Rtx-Wax).

The relative percentages of constituents (%) were calculated from the peak areas of the chromatograms measured on the nonpolar column (Rtx-1).

The analysis reveals that the EO from *A. graveolens* seeds is primarily composed of monoterpenes (71.3%), with a majority being oxygenated compounds (53.9%) and a smaller proportion being hydrocarbons (17.4%). The phenylpropanoid dillapiol is also present in significant quantities. The absence of sesquiterpenes is notable.

The major constituents identified in this EO are:

- Carvone: 43.5%
- Dillapiol: 26.7%
- Limonene: 15.4%

These results are illustrated in Figure 1.

Table 2. Chemical Composition of the EO from *A. graveolens* Seeds Collected in Errachidia

N° ^a	Composés	Ir ^b	Ir a ^c	Ir p ^d	% ^e
1	α -Pinene	936	930	1022	0,4
2	Sabinene	973	964	1119	0,2
3	α -Phellandrene	1002	997	1161	1,2
4	p-Cymene	1015	1011	1263	0,2
5	Limonene	1025	1022	1198	15,4
6	Camphre	1123	1120	1502	0,9
7	Dilletter	1170	1170	1510	0,6
8	E-Dihydrocarvone	1177	1177	1609	1,8
9	Carvone	1214	1219	1717	43,5
10	Piperitone	1228	1228	1706	6,5
11	Piperitenone oxyde	1335	1330	1930	0,6
12	Dillapiol (dimethoxysafrole)		1595	2332	26,7
TOTAL					98,00
Hydrocarbon monoterpenes					17,40
Oxygenated monoterpenes					53,90
Hydrocarbon sesquiterpenes					00,00
Oxygenated sesquiterpenes					00,00
Phenylpropanoide (Dillapiol)					26,70

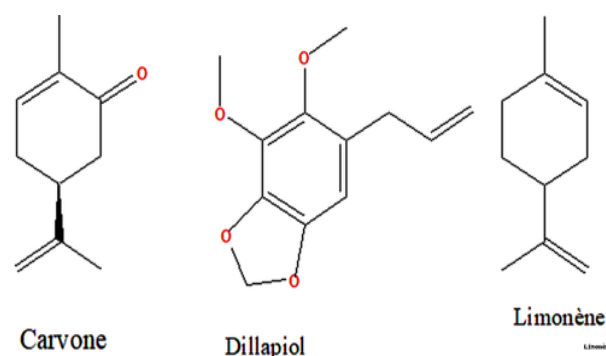


Figure 1. Chemical structures of the main constituents of the EO studied

The chemical profile of our essential oil presents similarities with those described in the literature. However, qualitative and quantitative differences were observed. Referring to studies by *Soltanie et al.* [30], our sample stands out with a higher carvone content and a lower dillapiol content compared to their findings. These variations may be explained by factors such as ecological conditions, the plant's developmental stage, genotype, and climatic and geographical conditions.

3.3. Gravimetric Measurements

3.3.1. Effect of Concentration

To evaluate the inhibitory effect of the essential oil, mass loss experiments were conducted by immersing C38 steel samples in 1M HCl solutions containing different essential oil concentrations (125 to 500 mg/L) at 298 K for 6 hours. Corrosion rates (W_{corr}), inhibition efficiencies (E_w %), and surface coverage rates (θ) were calculated based on the measured mass losses using the equations below:

$$W = \frac{\Delta m}{S \cdot t} \quad (1)$$

$$E_w = \frac{W_{\text{corr}(0)} - W_{\text{corr}(\text{inh})}}{W_{\text{corr}(0)}} \times 100 \quad (2)$$

$$\theta = \frac{E_w}{100} \quad (3)$$

Where:

Δm : Mass difference of the steel in mg before and after immersion in the corrosive solution.

S: Steel surface area in cm^2 .

t: Immersion time in hours.

$W_{\text{corr}(0)}$ and $W_{\text{corr}(\text{inh})}$ Corrosion rates in the absence and presence of the inhibitor, respectively, expressed in mg/h.cm^2 .

The results of these experiments are summarized in Table 3:

Table 3. Gravimetric Corrosion Results for C38 Steel in 1M HCl in the Absence and Presence of Various EO Concentrations at 298 K

Concentration (g/L)	W (mg/h.cm ²)	E _w (%)	$\theta(E_w/100)$
HCl 1M	0,169	-	-
0,125	0,111	34,40	0,3440
0,25	0,081	51,80	0,5180
0,375	0,071	58,01	0,5801
0,5	0,063	62,95	0,6295

The variation of corrosion rate (W_{corr}) of the steel in 1M HCl and the corresponding inhibition efficiency (E_w %) as a function of the different EO concentrations is shown in Figure 2.

