

Experimental, Computational and Phytochemical Screening of Plant Bio-Extract as Green Corrosion Inhibitors for Metals in Acid Media

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Abstract

The study aimed to validate the experimental, computational and phytochemical efficacy of plant bio extract from *elusine indica*, *cassytha filiformis* and *morus rubra* as metallic corrosion inhibitors in HCl and H₂SO₄ solutions. The plant leaves were collected from Nekede and Ihiagwa, Imo State, Nigeria and prepared. Phytochemical results showed all extracts exhibited very high (+++) alkaloid content, moderate (++) to very high (+++) phenolic content, trace (+) amounts of flavonoids, moderated (++) tannin levels, moderate (++) to very high (+++) terpenoid levels, saponin was absent in *Elusine indica* yet present (+) in others, phytates were moderate (++) in others but absent in *Elusine indica*, cardiac glycosides were detected at trace (+) levels in others and absent in *Morus rubra*. Alkaloid ranged from 983-1,335 mg/100 g, flavonoid from 58-293 mg/100 g, phenolic content from 38.7-89.4 mg GAE/g, saponin content from 10-165 mg/100 g, phytate from 35-90 mg/100 g, terpenoids from 235-920 mg/100 g, steroids had 28-217 mg/100 g, cardiac glycosides had 5–45 mg/100 g and tannins from 375–395 mg/100 g. Quantum chemical and molecular dynamics were conducted to ascertain their corrosion inhibition mechanisms on Fe(110) surfaces. Figures 4.93–4.98 (a–g) presented the optimized molecular structures, electron density distributions, electrophilic (F[−]) and nucleophilic (F⁺) Fukui functions, frontier molecular orbitals (HOMO and LUMO), and molecular dynamics snapshots of adsorption. The HOMO and LUMO orbitals were predominantly localized on heteroatoms (oxygen) and carbonyl groups, identifying them as primary adsorption centers. Mulliken charge analysis further confirmed these sites as reactive points for electron donation to the Fe surface. TD exhibited the highest EHOMO, while TD and CPS showed the lowest ELUMO. Binding energies ranged from 45.26 kcal/mol (PA) to 515.3 kcal/mol (HX). These results collectively validate these phytochemical molecules, via heteroatom-mediated chemisorption and surface coverage, are effective eco-friendly corrosion inhibitors. To fully validate the inhibition performance of these extracts, it is recommended that electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and surface morphology analyses be conducted to ascertain the inhibition mechanism.

Keywords: Corrosion, Phytochemicals, Quantum chemistry and Dynamics simulations.

1.0 Introduction

Corrosion of metals, particularly mild steel, in acidic environments such as hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) poses serious industrial challenges, leading to substantial damage, loss of functionality, and economic burden (Fouda & Tilp, 2021). Corrosion inhibitors mitigate material degradation by reducing the corrosion rate. Synthetic inhibitors are widely used for their effectiveness but are often environmentally hazardous, biodegradability, regulatory constraints and expensive (Onakpa *et al.*, 2025). In response, the recent trend in corrosion science has increasingly favored natural, plant-based extracts as sustainable, biodegradable, cost-effective alternatives (Medupin *et al.*, 2023).

Plant extracts are rich sources of phytochemicals including alkaloids, flavonoids, tannins, phenolic acids, terpenoids, and saponins, which can absorb onto metallic surfaces via electron-donation, π -electron interactions, and functional group binding, thus forming protective films that inhibit the electrochemical corrosion process (Gabsi *et al.*, 2023). Herbal preparations are the oldest and richest remedies in human health care, and today, the human being studies, tests and regains confidence in natural, effective remedies that have survived for several generations (Memete *et al.*, 2022). Adsorption of these compounds commonly follows established isotherms such as Langmuir or Freundlich, reflecting physico-chemical binding modes and enabling predictable modeling of inhibitor–substrate interactions. Numerous experimental studies confirm high inhibition efficiencies often exceeding 90 % for plant extracts in acidic media under optimized conditions (Palumbo *et al.*, 2023).

Quantum chemistry provides a fundamental theoretical framework for describing chemical reactivity and molecular interactions at the electronic and atomic levels through the application of quantum mechanical principles (Al-Amiery *et al.*, 2023). In corrosion science, approaches have become increasingly important for elucidating the inhibition mechanisms of organic and bio-based compounds by directly linking their electronic structure to adsorption behavior and corrosion protection efficiency on metal surfaces (Yang *et al.*, 2022). Recent advances in quantum chemical corrosion studies also emphasize the importance of local reactivity descriptors, which allow site-specific identification of reactive centers within inhibitor molecules (Shaker *et al.*, 2024). Quantum chemical methods have also played a crucial role in advancing the development of green and bio-based corrosion inhibitors, where experimental identification of active components and inhibition mechanisms is often complicated by the chemical complexity of plant extracts (Lgaz *et al.*, 2023). Dynamic simulation has become a critical theoretical tool for investigating corrosion inhibition mechanisms at the atomic and molecular levels by explicitly modeling time-dependent interactions between inhibitor molecules, metal surfaces, and corrosive media (Zhang *et al.*, 2020). It captures the real-time motion of atoms and molecules, enabling realistic observation of adsorption behavior, molecular orientation, surface coverage, and stability of inhibitor films under simulated corrosive conditions (Obot & Ebenso, 2021). In recent years, dynamic simulation has increasingly been integrated with other computational approaches to improve predictive reliability in corrosion studies. Its methods have also proven especially useful in the study of green and bio-based corrosion inhibitors (Verma *et al.*, 2021).

Herbal extract has been shown to inhibit corrosion of mild steel in acidic media, with efficiency increasing as concentration increased, and verified through electrochemical methods such as polarization and impedance spectroscopy (Sharma *et al.*, 2019). However, comprehensive studies combining qualitative and quantitative phytochemical characterization with practical corrosion inhibition assessment especially in HCl and H₂SO₄ environments remain scarce for *Elusine indica*, *Cassytha filiformis*, and *Morus rubra*. Thus, there is a clear

research gap in correlating the specific experimental, computational and phytochemical composition of these extracts with their efficacy as corrosion inhibitors. The study therefore aims to validate the metallic corrosion inhibition efficacy of bio extract from *elusine indica*, *cassytha filiformis* and *morus rubra* in HCl and H₂SO₄ solutions.

2.0 Materials and Methods

The materials used in this study include: Plant leaves (*Elusine indica*, *Cassytha filiformis* and *Morus rubra*), Ethanol (Analar grade), ammonium hydroxide silica gel and sprayed with Dragendorff compound, chloroform, hexane, HCl, Glacial acetic acid, acetone, methanol etc.

Extraction of the plant extracts: Plant leaves were collected from Nekede and Ihiagwa, Imo State, Nigeria. Leaves were sun dried for four days, ground to increase the surface area and stored. 30g each of the ground leaves was measured, soaked in 1000 ml of ethanol for 48 hrs, filtered. The extract-solvent mixture was concentrated and distilled. The plant extract was weighed and stored for the experimental, computational and phytochemical study.

2.1 Quantum Chemical Calculations and Dynamic Molecular Simulation Studies

Quantum chemical calculations method have a potential application towards the design and development of organic corrosion inhibitors in corrosion field. To this end, molecular simulation study was performed to simulate the adsorption structure of the key components of the plants extract. The quantum chemical parameters for the relative major constituents of the plant extracts were also computed and recorded.

