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## Inhibitive action of piperic acid on C38 steel corrosion in HCl solution

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### ABSTRACT

5-(1,3-benzodioxol-5-yl)penta-2,4-dienoic acid named piperic acid was obtained by hydrolysis of piperine and characterized by NMR and IR spectroscopies. Corrosion inhibition effect of piperic acid on C38 steel corrosion in 1 M HCl solution was investigated by weight loss method at various temperatures (298 - 353 K). Weight loss measurements indicated that piperic acid decreased the corrosion rate indicating that the natural compound forms a barrier against metal attack in acidic solution; then the efficiency increased with the inhibitor concentration to attain 90.4% at  $10^{-3}$  M. Temperature effect shows that inhibitory action decreases to attain 58.3% at 70°C. Activation parameters were evaluated. Piperic acid adsorption accords the Langmuir isotherm. Adsorption free enthalpy was determined and discussed. Attempts to explain 5-(1,3-benzodioxol-5-yl)penta-2,4-dienoic acid (piperic acid: III) were investigated as corrosion inhibitors for mild steel using density functional theory (DFT) at B3LYP/6-31G(d) level in comparison of piperine (I) and piperanone (II). Quantum chemical parameters most relevant to their potential action as corrosion inhibitors such as  $E_{HOMO}$  (highest occupied molecular orbital energy),  $E_{LUMO}$  (lowest unoccupied molecular orbital energy), the energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electron affinity (A), ionization potential (I), the absolute electronegativity ( $\chi$ ), the hardness ( $\eta$ ), the softness (S) and the number of electrons transferred ( $\Delta N$ ) have been calculated and discussed.

**Keywords:** Corrosion; Acid solutions; Green inhibitor; Piperic acid; Adsorption, DFT

### INTRODUCTION

The studies of corrosion inhibition find more and more papers on databases, for example more than twelve thousands papers are covered by Scopus. The most treated ones concerned steel in various media because of the wide applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes. The dissymmetry potentials between iron and hydrogen couples are the principal cause of the electrochemical attack. The aggressivity of hydrogen ion is inevitable in uninhibited acid and the use of inhibitors is necessary [1-5]. Researchers are unanimous that this kind of metal protection occurs by the adsorption of inhibitors on the metal surface. Then, compounds can adsorb on metal surface forming a barrier against hydrogen ions and then block or reduce the corrosion phenomena [6-9]. Although, synthetic compounds offer good anticorrosive effect; a risk of toxicity of these compounds to both human beings and environment is not excluded. In this later decade, researchers try to find new alternatives by using naturally occurring substances. Plant extracts and oils have become important as an environmentally acceptable, less toxic and biodegradable [10-14].

In our laboratories, numerous studies have been devoted on the corrosion inhibition by natural plant extracts or oils on steel in acidic solutions [15-18]. The infinite constituents in extract or oil exhibiting inhibitive action do not

permit to explain clearly the nature of the mechanisms of inhibition process. Some authors determined adsorption parameters such as free enthalpy, etc by using "concentration" of extract or oil in ml/l, ppm, g/l and suggested adsorption isotherm and physical or chemical adsorption. In our opinion, we always have reservations on these determinations because authors confuse with synthesised molecules that have a known weight and expressed in mol/l.

This inconvenience may be surpassed when works are made with isolated molecules. Several works were then conducted on pure components issued from plants as bguanine, iriine, pulegone, limonene, piperine, piperanine... [19-20]. This work is aimed to investigate the inhibitory effect of piperic acid (PA), obtained from piperine isolated from black pepper (BP) on C38 steel corrosion in 1 M HCl solution through weight loss measurements. Inhibition action is discussed on the basis of quantum parameters determined by DFT calculations and compared to those of piperine and piperanine.

## MATERIALS AND METHODS

### 2.1. Isolation of piperine

Piperine can be isolated in good yield from ground black pepper as described elsewhere [21,22]. Two methods of extractions of the piperine were used: extraction involving refluxing with  $C_2H_5OH$  (95%) or  $CH_2Cl_2$  and by means of a device of soxhlet ( $C_2H_5OH$  95%). With the extraction involving refluxing, we obtain a mixture of two products (piperine and piperanine). During the recrystallising in the ethanol, the piperine is soluble in the cold ethanol (Mp: 128 °C), and the other compound is piperanine soluble at hot temperature (Mp: 135 °C). We notice during these various manipulations of extractions, that the piperine is soluble in dichloromethane and in cold ethanol and the piperanine is soluble in dichloromethane and in hot ethanol. The piperine was purified and the structure is confirmed by NMR and IR analysis.

