

Article

Aqueous Extract of *Ammodaucus leucotrichus* L. as an Eco-Friendly Corrosion Inhibitor for Mild Steel Under Acid Pickling Conditions: Electrochemical, SEM/EDS, and DFT Study

Otmane Kharbouch ^{1,*} , Asmaa Oubihi ² , Omar Belhadj ³, Sara Cherrad ², Musa A. Said ⁴ , Elhachmia Ech-cihbi ⁵ , Moussa Ouakki ^{1,*}  and Younes Chhiti ^{1,6}

¹ Laboratory of Engineering, Sustainability and Innovation, National Higher School of Chemistry (NHSC), Ibn Tofail University, Kenitra P.O. Box 133-14000, Morocco

² Laboratory of Natural Resources and Sustainable Development, Department of Biology, Faculty of Science, Ibn Tofail University, Kenitra P.O. Box 133-14000, Morocco

³ Laboratory of Organic Chemistry, Catalysis and Environment, Faculty of Sciences, Ibn Tofail University, Kenitra P.O. Box 133-14000, Morocco; omar.belhadj@uit.ac.ma

⁴ Department of Chemistry, Faculty of Science, Islamic University of Madinah, Madinah 42351, Saudi Arabia

⁵ Laboratory of Physics and Chemistry of Inorganic and Organic Materials, Higher Normal School, Mohammed V University, Rabat, Morocco

⁶ Green Tech Institute (GTI), Mohammed VI Polytechnic University, Ben Guerir, Morocco

* Correspondence: otmane.kharbouch@uit.ac.ma (O.K.); moussa.ouakki1@uit.ac.ma (M.O.)

Abstract

The aqueous seed extract of *Ammodaucus leucotrichus* Cosson & Durieu (**AL-AE**), a Saharan annual herb of the family Apiaceae, was evaluated for the first time as a green corrosion inhibitor for mild steel in 1.0 M hydrochloric acid. GC-MS analysis after acetylation derivatization identified ten constituents representing 99.22% of the total detected area, with 17-pentatriacontene (47.69%), 2,4-di-tert-butylphenol (13.24%), and myo-inositol (8.62%) as the dominant species. Inhibition performance was assessed by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) over 25–100 ppm at 298–328 K. At 100 ppm and 298 K, **AL-AE** achieved 96.17% by EIS and 97.10% by PDP. Adsorption obeyed the Langmuir model with a standard free energy of adsorption of $-38.2 \text{ kJ mol}^{-1}$, consistent with a mixed physisorption–chemisorption mechanism. SEM/EDS confirmed protective film formation, with surface oxygen dropping from 34.9 to 4.1 wt%. Density functional theory (DFT) calculations at the B97-3c/CPCM (water) level in ORCA 6.1 identified 2,4-di-tert-butylphenol as the most reactive constituent, while Fukui index analysis based on Mulliken population analysis located the preferential adsorption sites on each molecule.

Keywords: *Ammodaucus leucotrichus*; aqueous extract; green corrosion inhibitor; mild steel; GC-MS; DFT; EIS



Academic Editor: Cheng Zhang

Received: 17 May 2026

Revised: 15 June 2026

Accepted: 22 June 2026

Published: 23 June 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and

conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Mild steel occupies a central place in the petrochemical, construction, and mechanical engineering sectors, chosen above all for its tensile strength and manufacturing cost. Its widespread use in equipment exposed to hydrochloric acid during pickling, descaling, and wellbore stimulation makes corrosion a persistent operational problem. Annual corrosion costs worldwide are consistently placed at 3%–5% of gross domestic product, a figure exceeding USD 2.5 trillion [1,2]. Adding an inhibitor at low concentration to the acid bath remains the most practical protective strategy for mild steel in industrial acid-cleaning operations [3].

Organic molecules carrying heteroatoms or pi-electron systems reduce corrosion by adsorbing on the Fe surface and donating electron density to vacant d-orbitals, which simultaneously blocks anodic dissolution and cathodic hydrogen evolution [4,5]. Synthetic inhibitors such as azole derivatives, Schiff bases, and imidazolines perform well in this role, but their toxicological and environmental profiles are increasingly subject to regulatory restriction [6]. The resulting demand for plant-based alternatives has grown considerably over the past decade, sustained by demonstrated efficiencies above 90% in 1.0 M HCl at concentrations below 500 ppm [7,8]. Within plant-derived preparations, aqueous extracts present practical advantages over essential oils. Ultrasound-assisted aqueous extraction requires no organic solvents and no distillation equipment, generates no flammable waste, and yields fractions rich in phenolics, polyols, and long-chain alkenes, all of which carry functional groups capable of donor–acceptor interaction with iron [9,10].

Ammodaucus leucotrichus Cosson & Durieu (Apiaceae), locally called hairy cumin (kammun es-sofi), grows across the arid and semi-arid zones of Morocco, Algeria, and Tunisia [11]. Its fruits carry a documented ethnomedicinal role for digestive and respiratory complaints [12]. Phytochemical surveys have confirmed the presence of monoterpenes, phenolic acids, polyols, and long-chain hydrocarbons in various organs [13]. Two earlier corrosion studies exist in the literature: one using the fruit essential oil with perillaldehyde (73.5%) as the active constituent [14], and one using odorized and deodorized aqueous fruit extracts for C38 steel [15]. Neither study characterized the aqueous seed extract by GC-MS after derivatization, and neither reported a combined electrochemical-DFT investigation at the sub-100 ppm level. All three published studies on *A. leucotrichus* as a corrosion inhibitor worked with fruit material from Morocco. Secondary metabolite profiles in this species vary with geographical origin and plant organ, and seeds from Kenitra carry a different chemical composition from the Moroccan fruits previously studied. Table 1 sets out the comparison.

Table 1. Methodological comparison of published studies on *Ammodaucus leucotrichus* and related works with the present study.

Species Organ	Origin	GC-MS	Conc. Range	DFT Level	MC/MD	REF
<i>A. leucotrichus</i> Fruits	Morocco (Errachidia)	Direct	>250 ppm	----	----	[15]
<i>A. leucotrichus</i> Fruits	Morocco (Errachidia)	Direct	>250 ppm	----	----	[14]
<i>A. leucotrichus</i> Fruits (PER)	Morocco (Errachidia)	Direct	>125 ppm	Gas phase	MC Fe(111)	[16]
<i>M. koenigii</i> Leaves	Indonesia (Surabaya)	----	>1000 ppm	----	----	[17]
<i>A. paniculata</i> Leaves	Malaysia (Terengganu)	Direct	>500 ppm	Gas phase	MD	[18]
<i>A. leucotrichus</i> Seeds	Morocco (Kenitra)	Acetylation derivatisation	25–100 ppm	CPCM (water)	MC	Present work

PER: perillaldehyde; MC: Monte Carlo; MD: molecular dynamics.

The present work fills that gap. An aqueous extract of *A. leucotrichus* seeds (AL-AE) was prepared by ultrasound-assisted extraction, profiled by GC-MS after acetylation, and tested as a corrosion inhibitor for mild steel in 1.0 M HCl at 25–100 ppm over 298–328 K. The protocol combined EIS, PDP, adsorption isotherm fitting, thermodynamic activation analysis, and SEM/EDS surface characterization, supplemented by DFT calculations at the B97-3c/CPCM(water) level in ORCA 6.1 and Fukui index analysis based on Mulliken population analysis. To the best of our knowledge, this is the first study to couple GC-MS profiling of the *A. leucotrichus* aqueous seed extract with a full electrochemical-DFT protocol.

2. Experimental Study

2.1. Extraction and Characterization

Seeds of *A. leucotrichus* were dried at ambient temperature in the dark before use. Five grams of ground seeds were subjected to ultrasound-assisted aqueous extraction at 50 kHz and 45 °C for 60 min. After filtration, the aqueous phase was lyophilized to yield a dry powder (**AL-AE**), stored at 4 °C in amber glass vials until use [9]. For GC-MS analysis, 5 mg of **AL-AE** was dissolved in 1 mL of acetic anhydride with four drops of anhydrous pyridine as a catalyst, heated at 50 °C for 20 min, cooled overnight, and hydrolyzed with 6 mL of ice-cold water under magnetic stirring in an ice bath for 2 h. Products were extracted with chloroform, neutralized with saturated NaHCO₃, dried over anhydrous Na₂SO₄, and the solvent was evaporated. Chromatographic analyses were performed on a Perkin Elmer Clarus 580 GC coupled with an SQ8S mass spectrometer, equipped with a capillary column (40 m × 180 µm i.d.), with helium carrier gas at 1.0 mL min^{−1}, injector at 250 °C in split–splitless mode, and an oven program rising from 60 °C to 250 °C at 4 °C min^{−1} held for 10 min. Identification relied on retention index comparison with published databases and mass–spectral fragmentation matching [19].

2.2. Electrochemical Study

All measurements were conducted in a conventional three-electrode cell using a PGZ100 potentiostat controlled by Voltamaster 4 software. Mild steel (1.0 cm² exposed area) served as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference; all potentials are reported versus SCE. Prior to each measurement, the electrode was immersed for 1200 s to stabilize the open circuit potential [20,21]. EIS was performed by applying a 10 mV sinusoidal perturbation over the frequency range 100 kHz to 100 mHz at the open circuit potential. PDP curves were recorded from −900 to −100 mV vs. SCE at 1 mV s^{−1}. Temperature-dependent experiments covered 298–328 K using a thermostatic double-walled cell. All measurements were performed in triplicate (n = 3), and reported values are arithmetic means. Test solutions consisted of 1.0 M HCl with **AL-AE** at 0, 25, 50, 75, and 100 ppm [22].

2.3. SEM/EDS

Mild steel coupons (1 cm²) were immersed in 1.0 M HCl for 6 h at 298 K, with and without 100 ppm **AL-AE**. After retrieval, specimens were rinsed with deionized water and dried in a desiccator. SEM images and EDS spectra were acquired at the UATRS-CNRST facility in Rabat [23].

2.4. DFT Methodology

Geometry optimizations and single-point energy calculations were performed using ORCA 6.1.1 with the B97-3c composite method and the CPCM(water) implicit solvent model [24]. The three principal **AL-AE** constituents, 17-pentatriacontene, 2,4-di-tert-butylphenol, and myo-inositol, were fully optimized in aqueous phase without symmetry constraints. Global reactivity descriptors were derived from the frontier molecular orbital energies following Koopmans theorem, using the work function of iron, $\phi_{\text{Fe}} = 4.82$ eV and $\eta_{\text{Fe}} = 0$ eV [25].

$$\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \quad (2)$$

$$\chi = \frac{-(E_{\text{LUMO}} - E_{\text{HOMO}})}{2} \quad (3)$$

$$\sigma = \frac{1}{\eta} \quad (4)$$

$$\Delta N = \frac{\varphi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \quad (5)$$

The local Fukui indices were computed from Mulliken population analysis on single-point calculations of the neutral (N), anionic (N + 1, charge = −1, multiplicity = 2), and cationic (N − 1, charge = +1, multiplicity = 2) species at the frozen neutral geometry [26].

$$f_k^+ = q(N + 1) - q(N) \quad (6)$$

$$f_k^- = q(N) - q(N - 1) \quad (7)$$

2.5. MC Simulation Method

Monte Carlo (MC) simulation was used to model how the main extract molecules interact with the mild steel surface [27]. The calculations were done using the Adsorption Locator module in Materials Studio 2017 with the COMPASS force field [28]. The steel surface was modeled using an Fe(110) crystal plane expanded into an (11 × 11) supercell. A simulation box was built over the iron slab and filled with 200 water molecules, 8 H₃O⁺ ions, and 8 Cl[−] ions. The simulation was run to find the most stable top and side views of the adsorption configurations for each molecule on the iron surface.

3. Result and Discussion

3.1. GC-MS Chemical Profiling

Table 2 presents the chemical composition of **AL-AE** as established by GC-MS. Ten constituents were resolved, collectively representing 99.22% of the total detected area. The extract is dominated by 17-pentatriacontene (47.69%), a C35 terminal alkene, followed by 2,4-di-tert-butylphenol (13.24%), myo-inositol (8.62%), 1,3-bis(1,1-dimethylethyl)benzene (6.25%), n-dotriacontane (6.19%), eicosane (4.81%), D-limonene (4.78%), dodecane 2,6,11-trimethyl (3.69%), tetrapentacontane (3.65%), and 1,2,3-propanetriol triacetate (0.30%).

Table 2. Chemical composition of **AL-AE** determined by GC-MS analysis after acetylation derivatization.