Density functional theory (DFT) calculations were carried out using the electronic structure program DMol3 using a Mulliken population analysis (Martinez and Metikos-Hukovic, 2003). The electronic parameters for the simulation involve the Perdew–Wang (PW) local correlation density functional and restricted spin polarization using the DND basis set. For core electrons at the lowest atomic orbitals the DFT semicore pseudopotentials (DSPP) was active (Bentiss *et al.*, 2005). The quantum chemical parameters were calculated for 2-heptanone (HP), 2-tridecene (TC), 2-hexanone (HX), 4-tetradecene (TT), cyclopentanone (CP), 1,3-dioxane (DX), Propanoic Acid (PA), cyclopentasiloxane (CPS), 3, 7 – Dimethyl (DM), 1, 3, 6 –octadiene (OD), Undecene (UC) and tridecane (TD) molecules in protonated forms. Self-consistent reaction field (SCRF) methods were used to perform calculations in aqueous solution. These methods model the solvent as a continuum of uniform dielectric constant, and the solute is placed in the cavity within it. The Self-Consistent Field (SCF) procedure was performed with a convergence of 10^{-5} and a Fermi smearing parameter of 0.005 Hartree to increase the rate of SCF convergence. The geometry optimization was achieved using the COMPASS force field and Smart minimization method. Quantum chemical parameters such as E_{HOMO} , E_{LUMO} , the energy gap ΔE ($E_{\text{LUMO}} - E_{\text{HOMO}}$), and adsorption energy were obtained for the molecules in order to predict its activity toward the Fe surface. The aforementioned parameters were determined after geometric optimization with respect to all nuclear coordinates.

2.2 Qualitative and Quantitative Analysis of Phytochemical Properties of the Extracts

The solvent free extract obtained was subjected to qualitative test for the identification of various plant constituent from the sample. Phytochemical characterization of genotypes is qualitative; data were collected on the presence or absence of the metabolites essential oils, anthraquinones, base alkaloids, weakly base alkaloids, phenols and tannins, quaternary salts, flavonoids, and saponins of the plant. Materials on which determinations were performed are shadow-dried and converted to dust using a laboratory mill. Thus, these processed materials

were exposed 10 times to hexane for fast removal. After this procedure, materials were kept under hexane for 24 hrs, filtered, and left for 5 to 7 days to allow the residual hexane to evaporate. This processed material was covered with ethanol and maintained for 24 hrs. A series of several filtering were performed until the liquid material turned into hyaline aspect. Assays were conducted with this liquid to determine the presence or absence of each one of the above-mentioned metabolites. For base and weakly base alkaloids, as well as for quaternary salts, the raw extract of ethanol evaporated until complete dryness received hydrochloric acid at 10%. Mixed material was passed through a separation funnel. The first separation was attained with chloroform. To the aqueous phase that remained in the funnel, a portion of ammonium hydroxide was added until it reached a basic PH, and then it was washed again with chloroform to obtain the second phase. The third phase had been left in the funnel. Using a capillary tube, a few drops of each one of the three phases were placed on plaques of silica gel and sprayed with Dragendorff compound. Assays in which the phase responded positively to the presence of alkaloids formed a black spot. With this test, it was easy to determine the type of alkaloids present on each phase (first, second, or third) reacted to the Dragendorff compound. These results were confirmed by treating the three phases with Meyer's reactive resulting in a white precipitate with a small amount of the raw extract.

Terpenoids: 1g of the sample was weighed and soaked with 10 ml of petroleum ether for 15mins to get the extract, the mixture was filtered using filter paper and the absorbance was read at a wave length of 420nm.

Flavonoids: 1g of the sample was extracted with 10 ml of 80% Methanol; it was allowed to stand for 2 hours, was filtered into a Petri dish and allowed to dry in the oven at 40⁰C. The Petri dish was weighed constantly as it dries.

Tannins: 1g of the sample was weighed and extracted with 25 ml of solvent mixture of 80:20 acetones, 10% of Glacial acetic acid was added to the mixture for 5 hours, the mixture was filtered and the absorbance was measured at 500nm. A standard graph with 10,20,30,40,50 mg/100g of Tannic Acid were made. The concentration of tannin was read taking into consideration the dilution factor.

Alkaloids: 1g of the sample (W) was weighed and added to 20ml of 10% Acetic Acid in Ethanol. The mixture was shaken and allows standing for 4 hours, it was filtered and the filtrate was evaporated to about a quarter of its original volume. One drop of concentrated Ammonia was added. The precipitate formed was filtered through a weighed (W₁) filter paper. The filter paper was left to dry in the oven at 60⁰C. The filter paper was weighed after it dries to constant weight.

$$\% \text{Alkaloids} = \frac{W_2 - W_1}{W} \times 100 \quad (3.1)$$

Where W is the weight of the sample, W₂ is the weight of the filter paper before the filtration of the precipitate and W₁ is the weight after the filtrate was dried to constant weight.

Steroids: 5g of the sample was added to 100ml of water, 0.1M Ammonium Hydroxide was added to take PH to 9.1. 2ml of petroleum ether, 3ml acetic anhydride and concentrated H₂SO₄ was added and the absorbance was read at 420nm.

Cardiac Glycosides: 1g of the sample was extracted with 40ml of water and was place in the oven at 100⁰C for 15min. 1ml of extract + 5ml of water were added to 2ml Glacial Acetic

Acid plus one drop of FeCl_3 . 1ml Concentrated H_2SO_4 was added and absorbance of the resulting solution was measured at 410nm.

Phytates: 1g of the sample was extracted with 0.2M HCl. 0.5ml of extract was added into 1ml Fe^{3+} solution e.g. Ferric Ammonium Sulphate. The tube in the water bath was heated for 30mins. 1ml of supernatant was added to 1.5 ml of 2, 2-Bipyridine solution. 519nm was measured with distilled water as blank.

Phenols/Phenolics/Phenolic Acids: 2ml of the extract was mixed with 0.5ml of Folin-Ciocalteu Reagent and 1.5ml Sodium Carbonate (20%). It was mixed for 15 sec and allowed to stand at 40°C for 30min to develop colour. A_{765} was measured and express as GAE/g Gallic Acid Equivalent.

Saponins: 1g of the sample was weighed and added to 5ml of 20% ethanol and heated with water bath at 55°C for 4hours. The residue was filtered and washed with 20% ethanol twice. The extract was reduced to 5ml in the oven. 5ml of petroleum ether was added to the concentrated extract inside a separating funnel. Petroleum ether layer was discarded and 3ml of butanol was added to it. The butanol layer was poured into a weighed petri dish and was put in the oven to evaporate to dryness and the residue was weighed.

3.0 Results and Discussion

3.1 Quatum and Chemical Computational Studies of Vital constituents of the Plant Extracts

The results of quatum computational studies as well as the dynamic simulation of the relative components of the plants extract are fully recorded. Figure 4.93 to 4.98 (a–g), showed the Optimized structure, Electron density, Electrophilic, Nucleophilic, HOMO, LUMO, Molecular dynamics model of the adsorption of single molecule of the various molecules on Fe. From our results, the HOMO and LUMO energy orbitals are mostly localized on the heteroatoms (O) and carbonyl groups present in the various molecules. Mulliken charge analysis was used to determine the adsorption centers of the inhibitor. The electron donating ability of the molecules is related with the E_{HOMO} . The value of E_{HOMO} shows the tendency of the molecules to donate electrons to the acceptor species with empty molecular orbitals. The tendency of a molecule to accept the electrons is related to E_{LUMO} (Bentiss *et al.*, 2007). As can be seen from Figure 4.93 to 4.98(e) and (f), the HOMO and the LUMO are distributed over the entire molecules studied due to the presence of lone electron pairs in the O atoms and the delocalization of p-electrons. The result so far suggests that the heteroatoms are the probable reactive sites for adsorption of most of the studied molecules on the metal surface. The adsorption of an inhibitor on metal surface can occur on the basis of donor–acceptor interactions between the lone electron pairs in heteroatoms together with the p-electrons of heterocyclic compound and the vacant d-orbital of the metal surface atoms (Chidiebere *et al.*, 2014). It is obvious that TD had the highest E_{HOMO} in the protonated form, showing that the electron-donating tendency of TD is greater than all the other molecules followed by PA, UC etc. Also, the LUMO energy is directly related to the electron affinity and shows the susceptibility of the molecule towards attack by nucleophiles. The lower the value of E_{LUMO} , the stronger the electron accepting ability of the molecule. It is clear that TD and CPS shows the lowest E_{LUMO} , making them the most likely molecules for the interaction of mild steel. Again, low values of the energy gap will provide good inhibition efficiencies, because the energy needed to excite an electron from the last occupied orbital will be low (Chidiebere *et al.*, 2014). A molecule with a low energy gap (ΔE) is expected to be more polarizable and is generally associated with high chemical reactivity and low kinetic stability, being regarded to as a soft molecule (Chidiebere *et al.*, 2015). The adsorption of inhibitor onto a metallic

surface occurs at the part of the molecule which has the greatest softness and lowest hardness (Schmitt and Bedbur, 1985). The result revealed that the order of the lowest energy gap value and lowest hardness is $DM < OD < CP < DX < HX < HP < TC < TT < PA < CPS < TD < UC$. If the studied molecules donate electrons to unoccupied d-orbital of metals and the electrons are accepted in the d-orbital of metals by using anti-bonding orbital to form covalent bond, the adsorption process is regarded as chemisorption, and there will be a relationship between the quantum chemical parameters and the inhibitive effect of the molecules. However, it is evident from the theoretical calculations that no direct correlation can be obtained.