### 2.2. Piperic acid Synthesis from hydrolysis of piperine

A mixture of an aqueous solution of potassium hydroxide (12g in 15 mL of water) and 3g of piperin in ethanol (25 mL) is refluxed for 2 h. After cooling to room temperature, the mixture, which is mostly the resulted salt, is transferred to a 50 mL Erlenmeyer flask containing 50 mL of water. The acidification of the solution by adding drop wise HCl afforded to the desired piperic acid. After filtration the product is recrystallized in absolute ethanol. Mp = 215°C. (Litt : Mp = 216 °C) [19-20].

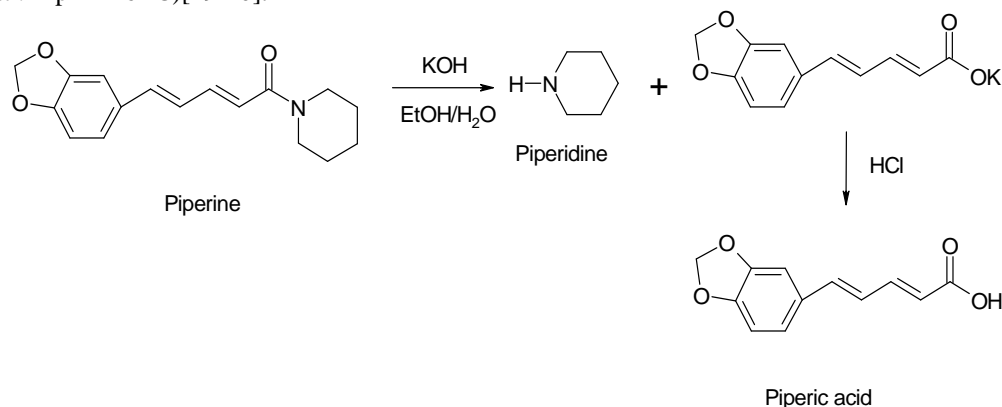


Fig. 1. Obtention of piperic acid from Piperine

### 2.2. Specimen preparation

C38 steel specimens having nominal composition of 0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance were used. Coupons were cut into  $2 \times 2 \times 0.5$  cm dimensions used for weight loss measurements. The exposed area was mechanically abraded with 220, 400, 800 and 1000 grades of emery papers, degreased with acetone and rinsed by distilled water before each experiment. About 1 M HCl solutions were prepared by dilution of 37% HCl (Merck) using distilled water. The concentration range of piperic acid was varied from  $7 \times 10^{-7}$  to  $10^{-3}$  M and the electrolyte used was 100 ml for each experiment.

### 2.3. Weight loss measurements

Experiments were performed with different concentrations of the inhibitor. The immersion time for the weight loss is 6 h at 35°C and 1h at other temperatures. The results of the weight loss experiments are the mean of three runs, each with a fresh specimen and 100 ml of fresh acid solution. The inhibition efficiency *IE*% was calculated using the following equation:

$$E_w \% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \quad (1)$$

where,  $W_{corr}$  and  $W_{corr/inh}$  are the corrosion rate of steel without and with inhibitors, respectively.

## RESULTS AND DISCUSSION

The gravimetric data obtained in the absence and presence of different concentrations of piperic acid are gathered in **Table 1**. The respective corrosion rate illustrated that the addition of piperic acid molecule decreases hugely corrosion rate. In other hand, natural molecule adsorbs on steel surface and consequently retards the corrosion process. The inhibition efficiency of PA increases with inhibitor concentration to attain its maximum (90.4%) at  $10^{-3}$  M. This behaviour indicates that nature molecule acts as a good inhibitor for the corrosion of C38 steel in HCl media [23].

