Jordan Journal of Chemistry https://doi.org/10.47014/17.2.1

ARTICLE

Theoretical Simulation of the Corrosion-inhibition Potentials of Triterpenoids on Aluminium Metal Surface

Abdullahi Muhammad Ayuba* and Ameenullah Abdullateef

Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, College of Natural and Pharmaceutical Sciences, Bayero University, P.M.B 3011, Kano, NIGERIA.

Received: 27th March 2022; Accepted:14th Oct. 2022

Abstract: The mechanism of the corrosion-inhibition action of three selected triterpenoid compounds including α -amyrin, β -amyrin and Lupeol on Al(110) surface was studied using computational methods including molecular dynamic simulations and quantum chemical calculations. The relative corrosion-inhibition performance of the studied compounds was investigated. Quantum chemical parameters including fraction of electron transfer (ΔN) from the inhibitor molecule to the Al(110) surface, energy gap (ΔE), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital (E_{HOMO}), global electrophilicity index (ω), global softness (σ), electronegativity (χ) and global hardness (η) were all computed. The local reactivity-indicating sites for electrophilic and nucleophilic attack were analyzed using Fukui indices, while molecular dynamic simulation was used to study their adsorption behavior on the surface of Al(110). Based on the interactions, the adsorption energy (E_{ads}) values obtained, –49.533 kcal/mol for $\alpha\text{-}$ amyrin, -48.284 kcal/mol for β -amyrin and -37.654 kcal/mol for lupeol, are all negative with correspondingly low magnitudes (less than -100 kcal/mol). This shows weak and unstable adsorption structures and relatively low corrosion inhibition, suggesting a physical adsorption mechanism with the trend: α -amyrin > β -amyrin > lupeol.

Keywords: Quantum parameters, Molecular dynamics, Fukui indices, Physical adsorption.

Introduction

Aluminium is one of the most useful and versatile metals with many applications in modern-day industries. This is due to its excellent thermal and electrical conductivity, good ductility, low cost, low density and its rather high natural abundance^[1]. Because of its relative corrosion-resistance capabilities, aluminium is extensively used in aviation and automobile industries, food containers and household appliances, as well as in other vital devices^[2]. Aluminium is known to possess a protective oxide layer which is amphoteric in nature and may be depleted when subjected to corrosive environments including acid, alkaline and salt solutions^[3,4].

Investigating corrosion inhibition of aluminium and its alloys is recently receiving a

lot of attention^[5–9]. The mechanism of the corrosion inhibition of aluminium is usually addressed using experimental techniques, but there is a need to search for alternative methods, because experimental methods are expensive and time-consuming. On the other hand, powerful modeling techniques have been shown to effectively correlate the inhibitor's efficiency in relation to its molecular properties and structure. The recent trend in theoretical chemistry using computational tools has provided researchers the opportunity to explore the structural and electronic properties of molecules and understand their contributions to molecular activity^[10]. The electronic and molecular properties of several natural corrosion inhibitors could be determined using molecular dynamic simulations and quantum chemical calculations^[11–17]. Literature reports, however, established that it is difficult to ascertain which of the properties, structural, molecular or electronic, is majorly responsible for controlling the inhibition efficiency of corrosion-inhibiting compounds^[12–14] and these properties are sometimes inferred to act simultaneously in controlling corrosion inhibition. For this reason, some triterpenoid compounds of similar structures were carefully selected with the intention of cancelling effects that may arise from structural contributions and allowing only those that are electronic in nature^[18,19]. Even though many researchers have reported in literature in this direction, there is always a need to search and develop new corrosion inhibitors that are more promising than those currently known.

This work aims at theoretically modeling some triterpenoids as potential corrosion inhibitors on aluminium metal surface using molecular dynamic simulations and quantum chemical methods, focusing on understanding the mechanism of the inhibition process^[20]. The authors reported earlier on the experimental use of Strichnos spinosa L. extract for the corrosion inhibition of aluminium in both 0.9 M HCl^[21] and 0.3 M HCl^[22] solutions. To further explain the corrosion-inhibiting behavior of the reported extract. these triterpenoids, which are structurally related, were sourced from literature^[23] to be some of the phytochemicals from the leaf extract of Strichnos spinosa L. that might be responsible for its corrosion-inhibiting activity on aluminium surface in HCl solutions.