	Compound	R.Time	%
1	D-Limonene	10.718	4.78
2	Benzene, 1,3-bis(1,1-dimethylethyl)	17.173	6.25
3	1,2,3-Propanetriol Triacetate	17.462	0.30
4	Dodecane, 2,6,11-trimethyl	17.924	3.69
5	Eicosane	23.519	4.81
6	2,4-Di-tert-butylphenol	23.925	13.24
7	n-Dotriacontane	29.380	6.19
8	Myo-inositol	37.389	8.62
9	Tetrapentacontane	51.774	3.65
10	17-Pentatriacontene	56.657	47.69
	Total identified %		99.22

As depicted in Figure 1, the principal constituents carry functional groups relevant to Fe surface interaction. 2,4-Di-tert-butylphenol presents a phenolic hydroxyl group capable of donating electron density to vacant Fe d-orbitals, while the two flanking tert-butyl substituents extend laterally over the surface, widening the adsorbed footprint and reducing accessible area [29]. Myo-inositol brings six equatorial hydroxyl groups on a cyclohexane scaffold, a geometry suited to flat adsorption on the Fe(110) plane with simultaneous multi-site anchoring [30]. 17-Pentatriacontene, although less obviously reactive, donates

pi-electron density through the vinyl terminus while its long hydrocarbon chain establishes a hydrophobic barrier against chloride penetration [31]. Chemical diversity in multi-component extracts is generally advantageous, since mixed adsorbate populations fill surface sites that no single molecule would cover [32].

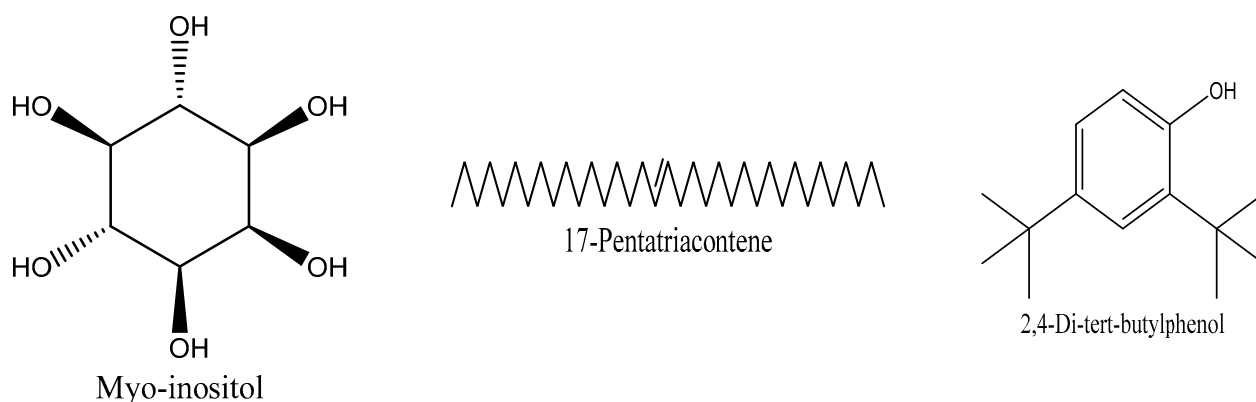


Figure 1. Molecular structures of the three principal constituents of **AL-AE** identified by GC-MS: 17-pentatriacontene, 2,4-di-tert-butylphenol, and myo-inositol.

3.2. Electrochemical Impedance Spectroscopy (EIS) Analysis

The Nyquist plots shown in Figure 2 exhibit single depressed capacitive arcs at each concentration, with diameters that grow steadily with **AL-AE** content. No Warburg diffusion tail appears at any concentration, confirming that the corrosion process remains charge-transfer controlled throughout. **AL-AE** acts by blocking the surface sites at which electron exchange occurs rather than by restricting mass transport [33]. In the Bode plots, the impedance modulus at low frequencies increases progressively, and the phase-angle peak broadens with concentration, both consistent with a surface film that grows in lateral coverage and effective thickness [34].

The arc depression reflects the heterogeneity of the corroded steel surface rather than a second time constant. It was reproduced using the equivalent circuit $R_s(CPE/R_{ct})$ shown in Figure 3, in which a constant phase element CPE replaces the ideal capacitor. The effective double-layer capacitance C_{dl} was extracted from the Brug formula from Q and n_{dl} [35]. The Brug formula is expressed as Equation (8):

$$C_{dl} = Q^{\frac{1}{n}} \times \left(R_s^{-1} + R_{ct}^{-1} \right)^{\frac{n-1}{n}} \quad (8)$$

where Q is the CPE magnitude ($\Omega^{-1} \text{ cm}^{-2} \text{ s}^n$), n is the CPE exponent (n_{dl}), R_s is the solution resistance ($\Omega \text{ cm}^2$), and R_{ct} is the charge transfer resistance ($\Omega \text{ cm}^2$).

The results presented in Table 3 confirm that **AL-AE** has a marked protective effect on the steel surface. The introduction of **AL-AE** at a concentration of just 25 ppm increases the R_{ct} value from 35.7 to 796.4 $\Omega \text{ cm}^2$, a factor of more than twenty-two, indicating that the main adsorbates achieve near-saturation surface coverage at concentrations well below the lowest tested. From 25 to 100 ppm, R_{ct} increases further to reach 932.2 $\Omega \text{ cm}^2$, yielding an inhibition efficiency of 96.17%, although the additional gain decreases as the remaining sites with lower affinity are progressively occupied. At the same time, C_{dl} decreases from 78.7 $\mu\text{F}/\text{cm}^2$ in the 1.0 M HCl to 44.4 $\mu\text{F}/\text{cm}^2$ at 100 ppm, reflecting a lower local dielectric constant and a greater effective double-layer thickness, as the organic molecules displace water and chloride from the metal-solution interface. The n_{dl} values (0.848–0.951) remain well above 0.8 at all concentrations, confirming a genuine capacitive response of the film with no significant diffusive contribution [36,37]. For context, marjoram extract

reached $R_{ct} = 301.5 \Omega \text{ cm}^2$ only at 500 ppm [35], and seed-derived inhibitors from related species typically require concentrations well above 100 ppm to approach similar surface coverage [34], whereas AL-AE reaches $932.2 \Omega \text{ cm}^2$ at 100 ppm.

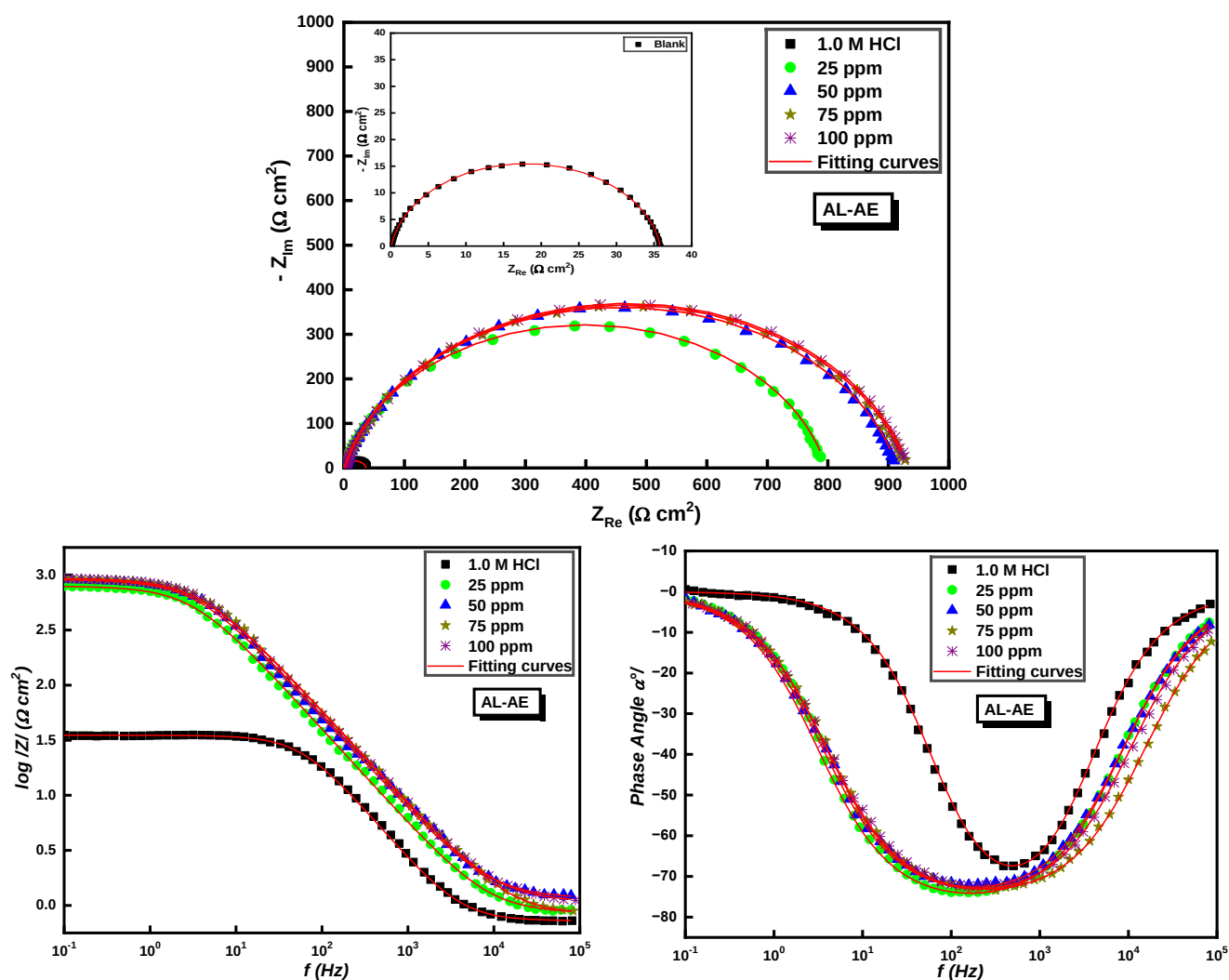


Figure 2. Nyquist and Bode plots for mild steel in 1.0 M HCl in the absence and presence of various concentrations of AL-AE at 298 K.

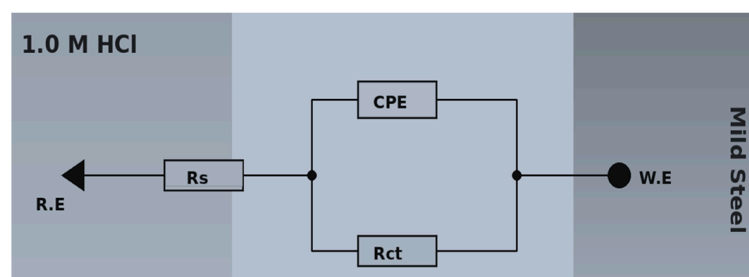


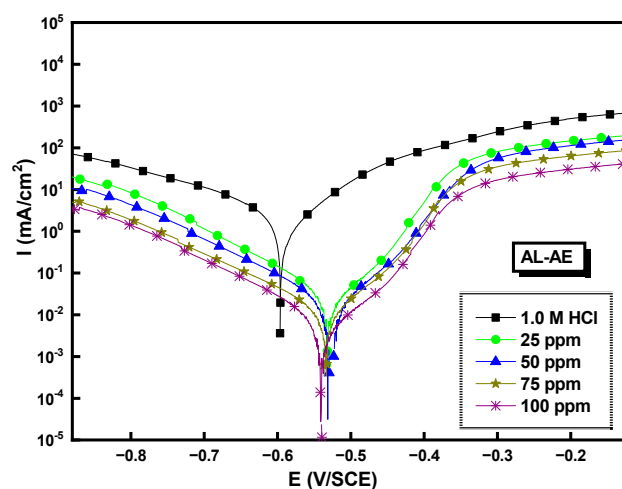
Figure 3. An equivalent electrical circuit used to fit the EIS spectra.

Table 3. EIS parameters for mild steel in 1.0 M HCl in the absence and presence of various concentrations of AL-AE at 298 K.

