

Computational Stimulation and Experimental Study on Corrosion Inhibition Qualities of *Emilia sonchifolia* Leaf Extract for Copper (CU131729) in Hydrochloric Acid

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Abstract

Copper corrosion inhibition by *Emilia sonchifolia* (ES) leaf extract has been studied in 2 M hydrochloric acid solution using electrochemical measurement, energy dispersive X-ray emission spectroscopy and surface examination techniques. Computational simulations were adopted to describe probable reactivity of individual ES leaf constituents and mechanism of interaction with copper crystal. Results obtained from potentiodynamic polarization revealed a shift in corrosion potentials of copper (CU131729) to more positive potentials in the presence of ES leaf extract with increased effect as inhibitor concentration increased and also a decrease in both current densities suggesting a mixed type inhibitor characteristics with pronounced anodic protection. Surface elemental characterization revealed presence of the inhibitor species in the corrosion products formed on corroded CU131729 surface confirming the formation of complex chelating ligands through interactions with the metal surface. Quantum chemical calculations and molecular dynamics simulations were employed to theoretically analyse the interactions of individual ES leaf constituent with copper surface at the molecular level and obtained results revealed strong and spontaneous adsorption with high binding energies which affirms observed quality inhibition action. Quantum chemical descriptors such as energy of HOMO and LUMO, energy gap, number of transferred electrons, global hardness and softness, electrophilicity, and interaction energy were computed and discussed.

Keywords

Copper Corrosion, *Emilia sonchifolia*, Surface Analysis, Quantum Chemical Calculation, Binding Energy, Passivation

1. Introduction

Increase of industrial activities in economic sectors such as marine, communication, domestic utility productions, electrical and electronics have engaged resourceful use of copper and alloy in respect of its good aesthetic and mechanical qualities. Copper is a type of material endowed with the ability to establish natural passive surface films in appropriate environmental conditions. This characteristic of copper makes it resistant to corrosion processes in numerous aqueous environments including chemical; however, chemical environments inhabiting chloride ions among others, undermine these qualities and permit corrosion process [1]-[8]. Corrosion process forms corrosion product and deposits on corroding copper surface which interferes with its electrical, thermal and mechanical qualities and also leads to huge economic loss and possible safety concerns [9] [10] [11]. The use of corrosion inhibitors in such situation is proven essential to augment the compactness of the surface passive layer formed on material surface and/or mitigate corrosion processes [12] [13] [14] [15]. The utilization of appropriate inhibitor is necessary taking into cognizance the corrosion mechanism of copper in chloride ion environments.

Among several developed strategies to contain copper corrosion, inhibitors of many-sided benefits that involve both environmental and economic friendliness boil down to the use of organic compounds. Organic compounds containing electronegative functional groups and conjugated p -electron within multiple bonds have been studied and proven to form compact thin films on metal surfaces which enhance the passivation potentials of metals during corrosion processes [6] [15] [16] [17]. Scientists have ruled out conventional and synthetic organic corrosion inhibitors with regard to their adverse effects on human health and the environment [18]. Biomass mass of plant origin contains numerous organic compounds and has been reported by several researchers to possess corrosion inhibitory characteristics for metals. Plant leaf is known to contain several organic compounds incorporating multiple bonds, unsaturated heterocyclic rings, aromatic rings, hetero-atoms, such as nitrogen, oxygen and sulfur within their structures and as such, do interact with metal surface through these species which reduces the surface area on the metal surface available for corrosion processes via electron exchange [19].

The past two decades have documented density functional theory (DFT) as a veritable tool in corrosion studies used for modeling the reactivity of constituent organic compound of plant leaf extracts on metal surfaces [20] [21] [22]. Quantum chemical methods appear to be adequate for pointing out the reactivity of

active electronic centers which is responsible for inhibition action [23]. The constituent compounds of some plant leaf extracts have been investigated for their inhibitory role and their electronic structures analyzed in order to elucidate the origin of their inhibition effect [22]. Presently, the synergy between plant leaf constituent molecules as regards the overall observed inhibition action is beyond the scope of quantum chemical calculations. However, attempt has been made in this study to report the effects of *Emilia sonchifolia* (ES) on copper corrosion in acidic chloride environment. The inhibitory role of ES was studied using potentiodynamic polarization to evaluate the inhibition efficiency and mechanism while elemental analysis of the corroded copper surface via energy dispersive x-ray emission spectroscopy (EDS) characterized the corrosion products. Theoretical approach using quantum chemical calculations were applied to some constituent molecules of ES disclosed by GC-MS spectrometry while molecular quench dynamics estimated the extent of binding energy.

2. Experimental

2.1. Material Preparation

The typical analysis of 99.9% Copper (CU131729) obtained commercially from Advent research materials Ltd., England OX294JA are recorded in **Table 1**.

The sheets were reduced to specimen mechanically and treated as described in our earlier work as well as the procedures for inhibitor preparation [24]. All reagents used were of analytical grade.

2.2. Electrochemical Measurement

Electrochemical experiments were conducted using a complete DC Voltammeter and Corrosion System VERSASTAT 3 with parameter as described in [24]. The pre-cut CU131729 specimen was coated in wax leaving a total exposed surface area of 1 cm² which was used as working electrode while a graphite rod and a saturated calomel electrode (SCE) were used for counter and reference electrode respectively. The working electrode was used as obtained but degreased with ethanol, and finally dried with acetone and warm air before usage. The inhibition efficiency of ES leaf extract was calculated using Equation (1) [6].

$$\text{Inhibition efficiency (\%)} = 1 - i_{\text{corr}} / i_{\text{corr}}^o \times 100 \quad (1)$$

where i_{corr} is the current density for the inhibited solution and i_{corr}^o is the current density of the uninhibited solution.