The data presented in Table 3 and Figure 2 show a notable variation in the corrosion rate and the inhibition efficiency of the essential oil (EO) depending on its concentration. It is evident that the corrosion rate of steel significantly decreases as the EO concentration increases. This phenomenon can be attributed to the physical and/or chemical adsorption mechanism of the EO molecules on the metallic surface. By attaching to the active sites of the steel, these molecules form a protective barrier that prevents corrosive ions from reaching the metal.

The inhibition efficiency of the EO increases proportionally with its concentration, reaching 62.95% at the maximum concentration studied. This progressive increase in efficiency supports the hypothesis that denser adsorption of EO molecules on the metallic surface occurs as the concentration increases. This adsorption leads to the formation of an increasingly thick and compact protective

film, thereby enhancing the inhibitory effect [31]. The numerical data show that adding 125 mg/L of *A. graveolens* seed essential oil to the corrosive medium reduces the corrosion rate by 34.4%, reaching a maximum of 62.95% at 500 mg/L.

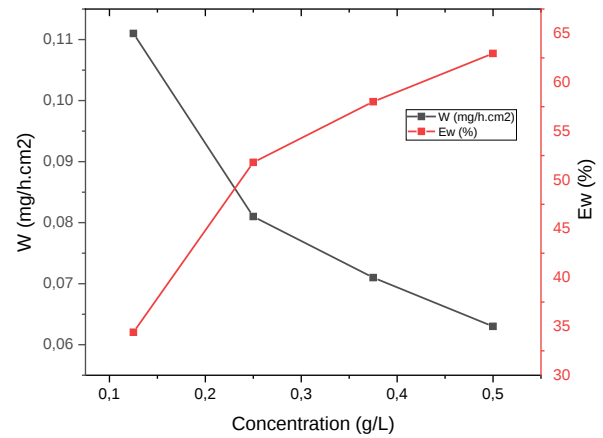


Figure 2. Variation of Corrosion Rate (W_{corr}) and Inhibition Efficiency (E_w %) of Carbon Steel C38 Corrosion in 1M HCl in the Absence and Presence of Different EO Concentrations at 298 K for 6 Hours of Immersion

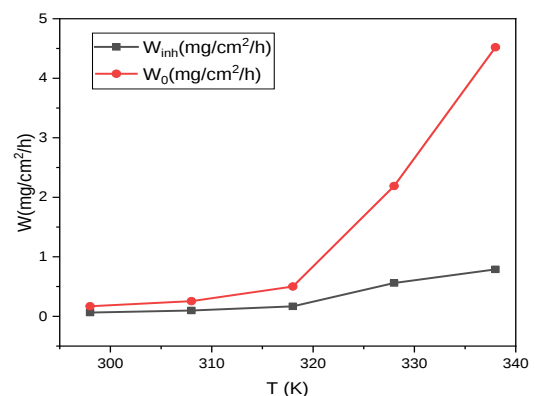
3.3.2. Effect of Temperature

Temperature has a considerable influence on the efficiency of corrosion inhibitors, as evidenced by numerous studies [22]. In this study, the impact of temperature on the inhibitory power of *A. graveolens* seed essential oil was evaluated using the gravimetric method. C38 steel samples were immersed for 6 hours in a 1M hydrochloric acid solution at different temperatures ranging from 298 K to 338 K, both in the absence and presence of a 0.5 g/L EO concentration. A controlled water bath (Memmert model WNE 22) was used to regulate the temperature. The corrosion rates and corresponding inhibition efficiencies are presented in Table 4.

Table 4. Effect of Temperature on the Corrosion of C38 Steel in 1M HCl in the Presence and Absence of 0.5 g/L EO for 6 Hours of Immersion

T (K)	$W_{\text{inh}}(\text{mg/cm}^2 \cdot \text{h})$	$W_0(\text{mg/cm}^2 \cdot \text{h})$	E _w %
298	0,063	0,169	62,95
308	0,098	0,255	61,60
318	0,168	0,500	66,40
328	0,560	2,190	74,43
338	0,789	4,520	82,54

These data are graphically represented in Figure 3.