Medium	Conc. (ppm)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	Q ($\mu\text{F S}^{n-1}$)	n_{dl}	C_{dl} ($\mu\text{F cm}^2$)	θ	η_{imp} %	SD ($\Omega \text{ cm}^2$)
1.0 M HCl	--	0.79	35.7	134	0.909	78.7	--	--	0.18
	25	0.85	796.4	95	0.864	63.3	0.9552	95.52	0.40
AL-AE	50	1.16	914.0	79	0.951	49.9	0.9609	96.09	0.46
	75	0.81	929.6	71	0.848	45.2	0.9616	96.16	0.27
	100	1.08	932.2	70	0.853	44.4	0.9617	96.17	0.41

3.3. Electrochemical PDP Measurements

Figure 4 presents the Tafel polarization curves for mild steel in 1.0 M HCl at 298 K, in the absence and presence of AL-AE at concentrations ranging from 25 to 100 ppm. In the uninhibited 1.0 M HCl, high current densities on both the anodic and cathodic branches indicate active iron dissolution and hydrogen evolution simultaneously. The introduction of AL-AE at the lowest tested concentration of 25 ppm already produces a substantial reduction in i_{corr} , from 965 to 42 $\mu\text{A}\cdot\text{cm}^{-2}$, and this suppression deepens progressively with concentration, reaching $i_{corr} = 28 \mu\text{A}\cdot\text{cm}^{-2}$ at 100 ppm (Table 4). The corresponding inhibition efficiency of 97.10% at 100 ppm confirms that AL-AE saturates the active surface sites at concentrations well below those commonly reported for plant-derived inhibitors [38].

**Figure 4.** Tafel polarization curves for mild steel in 1.0 M HCl in the absence and presence of various concentrations of AL-AE at 298 K.**Table 4.** Potentiodynamic polarization parameters for mild steel in 1.0 M HCl in the absence and presence of various concentrations of AL-AE at 298 K.

Medium	Conc. (ppm)	$-E_{corr}$ (mV/SCE)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$-\beta_c$ (mV.dec $^{-1}$)	η_{PP} %	SD ($\mu\text{A}\cdot\text{cm}^{-2}$)
1.0 M HCl	--	594	965	141	--	4.62
	25	528	42	121	95.65	0.21
AL-AE	50	530	36	123	96.27	0.18
	75	530	32	127	96.68	0.16
	100	538	28	128	97.10	0.14

The corrosion potential E_{corr} shifts from -594 mV/SCE in the 1.0 M HCl to -538 mV/SCE at 100 ppm, a net anodic displacement of 56 mV. Since this displacement remains within the ± 85 mV limit established for classifying mixed-type inhibitors [39], **AL-AE** is identified as a mixed-type inhibitor with anodic predominance. This classification means the extract reduces anodic iron dissolution more strongly than cathodic hydrogen evolution, without modifying either reaction mechanism. The cathodic Tafel slope β_c varies only from 141 to 128 mV/dec across all tested concentrations, confirming that the hydrogen evolution pathway is unchanged and that **AL-AE** operates exclusively through surface blocking rather than through catalytic modification [40].

The reduction in both partial reaction rates reflects the chemical nature of the adsorbed **AL-AE** film. The phenolic oxygen of 2,4-di-tert-butylphenol forms coordinate bonds with surface Fe atoms, blocking the anodic active sites where iron dissolution initiates. The multiple hydroxyl groups of myo-inositol contribute additional anchoring points across the surface, while the long C35 chain of 17-pentatriacontene creates a hydrophobic outer barrier that limits the access of aggressive Cl^- ions. These three mechanisms act simultaneously, which explains why anodic suppression is stronger than cathodic [41]. Haque et al. found the same pattern for *Thevetia peruviana* flower extract in 1 M HCl, where β_c held between 142 and 153 mV/dec from 50 to 1000 ppm, while the anodic branch dropped more sharply, a response attributed to preferential blocking of Fe dissolution sites by phenolic constituents [42]. The close agreement between EIS and PDP results, 96.17% and 97.10%, respectively, at 100 ppm, confirms the stability of the **AL-AE** film under both steady-state and dynamic measurement conditions. The slight difference between the two values arises from the inherently different perturbation modes: EIS operates at steady state with a small sinusoidal signal, while PDP involves a voltage sweep that can partially disturb the adsorbed layer. Consistency across both techniques validates the reliability of the inhibition efficiency values [43,44].

3.4. Influence of Temperature on Corrosion

Tafel polarization curves recorded at 298, 308, 318, and 328 K are presented in Figure 5 for mild steel in 1.0 M HCl, without and with 100 ppm **AL-AE**. The corresponding electrochemical parameters are summarized in Table 5. In the uninhibited system, the corrosion current density i_{corr} increases substantially with temperature, from $965 \mu\text{A}\cdot\text{cm}^{-2}$ at 298 K to $2183 \mu\text{A}\cdot\text{cm}^{-2}$ at 328 K. This continuous rise reflects the thermally accelerated kinetics of iron dissolution and hydrogen evolution, consistent with the Arrhenius behavior of charge-transfer-controlled electrochemical reactions [45].

Table 5. Effect of temperature on the potentiodynamic polarization parameters of mild steel in 1.0 M HCl in the absence and presence of 100 ppm **AL-AE**.

Medium	Temperature (K)	$-E_{\text{corr}}$ (mV/SCE)	i_{corr} ($\mu\text{A}\cdot\text{cm}^{-2}$)	$-\beta_c$ (mV.dec $^{-1}$)	η_{PP} %
1.0 M HCl	298	594	965	141	-
	308	595	1187	138	-
	318	603	1432	131	-
	328	599	2183	134	-
AL-AE	298	538	28	128	97.10
	308	541	49	127	95.87
	318	572	95	132	93.36
	328	582	212	138	90.29

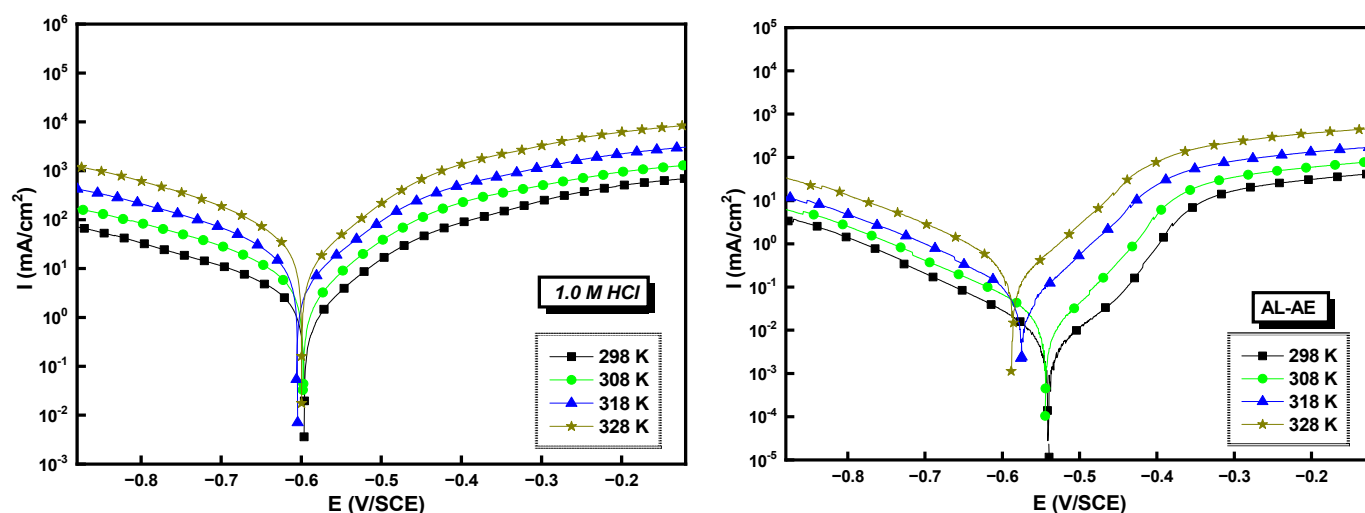


Figure 5. Tafel polarization curves for mild steel in 1.0 M HCl in the absence and presence of 100 ppm AL-AE at various temperatures (298–328 K).

In the presence of 100 ppm of AL-AE, i_{corr} values remain significantly lower than in the 1.0 M HCl at every temperature tested, ranging from 28 $\mu\text{A}\cdot\text{cm}^{-2}$ at 298 K to 212 $\mu\text{A}\cdot\text{cm}^{-2}$ at 328 K. The inhibition efficiency decreases from 97.10% at 298 K to 90.29% at 328 K, a reduction of about 7 percentage points over a 30 K interval. This decrease is moderate compared with many plant-derived inhibitors reported in the literature, which show inhibition efficiency values below 85% at 328 K. The fact that AL-AE maintains protection above 90% throughout the 298–328 K range places it among the thermally stable inhibitors at the concentrations tested [46].

The observed decrease in inhibition efficiency with temperature is consistent with a partial physisorption contribution to the adsorption mechanism. Physical adsorption is exothermic and reversible: as temperature rises, thermal energy promotes partial desorption of weakly bound molecules, reducing surface coverage. However, the persistence of efficiency above 90% at 328 K indicates that a significant fraction of the adsorbed AL-AE molecules is held by chemisorptive interactions, particularly the coordinate bonds between the phenolic and polyol hydroxyl groups of 2,4-di-tert-butylphenol and myo-inositol with surface Fe atoms. These bonds are sufficiently strong to resist thermal disruption at the temperatures relevant to industrial acid-cleaning operations [47,48]. These temperature-dependent results are internally consistent with the adsorption thermodynamics discussed in Section 3.5 and with the activation parameters derived in Section 3.4. A ΔG_{ads} value of $-38.2 \text{ kJ}\cdot\text{mol}^{-1}$ at 298 K, situated between the physisorption and chemisorption boundaries, naturally leads to a partial loss of surface coverage at elevated temperatures as the physisorptive component weakens, while the chemisorptive component maintains a functional protective layer [49,50].

Activation Parameters

The thermodynamic activation parameters E_a , ΔH_a , and ΔS_a were derived from the Arrhenius and Eyring–Polanyi plots shown in Figure 6, using the temperature dependence of i_{corr} reported in Table 5. The results are presented in Table 6. In the uninhibited 1.0 M HCl, the apparent activation energy $E_a = 21.3 \text{ kJ}\cdot\text{mol}^{-1}$ sits in the range commonly reported for mild steel in concentrated hydrochloric acid [51,52]. Values in this window tend to accompany charge-transfer-dominated dissolution, though a low E_a on its own cannot rule out a partial mass-transport contribution.

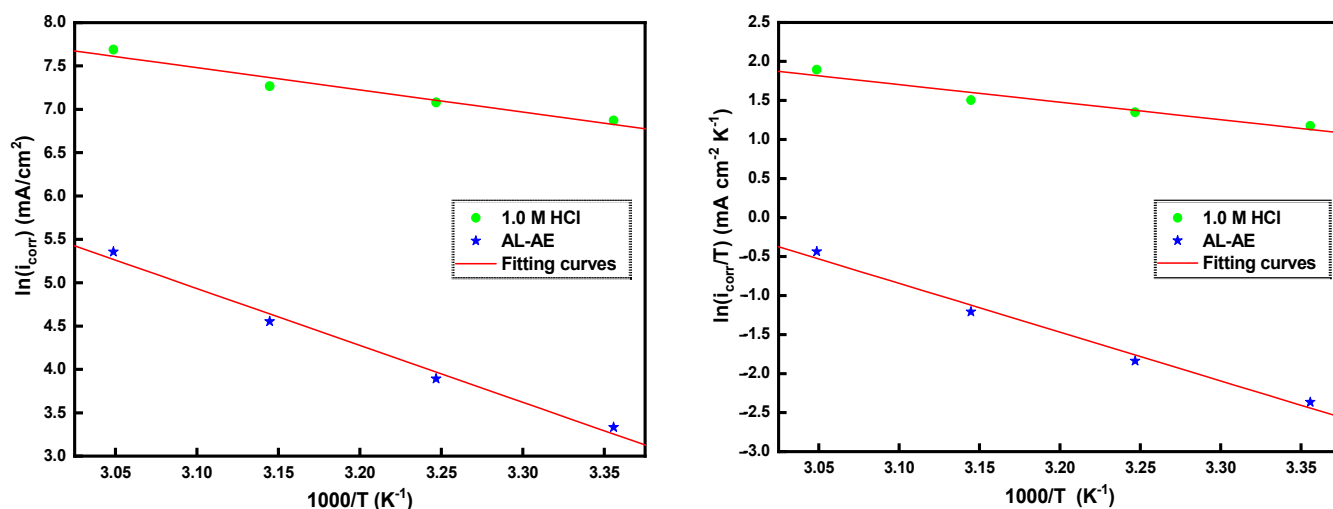


Figure 6. Arrhenius plots for mild steel corrosion in 1.0 M HCl in the absence and presence of 100 ppm of AL-AE.

Table 6. Thermodynamic activation parameters for mild steel corrosion in 1.0 M HCl in the absence and presence of 100 ppm AL-AE.