**Table 1: Effect of piperic acid on the steel corrosion in molar HCl solution**

Inhibitor	Concentration (M)	W (mg cm <sup>-2</sup> h <sup>-1</sup> )	E <sub>w</sub> %
Blank	1	1.13	-
piperic acid	$7 \times 10^{-7}$	0.73	35.5
	$1.25 \times 10^{-5}$	0.57	49.6
	$2.5 \times 10^{-5}$	0.137	87.8
	$5 \times 10^{-5}$	0.118	89.6
	$10^{-3}$	0.109	90.4

### Adsorption isotherm behaviour

The inhibition process is generally related to adsorption of inhibitor's species onto the metallic surface. Then, as illustrated Do, in his book [24], Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how many those components can be accommodated by a solid adsorbent... Various fundamental equations are shown, and to start with the proceeding we will present the most basic theory in adsorption: the Langmuir theory (1918). This theory allows us to understand the monolayer surface adsorption on an ideal surface. By an ideal surface here, we mean that the energy fluctuation on this surface is periodic and the magnitude of this fluctuation is larger than the thermal energy of a molecule (kT), and hence the troughs of the energy fluctuation are acting as the adsorption sites. If the distance between the two neighboring troughs is much larger than the diameter of the adsorbate molecule, the adsorption process is called localised and each adsorbate molecule will occupy one site. Also, the depth of all troughs of the ideal surface are the same, that is the adsorption heat released upon adsorption on each site is the same no matter what the loading is [25]. The Langmuir adsorption isotherm may be written in the following form:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \text{with} \quad K = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^{\circ}}{RT}\right) \quad (5)$$

where  $C$  is the concentration of inhibitor,  $K$  is the adsorptive equilibrium constant,  $\theta$  is the surface coverage and the standard adsorption free energy ( $\Delta G_{ads}$ ).

The relationship between  $C/\theta$  and  $C$  presents linear behaviour at all temperatures studied (Fig. 2) with slopes equal to unity (1.0125). The correlation factor is 0.99996. This suggests that the adsorption of henna extract on metal surface followed the Langmuir adsorption isotherm. From the intercepts of the straight lines  $C_{inh}/\theta$ -axis,  $K$  value calculated is 279212.6 L/mol. The standard free energy of adsorption ( $\Delta G_{ads}$ ) value deduced is -41.04 kJ/mol. The negative values of  $\Delta G_{ads}$  indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process.

Generally, an adsorption process suggests either physisorption or chemisorption.  $\Delta G_{ads}$  value lower than -40 kJ/mol are related to the chemisorption between charged molecule and charged metal [26-28].

### Determination of activation parameters

Weight loss measurements for C38 steel in molar HCl without and with  $10^{-3}$  mol L<sup>-1</sup> of piperic acid, in the temperature range 40–70 °C at 1 h of immersion, are shown in Table 2.

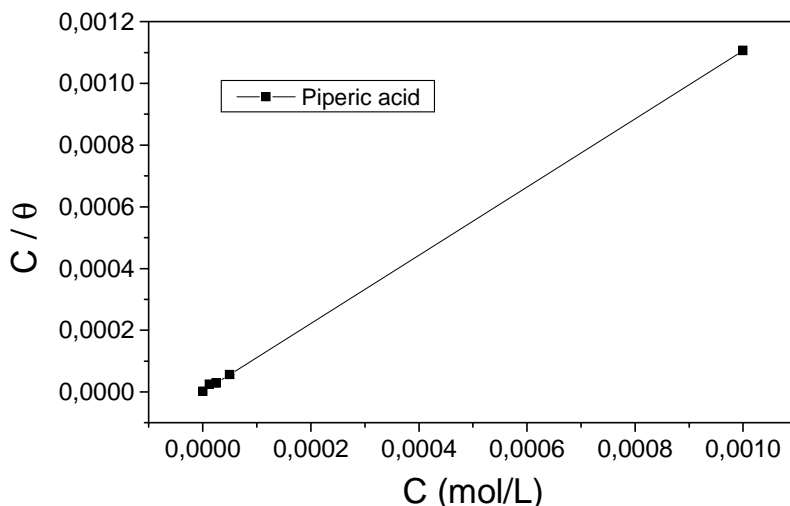


Fig. 2. Langmuir adsorption plot of PA on C38 steel in 1 M HCl at 35 °C

Table 2 : Corrosion data of steel in 1M HCl without and with  $10^{-3}$  mol L $^{-1}$  of piperic acid, in the temperature range 40–70 °C at 1 h

