

# Molecular Level Understanding of the Mechanism of Aloes Leaves Extract Inhibition of Low Carbon Steel Corrosion: A DFT Approach

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Quantum mechanics calculations have been applied within the framework of the density functional theory (DFT) to five major molecules of Aloes extract namely; Anthranol (AN), Aloin-Emodin (AE), Aloin Barbaloin (AB), Chrysophanol glycoside (CN) and Rutin (RT) recently investigated as corrosion inhibitor for mild steel in 1.0 M HCl in order to determine the structural and electronic parameters of the molecules responsible for imparting on the extract its high inhibition efficiency as corrosion inhibitor. The electronic parameters calculated include:  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap ( $\Delta\epsilon$ ) etc.. The calculated results show that all the molecules have high propensity as electron donors, have low  $\Delta\epsilon$  and  $\eta$  (high reactivity), are good nucleophiles characterized by low values of  $\omega$ , and the energy change associated with the charge transfer to the mild steel surface  $\Delta E$ , are all favourable (negative). Our result confirms the generally held assumption that there is a synergistic effect between the different organic molecules present in plant extracts towards enhancing the corrosion inhibition of these extracts on metals and alloys in varied aggressive media.

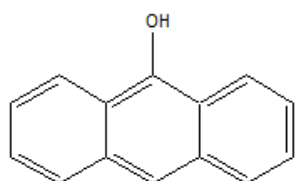
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**Keywords:** Mild steel; Aloes extract; DFT; Corrosion; Hydrochloric acid.

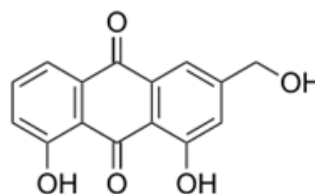
## 1. INTRODUCTION

Acid solutions especially hydrochloric acid with pH values below one are generally used for industrial acid cleaning, oil well acidification, petrochemical processes and acid pickling which generally leads to serious metallic corrosion [1]. An important method of protecting metallic materials against deterioration due to corrosion is by the use of inhibitors. Some chemicals are excellent inhibitors, but are quite toxic and readily absorbed through the skin [2]. Therefore, there is a growing

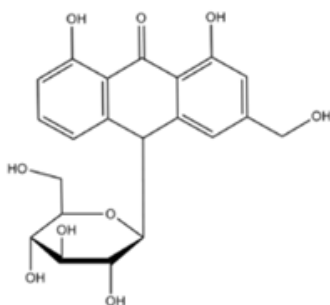
demand for corrosion inhibitors that are less toxic and biodegradable compared to current formulations. Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in the future [3]. Among the numerous organic compounds that have been tested and are applied industrially as corrosion inhibitors, those that are nontoxic are now far more strategic than in the recent past. In the past two decades, the research in the field of “green” corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or “zero” environmental impact [4].



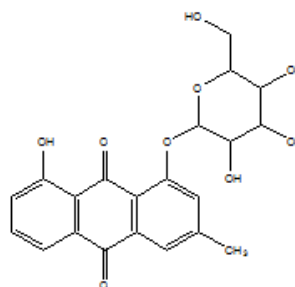
Anthranol (AN)



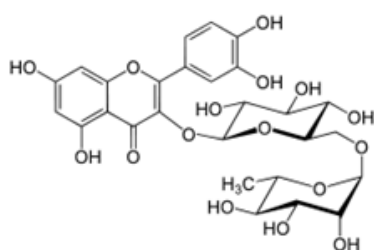
Aloin-Emodin (AE)



Aloin Barbaloin (AB)



Chrysophanol glycoside (CN)



Rutin (RT)

**Figure 1.** Structure of main constituents of Aloe leaves extract

The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted

by simple procedures with low cost and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by our research group and other authors [5-14]. Important reviews including extensive listing of various natural products from plant origin as corrosion inhibitors have recently been published [15, 16].

It has been reported that a number of the phytochemical constituents of plant extracts (including carbohydrates, organic and amino acids, alkaloids, tannins, flavonoids, etc.) have molecular and electronic structures bearing close similarities with those of conventional corrosion inhibitors and have been found to possess the ability to inhibit metal corrosion [17]. Despite the abundance and availability of many plant materials, only relatively few have been thoroughly investigated, and even at that, reports on the detailed mechanisms of the inhibition process are still scarce.

