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Computational Study of Corrosion Inhibition Potential of Watermelon Seed Ethanol Extract Compounds on Zinc Metal Surface in Acidic Medium

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Abstract: In the current computational study, the quantum chemical calculation and molecular dynamic simulation were performed on the compound's presence in Watermelon seed ethanol extract viz. (Pyridine-3-carboxylic acid [P3A], Linoleic acid [LA], Ascorbic acid [AA] and Thiamine [Th]). The quantum chemical calculation was executed by the means of the density functional theory (DFT) module of the material studio software, version 8.0. Electronic parameters for the calculation included DND basis set and B3LYP. Some global descriptors were studied to describe and correlate the reactivity of the molecule structures and their inhibition efficiency. First and second-order condensed Fukui functions were analyzed and local reactivity parameters were identified. Molecular dynamic simulation (MDS) of the interaction between a single molecule and the Zn (1 1 0) surface was performed using Forcite quench and the mechanism of physical adsorption was established. The result obtained was also found to be sufficient.

Keywords: *Watermelon seed extract, Zinc metal; Corrosion Inhibition; Density functional theory; Molecular dynamic simulation*

1. Introduction

Industrial processes including pickling, cleaning, oil acidification, chemical and electrochemical etching which involve the use of acid solutions on metals cannot be avoided (Vashi and Prajapati, 20217). The use of zinc metal is foremost in several construction works, possibly due to its superb cost effectiveness, mechanical and electrical properties. Like other metals, however, its degradation, when in contact with corrosion agents like acids, is a considerable issue for its application (Iorhuna et *al.*, 2023; Odewunmi et *al.*, 2015; Mihit et *al.*, 2010). However, proper implementation of corrosion control measures can save cost and safe guard the working environment (Sulaiman, 2017). This can be well achieved with the use of effective corrosion inhibitors. Most of the inhibitors used in the industries compose of some compounds that are toxic and have been facing a lot of criticisms due to their threat to human health and their environments (Arrousse et *al.*, 2021;

Usman, 2017; Zarrouk et *al.*, 2011). Hence, the research activities is now geared towards both exploring existing and developing new materials preferably eco-friendly materials that are capable of inhibiting metal corrosion in the presence of corrodent media (Lazrak et *al.*, 2021; Ahmad et *al.*, 2014; Barouni et *al.*, 2014). The efficiency of compounds extracted from plant materials toward corrosion inhibition have been reported by several authors (Ameh and Sani, 2015; El-Belghiti et *al.*, 2016; Chandrabhan et *al.*, 2018).

The efficiency of the corrosion inhibitors depends on the molecular structure of the inhibitor. The compounds, which can donate electrons to unoccupied orbitals of metal surface to form coordinate covalent bonds and can also accept free electrons from the metal surface by using their anti-bonding orbital to form feedback bonds, constitute excellent corrosion inhibitors (El-Belghiti et *al.*, 2016; Chandrabhan et *al.*, 2018).

With the advances in computer application and development of modeling software, the molecular modeling software has grown to be an effective technique to explore complex systems at molecular level. Molecular structure, electronic distribution density and detailed interaction energies can be obtained through this method, which is helpful for investigation of inhibition efficiency mechanism. Nowadays, much researches based on molecular modeling software were conducted to investigate the inhibition mechanism on micro to macroscopic scale (Ayuba et *al.*, 2018).

The molecular modeling software has been widely used to study the reaction mechanisms and interpret experimental results theoretically and to turn the chemical ambiguities. The computational study was executed on compounds presence in Watermelon seed ethanol extract (WSE) viz. (Pyridine-3-carboxylic acid [P3A], Linoleic acid [LA], Ascorbic acid [AA] and Thiamine [Th]) sourced from the literature in order to determine the relationship between molecular structures and their inhibition efficiencies on the corrosion of zinc (110) using quantum chemical calculation and molecular dynamic simulation.

2. Methodology

2.1 Density functional theory (DFT)

The quantum chemical calculations were performed on WSE compounds viz. Pyridine-3-carboxylic acid (P3A), Linoleic acid (LA), Ascorbic acid (AA) and Thiamine (Th) as reported in reported by (Okafor et *al.*, 2015; Gladvin et *al.*, 2017; Ait Aicha et *al.*, 2019). The global and local reactivity active sites of the molecules were evaluated. The simulations were performed by the means of density functional theory (DFT) electronic structure program DMol^3. Electronic parameters for the simulation included restricted spin polarization using the DND basis set and B3LYP local correlation density functional (Udowo, 2018).

The quantum chemical descriptors calculated in the current study are; E_{HOMO}, E_{LUMO}, absolute electronegativity (χ), global hardness (η), energy gap (ΔE_g), global softness (σ), ionization potential (I), electron affinity (A), global electrophilicity index (ω), energy of back donation ($\Delta E_{b\text{-}d}$) and the fraction of electrons transferred (ΔN).

