

## Quantum Chemical Assessment of Two Natural Compounds: Vasicine and Vasicinone as Green Corrosion Inhibitors.

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A theoretical study has been performed on the main Vasicine and Vasicinone molecules found in *Adhatoda vasica* plant extract using the Density Functional Theory (DFT). Through this study, the inhibitive effect of these two molecules to reduce the corrosion rate of mild steel in acidic medium is elucidated. The parameters such as dipole moment ( $\mu$ ),  $E_{HOMO}$ ,  $E_{LUMO}$ , energy gap ( $\Delta E$ ), global hardness ( $\eta$ ), chemical softness (S), electron affinity (A), ionization potential (I), the absolute electronegativity ( $\chi$ ), the fraction of electron transfer from the inhibitor molecule to the metallic atom ( $\Delta N$ ) and Mulliken charges have been calculated. All calculations have been carried out taking into account the Density Functional Theory (DFT) using the GAUSSIAN 03W computational program. The results showed that Vasicinone molecule is favorably adsorbed on the metal surface (Fe) through the electronegative density atoms as active centers of adsorption, and the theoretical conclusions were found to be in agreement with the experimental reported data.

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**Keywords:** Green Corrosion inhibitors; Vasicine; Vasicinone; Quantum Chemical Assessment, Density Functional Theory.

### 1. INTRODUCTION

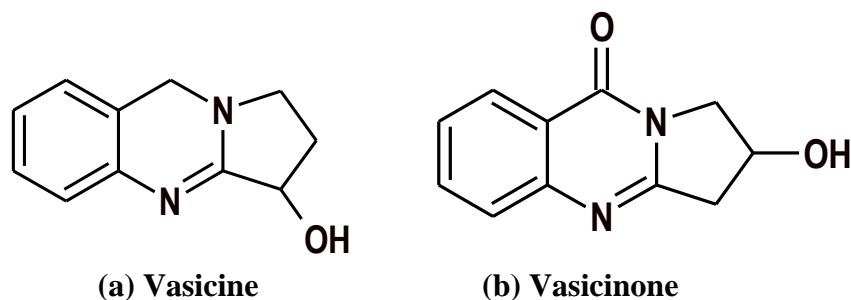
Mild steel is mostly used in industrial applications due to its availability and low cost [1]. Acidic solutions are used in many applications such as acidic cleaning, pickling and descaling processes [1,2]. Nowadays, corrosion in acidic media is a common phenomenon and a challenge to

scientists and engineers. The corrosion inhibitors is one of the best methods for metal protection against corrosion. Some organic compounds contain heteroatoms such as O, N and S, which act as good corrosion inhibitors [3,4]. However, during the synthesis of these inhibitors some hazardous substances are used, which together with the byproducts and waste materials are toxic for human beings and for the environment. Additionally, the synthesis of these organic compounds is expensive.

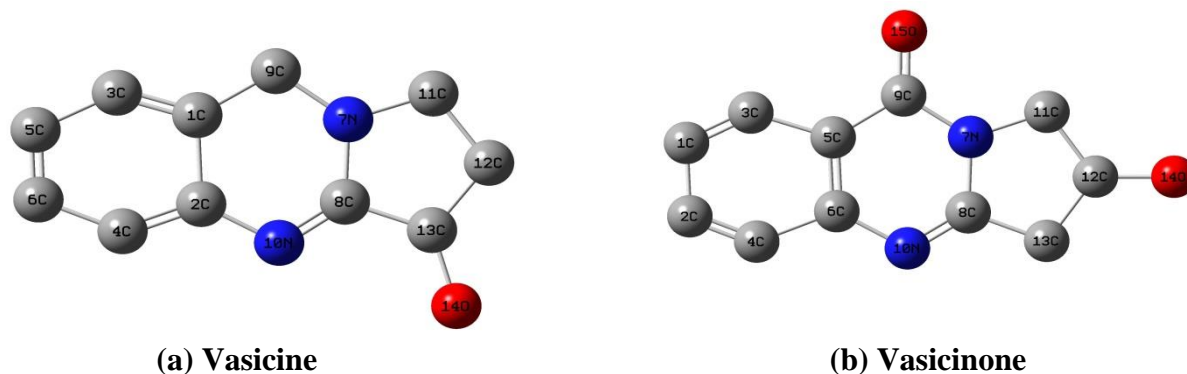
Green corrosion inhibitors are obtained from plant sources, which are biodegradable, eco-friendly and non-toxic [5,6]. The compounds containing in their chemical structure multiple  $\pi$ -bonds or/and heteroatoms generally exhibit good corrosion inhibiting properties, since the multiple  $\pi$ -bonds provide a plane molecular geometry, and the heteroatoms supply the lone electron pairs for coordinating the inhibitor molecule with the metal lattice. Such heteroatoms allow the compounds to coordinate with the corroding metal atoms through their  $\pi$ -electrons. Hence, protective films are formed on the metal surface and corrosion could be prevented [6]. Many phytochemical constituents of plant extracts including alkaloids, flavonoids, amino acids, tannins, carbohydrates, etc., and the natural compounds above mentioned, have molecular and electronic structures similar to those of the conventional corrosion inhibitors and have been found to possess the ability to inhibit a metal corrosion process [7].