2.3. Surface Examination

Representative snapshot of corroded CU131729 surface after 150 h of immersion

Table 1. Typical analysis of CU131729.

| Component | Ag | Bi | Pb | O | Others | Cu |
|----------------|------|-----|-----|------|--------|---------|
| Analysis (ppm) | <500 | <10 | <50 | <400 | <300 | balance |

were inspected by SEM on Vega Tescan scanning electron microscope with system pressure set at 6.9976×10^{-3} pa, emission current ranged between $101 - 105 \times 10^{-6}$ A, and magnification of 0.99502×10^3 . The dwell time was 145.80×10^{-6} s while internal chamber pressure varied at $7.5070 - 7.5335 \times 10^{-3}$ pa. The energy dispersive X-ray emission spectroscopy (EDS) was recorded in a VG TC INCA PentaFET x3 spectrometer with Mg K_X-ray source operated at accelerating voltage of 12.5 kV. A detailed procedure for the surface examination is reported in [25].

2.4. Quantum Chemical Analysis

The quantum chemical analysis was carried out using Materials Studio 4.0 engaging DMol³ and Atomistic Forcite Quench (AFQ). The geometry optimization for the phytochemical constituent of ES leaf extract and copper crystal was performed with delocalized internal coordinate optimizer on constituent molecules of ES leaf such as: 2-propen-1-ol 3-(p-hydroxyphenyl) (2-PHP), 3,5-Di-tert-bu-tylphenol (3-DBP), Ethyl 2-hydroxybenzyl sulfone (2-HBS), Z-9-Tetradecenal (9-ZTD) and 1,2-15,16-diepoxyhexadecane (1-EHD) as well as the copper crystal. Functional for geometry optimization in DMol³ was set to LDA at unrestricted spin PWC using zero symmetry charge while the core treatment of DFT semi-core pseudopotentials was set at DNP basis with k-point customized to 2x2x1 and other electronic parameters including orbital cutoff quality were set at fine. A density mixing charge of 0.2 was applied to the orbital occupation to speed up convergence alongside convergence tolerance maximum force of 0.002 Ha/A. Molecular dynamics stimulation was used to replicate interfacial interaction between single ES leaf constituent molecule and Cu(110) crystal using Forcite Quench at COMPASS forcefield while our stimulation parameters were set as reported in our earlier work [26]. The interaction energy (E_{Bind}), global hardness and softness, electrophilicity and number of transferred electrons were calculated as reported in our earlier work [26].

3. Results and Discussions

3.1. Electrochemical Measurement

The polarization curves for CU131729 specimen in aerated solution of 2 M HCl solution in the absence and presence of ES leaf extract is presented in **Figure 1** while the extracted electrochemical parameters are recorded in **Table 2**. As

Table 2. Corrosion parameters obtained for CU131729 in 2 M HCl solution in the absence and presence of *Emilia sonchifolia* leaf extract.

| Solution | Parameters | | | |
|-----------|---|------------------------|----------|--------------------|
| | i_{corr} (mA/cm ²) | E_{corr} (mV) | θ | IE_{PS} % |
| Blank | 2588.01 | 16.022 | - | - |
| 10 mg/L | 1627.03 | 33.117 | 0.3713 | 37.13 |
| 100 mg/L | 6.479 | 166.22 | 0.9975 | 99.75 |
| 1000 mg/L | 7.726 | 163.91 | 0.9970 | 99.70 |

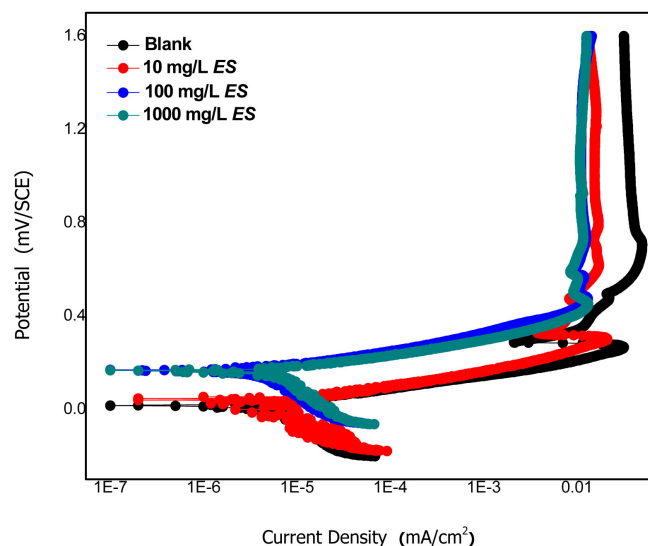
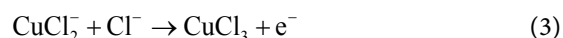


Figure 1. Polarization scans for CU131729 specimen in aerated solution of 2 M HCl solution in the absence and presence of *Emilia sonchifolia* leaf extract.