Electronegativity χ (eV) is defined as negative of chemical potential. For an N-electron system with total electronic energy E and an external potential v(r), the chemical potential (μ), has been defined as the first derivative of E with respect to N at constant v(r) as in equation 1,

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right) v(r) = \left(\frac{I+A}{2}\right) = \frac{-1}{2}\left(E_{HOMO} + E_{LUMO}\right) \qquad \textbf{Eqn. 1}$$

In equation 2, the global hardness η (eV) has been defined within DFT as the second derivative of E with respect to N at constant v(r)

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right) v(r) = \left(\frac{\partial \mu}{\partial N}\right) v(r) = \left(\frac{I-A}{2}\right) = \frac{-1}{2}\,(E_{HOMO} - E_{LUMO}) \qquad \textbf{Eqn. 2}$$

The mathematical expression of energy gap $\Delta E_g\ (eV)$ and global softness σ $(\mathrm{eV})^{-1}$ has been defined in equation 3 and 4 respectively.

$$\Delta E_g = E_{LUMO} - E_{HOMO} \qquad \textbf{Eqn. 3}$$

$$\sigma = \left(\frac{1}{\eta}\right) \qquad \textbf{Eqn. 4}$$

In equations 5 and 6, the Ionization potential $I(eV)$ (I) and Electron affinity $A\ (eV)$ are defined as the negative values of the energies of the highest occupied molecular orbital (E_{HOMO}) and of the lowest unoccupied molecular orbital (E_{LUMO}) respectively.

$$I: Ionisation\ energy\ (eV) = -E_{HOMO} \qquad \textbf{Eqn. 5}$$

$$A: Electron\ affinity\ (eV) = -E_{LUMO} \qquad \textbf{Eqn. 6}$$

These quantities above are related to the electronegativity (χ,) and global hardness (η).

Global electrophilicity index $\omega\ (eV)$ and energy of back donation $\Delta E_{b-d}\ (eV)$ are defined in equation 7 and 8 respectively.

$$\omega: Global\ electrophilicity\ index\ (eV) = \frac{E_{HOMO} + E_{LUMO}}{8} \qquad \textbf{Eqn. 7}$$

$$\Delta E_{b-d}: Back\ donation\ (eV) = \frac{E_{HOMO} - E_{LUMO}}{8} \qquad \textbf{Eqn. 8}$$

The fraction of electrons transferred (ΔN) from the inhibitor molecules to the zinc surface was calculated using equation 9.

$$\Delta N = \frac{(\chi_{Zn} - \chi_{inh})}{2(\eta_{Zn} - \eta_{inh})} \qquad \textbf{Eqn. 9}$$

χ_{Zn} and χ_{inh} are the absolute electronegativity of zinc metal and the inhibitor molecules respectively, and η_{Zn} and η_{inh} are the absolute hardness of zinc metal and the inhibitor molecules respectively.
The Local reactivity of the studied compounds was analyzed by means of the Fukui indices (FI) to assess regions of nucleophilic, electrophilic and radical attack.
The Fukui function f(r) is defined as the first derivative of the electronic density ρ(r) at a point r in space around the molecule at constant external potential v(r). Hence, using a scheme of finite difference approximations from Mulliken population analysis of atoms in the isolated compounds and depending on the direction of electron transfer, the equations 10, 11 and 12 are for electrophilic, nucleophilic and radical attack respectively. These functions/equations were condensed to the nuclei by using an atomic charge partitioning scheme, such as Mulliken population analysis and all calculations were done at the ground state geometry (Fransisco and Jose, 1994; Saranya *et al.*, 2015; Umaru and Ayuba, (2020b)):

$$f_{Ak}^{-} = q_{Ak}(N_A) - q_{Ak}(N_A - 1) \qquad \textbf{Eqn. 10}$$

$$f_{Ak}^{+} = q_{Ak}(N_A + 1) - q_{Ak}(N_A) \quad \textbf{Eqn. 11}$$

$$f_{Ak}^{0} = \frac{q_{Ak}(N_A+1) - q_{Ak}(N_A-1)}{2} \quad \textbf{Eqn. 12}$$

Where $q_{AK}(N_A)$ is the mulliken charge on atom k for N_A total electrons in the molecule, i.e., the electron density at a point r in space around the molecule. N_A + 1 correspond to an anion with an electron added to the LUMO of the neutral molecule; N_A - 1 corresponds to the cation with an electron removed from the HOMO of the neutral molecule.

