Communication in Physical Sciences, 2022, 8(4):530-542

Quantum Molecular Parameters for the Prediction of Corrosion Inhibition potentials of some Alkaloids in *Cryptocarya nigra* Stem

Babatunde T. Ogunyemi[1*] and Richard A. Ukpe

Received: 11 March 2022/Accepted 02 September 2022/Published online: 29 September 2022

Abstract: *In recent times, the corrosion industries is intensively concentrated in the deployment of ecofriendly inhibitors to replace existing ones that are relatively toxic. In this study,* ***a*** *quantum chemical investigation into the suitability of some natural products in the bark extract of cryptocarya nigra was studied. Molecular reactivity descriptors of six alkaloids reportedly found in the bark of Cryptocarya nigra were probed to elucidate their electronic structures and match their expected reactivity and predict potential toward corrosion inhibition using the quantum mechanical method. The result obtained from DFT/B3LYP/6-31G(d) calculations indicated that three of the constituent alkaloids (N-methylisococlaurine, methyllaurotetanine and 2-hydroxyathersperminine) displayed strong tendency towards corrosion inhibition with theoretical data matching reported experimental values in literature. However, noratherosperminine was shown to be better at inhibiting iron corrosion than the other five due to their low energy gap, higher* E_{HOMO}*, lower* E_{LUMO} *and* ΔN *values which would allow effective electron transfer and therefore better efficiency as a corrosion inhibitor. The relationship between the studied quantum parameters and reportedexperimental inhibition efficiency of the studied molecules is useful in predicting Cryptocarya nigra alkaloids inhibitors with suitable substituents capable of donating electrons to the surface of the metal.*

Keywords: *Quantum chemical descriptors; DFT; alkaloids; inhibition potential*

Babatunde T. Ogunyemi*
Department of Chemistry, Federal University Otuoke, Bayelsa State, Nigeria
Email: ogunyemibt@fuotuoke.edu.ng
Orcid id: 0000-0002-3634-488X

Richard A. Ukpe
Department of Chemistry, Federal University Otuoke, Bayelsa State, Nigeria
Email: ukpera@fuotuoke.edu.ng
Orcid id: 0000-0002-1010-4933

1.0 Introduction

The deterioration of metallic materials, known as corrosion, is caused by a spontaneous electrochemical reaction during interactions with the environment thus resulting in the loss of material properties (Zarras and Stenger-Smith, 2014; Parajli *et al*., 2022). As a result, both emerging and developed countries suffer significant economic and safety costs. A lot of industries are heavily affected by corrosion due to contact and subsequent electrochemical interaction between the metal and the corrodent. Corrosion of iron and its alloy has received deep concern because of the prevalence of several iron or iron alloys in several industrial installations. Some technologies are available for the protection of metals against corrosion, for example, galvanizing, cathodic or anodic protection, greasing, etc (Eddy*et al*., 2010). Despite the some success in some of yhr tested methods,

Corresponding Author: B. T. **Ogunyemi,** ogunyemibt@fuotuoke.edu.ng

the alternative of adding a substance (called corrosion inhibitor) that has the tendency to be adsorbed and retard the rate of corrosion is one of the best options. A corrosion inhibitor represents any compound with the potential to retard the rate of corrosion of metals when present in minute concentration (Eddy and Ita, 2011a-b). By interacting with and depositing on the metal surface, in the form of a protective layer, the inhibitor shields the surface from expected electrochemical; attack within the aggressive medium. From literature, it is known that some corrosion inhibitors are expensive, some are not easily accessible and may not be environmentally friendly. Consequently, the need to protect metal must be matched by approaches that also protect the environment, without initiating harmful impact on man (Marzorati *et al*., 2018).

Recently, heightened environmental awareness has completely restricted the use of traditional toxic inhibitors, and more emphasis are now on the exploration of eco-friendliness, cost effectiveness, and non-toxic green inhibitors (Faraj and Khan 2015) such as tea leaves(Hamdan and Haider, 2018), Rhizophora apiculate, *Musa paradisiaca* (Anjum *et al*., 2015), *Neolamarckia cadamba* (Raja et al., 2013), *Glycyrrhia glabra* extract (Alibakhshi *et al*., 2018), *Citrus aurantifolia* (Haldhar *et al*., 2019), *Rollinia occidentalis* (Alvarez *et al*., 2018), and *Hibiscus sabdariffa* (Oguzie, 2008). One of the technical reasons for the corrosion inhibition potentials of plant extracts is theta their extracts are either rich in alkaloids, thioaldehydes, rich nitrogen-containing compounds, aldehydes, sulfur-containing compounds or acetylenic compounds (Rani and Basu, 2012). Umoren *et al.*, 2008, stated that corrosion inhibition efficiency of these extracts is a result of their phytochemical components. Also, within the phytochemical molecules, the presence of organic molecules with oxygen, nitrogen, sulphur, and/or phosphorus in their structures is the key component of an extract towards corrosion inhibition.

Due to the abundant source of secondary metabolites, plant extracts, such as extract of *Cryptocarya nigra*, are widely used in traditional medicine. These metabolites have beneficial properties and have been shown to function as the basis for many important pharmacological drug compositions (Okafor *et al.*, 2008). Phytochemical and pharmacological investigations show that *Cryptocarya nigra*, extract is a prolific producer of alkaloids, chalcones, flavonoids, lactones, and a-pyrones (Saw and Chung 2015). Studies on alkaloids of this species in particular have been published and their anti-cholinesterase antiplasmodial, anti-bacterial, antioxidative and cytotoxicity have also been investigated (Wan Othman *et al*., 2017). However, the use of *Cryptocarya nigra* as a corrosion inhibitor has not been adequately investigated> However, three sets of alkaloids (atherosperminine, N-methyllaurotetanine and N-methylisococlaurine) from this plant have been investigated for their effectiveness in the inhibition of the corrosion of metals. The reported alkaloids are (MasFaize *et al.*, 2020). Faiz *et al*. (2020) also carried out experimental and theoretical investigation in some phytochemical constituents of the plant leaf and observed a strong correlation between the experimental inhibition efficiency and some quantum chemical descriptors. They observed that the isolated *N*-methyllaurotetanine, and atherosperminine exhibited excellent inhibition efficiency of 88.05 and 91.05%

