

# Adsorption and Quantum Chemical Studies on the Inhibition Potentials of *Afzelia Africana* Seed Extract for the Corrosion of mild Steel in 2M HCl Solutions

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**Abstract:** - The inhibitive action of the seed extract of *Afzelia Africana* on mild Steel corrosion in 2M HCl solutions was investigated using Phytochemical Screening, Weight loss and theoretical analysis. The results obtained at room temperature indicate that the *Afzelia Africana* seed (AAS) extracts functioned as good corrosion inhibitor in 2M HCl solutions. Inhibition efficiency was found to increase with extracts concentration but decreases with time. The inhibition efficiency increases gradually reaching a maximum value of 86.01% within the first 24 hours after which its inhibitory potency decreases with time. The kinetic study shows that the inhibitory action is a first order kinetics with the concentration of the seed extract of *Afzelia Africana* which is in tandem with the langmuir adsorption isotherm. Quantum studies revealed that inhibition was due to adsorption of active molecules leading to formation of a protective layer on surface of mild steel. Quantum chemical parameters such as highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) energy levels, HOMO-LUMO energy gap and electronic density were virtually identified. Quantum analysis demonstrated reactive centres of electrophilic and nucleophilic attack and strong inhibition properties of bioactive molecules of *Afzelia Africana* seed extract.

**Key Words:** Corrosion, Corrosion Inhibitors, Mild Steel, Weight Loss, Quantum Analysis

## I. INTRODUCTION

Corrosion of metals has been known as a major threat to the growth of industries that not only affect the structural integrity of manufacturing equipment but also has economic implications costing billions of dollars each year. Corrosion is a natural phenomenon commonly defined as the electrochemical oxidation/deterioration of metals as a result of their reaction with the surrounding environmental conditions. This phenomenon in view of the frequent use of different metals in modern life, is induced by the corrosion environment which can be atmospheric, acidic, alkaline, underground waste and combination of these [1], [2].

Myriad of the numerous corrosion problems encountered in the industries involves acids due to its usefulness in acid pickling, industrial cleaning, scrubbing, scraping and storing of steel structure. However, efforts are being made by many industries to combat this menace via electroplating, cathodic

protection and the addition of inhibitors. Corrosion inhibitors are substances which when added in small concentrations to an environment, effectively reduces the dissolution of the metals exposed to it [1], [3]-[5].

Literature reveals that several organic compounds containing hetero-atoms (N, O, P, and S) and conjugated diene exhibit corrosion inhibitive properties for mild steel in acidic medium. As a result of the know hazardous effect of most synthetic inhibitors such as Chromates, Silicates and organic amines coupled with environmental pollution, the need for eco-friendly, cost effective and nontoxic natural corrosion inhibitors of plant origin becomes very important and desirable [6]-[12].

The use of plant extracts as corrosion inhibitors cannot be over emphasized and the following plants have been investigated and found to possess inhibitory efficacy. *Gliricidia Sepium* [4], *Azadirachta indica* [13], *Pterocarpus soyauxii Taul* [14], *Brachystegia eurycoma* [7], *Boscia senegalensis* [15] and lots more.

*Afzelia africana* also known as Mahogany bean is an underutilized legume plant in the family of *Fabaceae* and sub family *Caesalpinaceae* [16]. *Afzelia africana* plants are largely cultivated in the Savannah, fringing forest and the drier parts of the forest regions of Africa. The *Afzelia africana* seeds (AAS) have waxy orange cup-like structure at their base and are used in Nigeria generally as soup thickening ingredient in much the same way as melon and *irvingia gabonensis* seeds as shown in figure 1.0. It is widely distributed and consumed by many African countries including Senegal, Sudan, Uganda, Tanzania, Sierra leone, Ghana and Nigeria [17]. It is widely known for its medicinal and biological activities and also as one of the richest sources of secondary metabolites in nature.

The use of computational methods have been extended to various fields via the developments in software one of which is the application of quantum chemical calculations (QCCS) in the corrosion studies. One can easily ascertain the

electronic and geometrical structure of the inhibitor by performing the quantum chemical calculations [18]-[19].

Aim of present study was to investigate the corrosion inhibition potentials and mechanism for mild steel in solution of 2M HCl acid with ethanolic extracts of *Afzelia Africana* seed (AAS) using weight loss and quantum studies.