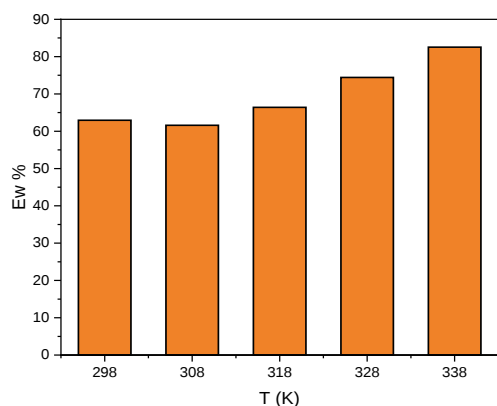


Figure 3. Variation of the Corrosion Rate (W_{corr}) of C38 Steel (a) in 1M HCl in the Absence and Presence of 0.5 g/L EO and the Corresponding Inhibition Efficiency (b) for 6 Hours of Immersion

The experimental results highlight a positive correlation between temperature and corrosion rate, both in the absence and presence of the essential oil (EO). This behavior is consistent with electrochemical principles, where increasing temperature generally enhances corrosion reactions.

In the pure corrosive solution (1M HCl), higher temperatures induce a rapid and regular increase in the corrosion rate, indicating accelerated metal dissolution. This phenomenon is explained by the increased thermal agitation of particles, which facilitates electrochemical reactions at the metal/solution interface.

In the presence of EO, the increase in temperature also leads to a rise in the corrosion rate but to a much lesser extent than in the absence of the inhibitor. This result confirms the inhibitory nature of the EO over the entire temperature range studied. Furthermore, the inhibition efficiency ($E_w\%$) exhibits a particular behavior: it increases with temperature, reaching a maximum value of 82.54% at 338 K.

Several mechanisms can explain the evolution of inhibition efficiency with temperature:

- **Adsorption:** Higher temperatures generally promote the adsorption of EO molecules on the metallic surface. Studies by *Ammar and El Khorafi* [32] suggest that this adsorption is linked to specific interactions between the inhibitor and the substrate.
- **Electron Density:** *Singh et al.* [33] propose that increasing temperature enhances the electron density around adsorption sites, strengthening the bonds between the inhibitor and the metal.
- **Surface Coverage:** *Putilova et al.* [34] argue that higher temperatures favor increased surface coverage by the inhibitor, leading to more effective protection.
- **Nature of Adsorption:** *Ivanov* [35] indicates that the mode of adsorption of the inhibitor evolves with temperature: physisorption dominates at lower temperatures, while chemisorption is favored at higher temperatures.

3.3.3. Thermodynamic Parameters

To better understand the adsorption mechanism of the inhibitor on the metal surface, the thermodynamic parameters of the corrosion process were determined.

Specifically, the apparent activation energy (E_a) was evaluated at different temperatures, both in the presence and absence of the optimal inhibitor concentration.

The Arrhenius equation, which describes the influence of temperature on the rate of a chemical reaction, was used [36]:

$$W_{\text{corr}} = k \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

where W_{corr} is the corrosion rate of the steel in (mm/yr), E_a is the activation energy (kJ.mol⁻¹), R is the perfect gas constant (8,32 J.K⁻¹.mol⁻¹), k is a pre-exponential factor, T is the absolute temperature in K.

By plotting the natural logarithm of the corrosion rate as a function of the inverse of the absolute temperature [$\ln(W) = f(1/T)$], we have drawn Arrhenius diagrams (Figure 4-a) and determined apparent activation energy values from the slopes of these lines. This energy represents the minimum energy barrier that must be crossed for the corrosion reaction to occur.

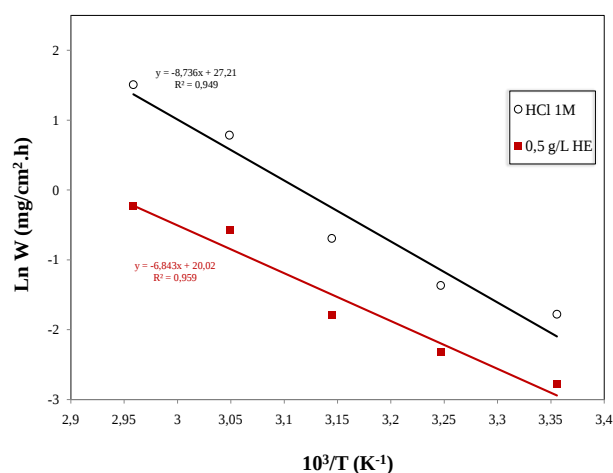
In addition, applying the state transition equation, we calculated the activation enthalpy (ΔH_a°) and activation entropy (ΔS_a°) from the same experimental data, representing transition state diagrams [$\ln(V/T) = f(1/T)$]. For these calculations, we used the Arrhenius transition equation or the activated complex equation [37]:

$$W_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\circ}{R}\right) \exp\left(-\frac{\Delta H_a^\circ}{RT}\right) \quad (5)$$

where h is Planck's constant (6.63×10^{-34} J.s), N is Avogadro's number (6.02×10^{23} mol⁻¹), $R/N = K_b = 1.38 \times 10^{-23}$ J.K⁻¹ is Boltzmann's constant.

Figure 4-b shows the variation of $\ln(W/T)$ as a function of $(1/T)$ with a slope equal to $(-\Delta H_a^\circ/R)$ and a coordinate at the origin equal to $[\ln(K_b/h) + \Delta S_a^\circ/R]$. The values of the activation enthalpies (ΔH_a°) and activation entropies (ΔS_a°) are given in Table 5.

These parameters, represented in the transition state diagrams (Figure 4-b), provide additional information on the reaction mechanism. The enthalpy of activation is related to the change in internal energy during the formation of the activated complex, while the entropy of activation is associated with the degree of order or disorder of the system during the transition from the initial to the activated state.



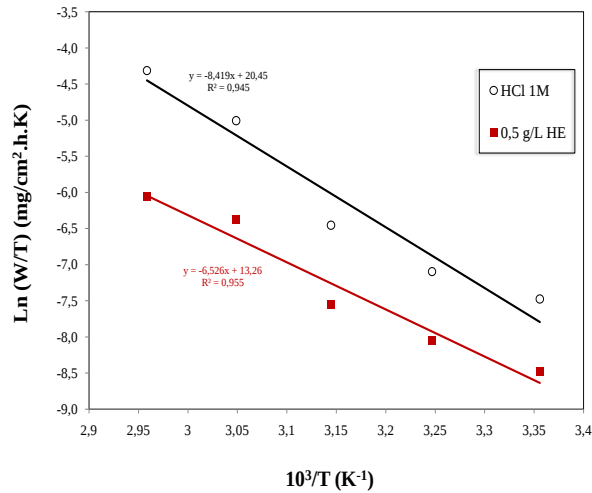


Figure 4. Arrhenius Diagrams (a) and Transition-State Diagrams (b) in the Absence and Presence of 0.5 g/L EO

Table 5. Thermodynamic Parameters for C38 Steel in 1M HCl in the Absence and Presence of 0.5 g/L EO

C (g/L)	E_a (KJ. Mol ⁻¹)	ΔS_a° (J. Mol ⁻¹ K ⁻¹)	ΔH_a° (KJ. Mol ⁻¹)
0	72,68	-27,54	70,05
0,5	56,39	-87,36	54, 30

The results in Table 5 clearly show a decrease in activation energy (E_a) in the presence of the essential oil at a concentration of 0.5 g/L. This decrease, coupled with the increase in inhibition efficiency with temperature, suggests strong adsorption of the inhibitor molecules on the metallic surface. Radovici (1965) previously emphasized that such a decrease in E_a is characteristic of a chemisorption process [38].

Moreover, the positive values of activation enthalpy (ΔH_a°) indicate an endothermic dissolution process of the steel. The simultaneous decrease in ΔS_a° and ΔH_a° in the presence of the inhibitor can be attributed to a change in the reaction mechanism induced by the inhibitor. Specifically, as highlighted by Noor *et al.* [39], the inhibitor preferentially acts on a specific step of the corrosion process, either slowing it down or completely inhibiting it, leading to an overall decrease in activation energy.

The negative values of the activation entropy (ΔS_a°) suggest a decrease in disorder during the formation of the activated complex, indicating an increased organization of the species involved in the rate-determining step. This observation aligns with the formation of a more structured activated complex in the presence of the inhibitor, attributed to the formation of bonds between the inhibitor molecules and the metallic surface [40,41,42,43,44].