Medium	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol.K)
1.0 M HCl	21.3	18.7	−125.4
100 ppm of AL-AE	54.6	52.0	−43.4

The rise in E_a to $54.6 \text{ kJ}\cdot\text{mol}^{-1}$ upon AL-AE addition points to a higher barrier for Fe dissolution, most likely because adsorbed molecules must be at least partially displaced before an Fe atom can leave the surface. This is consistent with surface blocking, though E_a alone is not a definitive mechanistic criterion. This interpretation is consistent with the Langmuir isotherm data, which indicate a K_{ads} of $50.37 \times 10^2 \text{ L g}^{-1}$, reflecting a strong surface affinity that a dissolving Fe atom must overcome [53].

The activation enthalpy ΔH_a follows the same direction, increasing from 18.7 to $52.0 \text{ kJ}\cdot\text{mol}^{-1}$ in the inhibited system. This rise confirms that the dissolution transition state is significantly more endothermic when AL-AE is adsorbed, again consistent with the need to partially disrupt inhibitor-surface interactions before an Fe atom can escape into solution. The relationship $\Delta E_a - \Delta H_a = RT$ is satisfied within experimental uncertainty, as expected for a condensed-phase process, which confirms the internal consistency of the thermodynamic data [54].

The activation entropy ΔS_a shifts from $-125.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ in the 1.0 M HCl to $-43.4 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ in the inhibited system. Both values are negative, as expected for an associative transition state in which the reacting species loses translational freedom. The large positive shift of $82 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ upon inhibitor addition indicates that the activated complex in the inhibited system has more conformational freedom than in the bare-surface case. This is physically reasonable: the partial desorption of a segment of the adsorbed film during the dissolution event allows greater molecular motion in the transition state compared with the highly constrained solvation environment around a bare Fe surface site [55]. Taken together, the three activation parameters form a thermodynamically self-consistent picture that confirms the surface-blocking mechanism inferred from EIS and PDP.

3.5. Adsorption Isotherm

In order to quantify the adsorption behavior of **AL-AE** on the surface of mild steel, the surface coverage values θ measured at 298 K were fitted to four classical adsorption isotherm models: Langmuir, Freundlich, Temkin and Frumkin. The fit plots are shown in Figure 7 and the corresponding parameters are listed in Table 7. The Langmuir model yields a correlation coefficient $R^2 = 1.00$ with a slope of 1.04, values significantly higher than those of the other three models: Freundlich and Temkin both give $R^2 = 0.927$, and Frumkin gives $R^2 = 0.905$. The Langmuir isotherm, therefore, provides the best statistical description of the adsorption process in the concentration range of 25 to 100 ppm [56].

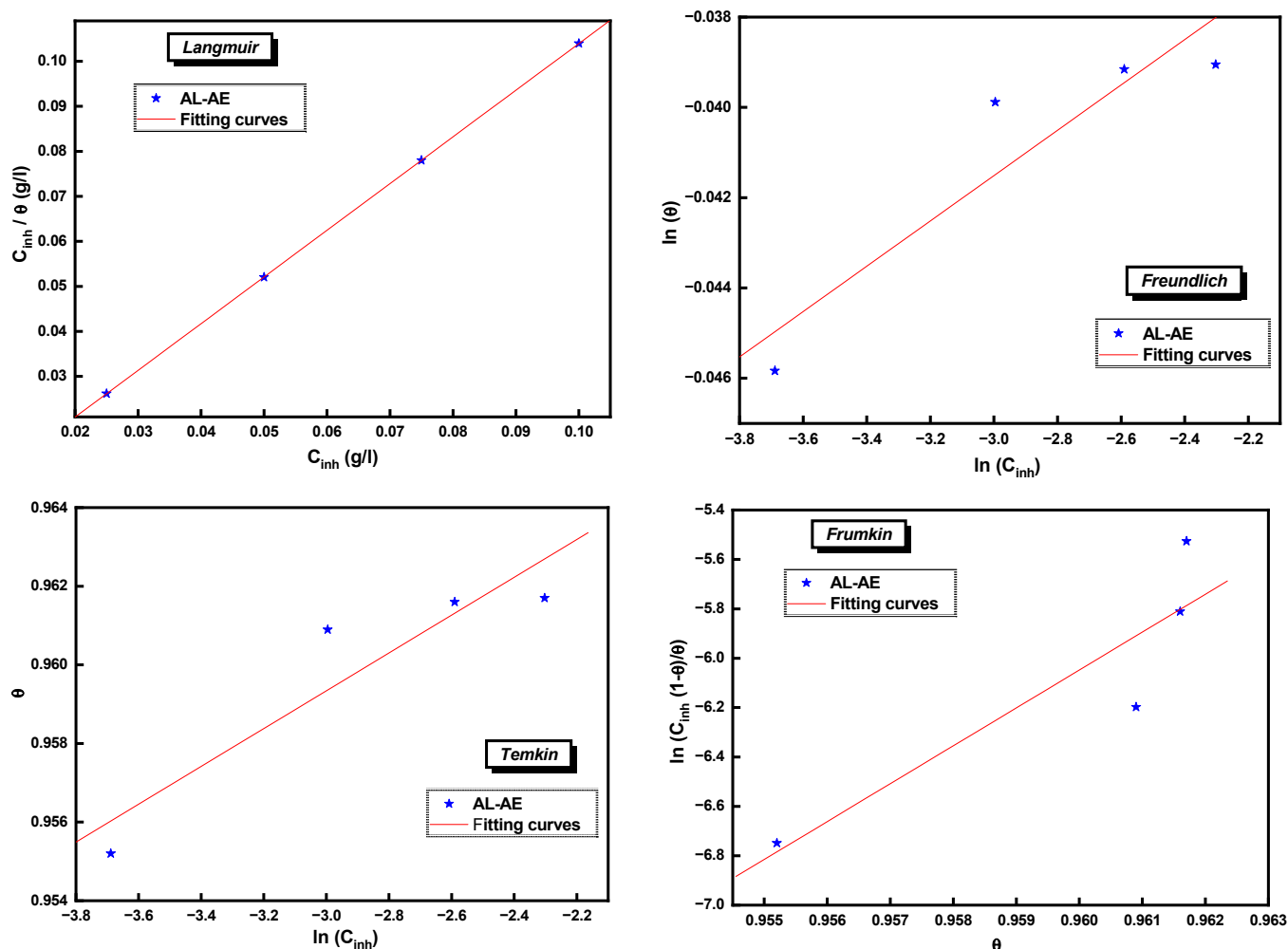


Figure 7. Adsorption isotherm plots for **AL-AE** on mild steel in 1.0 M HCl at 298 K.

Table 7. Parameters of adsorption isotherm models for **AL-AE** on mild steel in 1.0 M HCl at 298 K.

Isotherms	Parameters	
	R^2	1
Langmuir	K_{ads} (L/g)	$50.37 \cdot 10^2$
	Slope	1.04
	ΔG_{ads} (kJ/mol)	−38.2
Freundlich	R^2	0.92657
Temkin	R^2	0.92669
Frumkin	R^2	0.90479

The Langmuir model fits the adsorption data with $R^2 = 1.00$ and a slope of 1.04. For a ten-constituent extract like **AL-AE**, this fit is best read as an empirical effective description: the classical assumptions of a homogeneous surface with no lateral interactions between adsorbates hold reasonably well at the concentrations tested but are acknowledged approximations for a multi-component mixture. The slope of 1.04 signals a small departure from ideal Langmuir behavior, attributable to weak interactions between adjacent hydrocarbon chains or minor site-energy heterogeneity on the corroded Fe surface. The near-unity slope of 1.04 is consistent with this interpretation, as a slope of exactly 1.00 indicates ideal Langmuir behavior. The small deviation may reflect minor surface site energy heterogeneity or weak lateral interactions between the long hydrocarbon chains of adjacent 17-pentatriacontene molecules at high surface coverage. The adsorption equilibrium constant $K_{ads} = 50.37 \times 10^2 \text{ L.g}^{-1}$ is large, reflecting a strong affinity between the **AL-AE** constituents and the Fe surface. From K_{ads} and Equation (9), the standard free energy of adsorption $\Delta G_{ads} = -38.2 \text{ kJ.mol}^{-1}$ at 298 K, with CH_2O set to 1000 g/L, the mass concentration of pure water, matching the L/g units of K_{ads} . The literature conventionally distinguishes physisorption (ΔG_{ads} between 0 and -20 kJ.mol^{-1}) from chemisorption (below -40 kJ.mol^{-1}), with values between -20 and -40 kJ.mol^{-1} attributed to a mixed mechanism. The value of $-38.2 \text{ kJ.mol}^{-1}$ places **AL-AE** in this mixed regime [57,58].

$$\Delta G_{ads} = -RT \ln(K_{ads} \cdot C_{Solvent}) \quad (9)$$

The negative sign of ΔG_{ads} confirms that adsorption is thermodynamically spontaneous under the experimental conditions. The value of $-38.2 \text{ kJ.mol}^{-1}$ for **AL-AE** indicates a slightly stronger surface interaction, consistent with the higher inhibition efficiency of 97.10% at the low concentration of 100 ppm [59]. Lin et al. found ΔG_{ads} between -24.3 and -27.4 kJ/mol for Ipomoea batatas leaf extract on mild steel in 1.0 M HCl under the same Langmuir framework, with hydroxyl and phenolic groups sharing responsibility for the intermediate adsorption strength [60].

3.6. SEM/EDS

SEM/EDS analysis was used here to confirm macroscopic film formation and elemental shifts at the steel surface. It does not resolve nanoscale molecular interactions, functional-group preservation, or chemical bonding states at the interface, but it gives direct morphological evidence of whether a protective layer has formed. Figure 8 shows SEM micrographs and EDS spectra for mild steel coupons immersed for 6 h in 1.0 M HCl at 298 K, without and with 100 ppm of **AL-AE**. The surface from the uninhibited 1.0 M HCl shows extensive and severe damage: widespread corrosion pits, brittle iron oxide crusts, and transgranular cracks running along grain boundaries are clearly visible across the entire field of view. These morphological features are characteristic of the localized chloride-promoted dissolution that occurs when aggressive Cl^- ions concentrate at surface defects and sustain autocatalytic pit growth [61]. The corresponding EDS spectrum records 34.9% oxygen, reflecting the thick layer of iron oxides and hydroxides that accumulates as corrosion products during 6 h exposure.

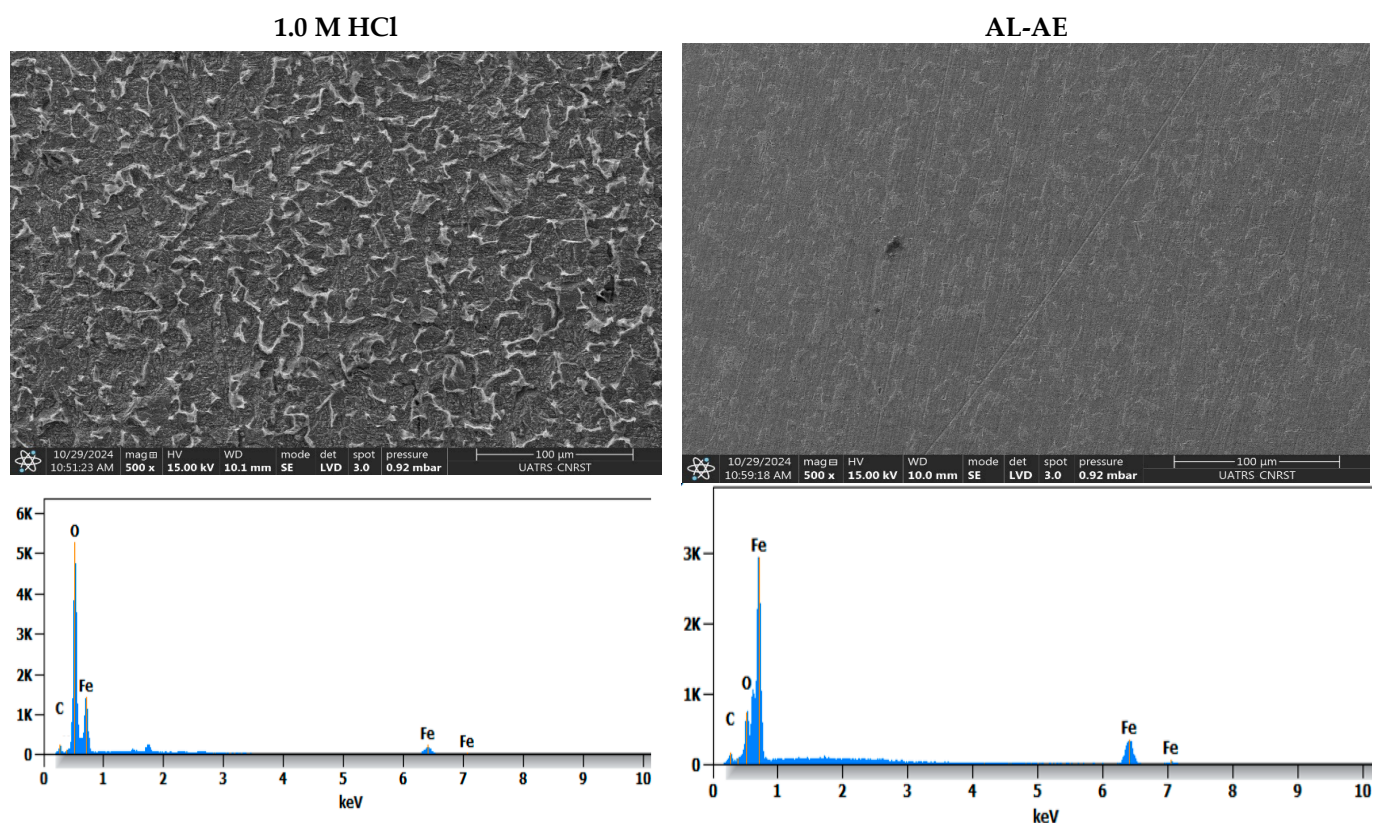


Figure 8. SEM/EDS spectra before and after 6 h of immersion in 1.0 M HCl, with and without AL-AE at 298 K.