Despite the reported works on this plant extract, literatures have not covered an investigation into the potentials of some other alkaloid extract of the plants. It is of note that some of the extracts may be active or inactive against the inhibition of corrosion. According to Eddy *et al*. (2020), computational chemistry is a unique tool in the investigation of the reactivity, adsorption, topological and other surface properties of a molecules. A success of such investigation can provide a guide towards the initiation of the experimental investigation, which are normally costly. Therefore, the present study aligned with already started modelling to probe the tendency of five alkaloids molecules in the bark extract of *Cryptocarya nigra*.

2.0 Materials and Method

All calculations described in this work were performed using version 2.4 of the Spartan 14 package (Spartan 14v112, 2013). The examined *Cryptocarya nigra* alkaloids: reticuline**,** methyllaurotetanine, methylisococlaurine, methyllaurotetanine, atherosperminine, 2-hydroxyathersperminine, noratherosperminine (Fig. 1) were optimized using density functional theory (DFT) at B3LYP (Becke, 1993), and the 6-31G(d) basis set (Parr and Yang, 1989). Density functional theory (DFT), has shown a lot of promise (Udhayakala *et al*., 2012) and seems to be sufficient for identifying the changes in electronic structure that are accountable for the inhibitory effect. In accordance with the approach of Hohenberg and Kohn (1964); Kohn and Sham (1965) DFT with 6-31G(d) basis set, which is an important tool in modern Molecular descriptors calculated were E_{HOMO} and E_{LUMO} levels while other parameters that dependent on these two functions were evaluated through equations 1-8 The electron affinity (EA) and ionization potential (IP) of the inhibitors studied were associated with the negative values of E_{HOMO} and E_{LUMO} in accordance with the Koopmans' theorem () as shown in equations 1 and 2

$$IP = -E_{HOMO} \qquad (1)$$

$$EA = -E_{LUMO} \qquad (2)$$

The application of equations 3 and 4, led to ' electronegativity (χ) and absolute hardness values respectively. Also, the global softness were evaluated from 5

$$\eta = \left(\frac{\delta\varepsilon^2}{\delta N^2}\right)_{v(r)} = \frac{E_{LUMO}+E_{HOMO}}{2} = \frac{IP-EA}{2} \qquad (3)$$

$$\chi = -\mu = \left(\frac{\delta\varepsilon}{\delta N}\right)_{v(r)} = -\frac{E_{LUMO}+E_{HOMO}}{2} = \frac{IP+EA}{2} \qquad (4)$$

$$S = \frac{1}{\eta} \qquad (5)$$

In order to assess the chemical reactivity of organic inhibitors, hardness, electronegativity and softness which are quantum chemical parameters are particularly useful. When an organic molecule makes contact with the metal surface, an electron flow begins between the two systems and tend to increase, until their chemical potentials are equal. Equation 6 was used to hypothetically determine the number of electrons moved (ΔN) (Eddy, 2020),

$$\Delta Nz = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \qquad (6)$$

χ_{Fe} and χ_{inh} are the absolute electronegativities of iron (Fe) and organic inhibitor respectively while η_{Fe} and η_{inh} are the hardness of iron (Fe) and inhibitor respectively. The number of electrons transferred was calculated using the theoretical absolute electronegativity value of iron ($\chi_{Fe} = 7$ eV/mole) and its theoretical absolute hardness ($\eta_{Fe} = 0\ eV/mole$) (Ogunyemi and Borisade, 2020).

Equation 7, was used to compute the tendency towards back donation of charges:

$$\Delta E_{(Back\ –\ donation)} = \frac{\mu}{4} \qquad (7)$$

Equation 8 was used to determine the electrophilicity index for each studied molecule (Parr *et al*., 1999). This parameter determines the stabilization energy produced when charges are introduced into a system from the outside. Additionally, it measures how readily chemical species receive electrons.

$$\omega = \frac{\mu^2}{2\eta} \qquad z \qquad (8)$$

when the values of μ and ω are low, it shows that inhibiting molecules is a more reactive nucleophiles while high values depict a more reactive electrophile.