Figure 1.0. *Afzelia Africana* seeds (AAS)

## II. MATERIALS AND METHODS

### 2.1. Collection of plant material and preparation of seed extracts

The study was carried out on *Afzelia Africana* seeds (Figure 1.0). the *Afzelia Africana* seeds were purchase from Eke-Okigwe market in Okigwe local government area of Imo state, Nigeria. The sample was dried and grounded into powder. Four hundred and fifty gram (450g) of the dehydrated and grounded seeds was soaked in a 500ml solution of ethanol for 48hrs. Sequentially, sufficient grams of the grounded seeds were measured into the ethanol and were extracted until the 450g of the grounded seeds were exhausted. After 48hrs, the samples were filtered using Whatman filter paper No.1 (QUALIGEN- Germany). The filtrates were further subjected to evaporation by rotatory evaporator at 358K in order to leave the sample free of the ethanol. The stock solutions of the extract obtained were used in preparing different concentrations of the extract by dissolving 1.0, 2.0 and 3.0g of the extract in 1L of 2M HCl respectively.

### 2.2. Phytochemical Screening on AAS

Screening of phytochemicals is significant for identification of bioactive principles present in plants. Phytochemical screening was carried out on AAS extracts by standard procedures [19]. Plant extracts were screened for reducing sugar, alkaloids, protein, phenols, flavonoids, amino acids, tannin, steroids, glycosides and carbohydrates.

### 2.3. Preparation of Specimen

The specimens were cut using a saw into the required dimension of 4 x 3 x 0.017cm then descaled by brushing with a emery paper. They were cleaned and dried with acetone, then stored properly in desiccators for further use. The elemental composition of mild steel specimen analyzed and used for this study with iron (Fe) having the highest elemental composition of 93.65%.

### 2.4. Gravimetric Techniques

One hundred millilitres (100ml) each of the 2.0M HCl solution was measured into four different beakers with one as the blank (uninhibited solution) and the remaining three labeled A to C containing different concentrations of the inhibitors ranging from 1.0g to 5.0g/100ml respectively. The test coupons were weighed before immersion in the acid solutions and the measurements were taken down. After weighing, the coupons were immersed in the acids solution. The coupon in each beaker was noted to avoid mix ups during the practical work. The immersion period was 24 hour interval, after 24 hour the coupons were retrieved from the acids, washed with tap water, degreased with ethanol and dried with acetone before the corresponding weights after immersion were recorded. The procedures were repeated for 96 hours i.e. for 4 days. The corresponding weights after immersion were recorded as well after each day. The differences in weight of the coupons were again taken as the weight loss [19]. The rate of corrosion (CR), inhibition efficiency (IE), and degree of surface coverage ( $\theta$ ) were obtained from the weight loss results. Rate constant and half life ( $t_{1/2}$ ) were also determined using the expressions below.

The corrosion rates (C.R) were computed using the formular:

$$C.R = \frac{\Delta W}{A \times T} \quad - \quad - \quad - \quad - \quad - \quad 1.1$$

Where:  $\Delta W$  = weight loss (g), A = total surface area of the test coupon ( $\text{cm}^2$ ), T = immersion time (min)

The inhibitor efficiency (IE) was computed using the relationship in equation 1.2.

$$\%IE = \frac{(C.R)_o - (C.R)_{inh}}{(C.R)_o} \times 100 \quad - \quad - \quad - \quad - \quad 1.2$$

Where:  $(C.R)_o$  and  $(C.R)_{inh}$  are the corrosion rates in the absence and presence of different concentrations of the inhibitor, respectively.

The surface coverage ( $\theta$ ) of the inhibitor was obtained from the experimental data using the equation 1.3 as follows:

$$\theta = \frac{(C.R)_o - (C.R)_{inh}}{(C.R)_o} \quad - \quad - \quad - \quad - \quad 1.3$$

The rate of the reaction as well as the values of the rate constant  $k$  of the reaction were evaluated using the Equation 1.4 and 1.5 as follows:

$$\log W_f = \log W_o - kt \quad - \quad - \quad - \quad - \quad 1.4$$

$$k = \frac{1}{t} \log \left( \frac{W_o}{W_f} \right) \quad - \quad - \quad - \quad - \quad 1.5$$

Where  $W_f$  = the final weight of metal after time, t,  $W_o$  = the initial weight of metal, t = the immersion time.

The half-life of the reaction was evaluated using Equation 1.6 as follows:

$$t_{1/2} = \frac{0.693}{k} \quad - \quad - \quad - \quad - \quad 1.6$$

Where  $k$  = the rate constant of the reaction.