The surface exposed to 100 ppm AL-AE is qualitatively different. Pit nucleation events are far less frequent, grain boundaries are visible and structurally intact under the electron beam, and the overall texture is noticeably smoother. This microscopic improvement results from the formation of a coherent organic adsorption film that covers the metal surface and prevents the localized acid attack responsible for pitting in the uninhibited system [62]. EDS analysis (Table 8) reveals that oxygen falls from 34.9 to 4.1% and iron rises from 63.1 to 94.4% when AL-AE is present. A reduction of 30.8% in surface oxygen content cannot be attributed to analytical scatter and represents a near-complete suppression of iron oxidation at the surface. The residual carbon of 1.5% is consistent with the presence of an organic film from adsorbed AL-AE constituents, since the test medium contains no carbonate species [63].

Table 8. EDS elemental composition (%) of mild steel surface after 6 h immersion in 1.0 M HCl at 298 K in the absence and presence of 100 ppm AL-AE.

	C	O	Fe	Total
1.0 M HCl	2.0	34.9	63.1	100.0
AL-AE	1.5	4.1	94.4	100.0

Taken together, the SEM imaging and EDS compositional data confirm that AL-AE forms a genuine protective surface layer that is chemically and morphologically distinct from the corrosion product layer observed in the 1.0 M HCl. The convergence of this surface evidence with the EIS data (R_{ct} rising from 35.7 to 932.2 $\Omega \text{ cm}^2$ at 100 ppm, a 26-fold gain, Table 2), the PDP data (97.10% efficiency), and the Langmuir thermodynamics ($\Delta G_{ads} = -38.2 \text{ kJ.mol}^{-1}$) provides a self-consistent, multi-technique account of the corrosion inhibition mechanism.

3.7. DFT Results

The optimized molecular geometries, frontier molecular orbital (HOMO/LUMO) density maps, and molecular electrostatic potential (MEP) surfaces for the three principal AL-AE constituents computed in aqueous phase at the B97-3c/CPCM(water) level are presented in Figure 9. The HOMO density represents the region from which each molecule can donate electron density toward the vacant d-orbitals of surface Fe atoms, serving as a primary site for potential electronic interaction with the metal surface. The LUMO density identifies sites capable of accepting electron density during back-donation from the metal. For 2,4-di-tert-butylphenol, both HOMO and LUMO density concentrate on the aromatic ring and the phenolic oxygen, confirming this fragment as the primary electronic interaction center with the Fe surface. For myo-inositol, the HOMO extends across the entire cyclohexane ring and all six hydroxyl oxygens, consistent with flat multi-site adsorption. For 17-pentatriacontene, HOMO density localizes near the C17=C18 vinyl bond, the only pi-electron-rich region in an otherwise sigma-framework molecule [64,65]. The MEP maps show that the most negative electrostatic potential zones coincide with HOMO-dense regions in all three molecules. These electron-rich zones are the molecular regions most likely to interact with positively charged Fe surface sites and with surface Fe_2^+ cations generated during anodic dissolution. The positive electrostatic potential zones correspond to hydrogen atoms and alkyl chain segments, which contribute to the hydrophobic character of the film rather than to direct electronic interaction with the metal [66].

The global DFT reactivity descriptors in Table 9 provide a quantitative ranking of the three constituents. Among them, 2,4-di-tert-butylphenol has the highest E_{HOMO} (−5.219 eV), the narrowest energy gap ΔE_{gap} (4.408 eV), the lowest hardness η (2.204 eV), the highest softness σ (0.454 eV^{-1}), and the largest ΔN (0.410). A higher E_{HOMO} means electrons in the outermost orbital are more easily donated to the Fe surface. A smaller ΔE_{gap} reflects greater molecular polarizability, favoring adaptation of the electron cloud to the surface geometry. The ΔN value of 0.410 exceeds the 0.3828 threshold for net electron donation to iron, confirming 2,4-DTBP as the dominant electron-transfer partner, despite representing only 13.24% of the extract [67]. Phenolic constituents with E_{HOMO} in the −5.2 to −5.4 eV range and ΔE_{gap} below 5.0 eV consistently rank as the dominant electron-transfer partners in mixed plant extracts tested under the same conditions, regardless of the botanical source [42].

Table 9. Global DFT reactivity descriptors for the three principal AL-AE constituents in aqueous phase.

Descriptor	Myo-Inositol (8.62%)	17-Pentatriacontene (47.69%)	2,4-Di-tert-butylphenol (13.24%)
E_{HOMO} (eV)	−6.050	−5.507	−5.219
E_{LUMO} (eV)	+0.125	−0.193	−0.810
ΔE_{gap} (eV)	6.175	5.315	4.408
η (eV)	3.087	2.657	2.204
σ (eV^{-1})	0.324	0.376	0.454
χ (eV)	2.963	2.850	3.015
ω (eV)	1.422	1.528	2.061
ΔN	0.301	0.371	0.410

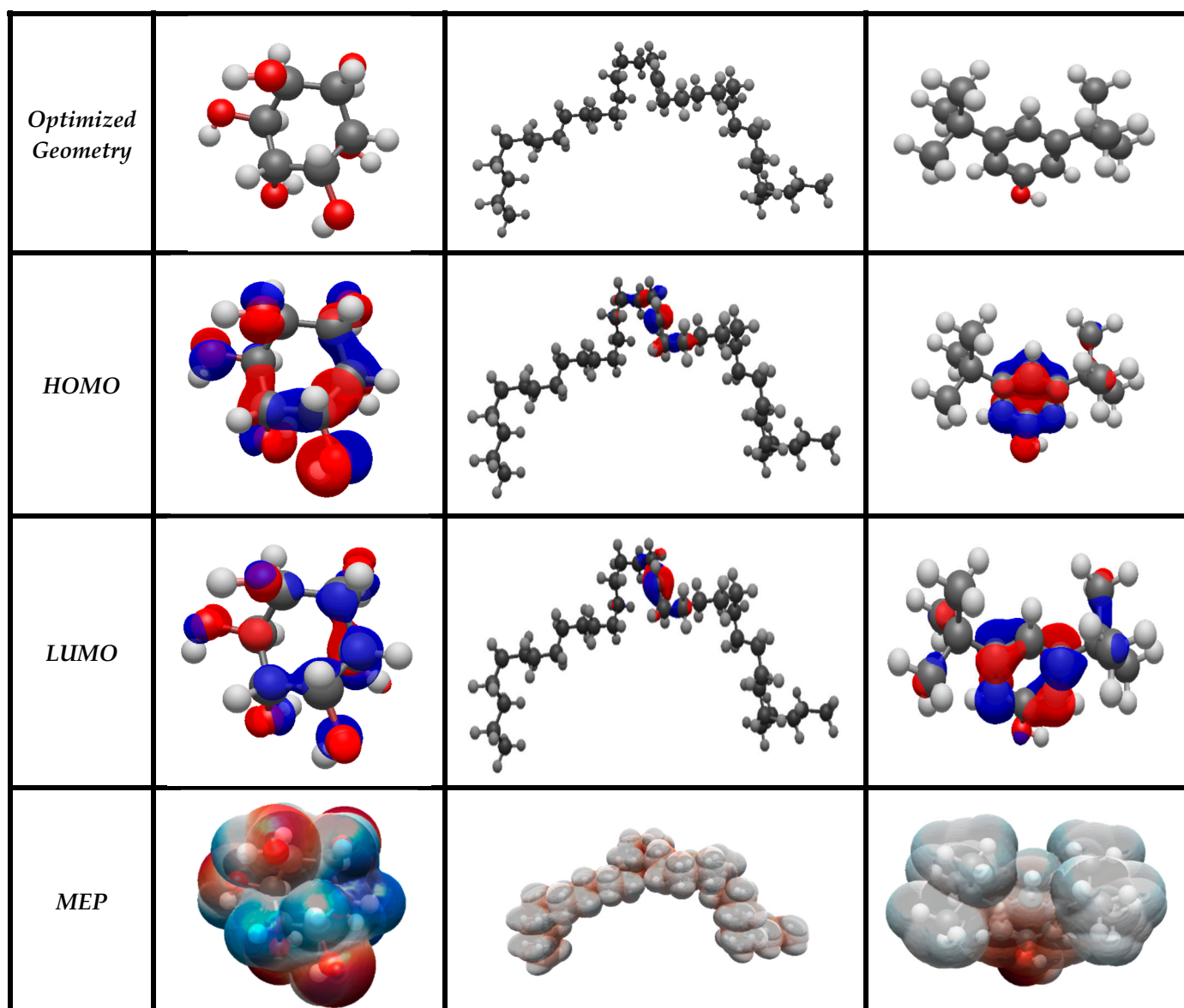


Figure 9. Optimized molecular geometries, frontier molecular orbitals (HOMO, LUMO), and molecular electrostatic potential (MEP) maps of the three principal AL-AE constituents in aqueous phase.

17-Pentatriacontene ranks second ($\Delta N = 0.371$, $\Delta E_{\text{gap}} = 5.315$ eV). While it interacts weakly through its terminal vinyl group, its main role is structural. Its long C35 chain forms a hydrophobic barrier that keeps chloride ions away from the steel surface, maintaining high protection even at 328 K [27,63]. On the other hand, myo-inositol has the lowest electron-donating power ΔN (0.301). Because it is a saturated polyol, it does not act as a pi-donor. Instead, it protects the surface through multi-site bonding. Its six equatorial hydroxyl groups donate electrons via oxygen lone pairs directly to the metal, creating a stable, tightly bound layer that resists being pushed away by water molecules [68].

The local Fukui indices f_k^+ and f_k^- , derived from Mulliken population analysis of the N , $N + 1$, and $N - 1$ species at frozen neutral geometry, are presented for the heavy atoms of each molecule in Figure 10. These indices identify the atomic sites most susceptible to nucleophilic attack (high f_k^+ , electron-donation centers during adsorption onto electrophilic Fe surface sites) and electrophilic attack (high negative f_k^- , electron-acceptance centers during back-donation from the metal).

