



Comparative study of skimmianine as an adsorptive inhibitor on Al (110) and Fe (111) crystal surface, using DFT and simulation method

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ABSTRACT

Aluminum and iron are very significant industrial materials that are used to make everything from car bodies to roofing sheets. Despite forming a layer of protection to prevent corrosion, they are still susceptible to corrosion in some environments. Using the local density function B3LYP under constrained spin polarization DNP+ basis in aqueous solution, a theoretical study on the corrosion inhibition of the two metals, aluminum and iron, was conducted in an effort to protect these metals. The goal was to obtain the stable geometry of the molecule skimmianine. These parameters included the (+) electron accepting power and (-) electron donating power as well as the energy gap (E), electronegativity (E), global hardness (E), and fraction of electron transfer (N) between the inhibitor molecule and the iron surface. As a result, it was determined that chemisorption was seen on the surface of the Fe crystal, while physisorption was described as the mode of interaction between the molecule and Al. According to the results of the Fukui functions, the heteroatoms in the molecule, such as the nitrogen, oxygen, and methylene (-CH₂-) functional groups, may act as the focal point for the selectivity of electron donation and acceptance between the metal and the skimmianine molecule. According to information on bond length and angle, the molecule was tetragonal planar on the surfaces of the aluminum and iron crystals.

1. Introduction

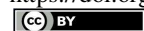
The necessity to safeguard aluminum and iron by different scientific techniques exists due to the fact that they are extremely important materials in building and other sectors. Metals like aluminum and iron become brittle and susceptible to corrosion when acid solutions are used during cleaning, pickling, oil well acidization, and acid descaling [5]. As a result of the high cost of stainless steel, aluminum and iron are the metals utilized to build most tanks in the oil sectors [3]. When exposed to the environment or aqueous solutions, aluminum and iron have the unusual property of having a comparatively low corrosion rate [4] because oxides develop as a protective coating on their surface. Nonetheless, in extremely corrosive or aggressive settings, it is still prone to corrosion [6–8]. These metals' high technical value and extensive variety of industrial and household uses have made corrosion avoidance of these materials a topic of interest [5]. The majority of

structural failures are linked to the sorts of materials being used, either as principal metals or in massive compositions (alloys) with either aluminum or iron [6–10]. Thus, it is necessary to prevent the metal from degrading in the environment by using inhibitors in order to lessen or eliminate this hazard [11].

In this regard, organic chemicals have found extensive usage as corrosion inhibitors, although the majority of them are costly and unfriendly to the environment [6]. Because of this, natural compounds of a plant origin are known to be readily available, affordable, and environmentally friendly, making them suitable inhibitors. Plant extracts from the leaves, bark, and roots are thought to be ecologically acceptable when used as compounds that prevent corrosion of metals and their alloys in a variety of conditions [8]. Several earlier investigations demonstrated that naturally occurring compounds with a plant origin may effectively be employed as metal corrosion inhibitors. Most inhibitor compounds derived from plants contain hetero atoms

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such O, N, S, and P, which have been shown to improve adsorption and inhibitory effectiveness [9–15].

The identification and evaluation of inhibitor potentials and process mechanisms were made simpler by the advent of computer-based programs to address corrosion issues. Most recently, attention has been focused on the use of the quantum chemical parameters approach and molecular dynamic simulation approaches to examine the inhibitory potentials of several of these phytochemicals [12].

Skimmianine is a fluoroquinoline alkaloid found in *skimia japonica*, a flowering plant in family Rutaceae that is native to Japan and China also known as 4,7,8-Trimethoxy-2,3-dihydro-furo[2,3-b] quinoline. It is utilized in the current investigation to compare the potential of inhibition on the surfaces of aluminium and iron metal surfaces: Al(110) and Fe(111) respectively. This was theoretically accomplished by the computation of quantum chemical parameters using molecular dynamics simulations of the molecule.

2. Results and Discussion

2.1 Quantum Chemical Calculations Molecular Geometry

The geometry of the skimmianine structure was fully optimized using density functional theory (DFT) with a B3LYP functional and DNP+ basis set in the aqueous phase. The geometry of the molecule on the surfaces of both Fe and Al was examined and is shown in Table 1 before and after simulation. The geometry revealed that the single bonds between the molecule's atoms were longer than the double bonds. Both before and after the simulation, C4-C5 seems to be the molecule's longest bond. All of the molecules' bond lengths were altered as a result of the experiment, this demonstrated that each molecule actively contributed to the metal surfaces' protection. The investigation of the bond angle before and after simulation of molecules was not entirely planar; the values ranged from 0 to 120, which suggested that the molecules might not have a flat orientation on the aluminum and iron surfaces to maximize surface adsorption. [10].