Methods

DFT calculations find excellent applications in exploring the corrosion inhibitors' molecular properties and their inhibition efficiencies. Therefore, DMol³ module package in the BIOVIA Material Studio 8.0 was used in this study for the DFT calculations with B3LYP (hvbrid) functional for the geometry optimization of the studied inhibitor molecules ^[24–29]. To recognize sites of electrophilic and nucleophilic attack on the studied molecules, Fukui indices of each atom in the molecules were also obtained using the same method^[30]. All the calculations were accomplished using the Becke-Lee-Yang-Par (BLYP) exchange correlation functional with generalized gradient approximation (GGA) and double numerical polarization (DNP) basis set^[31–32].

Computational tools in BIOVIA Material Studio 8.0 were also applied to conduct

molecular dynamic (MD) simulation to evaluate the interaction between the studied inhibitor molecules and the Al metal's surface through adsorption^[30]. This was achieved by constructing a 36.60 Å \times 36.60 Å \times 71.28 Å simulation box corresponding to the Al(110) surface with periodic boundary condition. The (110) face was chosen because of its stabilization and highdensity packed atoms. The created simulation box was initially optimized using FORCITE method and then subjected to MD simulation using Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. This COMPASS force field has been established to be an excellent force field used in predicting the properties of molecules during dynamic simulations^[33]. The COMPASS force field can be defined in functional form as presented in Eq. $1^{[34-36]}$:

$$E = E_{vdw} + E_{cross} + E_{oop} + E_{bond} + E_{angle} + E_{elec} + E_{torsion}$$
(1)

where E_{vdw} refers to van der Waals interactions, E_{cross} represents the energy of coupling, E_{oop} corresponds to out-of-plane angle coordinates, E_{angle} is the angle-bending component, E_{bond} is the bond stretching contribution, E_{elec} is the electrostatic interaction and $E_{torsion}$ is the torsional effect.

Quantum Chemical Calculations

The selected triterpenoid compounds were optimized and later subjected to quantum chemical calculations. To establish local and global reactivity sites in these molecules, as well as their active sites for nucleophilic and electrophilic attack, the electronic structure of the compounds was assessed through the lowest unoccupied molecular orbital and the highest occupied molecular orbital, which are both distributions of Frontier molecular orbitals and Fukui indices^[3,37]. The double numeric basis set with polarization (DNP) and Perdew Wang local correlation density functional were used to calculate the electronic parameters for the simulations. The regions of nucleophilic and electrophilic attack in the molecules were located by the use of Fukui local reactivity indices (FI)^[38]. Other parameters evaluated for these molecules included electronegativity (γ) , softness (σ) and global hardness (η). Hence, the total electronic energy (E) of an N-electron system the external potential of which is v(r); the electronegativity χ can be defined as the negative

of the chemical potential μ . The expression can be presented as in Eq. 2^[3].

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)v(r) \tag{2}$$

The second derivative of E with respect to the potential v(r) in relation to N is the hardness (η) of a molecule and is defined as given in Eq. 3^[3]:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right) v(r) = \left(\frac{\partial \mu}{\partial N}\right) v(r) \qquad (3)$$

To calculate ΔN , which is the number of electrons transferred from the inhibitor molecule to the aluminium metal, Eq. 4 is used^[1,3].

$$\Delta N = \frac{\chi_{Al} - \chi_{inh}}{2(\eta_{Al} - \eta_{inh})} \tag{4}$$

 χ_{inh} and χ_{Al} can be defined as the absolute electronegativity of the inhibitor molecule and aluminium metal, while η_{inh} and η_{Al} represent the absolute hardness of the inhibitor molecule and aluminium metal, respectively. The energy of the lowest unoccupied molecular orbital (E_{LUMO}) and highest occupied molecular orbital (E_{HOMO}) was used to derive a value for the ionization potential (A) and electron affinity (I) using Eqs. 5 and 6, respectively^[3,19]:

$$A = -E_{LUMO} \tag{5}$$

$$I = -E_{HOMO} \tag{6}$$

The electronegativity and hardness were calculated using values obtained from electron affinity (A) and ionization potential (I) as presented in Eqs. 7 and $8^{[3, 18-19]}$.