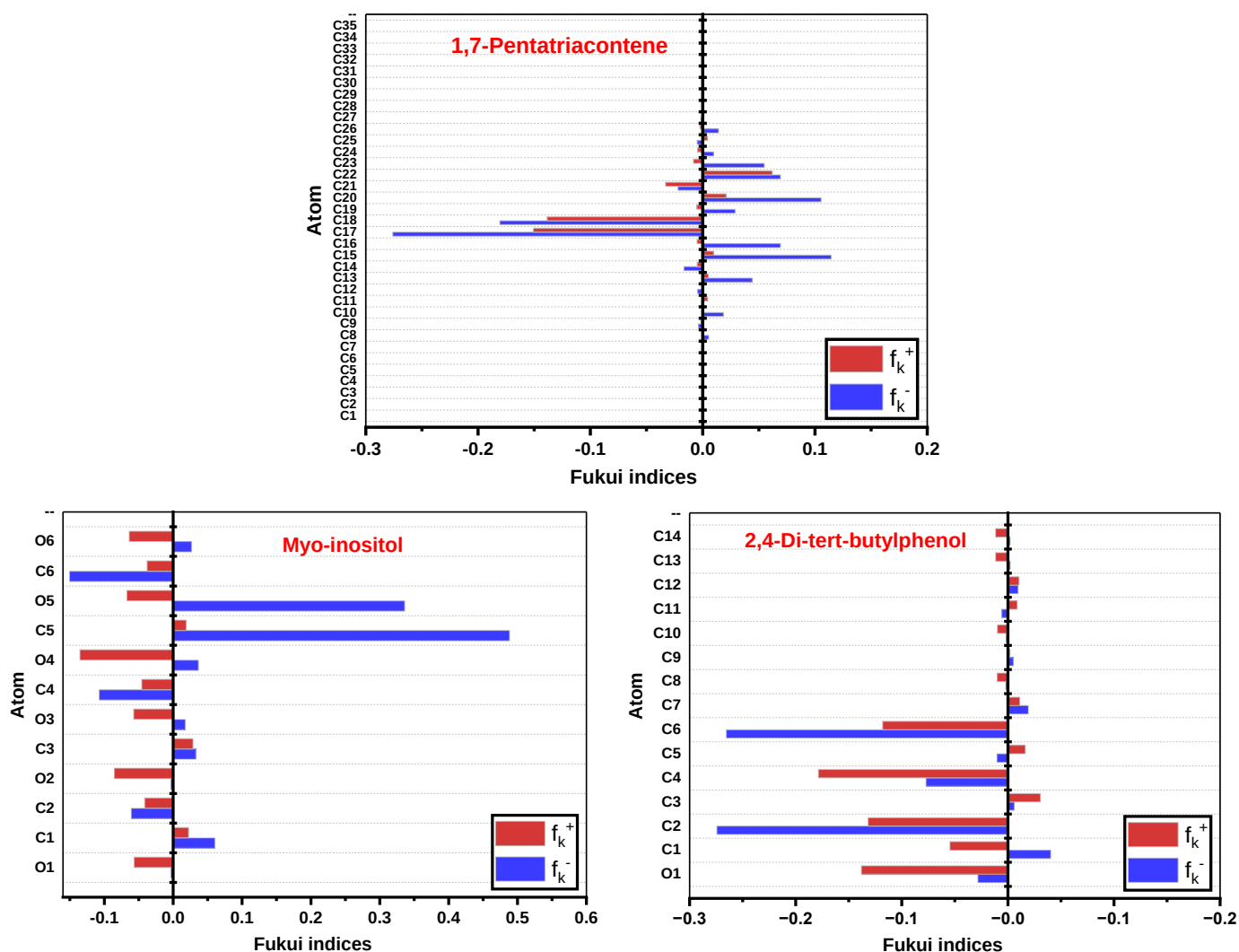


Figure 10. Fukui indices f_k^+ (red color) and f_k^- (blue color) for the heavy atoms of the three principal AL-AE constituents.

For myo-inositol, C5 carries the highest f_k^+ (+0.489), the primary electron-donation center toward surface Fe^{2+} . O4 shows the most negative f_k^- (−0.135), the main electron-acceptance site during back-donation. This distribution reflects the electronic reorganization when a cyclohexane polyol adopts a flat adsorption geometry on a corrugated surface, consistent with published studies on polyol adsorption on iron. For 2,4-di-tert-butylphenol, C2 (−0.274) and C6 (−0.265) show the largest f_k^+ values, corresponding to the ortho and para positions of highest pi-electron density in the phenolic ring. C4 carries the most negative f_k^- (−0.179). This pattern is consistent with a parallel adsorption geometry where the aromatic plane lies flat on the Fe surface, maximizing pi-orbital overlap with the metal d-bands, as also reported from DFT slab calculations for related phenolic inhibitors [69,70]. For 17-pentatriacontene, all significant Fukui values are confined to C15–C20, flanking the C17=C18 vinyl bond: C15 (+0.115) and C20 (+0.106) are the electron-donation centers, C17 (−0.151) and C18 (−0.139) are the electron-acceptance centers. The remaining 29 carbons of the chain show values near zero, confirming that the saturated backbone plays no electronic role and contributes exclusively through van der Waals contact and hydrophobic barrier formation. Adsorption through the vinyl terminus positions the chain in a standing-up or tilted configuration that creates the outer hydrophobic layer responsible for the thermal stability of inhibition efficiency above 90% at 328 K [71,72].

3.8. MC Simulation Results

Monte Carlo simulations (MCS) were performed to investigate how the principal extract constituents, (a) myo-inositol, (b) 17-pentatriacontene, and (c) 2,4-di-tert-butylphenol, interact with the mild steel surface in an acid environment. The top and side views of the lowest-energy configurations (Figure 11) show that the organic molecules orient themselves to maximize direct contact with the iron surface. This flat and aligned arrangement optimizes surface coverage, successfully creating a physical shield that blocks corrosive ions from reaching the substrate [73].

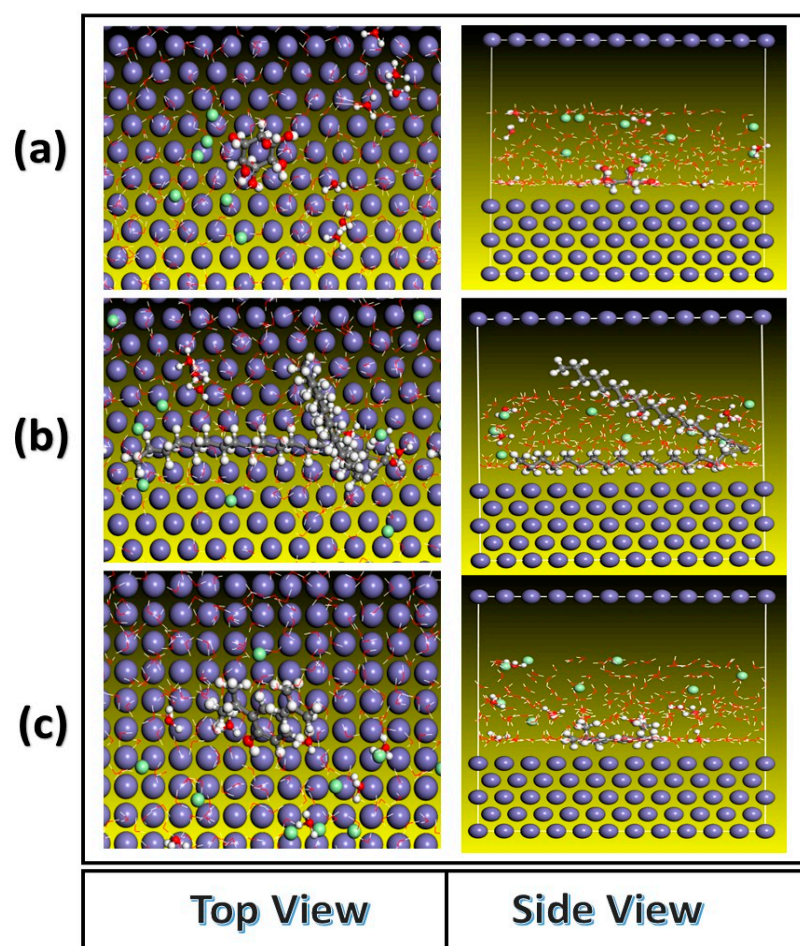


Figure 11. Top and side views of the lowest-energy adsorption configurations for (a) myo-inositol, (b) 17-pentatriacontene, and (c) 2,4-di-tert-butylphenol on the steel surface in an acid environment.

It is important to note that the high inhibition efficiency of the studied extract can be attributed to a synergistic effect among its various components. It is suggested that a synergistic interaction between all constituents within the extract contributes to the inhibition of mild steel corrosion in acidic environments. The different molecular structures work together by occupying different spaces on the metal surface to form a tight protective barrier.

4. Conclusions

The aqueous seed extract of *Ammodaucus leucotrichus* (AL-AE) was evaluated for the first time as a green corrosion inhibitor for mild steel in 1.0 M HCl. The results demonstrated outstanding inhibitory performance, with maximum inhibition efficiencies of 96.17% (EIS) and 97.10% (PDP) at 100 ppm and 298 K, positioning AL-AE among the most effective plant-derived inhibitors reported at such a low concentration. EIS analysis

confirmed the formation of a stable protective film at the metal-solution interface, reflected by a 26-fold increase in charge-transfer resistance. PDP measurements classified **AL-AE** as a mixed-type inhibitor with anodic predominance, maintaining protection above 90% up to 328 K. Adsorption obeyed the Langmuir isotherm with $\Delta G_{\text{ads}} = -38.2 \text{ kJ.mol}^{-1}$, indicating a spontaneous mixed physisorption–chemisorption mechanism. SEM/EDS confirmed the formation of the protective organic film, with surface oxygen falling from 34.9 to 4.1%. DFT calculations at the B97-3c/CPCM(water) level identified 2,4-di-tert-butylphenol as the most reactive constituent ($\Delta N = 0.410$, $\Delta E_{\text{gap}} = 4.408 \text{ eV}$), while Fukui index analysis located the preferential adsorption centers on each molecule responsible for the inhibition mechanism. Overall, these findings confirm that **AL-AE** is a highly effective, environmentally benign, and cost-efficient green inhibitor, making it a promising candidate for sustainable corrosion control in industrial acid-cleaning operations.

Author Contributions: Conceptualization, O.K. and M.O.; methodology, O.K. and A.O.; software, O.K.; validation, M.A.S. and M.O.; formal analysis, O.K. and A.O.; investigation, O.K., A.O., O.B. and S.C.; resources, M.A.S. and Y.C.; data curation, O.K. and A.O.; writing—original draft preparation, O.K.; writing—review and editing, M.A.S., E.E.-c., M.O. and Y.C.; visualization, A.O.; supervision, M.O. and Y.C.; project administration, O.K.; funding acquisition, M.A.S. and Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding authors.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Pourmohseni, M.; Rashidi, A.; Karimkhani, M. Preparation of corrosion inhibitor from natural plant for mild steel immersed in an acidic environment: Experimental and theoretical study. *Sci. Rep.* **2024**, *14*, 7937. [CrossRef] [PubMed]
2. Koch, G.; Varney, J.; Thompson, N.; Moghissi, O.; Gould, M.; Payer, J. International measures of prevention, application, and economics of corrosion technologies study. *NACE Int.* **2016**, *216*. Available online: <http://impact.nace.org/documents/Nace-International-Report.pdf> (accessed on 15 June 2026).
3. Mamand, D.M.; Qadr, H.M. Corrosion inhibition efficiency and quantum chemical studies of some organic compounds: Theoretical evaluation. *Corros. Rev.* **2023**, *41*, 427–441. [CrossRef]
4. Mehta, R.K.; Gupta, S.K.; Yadav, M. Studies on pyrimidine derivative as green corrosion inhibitor in acidic environment: Electrochemical and computational approach. *J. Environ. Chem. Eng.* **2022**, *10*, 108499. [CrossRef]
5. John, S.; Mathew, Z.P.; Augustine, C.; George, J.B.; Joseph, B.; Josh, M.S. Corrosion inhibition of mild steel in 1 M HCl using water soluble chitosan derivative of vanillin. *Int. J. Biol. Macromol.* **2024**, *262*, 130024. [CrossRef] [PubMed]
6. Ihamdane, R.; Tiskar, M.; Amri, A.E.; Lgaz, H.; Aldalbahi, A.; Outemsaa, B.; Lee, H.; Dagdag, O.; Dkhireche, N.; Loukili, A. Synergistic experimental-computational insights into the protective mechanism of Chinese star anise essential oil on mild steel. *Colloids Surf. A Physicochem. Eng. Asp.* **2025**, *720*, 137113. [CrossRef]
7. Thakur, A.; Kumar, A.; Kaya, S.; Benhiba, F.; Sharma, S.; Ganjoo, R.; Assad, H. Electrochemical and computational investigations of the *Thysanolaena latifolia* leaves extract: An eco-benign solution for the corrosion mitigation of mild steel. *Results Chem.* **2023**, *6*, 101147. [CrossRef]
8. Berrissoul, A.; Ouarhach, A.; Benhiba, F.; Romane, A.; Guenbour, A.; Dikici, B.; Bentiss, F.; Zarrouk, A.; Dafali, A. Assessment of corrosion inhibition performance of *origanum compactum* extract for mild steel in 1 M HCl: Weight loss, electrochemical, SEM/EDX, XPS, DFT and molecular dynamic simulation. *Ind. Crops Prod.* **2022**, *187*, 115310. [CrossRef]
9. Iraqi, O.; Aouji, M.; Oubihi, A.; Imtara, H.; Noman, O.M.; Mothana, R.A.; Tarayrah, M.; Taboz, Y.; Habsaoui, A. Exploring the chemical composition, antioxidant, and antibacterial properties of milk thistle (*Silybum marianum* L.). *Front. Sustain. Food Syst.* **2025**, *9*, 1551584. [CrossRef]