### 2.5. Quantum Chemical Analysis:

Quantum chemical calculations were used as a theoretical tool to support the experimental results and to explain the interaction between the inhibitor molecules and the steel surface. Density functional theory (DFT) was used to analyze the characteristics of the plant extracts and to describe the structural nature of the inhibitor on the corrosion process [20]-[21]. Structures of flavonol and alkaloid in AAS extracts were obtained from literature for computational analysis. 3-Dimensional (3D) structures were retrieved from structural database and was optimized (Fig.3) and taken as input file for quantum chemical studies. Mulliken population analysis determines nucleophilic and electrophilic reaction centers in compounds. According to PM3 (Parameterized Model number 3) theorem [22]-[23], the HOMO energy is related to the ionization potential (IE) whereas the LUMO energy is linked to the electron affinity (EA), as follows:

$$IE = -E_{\text{HOMO}} \quad - \quad - \quad - \quad - \quad - \quad 1.7$$

$$EA = -E_{\text{LUMO}} \quad - \quad - \quad - \quad - \quad - \quad 1.8$$

Other related parameters like electronegativity ( $\chi$ ), electronic chemical potential ( $\mu$ ), hardness ( $\eta$ ), and softness ( $\sigma$ ) can be expressed as:

$$\text{Electronegativity } (\chi): -\mu = \frac{IE+EA}{2} \quad - \quad - \quad - \quad - \quad 1.9$$

$$\text{Electronic chemical potential } (\mu): -\chi \quad - \quad - \quad - \quad - \quad 2.0$$

$$\text{Hardness } (\eta): = \frac{IE-EA}{2} \quad - \quad - \quad - \quad - \quad 2.1$$

Electronegativity, hardness, and softness have proved to be very useful quantities in chemical reactivity theory.

The global electrophilicity ( $\omega$ ) index was introduced by Parr (1999) as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by

$$\text{Electrophilicity } (\omega): = \frac{\mu^2}{2} \sigma \quad - \quad - \quad - \quad - \quad 5.4$$

Nucleophilicity ( $\epsilon$ ): nucleophilicity is the reciprocal of electrophilicity expressed as:

$$\epsilon = \frac{1}{\omega} \quad - \quad - \quad - \quad - \quad - \quad 5.5$$

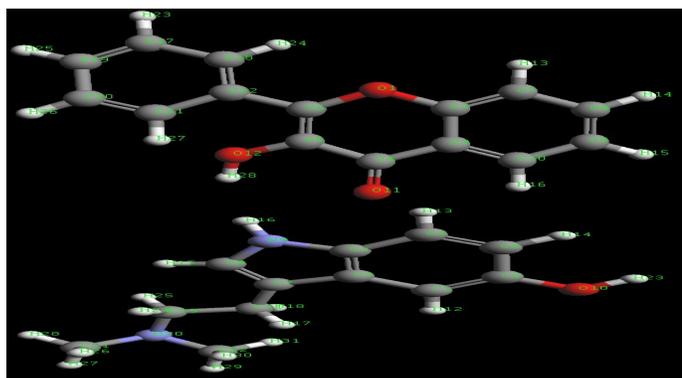


Figure1.1: Molecular structure of flavonol and alkaloid

## III. RESULTS and DISCUSSION

### 3.1. Phytochemical screening

The phytochemical constituents of AAS extract, as presented in Table 1, indicate the presence of tannins, saponins, et cetera. The presence of these compounds promotes the inhibition of mild steel in hydrochloric acid solution. Plant extracts are organic in nature and some of the constituents are tannins, alkaloids, proteins, polysaccharides, polycarboxylic acids, alkaloids, and so forth. These compounds are potential corrosion inhibitors for many metals in an acidic medium<sup>24</sup>.

Table 1: phytochemical constituents of AAS extract

Phytochemical constituent	Tannins	Flavonol	Amino acids	Alkaloid
Ethanol extract of AAS	+++	++	++	+

**Legend:** + = Sparingly Present; ++ = Moderately Present; +++ = Highly Present

### 3.2. Weight Loss Measurements

The weight loss of mild steel coupons due to their immersion in solutions of 2MHCl containing different concentrations of AAS extract was measured as shown in Table 2. The results clearly shows a general reduction in the original weight of the metal coupons in the presence of the inhibitor compared to the uninhibited solution (blank), indicating that ethanol extract of AAS inhibited the corrosion of mild steel in 2MHCl at the end of the corrosion monitoring process. This is further supported by the decrease in Corrosion rate and Rate constant as the concentration of the extract increases, this also is in tandem with what was observed in the inhibitory action of *Brachystegia eurycoma* seed extracts on the corrosion of mild steel<sup>25</sup>. This may be attributed to the adsorption of inhibitor on the mild steel surface, producing a barrier, which isolates the surface from the corrosion environment.