$$\chi = \left(\frac{I+A}{2}\right) = -\frac{E_{LUMO} + E_{HOMO}}{2} \tag{7}$$

$$\eta = \left(\frac{I-A}{2}\right) = -\frac{E_{LUMO} - E_{HOMO}}{2} \tag{8}$$

The reciprocal value of the global hardness was used to calculate the value of global softness, as reported in Eq. $9^{[18]}$.

$$\delta = \frac{1}{n} \tag{9}$$

The first-order derivative of electronic density q(r) at constant external potential v(r) with respect to the number of electrons N was used to define f(r), the Fukui function. Thus,

from the Mulliken population analysis using a scheme of finite difference approximations of atoms in the isolated compounds and depending on the direction of electron transfer, Eqs. 10–12 were derived^[39].

For nucleophilic attack.

$$f_k^+ = q_k(N+1) - q_k(N)$$
 (10)

For electrophilic attack.

$$f_{k}^{-} = q_{k}(N) - q_{k}(N-1)$$
(11)

For radical attack.

$$f_k^o = \frac{q_k(N+1) - q_k(N-1)}{2}$$
(12)

where N is the number of electrons in the neutral molecule, N+1 is the number of electrons in its anion (with an electron added to the LUMO of the neutral molecule) and N–1, is the number of electrons in the cation (with an electron removed from the HOMO of the neutral molecule), q_k is the gross charge of atom k in the molecule; i.e., the electron density at a point r in space around the molecule. Geometry of the ground state was used for all calculations, while the condensed nuclei functions were considered by using Mulliken population analysis with an atomic charge partitioning scheme, as presented in Eqs. 10–12.

Molecular Dynamic (MD) Simulations

Forcite quench molecular dynamic simulations modeling of the Al surface with a single molecule interaction was performed in the gas phase. This enabled the sampling of the interactions that are of lowest energy either as local or global minima^[3]. With the help of Smart algorithm and COMPASS force molecular field, simulations were conducted on a super cell of 7×6 dimensions. The Al crystal surface selected is the most stable surface and contain most densely packed atoms with (110) cleaved plane^[26]. The built Al slab was intended to avoid edge effects of molecules significantly larger in order being to accommodate the studied molecule for the docking and simulation processes. With the number-volume-energy (NVE) ensemble, the temperature was set at 350 K and 1 fs time step with 5 ps simulation time. The system was quenched every 250 steps with constrained Al(110) surface atoms. The single optimized molecule of each triterpenoid compound adsorbed onto the Al(110) surface was used to

determine the energetics of the adsorption and, therefore, correlated to the molecule's inhibition efficiency. Adsorption energy, E_{ads} , the energy of binding, $E_{binding}$, of the interaction of the inhibitor molecule and the Al(110) surface were calculated using Eqs. 13 and 14, respectively^[39,40].

$$E_{ads} = E_{total} - (E_{mol} + E_{Al}) \tag{13}$$

$$E_{binding} = -E_{ads} \tag{14}$$

where E_{total} represents the energy of the molecule-surface interaction, E_{Al} is the energy of the Al(110) surface and E_{mol} is the energy of the molecule in the gas phase.



Figure 1. Molecular structures of the triterpenoid compounds investigated: (a) α -amyrin (b) β -amyrin (c) Lupeol.

Results and Discussion

Quantum Chemical Parameters

Quantum chemical calculations find application in providing information about the reactivity and selectivity of studied inhibitor molecules^[41]. It has been established that most inhibitor molecules are in possession of regions and moieties capable of favorable interaction with metal surfaces. These regions provide helpful information in predicting the potentials of these inhibitors on selected surfaces of metals^[42]. The reactivity of the studied compounds is solely controlled by properties which are electronic in nature, including dipole moment, atom's partial charges, electron density, etc. Electronic properties of this type are influenced by the nature and type of functional groups located within the inhibitor molecules^[3,42]. Figs. 2–4 present snap shots of LUMO, HOMO, and optimized structures of the utilized triterpenoid compounds used in this study.