observed from the data, inhibition efficiency increased with increase in inhibitor concentration. Antonijevi and Radovanovic [11] in a review stated that the total polarization resistance of copper corrosion is a linear function of inhibitor concentration which is an indication of higher surface area coverage at higher concentration. Examination of **Figure 1** revealed a positive shift in corrosion potential (E_{corr}) which caused a decrease in the corrosion current density and consequently reduced both anodic and cathodic reactions occurring at the metals surface thereby, resulting in a reduced corrosion rate. This effect became pronounced with increase in ES leaf extract concentration and this could be attributed to action of the leaf extract enhancing passivation potential of the metal and/or improving the compactness of the surface films. The shift in E_{corr} with increasing inhibitor concentration is an indication of the fact that the inhibitor had a strong influence on the oxygen reduction than copper dissolution process [27]. The maximum E_{corr} was recorded for 100 mg/L with negligible decrease as inhibitor concentration increased and could be that at 100 mg/L, ES leaf extract had maximum surface interaction with the copper specimen. Further examination of the polarization scan revealed diminished distinct regions suggesting limited ingress of chloride ions into the developed surface passive film, which eventually opposed the forward process of corrosion reaction. This might be due to the moderation of the system current density and prevention of CuCl oxidation to CuCl_2^- and CuCl_3^- species. Sherif [7] stated that the formation of corrosion products on copper surfaces due to the hydrolysis of CuCl partially protects the metal and results in reduced chloride ion ingress at the surface, thus the reaction (Equation (2)) might be expected. However, Cu^{I} is also expected to be oxidized to Cu^{II} , as represented in reaction (Equation (3)) and this favours formation of soluble chloride complex species which undermines the protective surface layers.



Some authors agree that in dilute chloride solutions Cu_2O film is formed on the copper surface which acts as protective barrier to corrosion processes. However, in a scenario where CuCl is trapped underneath the Cu_2O film, the protective layer is damaged with initiation of pits [10] [28]. In the present study, it is proposed that the formation of cuprous oxide is favoured over soluble chloride complexes formation as a result of the compact surface films that diminished corrosion attack as also confirmed in the SEM micrographs. The presence of ES leaf extract in the chloride solution shifted the corrosion potential towards anodic potentials suggesting that the inhibitor had dominant effect on anodic dissolution of CU131729. Anodic dissolution of copper is generally controlled by the diffusion of soluble Cu^{II} species from the outer Helmholtz plane to the bulk solution as reported by Kosec *et al.* [29]. The diffusion of copper species was seen to decrease with increase in ES concentration as confirmed by the calculated inhibition efficiency suggesting that more inhibitor molecules were adsorbed on the surface until a limiting state. This effect confirms that ES leaf extract functioned by adsorption at the metal/electrolyte interface hence, enhanced the protectiveness of thin surface films as well as mitigate bulk mass transport mechanisms across the copper surface. The thin surface films behave as a resistor for electron transfer at the metal/electrolyte interface and may grow upon increasing the inhibitor concentration [30] [31].

Table 2 reveals that corrosion current density (i_{corr}) decreased upon the introduction of ES leaf extract and further decreased with increasing concentration which trend reversed minimally at 100 mg/L suggesting optimum inhibition efficiency of 99.7%. This validates that small amount of ES leaf extract can act as efficient inhibitor for copper surface in 2 M HCl via adsorption with maximum coverage that resists and retards intrusion of chloride ions on copper surface. The decrease in i_{corr} could be attributed to delayed formation of chloride complexes which degenerate into the bulk solution [3] and/or undergoes further oxidation to cupric ions which diffuses through the boundary layer. Moreover, both the anodic and cathodic current densities decreased in presence of ES leaf extract suggesting an action of mixed type inhibitor for copper corrosion in acid chloride solution however, with pronounced anodic effects. By considering the collective observations on the change in the Tafel slopes, change in current density, and the direction of change in corrosion potentials, the inhibition process appeared to be mixed type in nature with pronounced anodic effects.

3.2. Surface Elemental Analysis and Examination

The EDS elemental analysis for CU131729 surface corrosion products layer in 2 M HCl solution without and with ES leaf extracts are presented in **Figure 2**. The analysis revealed the presence of oxygen, chlorine and copper in absence of the inhibitor whereas the introduction of ES leaf extract incorporated nitrogen and

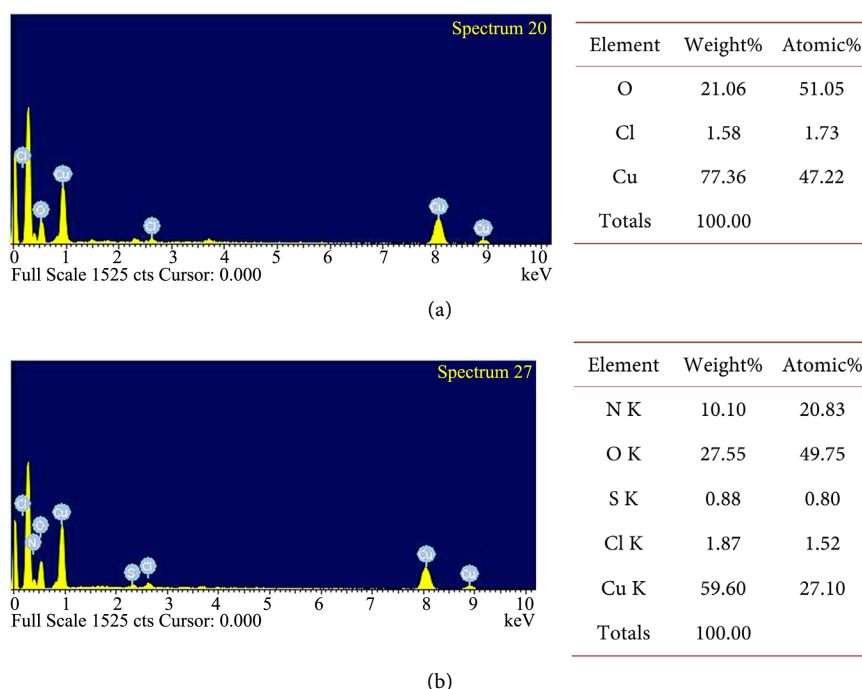


Figure 2. EDS analysis of the corrosion product layer on CU131729 surface in 2 M HCl solution (a) without inhibitor (b) with ES leaf extract.

sulphur atom in the corrosion product as well as reduced amount of chlorine atom, an indication that ES leaf extracts did interfere with chlorine ion access to CU131729 surface.