Table 2: Deduced data for inhibition efficiency, corrosion rate, rate constant and half life obtained from gravimetric method for mild steel in 2M HCl after 24hrs.

Concentration of inhibitor (g/l)	$\Delta W$ (g)	Corrosion Rate ( $\text{gcm}^{-3} \text{hrs}^{-1}$ ) $\times 10^3$	% IE	Rate Constant ( $\text{day}^{-1}$ ) $10^{-3}$	Half Life (days)
Blank	0.336	57.76	-----	1.90	3.65
1	0.144	24.75	57.2	0.79	8.77
2	0.096	16.50	71.43	0.52	13.33
3	0.046	8.08	86.01	0.25	27.72

The corrosion rate for the mild steel and the inhibition efficiency of the plant extract in 2M HCl containing different concentrations of the plant extracts as a function of time (in days) are also presented in figure 1.2-1.3.

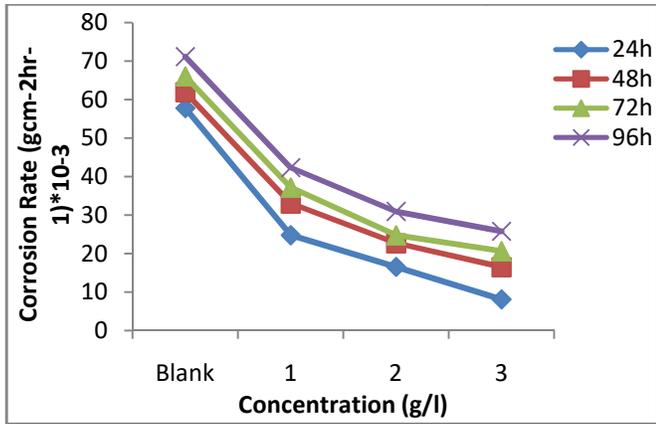


Figure 1.2: Variation of corrosion rate of AAS with concentration showing the effect of time

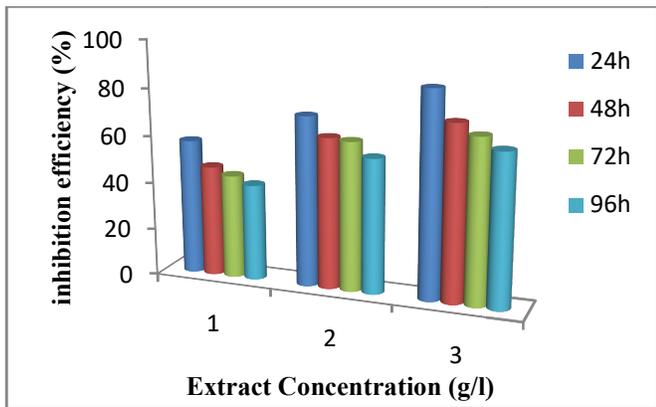


Figure 1.3: Variation of inhibition efficiency of AAS with concentration and time

The inhibition efficiency increased with increase in concentration of inhibitor from 1.0 to 3.0g/l at room temperature (Fig.1.3). Maximum inhibition efficiency was 86.01% in case of AAS /2MHCl for immersion period of 24h at a concentration of 3.0g/l (Fig.1.3). These results suggest that adsorption model arrangement and orientation of constituents present in *Azelia Africana* seed extract on surface of mild steel may change with time [26]. Decrease in inhibition efficiency thereafter with increasing time may be due to shift in adsorption and desorption equilibria which takes place simultaneously on prolonged exposure to corrosive media [27]. Adsorbed organic molecules prevent further interaction of metal with acid [28].

Figure 1.4 shows the plot of  $\log W_f$  against Time (hrs), for AAS extracts indicating a linear variation at all concentrations. The linearity of the plots confirmed a first order reaction kinetics with respect to the corrosion of mild steel in the acidic medium (1M HCl). This implies that the rate of the reaction was directly proportional to the concentration of the extracts [29]. From Table 2.0, the values of rate constant of the reaction decreases as the concentration of AAS extracts increased and were in agreement with the assertion that the rate of the reaction was directly proportional to the concentration of the blends of AAS extracts [30].

Since the rate of the reaction was first order, the half-life of the reaction which were determined using the expression for the half-life for a first order reaction, showed the time required for the concentration of AAS extracts to be reduced to half its initial value. Table 2.0, also shows that the half-life of the reaction increased as the concentration increased. The increase in half-life as the concentration of the extracts increased indicated a decrease in the dissolution rate of the mild steel and hence more protection of the metals by the AAS extracts<sup>7, 30</sup>.