In addition, it is important to note that the activation energy and activation enthalpy vary similarly as a function of inhibitor concentration, which verifies the thermodynamic relationship linking E_a and ΔH_a° , as described in: [45]

$$E_a - \Delta H_a^\circ = RT \quad (6)$$

R is the perfect gas constant (8.32 J-K⁻¹-mol⁻¹), T is the absolute temperature in K

3.3.4. Adsorption Isotherm and Standard Free Energy of Adsorption

To better understand the adsorption mechanism of *A. graveolens* seed essential oil on the steel surface and quantify its effectiveness, the experimental data were fitted to various adsorption isotherm models [46] (Langmuir, Frumkin, Temkin, and Freundlich). These models establish a relationship between the surface coverage (θ) by the inhibitor molecules and their concentration in the solution.

Our results demonstrate that the Langmuir isotherm provides the best description of the adsorption of our essential oil. The graphical representation of C/θ versus C (Figure 5) exhibits excellent linearity, confirmed by a correlation coefficient ($R^2 = 0,996$) and a slope (1.165) very close to 1.

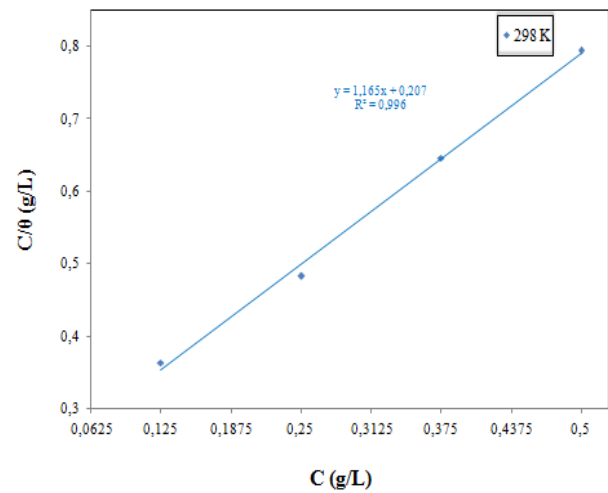


Figure 5. Langmuir Adsorption Isotherm of Carbon Steel C38 in 1M HCl in the Presence of *A. graveolens* Seed EO at 298 K

The excellent fit of our experimental data to the Langmuir isotherm suggests monolayer and homogeneous adsorption of the essential oil molecules on the steel surface, with negligible lateral interactions between adsorbed molecules [47].

The Langmuir isotherm equation is expressed as follows [48]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (7)$$

The Langmuir isotherm equation, presented in equation 7, is used to determine the adsorption equilibrium constant (K_{ads}). This constant is directly related to the standard free energy of adsorption (ΔG_{ads}°) by the following relationship:

$$\Delta G_{ads}^\circ = -RT \log (55.5 K_{ads}) \quad (8)$$

The value 55.5 represents the concentration of water in mol/L (1000 g/L), and R is the perfect gas constant. We then calculated the value of the standard free energy of adsorption ΔG_{ads}° which characterizes the interactions between the inhibitor molecules and the metal surface. The results are summarized in the following Table 6:

Table 6. Value of equilibrium constant K_{ads} and standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) at 298 K in the presence of *A. graveolens* seed EO

K_{ads} Langmuir (L/g)	$\Delta G^{\circ}_{\text{ads}}$ (KJ/Mol)
4,83	21,03

The values of the standard free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) tell us about the nature of the interactions between the inhibitor molecules and the metal surface. Generally speaking, for $\Delta G^{\circ}_{\text{ads}}$ values close to -20 kJ/mol or less negative, the type of adsorption involved is physisorption. This means that the inhibitory action is due to electrostatic interactions between the charged molecules and the metal charge. In contrast, values close to -40 kJ/mol or more negative are associated with chemisorption, where there is electron sharing or transfer from the inhibitor molecules to the metal surface to form covalent or coordination bonds. However, determining the type of adsorption when $\Delta G^{\circ}_{\text{ads}}$ is between -20 and -40 kJ/mol remains complex. It can be assumed that adsorption may simultaneously involve physisorption and chemisorption, a situation often referred to as mixed adsorption [34,49,50].

The negative value of $\Delta G^{\circ}_{\text{ads}}$ at 298 K indicates that the adsorption process is spontaneous and that the adsorbed layer on the steel surface is stable [33]. Furthermore, a $\Delta G^{\circ}_{\text{ads}}$ value close to -20 kJ/mol suggests that the inhibitory action of the studied EO is primarily due to electrostatic interactions between its components and the steel surface, corresponding to physical adsorption (physisorption).