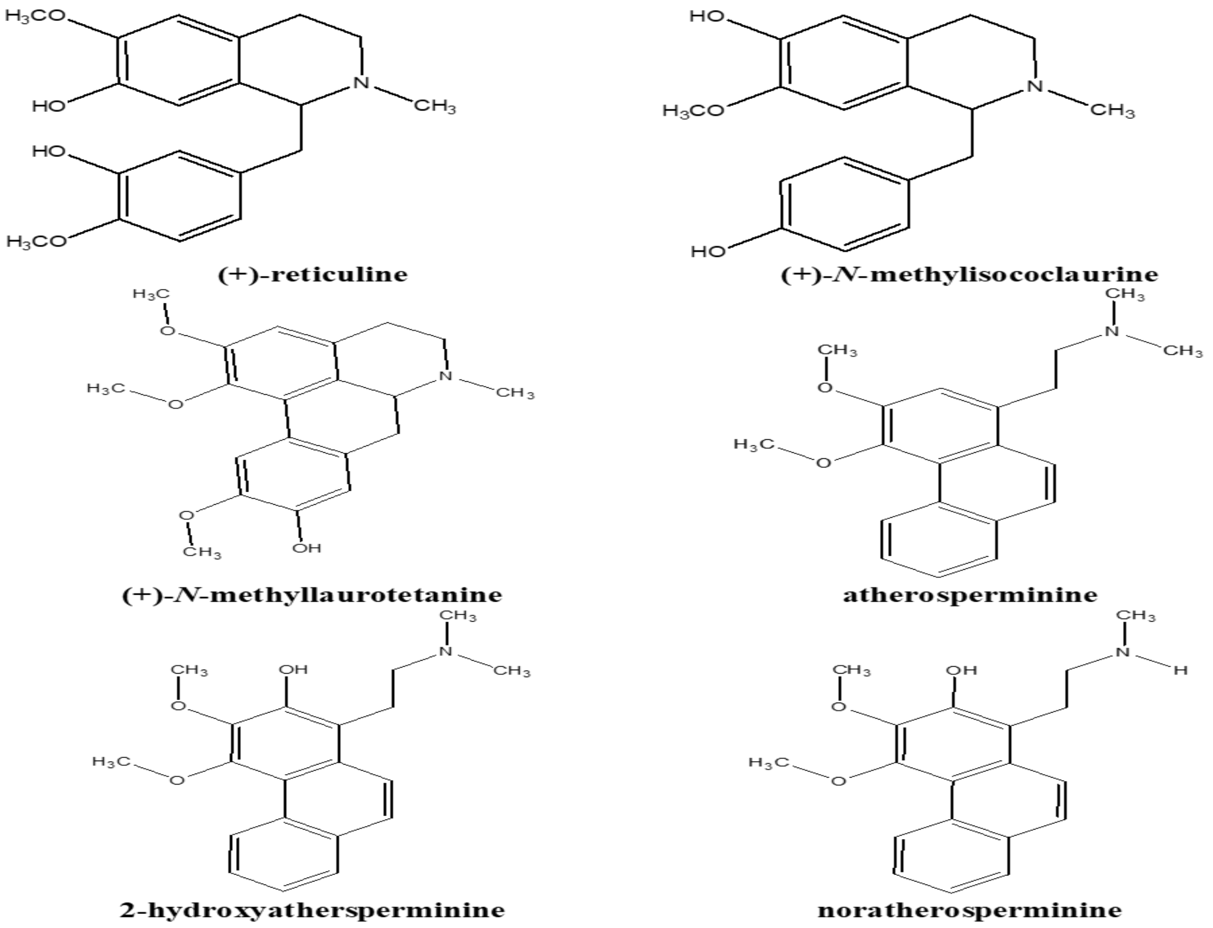
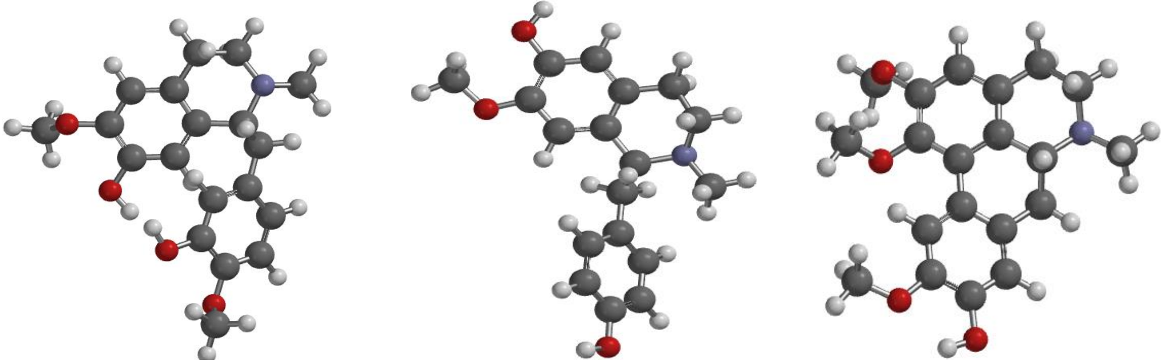


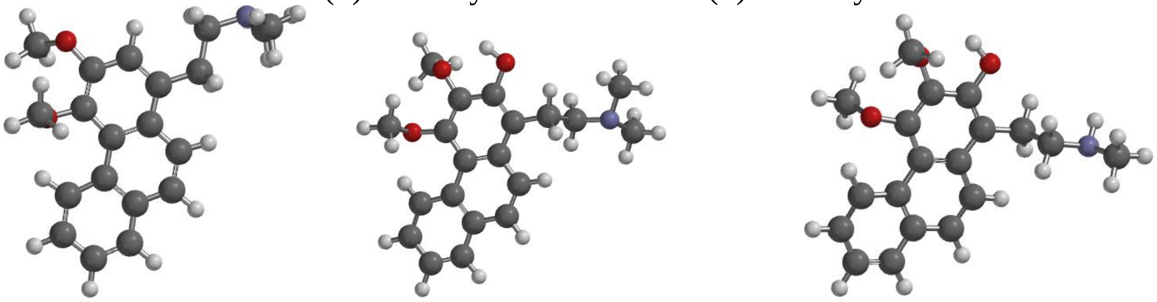
Fig. 1: structures of the studied *Cryptocarya nigra* alkaloids

3.0 Results and Discussion

3.1 Quantum Parameters

The corrosion inhibition potential of *Cryptocarya nigra* alkaloids: (Fig 1-5), was theoretically investigated using DFT/B3LYP/6-31G*. Their optimized geometric structures are presented in Fig. 2 while Table 1 displays their quantum parameters such as the energy gap (ΔE), solvation energy (E_{solv}), E_{HOMO}, dipole moment (DM), E_{LUMO}, Log P, chemical hardness (η), Ovality, electron affinity (EA), electronegativity (χ), global electrophilicity (ω), ionization potential (IP), softness (s), molecular weight (MW), polarizability and total electron transfer ΔN. The electrochemical impedance measurements of inhibitory effectiveness (Exp. I.E) for methylisococlaurine, methyllaurotetanine and atherosperminine reported by Mas-Faize *et al.,* (2020) showed a t a trend in the following order: methyllaurotetanine (88.27%) > methylisococlaurine (85.40 %) > atherosperminine (82.90 %) The electron-density region is often the highest occupied molecular orbital (HOMO) therefore, E_{HOMO} assesses the electron-donating ability of inhibitors. With increasing E_{HOMO}, the propensity of inhibitors to donate electrons to suitable orbitals at lower molecular energy levels increases. Therefore, the ability of inhibitors to transport electrons more effectively can increase the potency and efficiency of inhibitor molecules. As shown in Table 1, the order of E_{HOMO} values for the studied compounds is: methyllaurotetanine > methylisococlaurine > 2-hydroxyathersperminine > noratherosperminine > reticuline > atherosperminine. In the case of the experimentally reported alkaloids, methyllaurotetanine > methylisococlaurine > atherosperminine.