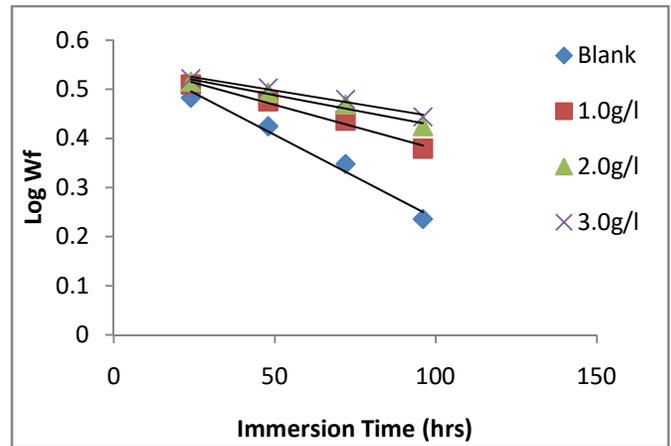


Figure 1.4: Variation of  $\log W_f$  with time for mild steel of in 2M HCl solutions containing AAS extract.

### 3.3. Adsorption Mechanism

Figure 1.5, shows the linear plots for Langmuir adsorption isotherm. The plots clearly revealed that the surface adsorption process of the AAS extracts on the mild steel surface obeyed the Langmuir adsorption isotherm as their linear regression approaches unity [31]. The plots support the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a monolayer protective film on the metal surface and producing uniform energies of adsorption onto the surface of the metal following Langmuir isotherm. It can therefore be inferred that physisorption occurred [4], [30].

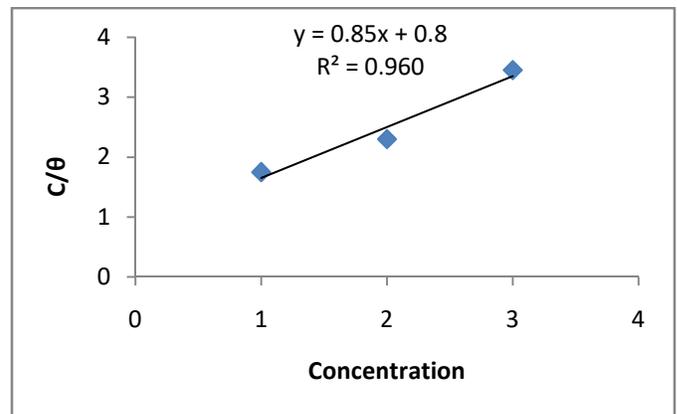


Figure 1.4: Langmuir adsorption isotherm plot for the adsorption of AAS on the surface of mild in 2M hydrochloric acid.

### 3.4. Theoretical and Quantum Chemical Studies:

Flavonol, and Alkaloid represent the most effective component of the AAS extract. Quantum chemical calculations have proved to be a veritable tool for studying corrosion inhibition mechanism [32]-[33]. Thus in the present investigation, quantum chemical calculation were performed using density functional theory (DFT) to explain the experimental results obtained in this study and to give an insight into the inhibition action of the AAS extract on the mild steel surface. The structures are sketched with ACD chemsketch and structural geometries were optimized to obtain a stable structure.

The calculated values of the quantum chemical parameters obtained using the Hartree-fock/ Density functional theory (HF-DFT) by Becke 3 Lee Yang Parr (B3LYP) method with 6-31G\* basis set of SPARTAN' 06 V112 program are presented in Table 3.0. The relation between inhibition efficiency of inhibitor and the quantum chemical calculation parameters like  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E$ ,  $\chi$ ,  $\eta$ ,  $\sigma$ ,  $\omega$ ,  $\epsilon$ , and dipole moment were investigated. Positive and negative regions in HOMO and LUMO orbitals, Mulliken charges, Electrostatic potential map of compounds were computed using ArgusLab 4.0.1[34]-[35]. Their examination is very important so as to determine the electronic properties of the compounds theoretically using PM3.