Lately, the corrosion inhibition of mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  adding *Adhatoda vasica* plant extract has been studied using the electrochemical impedance spectroscopy and the potentiodynamic polarization curves techniques together with the weight loss method, [2]. The *Adhatoda vasica* extract was reported to have two major constituents: Vasicine and Vasicinone compounds (Fig.1) [8]. The extract proved to be effective as corrosion inhibitor for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  through the adsorption of their molecules on the metal surface, which was confirmed by the Langmuir isotherm and the scanning electron microscopy [2]. The corrosion inhibition efficiency of *Adhatoda vasica* extract has been investigated in this research work by means of the quantum chemical assessment named Density Functional Theory (DFT).

The objective of this research was to analyze the inhibitive properties of the two major compounds of the *Adhatoda vasica* plant extract using the DFT calculations. The DFT calculations are commonly used to study the reaction mechanisms and to explain the experimental results as well as to solve chemical uncertainty [9]. The DFT is one the most powerful tool to explore the electronic structure levels in the molecules and to correlate such characteristics with the capacity as green corrosion inhibitors [10,11]. Such computations have been used to analyze the molecular electronic structures of organic inhibitors using some quantum chemical descriptors [12]. The survey of theoretical corrosion literature conferred by Gece 2008 demonstrates that quantum chemical could be a powerful tool to study the fundamental molecular-level processes associated with corrosion inhibition [13]. The chemical structures and their optimized molecular structures are seen in Figure 1 and Figure 2.



**Figure 1.** Basic chemical structure of main constituents of the *Adhatoda vasica* plant extract.



**Figure 2.** Optimized molecular structure of the main constituents of the *Adhatoda vasica* plant extract.

## 2. MATERIAL AND METHODS

In order to correlate the corrosion inhibition capability with the molecular orbital (MO) energy levels of both molecules, a quantum chemical evaluation was achieved. With this method, the capability of the inhibitor molecules to donate or accept electrons can be predicted with the analysis of the global reactivity parameters such as  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), global hardness ( $\eta$ ), chemical softness ( $S$ ), electrophilicity index ( $\omega$ ) and the fraction of electron transfer from the inhibitor molecule to the metallic atom ( $\Delta N$ ). All these parameters will provide the approaching to the mechanism of the interaction between the extract components and the mild steel surface (Fe).

In the present study all the calculations were carried out with the Gaussian 03 computational program for windows [14]. The molecular structure of Vasicine and Vasicinone was geometrically optimized using the functional hybrid B3LYP (Becke, three-parameter, Lee-Yang-Parr exchange-correlation function) [15] Density Function Theory formalism with electron basis set 6-31G ( $d, p$ ) for all atoms [16]. This approach has shown to yield favorable geometries for a wide variety of molecular systems. The geometry structure was optimized under no constraint. The obtained quantum chemical parameters were:  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electronegativity ( $\chi$ ), electron affinity ( $A$ ), global hardness ( $\eta$ ), chemical softness ( $\sigma$ ), ionization potential ( $I$ ), the global electrophilicity ( $\omega$ ), the fraction of the electron transfer ( $\Delta N$ ), the total energy (TE) and Mulliken charge on heteroatom [17].