Recently, the corrosion inhibition of mild steel in 1.0 M HCl by *Aloes* leaves extract has been studied using weight loss methods, potentiodynamic polarization and electrochemical impedance spectroscopy techniques [18]. The extracts proved to be effective corrosion inhibitor for mild steel in 1.0 M HCl. The plant extracts was reported to contain the following main constituents: Anthranol (AN), Aloin-emodin (AE), Aloin-Barbaloin (AB), Chrysophanol glucoside (CN) and Rutin (RT) (Fig.1). The presence of these compounds poses a considerable restriction to precise experimental determination of the contributions of the different constituents to the overall inhibiting effect, and understandable most researchers shy away from the subject. The use of the methodology of density functional theory (DFT) can in principle be used to overcome this problem. This is because DFT calculations have been widely used to study the reaction mechanisms and to interpret experimental results as well as to solve chemical ambiguities [19]. DFT is also a more useful approach to investigate the mechanisms of reaction in a molecule and its electronic structure levels [20, 21]. Furthermore, DFT calculations can also provide other reactivity indices such as the global indices which characterize the behaviour of a molecule towards a particular reagent (mild steel) in the framework of the HSAB theory [22]. Our approach in this investigation involve the analysis of the electronic parameters of key phytochemical constituents of the crude extract such as the highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ), the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta\varepsilon$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ), softness ( $S$ ), electrophilicity index ( $\omega$ ), electron charge transfer ( $\Delta N$ ) and energy change associated with the electron charge transfer from molecule to steel surface,  $\Delta E$ . These parameters will provide insights into the mechanism of the interaction of the extract components with mild steel surface.

## 2. THEORETICAL AND COMPUTATIONAL DETAILS

We carried out first-principle calculations using density functional theory (DFT) under the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implemented in Dmol<sup>3</sup> module using Material Studio Software Package Version 6.0 [23]. A double numerical basis set augmented with polarization functions (DNP) was employed to describe the valence electrons. The core electrons were described by the all-electron method. All the geometries

were fully optimized without symmetry constraints. Spin-unpolarization scheme was utilized throughout our calculation. The SCF and energy convergence threshold was set to be  $1.0 \times 10^{-5}$  Ha and  $2.0 \times 10^{-5}$  Ha, respectively. A continuum solvation method (COSMO) [24] was employed for an implicit description of the water environment. This dielectric continuum model simulates water by a macroscopic dielectric continuum characterized by a dielectric constant of 78.54, thus neglecting any atomistic nature but including implicitly configurational sampling. The above computational scheme has been widely utilized to study similar systems and has been demonstrated to be capable of providing excellent structural and energetic information [25, 26].

Density functional theory (DFT) has been found to be successful in providing insight into chemical reactivity and selectivity in terms of global molecular properties, such as electronegativity ( $\chi$ ) and chemical potential ( $\mu$ ) [27]. Thus, for an  $N$ -electron system with total electronic energy ( $E$ ) and an external potential  $v(r)$ ; the chemical potential ( $\mu$ ), which is also the negative of the electronegativity ( $\chi$ ), has been defined as the first derivative of the  $E$  with respect to  $N$  at constant  $v(r)$  [28]:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (1)$$

Equation (1) may be written as [29]:

$$\chi = -\mu = \left(\frac{I + A}{2}\right) \quad (2a)$$

$$\chi = -\frac{E_{LUMO} + E_{HOMO}}{2} \quad (2b)$$

where  $I$  and  $A$  are the ionization potential and electron affinity [30, 31].

The hardness  $\eta$  of an electronic system is defined as [32]:

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N}\right)_{v(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r)} \quad (3)$$

The global softness ( $S$ ), is the inverse of global hardness and is given as [33]:

$$S = \frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} \quad (4)$$

In terms of the energies of HOMO and LUMO molecular orbitals, hardness is given as [34, 35]:

$$\eta = \frac{I - A}{2}, \quad \eta = -\frac{E_{LUMO} - E_{HOMO}}{2} \quad (5)$$

The global softness, on the other hand, can be connected with the fluctuation of the particle number as [33]:

$$\frac{1}{kT} [\langle N^2 \rangle - \langle N \rangle^2] = \left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,v} \quad (6)$$

Comparing Equations (4) and (6), the softness,  $S$ , becomes:

$$\frac{1}{kT} [\langle N^2 \rangle - \langle N \rangle^2] = S \quad (7)$$

It has been reported that the more stable molecular structure has the largest HOMO-LUMO energy gap [36]. Therefore, an electronic system with a larger HOMO-LUMO gap should be less

reactive than one having a smaller gap. This relationship is based on the Maximum Hardness Principle [37], which states that ‘there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible’. This principle is among the most widely accepted electronic principles of chemical reactivity and a formal proof of this principle was given by Parr and Chattaraj [38].