	Temperature °(C)	$W_{corr}$ (mg.cm $^{-2}$ .h $^{-1}$ )	$E_w$ (%)
1M HCl	40	2.604	-
	50	4.834	-
	60	9.781	-
	70	13.235	-
piperic acid	40	0.175	93.2
	50	0.381	92.1
	60	0.807	89.6
	70	5.516	58.3

The activation energies ( $E_a$ ) for the corrosion of C38 steel in the absence and presence of different concentrations of BP extract and piperine were calculated using Arrhenius-type equation:

$$W_{corr} = A e^{-\frac{E_a}{RT}} \quad (2)$$

where  $E_a$  is the activation corrosion energy;  $R$  is the universal gas constant;  $A$  is the Arrhenius pre-exponential factor,  $T$  is the absolute temperature and  $W_{corr}$  is corrosion rate. Arrhenius plots for the corrosion rate of C38 steel in 1 M HCl are shown in Fig. 54. Values of  $E_a$  for C38 steel in were evaluated from the slope of  $\log W$  versus  $1/T$  plots and given in Table 3. The enthalpy of activation ( $\Delta H^*$ ) and the entropy of activation ( $\Delta S^*$ ) for the corrosion of C38 steel in HCl may be estimated using the transition-state equation:

$$W_{corr} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (3)$$

where  $k_B$  is the Boltzmann's constant and  $h$  is the Planck's constant. Fig. 3 shows a plot of  $\log(W/T)$  versus  $1/T$ . Straight lines are obtained with a slope of  $-\Delta H^*$  and from the intercepts of  $\log(W/T)$ -axis,  $\Delta S^*$  values were calculated and are given in Table 2.

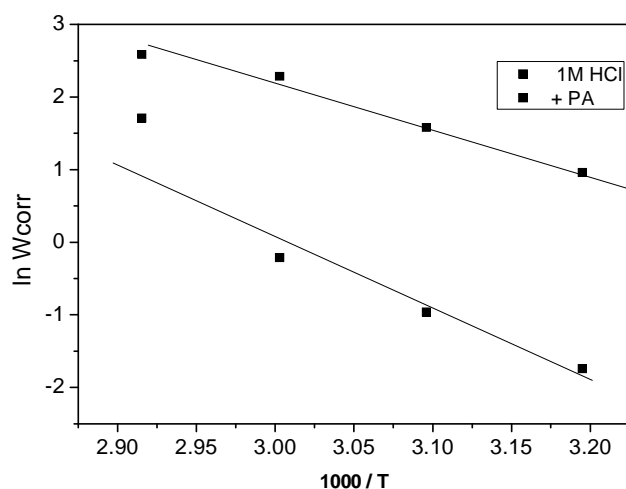


Fig. 3. Arrhenius plots of  $\log(W)$  versus  $1/T$  at different concentrations of BP extract and piperine

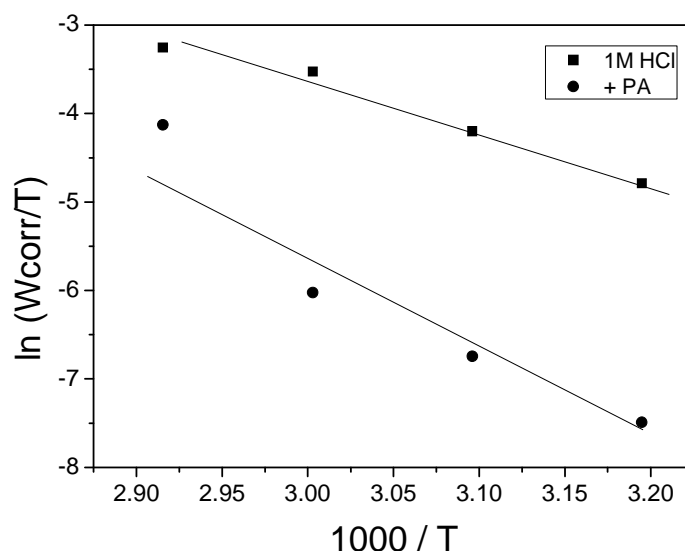


Fig. 4. Transition-state plots of  $\log(W/T)$  versus  $1/T$  in 1 M HCl in absence and presence of various concentrations of BP extract and piperine

Table 3 : Activation parameters of steelin 1 M HCl in absence and presence of various concentrations of BP extract and piperine