2.2 Frontier molecular orbitals

The ideal structure, total electron density, HOMO orbitals, and LUMO orbitals of the molecules under investigation are displayed in Figure 2. Given the total electron density of the molecules, it was possible that the entire molecule could enhance the inhibition of corrosion on metal surfaces during the inhibition phase. The oxygen atom is represented by the red color, the nitrogen atom by the blue color, the core carbon atom by the gray color, and the hydrogen atom by the white color

2.3 Fukui Functions

The Fukui function, which quantifies local reactivity, may be used to interpret the relative reactivity of several

atomic locations within a molecule [10]. Due to the presence of several substituted hetero-atoms, the condensed Fukui Ffunction and the local reactivity indices allow for the description of the various molecular components. Fukui indices are descriptors that identify the attack type (radical, electrophilic, or any combination of the three). The atoms' large negative charge densities imply that there are a lot of potential reactive sites where molecules can be adsorbed. It would be interesting to learn more about the active areas for the compounds' potential radical attacks given the possibility of using the investigated chemicals as inhibitors.

Table 1. Optimized geometric parameters of Skimmianine before and after corrosion inhibition on Aluminium and Iron surfaces.

Bond length	Optimized (nm)	Al (nm)	Fe (nm)
C1-C2	1.398	1.397	1.400
C2-C3	1.410	1.408	1.412
C3-C4	1.375	1.377	1.380
C4-C5	1.387	1.391	1.389
C5-C6	1.414	1.415	1.414
C5-C10	1.417	1.421	1.419
C10-C9	1.370	1.369	1.370
C9-C8	1.406	1.407	1.406
C8-N7	1.330	1.325	1.330
N7-C4	1.360	1.356	1.362
C10-O14	1.387	1.389	1.386
O14-C15	1.422	1.423	1.423
C8-O11	1.388	1.389	1.391
O11-C12	1.436	1.424	1.438
C12-C13	1.540	1.536	1.391
C3-O16	1.397	1.400	1.438
O16-C17	1.424	1.422	1.402
C2-O18	1.392	1.395	1.392
O18-C19	1.423	1.423	1.427
Bond Angle	Optimized (°)	Al (°)	Fe (°)
O18-C2-C3	119.193	117.652	120.596
O18-C2-C1	121.543	122.324	120.261
C2-C3-O16	122.100	116.596	124.005
C4-N7-C8	118.271	118.983	118.442
N7-C8-O11	119.332	118.823	119.439
C8-O11-C12	102.575	100.580	103.028
C10-O14-C15	117.320	120.307	115.519

Table 2 shows the outcomes of the condensed dual descriptor calculation using both $f_2^+(M)$ Mulliken atomic charges. The Mulliken atomic spin densities $P_{k^+}(M)$ and $P_{k^-}(M)$ correspond to the electrophilic and nucleophilic Parr functions, respectively. The results of the local reactivity descriptors in Table 2 showed that

the atoms in the molecule will function as electrophilic sites for a nucleophilic attack and that C10 will be the favored locations for such an assault [8]. The molecules are attacked by electrophiles at O16. As seen in Table 2 and Figure 3, the second Fukui function (dual descriptor) often showed that the molecule has a greater potential for nucleophilic attack, which is why $f^2(M)$ has more positive values than the negative.

Table 2: showing the Fukui function of the molecule in Milliken values.

Atom	$P_k^+(M)$	$P_k^-(M)$	$f^2(M)$
C (1)	0.054	0.038	0.016
C (2)	0.045	0.059	-0.014
C (3)	0.049	0.085	-0.036
C (4)	0.03	0.033	-0.003
C (5)	0.029	0.026	0.003
C (6)	0.072	0.079	-0.007
N (7)	0.073	0.066	0.007
C (8)	0.054	0.03	0.024
C (9)	0.06	0.046	0.014
C (10)	0.083	0.029	0.054
O (11)	0.045	0.022	0.023
C (12)	0.011	0.009	0.002
C (13)	0.019	0.011	0.008
O (14)	0.044	0.024	0.02
C (15)	0.015	0.01	0.005
O (16)	0.026	0.089	-0.063
C (17)	0.009	0.022	-0.013
O (18)	0.026	0.056	-0.03
C (19)	0.011	0.016	-0.005

2.4. Frontier orbital energies

Global reactivities such as Ionization energy (IP), electron affinity (EA) and other functions which describe the reaction behaviors of molecules were calculated. Such reactivity includes: electronegativity (χ), (ω) electrophilicity, global hardness (η), (ω^-) electron donating power, (ω^+) electron accepting power global softness (σ) global indices that describe the reactivity of a molecule in terms of the initial electron distribution in the molecule. Others includes fraction of electron transfer (ΔN). The ELUMO Eigen value indicates a molecule's potential to accept electrons from the p-orbital of the aluminum surface, while the EHOMO Eigen value illustrates a molecule's capacity to transmit electrons to the empty orbitals of the p-orbitals of the aluminum surface [2,7]. In Table 2, the compounds' Eigen energies are shown. The results show that the border orbital energies are equivalent to those that Nyijeme et al. reported in their independent