**Table 3.0:** Quantum Chemical Parameters of AAS Phytoconstituents

Component Parameters	Flavonol	Alkaloid
$E_{\text{HOMO}}$ (eV)	-0.3301	-0.3052
$E_{\text{LUMO}}$ (eV)	-0.0370	-0.0020
$\Delta E_{(\text{LUMO-HOMO})}$ (eV)	0.2931	0.3032
EA (eV)	0.0370	0.0020
IE (eV)	0.3301	0.3052
$\chi$ (eV)	0.1836	0.1536
$\eta$ (eV)	0.1466	0.1516
$\sigma$ (eV <sup>-1</sup> )	6.8213	6.5963
$\omega$ (eV)	0.1150	0.0778
$\epsilon$ (eV)	8.6957	12.8535
$\mu$ (debye)	1.7189	3.0395

For a molecule to be effective corrosion inhibitor, it must donate electrons to the vacant d orbital of the metal for bonding and as well receive free electrons from the metal surface. The reactive ability of the inhibitor is considered to be closely related to their frontier molecular orbitals, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [36]. The highest occupied molecular orbital (HOMO) is usually the region of high electron density, therefore is often associated with the electron donating ability of the molecule and lowest unoccupied molecular orbital (LUMO) is associated with the electron accepting ability of the inhibitor molecule from the metal. The optimized geometry of the components of AAS extract is shown in Figure 1.1. The positive and negative

phases of orbital are represented by two colours, blue regions represent an increase in electron density and red region represents a decrease in electron density [37].

The Positive and negative regions in HOMO and LUMO orbitals of flavonol and alkaloid components of AAS extract were plotted and are shown in Figure 1.5-1.6 respectively. From the Figure 1.5-1.6, It can be seen that the frontier orbitals, the HOMO and the LUMO were distributed all around each molecule most dominated by bonded heteroatoms (oxygen atoms and Nitrogen atoms of both amino and carboxylic group) and some of the carbon atoms basically those containing unsaturated bonds in their molecule, and on the entire aromatic rings. These regions are the sites at which electrophiles attack and represent the active centers, with the utmost ability to bond to the metal surface, whereas the LUMO orbital can accept the electrons in the d-orbital of the metal using antibonding orbitals to form feedback bonds [38], [39]. It has been reported that excellent corrosion inhibitors are usually those organic compounds that does not only offer electrons to unoccupied orbital of the metal but also accept free electrons from the metal [40]-[42]. It is also well documented in literature that the higher the HOMO energy of the inhibitor, the greater its ability of offering electrons to unoccupied d-orbital of the metal, and the higher the corrosion inhibition efficiency. It is evident from Table 3.0 that flavonol had the highest value of  $E_{\text{HOMO}}$  -0.3301 (ev) and increased in the order: Fla>Alk which suggest that flavonol would be better adsorbed on the metal surface than alkaloid.  $E_{\text{LUMO}}$  represent the ability of the molecule to accept electrons from a donor reagent and the lower the value of  $E_{\text{LUMO}}$ , the greater the tendency of the molecule to accept electrons. Results from Table 3.0 also show that alkaloid had the lowest value of  $E_{\text{LUMO}}$  -0.0020 (ev) and decreases in the order: Alk<Fla which suggest that alkaloid will readily accept electron from the metal than flavonol. The above assertion indicate that AAS extract is a good corrosion inhibitor capable of donating electrons to the mild steel surface, by forming an inhibition barrier [43]. This also confirms that the presence of this component molecules in the seed extract increases its inhibition efficiency which is in line with the experimental results.