	$E_a$ (kJ/mol)	$\Delta H_{ads}^\circ$ (kJ/mol)	$\Delta S_{ads}^\circ$ (J/mol.K)	$E_a - \Delta H^*$
Blank	50.01	47.25	-178.07	2.76
Piperic acid	98.42	95.69	-172.10	2.73

The collected data in Tables 3 and 4 indicate that the addition of both BP extract and piperine leads to an increase in the activation  $E_a$  and  $\Delta H^*$  to values greater than that of the free solution. Moreover, the average difference value of the  $E_a - \Delta H^*$  is 2.6 kJ/mol which is approximately equal to the value of  $RT$  (2.63 kJ/mol) at the average temperature (238 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known equation of perfect gas [23]:

$$E_a - \Delta H^* = RT \quad (4)$$

It is pointed out in the literature that positive sign of the enthalpies reflects the endothermic nature of the steel dissolution process. The presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank.

Large and negative values of entropies show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

#### 4. Quantum-chemical calculations

Quantum chemical calculations have been widely used to study the reactivity of organic compounds [29-31]. The inhibition potentials of three piperine derivatives: 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)penta-2,4-dien-1-one (piperine: I), 5-(1,3-benzodioxol-5-yl)-1-(piperidin-1-yl)pent-2-en-1-one (piperanine: II) and 5-(1,3-benzodioxol-5-yl)penta-2,4-dienoic acid (piperic acid: III), see **Figure 5**, have been elucidated using quantum chemical calculations based on density functional theory (DFT). Hence, we have investigated the relationship between the molecular, the electronic structure and the inhibition efficiency of the three studied molecules.

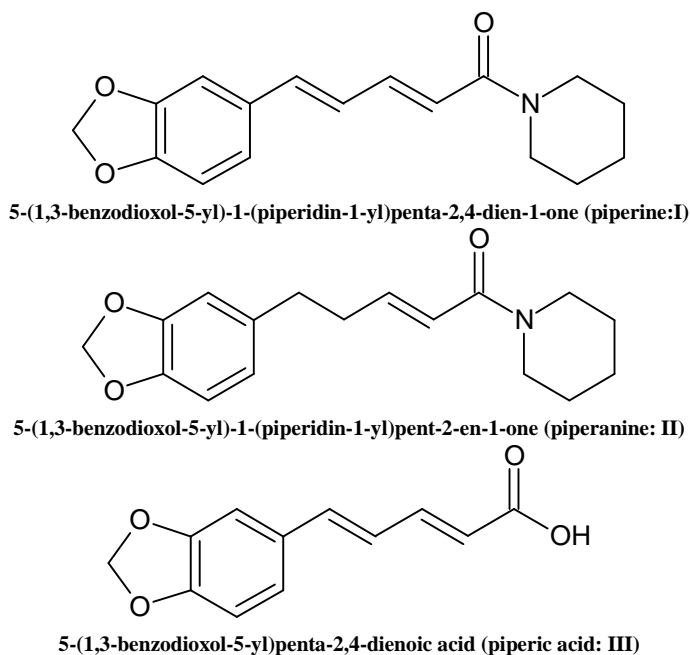


Figure 5: Names, molecular structures and the abbreviations of the inhibitors investigated.

Full geometry optimizations (**Figure 6**) with no constraints of the three molecules under study (I, II and III) were performed using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) [32-34] and the 6-31G\* orbital basis sets for all atoms as implemented in Gaussian 09 program [35]. This approach has been proved to be a very powerful tool for studying corrosion inhibition mechanism [36-38].

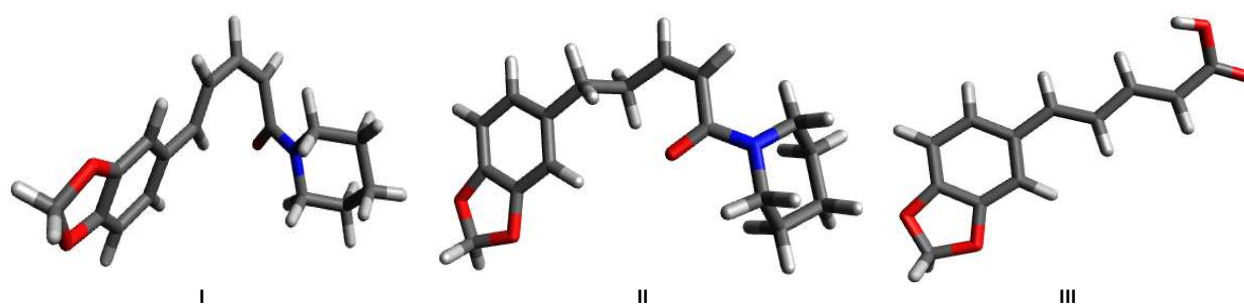


Figure 6: Optimized structures of the compounds I, II and III as calculated at the B3LYP/6-31G\* level