(+)-reticuline (+)-*N*-methylisococlaurine (+)-*N*-methyllaurotetanine


atherosperminine 2-hydroxyathersperminine noratherosperminine

● ● ● ● ●
C O N S H

Fig. 2: Geometry of the *Cryptocarya nigra* alkaloids optimized by DFT/B3LYP/6-31G (d) methods.

This order agrees with the experimental inhibition efficiency reported in the literature. Therefore, the best inhibitors to provide electrons to the corresponding vacant d-orbital of the metal ion are methyllaurotetanine and methylisococlaurine. However, it is important to note that electrons are not only donated to the empty d orbitals of the metal ion during the electron transfer process between the metal and the inhibitor. The inhibitor molecule also accepts an electron from the d-orbital of the metal, forming a feedback bond that is a function of E_{LUMO}. By measuring the E_{LUMO} values of studied molecules, it was possible to determine the ability of the analyzed molecules to incorporate metal ions.

The E_{LUMO} values (Table 1) for studied alkaloids range from -0.93 to 0.02 with the following order of levels: noratherosperminine < 2-hydroxyathersperminine < atherosperminine < methyllaurotetanine < methylisococlaurine < reticuline indicating that atherosperminine molecules had a better tendency to accept electrons from the corresponding metal ion more than other molecules. The values of the highest occupied and lowest unoccupied molecular orbital energies (HOMO and LUMO) for experimentally reported methylisococlaurine, methyllaurotetanine and atherosperminine show that atherosperminine and methylisococlaurine have improved adsorption and better inhibition efficiency than 2-hydroxyathersperminine on the surface of the metal surface. This order agrees with the experimental inhibition efficiency reported in the literature.

The energy difference (E) between E_{HOMO} and E_{LUMO} of an inhibitor determines the chemical reactivity of the inhibitor leading to adsorption to the metal ion surface. In general, the higher the reactivity of the metal ion with the corrosion inhibitor, the lower the ΔE value and the higher the binding capacity on the metal surface, thus increasing the inhibition efficiency (%IE) of the inhibitor.

Table 1. Quantum chemical reactivity descriptors of Molecules calculated with DFT/B3LYP/6-31G(d)

Quantum descriptors	**reticuline**	**Methyl isococlaurine**	**Methyl laurotetanine**	**Athero sperminine**	**2-hydroxy athersperminine**	**Norathero sperminine**
E_{HOMO} (eV)	-5.50	-5.26	-5.14	-5.68	-5.44	-5.45
E_{LUMO} (eV)	0.02	-0.34	-0.56	-0.70	-0.94	-0.93
ΔE (eV)	5.48	4.92	4.58	4.98	4.50	4.52
η (eV)	2.76	2.56	2.29	2.49	2.25	2.26
S(eV^{-1})	0.36	0.391	0.434	0.401	0.444	0.442
ΔN	0.792	0.839	0.889	0.765	0.846	0.843
Log P	-2.08	-1.10	-2.95	-0.08	-1.48	-1.86
Ovality	1.52	1.47	1.49	1.51	1.50	1.48
PSA	53.32	46.23	38.21	13.85	30.60	40.33
polarizability	67.94	65.79	68.65	68.35	68.62	67.09
E_{solv} (kJ/mol)	-44.03	-40.80	-41.85	-17.76	-23.49	-31.03
IP	5.50	5.26	5.14	5.68	5.44	5.45
EA	-0.02	0.14	0.56	0.70	0.94	0.93
X	2.63	2.7	2.91	3.19	3.19	3.19
Ω	1.421	1.424	1.841	2.043	2.261	2.251
V	343.55	315.98	349.54	347.10	349.00	330.19
Area	360.27	330.35	357.14	361.50	360.38	342.88
DM (debye)	1.40	2.07	2.41	0.68	2.17	2.55
$\Delta E_{back-donation}$	-0.662	-0.675	-0.7275	-0.7975	-0.7975	-0.7975
MW (amu)	329.396	299.37	341.41	311.425	325.41	311.38
Energy (au)	-1093.46	-978.96	-1131.58	-982.35	-1056.37	-1017.07

Note: DM= dipole moment, η = hardness, s=softness, V=Volume M.W=Molecular Weight, ΔN=Electron transfer, ΔE = energy difference, χ=electronegativity and ω=global electrophilicity index

The chemical reactivity of the inhibitors resulting in adsorption on the metallic ion surface is a function of energy difference (ΔE) between the E_{HOMO} and E_{LUMO} of the inhibitor. Generally, higher reactivity between metallic ion and corrosion inhibitor is a result of a decrease in the value of ΔE and increases the binding ability on the surface of the metal which consequently increases in inhibition efficiency (%IE) of the inhibitor. The value of ΔE is in the following order: 2-hydroxyathersperminine < noratherosperminine < atherosperminine < methylisococlaurine < 2-hydroxyathersperminine < reticuline.