Second order Fukui function (f^2) known as the dual descriptor Δf(k), is another local descriptor introduced by Morell *et al.* (Ayuba and Umar, 2021). It has been defined as the difference between nucleophilic and electrophilic Fukui functions as in equation 13.

$$f^2(r) = f_k^+ - f_k^- \quad \textbf{Eqn. 13}$$

If $f^2(r) > 0$, then site k prefers nucleophilic attack, whereas if $f^2(r) < 0$; then site k prefers an electrophilic attack. This indicates that $f^2(r)$ serves as an index of selectivity towards nucleophilic or electrophilic attacks (Belghiti et *al.*, 2019).

2.2 Molecular dynamic simulation (MDS)

Molecular dynamic simulation of the interaction between a single molecule of the WSE compounds and the Zn(110) surface was performed using Forcite quench module in BIOVIA Material studio 8.0 packages (Accelrys; presently BIOVIA, Dassault Systems, USA) in order to determine the global energy minimum (Belghiti et *al.*, 2017). Calculations were carried out in an 8 x 7 super-cell using the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field and the Smart algorithm. Of the many kinds of Zn surfaces, Zn (1 1 0) is the most densely packed and also the most stable (Ayuba et *al.*, 2018). The Zn crystal was cleaved along the (1 1 0) plane. The Zn slab built for the simulation process was significantly larger than the inhibitor molecules in order to avoid edge effects during docking. Temperature was fixed at 350 K, with NVE (micro canonical) ensemble, with time step of 1 fs and simulation time of 5 ps. The system was quenched every 250 steps.

Surface atoms were constrained. Optimized structure of the inhibitor molecules were used for the simulation. Adsorption of a single molecule of the Pyridine-3-carboxylic acid (P3A), Linoleic acid (LA), Ascorbic acid (AA) and Thiamine (Th) from watermelon seed ethanol extract onto the Zn (1 1 0) surface provides access to the interaction energies and its effect on the inhibition efficiency of the molecule. Hence, the interaction energy ($E_{interaction}$) and binding energy ($E_{binding}$) between single compound and Zn (1 1 0) surface was calculated using equation 14 and 15 respectively (Ayuba and Abdullateef, 2020).

$$E_{interaction} = E_{system} - (E_{molecule} + E_{Zn(110)}) \quad \textbf{Eqn. 14}$$

$$E_{binding} = -E_{interaction} \quad \textbf{Eqn. 15}$$

Where, E_{system}, $E_{molecule}$ and $E_{Zn(1\ 1\ 0)}$ correspond to the total energies of the adsorbed Zn-molecule interaction in a gas phase, single molecule of the WSE inhibitor and the Zn (1 1 0) slab respectively.

3. Results and Discussion

3.1 Density functional theory (DFT)

The calculated values of molecular quantum chemical parameters such as; E_{HOMO}, E_{LUMO}, absolute electronegativity (χ), global hardness (η), energy gap (ΔE_g), global softness (σ), ionization potential (I), electron affinity (A), global electrophilicity index (ω), energy of back donation (ΔE_{b-d}) and the fraction of electrons transferred (ΔN) are presented in Table 1. While Figures 1 – 4 (a – d), show the geometry optimized structures, total electron density, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) structures of the studied inhibitors compounds.