The quantum chemical parameters of the three studied molecules such as  $E_{\text{HOMO}}$  (highest occupied molecular orbital energy),  $E_{\text{LUMO}}$  (lowest unoccupied molecular orbital energy), the energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electron affinity (EA), ionization potential (IP), the absolute electronegativity ( $\chi$ ), the global electrophilicity index ( $\square$  in the hardness ( $\eta$ ), the softness ( $S$ ) and the number of electrons transferred ( $\Delta N$ ) were calculated and gathered in Table 4. The frontier orbital HOMO and LUMO of a chemical species are very important in defining its reactivity. A good correlation has been found between the speeds of corrosion and  $E_{\text{HOMO}}$  that is often associated with the

electron-donating ability of the molecule. Survey of literature shows that the adsorption of the inhibitor on the metal surface can occur on the basis of donor-acceptor interactions between the  $\pi$ -electrons of the heterocyclic compound and the vacant d-orbital of the metal surface atoms [39], high value of  $E_{\text{HOMO}}$  of the molecules shows its tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. Increasing values of  $E_{\text{HOMO}}$  facilitate adsorption and therefore enhance the inhibition efficiency, by influencing the transport process through the adsorbed layer. Similar relations were found between the rates of corrosion and  $\Delta E$  ( $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ ) [40-42]. The energy of the lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower the value of  $E_{\text{LUMO}}$ , the more probable the molecule would accept electrons. Consequently, concerning the value of the energy gap  $\Delta E$ , larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the  $\Delta E$  will render good inhibition efficiency, because the energy required to remove an electron from the lowest occupied orbital will be low [43]. Another method to correlate inhibition efficiency with parameters of molecular structure is to calculate the fraction of electrons transferred from inhibitor to metal surface. According to Koopman's theorem [44],  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  of the inhibitor molecule are related to the ionization potential (IP) and the electron affinity (EA), respectively. The ionization potential and the electron affinity are defined as  $\text{IP} = -E_{\text{HOMO}}$  and  $\text{EA} = -E_{\text{LUMO}}$ , respectively. Then absolute electronegativity ( $\chi$ ) and global hardness ( $\eta$ ) of the inhibitor molecule are approximated as follows [43]:

$$\chi = \frac{I + A}{2} \quad (1)$$

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

As hardness ( $\eta$ ), softness ( $S$ ) is a global chemical descriptor measuring the molecular stability and reactivity and is given by:

$$S = \frac{1}{\eta} \quad (3)$$

The chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [45].

The global electrophilicity index was introduced by Pearson [46] as a measure of energy lowering due to maximal electron flow between donor and acceptor and is given by:

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

According to the definition, this index measures the propensity of chemical species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of  $\mu$ ,  $\omega$ ; and conversely a good electrophile is characterized by a high value of  $\mu$ ,  $\omega$ . This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge  $\Delta N$  from the environment. Thus the fraction of electrons transferred from the inhibitor to metallic surface,  $\Delta N$ , is given by [47]:

$$\Delta N = \frac{\chi_{\text{Fe}} - \chi_{\text{inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{inh}})} \quad (5)$$

Where  $\chi_{\text{Fe}}$  and  $\chi_{\text{inh}}$  denote the absolute electronegativity of iron and inhibitor molecule respectively.  $\eta_{\text{Fe}}$  and  $\eta_{\text{inh}}$  denote the absolute hardness of iron and the inhibitor molecule respectively. In order to calculate the fraction of electrons transferred, a theoretical value of  $\chi_{\text{Fe}} = 7.0$  eV [46] and  $\eta_{\text{Fe}} = 0$  by assuming that for a metallic bulk  $\text{IP} = \text{EA}$  [48] because they are softer than the neutral metallic atoms.