The global electrophilicity index ( $\omega$ ) was introduced by Parr et al. [39] and is given by:

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

Using the parabolic model, it was shown that global electrophilicity index ( $\omega$ ), can also be written as [40]:

$$\omega = \frac{(I + A)^2}{8(I + A)} \quad (9)$$

The electron charge transfer,  $\Delta N$ , from base B to acid A, and the associated energy change  $\Delta E$  is given as [31]:

$$\Delta N = \frac{\mu_B - \mu_A}{2(\eta_A + \eta_B)} \quad \text{and} \quad \Delta E = -\frac{(\mu_B - \mu_A)^2}{2(\eta_A + \eta_B)} \quad (10)$$

Substituting the subscripts A and B by metal and mol to designate a metal surface and a molecule, respectively, and replacing the  $\mu$  by  $-\chi$  gives:

$$\Delta N = \frac{\chi_{metal} - \chi_{mol}}{2(\eta_{metal} + \eta_{mol})} = \frac{\Phi - \chi_{mol}}{2\eta_{mol}} \quad (11a)$$

$$\Delta E = -\frac{(\chi_{metal} - \chi_{mol})^2}{4(\eta_{metal} + \eta_{mol})} = -\frac{(\Phi - \chi_{mol})^2}{4\eta_{mol}} \quad (11b)$$

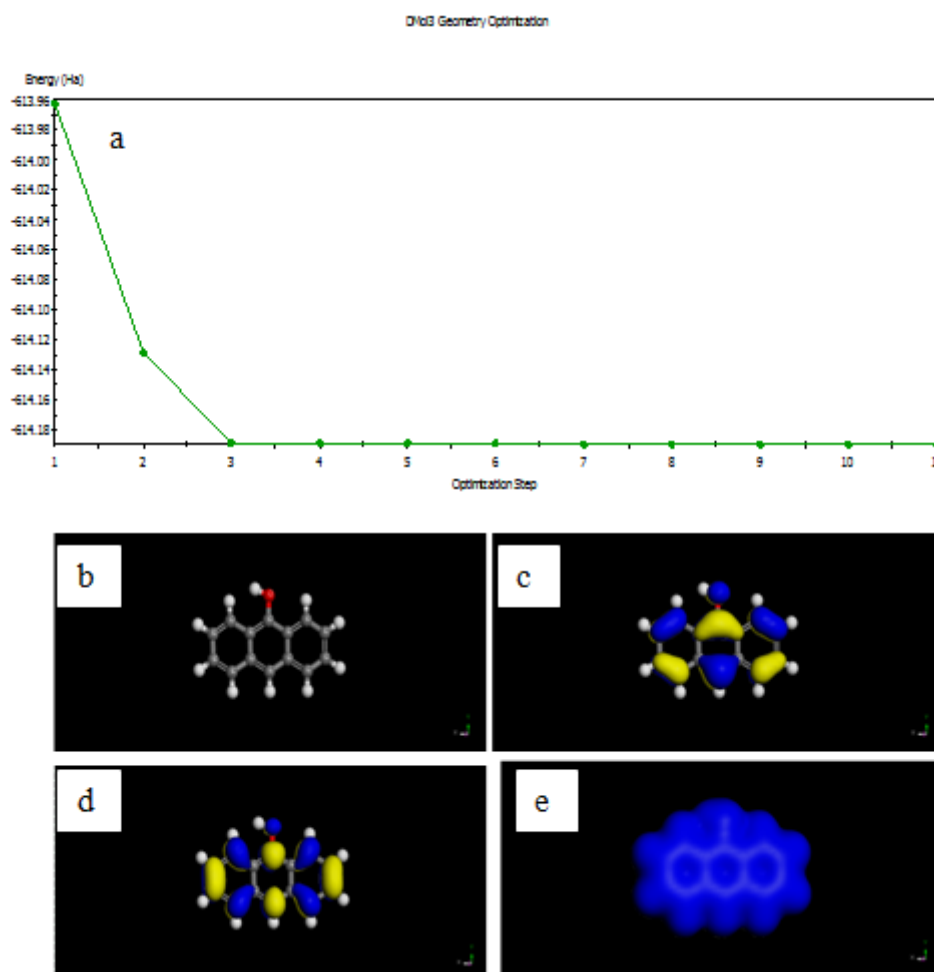
In the second equality of Eqs 11a and 11b, the electronegativity of metal surface is replaced by the work function for Fe (110) surface,  $\Phi$ , theoretically equals 4.82 eV and the hardness,  $\eta_{metal}$  which equals 0 eV for bulk metals [41].