The local reactivity of the molecules was analyzed by means of the Fukui indices (FI) to also assess the reactive regions in terms of nucleophilic (F^+) and electrophilic (F^-) behavior. Figure 4.93 to 4.98 (c & d) shows that the F^- functions correspond with the HOMO locations, indicating the sites through which the molecules could be adsorbed on the metal surface, whereas F^+ correspond with the LUMO locations, showing sites through which the molecules could interact with the nonbonding electrons in the metal. Molecular dynamics simulation was carried out to model different low energy adsorption configurations of the molecules on the Fe surface (Oguzie *et al.*, 2010). The Fe crystal was cleaved along the (110) plane because it has a density packed surface and the most stabilization at this position. Calculations were carried out in a 12×10 supercell using the COMPASS force field and the Smart algorithm with NVE (microcanonical) ensemble, a time step of 1 fs, and simulation time 5 ps. The geometry of the lower layers of the slab was constrained. The temperature was fixed at 350 K. Simulation was done using the optimized structure of the molecules and Fe. The system was quenched every 250 steps. Figure 4.93 to 4.98 (f) in each case shows the side views of the optimized (lowest energy) adsorption structures for the molecules on the Fe (110) surface from our simulation. The binding energy (E_{Bind}) which is important in characterizing the adsorption of molecules onto the Fe surface was estimated using the equation:

$E_{\text{Bind}} = E_{\text{total}} - (E_{\text{inhibitor}} + E_{\text{surface}})$, where $E_{\text{inhibitor}}$, E_{surface} , and E_{total} represent the energy of a single molecule of DM, OD, CP, DX, HX, HP, TC, TT, PA, CPS, TD, UC on the Fe slab without adsorption, and the total energy of the system containing a molecule and Fe surface, respectively. The obtained adsorption energy values are shown with HX (515.3 kcal/mol) as the highest and PA the lowest (45.26 kcal/mol). The obtained values were calculated by averaging the energies of five structures of lowest energy in each case. The estimated negative values of E_{Bind} of the molecules point towards their adsorption ability on the Fe surface (Oguzie *et al.*, 2012).

3.2 Electronic Properties and Molecular Dynamics of the Adsorption of Molecules of Various Compounds on Fe (110)

The optimized molecular geometry presented in panel (a) represents the lowest-energy conformation of the inhibitor species obtained via density functional theory (DFT) optimization. The geometric features such as bond lengths, ring conformations, and the positioning of heteroatoms inform reactivity tendencies because they determine how easily functional groups can interact with the metal surface (Sun *et al.*, 2022). Panel (b) shows the electron density distribution profile of the inhibitor. Electron density mapping highlights regions of high electron probability, often localized on heteroatoms or π systems. These high-density regions are more chemically reactive and likely to donate electron density to surface metal atoms during adsorption (Ahamad *et al.*, 2019). Panels (c) and (d) display the electrophilic (F^-) and nucleophilic (F^+) Fukui function maps, respectively. Local reactivity descriptors, like Fukui indices, provide site-specific predictions of where a molecule is most likely to donate or accept electron density during interaction with a surface (Yang *et al.*,

2022). Panels (e) and (f) illustrate the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively. Frontier molecular orbital theory has become a cornerstone in understanding corrosion inhibitor reactivity because the HOMO represents the electron-donating capability of the molecule, while the LUMO reflects its ability to accept electron density from the surface. Panel (g) presents a representative snapshot from a molecular dynamics (MD) simulation of the inhibitor on the Fe(110) surface under dynamic conditions. Molecular dynamics simulations extend static quantum chemical insights by modeling time-dependent interactions among inhibitor molecules, solvent, ions, and the metal surface (Obot & Ebenso, 2021).

CASSYTHA FILIFORMIS LEAF

Cyclopentanone

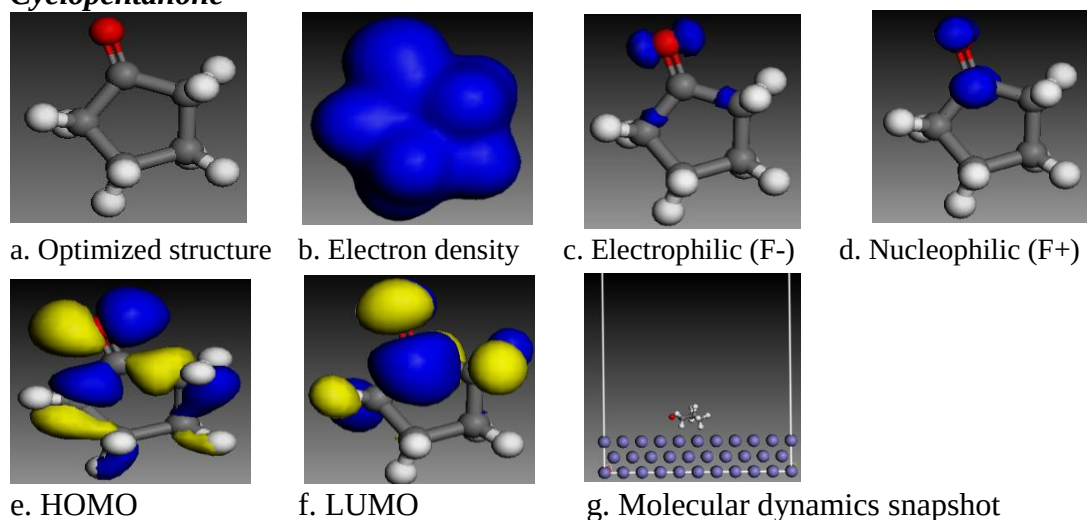
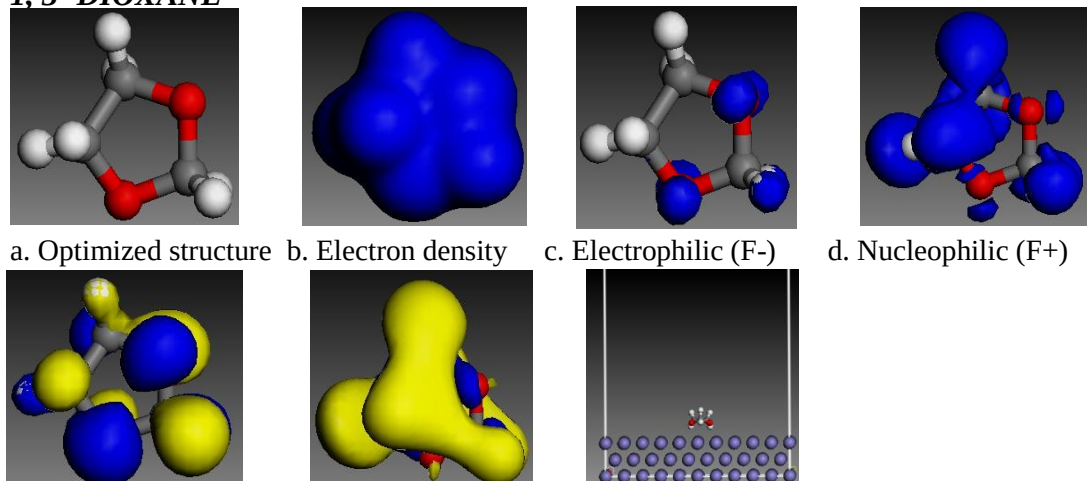


Figure 3.1: Electronic properties of CP: (a) Optimized structure, (b) Electron density, (c) Electrophilic f (-), (d) Nucleophilic f (+), (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of CP on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss. Inhibitors that adopt flat or near-parallel orientations tend to maximize surface contact, increasing multi-site interactions and forming a denser protective barrier against corrosive species (Lgaz *et al.*, 2023). Taken together, the panels (a–g) form a mechanistic chain explaining inhibitor adsorption on Fe(110).