research to be appropriate for a corrosion inhibitor. [11]. Therefore, the research's objective is to examine the adsorptive behavior of skimianine on two significant surfaces, Al(110) and Fe(111). In order to achieve this goal, the percentage of electron transfer (N) is extremely real. Though the surface with the highest value of fraction of electron transfer is considered to provide more inhibitive potential, the efficiency of the inhibition is directly proportional to the electron donating ability of the molecules [23-24]. According to Table 2, ΔN_{Fe} will be more effective in the transfer of electron between the molecule and the surface rather than ΔN_{Al} . The ω^- electron donating power and ω^+ electron accepting power of the molecules were calculated. It follows that a larger (ω^+) electron accepting power value corresponds to a better capability of accepting charge, whereas a smaller value of (ω^-) electron donating power value of a system makes it a better electron donor. The results from Table 3 clearly indicate that Skimianine is an electron donating molecule, with the same result predicted by all the density functionals considered in this study.

Table 3. Values of structural and electronic properties of Skimianine calculated using DFT at B3LYP functional and (DNP+) basis set in the aqueous phase

Properties	Skimianine
EHOMO (eV)	-4.995
ELUMO (eV)	-1.876
ΔE (eV)	3.119
Molecular Area [\AA^2]	264.449
Molecular Volume [\AA^3]	273.385
Ionization Potential (I) (eV)	4.995
Electron Affinity (A) eV	1.876
Global Softness (η)	1.559
Global Hardness (σ)	0.641
Absolute Electronegativity (χ)	3.436
Fraction of electron transfer Al (ΔN)	0.694
Fraction of electron transfer Fe (ΔN)	1.143
electron donating powers (ω^-)	5.697
electron accepting powers (ω^+)	2.261

2.5. Dynamic Simulation of Molecules

Skimianine, modeled on the surfaces of Al (110) and Fe (111), provides insight into how molecules interact with metal surfaces to lessen the severity of corrosion when exposed to hazardous environments [18-20]. Due to their great atomic coverage and density on the surface, the densely populated surface of the Aluminum Al (110) and Fe (111) crystals was selected to produce an accurate result. [17,20]. Figure 4 displays the image of the Skimianine on the Al and Fe surface following simulation. The potential for the inhibition of the molecule on the surface of the simulated metals is explained by the parameters of the estimated molecular dynamics [15]. Total energy (kinetic and potential), as

well as surface energy, molecule energy, adsorption energy, and binding energy, were the parameters that were determined [12]. determining out the type of inhibition present on the two surfaces. The statistical data for binding energy, adsorption, total potential and kinetic energy of the system, molecule and surface energy, are shown in Fig 4.

2.6. Mechanism of inhibition

Any corrosion inhibitor's first process involves determining the extent of the inhibitor's surface adsorption [7,9, 15]. The Skimmianine molecules on Al and Fe surfaces were compared, and the results show that the molecules are practicable and spontaneous on the surfaces because there is a negative adsorption energy on the surfaces. [10,21] The simulation's binding and adsorption energies on the surface of Al were both less than -100Kcal/mol, pointing to a physical adsorption mechanism [2, 5, 10–11]. The value of adsorption was larger than -100Kcal/mol because it was higher with Fe surfaces and an inhibition type that was confirmed to be chemisorption. According to this value, Nyijime et al. determined in a different experiment that

the amount of binding energy would need to be less than 100 Kcal/mol for a mechanism to be physisorption [11,15]. As a result, the binding energy value for the compound Skimmianine's mechanism is less than 100 kcal/mol in the surface order of Fe > Al. This outcome indicates that iron can maintain the molecule on its surface longer than it can with an aluminum surface because the molecule on an aluminum surface has a lower binding and adsorption value[24]

Table 5. Calculated molecular dynamic simulation parameters for the studied molecule

Properties	Al surface	Fe Surface
Total Kinetic Energy	26.3999±7.9	24.1916±0.0
Total potential Energy	45.5870±0.7	-7.2072±0.5
Energy of the molecule	46.5390±0.6	110.719±0.6
Energy of the surface	0.000±0.0	0.000±0.0
Adsorption Energy	-0.9525±0.0	-117.926±0.0
Binding Energy	0.9525±0.0	117.926±0.0