### 3. RESULTS AND DISCUSSION

#### 3.1. Frontier Orbitals

Figures 2-6 show (a) the optimization progress, (b) optimized geometry, (c) the HOMO density distribution, (d) the LUMO density distribution and (e) the total electron density plots for Anthranol (AN), Aloin-Emodin (AE), Aloin Barbaloin (AB), Chrysophanol glycoside (CN) and Rutin (RT) respectively, which constitute the main constituents of Aloes extract obtained using DFT calculations. The electronic distributions of the molecules appear somewhat different, which is expected since their molecular structures are different. The HOMO regions for the molecules are the sites at which electrophiles attack and represent the active centers with the utmost ability to interact with the metal surface atoms. On the other hand, the LUMO orbitals predict the regions where the molecules can accept electrons from the metal using antibonding orbitals to form feedback bonds [42]. We observe that the HOMO orbitals of AN and AE are on the entire molecule. HOMO orbitals of AB and CN are

over the three fused six-membered aromatic rings containing C=O and OH groups together with several  $\pi$ -electrons.

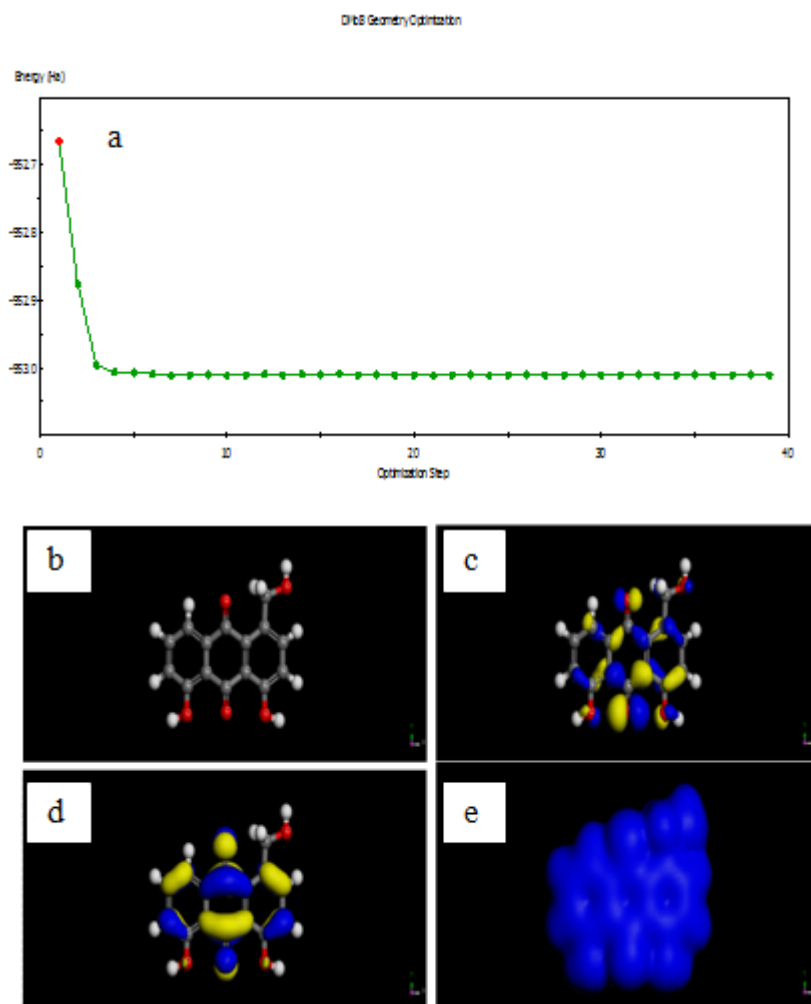


**Figure 2.** Electronic properties of Anthranol (AN): (a) optimized progress (b) optimized structure, (c) HOMO orbital, (d) LUMO orbital and (e) total electron density (atom legend: white H, light gray C and red O).