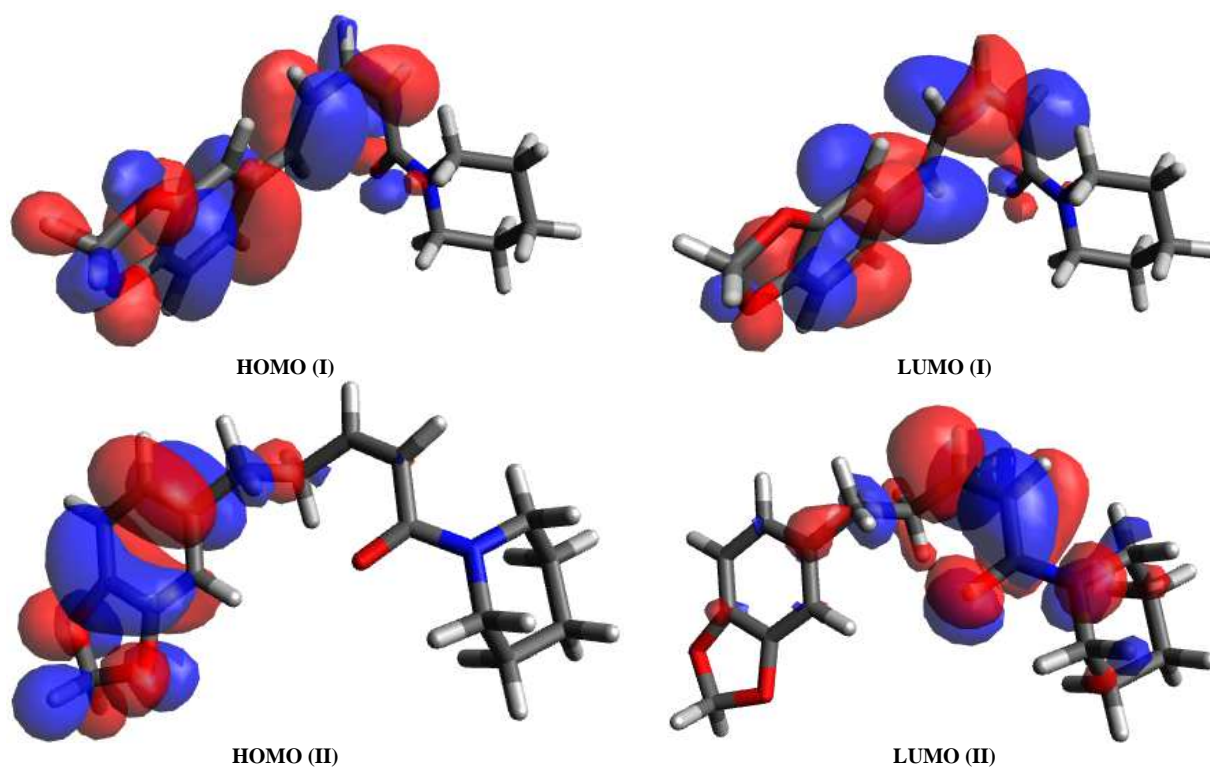
**Table 4:** Calculated quantum chemical parameters of the studied molecules

	I	II	III
$E_{\text{HOMO}}$ (eV)	-5.270031089	-5.267309949	-5.714393188
$E_{\text{LUMO}}$ (eV)	-1.268323174	-0.670760915	-2.122488898
$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ (eV)	4.001707915	4.596549034	3.59190429
$IP = -E_{\text{HOMO}}$ (eV)	5.270031089	5.267309949	5.714393188
$EA = -E_{\text{LUMO}}$ (eV)	1.268323174	0.670760915	2.122488898
$\chi$ (eV)	3.269177132	2.969035432	3.918441043
$\eta$ (eV)	2.000853958	2.298274517	1.795952145
$\mu$ □□□□□□□□	3.70	3.48	7.44
$\omega$	3.421039289	2.63467221	15.41065561
S	0.499786602	0.435109032	0.556807709
$\Delta N$	0.932307642	0.876954545	0.857917892
IE (%)	98.9 [19]	97.5 [20]	90.4

The inhibition effect of a given compound is usually ascribed to adsorption of the molecule on metal surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. When chemisorption takes place, one of the reacting species acts as an electron pair donor and the other one act as an electron pair acceptor. The energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) measures the tendency towards the donation of electron by a molecule. In this context, survey of **Table 4** shows that, the highest value of  $E_{\text{HOMO}}$  -5.270031089 (eV) and -5.267309949 (eV) of compounds I and II, respectively indicates the better inhibition efficiency than the other compound III. The fact that  $E_{\text{HOMO}}$  of inhibitors I and II are almost the same is in good agreement with the comparable experimental inhibition efficiency (IE) for these compounds.