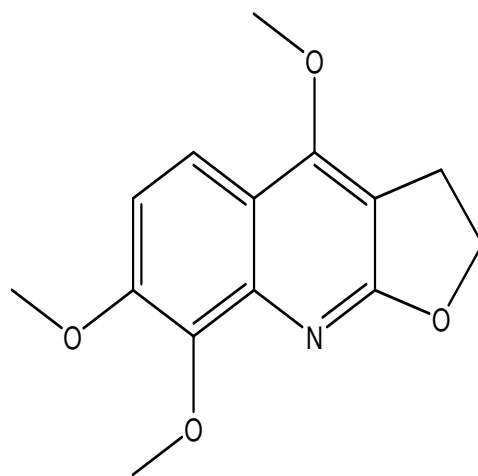
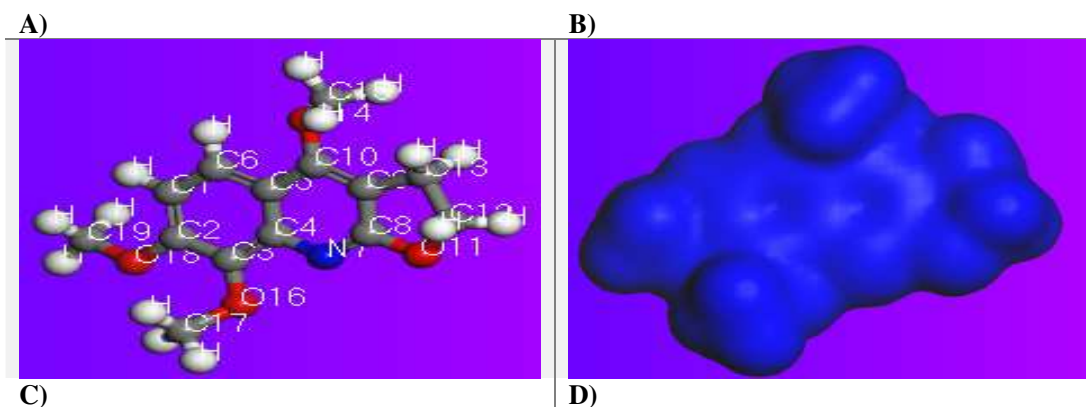


Fig. 1. Structure of the molecule Skimmianine (4,7,8-Trimethoxy-2,3-dihydro-furo[2,3-b] quinoline)



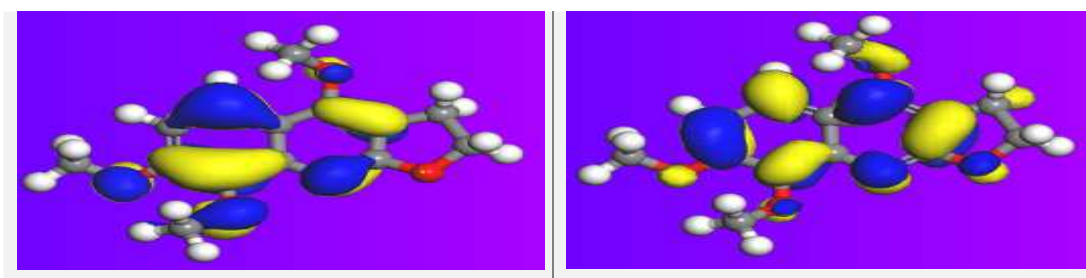


Figure 2. Structure of Skimmianine (A) Optimized Geometry (B) Total Electron Density (C) Highest Occupied Molecular Orbital (D) Lowest Unoccupied Molecular Orbital