Molecular geometry is usually considered when choosing compounds for intended inhibition on corrosion metals, because appropriate geometries are known to enhance metal-corrosion inhibition. Molecules which possess planar geometries are known to relatively inhibit better the corrosion of metals than those with non-planar geometry^[43]. This may be attributed to having better chances of covering a wide area when relatively compared to those which are less planar on the surface of the metal. Moreover, it is observed that those with planar geometries almost have all their atoms and structural moieties in intimate interaction with the metal's surface during the inhibitor-metal process.

Figs. 2-4 show that the Frontier orbitals of the investigated triterpenoids are relatively similar, since the compounds are similar in their functional groups/moieties and structures. The main structural difference between β -amyrin and that of α -amyrin is the presence of an additional methyl group in β -amyrin and therefore, both are expected to have similar adsorption characteristics. Lupeol has the same hydroxyl functional group position as amyrin, but with one of its six-membered fused rings substituted with a five-membered ring. This may have resulted in it having a slight change in position of its Frontier orbitals, which may result in a variation of its nature and characteristics of adsorption^[18].



Figure 2. Optimized structure of α -amyrin molecule with the HOMO (a) and LUMO (b) orbitals shown.



Figure 3. Optimized structure of β-amyrin molecule with the HOMO (a) and LUMO (b) orbitals shown.



Figure 4. Optimized structure of lupeol molecule with the HOMO (a) and LUMO (b) orbitals shown.

The results reported in Table 1 are those of the calculated quantum parameters known to qualify the reactivity of the utilized triterpenoid compounds in this study. The reported

parameters comprised of global softness, absolute (global) hardness, the gap in energy (ΔE) , E_{LUMO} , E_{HOMO} , ionization potential, electron affinity, electrophilicity index, absolute electronegativity and ΔN . Aluminium is considered, according to hard-soft acid and base (HSAB) concept, to be a Lewis acid because of its empty d-orbital which is available to accept electron pairs. The electronegativity difference is known to drive the transfer of electrons between aluminium and the inhibitor molecules, while the resistance of the electron transfer is the result of the sum of the hardness parameters. To calculate ΔN , the electronegativity of the aluminium bulk is obtained theoretically to be $\chi_{Al} = 5.6$ eV and the value of its global hardness is zero ($\eta_{Al} = 0$). This is based on the assumption that I = A for bulk metals known to be softer than the metallic atoms which are neutral in nature^[44]. The Frontier Molecular Orbital (FMO) theory, which is an example of molecular orbital theories, describes chemical reactivity in terms of the reacting species LUMO and HOMO interactions. This process is believed to be responsible for the transfer of electrons from the triterpenoid compound onto the aluminium metal's surface^[41]. Since the ability to donate electrons is based on the $E_{\mbox{\scriptsize HOMO}}$ value, compounds with higher E_{HOMO} values are likely to donate electrons to entities with electron-deficient centers^[45]. Therefore, higher E_{HOMO} compounds are likely to possess better inhibition efficiencies on metal surface corrosion.

The results presented in Table 1 show that the triterpenoid with the highest value of E_{HOMO} is α -amyrin with a numerical value of -5.470 eV, while lupeol possesses the lowest value for E_{HOMO} (-6.077 eV) among the three studied compounds. Since E_{LUMO} predicts the potential to accept electrons, molecules with higher E_{LUMO} values have, high tendency of interaction with a nucleophile^[46]. As shown in Table 1, E_{LUMO} is highest for lupeol (-1.061 eV) and lowest for α -amyrin (-1.306 eV).

Another important parameter that can be used to qualify stability and reactivity of compounds with respect to interaction with metal's surface is the energy gap (ΔE) between E_{LUMO} and E_{HOMO} . High ΔE value is thus related to high stability of the compound and subsequently low reactivity tendency, while low ΔE values indicate high reactivity and low stability^[47]. As can be seen, ΔE is highest for lupeol (5.016 eV) and lowest for α -amyrin (4.164 eV).

The resistance to charge transfer can be described by the global hardness (n) of the molecule. High values of global hardness imply high resistance to the transfer of atomic charges. Accordingly, global hardness with low values corresponds to easy interaction between the metal surface and the inhibitor molecules. Global softness (σ) can be also used to express the extent of interaction between the metal surface and the inhibitor molecules. Regions with a high value of global softness in the studied molecules are expected to interact better with the metal surface. The results presented show that lupeol has a value of global hardness of 2.508, which is relatively highest when compared to the other two compounds while α -amyrin possesses the lowest value (1.574). Accordingly, α -amyrin shows the highest value of global softness (0.480) while lupeol shows the lowest value (0.399).