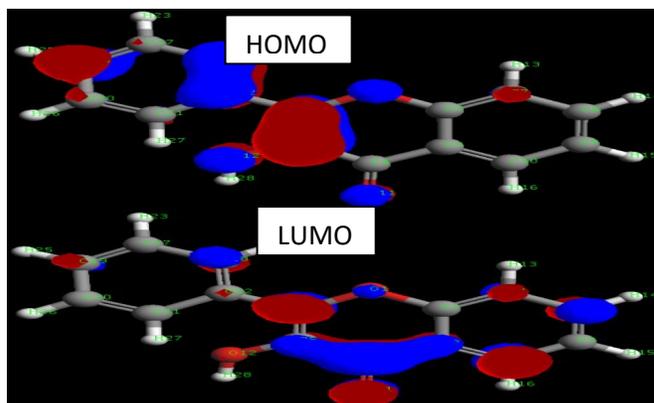


Figure 1.5: HOMO and LUMO orbitals of Flavonol

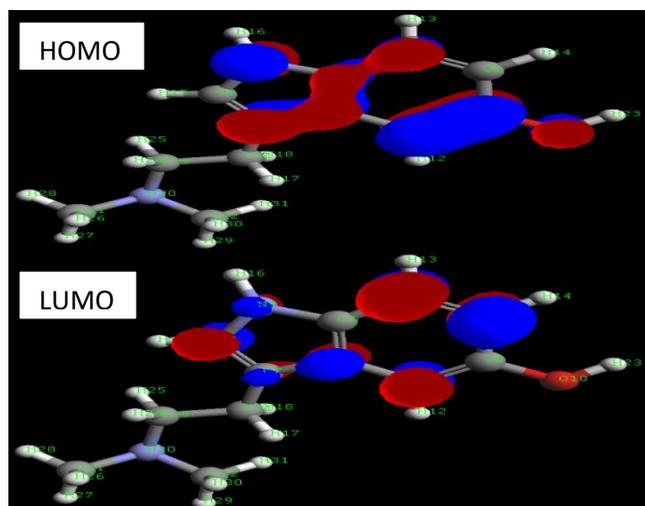


Figure 1.6: HOMO and LUMO orbitals of Alkaloid

Apart from  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , energy gap ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) is another essential quantum chemical parameter for explaining surface adsorptive behaviour of the inhibitor molecules. Generally, Larger value of  $\Delta E$  implies that the inhibition efficiency of the inhibitor is less due to low reactivity with the metal surface and lower value of  $\Delta E$  implies that the inhibitor is having higher inhibition efficiency due to high reactivity with metal surface. Low values of the energy gap ( $\Delta E$ ) will provide good inhibition efficiencies, because the excitation energy to remove an electron from the last occupied orbital will be low [22]. A molecule with a low energy gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed soft molecule<sup>44</sup>. In this study, Table 3.0 shows the lower values of  $\Delta E_{(\text{LUMO-HOMO})}$  in the following order Flavonol ( $0.2931$ ) < Alkaloid ( $0.3032$ ). The adsorption of inhibitor onto a metallic surface occurs at the part of the molecule which has the greatest softness and lowest hardness [45].

Chemical hardness ( $\eta$ ) and softness ( $\sigma$ ) are significantly related to the band gap (HLG). They are important properties to measure the stability and reactivity of a molecule. A soft molecule has a small energy gap and a hard molecule has a large energy gap [36]. According to Pearson, hard molecules with large energy gaps cannot act as good corrosion inhibitors [46]. Conversely, soft molecules with small energy gaps are efficient corrosion inhibitors because they can easily donate electrons to metal atoms at the surface. Table 3.0 reveal that constituent of AAS extract have greater values of softness ( $\sigma$ ) and lower values of hardness ( $\eta$ ). The softness ( $\sigma$ ) values of the studied extract increases in the order: Flavonol ( $6.8213$ ) > Alkaloid ( $6.5963$ ) and the corresponding hardness values decreases in the reverse form of the order: Flavonol ( $0.1466$ ) < Alkaloid ( $0.1516$ ). This confirmed the extract molecule as efficient corrosion inhibitor

Moreover the mapping of molecular electrostatic potential (ESP) can allow an observation of the regions of high and low electron density in an organic corrosion inhibitor molecule.

This can help determine the possible sites in the inhibitor molecule which are susceptible to undergo adsorption interaction with a metal surface [47], [48], [50]. The ESP mapping of the Component of AAS extract are displayed in Figure 1.7. The different values of ESP are shown in different colours where the most negative ESP regions are shown in red colour i.e. regions rich in electron, blue colour shows the region of the most positive ESP that is electron deficiency while the green colour shows the regions with zero ESP values [47] - [50]. It can be seen that in the Component of AAS extract, the most negative potential (red color) is around the heteroatoms (oxygen and nitrogen). Upon protonation at nitrogen, a deep blue coloured region can be observed around the nitrogen atoms showing a deficiency of electrons and the possible centre's susceptible for undergoing physical adsorption via electrostatic interaction.