1, 3- DIOXANE



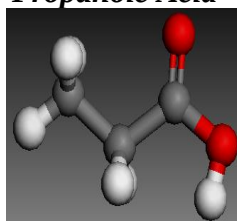
e. HOMO f. LUMO g. Molecular dynamics snapshot

Figure 3.2: Electronic properties of DX: (a) Optimized structure (b) Electron density, (c) Electrophilic $f(-)$, (d) Nucleophilic $f(+)$, (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of DX on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

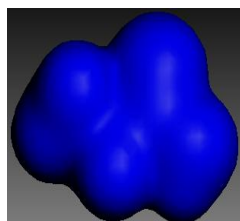
The optimized structure shown in panel (a) represents the minimum-energy conformation of 1,3-dioxane obtained through density functional theory optimization. This cyclic ether molecule adopts a relatively stable chair-like geometry, which minimizes steric strain while positioning the two oxygen atoms symmetrically within the ring (Li *et al.*, 2023). The electron density distribution illustrated in panel (b) reveals a clear localization of electron density around the oxygen atoms within the dioxane ring. These high-density regions correspond to lone-pair electrons, which are known to be the primary contributors to metal–inhibitor interactions in oxygen-containing organic compounds. The electrophilic Fukui function (F^-) shown in panel (c) identifies molecular regions susceptible to electrophilic attack, or more specifically, regions that can accept electron density. For adsorption phenomena, these regions play a role in stabilizing the inhibitor–metal complex through back-donation of electrons from the metal surface to the molecule after initial adsorption has occurred. The nucleophilic Fukui function (F^+) depicted in panel (d) highlights the regions most capable of donating electrons. In 1,3-dioxane, the highest F^+ values are concentrated around the oxygen atoms, confirming their role as primary adsorption centers. The frontier molecular orbitals further clarify the electronic reactivity of 1,3-dioxane. The HOMO distribution shown in panel (e) is predominantly localized around the oxygen atoms, indicating that these atoms are the most probable electron-donating sites during adsorption. The LUMO distribution presented in panel (f) represents regions capable of accepting electron density from the metal surface. For 1,3-dioxane, the LUMO is distributed around the ring system, including areas near the oxygen atoms, suggesting the molecule’s ability to participate in back-bonding interactions. The molecular dynamics snapshot shown in panel (g) provides time-dependent insight into the adsorption behavior of 1,3-dioxane on the Fe(110) surface under simulated conditions. The snapshot reveals that 1,3-dioxane tends to orient itself such that the oxygen atoms are directed toward the Fe surface, allowing sustained interaction through lone-pair donation. This orientation maximizes contact between the molecule and the metal, even though the molecule lacks bulky substituents or extended π -systems (Obot & Ebenso, 2021). Collectively, these results indicate that 1,3-dioxane can contribute to corrosion inhibition through physically stable and electronically favorable adsorption, particularly when present as part of a complex phytochemical extract.

MORUS RUBRA ROOT

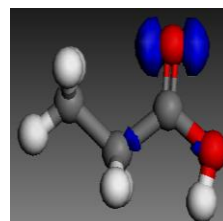
Propanoic Acid



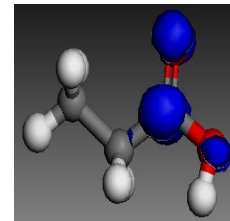
a. Optimized structure



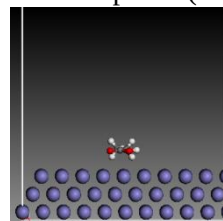
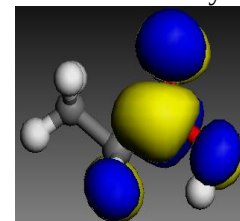
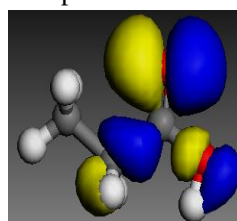
b. Electron density



c. Electrophilic (F^-)



d. Nucleophilic (F^+)



e. HOMO

f. LUMO

g. Molecular dynamics snapshot

Figure 3.3: Electronic properties of PA: (a) Optimized structure (b) Electron density, (c) Electrophilic $f(-)$, (d) Nucleophilic $f(+)$, (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of PA on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

The optimized structure shown in panel (a) represents the lowest-energy conformation of propanoic acid obtained through density functional theory calculations. The molecule adopts a relatively linear alkyl chain terminating in a carboxylic acid functional group. This functional group is of particular importance in corrosion inhibition because it contains two oxygen atoms with lone-pair electrons capable of interacting with metal surfaces. The electron density distribution illustrated in panel (b) shows pronounced electron localization around the carboxylate moiety, especially on the carbonyl oxygen and hydroxyl oxygen atoms. These electron-rich regions serve as the primary active centers for metal–inhibitor interaction. Electron density mapping is a crucial tool in corrosion studies because it reveals where electron donation to metal atoms is most likely to occur. The electrophilic Fukui function (F^-) presented in panel (c) identifies regions of the molecule that are most susceptible to electrophilic attack, or equivalently, regions capable of accepting electron density. In the context of adsorption on Fe(110), these sites are relevant for back-donation processes, where electron density is transferred from filled metal orbitals into antibonding or low-lying orbitals of the inhibitor molecule. Panel (d) shows the nucleophilic Fukui function (F^+), which highlights molecular regions most capable of donating electrons.

The HOMO distribution shown in panel (e) is concentrated around the oxygen atoms of the carboxyl group, confirming their role as primary electron donors during adsorption. A HOMO localized on heteroatoms is indicative of favorable interaction with metal surfaces, even for small molecules with limited structural complexity. The LUMO distribution in panel (f) reveals regions capable of accepting electron density from the Fe surface. In propanoic acid, the LUMO is partially distributed over the carboxyl group, enabling back-donation from metal orbitals into the molecule. The molecular dynamics snapshot shown in panel (g) provides a time-resolved perspective of the adsorption behavior of propanoic acid on the Fe(110) surface. Molecular dynamics simulations incorporate thermal motion, solvent effects, and surface heterogeneity, offering a more realistic depiction of adsorption compared to static quantum chemical calculations. The snapshot typically shows propanoic acid adsorbed with the carboxyl group oriented toward the Fe surface, enabling continuous interaction through oxygen atoms. This orientation maximizes electrostatic and coordination interactions while allowing the alkyl chain to extend away from the surface (Azeez *et al.*, 2024). Collectively, these findings indicate that propanoic acid contributes to corrosion inhibition primarily through carboxyl-mediated adsorption and surface site blocking, supporting its role as an effective component of plant-based corrosion inhibitor systems.