Electronegativity (χ) is another important chemical reactivity parameter of compounds. It describes the ability of a group of atoms or an atom to draw electrons towards themselves itself^[44]. Therefore, with entities high electronegativity values are capable of drawing electrons from other entities with lesser electronegativity. From the results presented in Table 1, the highest electronegativity value (3.566 eV) is reported for lupeol, while the least value (3.388 eV) is reported for α -amyrin. Global electrophilicity index (ω) is another important parameter that can be used to support electronegativity. High global electrophilicity index is an indication of the molecule being an electrophile; i.e., a molecule that has the potential of accepting electrons, while molecules with high potential of donating electrons are characterized by low values of electrophilicity index and are considered nucleophiles^[44]. Table 1 shows that the value of the electrophilicity index is highest in α -amyrin (2.757), while it is lowest in β -amyrin (2.529). For such a reason, it can be inferred that α -amyrin would be a better electrophile than β -amyrin and vice versa. When the triterpenoids are compared with respect to their relative values of electrophilicity index, the aluminium metal's p-orbital would better accept electrons from β -amyrin than others.

Electronic property	Lupeol	β-Amyrin	a-Amyrin
HOMO (at orbital number)	238	238	238
LUMO (at orbital number)	239	239	239
E _{HOMO} (eV)	-6.077	-5.809	-5.470
E _{LUMO} (eV)	-1.061	-1.096	-1.306
$\Delta E (eV)$	5.016	4.713	4.164
Ionization potential (IP) (eV)	6.077	5.809	5.470
Electron affinity (EA) (eV)	1.061	1.096	1.306
Absolute/global hardness (η)	2.508	2.357	2.082
Global softness global softnes (σ)	0.399	0.424	0.480
Absolute electronegativity (χ)	3.566	3.453	3.388
Fraction of electrons transferred (ΔN)	0.406	0.455	0.531
Global electrophilicity index (ω)	2.535	2.529	2.757

Table 1. Electronic quantum chemical parameters of the triterpenoid molecules

The fraction of electron(s) (Δ N) transferred from the inhibitor molecule to the metal is highest in α -amyrin with an observed trend of α amyrin > β -amyrin > lupeol. It was reported that values of Δ N less than 3.6 indicate an increase in the ability to donate electrons by the molecules, which also results in an increase in inhibition efficiency, while those molecules with Δ N values are greater than 3.6 have their inhibition efficiencies decreased when their electron donating ability is increased^[44]. from the results reported in Table 1, it is clear that all the studied triterpenoids have their Δ N values less than 3.6 and therefore, their inhibition efficiency will increase with electron donating abilities.

The local reactivity presented in Table 2 is the result of the analysis of the various regions in molecules for electrophilic and nucleophilic behavior using Fukui indices. The region for electrophilic attack is indicated as f^- which is an indication of an electron-release region or an electron-rich center, while f^+ denotes the region for nucleophilic attack or is characterized by the tendency to attract electrons. The highest Mulliken and Hirshfeld charges for electrophilic (f^{-}) and nucleophilic (f^{+}) points of attack in the compounds are as presented in Table 2. Hirshfeld values are relatively higher when compared to those of Mulliken and will be used to describe the local reactivities of the compounds. The carbon atom C(12) shows Hirshfeld values of 0.030, 0.024 and 0.025 for lupeol, β -amyrin and α -amyrin, respectively, representing the highest nucleophilic points of attack in these compounds. These carbon atoms (the highest electron-deficient point) are identified to be the methyl di-substituted carbon atoms adjacent to those carrying the only hydroxyl moiety in the compounds. The electrophilic points (electron-rich centers) of attack in these compounds are O(23) with a Hirshfeld value of 0.026 for α -amyrin, O(23) with a Hirshfeld value of 0.025 for β -amyrin and O(22) with a Hirshfeld value of 0.031 for lupeol (Figure 5). The only moiety in these compounds containing an oxygen atom is the hydroxyl group attached to the α -carbon to the f⁺ carbons in these compounds.