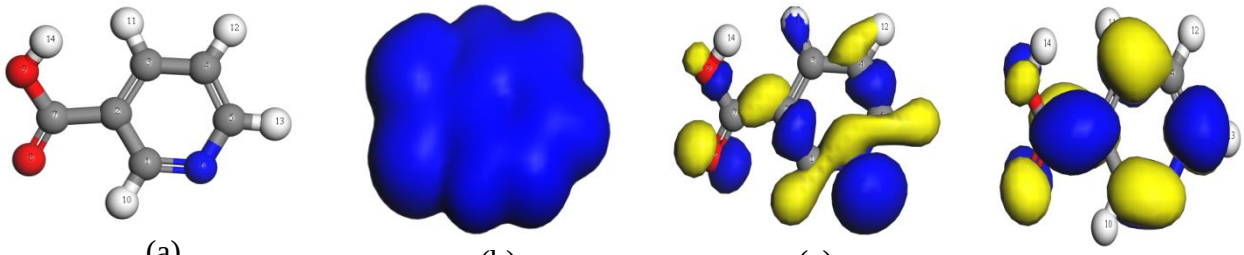
Table 1: Quantum chemical parameters

DFT descriptors	Pyridine-3-carboxylic acid	Ascorbic acid	Linoleic acid	Thiamine
HOMO (orbital number)	32	46	78	79
LUMO (orbital number)	33	47	79	80
E_{HOMO} (eV)	-0.273623	-0.236390	-0.234007	-0.204718
E_{LUMO} (eV)	-0.070883	-0.037818	-0.036445	-0.029185
ΔE_g: Energy gap (eV)	0.202740	0.198572	0.197562	0.175533
ΔE_{b-d}: Energy of back donation (eV)	-0.025343	-0.024822	-0.024695	-0.021942
Molecular mass (g/mol)	123.1094	176.1200	280.4472	265.3550
χ; Electronegativity (eV)	0.172253	0.137104	0.135226	0.116952
η: Global Hardness (eV)	0.101370	0.099286	0.098781	0.087767
σ: Global Softness (eV)	9.864852	10.071913	10.123404	11.393869
I: Ionization potential (eV)	0.273623	0.236390	0.234007	0.204718
A: Electron affinity (eV)	0.070883	0.037818	0.036445	0.029185
ω: Global electrophilicity index (eV)	-0.172253	-0.137104	-0.135226	-0.116952
ΔN: Fraction of Electrons Transferred	0.308040	0.315093	0.315418	0.317765

According to (Oguzie et *al.*, 2015), reveals that the molecules that possess higher values of E_{HOMO} have greater tendency to donate electrons while those molecules that possess lower values of E_{LUMO} have greater tendency to accept electrons from electron rich species. In WSE compounds Linoleic acid has high tendency to donate electrons while Pyridine-3-carboxylic acid has great potentials to accept electrons due to the highest E_{HOMO} and lowest E_{LUMO} values respectively.

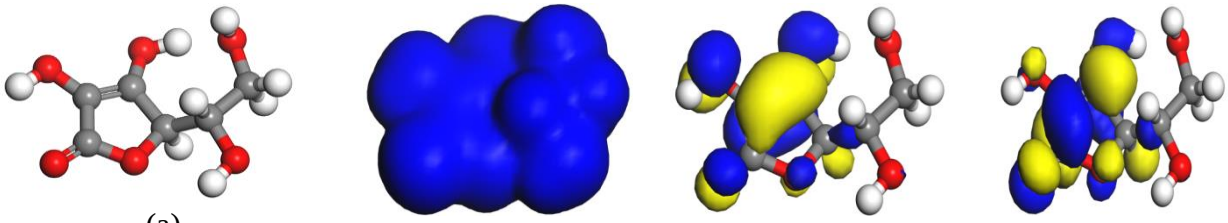
More details regarding the reactivity of the inhibitor compounds towards the zinc surface can be obtained through the energy gap (ΔE_g). The energy gap of the molecule can be directly related to its stability and consequently its tendency to react. Udowo (2018), stated that the higher values of energy gap are associated with high stability of the compound and therefore a low tendency to react while lower values are associated with low stability of the compound and hence a high tendency to react with other chemical species. The trend observed in energy gap values in inhibitor compounds, are in

increasing order (Linoleic acid < Pyridine-3-carboxylic acid). This indicates that Linoleic acid has low stability and hence a high tendency to adsorbed on zinc surface.



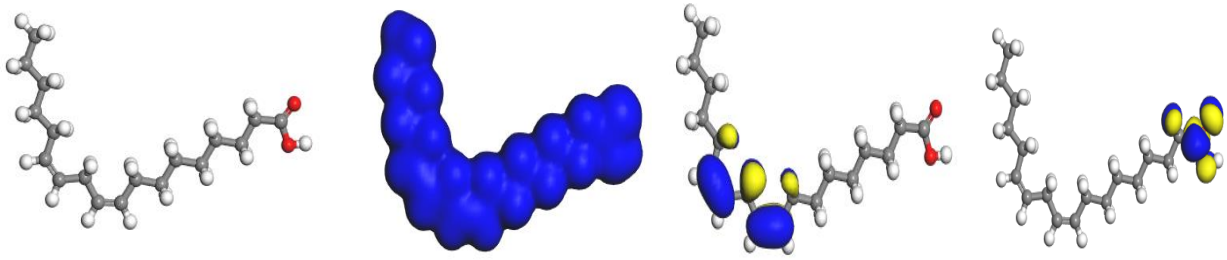
(a) (b) (c) (d)

Figure 1: Structural properties of Pyridine-3-carxylic acid: (a) optimized structure (b) total electron density (c) HOMO orbital and (d) LUMO orbital



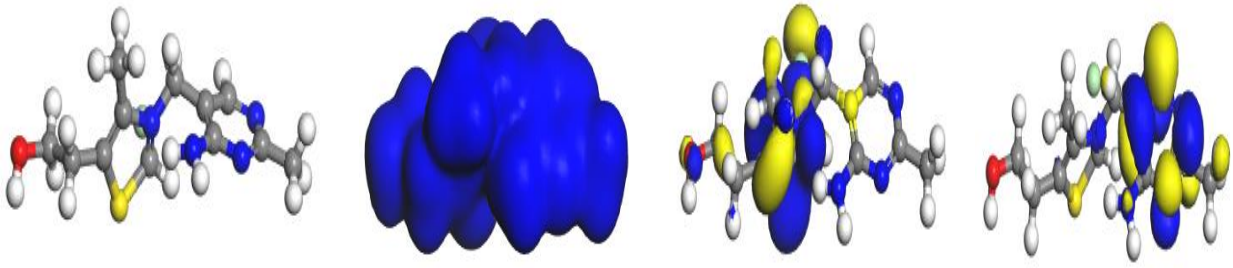
(a) (b) (c) (d)