Finally, the HOMO orbitals of RT is located on the three six-membered rings containing several OH groups and a C=O group. Similarly, the LUMO orbitals show the same behaviour for all the molecules studied as the HOMO orbitals. These active sites ensure strong interaction of each molecule with the metal surface.

### 3.2. Global descriptors

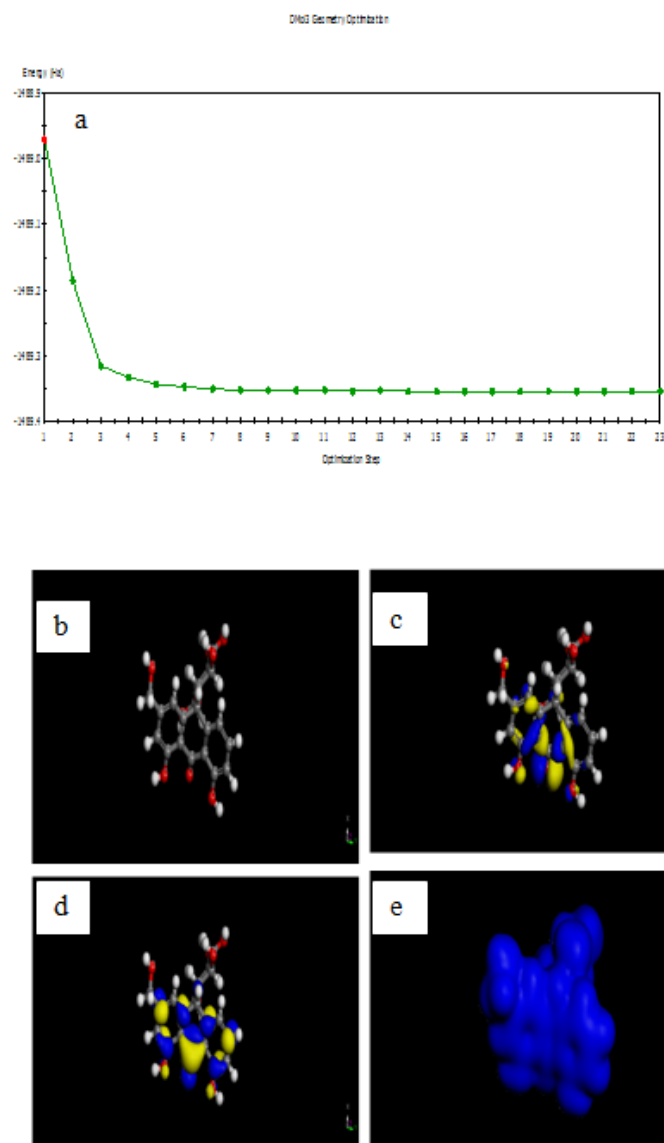
Quantum chemical parameters of the major molecules responsible for the inhibitive effect of Aloes extract and adsorption mechanism on mild steel are shown in Tables 1 and 2.



**Figure 3.** Electronic properties of Aloin-Emodin (AE): (a) optimization progress (b) optimized structure, (c) HOMO orbital, (d) LUMO orbital and (e) total electron density (atom legend: white H, light gray C and red O).

**Table 1.** Calculated quantum chemical properties for the most stable conformations of the major effective components of cactus extracts AN, AE, AB, CN and RT in aqueous phase using DFT at GGA/PBE/DNP level.

Properties	AN	AE	AB	CN	RT
Total Energy (Ha)	-613.96	-952.66	-1479.57	-1488.13	-2248.83
$E_{\text{HOMO}}$ (eV)	-4.76	-5.54	-5.23	-5.87	-5.54
$E_{\text{LUMO}}$ (eV)	-3.17	-4.59	-3.62	-3.57	-2.46
$\Delta\varepsilon$ (eV)	1.59	0.95	1.61	2.30	3.08