The ground state geometry of the inhibitor as well as the nature of its frontier molecular orbitals, namely, the HOMO and LUMO are involved in the activity properties of the inhibitors. Noteworthy, the shape of the HOMO and LUMO is structural dependant as shown in **Figure 7**. The electron density of the HOMO location in the inhibitors under study is mostly distributed on the atoms having a delocalized character indicating that these are the favorite sites for adsorption

Besides, the HOMO and LUMO are delocalised on the entire molecule III (due to the planarity of this molecule) while they are strongly localized for the molecules I and II (due to non planarity of these molecules).





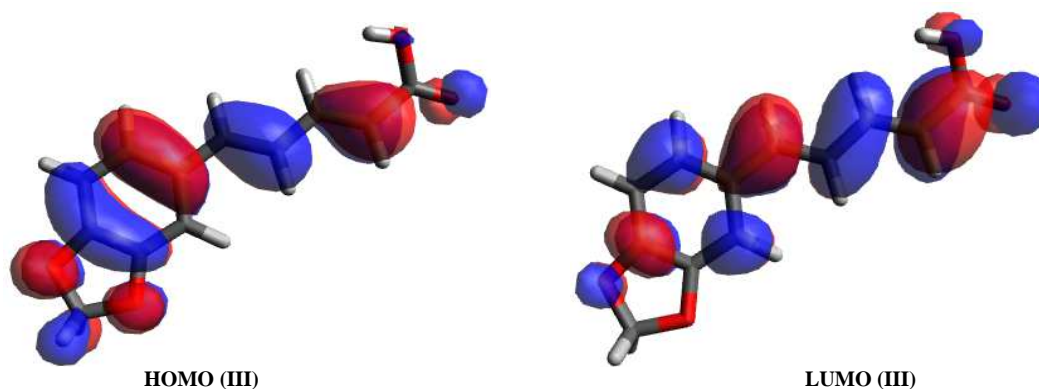


Figure 7: Schematic representation of HOMO and LUMO molecular orbital of studied molecules

The molecule III having the lowest values of  $E_{LUMO}$ , energy gap and hardness could have a better performance as corrosion inhibitor. When considering the global electrophilicity index ( $\omega$ ) which is the measure of the electrophilic tendency of a molecule, we find that the inhibitor III with high electrophilicity index value than the other compounds, has the highest inhibition efficiency. In our study, there is no direct relationship between on the one hand IE (%) and in the other hand  $E_{LUMO}$ , energy gap, hardness, electrophilicity index and dipole moment.

Interestingly, the values of the number of electrons transferred ( $\Delta N$ ) show that the inhibition efficiency resulting from electron donation agrees with Lukovits's study [49]. If  $\Delta N < 3.6$ , the inhibition efficiency increases by increasing electron-donating ability of these inhibitors to donate electrons to the metal surface and it increases in the following order: III < II < I. The results indicate that  $\Delta N$  values correlates strongly with experimental inhibition efficiencies. Thus, the highest fraction of electrons transferred is associated with the best inhibitor I, while the least fraction is associated with the inhibitor that has the least inhibition efficiency III.

### CONCLUSION

The study of effect of black pepper and piperine on the corrosion of steel in molar HCl conducted by weight loss method may draw the following conclusions:

1. The BP extract acts as an efficient inhibitor for corrosion of C38 steel in HCl medium; the inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 95.8% at 2 g/L.
2. Addition of isolated molecule of piperine also gives an opportunity to use these natural compounds as efficient inhibitor for C38 steel. Its inhibition attains 99% at  $10^{-3}$ M.
3. Temperature effect shows that piperine exhibits constant efficiency until 60°C which is recommended for industrial descaling.
- 4- Piperine adsorbs on the metal surface according to the Langmuir isotherm with more probable chemisorption phenomenon.
- 5- DFT calculations correlate strongly with experimental results and reveal that the inhibition efficiency grows in the following order: piperic acid < piperanine < piperine.

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