Quantum Chemical study of Citrus aurantium leaves extracts as a sustainable corrosion inhibitor of mild steel in sulfuric acid

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A B S T R A C T

Corrosion inhibition of mild steel in 1M H_2SO_4 was investigated in absence and presence of citrus aurantium leaves extracts as a friendly inhibitor. Quantum chemical calculations based on PM3 and QSAR methods were done to evaluate the relationship between the molecular structure of citrus aurantium leaves extracts and their inhibition efficiencies. The quantum chemical parameters such as E_{HOMO}, E_{LUMO}, energy gap, dipole moment, hardness, softness, the fractions of electrons transmit, electrophilicity index, etc were calculated and used. Furthermore, regression equations were proposed using the nonlinear regression analysis.

INTRODUCTION

Mild steel corrosion phenomena has become important particularly in acidic media because of the increased industrial applications of acid solutions, such as, acid pickling, industrial cleaning, acid descaling, oil well acid in oil recovery and the petrochemical processes (Khadom *et al*., 2010; Asipita *et al*., 2015; Khadom *et al*., 2009). Among the acid solutions, sulfuric acid is one of the most widely used chemicals. Sulfuric acid contact may cause damage to metal surface. This damage must be controlled by using one of corrosion prevention methods. Using inhibitors is an important method of protecting materials against deterioration due to corrosion, especially in acidic media (Khadom and Yaro, 2011). Organic anticorrosion materials synthetic industrially may cause a great negative effect on the environment. The organic inhibitors are gotten from the organic extraction of plants and vegetable extract, these extract are effective, economical and eco- friendly (Yaro *et al*., 2013; Yaro *et al*., 2011; Rosliza and Nik, 2014). The known risky effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media (Chaieb *et al*., 2005; Chaieb *et al*., 2004; Chauhan and Gunasekaran, 2007; El-Etre *et al*., 2005)**.** Fruits may contains different chemicals materials (El Sohaimy *et al*., 2015). Citrus aurantium leaves (CAL) are very common, available and cheap plants in Diyala governorate/Iraq. In our previous works (Hassan *et al*., 2016 a, b), the naturally corrosion inhibitor (CAL) was extracted and tested to control the corrosion of mild steel in 1M H_2SO_4 at different operating condition. In present work, theoretical quantum chemical calculations were carried out to describe the interaction between the inhibitor molecule and the surface, as well as the properties of this inhibitor concerning their reactivity. Linalool and Linalyl acetate are the most important component which consist more than 75 % of CAL

components (Mohammad-Bagher *et al*., 2012; Abderrezak *et al*., 2014). The chemical structure of these component were shown below
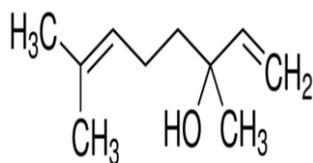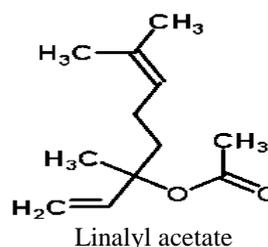
Linalool   Linalyl acetate

Theoretical And Quantum Chemical Backgrounds:

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. According to PM3 theorem (Gece, 2008), the HOMO energy is related to the ionization potential (IE) whereas the LUMO energy is linked to the electron affinity (EA), as follows:

$$IE = -E_{HOMO} \tag{1}$$

$$EA = -E_{LUMO} \tag{2}$$

Then, the electronegativity (χ), the chemical potential (μ) and the global hardness (η) were evaluated, based on the finite difference approximation, as linear combinations of the calculated IE and EA (Pearson, 1988):

$$\chi = -\mu = \frac{IE + EA}{2} \tag{3}$$

$$\eta = \frac{IE - EA}{2} \tag{4}$$

The softness (σ) is the inverse of the global hardness (Sastri, 1997).

$$\sigma = \frac{1}{\eta} \tag{5}$$

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 (Sastri, 1997). The global electrophilicity (ω) 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

$$\omega = \frac{\mu^2}{2}\sigma \tag{6}$$

The fraction of transferred electrons (ΔN), evaluating the electronic flow in a reaction of two systems with different electronegativities, in particular case; a metallic surface and an inhibitor molecule was calculated according to Pearson theory (Obot and Obi-Egbedi, 2010) as:

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

Where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and inhibitor molecule respectively, η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule respectively. In this study, we use the theoretical value of $\chi_{Fe}= 7.0eV$ and $\eta_{Fe}= 0.0eV$ for the computation of number of transferred electrons (Pearson, 1988). The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as a resistance (Gomez *et al*., 2006).