However, the increase in inhibition efficiency with temperature suggests the presence of chemisorption processes as well, involving the formation of chemical bonds between the inhibitor and the metal. This observation aligns with the findings of Ivanov [35] and

Putilova et al. [34], who demonstrated that the nature of adsorption can evolve with temperature, transitioning from physisorption at lower temperatures to chemisorption at higher temperatures.

Thus, our results suggest a combined adsorption mechanism, involving both physical and chemical interactions. This mixed adsorption behavior is common when $\Delta G^{\circ}_{\text{ads}}$ falls within an intermediate range (-20 to -40 kJ/mol). It is important to note that fitting experimental data to an isotherm model alone cannot definitively determine the adsorption mechanism. Additional experimental techniques, such as infrared spectroscopy, electron microscopy, or surface studies, may be necessary to confirm the exact nature of interactions at the metal/inhibitor interface [51].

3.4. Correlation Between the Molecular Structure of the Three Main EO Compounds and Their Corrosion Inhibition Effect

The essential oil (EO) of *A. graveolens*, a complex mixture of 12 components primarily comprising carvone, dillapiol, and limonene, was extensively studied through quantum chemical calculations. These simulations modeled the interaction of these molecules with the C38 steel surface, offering insights into their corrosion inhibition mechanism. The results, presented in Figures 6, 7, and 8 and Table 7, detail the adsorption structures, electronic distributions, and quantum chemical properties of these compounds, including E_{HOMO} , E_{LUMO} , ΔE , dipole moment (μ), and the total energy of the three main components in their neutral form. These properties reveal their potential to form bonds with the metal and inhibit corrosive reactions.

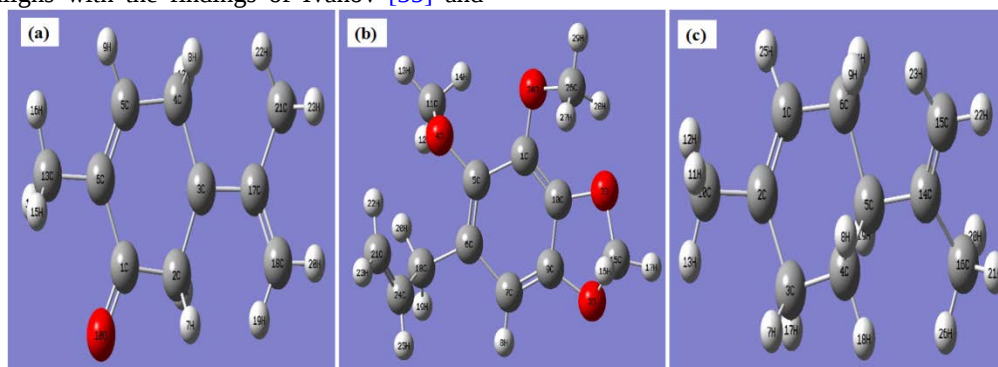


Figure 6. Optimized Structures Using DFT at the B3LYP/6-31G(d,p) Level for Carvone (a), Dillapiol (b), and Limonene (c)

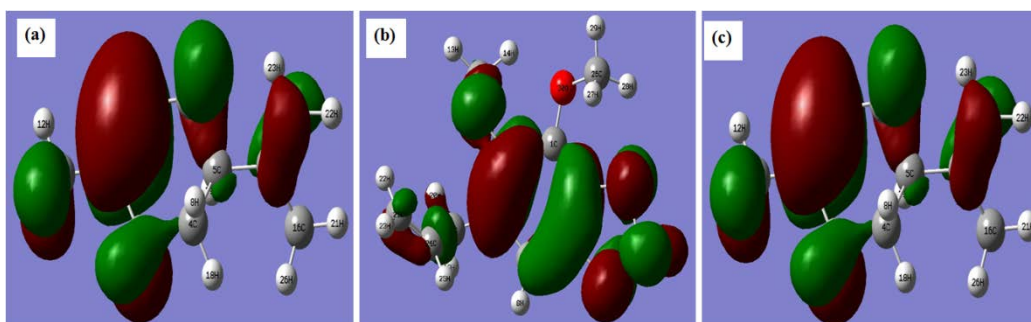


Figure 7. HOMO Electron Density Distribution Using DFT at the B3LYP/6-31G(d,p) Level for Carvone (a), Dillapiol (b), and Limonene (c)