2.1. Global quantities

The adsorption of atoms of the inhibitor molecules were predicted by the frontier orbital theory shows the interactions between the inhibitor molecules and the surface metal atoms (Fe). According to the DFT-Koopmans' theorem [18], the ionization potential (I) can be approximated as the negative value of the highest occupied molecular orbital energy ( $E_{HOMO}$ ), such as shown in equation 2,

$$I = -E_{HOMO} \dots\dots\dots(2)$$

The negative value of the lowest unoccupied molecular orbital energy ( $E_{LUMO}$ ) is similarly related to the electron affinity A [19] such as shown in equation 3,

$$A = -E_{LUMO} \dots\dots\dots(3)$$

The electronegativity ( $\chi$ ) and the global hardness ( $\eta$ ) can be determined by the values of I and A. The electronegativity is the measure of the power of an atom or group of atoms to attract electrons towards them [19,20]. The electronegativity was estimated using the following equation:

$$\chi = \frac{I+A}{2} \dots\dots\dots(4)$$

The global hardness ( $\eta$ ) measures the resistance of an atom to a charge transfer [20,21]. The chemical hardness was estimated using the following equation:

$$\eta = \frac{I-A}{2} \dots\dots\dots(5)$$

The chemical softness ( $\sigma$ ) is the measure of the capacity of an atom or group of atoms to receive electrons [20,21]. This parameter is the inverse of the global hardness and it was estimated using the following equation:

$$\sigma = \frac{1}{\eta} \dots\dots\dots(6)$$

When two systems (inhibitor and Fe) are brought together and have different electronegativities, the electrons will flow from the lower electronegativity  $\chi_{inh}$  to the higher electronegativity  $\chi_{Fe}$  until their chemical potentials become equal [19]. The fraction the electron transfer was calculated through the equation 7 [21]:

The number of the electron transfer ( $\Delta N$ ) was also calculated [36] using the next equation.

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \dots\dots\dots(7)$$

Where  $\chi_{Fe}$  and  $\chi_{inh}$  indicate the absolute electronegativity of the iron and the green molecule of inhibitor respectively,  $\eta_{Fe}$  and  $\eta_{inh}$  denote the absolute hardness of the iron and the green molecule of inhibitor respectively.

In this study, it was used the theoretical value of  $\chi_{Fe}=7.0$  eV/mol and  $\eta_{Fe} = 0$  eV/mol, assuming that for a metallic bulk  $I = A$  [22-24].

The predisposition of a chemical species to accept electrons is measured by the electrophilicity index ( $\omega$ ) [25], which was estimated using the following equation:

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

A good nucleophile species is characterized by having low values of  $\mu$  and  $\omega$ ; conversely a good electrophile species is characterized by having high values of  $\mu$  and  $\omega$ . This new reactivity index ( $\omega$ ) measures the stabilization of the energy when the system acquires an additional electronic charge  $\Delta N$  from the environment.

### 3. RESULTS AND DISCUSSION

To investigate the electronic structure of both molecules (Vasicine and Vasicinone) together with some quantum chemical parameters such as the highest occupied molecular orbital energy ( $E_{\text{HOMO}}$ ), the lowest unoccupied molecular orbital energy ( $E_{\text{LUMO}}$ ), the energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), ionization potential ( $I$ ), electron affinity ( $A$ ), electronegativity ( $\chi$ ), global hardness ( $\eta$ ), chemical softness ( $\sigma$ ), the global electrophilicity ( $\omega$ ), the fraction of electron transfer ( $\Delta N$ ) and the total energy (TE) were determined and the results are given in Table 1.

**Table 1.** Calculated quantum chemical parameters of the studied compounds.

| Quantum chemical parameters                  | Vasicine molecule<br>( $\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$ ) | Vasicinone molecule<br>( $\text{C}_{11}\text{H}_{10}\text{N}_2\text{O}_2$ ) |
|----------------------------------------------|-------------------------------------------------------------------------|-----------------------------------------------------------------------------|
| $E_{\text{HOMO}}$ (eV)                       | -8.65                                                                   | -8.92                                                                       |
| $E_{\text{LUMO}}$ (eV)                       | -7.86                                                                   | -8.32                                                                       |
| $\Delta E$ (L-H) (eV)                        | 0.79                                                                    | 0.60                                                                        |
| Dipole Moment ( $\mu$ ) Debye                | 3.29                                                                    | 1.16                                                                        |
| Ionization Potential ( $I$ ) (eV)            | 8.65                                                                    | 8.92                                                                        |
| Electron Affinity ( $A$ ) (eV)               | 7.86                                                                    | 8.32                                                                        |
| Electronegativity ( $\chi$ ) (eV)            | 8.25                                                                    | 8.62                                                                        |
| Global hardness ( $\eta$ ) (eV)              | 0.39                                                                    | 0.30                                                                        |
| Chemical Softness ( $\sigma$ )               | 2.56                                                                    | 3.33                                                                        |
| Global electrophilicity ( $\omega$ )         | 13.84                                                                   | 2.23                                                                        |
| Fraction of electron transfer ( $\Delta N$ ) | -1.60                                                                   | -2.70                                                                       |
| Total Energy (eV)                            | -16413.69                                                               | -18446.41                                                                   |