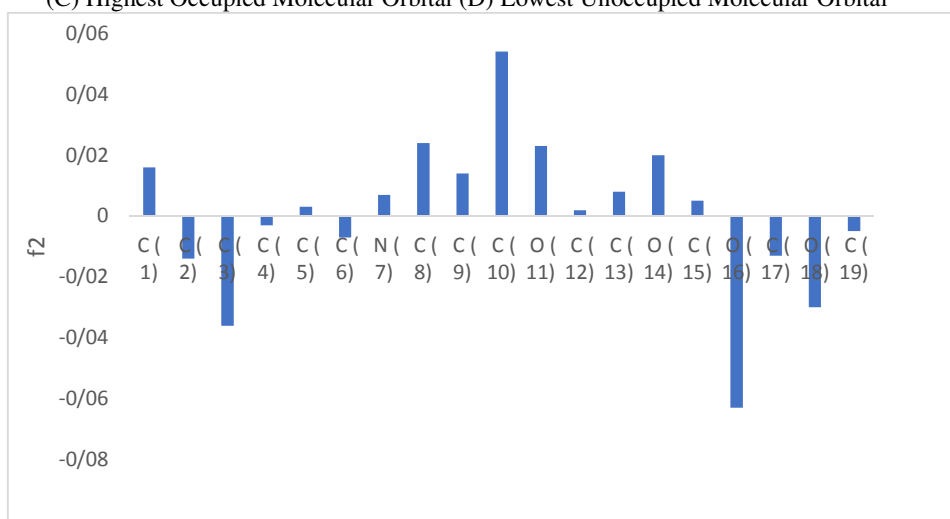


Figure 3. Graphical representation of Fukui second function

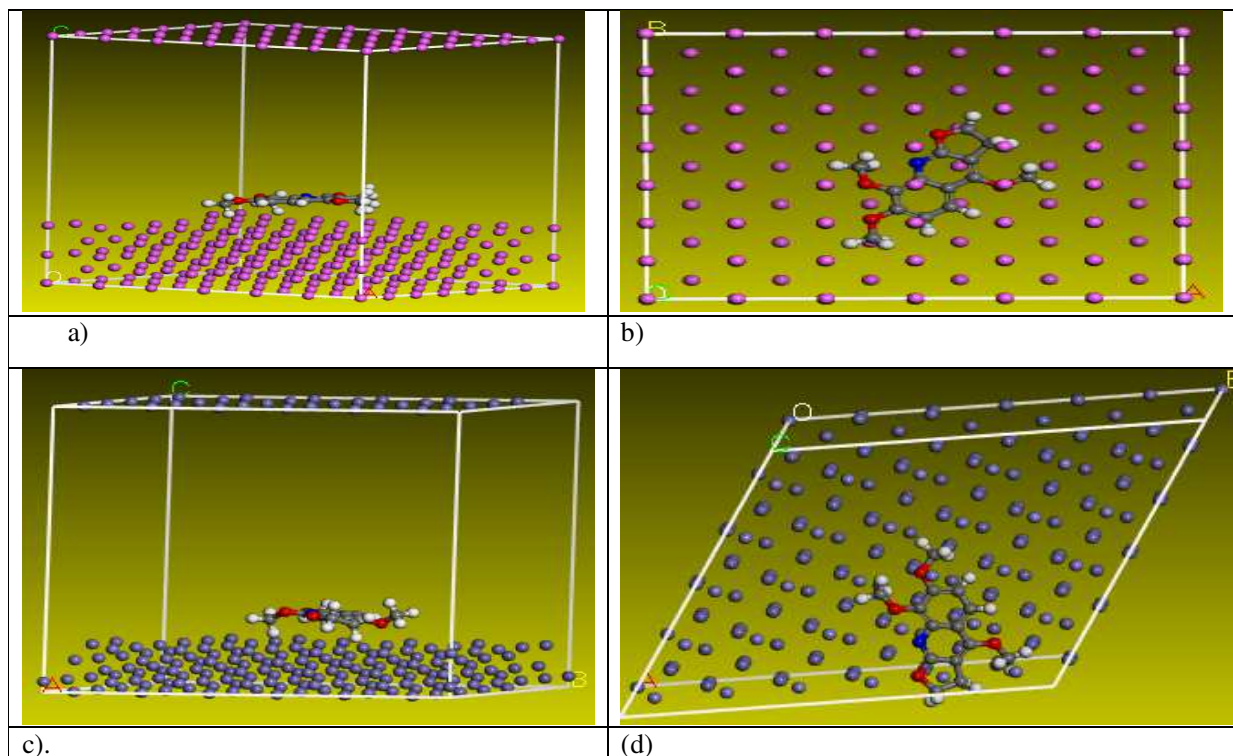


Figure 4. (a) Side view of molecule on of Al_{sur} . (b) Top view of molecule on of $Al_{surface}$
 (c) Side view of molecule on of $Fe_{surface}$ (d) Top view of molecule on of $Fe_{surface}$

3. Experimental

Computational Methods

3.1 Sketching and Geometric Optimization of the molecules

ChemDraw Ultra 7.0.3 CambridgeSoft was used to create sketches of the investigated compounds. Each molecular structure needs to be optimized once it has been constructed to bring it to a stable configuration. The atoms' coordinates are changed iteratively during this process to bring the structure's energy to a stationary point or where the forces acting on the atoms are zero. During the energy reduction, a relative minimum on the energy hyper surface was sought after. It is anticipated that the geometry corresponding to this structure will closely resemble the system's real physical structure when it is in equilibrium [6-8]. The molecules' torsional and conformational energies were reduced using DMol3 optimization, a feature of BIOVIA Materials Studio 8.0. (Accelrys, Inc.). From ChemDraw, the chemicals were imported into Materials Studio. The following parameters were used to do the optimization: limited spin polarization DNP+ basis for DFT-D. B3LYP was chosen as the local density functional in the water solvent [1-3].

3.2. Quantum Chemical Parameters Calculations

Calculations involving quantum chemistry were performed using the Dmol3 modules included in the Material studio 8.0 (from Accelrys Inc.) program. Dmol3 is software that computes the electronic characteristics of molecule clusters, surfaces, and crystalline solid materials from the first principle using the density functional theory (DFT) and a numerical radial function basis set. [12]. The double numeric with polarization (DNP) basis set and the functional methods B3LYP from the name Becke for the exchange portion and Lee, Yang, and Parr for the correlation component were used to do the density functional theory (DFT) computations. Because it is the best set available in Dmol3, this base set was chosen. [13].