Table 2. First-order Fukui indices for the triterpenoid molecules.

Molecule	Nucleophilic (f ⁺)			Electrophilic (f ⁻)				
	Mulliken		Hirshfeld		Mulliken		Hirshfeld	
	Atom	Value	Atom	Value	Atom	Value	Atom	Value
α-amyrin	O(23)	0.012	C(12)	0.025	O(23)	0.012	O(23)	0.026
β-amyrin	C(27)	0.013	C(12)	0.024	O(23)	0.016	O(23)	0.025
Lupeol	C(23)	0.018	C(12)	0.030	C(23)	0.019	O(22)	0.031



Figure 5. Atom labeling in a) lupeol, b) α-amyrin and c) β-amyrin.

Molecular Dynamic Simulations

Quench molecular dynamic method of simulation was used to study the adsorptive interaction between the surface of aluminium and each triterpenoid compound. This is intended to simulate the experimental corrosion inhibition processes that may be possible between the inhibitor and the metal surface. This will allow the display of many different lowenergy configurations of the interaction of the molecules with the aluminium surface in order to identify configurations with the lowest energy, called the local minima. Calculation of both binding energy (E_{bind}) and adsorption energy (E_{ads}) of the aluminium surface interaction with the inhibitor molecules provides a quantitative description of the interaction process. Stable adsorptive interaction between the inhibitor molecules and the metal surface is known to have negative E_{ads} values. Figure 6 and Table 3 contain the simulation results for the analyzed interaction between Al(110) surface and the triterpenoid molecules. The total energy for each molecule was calculated through taking the average of five lowest energies which are configurations that are the most stable. E_{ads} values obtained for the interaction are: -49.533 kcal/mol for α -amyrin, -48.284 kcal/mol for β amyrin and -37.654 kcal/mol for lupeol, which are all negative with correspondingly low magnitudes, suggesting unstable adsorption and relatively structures low corrosion inhibition. A study of the effect of Eads, molecular size and the number of -OH groups indicates that a better correlation is obtained between molecular size and the energy values of adsorption on the Al(110) metal surface. The low binding energy observed in this study is an indication of the low affinity of the studied molecules to the Al(110) surface. This may invariably account for a low inhibition efficiency of the triterpenoids, expected to be observed when experimentally tested. Also, it is reported in Table 3 that the values of the interaction of the triterpenoids with the metal surface are all less than -100 kcal/mol. Simulations of this type of molecular dynamics are devoid of covalent interactions which are characteristically specific in nature. Values of adsorption energy less than or equal to -100 kcal/mol were reported in literature to be supportive of the mechanism of physical adsorption interactions^[48]. Values of adsorption energies that are more negative are an indication of increased inhibition efficiency^[49]. A trend in Table 3 can be observed with respect to the inhibition efficiencies of the triterpenoids in relation to their binding or adsorption energies to be: α -amyrin > β -amyrin > lupeol.



Figure 6. Adsorption of a single β -amyrin molecule on aluminium (110) surface.

Molecules	Total Potential Energy (kcal/mol)	Energy of Molecule (kcal/mol)	Energy of Al(110) Surface (kcal/mol)	Adsorption Energy (kcal/mol)	Binding Energy (kcal/mol)
α-amyrin	-296.37	-89.84	0.00	-49.53	+49.53
β-amyrin	-58.11	-35.66	0.00	-48.28	+48.28
Lupeol	-20.72	-3.07	0.00	-37.65	+37.65

Table 3. Parameters for the interaction of Al(110) surface with single molecules in the gas phase.

Conclusion

Three triterpenoid compounds; namely, lupeol, β -amyrin and α -amyrin, were studied with the intention to predict the mechanism of their corrosion inhibition on Al(110) surface in the gas phase. Parameters including the fraction of electron transfer (ΔN) from the inhibitor molecules to the Al(110) surface, energy gap (ΔE) , energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy of the highest occupied molecular orbital (E_{HOMO}), global electrophilicity index (ω), global softness (σ), electronegativity (χ) and global hardness (η) , were all computed. Local reactivity sites of the molecules were analyzed using Fukui indices and the adsorption pattern and behavior of the molecules on the Al(110) surface were studied using quench