Cyclopentasiloxane

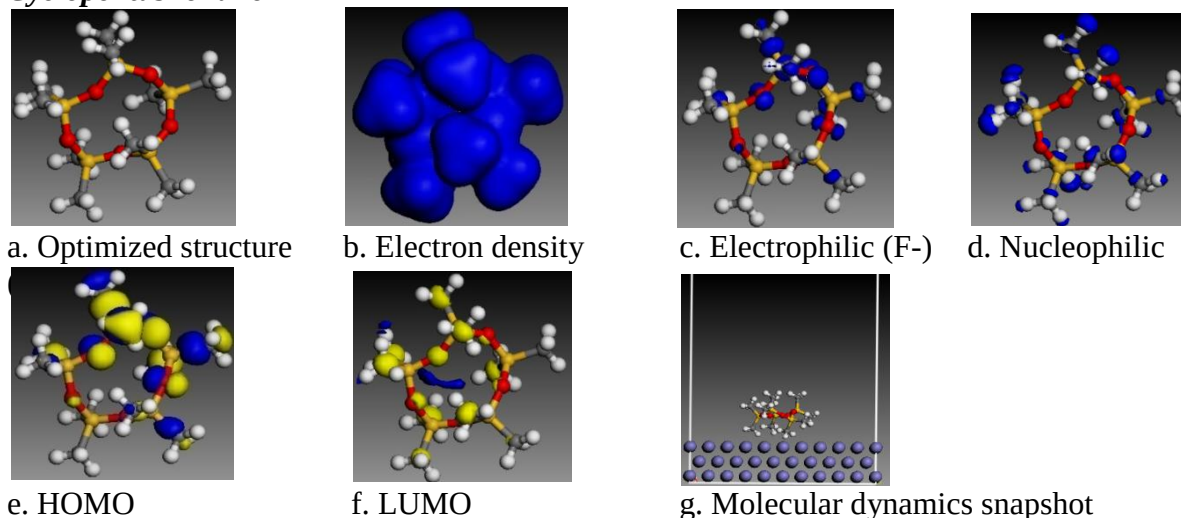


Figure 3.4: Electronic properties of CPS: (a) Optimized structure (b) Electron density, (c) Electrophilic $f(-)$, (d) Nucleophilic $f(+)$, (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of CPS on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

The optimized structure shown in panel (a) represents the minimum-energy conformation of cyclopentasiloxane as obtained from density functional theory optimization. The molecule adopts a puckered cyclic geometry due to the flexible Si–O–Si linkages, which reduces ring strain and allows conformational adaptability which is important for adsorption processes, as it enables the molecule to rearrange and orient itself favorably upon approaching the Fe(110) surface (Gholami *et al.*, 2024). The electron density distribution illustrated in panel (b) reveals that electron density is predominantly localized around the oxygen atoms in the siloxane backbone. These oxygen atoms possess lone-pair electrons that serve as the primary electron-donating centers during adsorption. The electrophilic Fukui function (F^-) shown in panel (c) highlights regions of the molecule that are capable of accepting electron density. For cyclopentasiloxane, these regions are typically distributed around the Si–O bonds, particularly near the oxygen atoms adjacent to silicon centers. The nucleophilic Fukui function (F^+) presented in panel (d) identifies regions most capable of donating electrons. In cyclopentasiloxane, high F^+ values are localized on the oxygen atoms of the siloxane ring, confirming their role as the dominant adsorption centers. These nucleophilic oxygen atoms donate electron density to vacant d-orbitals of surface Fe atoms, initiating adsorption. The HOMO distribution shown in panel (e) is mainly localized around the oxygen atoms in the siloxane backbone, indicating that these atoms are the primary electron donors during interaction with the Fe surface. The LUMO distribution depicted in panel (f) represents regions capable of accepting electron density from the metal surface. In cyclopentasiloxane, the LUMO is distributed over the siloxane ring, including regions near the Si–O framework, allowing the molecule to accept back-donated electrons from Fe atoms. This donor–acceptor synergy between HOMO and LUMO orbitals stabilizes the adsorbed complex and enhances resistance to desorption under aggressive acidic conditions. The molecular dynamics snapshot shown in panel (g) provides dynamic insight into the adsorption behavior of

cyclopentasiloxane on the Fe(110) surface. Molecular dynamics simulations account for thermal motion, solvent interactions, and competitive adsorption processes, offering a realistic depiction of inhibitor behavior under simulated corrosion conditions. The snapshot typically shows cyclopentasiloxane adsorbed in a flattened or slightly tilted orientation which maximizes multi-site interaction and enhances surface coverage, forming a hydrophobic protective layer that impedes the access of corrosive ions such as chloride and sulfate (Obot & Ebenso, 2021).

ELEUSINE INDICA LEAF

3, 7 – Dimethyl

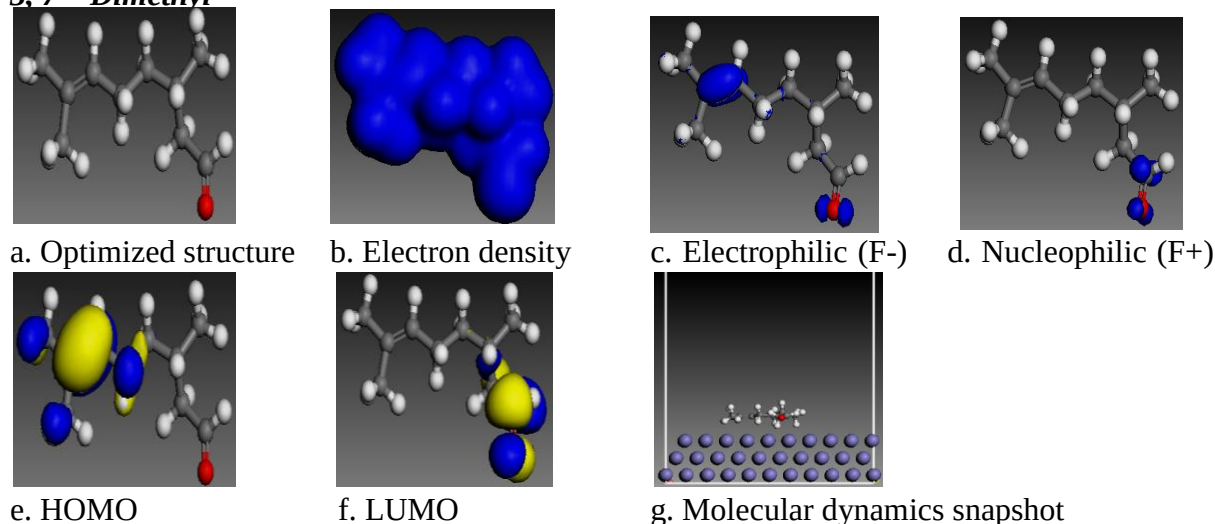


Figure 3.5: Electronic properties of DM: (a) Optimized structure (b) Electron density, (c) Electrophilic f^- , (d) Nucleophilic f^+ , (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of DM on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

The optimized structure shown in panel (a) represents the minimum-energy conformation of the 3,7-dimethyl molecule obtained via density functional theory optimization. The geometry reflects a distribution of methyl substituents that introduces asymmetry into the molecular framework. The electron density distribution illustrated in panel (b) reveals a relatively uniform distribution across the hydrocarbon skeleton, with slightly enhanced regions near carbon atoms bonded to methyl groups. Such electron density profiles indicate that while there are no pronounced electron-rich centers, the methyl-substituted carbon framework can still engage in van der Waals interactions and weak electron sharing with surface iron atoms. The electrophilic Fukui function (F^-) shown in panel (c) identifies regions of the molecule that may accept electron density. For molecules without classical heteroatoms, the electrophilic Fukui response is typically lower and more diffused across the carbon framework. This suggests that 3,7-dimethyl is less capable of stabilizing back-donation from filled metal orbitals compared to polar inhibitors (Yang *et al.*, 2022). The nucleophilic Fukui function (F^+) presented in panel (d) highlights regions most capable of donating electron density. For 3,7-dimethyl, higher F^+ values may be modestly localized around carbon atoms in methyl groups because alkyl substituents can slightly increase local electron density through hyperconjugation. The HOMO distribution shown in panel (e) is delocalized over the hydrocarbon framework, reflecting the relative non-polarity of the molecule. Although the HOMO does not exhibit distinct electron-donating centers like those seen in heteroatom-rich

inhibitors, its delocalization indicates potential for broad, low-intensity interactions with the metal surface, primarily through weak electron sharing and dispersion forces (Verma *et al.*, 2021). The LUMO distribution in panel (f) also appears delocalized over the carbon skeleton, indicating regions where the molecule could accept electron density from the metal surface. In the absence of strong electrophilic centers, such acceptance is limited and typically contributes minimally to adsorption stabilization. The molecular dynamics snapshot shown in panel (g) provides a time-resolved perspective of how 3,7-dimethyl interacts with the Fe(110) surface under dynamic, thermally active conditions. While static electronic descriptors suggest only modest intrinsic reactivity, dynamic simulation captures the influence of thermal motion, solvent effects, and surface polarization on adsorption behavior. The snapshot typically shows 3,7-dimethyl molecules oriented such that their carbon framework lies close to the surface which maximizes surface contact and can contribute to partial surface coverage, which may reduce available reactive sites and hinder corrosive ion adsorption (Azeez *et al.*, 2024).