According to Koopman's theory, the energy of the border molecular orbital, the energy of the highest occupied molecular orbital (EHOMO), and the energy of the lowest unoccupied molecular orbital (ELUMO) are connected in equation (2) and (3), respectively (3) [14-17].

$$IE = -EHOMO \quad (1)$$

$$EA = -ELUMO \quad (2)$$

The value of global hardness (η), according to Pearson, is roughly described as given in equation (3). The global softness (S) of the system, as shown in Equation 4, is the opposite of the global hardness. $\eta = \frac{IE-EA}{2}$ (3)

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

The energy gap of the molecules is calculated using the relation given in equation 5. The energy gap is a parameter that, determine in the

$$\Delta Eg = ELUMO - EHOMO \quad (5)$$

The fraction of electrons transferred from the inhibitor to Fe-surface, ΔN , this is calculated by using equation 6. The half electron transfer of the molecules is a parameter that demonstrate

$$\Delta N = \frac{\chi^{Fe} - \chi^{Inh.}}{2(\eta^{Fe} + \eta^{Inh})} \quad (6)$$

According to the simple charge transfer model for donation and back donation of charges, when a molecule receives a certain amount of charge, ΔN^+ , then: $\Delta E^+ = \mu^+ \Delta N^+ + \frac{1}{2} \eta (\Delta N^+)^2$ and when a molecule back-donates a certain amount of charge, ΔN^- , then: $\Delta E^- = \mu^- \Delta N^- + \frac{1}{2} \eta (\Delta N^-)^2$ Assuming the amount of charge back-donation is equal to the amount of charge received, the total energy change will be approximately be the sum of the contributions [15-18].

$$\Delta E_t = \Delta E^+ + \Delta E^- \quad (7)$$

$$= (\mu^+ - \mu^-) \Delta N^+ + \frac{1}{2} \eta (\Delta N^+)^2 + \frac{1}{2} \eta (\Delta N^-)^2$$

$$= (\mu^+ - \mu^-) \Delta N^+ + \eta (\Delta N^+)^2$$

But the most favorable condition corresponds to the case when the total energy change (ΔE back-donation) becomes minimum with respect to ΔN^+ , which implies that:

$$\Delta N^+ = -(\mu^+ + \mu^-) / 2 \eta.$$

$$\Delta E_{bd} = (\mu^+ - \mu^-)^2 / 4 \eta = \frac{-\eta}{4} \quad (8)$$

The electron donating (ω^-) and electron accepting (ω^+) powers of the molecules has been defined as shown in the equations 9 and 10 [19]

$$\omega^- \approx \frac{(3I+A)^2}{16(I-A)} \quad (9)$$

$$\omega^+ \approx \frac{(I+3A)^2}{16(I-A)} \quad (10)$$

$$\chi = \text{Absolute electronegativity (eV)} \quad \chi = \frac{I+A}{2} = \frac{-1}{2}(E_{HOMO} - E_{LUMO}) \quad (11)$$

The second order Fukui function (f^2) the dual descriptor $\Delta f(k)$, was used in describing the donating and acceptability of the molecule and the metal which has theoretical electronegativity value ($\chi_{Fe}=7.0\text{eV}$), ($\chi_{Al}=5.6\text{eV}$) and a global hardness of 0eV [2-5].The second Fukui function has been defined as the difference between nucleophilic and electrophilic Fukui functions as in Equation. 11. 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 [14, 19-20]

$$f(k)^+: \text{ (for nucleophilic attack)} = qk(N+1) - qk(N) \quad (12)$$

$$f(k)^-: \text{ (for electrophilic attack)} = qk(N) - qk(N-1) \quad (13)$$

$$f(r) = f^+ - f^- = f^2 \quad (\text{Fukui function}) \quad (14)$$

3.3. Molecular Dynamics Simulation

To simulate a realistic portion of the surface, calculations were performed using the COMPASS FORCEFIELD and Smart ALGORITHM in a simulation box of 17 x 12 x 28 with a periodic boundary condition. The fractional depth of 3.0 was used to split the Fe crystals along the (1 1 1) Plane and Al along (110). Prior to optimizing the iron surface, the lower layers' shape was limited. In order to minimize edge effects, the iron surface was then increased into a 10 x 10 supercell. [1-4]. A tradeoff between a system with too much kinetic energy, where the molecule desorbs from the surface, and a system with insufficient kinetic energy, where the molecule cannot move across the surface, was made by fixing the temperature at 350 K to quench the molecules on the surface. [1-2, 21]. The NVE (microcanonical) ensemble was used to set the temperature, with a time step of 1 fs and simulation duration of 5 ps. For the purpose of obtaining the statistical values of the energies on the surface of Al and Fe, the system was programmed to quench every 250 steps on the both surfaces. Different interactions were produced using force tailored molecular and surface architectures. Using the relationship in equation 14, the binding energy between the inhibitors and the metal surfaces were estimated. [22-24].