Figure 2: Structural properties of Ascorbic acid: (a) optimized structure (b) total electron density (c) HOMO orbital and (d) LUMO orbital



(a) (b) (c) (d)

Figure 3: Structural properties of Linoleic acid: (a) optimized structure (b) total electron density (c) HOMO orbital and (d) LUMO orbital



(a) (b) (c) (d)

Figure 4: Structural properties of Thiamine: (a) optimized structure (b) total electron density (c) HOMO orbital and (d) LUMO orbital

Note: Atom legend: *white* H, *light gray* C, *red* O, *yellow* S and *blue* N. The isosurfaces (larger lobes) depict the electron density difference; the *darker* regions show electron accumulation, whereas the *lighter* regions show electron

Global hardness (η) is the molecular properties that assist in the reactivity and selectivity of the inhibitor compounds, also provides more insight with respects to the resistance of an atom to a charge transfer of the molecule. The associations of adsorption process between inhibitor compounds and zinc surface is well establish with the compound that possess lower values of global hardness and subsequently high value of global softness (Umaru and Ayuba, 2020). The trends observed in global hardness is increasing order (Linoleic acid < Pyridine-3-carboxylic acid). This indicate that there was high tendency for a well establish adsorption interaction between Linoleic acid and zinc surface due to their lowest values of global hardness and consequently highest values of global softness compared with other investigated inhibitor compounds.

Electronegativity (χ) is one of the essential chemical reactivity parameters of these compounds. It provides information regarding the electron density within the molecule. In other words, electronegativity is a measure of the power of an atom or a group of atoms to attract electrons towards it (Ayuba and Abdullateef 2020; Ansari et *al.*, 2024). This means that the atom or group of atom with the highest value of electronegativity possess great power to attract electrons towards its direction. The electronegativity trends observed are in decreasing order were (Pyridine-3-carboxylic acid > Linoleic acid). This indicates that Linoleic acid has the lowest electronegativity and hence great tendency to adsorb on zinc surface.

The fraction of electrons transferred (ΔN) are in decreasing order of (Pyridine-3-carboxylic acid < Linoleic acid). Based on the trend observed, it has been found that Linoleic acid has the highest values of fraction of electrons transferred (ΔN) compared to other compounds of the inhibitor. It was reported by Tharini et *al.* (2016), that if ΔN value < 3.6, inhibition efficiency increases with increasing values of electron donating ability of the molecules, while value of ΔN > 3.6 indicate a decrease in inhibition efficiency with increase in electron donating ability of the molecules. With this regard ΔN values of all the studied compounds are < 3.6 and therefore linoleic acid was found to have high inhibition efficiency compared to other compounds of the inhibitor.

The local reactivity of the investigated inhibitor compounds were analyzed by means of the Fukui indices (FI) and are presented in Figures 5 - 8. The regions of the studied inhibitor compounds presence in WSE observed to have the highest values of Mulliken and Hirshfeld charges with respect to Fukui electrophilic attack (f^-) and nucleophilic attack (f^+) are presented in Table 2.