1, 3, 6 –octadiene

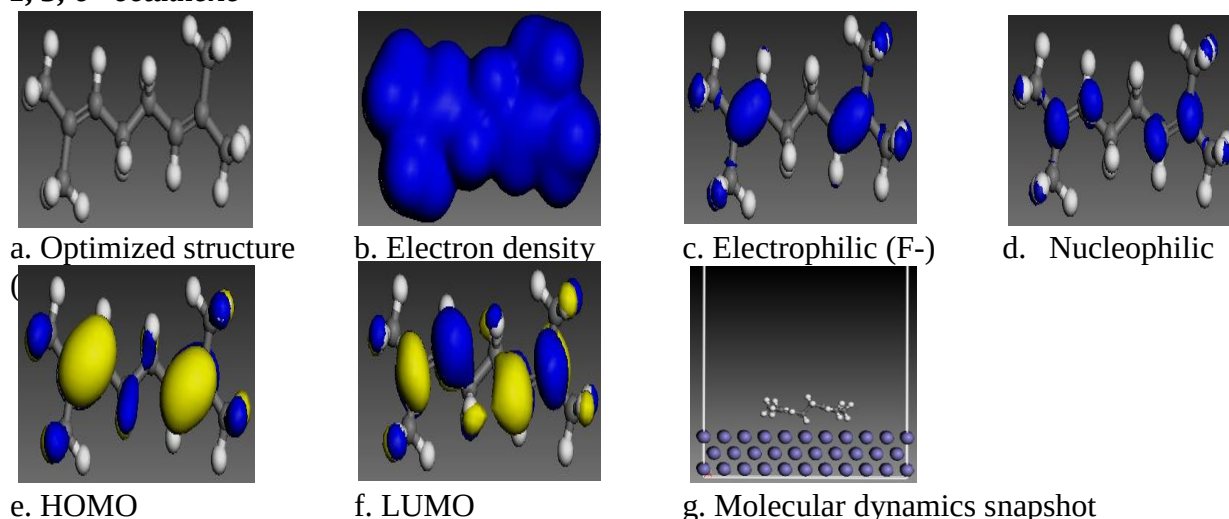


Figure 3.6: Electronic properties of OD: (a) Optimized structure (b) Electron density, (c) Electrophilic $f(-)$, (d) Nucleophilic $f(+)$, (e) HOMO, (f) LUMO, (g) Molecular dynamics model of the adsorption of single molecule of OD on Fe (110) surface. Atom legend: white = H; gray = C; red = O; purple = P. The blue and yellow isosurfaces depict the electron density difference: the blue regions show electron accumulation while the yellow regions show electron loss.

The optimized structure shown in panel (a) represents the minimum-energy conformation of 1,3,6-octadiene obtained through density functional theory (DFT). The molecule consists of a linear hydrocarbon chain with three carbon-carbon double bonds at positions 1, 3, and 6, which impart regions of π electron density. These unsaturated sites introduce potential for electron sharing and surface interaction, even in the absence of heteroatoms. The electron density distribution illustrated in panel (b) highlights regions of high electron probability along the π bonds. These regions of delocalized electrons are more chemically reactive than saturated portions of the chain and serve as potential centers for interaction with the Fe(110) surface. The electrophilic Fukui function (F^-) shown in panel (c) identifies parts of the molecule that are capable of accepting electron density. For 1,3,6-octadiene, regions adjacent to the double bonds exhibit higher electrophilic susceptibility, indicating potential for back-donation from filled metal orbitals into the π^* antibonding orbitals of the inhibitor. The duality of electron flow donation from inhibitor to metal and back-donation from metal to

inhibitor facilitates a more stable adsorption complex (Rajendran *et al.*, 2024). The nucleophilic Fukui function (F^+) in panel (d) highlights areas most capable of donating electron density. For 1,3,6-octadiene, the highest nucleophilic values are associated with the carbon atoms involved in π bonds. These unsaturated sites provide a reservoir of electron density that can be donated to vacant d-orbitals of surface Fe atoms, initiating adsorption (Zhang *et al.*, 2020). Panel (e) illustrates the HOMO distribution, which is primarily localized over the π bonds of the molecule. A HOMO concentrated on unsaturated carbon–carbon bonds indicates significant electron-donating capacity, which facilitates chemisorptive interactions with surface iron atoms. The LUMO distribution shown in panel (f) characterizes regions capable of accepting electron density from the metal surface. In 1,3,6-octadiene, the LUMO is also distributed along the double bond framework, suggesting that the molecule can participate in back-donation from metal orbitals into its π^* orbitals. This back-bonding mechanism complements the primary electron donation from the HOMO and contributes to adsorption stabilization (Sun *et al.*, 2022). Panel (g) presents a molecular dynamics snapshot of 1,3,6-octadiene adsorbed on the Fe(110) surface under dynamic, thermally active conditions. Molecular dynamics simulations account for thermal motion, solvent effects, and competitive adsorption phenomena that static quantum chemical calculations alone cannot capture. In the MD snapshot, 1,3,6-octadiene tends to orient itself such that its π electron regions are proximal to the Fe surface, maximizing interaction potential through surface polarization and weak π –d orbital overlap. This orientation enhances surface coverage and contributes to partial inhibition of corrosive ion access (Azeez *et al.*, 2024).

Table 3.1: Computed Quantum Chemical Parameters and Binding Energies for the Molecules Studied

MOLECULE	E_{HOMO}	E_{LUMO}	ENERGY GAP (ΔE)	BINDING ENERGY (E_{BIND}) kcal/mol
CASSYTHA FILIFORMIS				
LEAF	- 5.337	- 1.514	3.823	- 54.48
Cyclopentanone	- 5.750	- 1.866	3.884	- 46.23
1, 3- Dioxane				
MORUS RUBRA ROOT				
Propanoic Acid	- 7.196	- 1.714	5.482	- 45.26
Cyclopentasiloxane	- 6.798	0.056	6.854	- 115.3
ELEUSINE INDICA LEAF				
3, 7 - Dimethyl	- 5.428	-1.756	3.672	- 101.7
1, 3, 6 -octadiene	-5.435	-1.761	3.674	- 104.7

Table 3.1 presents the computed frontier molecular orbital energies, energy gaps, and binding energies for selected phytochemical constituents identified from *Cassytha filiformis* leaf, *Morus rubra* root, and *Eleusine indica* leaf extracts. In the *Cassytha filiformis* leaf extract, cyclopentanone exhibits an E_{HOMO} value of -5.337 eV, which is higher than that of 1,3-dioxane (-5.750 eV). This suggests that cyclopentanone possesses a stronger tendency to donate electrons to the metal surface compared to 1,3-dioxane, enhancing its adsorption interaction. This observation is consistent with established quantum chemical principles linking higher E_{HOMO} values with increased inhibition performance (Obot *et al.*, 2019). The lowest unoccupied molecular orbital energy (E_{LUMO}) reflects the ability of a molecule to accept electrons from the metal surface through back-donation. Lower E_{LUMO} values favor acceptance of electron density from filled metal orbitals, stabilizing the adsorbed inhibitor–metal complex. In this study, cyclopentanone shows a slightly lower E_{LUMO} (-1.514 eV)

than 1,3-dioxane (-1.866 eV), indicating that both molecules are capable of participating in back-donation interactions, although 1,3-dioxane may exhibit marginally stronger electron-accepting ability. Such donor–acceptor duality is widely reported as a key mechanism in corrosion inhibition by organic compounds (Gece, 2020).