$$\text{Binding Energy} = E_{\text{total}} - (E_{\text{inhibitor}} + E_{\text{Fe surface}}) \quad (14)$$

4. Conclusion

The outcome of this study showed that Skimmianine's established adsorption or binding energy on the surface of aluminum is comparatively low, indicating a physical adsorption process. In contrast, Fe's adsorption energy was larger than that of aluminum. The usefulness of the molecule as a possible corrosion-inhibiting molecule is demonstrated by the frontier energy values and Fukui function. Both E_{HOMO} and E_{LUMO} were assessed, and it was discovered that they both produced an energy gap necessary for the effective transmission of electrons. In the study, atoms like nitrogen, oxygen, and methylene group (-CH₂) were in charge of the electron transfer between the molecule and the vacant p-orbital on the surface of the aluminium and iron crystals. The inhibitive molecule can donate more electrons than it can accept from the vacant d and p orbitals of Fe and Al, respectively, according to the donating and accepting power and Fukui second function.

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References

- [1] H. A. AlMashhadani and K. A. Saleh, "Electrochemical Deposition of Hydroxyapatite Co-Substituted By Sr/Mg Coating on Ti-6Al-4V ELI Dental Alloy Post-MAO as Anti-Corrosion", Iraqi Journal of Science, vol. 61, no. 11 (2020) 2751–2761., <https://doi.org/10.24996/ijcs.2020.61.11.1>.
- [2] L. Afandiyeva, V. Abbasov, L. Aliyeva, S. Ahmadbayova, E. Azizbeyli, and HM. El-Lateef Ahmed, "Investigation of organic complexes of imidazolines based on synthetic oxy-and petroleum acids as corrosion inhibitors", Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 37 (2018);373-9. <http://https://doi.org/10.30492/ijcce.2018.34146>.
- [3] H. Jafari, F. Mohsenifar, and K. Sayin, "Effect of alkyl chain length on adsorption behavior and corrosion inhibition of imidazoline inhibitors", Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 37 (2018) 585-103., <https://doi.org/10.30492/ijcce.2018.29779>.
- [4] S. Elmi, M.M. Foroughi, M. Dehdab, and M. Shahidi-Zandi, "Computational evaluation of corrosion inhibition of four quinoline derivatives on carbon steel in aqueous phase", Iranian Journal of Chemistry and Chemical Engineering (IJCCE), vol. 381 (2019)185-200., <https://doi.org/10.30492/ijcce.2019.29776>.
- [5] B.N. Noorollahy, H.R. Hafizi-Atabak, F. Atabaki, M. Radvar, and S. Jahangiri, "Electrochemical measurements for the corrosion inhibition of mild steel in 0.5M HCl using poly (epichlorohydrin) derivatives", Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 39 (2020): 4113-25,.
- [6] L.T. Popoola, T.A. Aderibigbe, and MA. Lala, "Mild steel corrosion inhibition in hydrochloric acid using cocoa pod husk-ficus exasperata: extract preparation optimization and characterization" Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 2 (2022)482-92., <https://doi.org/10.30492/ijcce.2021.114540.3752>.
- [7] R. M. Kubba and N. M. Al-Joborry, "Theoretical study of a new oxazolidine -5- one derivative as a corrosion inhibitor for carbon steel surface", Iraqi Journal of Science, 5 (2021)1396–1403., <https://doi.org/10.24996/ijcs.2021.62.5.1>
- [8] K. A. K. Al-Rudaini and K. A. S. Al-Saadie, "Milk Thistle Leaves Aqueous Extract as a New Corrosion Inhibitor for Aluminum Alloys in Alkaline Medium", Iraqi Journal of Science 2 (2021):363–372. <https://doi.org/10.24996/ijcs.2021.62.2.2>
- [9] M. A. Mohammed and R. M. Kubba, "Experimental Evaluation for the Inhibition of Carbon Steel Corrosion in Salt and Acid Media by New Derivative of Quinolin-2-One", Iraqi Journal of Science, 8 (2020)1861–1873. <https://doi.org/10.24996/ijcs.2020.61.8.2>
- [10] S. Mammeri, N. Chafai, H. Harkat, R. Kerkour, and S. Chafaa, "Protection of steel against corrosion in acid medium using dihydropyrimidinone derivatives: experimental and DFT study", Iranian Journal of Science and Technology, Transactions A: Science, .5 (2021)1607-19, <https://doi.org/10.1007/s40995-021-01140-1>.
- [11] T.V. Kumar, J. Makangara, C. Laxmikanth, and NS. Babu, "Computational studies for inhibitory action of 2-mercapto-1-methylimidazole tautomers on steel using of density functional theory method (DFT)", International Journal of Computational and Theoretical Chemistry, 4 (2016) 1-6. <http://doi: 10.11648/j.ijctc.20160401.11>.
- [12] T.O. Esan, OE. Oyenyin, A. Deola, and NI. Olanipekun, "Corrosion inhibitive potentials of some amino acid