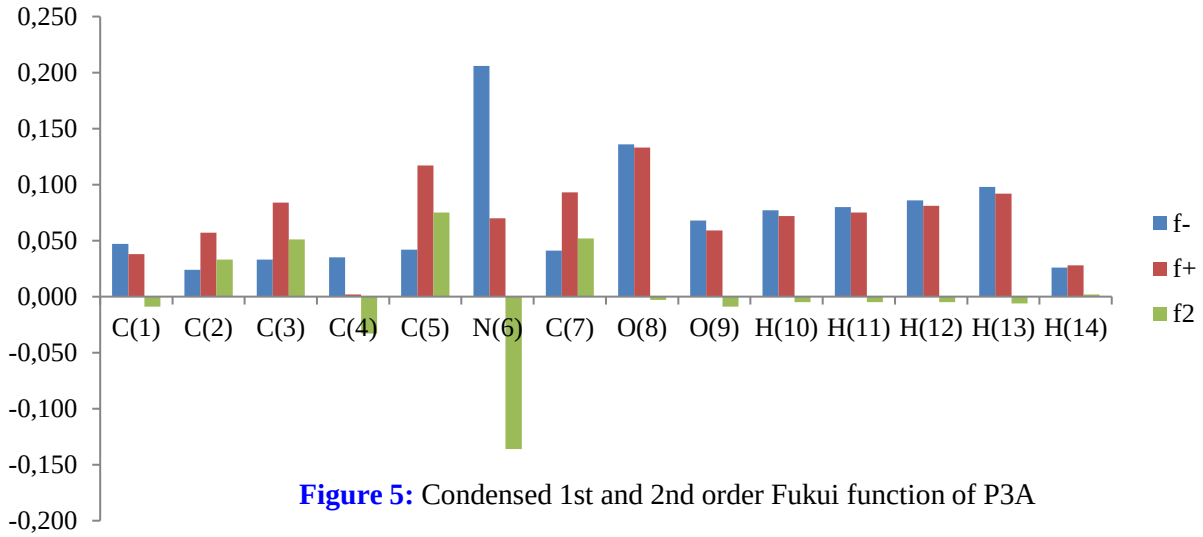


Figure 5: Condensed 1st and 2nd order Fukui function of P3A

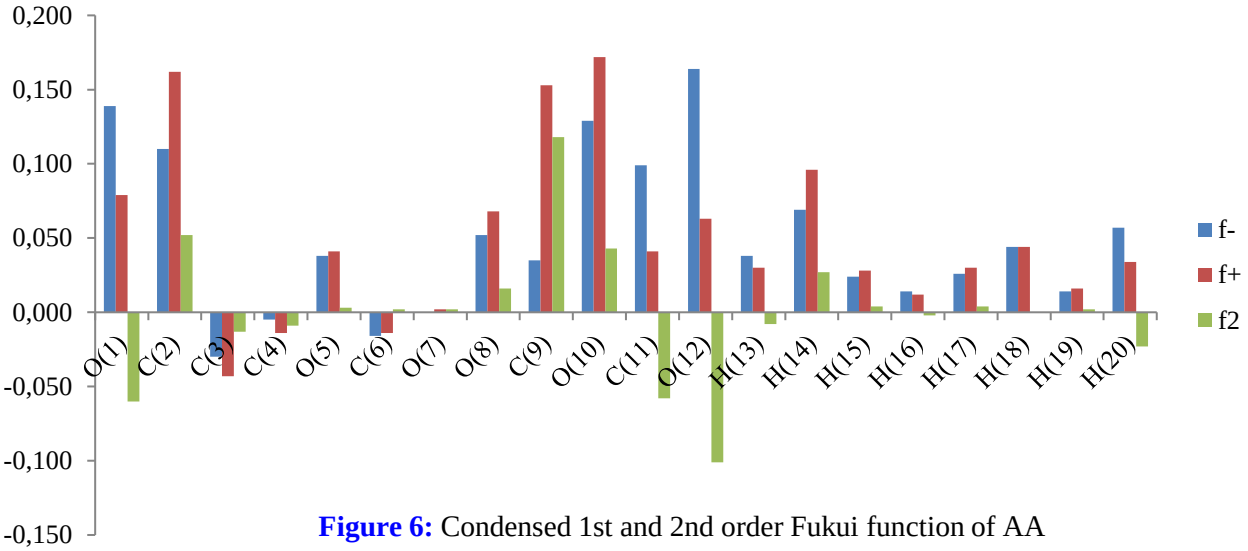


Figure 6: Condensed 1st and 2nd order Fukui function of AA

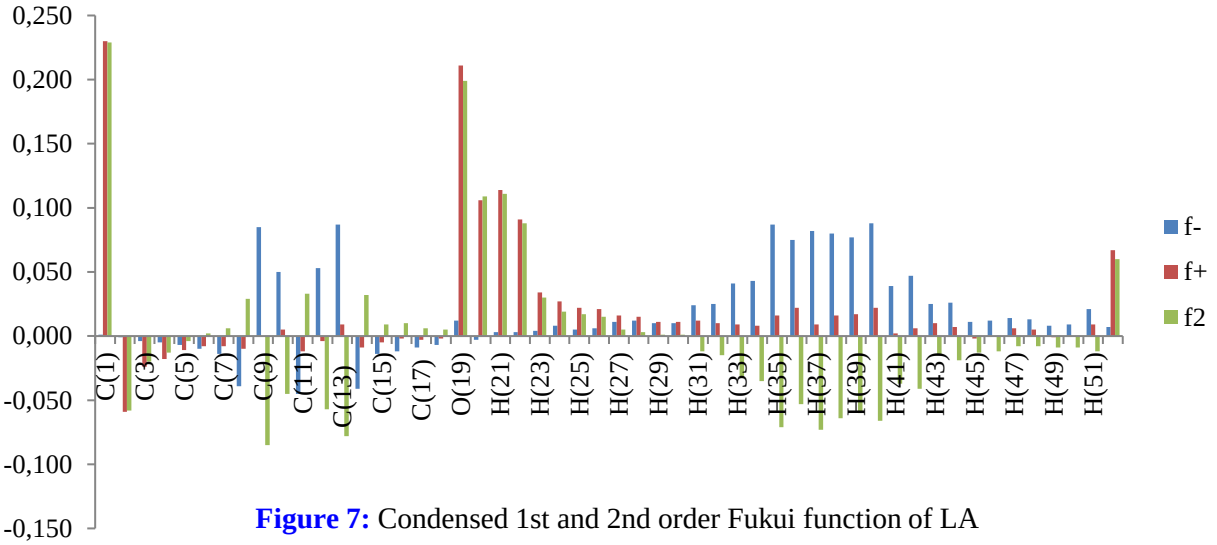


Figure 7: Condensed 1st and 2nd order Fukui function of LA

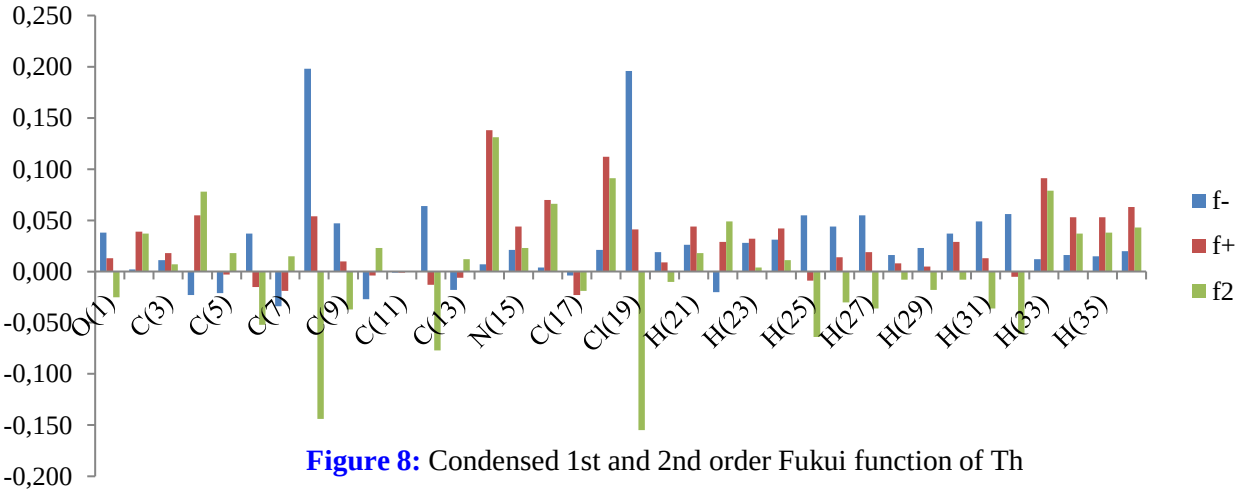


Figure 8: Condensed 1st and 2nd order Fukui function of Th

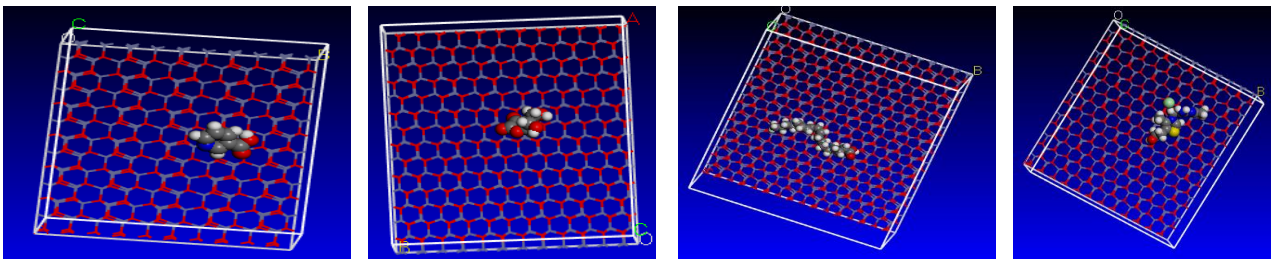
Table 2: Highest values of Mulliken and Hirshfeld charges with respect to condensed fukui functions of the studied molecules

Molecules	Electrophilic attack (f^-)		Nucleophilic attack (f^+)	
	Mulliken	Hirshfeld	Mulliken	Hirshfeld
Pyridine-3-carboxylic acid	N (6), 0.206	N (6), 0.234	O (8), 0.133	O (8), 0.130
Ascorbic acid	O (12), 0.164	O (12), 0.156	O (10), 0.172	O (10), 0.171
Linoleic acid	H (40), 0.088	C (13), 0.118	C (1), 0.230	O (19), 0.195
Thiamine	S (8), 0.198	S (8), 0.171	C (14), 0.138	C (14), 0.133