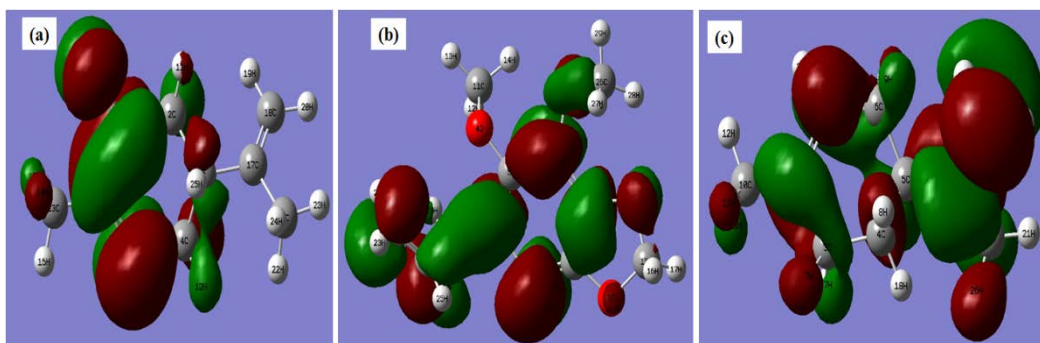


Figure 8. LUMO Electron Density Distribution Using DFT at the B3LYP/6-31G(d,p) Level for Carvone (a), Dillapiol (b), and Limonene (c)

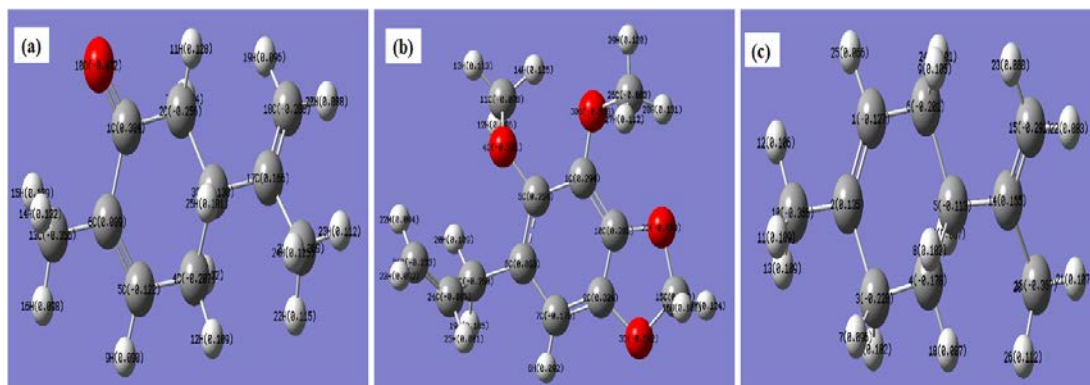


Figure 9. Mulliken Population Analysis Showing Charge Distribution for Carvone (a), Dillapiol (b), and Limonene (c) Using DFT at the B3LYP/6-31G(d,p) Level

As shown in Figure 7, the frontier molecular orbitals (HOMO) of carvone and limonene exhibit high electron density in the conjugated systems of the cyclohexenone ring and propylene fragments, while that of dillapiol is concentrated on its saffrole motif. These high electron-density regions, which are likely to interact with electrophilic sites on the metallic surface, constitute preferred adsorption sites.

The analysis of the LUMO orbitals (Figure 8) reveals a more diffuse distribution for limonene, whereas those of carvone and dillapiol are localized on specific regions of the molecule (the conjugated system of the cyclohexenone ring).

In addition, Mulliken analysis (Figure 9) is a means of estimating inhibitor adsorption centers by calculating the charge distribution over the entire molecule skeleton [52]. This analysis makes it possible to identify atoms carrying partial negative charges, likely to form bonds with the metal surface via a donor-acceptor mechanism [53]. The combination of this information makes it possible to propose a model for the adsorption of molecules on the surface of C38 steel, thus explaining their inhibiting effect.

The Mulliken charge density analysis (Figure 9) shows that the oxygen atoms in carvone and dillapiol are the most likely sites to interact with the metallic surface due to their high electron density. In contrast, for limonene, the adsorption-active sites are the carbons in positions 3, 4, 5, 6, 15, and 16.