10. Mouats, N.; Djellali, S.; Ferkous, H.; Sedik, A.; Delimi, A.; Boublia, A.; Rachedi, K.O.; Berredjem, M.; Cukurovali, A.; Alam, M. Comprehensive investigation of the adsorption, corrosion inhibitory properties, and quantum calculations for 2-(2,4,5-trimethoxybenzylidene) hydrazine carbothioamide in mitigating corrosion of XC38 carbon steel under HCl environment. *ACS Omega* **2024**, *9*, 27945–27962. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Mostafa, E.; Bouknana, S.; Idrissi, A.; Daoudi, N.E.; Bnouham, M. *Ammodaucus leucotrichus* Coss. & Durieu Apiaceae. In *Ethnobotany of Northern Africa and Levant*; Springer: Berlin/Heidelberg, Germany, 2023; pp. 1–6.
12. Laroui, H.; Guemmaz, T.; Zerargui, F.; Saffidine, K.; Guenifi, S.; Arrar, L.; Khennouf, S.; Zengin, G.; Baghiani, A. Antioxidant and anti-inflammatory potentials of *Ammodaucus leucotrichus* Coss. & Durieu seeds' extracts: In vitro and in vivo studies. *J. Ethnopharmacol.* **2024**, *326*, 117964. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Bairagi, H.; Vashishth, P.; Sehrawat, R.; Shukla, S.K.; Mangla, B. Impact of novel ZnO/PAA nanocomposite as corrosion inhibitor on mild steel in 5% HCl. *Mater. Chem. Phys.* **2024**, *315*, 128958. [\[CrossRef\]](#)
14. Manssouri, M.; El Ouadi, Y.; Znini, M.; Costa, J.; Bouyanzer, A.; Desjobert, J.; Majidi, L. Adsorption proprieties and inhibition of mild steel corrosion in HCl solution by the essential oil from fruit of Moroccan *Ammodaucus leucotrichus*. *J. Mater. Environ. Sci.* **2015**, *6*, 631–646.
15. Manssouri, M.; Znini, M.; Ansari, A.; Bouyanzer, A.; Faska, Z.; Majidi, L. Odorized and deodorized aqueous extracts of *Ammodaucus leucotrichus* fruits as green inhibitor for C38 steel in hydrochloric acid solution. *Der Pharma Chem.* **2014**, *6*, 331–345.
16. Manssouri, M.; Znini, M.; Lakbaibi, Z.; Ansari, A.; El Ouadi, Y. Experimental and computational studies of perillaldehyde isolated from *Ammodaucus leucotrichus* essential oil as a green corrosion inhibitor for mild steel in 1.0 M HCl. *Chem. Pap.* **2021**, *75*, 1103–1114.
17. Pradityana, A.; Khosfirah, F.; Biwai, F.N.; Shidieqy, R.H.A.; Hakim, M.L.; Santosa, P.I.; Nik, W.M.N.W. Curry leaf extract (*Murraya Koenigii* (L.) Spreng) as a corrosion inhibitor of ASTM A36 steel in H₂SO₄ solution. *Results Eng.* **2024**, *24*, 103037. [\[CrossRef\]](#)
18. Kamaruzzaman, W.M.I.W.M.; Shaifudin, M.S.; Nasir, N.A.M.; Badruddin, M.A.; Yusof, N.; Adnan, A.; Aziz, N.A.; Nik, W.M.N.W.; Haque, J.; Murmu, M. Experimental, DFT and molecular dynamic simulation of *Andrographis paniculata* as corrosion inhibitor for mild steel in artificial seawater. *Mater. Chem. Phys.* **2024**, *312*, 128642.
19. Oubihi, A.; Ouakki, M.; Ech-Chebab, A.; Assiri, E.H.E.; Tarfaoui, K.; Galai, M.; Touhami, M.E.; Ouhssine, M.; Guessous, Z. Corrosion inhibition in 1M HCl of mild steel with *Thymus leptobotrys* Murb essential oil (TLMEO): Electrochemical measurements and Density Function Theory (DFT) and Molecular Dynamics (MD) simulations. *J. Appl. Electrochem.* **2024**, *54*, 1279–1297. [\[CrossRef\]](#)
20. Daoudi, W.; Dagdag, O.; Verma, C.; Berdimurodov, E.; Oussaid, A.; Berisha, A.; Oussaid, A.; Abboud, M.; El Aatiaoui, A. *Rosmarinus officinalis* L. Oil as an Eco-Friendly corrosion inhibitor for mild steel in acidic Solution: Experimental and computational studies. *Inorg. Chem. Commun.* **2024**, *161*, 112030. [\[CrossRef\]](#)
21. Himeur, T.; Rouibah, K.; Ferkous, H.; Boublia, A.; Rachedi, K.O.; Harrouche, K.; Boulechfar, C.; Abdennouri, A.; Benguerba, Y. Unlocking the power of *Inula Viscosa* essential oil: A green solution for corrosion inhibition in XC48 steel within acidic environments. *Process Saf. Environ. Prot.* **2024**, *187*, 1422–1445. [\[CrossRef\]](#)
22. Haddou, S.; Zaidi, K.; Dagdag, O.; Hbika, A.; Adil Mahraz, M.; Bouhrim, M.; Alqahtani, A.S.; Noman, O.M.; Kim, H.; Aouniti, A.; et al. Theoretical and Electrochemical Evaluation of *Cannabis sativa* L. Extracts as Corrosion Inhibitors for Mild Steel in Acidic Medium. *ChemistryOpen* **2025**, *14*, e202400273. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Aboubi, M.E.; Hmada, A.; Kharbouch, O.; Saber, I.; Safi, Z.; Hsissou, R.; Wazzan, N.; Bikri, S.; Dkhireche, N.; Aouane, E.M. Theoretical and electrochemical investigation of citrus limon peel essential oil as green corrosion inhibitor for mild steel in 1 M HCl. *Next Mater.* **2025**, *9*, 101259. [\[CrossRef\]](#)
24. Neese, F. Software update: The ORCA program system—Version 5.0. *WIREs Comput. Mol. Sci.* **2022**, *12*, e1606. [\[CrossRef\]](#)
25. Koopmans, T. Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atoms. *Physica* **1934**, *1*, 104–113. [\[CrossRef\]](#)
26. Koch, W.; Holthausen, M.C. *A Chemist's Guide to Density Functional Theory*; John Wiley & Sons: Hoboken, NJ, USA, 2015.
27. Karezani, E.; Hallajisani, A.; Asgarpour Khansary, M. A quantum mechanics/molecular mechanics (QM/MM) investigation on the mechanism of adsorptive removal of heavy metal ions by lignin: Single and competitive ion adsorption. *Cellulose* **2017**, *24*, 3131–3143.
28. Azgaou, K.; Chkirate, K.; Ech-chihbi, E.; Saufi, H.; Ksama, S.; Benmessaoud, M.; Essassi, E.M.; Sebbar, N.K.; El Hajjaji, S. Electrochemical and surface analysis of a novel pyrazole derivative for corrosion protection of C38 steel in 1 M HCl solution. *J. Electroanal. Chem.* **2026**, *1013*, 120142. [\[CrossRef\]](#)
29. El Nemr, A.; Elhebshi, A.; Ashour, I.; El-Deab, M.S.; Barghout, N.A.; Eddy, N.O.; Ragab, S. Camphor tree bark extract as green corrosion inhibitor of LCS in 0.5 M H₂ SO₄ with and without salt effect. *J. Chin. Chem. Soc.* **2024**, *71*, 174–196. [\[CrossRef\]](#)
30. Paul, P.K.; Yadav, M. Investigation on corrosion inhibition and adsorption mechanism of triazine-thiourea derivatives at mild steel / HCl solution interface: Electrochemical, XPS, DFT and Monte Carlo simulation approach. *J. Electroanal. Chem.* **2020**, *877*, 114599. [\[CrossRef\]](#)

31. Acidi, A.; Sedik, A.; Rizi, A.; Bouasla, R.; Rachedi, K.O.; Berredjem, M.; Delimi, A.; Abdennouri, A.; Ferkous, H.; Yadav, K.K.; et al. Examination of the main chemical components of essential oil of *Syzygium aromaticum* as a corrosion inhibitor on the mild steel in 0.5 M HCl medium. *J. Mol. Liq.* **2023**, *391*, 123423. [\[CrossRef\]](#)
32. Al-Amiry, A.A.; Isahak, W.N.R.W.; Al-Azzawi, W.K. Corrosion Inhibitors: Natural and Synthetic Organic Inhibitors. *Lubricants* **2023**, *11*, 174. [\[CrossRef\]](#)
33. Lukovts, I.; Kálmán, E.; Zucchi, F. Corrosion Inhibitors—Correlation Between Electronic Structure and Efficiency. *Corrosion* **2001**, *57*, 3–8. [\[CrossRef\]](#)
34. Elfarhani, F.; Faydy, M.E.; Ouakki, M.; Benzekri, Z.; Boukhris, S.; Elfakir, Z.; Bouzakraoui, S.; Benhiba, F.; Zarrouk, A.; Touhami, M.E. Unraveling the Adsorption and Corrosion Resistance Mechanisms of Pyran-Pyrazole Analogs for Carbon Steel Corrosion in Hydrochloric Acid Based on Practical Approaches and Theoretical Calculations. *J. Bio-Tribo-Corros.* **2024**, *10*, 33. [\[CrossRef\]](#)
35. Aribou, Z.; Ouakki, M.; Khemmou, N.; Sibous, S.; Ech-chihbi, E.; Benzekri, Z.; Galai, M.; Boukhris, S.; AlObaid, A.A.; Warad, I.; et al. Detailed experimental of indazole derivatives as corrosion inhibitor for brass in acidic environment: Electrochemical/theoretical/surface studies. *J. Appl. Electrochem.* **2024**, *54*, 393–411. [\[CrossRef\]](#)
36. Kumar, H.; Yadav, V. Highly efficient and eco-friendly acid corrosion inhibitor for mild steel: Experimental and theoretical study. *J. Mol. Liq.* **2021**, *335*, 116220. [\[CrossRef\]](#)
37. Hjouji, K.; Atemni, I.; Haldhar, R.; Ouakki, M.; Ainane, T.; Taleb, M.; Kim, S.-C.; Rais, Z. Green corrosion inhibition of mild steel in acidic media using *Datura stramonium* seed extract: A study for sustainable engineering applications. *Chin. J. Chem. Eng.* **2025**, *80*, 281–302. [\[CrossRef\]](#)
38. Sabiha, M.; Kerroum, Y.; El Hawary, M.; Boudalia, M.; Bellaouchou, A.; Hammani, O.; Amin, H.M. Investigating the adsorption and corrosion protection efficacy and mechanism of marjoram extract on mild steel in HCl medium. *Molecules* **2025**, *30*, 272. [\[CrossRef\]](#) [\[PubMed\]](#)
39. Ruiyu, B.; Wei'an, H.; Jianghong, J.; Yanming, Z.; Yunfeng, L.; Zengbao, W. Multiscale Computational Study of Corrosion Inhibition Mechanism for Five Cyclic Amino Acids Based on Density Functional Theory (DFT) and Molecular Dynamics (MD) Simulations. *J. Chin. Soc. Corros. Prot.* **2025**, *46*, 261–272.
40. Mortadi, K.; El Amri, A.; Ouakki, M.; Hsissou, R.; Jebli, A.; Lebkiri, A.; Safi, Z.; Wazzan, N.; Berisha, A.; Cherkaoui, M. Electrochemical and theoretical studies on a bioactive *Juniperus oxycedrus* essential oil as a potential and ecofriendly corrosion inhibitor for mild steel in 1.0 M HCl environment. *Inorg. Chem. Commun.* **2024**, *162*, 112196. [\[CrossRef\]](#)
41. Tluangi, L.; Mishra, R.K.; Rajan, J.P.; Malviya, M.; Pathak, R.; Singh, A.K.; Sehrawat, R.; Sharma, D.K.; Pandey, S.K.; Mangla, B. Green corrosion inhibition of mild steel in acidic media: Electrochemical behavior and theoretical studies of *Zingiber mioga* essential oil. *Environ. Sci. Pollut. Res.* **2026**, *33*, 275–290. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Haque, J.; Verma, C.; Srivastava, V.; Nik, W.W. Corrosion inhibition of mild steel in 1M HCl using environmentally benign *Thevetia peruviana* flower extracts. *Sustain. Chem. Pharm.* **2021**, *19*, 100354. [\[CrossRef\]](#)
43. Gadow, H.S.; Fakeeh, M. Green inhibitor of carbon steel corrosion in 1 M hydrochloric acid: *Eruca sativa* seed extract (experimental and theoretical studies). *RSC Adv.* **2022**, *12*, 8953–8986. [\[CrossRef\]](#) [\[PubMed\]](#)
44. Ou-Ani, O.; Zgueni, H.; Oucheikh, L.; Youssefi, Y.; Salah, M.; Matine, A.; Mabrouk, E.H.; Oubair, A.; Chebabe, D.; Znini, M. Experimental and theoretical studies of the effect of *Ballota hirsuta* essential oil on carbon steel corrosion in a molar concentration of HCl. *J. Mol. Struct.* **2025**, *1332*, 141657. [\[CrossRef\]](#)
45. Mahraz, M.A.; Salim, R.; Loukili, E.H.; Laftouhi, A.; Haddou, S.; Elrherabi, A.; Bouhrim, M.; Herqash, R.N.; Shahat, A.A.; Eto, B. Ephedra fragilis plant extract: A groundbreaking corrosion inhibitor for mild steel in acidic environments—electrochemical, EDX, DFT, and Monte Carlo studies. *Open Life Sci.* **2025**, *20*, 20221050. [\[PubMed\]](#)
46. Shahini, M.; Ramezanzadeh, M.; Bahlakeh, G.; Ramezanzadeh, B. Superior inhibition action of the Mish Gush (MG) leaves extract toward mild steel corrosion in HCl solution: Theoretical and electrochemical studies. *J. Mol. Liq.* **2021**, *332*, 115876. [\[CrossRef\]](#)
47. Yıldız, R.; Arslanhan, S.; Döner, A.; Baran, M.F. Corrosion behavior of mild steel in 1 M HCl with *Cyclotrichium niveum* as a green inhibitor. *Mater. Chem. Phys.* **2024**, *312*, 128654. [\[CrossRef\]](#)
48. Chaouche, R.; Tiskar, M.; Larhlid, I.; Ihamdane, R.; El Amri, A.; Ait Mansour, A.; Hsissou, R.; Salghi, R.; Cheikhi, N.; Chaouch, A. Exploring of the *Origanum Compactum* essential oil as an ecofriendly corrosion inhibitor for mild steel in 1M HCl environment: Experimental, DFT, MD, DFTB and PDOS approaches. *J. Mol. Struct.* **2025**, *1327*, 141112. [\[CrossRef\]](#)
49. Rizi, A.; Sedik, A.; Acidi, A.; Rachedi, K.O.; Ferkous, H.; Berredjem, M.; Delimi, A.; Abdennouri, A.; Alam, M.; Ernst, B.; et al. Sustainable and Green Corrosion Inhibition of Mild Steel: Insights from Electrochemical and Computational Approaches. *ACS Omega* **2023**, *8*, 47224–47238. [\[CrossRef\]](#) [\[PubMed\]](#)
50. Lashgari, S.M.; Bahlakeh, G.; Ramezanzadeh, B. Detailed theoretical DFT computation/molecular simulation and electrochemical explorations of *Thymus vulgaris* leave extract for effective mild-steel corrosion retardation in HCl solution. *J. Mol. Liq.* **2021**, *335*, 115897. [\[CrossRef\]](#)