The EDS spectra recorded appreciable amount of oxygen atoms confirming that the corrosion product that developed on CU131729 surface was predominantly CuO and/or Cu₂O with surface amounts of (N-Cu-S)ads and (ES-Cu)ads with traces of (ES-Cu-Cl)ads. The possibility of a synergy between species at the corroded surface forming weak bonds with the metal surface is not ruled out. It is known that Cl⁻ ions actually influence the stability of cuprite surface films based on the replacement of O²⁻ ions in the surface films and also balances up the charge in p-Cu₂O structure as Cu⁺ ions migrate towards the oxide/electrolyte interface and chlorine ions diffuses underneath the oxide film to enact a rupture [32]. Accordingly, Oguzie *et al.* [33] reported that when the O₂ content of material surface film is reduced, there is disruption of the structural order which enhances breakdown of the oxide film. However, the EDS spectrum reveals that the presence of ES leaf extract in the system caused appreciable amount of oxygen and also of nitrogen and sulphur atoms on the surface as was disclosed attesting to the fact that ES leaf extract did contend with Cl⁻ ion intrusion and stabilized the oxide surface films formed. The effect is supposed to enhance the passivation potentials of CU131729 surface. This agrees with results obtained from the polarization scans which showed high inhibition efficiency in the acid solution. Furthermore, the complex (N-Cu-ES)ads and (S-Cu-ES)ads formed on the copper surface did suppressed copper dissolution and prevented cuprous chloride formation hence, inhibited corrosion of copper surface in 2 M HCl. The

corrosion inhibition process is associated with formation and growth of stable surface thin film on CU131729 surface through the process of complexation of the constituent organic molecules of ES leaf extract [11]. ES leaf extract is assumed to be incorporated onto the cuprite surface film and did enhance its compactness which in turn mitigated the formation of copper chloride complexes and further dissolution processes. The proof of this is seen in the SEM micrographs (Figure 3) showing fewer pits and holiday (non-active) regions on CU131729 surface in the presence of ES leaf extracts indicating a greater resistance to corrosion process on CU131729 surface. This, as reported by some researchers points to a process that enhances the stability and compactness of passive surface films formed on metal surfaces deployed in service environments [34].

Micrographs of CU131729 specimen in 2 M HCl solution in the absence of the inhibitor was severely corroded and is seen to have high density irregular pits arising from the formation of cuprous chloride and oxychloride soluble complexes which migrated into the bulk solution. The presence of chlorine ions in the system clearly interfered with peculiar surface processes, via impairing the surface barrier properties and introduce passivation breakdown due to local surface reactivity. This is due to specific action of chloride ions in undermining formed cuprite surface films however, the introduction of ES leaf extract contained these processes to a great extent and suppressed the interaction of chloride ions with the passivating film and/or slowing down of their access to it. Madkour and Elshamy [35] reported that copper activation occurs only after a certain incubation period, during which a thin layer of CuCl is formed, which further facilitates the rapid dissolution of copper. Micrographs for CU131729 surface in 2 M HCl solution in the presence of ES leaf extracts showed spherical, irregularly shaped pits with holiday regions on the surface that was not corroded due to the adsorption of ES leaf extract on the surface. This is attributed to the action of the inhibitor via adsorption and forming chelating complex ligands

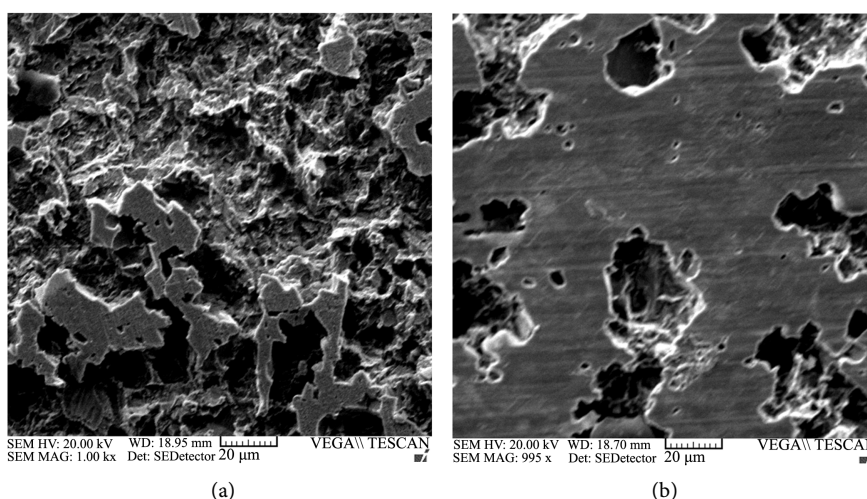


Figure 3. SEM micrographs of CU131729 surface after immersion for 150 h in 2 M HCl solution (a) without inhibitor (b) with ES leaf extracts.

with the copper surface film that prevented Cu^+ cations travelling through the oxide film towards the bulk medium [36]. An indication that ES leaf extract through adsorption dispossessed the incorporation of chloride ions onto the Cu_2O films and prevented the possible formation of CuCl and other chloride complexes at the metal/electrolyte interface.