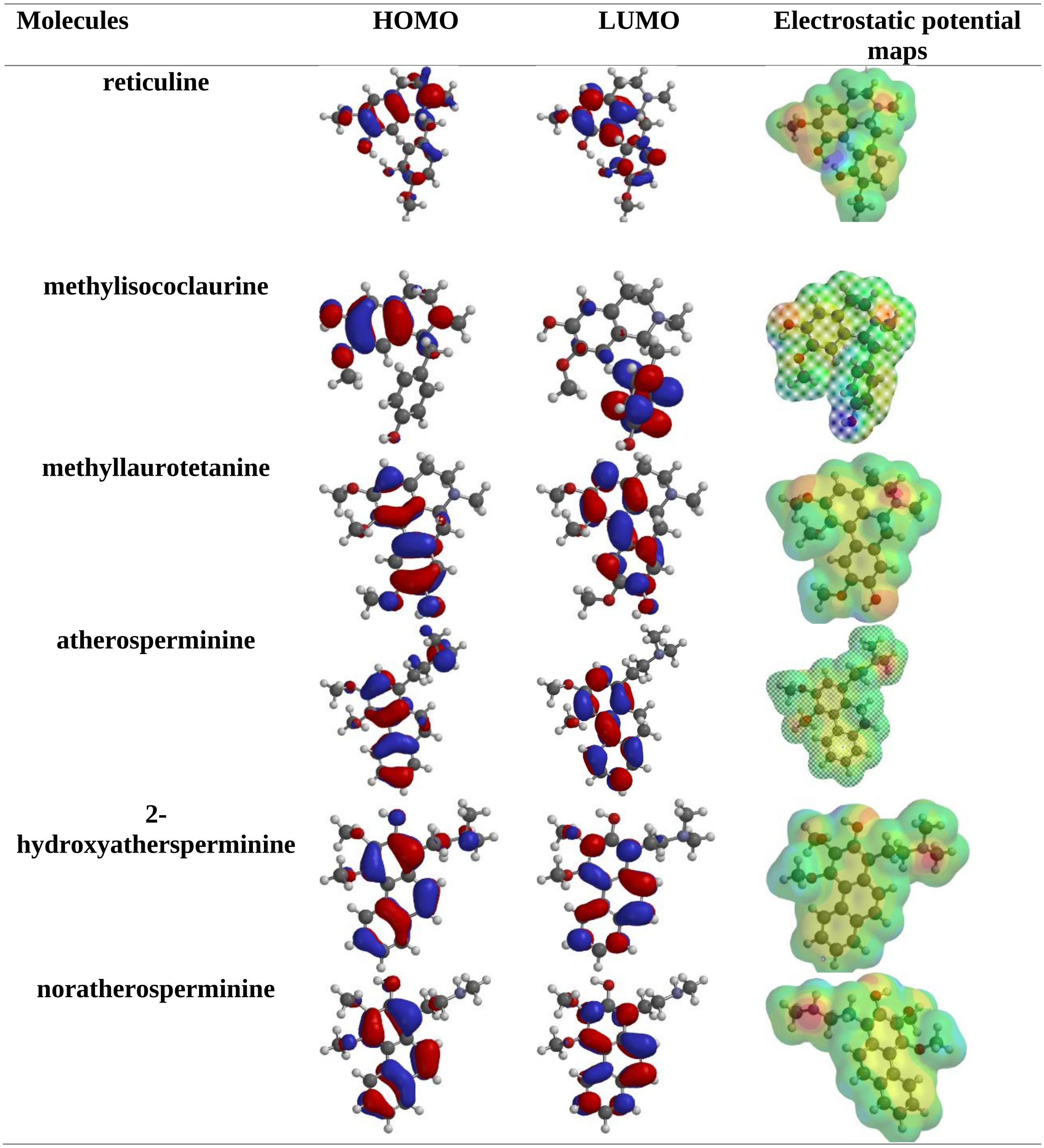


Fig. 3. HOMO (left) and LUMO (middle) frontier molecular orbitals and molecular electrostatic potential maps (right) of Optimized molecular structures of a molecule determined by DFT/B3LYP/6-31G*.

However, the value of ΔE for the first three molecules (Table 1) is 4.92 5.12 eV (methylisococlaurine), 4.58eV(methyllaurotetanine), 4.98 eV (atherosperminine) respectively.

2-hydroxyathersperminine and 2-hydroxyathersperminine are structural modifications of atherosperminine as shown in Figs. 1 and 2. Structural modification of lowest inhibition efficiency inhibitor atherosperminine with hydroxyl group as presented in 2-hydroxyathersperminine destabilizes HOMO and LUMO by increasing the HOMO and decreasing the LUMO. This destabilization also decreases the energy difference by 0.48 and 0.46 eV respectively for both 2-hydroxyathersperminine and noratherosperminine.

This destabilization and reduction in energy difference might improve the inhibition efficiency of 2-hydroxyathersperminine and noratherosperminine more than 2-hydroxyathersperminine and even atherosperminine. An infinitesimal change was observed from the HOMO, LUMO and band gap of noratherosperminine when one of the side chain methyl ($-CH_3$) groups is substituted with hydrogen in 2-hydroxyathersperminine. Hence 2-hydroxyathersperminine and noratherosperminine are predicted to have similar inhibition efficiency which is also expected to be higher than that of atherosperminine. However, the infinitesimal change in the energy gap in methyllaurotetanine, 2-hydroxyathersperminine and noratherosperminine makes it difficult theoretically predict molecules with better inhibition efficiency. Hence other parameters are to be examined.

When the frontier molecular orbital density distribution of the studied *Cryptocarya spp.* alkaloids (Fig. 3) were analyzed, it was discovered that the electron density on the HOMO is mainly localized on oxygen, nitrogen atoms, and some areas containing carbon atoms in rings A and B, of reticuline and methylisococlaurine showing that these atoms are the most preferable adsorption sites. The bigger lobes in HOMO mean the largest contribution to molecular orbitals. The carbon atoms lobes in rings A and B in methyllaurotetanine and atherosperminine are bigger than the carbon lobes in methylisococlaurine. This makes methyllaurotetanine have the highest tendency to offer electrons to the unoccupied orbital of the metal. The LUMO electron densities are distributed over constituent atoms of all the methylisococlaurine. The widely distributed LUMO electron density around the ring C of methyllaurotetanine is an indication of favorable interactions of the molecules with electron-rich metallic orbitals.