For the *Cassytha filiformis* constituents, cyclopentanone and 1,3-dioxane show comparable ΔE values of 3.823 eV and 3.884 eV, respectively, suggesting similar reactivity levels. However, the slightly lower ΔE of cyclopentanone supports its enhanced adsorption tendency relative to 1,3-dioxane. These trends align with recent computational corrosion studies demonstrating that inhibitors with moderate to low ΔE values tend to exhibit superior inhibition efficiencies in acidic media (Al-Amiery *et al.*, 2023). In the *Cassytha filiformis* group, cyclopentanone exhibits a binding energy of -54.48 kcal/mol, which is significantly more negative than that of 1,3-dioxane (-46.23 kcal/mol). Strong binding energies are often associated with mixed physisorption–chemisorption mechanisms, which enhance surface coverage and corrosion protection (Gholami *et al.*, 2024). For the *Morus rubra* root extract, propanoic acid and cyclopentasiloxane display markedly different electronic and adsorption characteristics. Propanoic acid has an EHOMO of -7.196 eV, indicating relatively weak electron-donating ability compared to cyclopentasiloxane (-6.798 eV). However, propanoic acid exhibits a much lower ELUMO value (-1.714 eV) than cyclopentasiloxane (0.056 eV), suggesting a stronger ability to accept electron density from the metal surface. Despite its lower electron-donating capacity, propanoic acid’s polar carboxyl group enhances interaction with the metal surface through electrostatic attraction and hydrogen bonding, contributing to its adsorption behavior (Rajendran *et al.*, 2024). The ΔE values for propanoic acid (5.482 eV) and cyclopentasiloxane (6.854 eV) indicate that cyclopentasiloxane is less reactive electronically. Nevertheless, cyclopentasiloxane exhibits a remarkably high binding energy of -115.3 kcal/mol, far exceeding that of propanoic acid (-45.26 kcal/mol). This suggests that cyclopentasiloxane adsorbs very strongly on the iron surface, likely due to its larger molecular size, flexible siloxane framework, and multiple interaction sites that promote extensive surface contact. Such behavior has been reported for silicon-containing organic inhibitors, where high binding energies arise from enhanced surface affinity and dispersion interactions (Zhang *et al.*, 2020). In the *Eleusine indica* leaf extract, 3,7-dimethyl and 1,3,6-octadiene exhibit very similar EHOMO values (-5.428 eV and -5.435 eV, respectively) and nearly identical ELUMO values (-1.756 eV and -1.761 eV). These similarities indicate comparable electron-donating and electron-accepting abilities, which is further supported by their nearly identical ΔE values of 3.672 eV and 3.674 eV. Such small energy gaps suggest high molecular reactivity and favorable interaction with the metal surface (Sun *et al.*, 2022; Li *et al.*, 2023). The binding energies of 3,7-dimethyl (-101.7 kcal/mol) and 1,3,6-octadiene (-104.7 kcal/mol) are highly negative, indicating strong and stable adsorption on the iron surface. Despite lacking heteroatoms, these unsaturated hydrocarbons possess π -electron systems that can interact effectively with the metal surface through π -d orbital interactions and dispersion forces. The strong binding energies observed support the notion that π -electron-rich hydrocarbons can significantly contribute to corrosion inhibition, especially when acting synergistically with other extract constituents (Lgaz *et al.*, 2023).

3.3 Qualitative Phytochemical Characteristics of the Plant Extracts

The result of the qualitative analysis is shown in Table 1. Alkaloids are nitrogen-containing organic molecules that readily donate lone-pair electrons, enabling strong interactions with metal surfaces and contributing significantly to corrosion inhibition via chemisorption and complex formation (Lebrini, 2024). In this study, all extracts exhibited very high (+++) alkaloid content, suggesting robust inhibitory potential. This aligns with evidence from studies on eucalyptus bark extract, which contains alkaloids among its constituents and

achieved up to 98.2% inhibition efficiency against mild steel in 5% HCl, attributed to mixed adsorption following Langmuir behavior (Aslam *et al.*, 2023). Therefore, the high alkaloid levels in these extracts are likely to translate into similarly excellent corrosion protection when tested under acidic conditions. Phenolic compounds, possessing hydroxyl groups and conjugated aromatic rings, enable adsorption through electron donation and hydrogen bonding, forming protective layers on metal surfaces (Murungi & Sulaimon, 2023). The result showed very high (+++) phenolic content in *Cassythia filiformis* and moderate (++) levels in both *Elusine indica* and *Morus rubra*. This suggests a particularly strong inhibition potential for *C. filiformis*, consistent with reports that extracts rich in phenolics, such as eucalyptus leaf extract achieving 88% efficiency in HCl, perform well by increasing charge-transfer resistance and following Langmuir adsorption (Abdel-Gaber *et al.*, 2023). Flavonoids, as polyphenolic constituents, engage in π - π stacking and hydrogen bonding with metal surfaces, aiding adsorption and inhibition even at trace levels (Bandeira *et al.*, 2025). In this study, all extracts contained trace (+) amounts of flavonoids, which may still provide synergistic benefits when combined with major phytochemicals. Similar observations were made in *Justicia secunda* leaf extract containing trace flavonoids alongside alkaloids, tannins, saponins, and steroids achieving 94% inhibition efficiency in acid media (Murungi & Sulaimon, 2023). Tannins are high-molecular-weight polyphenols that strongly complex with metal ions, forming stable, adherent films that prevent acid-induced corrosion (Lebrini, 2024). All extracts demonstrated moderate (++) tannin levels, which is consistent with numerous studies where moderate-to-high tannin content correlated with inhibition efficiencies between 85% and 95% in similar environments. Therefore, the tannin content across suggests effective film formation and corrosion shielding. Terpenoids such as mono-, sesqui-, and diterpenes possess conjugated systems and oxygen-containing functional groups that enable strong hydrophobic and π interactions with steel surfaces. In this study, *Cassythia filiformis* had very high (+++) terpenoid levels, while *Eleusine indica* and *Morus rubra* showed moderate (++) concentrations. A corresponding study observed that terpenoid-rich eucalyptus bark extract delivered marked inhibition in 5 % HCl via spontaneous mixed adsorption, demonstrating excellent efficacy (Aslam *et al.*, 2023). Thus, the abundant terpenoids in *C. filiformis* likely contribute positively to its adsorption film quality and corrosion resistance.

Table 3.2: Qualitative Phytochemical Characteristics of Ethanolic Bio-Extract for Corrosion Inhibition of Metals in Acid Media

Parameters	Eleusine indica	Cassythia filiformis leaf	Morus rubra root
Alkaloids	+++	+++	+++
Cardiac Glycosides	+	+	-
Flavonoids	+	+	+
Phenolics	++	+++	++
Phytates	+	++	++
Saponins	-	+	+
Terpenoids	++	+++	++
Steroids	++	-	+
Tannins	++	++	++

+++ = **Highly Concentration**, ++ = **Concentrated**, + = **intrace**, - = **absence or too little to identified qualitatively**.

Saponins are amphiphilic glycosides that reduce interfacial tension and promote uniform distribution of inhibitory molecules across the metal surface. It was absent in *Elusine indica* yet present (+) in *Cassythia filiformis* and *Morus rubra*. Studies have shown that saponins enhance inhibitor film stability and synergize with other phytochemicals, improving coverage

and adhesion (Aslam *et al.*, 2023). Therefore, their presence likely boosts inhibition performance in the two extracts by facilitating cohesive surface film formation. Phytates are highly effective chelators of iron ions, forming precipitates that mitigate localized corrosion. In this study, phytates were moderate (++) in *Cassytha filiformis* and *Morus rubra*, but absent in *Eleusine indica*. Although less commonly examined, recent research underscores their utility in enhancing corrosion resistance via ion-sequestration and film formation, particularly in acidic environments (Ahanotu *et al.*, 2024). Thus, the presence of phytates is advantageous in improving inhibition performance. Cardiac glycosides feature oxygen-rich glycone structures capable of hydrogen bonding, though they typically show limited direct inhibition (Nakumara *et al.*, 2020). In this study, they were detected at trace (+) levels in *Eleusine indica* and *Cassytha filiformis* and were absent in *Morus rubra*. Other studies indicate that glycosides often contribute minimally unless present in synergy with more active compounds like tannins or phenolics. Steroids are cyclic terpenoidal molecules that can produce hydrophobic interactions with metal surfaces, leading to barrier film formation. These were found at moderate (++) levels in *Eleusine indica*, trace (+) in *Morus rubra*, and absent in *Cassytha filiformis*. Previous research indicates that the presence of steroids alongside phenolics and tannins may enhance inhibitor performance by adding hydrophobic film integrity (Aslam *et al.*, 2023). Thus, steroid presence in *E. indica* and *M. rubra* may marginally contribute to corrosion resistance.