The Fukui indices (f^-) measures reactivity with respect to electrophilic attack that is the potency of the molecule to release electrons, whereas Fukui indices (f^+) is a measure of reactivity relating to nucleophilic attack or ability of the molecule to attract electrons (Umaru and Ayuba, 2020; Fransisco and Jose 1994). It was observed that P3A has the highest Mulliken and Hirshfeld values in the fukui indices (f^-) electrophilic attack resulting the potency of the molecule to release electrons on the zinc metal surface.

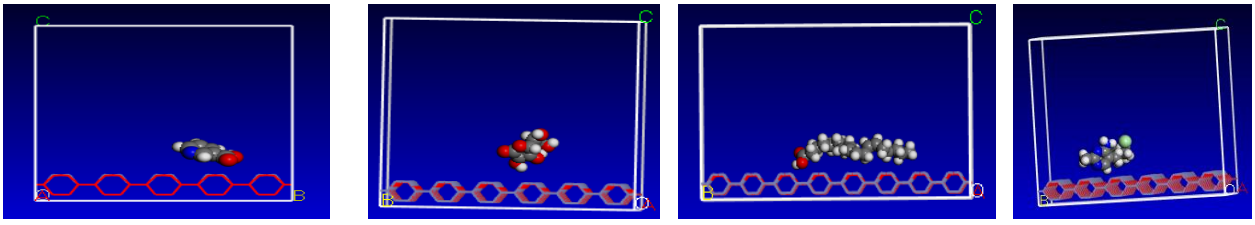
3.2 Molecular Dynamic Simulation (MDS)

Figures 9 and 10 (a-d) represents the snapshots of the top and side views respectively of the lowest energy of the Molecular dynamics simulation for the interaction between a single molecule and the Zn (1 1 0) surface which was performed using Forcite quench module in Material Studio. The total energies were calculated by averaging the energies of the five (5) most stable representative adsorption configurations.



(a) (b) (c) (d)

Figure 9: Top view of the most stable configuration (a) Zn-P3A system (b) Zn-AA system (c) Zn-LA system and (d) Zn-Th system



(a) (b) (c) (d)

Figure 10: Side view of the most stable configuration (a) Zn-P3A system (b) Zn-AA system (c) Zn-LA system and (d) Zn-Th system

From Table 3, the obtained $E_{interaction}$ values for Pyridine-3-carboxylic acid, Ascorbic acid, Linoleic acid and Thiamine are; -19.7729, -22.4688, -30.2052 and -48.1198 kcal/mol respectively. The values are all negative and of considerable magnitude, suggesting stable adsorption structures, showing that the large negative values of $E_{interaction}$ are more strongly adsorbed on the Zn metal surface. It has also been reported that the more negative the interaction energy of the inhibitor metal surface is, the better the adsorption of the inhibitor onto the metal surface and subsequently the higher the inhibition efficiency (Ayuba and Abdullateef, 2020; Umaru and Ayuba, 2020; Hbika *et al.*, 2023; Jafil *et al.*, 2024). It can be observed from **Table 3** that a trend could be inferred in terms of inhibition efficiencies of the inhibitors in respect of their adsorption energies as follows: Thiamine > Linoleic acid > Ascorbic acid > Pyridine-3-carboxylic acid.

Table 3: Energies descriptors for the lowest adsorption configuration for Zn-Inhibitor systems

Compounds	Interaction parameters (kcal/mol)				
	E_{system}	$E_{interaction}$	$E_{molecule}$	$E_{Zn(110)}$	$E_{binding}$
Pyridine-3-carboxylic acid	-33.0537	-19.7729	-13.2807	0.0000	19.7729
Ascorbic acid	-6.2007	-22.4688	15.0281	0.0000	22.4688
Linoleic acid	-90.2382	-30.2052	-60.0330	0.0000	30.2052
Thiamine	-148.3971	-48.1198	-100.2773	0.0000	48.1198

Conclusion

The results obtained from quantum chemical calculations and molecular dynamic simulations unequivocally demonstrated the potency of the compounds present in Watermelon Seed Extract (WSE) to adsorb onto the zinc metal surface. Notably, all the compounds tested exhibited remarkable inhibition efficiency, underscoring their potential as effective corrosion inhibitors.

The findings of this study suggest that WSE-derived compounds could be explored as eco-friendly and sustainable alternatives for corrosion protection in various industrial applications. The adsorption of these compounds onto the zinc metal surface could provide a barrier against corrosive agents, thereby reducing the risk of corrosion-related damage.

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