The Molecular Electrostatic Potential (MEP) gives information about all the electronic components of the molecule and the region/reactive sites for electrophilic and nucleophilic attack. The size, shape, charge density and reactive sites of a broad range of organic materials could be defined clearly by using the electron density isosurface produced by the MEP surface (Bharanidharani and Myvizhi, 2018). The MEP map shows different values of electrostatic potential in different colors: red, yellow, green, light blue, and blue. The red and yellow regions on the MEP map are associated with the active electrophilic region, and the light blue and blue regions are associated with the active nucleophilic regions. The MEP map of the studied molecules is depicted in Fig. 3 (right). As shown, the more electron-rich regions (red) are located on the nitrogen and oxygen atoms; therefore, nitrogen and oxygen atoms represent the most electrophilic active sites. The nucleophilic reactions occur with hydrogen atoms (blue color).

Electronegativity, softness and chemical hardness, softness which are defined as reactivity indices as derivatives of electronic energy (E) with respect to several electrons (N) at a constant external potential t (r), were determined to further evaluate the inhibitor reactivity and stability that predict the adsorption and inhibition efficiency of the studied molecules. Chemical stability is closely related to chemical hardness: harder molecules are less reactive (principle of maximum hardness). The absolute hardness and softness reactivity descriptors are associated with the description of hard and soft solutions through the theory of acid and base (Kabanda *et al.*, 2012). The large energy gaps of hard molecules prevent them from being effective corrosion inhibitors. As a result of their ease in donating electrons to metal atoms at the surface, a soft molecule with a small. the energy gap is an effective corrosion inhibitor. The values of the absolute hardness for molecules 1 to molecule 6 are 2.56 (methylisococlaurine), 2.30 (methyllaurotetanine), 2.49 (atherosperminine, 2.25(2-hydroxyathersperminine) and 2.26(noratherosperminine). These results show that methyllaurotetanine has the lowest hardness value while molecule 1 has the highest hardness value when compared with other studied molecules. This trend is consistent with the general belief that hard molecules should have a large energy gap. The softness values for studied Alkaloids are 0.391 (methylisococlaurine), 0.434(methyllaurotetanine), 0.401(atherosperminine), 0.444(2-hydroxyathersperminine) and 0.442(noratherosperminine). It is therefore expected also, that molecule 2-hydroxyathersperminine and noratherosperminine should have higher inhibition efficiency than methylisococlaurine, methyllaurotetanine and atherosperminine. These outcomes were anticipated because the compounds under study all exhibit the same pattern of ΔE values for hardness. The ability of an inhibitor to bind to the metallic surface as the E_{HOMO} increased and the E_{LUMO} decreased can be used to predict better adsorption or enhanced inhibition potential (as in the case of methyllaurotetanine), but these parameters are also insufficient to determine how effective the inhibitor is at inhibiting. So, it's important to take into account other factors like electronegativity.

Electronegativity is related to an atom's propensity to draw the shared pair of electrons to itself within a molecule. A molecule's adsorption on an iron surface is enhanced by its increased electronegativity. According to table 1, the examined compounds' electronegativity levels are listed in the following order: reticuline < methylisococlaurine < methyllaurotetanine < atherosperminine ≈ 2-hydroxyathersperminine ≈ noratherosperminine . Additionally, the order of reticuline > methylisococlaurine > methyllaurotetanine > atherosperminine > 2-hydroxyathersperminine describes the difference in electronegativity between the inhibitor and the metal. According to Sanderson's principle of electronegativity equalization, reticuline with a low electronegativity difference and large electronegativity gets to equalization quickly and, as a result, high reactivity is anticipated, which in turn indicates that the molecule has a high inhibition efficiency. This is yet another conclusion that is entirely consistent with the results of the experiment.

The direction of the corrosion inhibition process is predicted by the dipole moment (DM). It is described as the result of the separation distance and the magnitude of the separated charge. It offers details on a molecule's polarity of the bonds and distribution of its electrons (Ebenso *et al.*, 2010). Inhibitors with strong dipole moment, tend to bind to metallic surfaces more readily, improving inhibition. As the dipole moment increases, the deformability energy also rises. The dipole moment of the studied molecules is observed in the following order: noratherosperminine > methyllaurotetanine > 2-hydroxyathersperminine >

methylisococlaurine > atherosperminine. The hydroxyl group in 2-hydroxyathersperminine increases the dipole moment when compared to atherosperminine while the absence of methyl group in the side chine of noratherosperminine further improves its dipole moment. As a result, it is predicted that noratherosperminine with a dipole moment of 2.55 Debye should adhere to the metal's surface more readily than 2-hydroxyathersperminine given that the effectiveness of inhibition is increased by the adsorption of polar compounds with greater dipole moments. The studied molecules' polarizability trends are as follows: noratherosperminine > 2-hydroxyathersperminine > methyllaurotetanine > methylisococlaurine > atherosperminine, suggesting that 2-hydroxyathersperminine and noratherosperminine may have higher inhibitory efficiency than methyllaurotetanine and methylisococlaurine. Therefore, APA molecules exhibit greater dipole moments than BIA molecules in our investigation. This result supports the experimental results in Table 1 and suggests that APA inhibits more effectively than BIA.