3.3. Quantum Chemical Analysis

Quantum chemical calculations on frontier orbital distribution, Fukui indices and atomic charges were done in gas phase for all stimulations on some constituent molecules of ES leaf extract for the purpose of appreciating the reactive regions within each molecule as an inhibitor. Electronic parameters of compounds provide useful insights about reactive tendency in respect of donation/back-donation of electrons between a compound and metal surface. The optimized structures of constituent ES leaf molecules; 2-PHP, 3-DBP, 2-HBS, 9-ZTD and 1-EHD were analyzed for frontier molecular orbital density distributions; with Mulliken population charges, Funki indices and total electron density which results are presented in **Figure 4**. The computed Mulliken atomic charges are recorded in **Table 3** for centers with high value charges. The chemistry of interaction theory suggests that all chemical interactions are driven by either electrostatic or orbital properties and these descriptors are eminent for molecular physicochemical

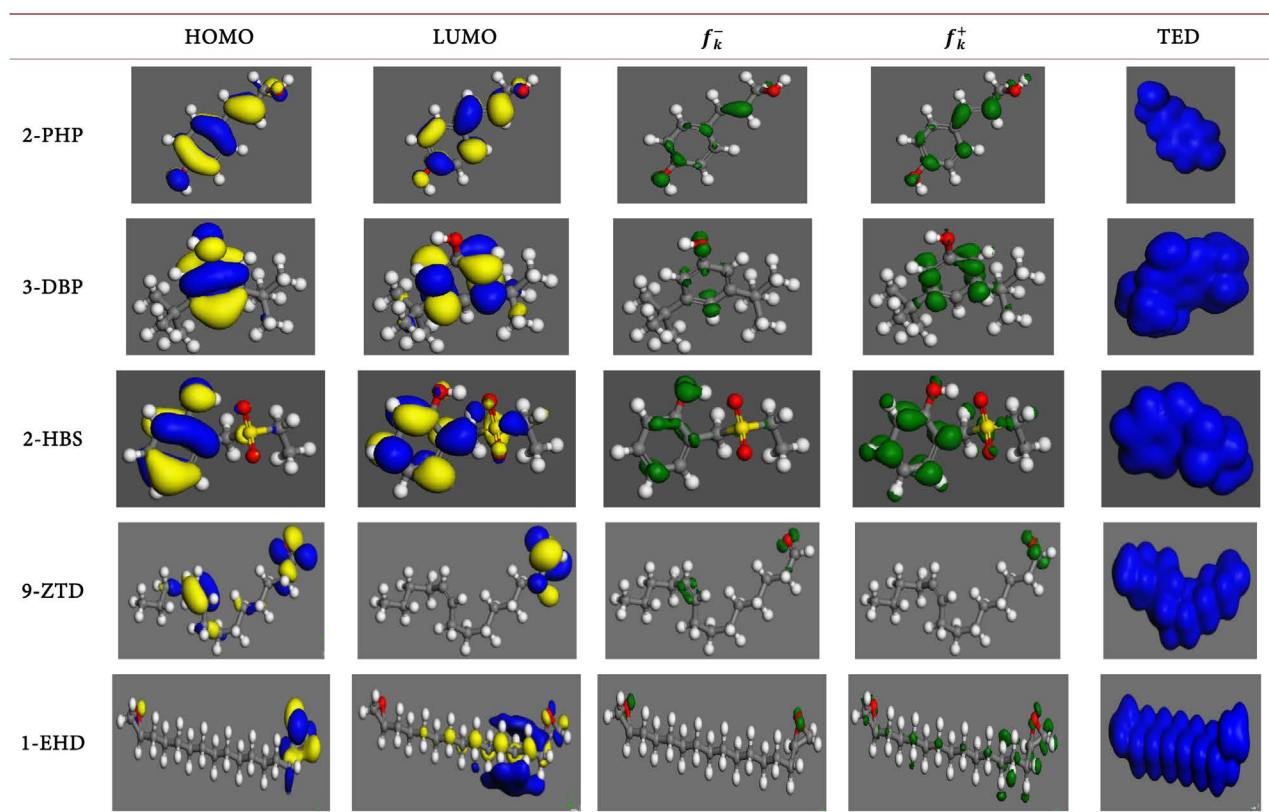


Figure 4. Geometry optimized structure and Fukui indices plots for ES leaf extract constituents obtained from GCMS chromatogram [C, gray; H, white; S, yellow; O, red].

Table 3. Computed Fukui functions with Mulliken atomic charges of ES leaf extracts' molecular composition in gas phase.

| | | | | | | |
|-------|------------------|--------------------|--------------------|---------------------|---------------------|---------------------|
| 2-PHP | f_k^- | C(1) 0.039 | C(3) 0.033 | C(4) 0.025 | O(10) 0.027 | O(11) 0.096 |
| | f_k^+ | 0.037 | 0.011 | 0.066 | 0.004 | 0.055 |
| | Mulliken Charges | -0.147 | -0.161 | -0.134 | -0.483 | -0.441 |
| 3-DBP | f_k^- | C(1) 0.062 | O(7) 0.136 | C(9) -0.021 | C(13) -0.020 | C(14) -0.018 |
| | f_k^+ | 0.096 | 0.042 | -0.021 | -0.021 | -0.019 |
| | Mulliken Charges | -0.208 | -0.448 | -0.296 | -0.243 | -0.295 |
| 2-HBS | f_k^- | O(7) 0.155 | C(8) -0.019 | C(11) -0.010 | O(12) 0.035 | O(13) 0.016 |
| | f_k^+ | 0.045 | -0.02 | -0.013 | 0.043 | 0.032 |
| | Mulliken Charges | -0.473 | -0.316 | -0.340 | -0.336 | -0.433 |
| 9-ZTD | f_k^- | C(1) -0.010 | C(4) -0.025 | C(7) -0.028 | C(9) -0.018 | C(13) -0.020 |
| | f_k^+ | -0.003 | -0.004 | -0.004 | -0.010 | -0.094 |
| | Mulliken Charges | -0.280 | -0.254 | -0.247 | -0.200 | -0.244 |
| 1-EHD | f_k^- | C(2) -0.019 | C(3) -0.015 | C(11) -0.010 | C(13) -0.020 | O(16) 0.198 |
| | f_k^+ | -0.037 | -0.034 | -0.074 | -0.040 | 0.012 |
| | Mulliken Charges | -0.194 | -0.189 | -0.189 | -0.204 | -0.431 |