References

- [1] Ayuba, A. M.; Abubakar, M., J. Sci. Tech. 2021, 13, 47–56.
- [2] Emad, E. E.; Yasser, M. A., *Int. J. Electrochem. Sci.* **2018**, *13*, 4319–4337.
- [3] Ayuba, A. M.; Uzairu, A.; Abba, H.; Shallangwa, G. A., J. Mater. Environ. Sci. 2018, 9, 3026–3034.
- [4] Khaled, K. F., *Electrochim. Acta*, **2010**, *55*, 5375–5383.
- [5] Elabbasya, H. M.; Fouda, A. S., *Green Chem. Lett. Rev.* **2019**, *12*, 332–342.
- [6] Emad, E. E.; Saedah, A., *Green Chem. Lett. Rev.* **2019**, *12*, 31–48.
- [7] Fouda, A. A.; Ali, A. H., Zastita Materijala, 2018, 59,126–140.

molecular dynamic simulations. The calculated energies of adsorption were -49.533 kcal/mol for α -amyrin, -48.284 kcal/mol for β -amyrin and -37.654 kcal/mol for lupeol, indicating physical adsorption mechanism. The study revealed that based on the adsorption energies, the expected order of inhibition efficiency of the three triterpenoids investigated is: α -amyrin > β -amyrin > lupeol.

Acknowledgement

Dr. David Ebuka Arthur, Department of Pure and Applied Chemistry, Faculty of Science, University of Maiduguri, Nigeria is well appreciated and acknowledged for his contribution in the installation of the software programme used for this work.

- [8] Fouda, A. S.; Abou Shahba, R. M.; El-Shenawy, A. E.; Seyam, T. J. A., *Int. J. Electrochem. Sci.* 2018, *13*, 7057–7075.
- [9] Oguzie, E. E.; Chidiebere, M. A.; Ibe, F. C.; Ogukwe, C. E.; Adindu, C. B., *Intern. Lett. Chem. Phy. Astr.* 2017, 73, 9–21.
- [10] Verma, C.; Quraishi, M. A.; Kluza, K.; Makowska-Janusik, M.; Olasunkanmi, L. O.; Ebenso, E. E., *Sci. Rep.* 2017, 7, 44432 (17 pages).
- [11] Ansari, K. R.; Quraishi, M. A., Phys. E, 2015, 69, 322–331.
- [12]Obot, I. B.; Gasem, Z. M.; Umoren, S. A., Int. J. Electrochem. Sci. 2014, 9, 510–522.

Ayuba and Abdullateef.

- [13] Obot, I. B.; Gasem, Z. M.; Umoren, S. A., Int. J. Electrochem. Sci. 2014, 9, 2367–2378.
- [14]Obot, I. B.; Macdonald, D. D.; Gasem, Z. M., *Corr. Sci.* 2015, 99, 1–30.
- [15] Obot, I. B.; Obi-Egbedi, N. O.; Ebenso,
 E. E.; Afolabi, A. S.; Oguzie, E. E., *Res. Chem. Intermed.* 2013, *39*, 1927–1948.
- [16] Verma, C.; Quraishi, M. A.; Olasunkanmi, L. O.; Ebenso, E. E., *RSC Adv.* 2015, *104*, 85417–85430.
- [17] Yadav, M. D.; Sharma, D.; Kumar, S.;
 Bahadur, I.; Ebenso, E. E., *Int. J. Electrochem. Sci.* 2014, 9, 6580–6593.
- [18] Ayuba, A. M.; Abubakar, M., Alger. J. Eng. Technol. 2021, 4, 66–73.
- [19] Usman, B.; Jimoh, I.; Umar, B., *Appl. J. Envir. Eng. Sci.* **2019**, *5*, 66–67.
- [20] Khaled, K. F.; Abdel-Shafi, N. S.; Al-Mobarak, N. A., *Int. J. Electrochem. Sci.* 2012, 7, 1027–1044.
- [21] Ayuba, A. M.; Abdullateef, A., J. App. Sci. Env. Stud. **2021**, *4*, 336–348.
- [22] Ayuba, A. M.; Abdullateef, A., *Alg. J. Eng. Tech.* **2020**, *3*, 28–37.
- [23] Hoet, S.; Pieters, L.; Muccioli, G. G.; Habib-Jiwan, J.; Opperdoes, F. R.; Quetin-Leclerc, J., *J. Nat. Prod.* 2007, 70, 1360–1363.
- [24]Becke, D. A., J. Chem. Phys. 1986, 84, 4524–4529.
- [25]Becke, D. A., J. Chem. Phys. **1993**, 98, 5648–5652.
- [26]Lee, C.; Yang, W.; Parr, G. R., *Phys. Rev. B.* **1988**, *37*, 785–789.
- [27] Banerjee, P.; Company, A.;
 Weyhermuller, T.; Bill, E.; Hess, C. R., *Inorg. Chem.* 2009, 48, 2944–2955.
- [28] Banerjee, P.; Sproules, S.; Weyhermuller, T.; George, S. D.; Wieghardt, K., *Inorg. Chem.* 2009, 48, 5829–5847.