The number of electrons transferred (ΔN) in *Cryptocarya nigra* alkaloids indicates whether or not it can donate electrons to the metal surface. A higher value for N suggests a greater propensity to donate electrons to an electron-deficient location, which in turn indicates a greater propensity to interact with and adsorb on a metallic surface. The range of ΔN values for the alkaloids under study is 0.765–0.889 e-. The least effective inhibition is provided by organic compounds with low ΔN. (Udhayakala *et al*., 2012). The trend of ΔN results for methylisococlaurine, methyllaurotetanine and atherosperminine as shown in Table 1 follow the trend of their measured inhibition efficiency in the experiment. This indicates that methyllaurotetanine has a higher inhibitory efficiency than methylisococlaurine due to the greater electron transfer (ΔN) that is connected with it. Moreover, 2-hydroxyathersperminine is expected to transfer more electrons than noratherosperminine and more than methylisococlaurine and atherosperminine. The electronic back donation, is also possible wherein electrons from metal are transferred back to the molecules that hinder them. Back donation charges (Table 1) which range between -0.675 and -0.797 e-, demonstrate that the inhibitor-metal interaction process can result in electron back donation because their values are less than zero. When both $\eta > 0$ and $\Delta E_{\text{back-donation}}$ are greater than zero, the charges transferred to the molecule are energetically preferred. Therefore, studied molecules are energetically favourable in transferring electrons back to themselves. Specifically, APA molecules are more favoured than BIA molecules. This outcome supports the idea that, if both charge transfer and reverse donation occur (i.e., to the molecule and from the molecule, respectively), the energy changes directly proportional to the molecule's hardness.

The *Cryptocarya nigra* alkaloids under study were weighed and measured in volume in order to determine the molecular size and their molecular coverage capability on the metal surface. Additionally, as these parameters rise in value, the molecules' potential to inhibit corrosion rises (Quraishi *et al*., 2010). methyllaurotetanine and 2-hydroxyathersperminine have higher values for weight and volume (327 amu and 325 amu, respectively) than other molecules. Therefore, it is expected that methyllaurotetanine and 2-hydroxyathersperminine will cover more on the surface of metal than other molecules.

4.0 Conclusion

In order to understand their electronic structures, reactivity, and anticipate their effectiveness toward corrosion inhibition using the quantum mechanical approach, the molecular reactivity descriptors of examined compounds were probed. The outcome of DFT/B3LYP/6-31G(d) reveals a relationship between the investigated quantum parameters and the inhibitory efficacy of *Cryptocarya nigra* alkaloids as assessed experimentally. It was discovered that the correlations can be used to anticipate inhibitors of the *Cryptocarya nigra* alkaloids with proper substituents that can give electrons to the metal's surface. According to theory, methyllaurotetanine and 2-hydroxyathersperminine should be more effective at inhibiting corrosion than the other three because of their greater E_{HOMO}, lower E_{LUMO}, and higher ΔN values, which would allow for more efficient electron transfer. The use of computational tools suggests an initial dry-lab approach, followed by a wet-lab procedure, as opposed to the conventional method of identifying new corrosion inhibitors in a wet lab.

5.0 References

Alibakhshi E., Ramezanzadeh M., Bahlakeh G., Ramezanzadeh B., Mahdavian M. & Motamedi M., (2018) *Glycyrrhiza glabra* leaves extract as a green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution: Experimental, molecular dynamics, Monte Carlo and quantum mechanics study, *Journal of Molecular Liquid*, 255, pp. 185–198.

Alvarez P.E., Fiori-Bimbi M.V., Neske A., Brand´an S. A. & Gervasi C.A., (2018) *Rollinia occidentalis* extract as green corrosion inhibitor for carbon steel in HCl solution, *Journal of Industrial and Engineering. Chemistry*, 58, pp. 92–99.

Becke, A.D. (1993) Density-functional thermochemistry. III. The role of exact exchange, *Journal of Chemical Physics*, 98, pp. 5648−5652.

Bharanidharani S. & Myvizhi P., (2018) *International Journal of Pure and Applied Mathematics, 119, 6769.*

Custodio D. L. and da V. Junior V. F., (2014) Lauraceae alkaloids, RSC Advance, 4(42), 21864–21890.

Ebenso, E. E.., Isabirye, D. A. & Eddy, (2010) Adsorption and quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium", International. journal of molecular Science. 11, 6, pp(6) (2010) 2473-98.

Eddy, N. O. (2020)._Theoretical chemistry study on the toxicity of some polychlorobiphenyl (PCB) compounds using molecular descriptors. *Scientific Africana*, 10, doi:10.1016/j.sciaf.2020.e00587.

Eddy, N. O., Odoemelam, S. A., Ogoko, E. C., Ukpe, R. A., Garg, R. and Anand, B. (2022). Experimental and quantum chemical studies of synergistic enhancement of the corrosion inhibition efficiency of ethanol extract of *Carica papaya* peel for aluminum in solution of HCl. *Results in Chemistry*, 100290,https://doi.org/10.1016/j.rechem. 2022.100290.

Eddy, N. O. & Ita, B. I. (2011). Experimental and theoretical studies on the inhibition potentials of some derivatives of cyclopenta-1,3-diene. *International Journal of Quantum Chemistry* 111, 114, pp. 3456-3473. doi10.1002/qua.

Eddy, N. O. & Ita, B. I. (2011). Theoretical and experimental studies on the inhibition potentials of aromatic oxaldehydes for the corrosion of mild steel in 0.1 M HCl. *Journal of Molecular Modeling* 17: 633-647. DOI:10.1007/s00894-010-0749.

Eddy, N. O., Odoemelam, S. A. & Ibiam E (2010). Ethanol extract of *Occimium gratissimum* as a green corrosion inhibitor for mild steel in H_2SO_4. *Green Chemistry Letters and Review*, 3, 3, pp. 165-172.

DOI: 10.1080/17518251003636428, Faraj, L.; Khan, G.M. (2015) Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes-A. Int. J. Electrochemical. Science., 10, pp. 6120–6134.

Faiz, M., Awanng, K. & Hussin, H.(2020). Corrosion inhibition on mild steel in 1 M HCl solution by *Cryptocarya nigra* extracts and three of its constituents (alkaloids). *RSC Adv.*, 2020,10, 6547-6562. https://doi.org/10.1039/C9RA05654H

Haldhar, D. Prasad & Bhardwaj N., (2019) Extraction and experimental studies of *Citrus aurantifolia* as an economical and green corrosion inhibitor for mild steel in acidic media J. Adhes. Sci. Technol., 33(11), 1169–1183.