features [35]. Accordingly, energy of HOMO is related to electron donating ability of a molecule which increases with increase in E_{HOMO} values whereas LUMO energy value is a pointer to molecules' ability to accept electrons with anti-bonding orbital which increases with increase in E_{LUMO} values. Molecules having high E_{HOMO} values induce the affinity to donate electrons to appropriate acceptor sites on the metal surface with low-energy unfilled d-orbital whereas large E_{LUMO} values would imply enhanced ability of the molecule to accept electrons via back-donation from the metal surface. This interaction causes an electrostatic bond to be established between the inhibitor molecule and metal surface thereby reducing sites on the metal available for corrosion attack by the corrosive environment. Herrag *et al.* [37] reported that excellent corrosion inhibitors are usually molecules that not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal using their anti-bond orbital to form stable chelates.

Similarly, molecules with planar geometry have been reported to exhibit higher inhibition efficiency than corresponding molecules with less planar geometry [38] [39] [40]. As seen from **Figure 4**, 2-PHP has a planar geometry with populations of HOMO density focused mainly around the phenyl ring and car-

bon chain with double bond while the LUMO densities were mainly located around the benzene cyclic. This suggests that 2-PHP could undergo a back donation as well as donates electrons at the same region and as a result, form stable chelates with the metal using their anti-bond orbital. 2-PHP adsorption on Cu(110) crystal is lateral (**Table 5**) and engages the delocalized pairs of π -electrons within the electron rich centers for surface interaction. 3-DBP could be seen to have similar HOMO and LUMO population distributions majorly located on the phenyl carbon ring. This also is attributed to the presence of delocalized π -electrons within the ring and electron pair containing oxygen atom attached to it. Hence, 3-DBP could interact with the vacant d orbital of copper atoms and donate electrons as well as accept electrons through anti-bonding orbitals thereby forming coordinate electrostatic chelate bonds. Generally, negatively charged sites in a molecule are susceptible to electrophile attacks. As observed in **Figure 4**, the LUMO electron density for 2-HBS is concentrated on the benzyl member and sulfone link suggesting the active sites which had strong ability of electrostatic bonding to the metal surface. On the other hand, the HOMO density plot was mainly distributed on the oxy- and benzyl-atoms thus signifying the active regions for transferring electrons from 2-HBS to copper surface. The hetero-atoms having electron rich centers are required for bonding unfilled 3d orbitals of Cu atom hence, formation of chelate bonds via adsorption on copper surface is achieved [39]. Comparison of LUMO and HOMO density plot for 9-ZTD reveals that, C1 has higher negative charges as confirmed by the Mulliken population charges computed in **Table 3** and this could be the main adsorption site on the molecule which interacts with Cu(110) crystal. The negative charges however spread to C4 and had presence at C9 indicating that the molecule did interact with the metal surface in a parallel adsorption mode (**Table 5**). The LUMO and HOMO density for 1-EHD is chiefly located at the epoxyl atom (O16). **Table 3** reveals high f and f^* values for 1-EHD indicating that the molecule underwent both donating and back donating of electrons with the copper surface at these active regions. This is confirmed in **Table 4** showing high number of electrons transferred between the molecule and Cu(110) crystal. The individual characteristics of ES leaf extract give an indication in agreement with the obtained high inhibition efficiency got from the electrochemical measurement.

Table 4. EHOMO, ELUMO, energy gap (ΔE), and Binding energy (E_{Bind}) from the molecular dynamic simulations for DM leave extract molecular compositions.

| | EHOMO (Ha) | ELUMO (Ha) | ΔE (Ha) | η (Ha) | χ (Ha) | σ (Ha) | μ (Ha) | E_{Bind} (kcal/mol) | ΔN (kJ/mol) |
|-------|---------------|---------------|--------------------|----------------|----------------|------------------|---------------|---------------------------------|------------------------|
| 2-PHP | -0.1911 | -0.0675 | 0.1236 | 0.0618 | 0.1293 | 16.1812 | -0.1293 | -41.76 | 0.3810 |
| 3-DBP | -0.1978 | -0.0379 | 0.1599 | 0.0800 | 0.1179 | 12.5000 | -0.1179 | -102.7 | 0.1828 |
| 2-HBS | -0.2065 | -0.0592 | 0.1473 | 0.0737 | 0.1329 | 13.5685 | -0.1329 | -49.53 | 0.2950 |
| 9-ZTD | -0.2146 | -0.0717 | 0.1429 | 0.0715 | 0.1432 | 13.9860 | -0.1432 | -70.98 | 0.2321 |
| 1-EHD | -0.2263 | 0.0364 | 0.2627 | 0.1314 | 0.0950 | 7.6104 | -0.0950 | -78.5 | 0.3097 |