The calculated electronic properties (Table 7) indicate that the three molecules can act as electron donors to the vacant orbitals of the metallic surface due to their low differences in E_{HOMO} values [54]. However, carvone, with its low E_{LUMO} and small ΔE , proves to be a more effective electron acceptor, thus favoring the formation of a bond with iron. Additionally, its high dipole moment suggests a

strong interaction with the metallic surface.

Table 7. Molecular Properties Calculated Using DFT at the B3LYP/6-31G(d,p) Level for the Three Main Constituents in Their Neutral Form

	Carvone	Dillapiol	Limonène
Total energy E_T (a.u)	-464.715	-766.534	-390.699
E_{HOMO} (a.u)	-0.23726	-0.19902	-0.22545
(eV)	-6,45	-5,41	-6,13
E_{LUMO} (a.u)	-0.04521	0.00556	0.02759
(eV)	-1,23	0,15	0,75
$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (a.u)	0.19205	0.20459	0.25304
(eV)	5,22	5,56	6,88
Dipole moment μ (debye)	3.46	1.84	0.65

Theoretical calculations (Table 7) demonstrate that the three molecules exhibit a similar capacity to donate electrons to the metallic surface, as evidenced by the small differences between their HOMO energies [55]. This small energy difference (ΔE) leads to an increased inhibitory efficiency of the molecule, as the excitation energy required to remove an electron from the last occupied orbital is low [56].

Moreover, carvone, with its lowest E_{LUMO} value and smallest ΔE , emerges as the best electron acceptor among the three molecules, promoting the formation of a stable [Fe-carvone] complex on the metal surface [57]. Its high dipole moment ($\mu=3.46$ Debye), which exceeds that of water ($\mu=1.84$ Debye), also suggests preferential adsorption on the metallic surface via a substitution mechanism with adsorbed water molecules [56]. Considering all calculated parameters and molecular structures, carvone appears to significantly contribute to the inhibitory performance of *A. graveolens* essential oil.

It is important to note that the relative efficiency of each molecule may vary depending on experimental conditions. The calculations presented here concern isolated molecules in the gas phase and do not account for solvent effects or protonation.

Theoretical calculations, combined with experimental results, allow us to deduce the following inhibition mechanism: the essential oil of *A. graveolens*, rich in carvone, dillapiol, and limonene, owes its inhibitory activity to the presence of active sites such as oxygen atoms, functional groups, and π -electrons, which are characteristic of classical corrosion inhibitors. These three compounds, representing 85.6% of the oil's overall composition, can adsorb onto the C38 steel surface via various mechanisms.

In acidic environments, neutral molecules can form bonds with the metallic surface through electron sharing or transfer (chemisorption mechanism), while protonated forms may be attracted to the negatively charged surface (due to the presence of Cl^- anions near the interface) via electrostatic interactions, i.e., a physisorption mechanism. It is also possible that minor components of the essential oil play a role, either synergistically or competitively, with the three major compounds.

4. Conclusion

The gravimetric study conducted on C38 steel in a 1M hydrochloric acid medium highlighted the significant inhibitory effect of essential oil extracted from *Anethum graveolens* seeds. The results demonstrate a notable reduction in the corrosion rate in the presence of the inhibitor, with a maximum efficiency of 62.95% achieved at 298 K with a concentration of 0.5 g/L. Thus, *A. graveolens* essential oil proves to be an excellent inhibitor in a 1M HCl medium.

The effect of temperature in the presence of 0.5 g/L of the oil was studied within the range of 298 to 338 K, revealing that increasing temperature enhances inhibitory activity, reaching 82.54% at 338 K. Furthermore, the various tested isotherms (Langmuir, Temkin, and Frumkin) demonstrated that the adsorption of the essential oil follows the Langmuir isotherm model.

Thermodynamic parameters calculated from Arrhenius plots and the Langmuir isotherm suggest a mixed adsorption mechanism, combining physical (physisorption) and chemical (chemisorption) interactions of the essential oil molecules with the steel surface.

Density Functional Theory (DFT) calculations confirmed this hypothesis by identifying oxygen atoms and π -electrons in the main constituents of the essential oil as the active sites responsible for adsorption on the metallic surface. The formation of coordination bonds, involving charge transfer between the heteroatoms of the inhibitor and the vacant orbitals of the metal, is the favored adsorption mechanism. This process also involves the displacement of water molecules from the C38 steel surface. Additionally, electrostatic interactions between the inhibitor cations and chloride anions present near the metallic surface contribute to the stability of the adsorbed film.

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