In agreement with Wang [26], the frontier orbital (the highest occupied molecular orbital energy  $E_{\text{HOMO}}$  and the lowest unoccupied molecular orbital energy  $E_{\text{LUMO}}$ ) of the chemical natural compounds play the main role in describing the reactivity.

As  $E_{\text{HOMO}}$  is often a measure of the electron donating ability of an inhibitor molecule, a high value of  $E_{\text{HOMO}}$  is likely an indicator of the donated electrons flow of the inhibitor molecule to a suitable acceptor molecule with a lower molecular orbital energy. Therefore, the increase of the value of  $E_{\text{HOMO}}$  facilitates the adsorption of the inhibitor on the metal surface due to the influence of the

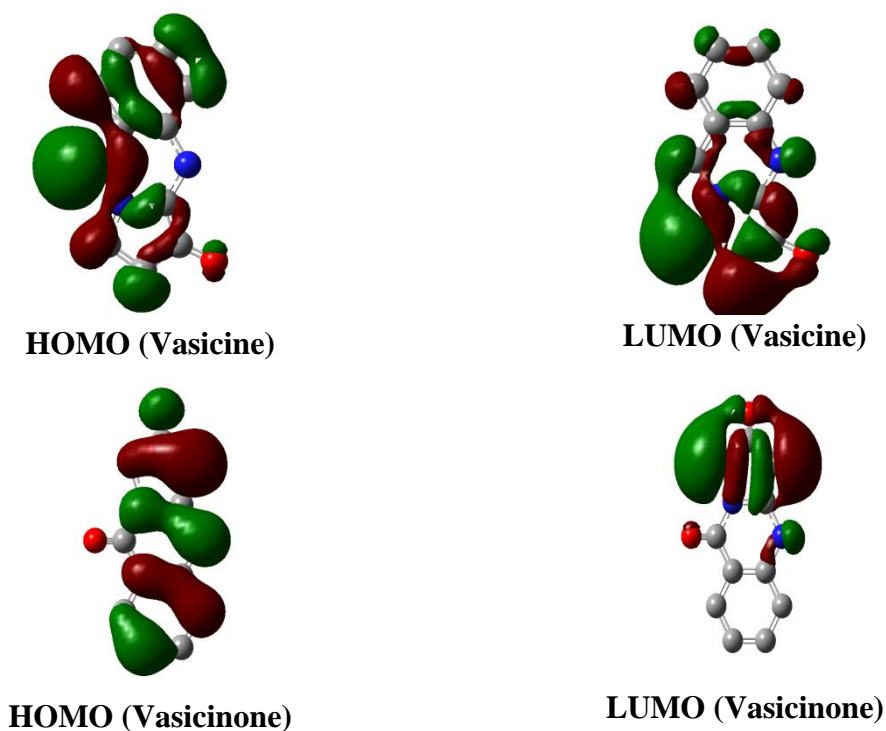
transport process.  $E_{\text{LUMO}}$  indicates the ability of the molecule to receive electrons. In conclusion, an increase of the value of  $E_{\text{HOMO}}$  level and a decrease of the value of  $E_{\text{LUMO}}$  level show an increment in the binding ability between the inhibitor molecule and the metal surface [27]. The frontier molecular orbital (FMO) diagrams of compound 1 (Vasicine) and compound 2 (Vasicinone) is represented in figure 3.

According to the FMO theory approach of chemical reactivity, the transition of electrons is due to the interaction between HOMO and LUMO energies of reacting species [28]. The higher value of  $E_{\text{HOMO}}$  indicates, the greater ability of offering electrons to unoccupied *d*-orbital of the metal, and therefore the higher corrosion inhibition efficiency through a better adsorption. The higher value of  $E_{\text{HOMO}}$  of -8.92 (eV) indicates the inhibition efficiency of Vasicinone.