- [29] Joy, S.; Krämer, T.; Paul, N. D.; Banerjee, P.; McGrady, J. E.; Goswami, S., *Inorg. Chem.* **2011**, *50*, 9993–10004.
- [30]BIOVIA Materials Studio 8.0, Manual, Accelrys, Inc, San Diego, CA, **2008**.
- [31]Cao, Z.; Tang, Y.; Cang, H.; Xu, J.; Lu,
 G.; Jing, W., Corros. Sci. 2014, 83, 292–298.
- [32]Ciezak, J. A.; Trevino, S. F., J. Phys. Chem. A, 2006, 110, 5149–5155.
- [33] Chakraborty, T.; Hens, A.; Kulashresth, S.; Murmu, N. C.; Banerjee, P., *Physica E*, **2015**, *69*, 371–377.
- [34] Sun, H., J. Phys. Chem. B, **1998**, 102, 7338–7364.
- [35]Sun, H.; Ren, P.; Fried, J. R., Comput. Theor. Polym. Sci. **1998**, 8, 229–246.
- [36]Bunte, S. W.; Sun, H., J. Phys. Chem. B, **2000**, *104*, 2477–2489.
- [37] Shehu, N. U.; Gaya, U. I.; Muhammad, A. A., App. Sci. Eng. Prog. 2019, 12, 186–197.
- [38]Singh, P.; Ebenso, E. E.; Obot, I. B.; Olasunkanmi, L. O.; Quraishi M. A., J. Phys. Chem. 2016, 120, 3408–3419.
- [39]Lgaz, A. H.; Salghi, R.; Chaouiki, A.; Shubhalaxmi, J. S.; Bhat, K. S., *Cog. Eng.* 2018, 5, 144–1585.
- [40]Zhao, X.; Zhang, X.; Ji, L.; Hu, H.; Li, Q., Corr. Sci. 2014, 83, 261–271.
- [41] Udhayakala, P.; Samuel, A.; Rajendiran, T. V.; Gunasekaran, S., *Der. Pharma. Chemica*, 2013, *5*, 111–124.
- [42] Olasunkanmi, L. O.; Obot, I. B.; Kabanda, M. M.; Ebenso, E. E., J. Phys. Chem. 2015, 119, 16004–16019.
- [43] Cao, Z.; Tang, Y.; Cang, H.; Xu, J.; Lu,
 G.; Jing, W., Corros. Sci. 2014, 83, 292–298.
- [44] Martinez, S., *Mater. Chem. Phys.* **2002**, 77, 97–102.

- [45] Eddy, N. O.; Awe, F. E.; Gimba, C. E.;
 Ibisi, N. O.; Ebenso, E. E., *Int. J. Electrochem. Sci.* 2011, 6, 931–957.
- [46] Singh, A. K.; Khan, S.; Singh, A.; Quraishi, S. M.; Quraishi, M. A.; Ebenso, E. E., *Res. Chem. Intermed.* 2013, 39, 1191–1208.
- [47]Eddy, N. O.; Stoyanov, S. R.; Ebenso,E. E., *Int. J. Electrochem. Sci.* 2010, *5*, 1127–1150.
- [48] John S.; Joseph, A., *Mat. Chem. Phys.* **2012**, *133*, 1083–1090.
- [49] Awe, F. E.; Idris, S. O.; Abdulwahab, M.; Oguzie, E. E., *Cog. Chem.* 2015, *1*, 1–14.