Inhibition efficiency is also closely related to reactivity of molecular orbital in response to the whole molecular continuum [41]. The optimized geometries used for the calculations of condensed Fukui functions are shown in Figure 4. As observed, the plots for Fukui functions support the trend of the frontier molecular orbital calculations with less dense population and minimal variation. Table 3 records values for f^+ which measures the molecule reactivity with regard to electrophilic attack or the tendency to donate electrons, whereas the measure of reactivity relating to nucleophilic attack or propensity of the molecule to accept electrons is measured by f^- values [42]. For simplicity, only species with high Mulliken population charges are recorded in Table 3. The recorded high values of Mulliken population charges suggest species within the molecule that might readily be adsorption active centers via electron interaction and formation of stable chelate coordinate bonds with copper surface which in turn reduces sites available for corrosion and dissolution process is mitigated.

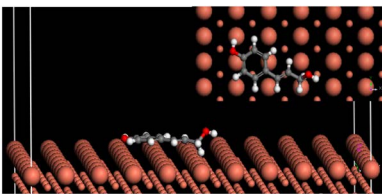
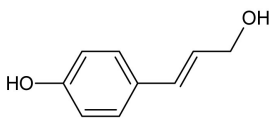
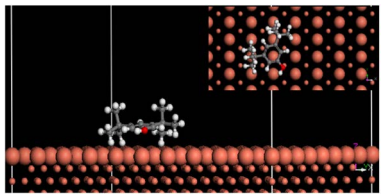
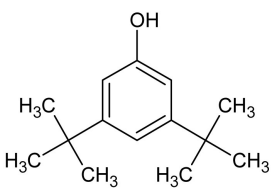
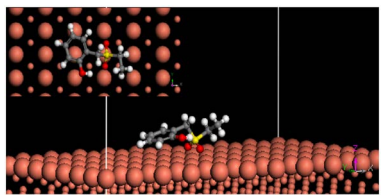
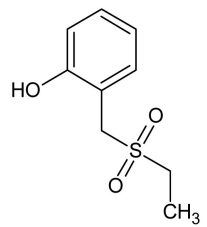
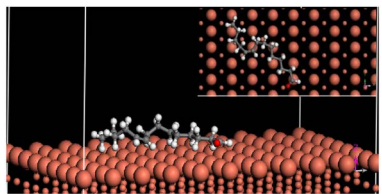
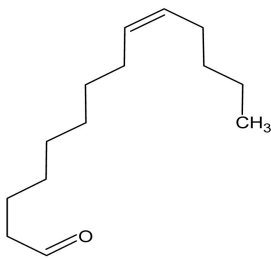
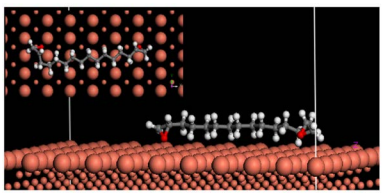
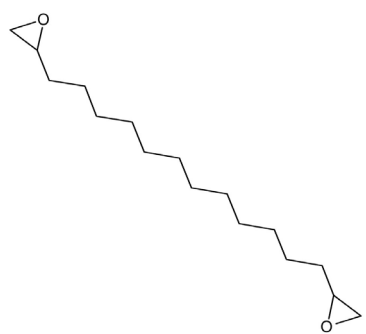
In order to calculate the number of transferred electrons (ΔN), a theoretical value for absolute electronegativity of copper crystal according to Pearson was used $\chi_{\text{Cu}} \approx 463.1 \text{ kJ}\cdot\text{mol}^{-1}$, and a global hardness of $\eta_{\text{Cu}} \approx 0$, by assuming that for a metallic bulk $I = A$, bearing that metallic bulk is softer than neutral metallic atoms [35]. Examination of Table 4 reveals that the planar molecular structure of 2-PHP coupled with the presence of hetero- and oxy- atoms contributed to a lowered value of global hardness and also increased the fraction of transferred electrons between copper crystal. As expected, 2-PHP displayed a low energy gap (ΔE) which is credited with high inhibition efficiency and easily polarized molecule. The number of transferred electrons among the studied molecules of ES leaf extract increased in the order; 2-PHP < 1-EHD < 2-HBS < 9-ZTD < 3-DBP. Wang and Xiao [43] claimed that inhibitor molecule adsorption onto a metallic surface occurs with increased greater softness and lower hardness. This infers that 2-PHP had more contributions in the overall inhibition continuum of ES leaf extracts considering its low-energy gap value and high global softness values that is a pointer to being more polarizable, low kinetic stability and high chemical reactivity among other factors [42] [44] [45]. Occurrence at the copper/inhibitor interface could be likened to Sanderson's electronegativity equalization principle which infers that electron transfer at the interface continues until their electronegativity values become equal with each other [46]. This difference in electronegativity drives the interfacial electron transfer among the studied molecules and is seen to decrease in order, 1-EHD < 3-DBP < 2-PHP < 2-HBS < 9-ZTD. However, if the value of ΔN is greater than 3.6, then inhibition efficiency of molecules increases with increase in electron donating ability with the metal surface [47]. It can be deduced from the calculated data (Table 4) that the major mechanism for the adsorption process of studied inhibitor molecules of ES leaf extracts is principally governed by the donation of electrons from inhibitor molecules to the copper surface. A similar observation has been reported for copper crystals elsewhere [35].