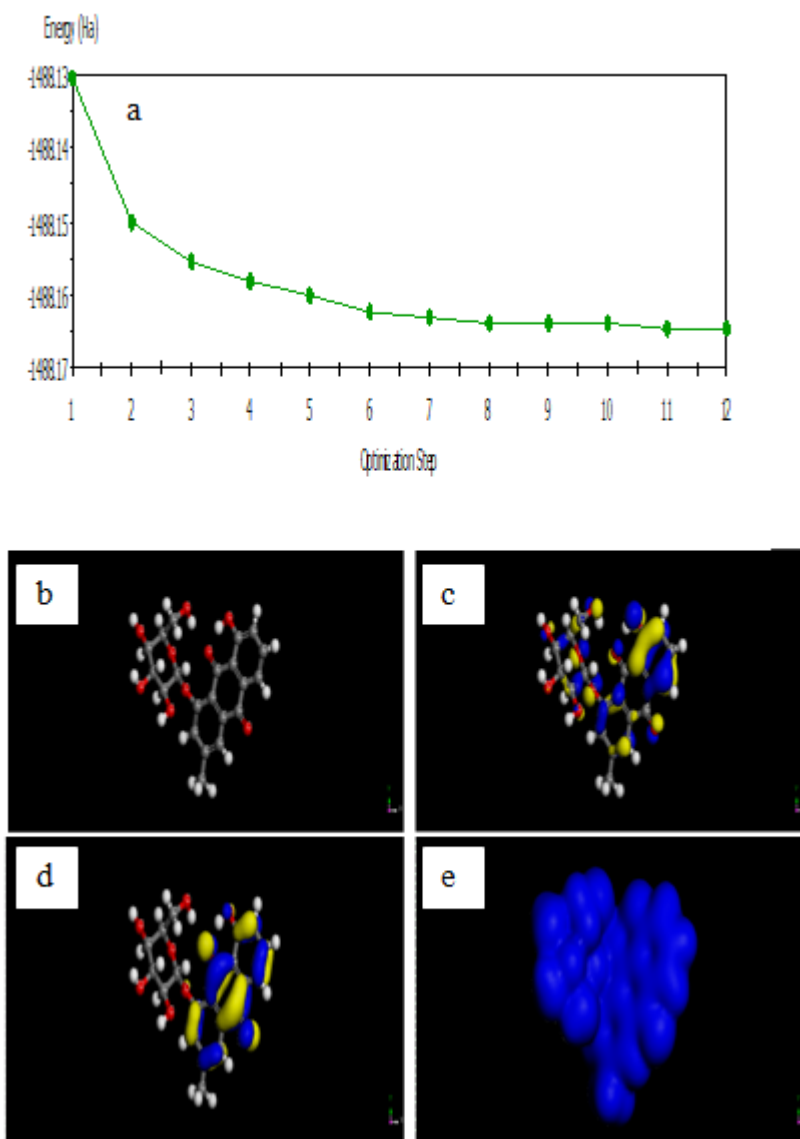


**Figure 4.** Electronic properties of Aloin Barbaloin (AB): (a) optimization progress (b) optimized structure, (c) HOMO orbital, (d) LUMO orbital and (e) total electron density (atom legend: white H, light gray C and red O).

**Table 2.** Calculated quantum chemical descriptors for the most stable conformations of the major effective components of cactus extracts AN, AE, AB, CN and RT in aqueous phase using DFT at GGA/PBE/DNP level.

Descriptors	AN	AE	AB	CN	RT
$I$	4.76	5.54	5.23	5.87	5.54
$A$	3.17	4.59	3.62	3.57	2.46
$\chi$	3.96	5.06	4.42	4.72	4.00
$\eta$	0.79	0.47	0.81	1.15	1.54
$S$	1.26	2.12	1.23	0.86	0.64
$\omega$	0.99	1.26	1.10	1.18	1.00
$\Delta N$	0.54	-0.25	0.24	0.04	0.26
$\Delta E$	-0.23	-0.03	-0.05	-0.002	-0.09