51. Ansari, A.; Youssefi, Y.; Tanghourte, M.; Ouassou, N.; Asoufar, N.; Znini, M.; Lgaz, H.; Mabrouk, E.H.; Azrour, M.; Lee, H.-S.; et al. Assessment of Warionia saharea Essential Oil as a Green Corrosion Inhibitor for Mild Steel in HCl: Experimental and Computational Studies. *Coatings* **2024**, *14*, 1164. [[CrossRef](#)]
52. Azzouni, D.; Alaoui Mrani, S.; Bertani, R.; Alanazi, M.M.; En-nabety, G.; Taleb, M. Experimental and Theoretical Investigation of the Inhibitor Efficiency of Eucalyptus globulus Leaf Essential Oil (EuEO) on Mild Steel Corrosion in a Molar Hydrochloric Acid Medium. *Molecules* **2024**, *29*, 3323. [[CrossRef](#)] [[PubMed](#)]
53. Monteiro, H.L.; Ribeiro, A.F.; Joyce Correia Modesto, M.; Helena De Aguiar Andrade, E.; Souza, J.A.D.S.; Nero, J.D.; Silva Rente, A.D.F.; Noce, R.D.; Souza, J.P.I.D.; Alberto Brito Da Silva, C., Jr.; et al. Investigation of the Anticorrosive Activity of *Piper divaricatum* Essential Oil on Steel in 1 M HCl. *ACS Omega* **2024**, *9*, 45348–45357. [[CrossRef](#)] [[PubMed](#)]
54. Ouakki, M.; Ech-chihbi, E.; Chahmout, H.; Aribou, Z.; Lachhab, R.; Kharbouch, O.; Rbaa, M.; Cherkaoui, M. High-efficiency imidazole derivatives as corrosion inhibitors for mild steel in sulfuric acid: Experimental and theoretical analysis. *J. Mol. Liq.* **2025**, *433*, 127922. [[CrossRef](#)]
55. Song, X.; Zhang, Y.; Yan, C.; Jiang, W.; Chang, C. The Langmuir monolayer adsorption model of organic matter into effective pores in activated carbon. *J. Colloid Interface Sci.* **2013**, *389*, 213–219. [[CrossRef](#)] [[PubMed](#)]
56. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. [[CrossRef](#)]
57. Zheng, Q.; Liang, C.; Jiang, J.; Li, S. Understanding anti-corrosion mechanisms of the 2,6-dithiopurine (DTP) inhibitor molecule on iron surfaces. *J. Environ. Chem. Eng.* **2024**, *12*, 113176. [[CrossRef](#)]
58. Döner, A.; Yıldız, R.; Arslanhan, S.; Baran, M.F. A comprehensive analysis of Arum dioscoridis plant leaf extract as a corrosion inhibitor for mild steel in 1 M HCl: Synthesis, characterization, surface analysis observations, experimental and DFT studies. *J. Taiwan Inst. Chem. Eng.* **2025**, *169*, 105955. [[CrossRef](#)]
59. Carmona-Hernandez, A.; Barreda-Serrano, M.C.; Saldarriaga-Noreña, H.A.; López-Sesenes, R.; González-Rodríguez, J.G.; Mejía-Sánchez, E.; Ramírez-Cano, J.A.; Orozco-Cruz, R.; Galván-Martínez, R. Insight into the corrosion inhibition performance of Pistia stratiotes leaf extract as a novel eco-friendly corrosion inhibitor for mild steel in 1 M HCl solution. *Molecules* **2024**, *29*, 5243. [[CrossRef](#)] [[PubMed](#)]
60. Lin, B.; Zhou, X.; Duan, T.; Zhao, C.; Zhu, J.; Xu, Y. Experimental and theoretical study on corrosion inhibition and adsorption performance of Ipomoea batatas L. leaf extract for mild steel. *Arab. J. Chem.* **2024**, *17*, 105410. [[CrossRef](#)]
61. Azeez, Y.H.; Mamand, D.M.; Omer, R.A.; Awla, A.H.; Omar, K.A. Investigation of corrosion inhibition and adsorption properties of quinoxaline derivatives on metal surfaces through DFT and Monte Carlo simulations. *Corros. Rev.* **2024**, *42*, 775–793. [[CrossRef](#)]
62. Boutoumit, A.; Elhawary, M.; Bellaouchou, A.; Boudalia, M.; Hammani, O.; José Garcia, A.; Amin, H.M.A. Electrochemical, Structural and Thermodynamic Investigations of Methanolic Parsley Extract as a Green Corrosion Inhibitor for C37 Steel in HCl. *Coatings* **2024**, *14*, 783. [[CrossRef](#)]
63. Al-Amiery, A.; Isahak, W.N.R.W.; Al-Azzawi, W.K. Multi-method evaluation of a 2-(1,3,4-thiadiazole-2-yl)pyrrolidine corrosion inhibitor for mild steel in HCl: Combining gravimetric, electrochemical, and DFT approaches. *Sci. Rep.* **2023**, *13*, 9770. [[CrossRef](#)] [[PubMed](#)]
64. Razali, N.Z.K.; Wan Hassan, W.N.S.; Sheikh Mohd Ghazali, S.A.I.; Mohd Shotor, S.N.; Dzulkifli, N.N. DFT, Fukui indices, and molecular dynamic simulation studies on corrosion inhibition characteristics: A review. *Chem. Pap.* **2024**, *78*, 715–731. [[CrossRef](#)]
65. Parr, R.G.; Yang, W. Density functional approach to the frontier-electron theory of chemical reactivity. *J. Am. Chem. Soc.* **1984**, *106*, 4049–4050. [[CrossRef](#)]
66. Guo, L.; Kaya, S.; Obot, I.B.; Zheng, X.; Qiang, Y. Toward understanding the anticorrosive mechanism of some thiourea derivatives for carbon steel corrosion: A combined DFT and molecular dynamics investigation. *J. Colloid Interface Sci.* **2017**, *506*, 478–485. [[CrossRef](#)] [[PubMed](#)]
67. Khamis, E.; Abdel-Gaber, A.M.; Morshidy, M.; Mohamed, M.E. Eco-friendly inhibitors for sustainable corrosion protection of mild steel under oilfield acidizing conditions. *Sci. Rep.* **2025**, *15*, 42549. [[CrossRef](#)] [[PubMed](#)]
68. Carranza, M.S.S.; Reyes, Y.I.A.; Gonzales, E.C.; Arcon, D.P.; Franco, F.C. Electrochemical and quantum mechanical investigation of various small molecule organic compounds as corrosion inhibitors in mild steel. *Heliyon* **2021**, *7*, e07952. [[CrossRef](#)] [[PubMed](#)]
69. Fernine, Y.; Salim, R.; Arrousse, N.; Haldhar, R.; Hajjaji, F.E.; Kim, S.-C.; Touhami, M.E.; Taleb, M. Anti-corrosion performance of Ocimum basilicum seed extract as environmental friendly inhibitors for mild steel in HCl solution: Evaluations of electrochemical, EDX, DFT and Monte Carlo. *J. Mol. Liq.* **2022**, *355*, 118867. [[CrossRef](#)]
70. Melhi, S.; Bedair, M.A.; Alosaimi, E.H.; Younes, A.A.; El-Shwiniy, W.H.; Abuelela, A.M. Effective corrosion inhibition of mild steel in hydrochloric acid by newly synthesized Schiff base nano Co (II) and Cr (III) complexes: Spectral, thermal, electrochemical and DFT (FMO, NBO) studies. *RSC Adv.* **2022**, *12*, 32488–32507. [[CrossRef](#)] [[PubMed](#)]
71. Km, S.; Praveen, B.M.; Devendra, B.K. A review on corrosion inhibitors: Types, mechanisms, electrochemical analysis, corrosion rate and efficiency of corrosion inhibitors on mild steel in an acidic environment. *Results Surf. Interfaces* **2024**, *16*, 100258. [[CrossRef](#)]

72. Bazanov, D.R.; Avdeev, Y.G.; Nenasheva, T.A.; Luchkin, A.Y.; Mazur, D.M.; Makarychev, Y.B.; Andreeva, T.E.; Marshakov, A.I.; Kuznetsov, Y.I. Aldehyde–Aminotriazole Condensation Products as Novel Corrosion Inhibitors for Mild Steel in Hydrochloric Acid. *Polymers* **2025**, *17*, 2761. [[CrossRef](#)] [[PubMed](#)]
73. Ouakki, M.; Aribou, Z.; El Hajri, F.; Ech-chihbi, E.; Benzekri, Z.; Lachhab, R.; Srhir, B.; Patrick, M.; Almeer, R.; Galai, M. A study on the corrosion inhibition impact of newly synthesized quinazoline derivatives on mild steel in 1.0 M HCl: Experimental, surface morphological (SEM-EDS and FTIR) and computational analysis. *Int. J. Electrochem. Sci.* **2024**, *19*, 100795. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.