3.4 Quantitative Phytochemical Characteristics of the Plant Extracts

The result of the quantitative analysis is shown in Table 4.2. This data shows *Morus rubra* has the highest alkaloid levels (1,335 mg/100 g), followed by *Cassytha filiformis* (1,145 mg/100 g) and *Eleusine indica* (983 mg/100 g). Similar findings in pomegranate aril extract yielded strong corrosion inhibition in 1 M HCl due to abundant alkaloids forming protective layers (Xiao *et al.*, 2024). Higher alkaloid content in the extracts likely correlates with superior inhibition via strong film-forming abilities. Flavonoids as polyphenolic molecules enhance inhibition through π interactions and hydrogen bonding on metal surfaces. *Morus rubra* again leads, with 293 mg/100 g, while *Cassytha filiformis* (85 mg/100 g) and *Eleusine indica* (58 mg/100 g) have moderate contents. Studies on olive leaf extract showed flavonoid-rich inhibitors provide robust protection in acidic media (Nazari *et al.*, 2023). Thus, high flavonoid content suggests significantly improved anticorrosive efficiency, especially for *Morus rubra*.

Table3.3: Quantitative Phytochemical Characteristics of Ethanolic Bio-Extract for Corrosion Inhibition of Metals in Acid Media

Parameters	Eleusine indica	Cassytha filiformis	Morus rubra
Alkaloids (mg/100g)	955	1150	1325
	995	1125	1350
	980	1135	1335
Cardiac Glycosides (mg/100g)	45	45	5
	40	45	5
	35	40	5
Flavonoids (mg/100g)	60	70	295
	50	95	290
	65	85	295
Phenolics (GAE/g)	38.7	89.2	63.4
	38.4	89.7	63.6
	38.8	89.4	63.1
Phytates (mg/100g)	25	80	85
	30	75	90
	45	80	90
Saponins (mg/100g)	10	110	145
	10	105	130
	10	125	165
Terpenoids (mg/100g)	260	940	235
	275	910	225
	245	905	250
Steroids (mg/100g)	210	30	60
	225	30	70
	215	25	75
Tannins (mg/100g)	390	300	385
	375	340	360
	400	315	395

Phenolics are well-known for strong adsorption and metal ion chelation. *Cassytha filiformis* has the highest phenolic content (89.4 mg GAE/g), with *Morus rubra* (63.4 GAE/g) and *Eleusine indica* (38.7 GAE/g). This mirrors findings where terpenoids and phenolics in eucalyptus extracts gave excellent protection (>95 % efficiency) in HCl systems (Aslam *et al.*, 2023). The elevated phenolic levels in the extracts should enhance corrosion inhibition by forming dense protective films. Saponins function as surfactants, facilitating even film formation across metal surfaces (Nazari *et al.*, 2023). These extracts showed *Morus rubra* had the highest saponin content (145-165 mg/100 g), *Cassytha filiformis* (110-125 mg/100 g), and *Eleusine indica* minimal (10 mg/100 g). This aligns with avocado leaf studies where saponins helped spread inhibitor coverage in alkaline or saline environments (El-Gendy *et al.*, 2024). Thus, saponin-rich extracts may offer superior inhibition due to better film uniformity. Phytates bind iron ions, reducing corrosion via a chelation mechanism (Nazari *et al.*, 2023). These data showed *Morus rubra* (90 mg/100 g) and *Cassytha filiformis* (80 mg/100 g) lead, while *Eleusine indica* lags (35 mg/100 g). Though phytates are less studied, grape seed extract with similar phytate levels showed improved corrosion protection (Camacho *et al.*, 2024). Thus, high phytates may strengthen metal passivation. Terpenoids adsorb strongly

onto metal surfaces via conjugated double bonds, forming hydrophobic barriers (Bandeira *et al.*, 2025). *Cassytha filiformis* presents a remarkably high level (920 mg/100 g), while *Eleusine indica* (260 mg/100 g) and *Morus rubra* (235 mg/100 g) are moderate. This parallels olive leaf and eucalyptus findings where terpenoids were primarily credited for strong inhibition (Aslam *et al.*, 2023). Steroids form hydrophobic, planar films that hinder corrosive ion ingress. *Eleusine indica* has 217 mg/100 g steroids, *Morus rubra* 68 mg/100 g, and *Cassytha filiformis* 28 mg/100 g. Studies on flower extracts demonstrated steroids, together with phenolics, improved film robustness in acid media (Xiao *et al.*, 2024). Their presence in these extracts likely enhances barrier properties. Cardiac glycosides are oxygen-rich compounds forming weak hydrogen-bonded surface films. *E. indica* and *C. filiformis* contain 40–45 mg/100 g, but *M. rubra* has minimal (5 mg/100 g). Tannins strongly complex with metal ions forming robust protective films. The extracts are rich (375–395 mg/100 g), aligning with peanut hull studies where tannin levels exceeding 300 mg/100 g yielded >90% inhibition in HCl (Camacho *et al.*, 2024).

4.0 Conclusion and Recommendations

The quantum chemical and molecular dynamics studies of plant extract constituents show that heteroatoms such as oxygen in carbonyl, hydroxyl, and siloxane groups act as primary adsorption centers on Fe(110) surfaces. The HOMO and LUMO distributions, together with Fukui function analyses, indicated that these molecules can both donate and accept electrons, facilitating strong chemisorption. Molecules with high EHOMO and low ELUMO values demonstrate greater electron-donating and accepting tendencies, correlating with higher inhibition efficiency. Molecular dynamics simulations reveal that the molecules adopted flat orientations on the Fe surface, maximizing contact and surface coverage. Calculated adsorption energies confirm stable molecule–metal interactions, while small HOMO–LUMO gaps suggest high chemical reactivity and polarizability. The phytochemical profiling of the ethanolic extracts of *Eleusine indica*, *Cassytha filiformis*, and *Morus rubra* revealed a rich presence of bioactive compounds known to contribute to corrosion inhibition in acidic media. Among these, *Morus rubra* exhibited the highest levels of alkaloids. These phytochemicals are recognized for their ability to adsorb onto metal surfaces, creating a protective barrier that limits corrosion in aggressive environments such as hydrochloric or sulfuric acid solutions. The results suggest that all three plant extracts have considerable potential as green corrosion inhibitors. *Cassytha filiformis* stands out in terms of phenolic and terpenoid content, implying a strong adsorption capacity and likely superior inhibition efficiency. *Morus rubra*, with its high alkaloid and flavonoid content, may exhibit inhibition through complex formation and π -electron interactions.

To fully validate the inhibition performance of these extracts, it is recommended that electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and surface morphology analyses (e.g., SEM, AFM) be conducted to elucidate the inhibition mechanism. Furthermore, isolation and structural characterization of individual compounds (via GC-MS, LC-MS/MS, and NMR) from the most active extracts, particularly *Cassytha filiformis* and *Morus rubra*, would help identify the most potent phytochemicals responsible for corrosion inhibition. Experimental validation is recommended to confirm theoretical predictions, and synergistic formulations of multiple phytochemicals could further enhance inhibition performance. Optimizing inhibitor concentration and exploring molecular modifications with additional heteroatoms may improve surface adsorption and protection. These findings support the potential industrial application of plant-based inhibitors as sustainable alternatives to conventional chemical corrosion inhibitors.

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