Hamdan, A.B., & Haider F.I., (2018) Study on tea leaves extract as green corrosion inhibitor of mild steel in hydrochloric acid solution, IOP Conference Series Material Science Engineering, 290, pp. 12–86.

Ji, G, Anjum S., Sundaram S. & Prakash R., (2015) *Musa paradisica* peel extract as green corrosion inhibitor for mild steel in HCl solution, Corrosion Science., 90, 107–117.

Kabanda M. M., Shukla S. K., Singh A. K, Murulana L. C., & Ebenso E. E., (2012) “Electrochemical and Quantum Chemical Studies on Calmagite and Fast Sulphone Black F Dyes as Corrosion Inhibition for Mild Steel in Hydrochloric Medium”. International Journal of *Electrochemical Science*, 7, 8813-8831.

Karki, N.; Neupane, S.; Chaudhary, Y.; Gupta, D.K.; Yadav, A.P. (2020) Berberis aristata: A highly efficient and thermally stable green corrosion inhibitor for mild steel in acidic medium. Anal. Bioanal. Electrochem. 12, 970–988.

Lopez, N. and Illas, F. (1998) Ab Initio Modeling of the Metal-Support Interface: The Interaction of Ni, Pd and Pt on MgO(100). Journal of Physical Chemistry B, 102, 1430.

Marzorati, S.; Verotta, L.; Trasatti, S.P. (2018) Green corrosion inhibitors from natural sources and biomass wastes. Molecules, 24, 48.

Mas Faiz, Azeana Zahari, Khalijah Awang and Hazwan Hussin (2020) Corrosion inhibition on mild steel in 1 M HCl solution by *Cryptocarya nigra* extracts and three of its constituents (alkaloids) RSC Advance., 10, 6547–6562 | 6547

Ogunyemi B. T and Borisade G. S., (2020) Theoretical Modeling of Iminoisatin Derivatives as Corrosion Inhibitors of Steel in Acid Solution”, *FUDMA Journal of Sciences (FJS*), 4, 672 – 678,

Oguzie E.E., (2008) Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel, Corrosion. Science, 50(11), 2993–2998.

Oguzie, E. E. (2006). Adsorption and corrosion inhibitive properties as *Azadirachta indica* in acid solutions, *Pigment and Resin Technology, 35 (6),* 334-340.

Okafor P.C., Ikpi, M.E., Uwah, I.E., Ebenso, E.E., Ekpe, U.J., & Umoren, S.A. (2008). Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corrosion Science, 50 (8),* 2310-2317.

Parajuli, D.; Sharma, S.; Oli, H.B.; Bohara, D.S.; Bhattarai, D.P.; Tiwari, A.P.; Yadav, A.P. (2022) Comparative Study of Corrosion Inhibition Efficacy of Alkaloid Extract of Artemesia vulgaris and Solanum tuberosum in Mild Steel Samples in 1 M Sulphuric Acid. Electrochemical 3, 416–433.

Parr R. G, Szentpaly L.V., Liu S. (1999) Electrophilicity index”, *Journal* of the American *Chemical Society.* 121 1922–1924.

Parr R. G, Yang W. (1984) Density functional approach to the frontier electron theory of chemical reactivity. *Journal of the American Chemical Society*, 106:4049-4050

Parr, R.G. and Yang, W. (1989) Density Functional Theory of Atoms and Molecules. Oxford University Press, New York.

Pearson R. G., (1993) The principle of maximum hardness", *Account of Chemical Research*. 26 250–255

Quraishi, M. A., Singh, A., Singh, V.K., Yadav, D. K., & Singh, A.K. (2010). Green steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* Leaves. *Materials Chemistry and Physics*, 122, 1, pp. 114-122.

Raja, P. B., Qureshi, A. K., Rahim, A. A., Osman, H. & Awang, K. (2013) Neolamarckia Cadamba Alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media. *Corrosion Science*, 69, pp.292-301

Rani, B. & Basu, B. B. J. (2012) Green inhibitors for corrosion protection of metals and alloys: An overview. *International Journal of Corrosion*, 380217.

Saw L. G. & Chung R. C. K (2015) the flora of Malaysia projects, Rodriguesia, 66, 4, pp. 947–960.

Spartan 14v112 (2013) Wavefunction, Inc., Irvine.

Udhayakala, P., Rajendiran, T.V. & Gunasekaran, S. (2012) Theoretical Evaluation on the Efficiencies of Some Flavonoids as Corrosion Inhibitors on Copper. Journal of Chemical, *Biological and Physical Sciences, Section A: Chemical Sciences*, 2, 1151-1165

Udhayakalaa, P. Rajendiranb T.V. and Gunasekaranc S., (2012) *Der Pharma Lettre*, 4 , 1285.

Umoren, S.A., Obet, I. B., Akpabio, L.E., & Etuk, S. E. (2008). Adsorption and corrosive inhibitive properties of *Vigna unguiculata* in alkaline and acidic media. *Pigment and Resin Technology*, 37 , 2, pp. 98-105.

Wan Othman W. N. N., Sivasothy Y., Liew S. Y., Mohamad J., Nafiah M. A., Ahmad K., Awang K., et al., (2017) Alkaloids from *Cryptocarya densiflora* Blume (Lauraceae) and their cholinesterase inhibitory activity, Phytochemical Letter, 21, pp. 230–236.

Zarras, P.; Stenger-Smith, (2014), J. Corrosion processes and strategies for prevention: An introduction. In Handbook of Smart Coatings for Materials Protection; Elsevier: Amsterdam, The Netherlands, pp. 3–28.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data public

Competing interest

The authors declared no conflict of interest.

There is no source of external funding

Authors Contributions

BT Ogunyemi and RA Ukpe designed the project, BT Ogunyemi performed the *in computioanl* experiment. Both authors analysed the data and prepared the manuscript.