To fully understand the theoretical mechanism of the inhibition action of ES leaf extract, molecular dynamics was engaged to stimulate single inhibitor molecule atop Cu(110) surface in the gas phase devoid of imaginary boundaries. Quench molecular dynamics is used to establish the global energy minimum out of many local energy minima through sampling different possible low energy configurations [31]. Thus, this work engaged molecular dynamics simulation to calculate the binding energies between individual inhibitor molecule and Cu(110) crystal with the results recorded in **Table 4**. The obtained results revealed that the binding energies (E_{Bind}) calculated from the interaction between individual inhibitor molecule and copper crystal was reasonably high suggesting a strong and spontaneous adsorption [32]. The values also give credence to the observed inhibition efficiency of 99.75% obtained from the electrochemical measurement. It is imperative to understand that high binding energy leads to a more stable inhibitor/surface interaction and hence corrosion processes are contained. The E_{Bind} and ΔN values affirm the high inhibition efficiency results gotten from electrochemical polarization and surface analysis. It could also be seen that 2-PHP has the highest binding energy which supports the factor that molecular mechanics for isolated molecule depends on molecule geometry and relies forces between atoms which is minimized to ascertain the minimum strain reactivity [39]. The data obtained from the computations supports the results obtained from electrochemistry and surface morphology studies.

The schematic representative snapshots of the adsorption behavior for single inhibitor molecule on Cu(110) crystal have been presented in **Table 5** along with the molecular structures of the studied ES leaf extract constituents. The representative snapshots indicate the optimum equilibrium adsorption configurations of the studied molecules on Cu(110) crystal. A clear close contact pattern between the inhibitor and the metal is observed in that the molecular backbone of the inhibitor aligns itself systematically along electron deficient areas atop the copper crystal [20]. Moreover, the hetero atoms had very close interaction with the crystal surface after stimulation indicating that they are the chief adsorption centers that form thin compact films on the metal surface at the metal/electrolyte interface while blocking intrusion of corrosive species and/or enhancing the metals' passivation potentials [25]. This is an indication that the ES leaf extract constituents could effectively inhibit corrosion of copper in acid chloride media.

The effect could be attributed to the idea that constituent molecules of ES leaf extract adsorbed closely at the metal/electrolyte interface on the basis of electron donor-acceptor interactions between p -electrons, antibonding lone pairs of heteroatom and unfilled $3d$ copper orbital [45] [46] [47]. The inhibitor molecules probably formed coordinate chelating ligands with the copper crystal through electrons rich centers hence, acting as compact thin films that protected the copper surface along with augmenting of copper passive films. The high value of binding energy for 2-PHP and 2-HBS is attributed to existence of favourable electronic properties such as electron rich centers, planar geometry among

Table 5. Molecular structures of ES leaf constituents and snapshots of side and top view of the lowest energy adsorption minima for single inhibitor molecule simulated on Cu(110) surface.

| | Inhibitor Molecule Simulated atop Cu(110) crystal | Molecular Structure |
|-------|--|---|
| 2-PHP |  |  |
| 3-DBP |  |  |
| 2-HBS |  |  |
| 9-ZTD |  |  |
| 1-EHD |  |  |

others. Electron rich centers are known to enhance electrostatic interaction with material surface so also, the presence of p- π conjugation system at the oxygen atoms resulted in a dissociative adsorption which is favourable to crack intra-molecular bond of the adsorbate crystal [26]. Furthermore, oxy-groups are usually known to hydrolyze in acidic/near neutral solution and are suitable to displace water molecules at the metal surface which favours corrosion inhibition

[41] [44]. The noble value of E_{bind} obtained for 2-PHP infers a probable chemisorption as electron donation and back-donation were observed to be at the same sites. The presence of lone pair electrons and electron rich multiple bonds provided electrons to the unfilled $3d$ orbital at the copper surface thereby forming a protective thin layer via adsorption. Such protective thin films enhances the metals' passivation qualities and as such, acts as steric barrier that hinders the activeness of corrosion process at the metal surface hence, protection of the metal is achieved. This passivation enhancing effect is ascribed to the adsorbed organic molecules of ES leaf extract which actually modified the nature of electron transfer processes across the metal/electrolyte interface.

4. Conclusions

The study engaged both experimental and theoretical approach to evaluate ES leaf extract for corrosion inhibition of CU131729 in 2 M HCl solution and the conclusions that may be drawn from the study are the following:

- 1) Copper corrosion inhibition of in acid solution by ES leaf extract is achieved on the basis of adsorption via formation of electrostatic chelate bonds through heteroatoms.
- 2) Polarization measurements show that Inhibition efficiency (IE%) values increase with the inhibitor concentration resulting in a decrease in anodic and cathodic current density acting essentially as a mixed-type inhibitor. The E_{corr} values shifted towards the positive direction which suggests dominant anodic protection.
- 3) Characterization of the surface corrosion product revealed the presence of nitrogen and sulphur, and increased amount of oxygen indicates the formation of copper oxides and complex chelating ligand bonding of the inhibitor molecules ($\text{N-Cu-S}_{\text{ads}}$, $\text{ES-Cu-Cl}_{\text{ads}}$) took place at the metal surface. The adsorption might be assisted by hydrogen bonds and synergy between ES leaf constituents.
- 4) The theoretical quantum study revealed strong and spontaneous adsorption with high binding energies which affirms the high inhibition efficiency recorded by the experimental methods. The quantum mechanical approach may well be able to foretell molecule structures that are better for corrosion inhibition.
- 5) Equilibrium adsorption configurations based on forcite quench stimulation for individual molecules of ES leaf on Cu(110) have been presented.
- 6) The collective results confirm that ES leaf molecules adhered strongly on the copper surface and aided the compactness of the passive film formed thereby mitigating corrosion processes from occurring on the surface.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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