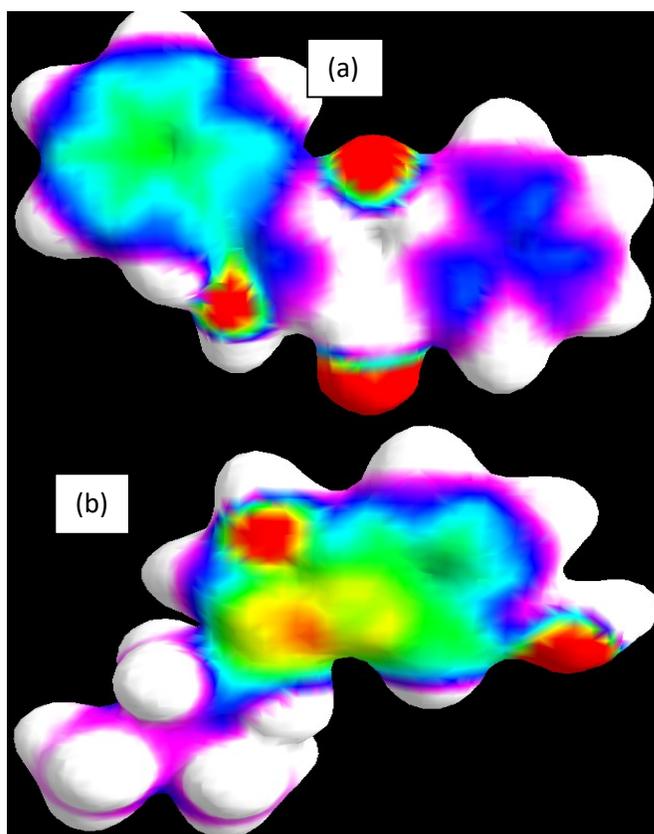


Figure 1.7: ESP Optimized mapped density of (a) Flavonol and (b) Alkaloid

### 3.5. Mulliken Charge Distribution of Flavonol and Alkaloid

Mulliken population analysis is mostly used for calculation of charge distribution in a molecule [38]. Mulliken charge distribution of flavonol and alkaloid are presented in Table 4.0. It shows Mulliken charge distribution of all heteroatoms and some of carbon atoms are negatively charged. Thus, considered as active sites for adsorption process of inhibitor molecule onto the mild steel surface [51]. More negative the atomic charges of adsorbed centre, more easily atom donates its electron to unoccupied orbital of the metal [52]. The inhibition efficiency of inhibitors under study depends on

presence of electronegative atoms in their molecular structure. It can be readily observed that oxygen atoms and most of the carbon atoms have higher charge densities/negative charges. Flavonol has more electronegative O11 and O12 with charges -0.3576 and -0.2357. In Flavonol, C21, C9, C7, O11 and O12 are most susceptible sites for electrophilic attacks as they present highest values of negative charge. On other hand, C4 in Flavonol is the most susceptible sites for the nucleophilic attacks as its present the highest values of positive charge. The regions of highest electron density are generally sites to which electrophiles can attack [52]. Alkaloid has O10, C8, C22, C5, C21 and C22 as the most susceptible sites for electrophilic attack as they offer the highest values negative charge. The susceptible sites for nucleophilic attacks possess highest values of positive charge at N9. O and C atoms were active centers that possess strong ability of bonding to metal surface. Therefore, Flavonol and Alkaloid can accept electrons from metal through these atoms and hence these compounds could serve as good corrosion inhibitor against metal surface protection.

Table-4: Mulliken Charge Distribution on Flavonol and alkaloid

Atomic Charges on Flavonol			Atomic Charges on Alkaloid		
1	O	0.1185	1	C	-0.1902
2	C	0.0993	2	C	-0.0442
3	C	-0.2138	3	C	-0.2005
4	C	0.3705	4	C	-0.1394
5	C	-0.0914	5	C	-0.2596
6	C	0.0929	6	C	0.0637
7	C	-0.2413	7	C	-0.1367
8	C	-0.1319	8	C	-0.2989
9	C	-0.2373	9	N	0.1830
10	C	-0.0735	10	O	-0.2452
11	O	-0.3576	11	C	-0.1708
12	O	-0.2357	12	H	0.2166
13	H	0.2185	13	H	0.1947
14	H	0.2001	14	H	0.1928
15	H	0.2067	15	H	0.2328
16	H	0.2251	16	H	0.1181
17	C	-0.2013	17	H	0.1299
18	C	-0.1620	18	H	0.1430
19	C	-0.1807	19	C	-0.1985
20	C	-0.2000	20	N	-0.1021
21	C	-0.2243	21	C	-0.2714
22	C	-0.0540	22	C	-0.2835
23	H	0.1951	23	H	0.2188
24	H	0.2070	24	H	0.1030
25	H	0.1917	25	H	0.1217
26	H	0.1947	26	H	0.0839
27	H	0.2967	27	H	0.1118
28	H	0.2250	28	H	0.1108
			29	H	0.1092
			30	H	0.0937
			31	H	0.1136

#### IV. CONCLUSION

From the above results and discussions, the following conclusion was drawn:

- ❖ All the studied phytochemical constituent of the seed extracts acts as an effective corrosion inhibitor of mild steel in 2M hydrochloric acid solution and their inhibition efficiency increases with increase in the concentration of the seed extracts with maximum efficiency obtained at an optimum concentration of 3.0g/l within the first 24 hours.
- ❖ The adsorption data was best fitted into Langmuir adsorption models.
- ❖ Phytochemical screening, weight loss measurements, and quantum analysis confirmed the corrosion preventive property of *Azelia Africana* seed (AAS) in 2M HCl medium. The investigation shows *Azelia Africana seed* (AAS) extract as an excellent inhibitor for mild steel corrosion in 2M HCl.

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