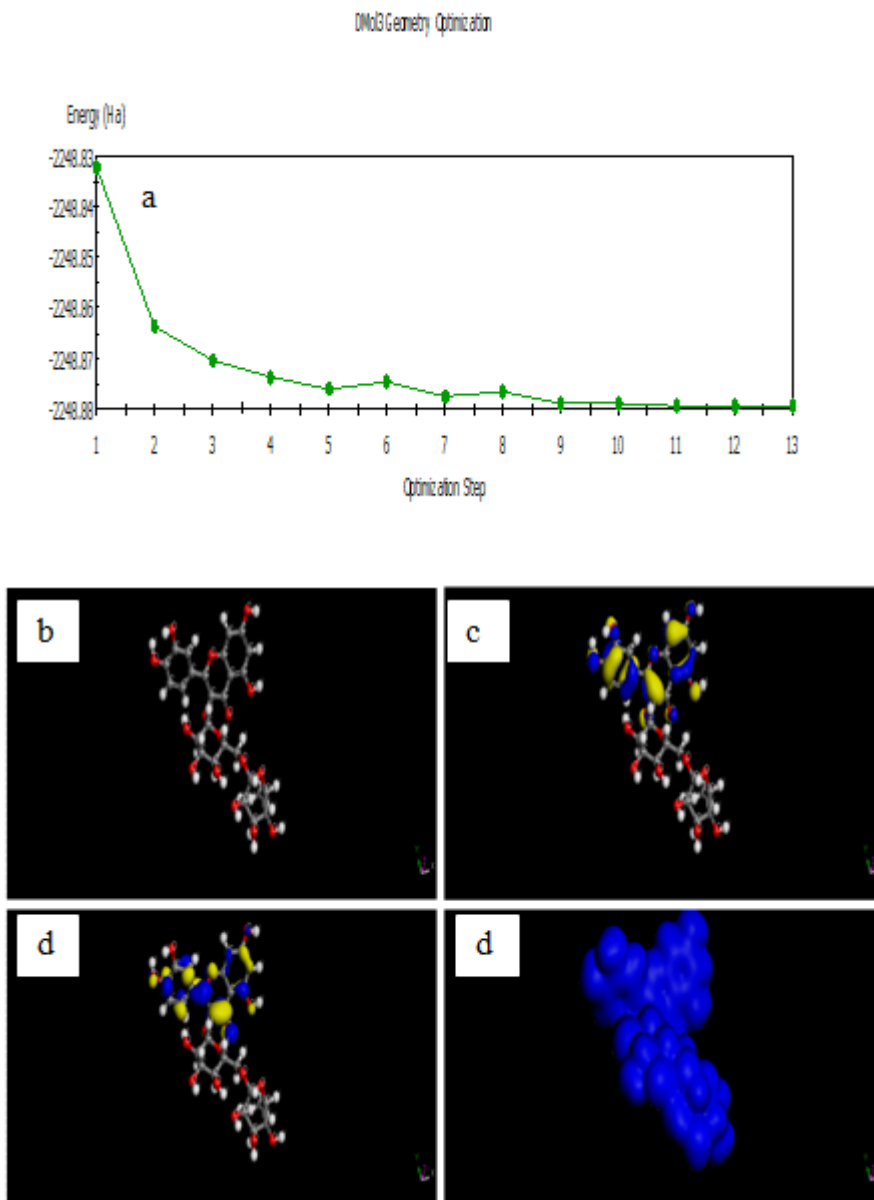




**Figure 5.** Electronic properties of Chrysophanol glycoside (CN): (a) optimization progress (b) optimized structure, (c) HOMO orbital, (d) LUMO orbital and (e) total electron density (atom legend: white H, light gray C and red O).

It has been documented that the higher the energy level of HOMO, the less is the value of the ionization potential and the easier for electrons to be easily donated [43]. Organic substances with less negative HOMO value corresponds to lower  $I$  values and is expected to have greater adsorption ability to metal surface. Thus, if the energy of HOMO level was decisive for the inhibitive properties of the extract constituents on the steel surface, the ranking of the compounds would be: AN > AB > AE = RT > CN.

It is well known that the lower the value of  $E_{LUMO}$ , the more probable it is that the molecule would accept electrons from the metal [44]. Our calculations show that AE has the lowest  $E_{LUMO}$ , so it has the greatest ability to interact with the metal surface. The ranking of the molecules according to their ability to accept electrons from mild steel is: AE > AB > CN > AN > RT.



**Figure 6.** Electronic properties of Rutin (RT): (a) optimization progress (b) optimized structure, (c) HOMO orbital, (d) LUMO orbital and (e) total electron density (atom legend: white H, light gray C and red O).

The separation energy,  $\Delta\epsilon = (E_{\text{LUMO}} - E_{\text{HOMO}})$  is a parameter which determines the reactivity of a molecule towards a metallic surface and is a very important stability index [45]. As  $\Delta\epsilon$  decreases, the reactivity of the molecule increases leading to increased adsorption on the metal surface. The calculations from Table 1, show the following increasing reactivity abilities of the molecules towards steel:  $\text{AE} > \text{AN} > \text{AB} > \text{CN} > \text{RT}$ .