- derivatives of 1, 4-naphthoquinone– DFT calculations”, *Advanced Journal of Chemistry-Section A*, 4 (2022):263-270.,
<https://doi.org/10.22034/ajca.2022.353882.1321>.
- [13] R. M. Kubba, N. M. Al-Joborry, and N. J. Al-lami, “Theoretical and Experimental Studies for Inhibition Potentials of Imidazolidine 4-One and Oxazolidine 5-One Derivatives for the Corrosion of Carbon Steel in Sea Water”, *Iraqi Journal of Science*, 11 (2020)2776–2796.
<https://doi.org/10.24996/ijcs.2020.61.11.3>
- [14] Z. Yavari, M. Darijani, and M. Dehdab, “Comparative theoretical and experimental studies on corrosion inhibition of aluminum in acidic media by the antibiotics drugs”, *Iranian Journal of Science and Technology, Transactions A: Science*, 4 (2018):1957-67.
<https://doi.org/10.1007/s40995-017-0358-y>.
- [15] N. M. Al-Joborry and R. M. Kubba, “Theoretical and Experimental Study for Corrosion Inhibition of Carbon Steel in Salty and Acidic Media by A New Derivative of Imidazolidine 4-One”, *Iraqi Journal of Science*, vol. 61, no. 8 (2020) 1842–1860.,
<https://doi.org/10.24996/ijcs.2020.61.8.1>
- [16] S. John, J. Joy, M. Prajila, and A. Joseph, “Electrochemical, quantum chemical, and molecular dynamics studies on the interaction of 4- amino- 4H, 3, 5- di (methoxy)- 1, 2, 4-triazole (ATD), BATD, and DBATD on copper metal in 1NH₂SO₄”, *Materials and Corrosion*, 11 (2011)1031-41.
<https://doi.org/10.1002/maco.201005938>.
- [17] M.E. Belghiti, S. Echihi, A. Dafali, Y. Karzazi, M. Bakasse, H. Elalaoui-Elabdallaoui, LO. Olasunkanmi, EE. Ebenso, and M. Tabyaoui, “Computational simulation and statistical analysis on the relationship between corrosion inhibition efficiency and molecular structure of some hydrazine derivatives in phosphoric acid on mild steel surface”, *Applied Surface Science*, 49(2019)707-22.,
<http://doi.org/10.1016/j.apsus.2019.04.125>.
- [18] M. M. Kadhim, L. A. A. Juber, and A. S. M. Al-Janabi, “Estimation of the Efficiency of Corrosion Inhibition by Zn-Dithiocarbamate Complexes: a Theoretical Study”, *Iraqi Journal of Science*, vol. 62, no. 9 (2021) 3323–3335. [https://doi.org/10.24996/ijcs.2021.62.9\(SI\).3](https://doi.org/10.24996/ijcs.2021.62.9(SI).3)
- [19] D. Glossman-Mitnik, “Computational study of the chemical reactivity properties of the rhodamine B molecule, international conference on computational science, ICCS”, *Procedia Computer Science*, 18 (2013)816 – 825., doi: 10.1016/j.procs.2013.05.246.
- [20] A. Nahlé, R. Salim, F. El Hajjaji, MR. Aouad, M. Messali, E. Ech-Chihbi, B. Hammouti, and M. Taleb, “Novel triazole derivatives as ecological corrosion inhibitors for mild steel in 1.0 M HCl: experimental & theoretical approach”, *RSC advances*.7(2021)4147-62.,
<http://doi: 10.1039/D0RA09679B>.
- [21] N.O. Eddy, PO. Ameh, and NB. Essien, “Experimental and computational chemistry studies on the inhibition of aluminium and mild steel in 0.1 M HCl by 3-nitrobenzoic acid”, *Journal of Taibah University for Science*, 5 (2018)545-56.
<https://doi.org/10.1080/16583655.2018.1500514>.
- [22] J.K. Gibson, “Bond dissociation energies reveal the participation of d-electrons in f-element Halides bonding”, *The Journal of Physical Chemistry A*, 2, (2022) 272-285 <https://doi.org/10.1021/acs.jpca.1c09090>.
- [23] T. A. Nyijime, H. F. Chahul, A. M. Ayuba, F.Iorhuna. Theoretical Investigations on Thiadiazole Derivatives as Corrosion Inhibitors on Mild Steel. *Adv. J. Chem. A*, 2 (2023) 141-154. DOI: 10.22034/AJCA.2023.383496.1352
- [24] F. Iorhunaa, N.A.Thomas, S.M. Lawal. Theoretical properties of Thiazepine and its derivatives on inhibition of Aluminium Al (110) surface. *Alger. J. Eng. Technol.*, 1 (2023) 43-51. DOI: <https://doi.org/10.57056/ajet.v8i1.89>