$\Delta E$  (energy gap  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) is an important parameter as a function of reactivity of the inhibitor molecule towards the adsorption on the metallic surface. As  $\Delta E$  decreases, the reactivity of the molecule increases leading to a better inhibition efficiency [26,28,29]. A molecule with a low energy gap is more polarizable and is generally associated to the high chemical activity and low kinetic stability, such molecule is called "soft molecule" [27]. The results in table 1 shows that Vasicinone has the lowest energy gap (0.60 eV) compared to that of Vasicine (0.79 eV), which means that Vasicinone could have a better performance as corrosion inhibitor.

From figure 3, it could be seen that both molecules might have different HOMO and LUMO energy distributions. The HOMO densities were mainly located on the entire molecules (Vasicine and Vasicinone), whereas the LUMO densities were concentrated on a localized zone. This kind of structure is difficult to form chemical bond active centers, which proves the probability of physical adsorption between the interaction sites [28].

The dipole moment ( $\mu$ ) is a significant and mostly used electronic parameter that results from non-uniform charges allocation on the various atoms in the molecule [13, 24, 29]. The dipole moment is the measure of the polarity of a polar covalent bond. A big value of the dipole moment most likely increases the adsorption between the natural compound (inhibitor) and the metal surface [26, 30]. The energy of the deformability of the molecule rises with the increase in  $\mu$ , making the natural compound easier to be adsorbed on the metal surface (Fe). With the increment of the dipole moment ( $\mu$ ), the volume of the green inhibitor molecule also increases, thereby the contact area between the inhibitor molecule and mild steel surface increases, as a result the corrosion inhibition ability also increases. The value of the dipole moment ( $\mu$ ) obtained in this study was 3.29 Debye for Vasicine and 1.16 Debye for Vasicinone (Table 1). No significant relationship has been found between the dipole moment values and inhibition efficiencies [13]. However, the high value of the dipole moment indicates that the adsorption between the natural compound and the metal surface probably increases.



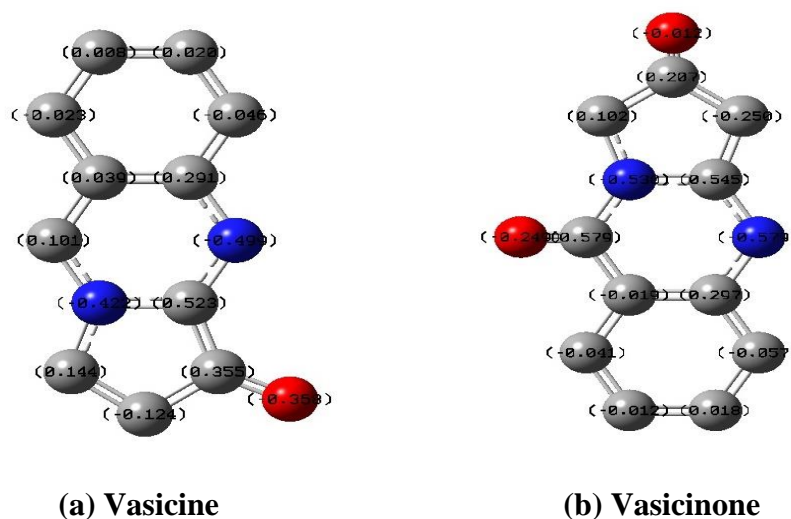
**Figure 3.** The HOMO and LUMO representation of Vasicine and Vasicinone molecules.

Ionization energy is one of the fundamental indicators of the chemical reactivity. High values of the ionization energy evidence the chemical inertness and strong stability, whereas small ionization energy denotes high reactivity of the atoms and molecules [31]. The lower ionization energy of 8.65 eV for the Vasicine molecule indicates the higher inhibition efficiency compared to that of the Vasicinone molecule, which had ionization energy of 8.92 eV (see Table 1).