The general rule as suggested by HSAB principle is that hard acids prefer to co-ordinate to hard bases and soft acids prefer to co-ordinate to soft bases. Metal atoms are known as soft acids. Hard molecules have a high HOMO-LUMO gap and soft molecules have a small HOMO-LUMO gap [46]. Thus, soft bases (organic heterocyclic molecules) are most effective for metal interactions. Hardness of

the molecules increases in the following order: RT > CN > AB > AN > AE while softness which is the inverse of hardness has the opposite effect: AE > AN > AB > CN > RT. The trend shows the RT is the least reactive of the compounds studied while AE is the most reactive towards steel surface.

### 3.3. Electron transfer processes

To obtain a clear picture of the interaction between the molecules studied and mild steel surface, intermolecular parameters such as a charge transfer descriptors and the associated energy change should be taken into account [47]. Corrosion inhibition of mild steel by organic inhibitors (present in plant extracts) in acidic media is a complex process and is mainly influenced by charge transport.

Electrophilicity is an index which measures the propensity of chemical specie to accept electrons. The higher the value of  $\omega$ , the higher the capacity of the molecule to accept electrons. Thus, a good nucleophile is characterized by low values of  $\mu$  and  $\omega$ ; whereas a good electrophile is characterized by high values of  $\mu$  and  $\omega$ . It is clear in Table 2 that the molecules have low electrophilicity index values and are good nucleophiles.

The amount of charge transfer,  $\Delta N$ , between the molecules and the mild steel Fe (110) surface as calculated is given in Table 2. A positive value of  $\Delta N$  indicates that the molecules act as an electron acceptor, while a negative value of  $\Delta N$  indicates that the molecules act as electron donors [41]. Thus, from Table 2, all the molecules studied act as electron acceptors except AE which acts as electron donor. According to Lukovits, if  $\Delta N < 3.6$ , the molecules can be assumed to possess charge transfer ability towards the metal surface [48]. The molecules studied possess charge transfer abilities towards mild steel.

The energy change ( $\Delta E$ ) associated with the charge transfer process were all negative and exothermic indicating a favourable transfer of charge process from the organic molecules onto steel surface.

### 3.4. Mechanism of inhibition of Aloes extract on mild steel corrosion

The main constituents of extract of Aloes are Anthranol, Aloin-emodin, Aloin-Barbaloin, Chrysophanol glucoside and Rutin. The high performance of Aloes extract may be due to the synergistic effect of these compounds. As observed from Tables 1 and 2, the obtained quantum chemical parameters for the major constituents do not show any well-defined and clear cut correlation, and none was actually expected, since the molecules differ considerably in their chemical structures and we do not yet know their individual inhibition efficiencies. Furthermore, according to the HOMO and LUMO orbitals presented earlier, the adsorption of these compounds on the steel surface can be attributed to the presence of oxygen atoms,  $\pi$ -electrons and aromatic/heterocyclic rings. Therefore, the possible reaction centers are unshared electron pairs of heteroatoms and  $\pi$ -electrons of aromatic/heterocyclic ring. The organic molecules may adsorb on the metal/acid solution interface by one and/or more of the following ways: (1) donor-acceptor interactions between the  $\pi$ -electrons of

aromatic rings and vacant d-orbital of surface iron atoms, and (2) interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms. These processes drastically reduce the transport of aggressive ions to the metal surface thereby controlling the corrosion of the mild steel.

#### 4. CONCLUSIONS

Density functional theory (DFT) has successfully been used to gain some insights into chemical reactivity and mechanism of corrosion inhibition of Aloes extracts at the molecular level. The calculated results show that all the molecules (constituting Aloes extract major constituents) have high propensity for donating electrons, have low  $\Delta\epsilon$  and  $\eta$  (high reactivity), are good nucleophiles which is characterized by low values of  $\omega$ , and the energy change associated with the charge transfer to the mild steel surface  $\Delta E$ , are all favourable (negative). Our result confirms the generally held assumption that there is a synergistic effect between the different organic molecules present in plant extracts towards enhancing the corrosion inhibition of these extracts on metals and alloys in varied aggressive media.

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