Global hardness and chemical softness are important properties associated with the molecular stability and reactivity. It is apparent that the global hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of the chemical reactions. A hard molecule has a large energy gap and a soft molecule has a small energy gap [32]. In our present study, Vasicinone has a lower global hardness value (0.30 eV) compared to that of the Vasicine, whose value is 0.39 eV. Generally, the inhibitor molecule shows high inhibition efficiency if it has the smallest value of the global hardness (hence the highest value of global softness) [29]. For the straightforward electron transfer, the adsorption could occur in that part of the molecule where the chemical softness (which is a local property) has the highest value [33]. Noticing that Vasicinone (with the chemical softness value of 3.33 eV), has the high inhibition efficiency compared to Vasicine, whose value is 2.56 eV. Vasicinone, as the best green inhibitor has a total energy of -18446.41 eV. Such result indicates that the Vasicinone molecule will mainly be adsorbed through the active adsorption centers of the metal surface [24].

The value of  $\Delta N$  has been previously reported in the literature, showing that the value of  $\Delta N$  evidences an inhibition effect as a result of the electrons donation through the lone electron pairs from the heteroatoms [13,34]. In accordance with the Lukovits's study [34], if the value of  $\Delta N < 3.6$ , the

inhibition efficiency increases with the increase of the electron donating capacity of the inhibitor on the metal surface, and the adsorption of the green inhibitor on the metal surface could be possible. Also, it was observed that the inhibition efficiency increases with an increment of the values of  $\Delta N$  [35]. The Mulliken charges of Vasicine and Vasicinone molecule are shown in Figure 4 and Table 2.



**Figure 4.** Mulliken charges on the atoms of Vasicine and Vasicinone molecules.

**Table 2.** Calculated Mulliken charges of Vasicine (C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O) and Vasicinone (C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>) molecules.

| Atom Positions | Atoms | Mulliken Charges |               |
|----------------|-------|------------------|---------------|
|                |       | Vasicine         | Vasicinone    |
| 1              | C     | 0.039            | -0.012        |
| 2              | C     | 0.291            | 0.018         |
| 3              | C     | -0.023           | -0.041        |
| 4              | C     | -0.046           | -0.057        |
| 5              | C     | 0.008            | -0.019        |
| 6              | C     | 0.020            | 0.297         |
| 7              | N     | <b>-0.422</b>    | <b>-0.530</b> |
| 8              | C     | 0.523            | 0.545         |
| 9              | C     | 0.101            | 0.579         |
| 10             | N     | <b>-0.499</b>    | <b>-0.579</b> |
| 11             | C     | 0.144            | 0.102         |
| 12             | C     | -0.124           | 0.207         |
| 13             | C     | 0.355            | -0.250        |
| 14             | O     | <b>-0.368</b>    | -0.012        |
| 15             | O     | -----            | -0.249        |



It is clear that the nitrogen atoms as well as the oxygen bonded carbon atoms carry the negative charge centers, which could give electrons to the mild steel surface and form coordinate covalent bonds, which suggests that the active centers with charge excess could act as a nucleophilic reagent. Such statement is a general agreement of different authors [36-39].

#### 4. CONCLUSIONS

The inhibition efficiency of the Vasicine and Vasicinone molecules, which are present as major components in *Adhatoda vasica* plant extract, has been investigated utilizing the DFT quantum chemical assessment. The inhibition efficiency increases with the increase in  $E_{\text{HOMO}}$ , and the decrease in  $E_{\text{LUMO}}$  and the energy gap ( $\Delta E$ ). Both, the global hardness ( $\eta$ ) and the chemical softness ( $\sigma$ ) confirm the inhibition efficiency of the molecules in the next order: Vasicinone > Vasicine. The calculated  $E_{\text{HOMO}}$  and the energy gap ( $\Delta E$ ) show reasonably good correlation with the corrosion inhibition efficiency.

The total energy of the best inhibitor (Vasicinone) was the more negative value of the two studied molecules. This outcome indicates that Vasicinone is adsorbed on the active centers of the metal surface. In this study, a direct relationship between the inhibition efficiency, the number of electron transfer ( $\Delta N$ ) and the dipole moment ( $\mu$ ) is not evident. The quantum chemical assessment is a viable method to predict the chemical structure and the molecule suitability to be a green inhibitor.

The interesting results of DFT quantum chemical evaluation motivate the evaluation of the corrosion inhibition efficiency separately for Vasicine and Vasicinone for the mild steel in acid solution. Such results were correlated to the experimental electrochemical results for Vasicine and Vasicinone as pure compounds.

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