Methodology And Experimental Data:

The corrosion reaction of mild steel in 0.5, 1, and 1.5 M H_2SO_4, at 30, 40, 50 and 60 ℃, in absence and presence of 2, 4, 6, 8 and 10 ml of CAL as a corrosion inhibitor was studied in our previous works (Hassan *et al*., 2016 a,b). Two software were used in simulation of these variables. STATISTICA 7 software was used to estimate the coefficients of suggested models. This software based on *Levenberg-Marquardt* estimation method. While the other software was *ArgusLab 4.0.1 package*. This program optimizes the surface structure of inhibitor molecule and selects the best surface area for distribution of charges.

RESULTS AND DISCUSSION

Quantum chemical studies:

Linalool and Linalyl acetate represent the most effective component of CAL (Mohammad-Bagher *et al*., 2012; Abderrezak *et al*., 2014). Quantum chemical calculations are proven to be a very powerful tool to know

the inhibition mechanism and to emphasis the experimental data (Martinez and Tagljar, 2003; Ma _et al_., 2006). Through the method of quantum chemical calculations, the structural parameters, such as the frontier molecular orbital (MO), HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), dipole moment (d), the fraction of electrons (ΔN) transfer from inhibitors to metal surface, and other quantum parameters were calculated and correlated. The optimized minimum energy geometrical configurations of test compounds are given in Fig. 1. The computed quantum chemical parameters are summarized in Table 1. It has been well documented in literature that (Ma _et al_., 2006) higher the value of E_{HOMO} of the inhibitor, greater is the ease of inhibitor to offer electrons to unoccupied d orbital of metal atom and higher is the inhibition efficiency of the inhibitor. Further lower the E_{LUMO}, easier is the acceptance of electrons from metal atom to form feedback bonds. The gap between HOMO–LUMO energy levels of molecules was another important parameter that needs to be considered. Smaller the value of ΔE of an inhibitor, higher is the inhibition efficiency of that inhibitor (Gao and Liang, 2007). These indicate that both Linalool and Linalyl acetate inhibition effect is the same. Further higher values of dipole moment will favor the enhancement of corrosion inhibition (Lebrini _et al_., 2007). The dipole moment values stands in the approximately same order that support our findings. Values of X and η were calculated by using the values of IE and EA obtained from quantum chemical calculation. The fraction of electrons transferred from inhibitor to the iron molecule (ΔN) was calculated. According to other reports (Gece, 2008), value of ΔN showed inhibition effect resulted from electrons donation. In this study, the CAL was the donators of electrons while the mild steel surface was the acceptor. These components were bound to the mild steel surface, and thus formed a protective inhibition adsorption film.

Mulliken charge distributions:

The Mulliken charge distributions of Linalool and Linalyl acetate are presented in Tables 2 and 3. It can be readily observed that oxygen and most of carbon atoms have higher charge densities. The regions of highest electron density are generally the potential sites for the electrophiles attacked (Lukovits _et al_., 2001; Gece, 2008). The use of Mulliken population analysis to probe adsorption center of inhibitors has earlier been reported (Musa _et al_., 2010). Based on the calculations, the highest electron densities were located on O and C atoms implied that the O and C atoms were the active centers, which have the strongest ability of bonding to the metal surface. On the other hand, HOMO (Fig. 1, B) was mainly distributed on the area containing O and C atoms and this area is probably the primary site of the bonding.

Quantitative structure-activity relationship:

Quantitative structure-activity relationship (QSAR) was used to relate the corrosion inhibition efficiency and molecular structures of the compounds under investigations. The QSAR approach is effectively sufficient to prediction the inhibitor effectiveness using the theoretical approach; it may be used to find the optimal group of parameters for predicting the suitability of the molecule to be a corrosion inhibitor. In addition, it may also be used to find the optimal group of quantum chemical parameters that could predict the structure and the suitability of the molecule to be a potential inhibitor. Attempts are made to find a relationship between the experimental inhibition efficiencies and some quantum chemical parameters (Obot and Obi-Egbedi, 2010). The following proposed regression analysis was used to correlate inhibitor concentration (C_i) and QSAR parameters with the experimental inhibition efficiencies $Eff_{exp}\%$. The linear model approximates corrosion inhibitor efficiency ($Eff_{cal}\%$) as in eq. 8 (El Ashry _et al_., 2006):

$$Eff_{cal}\% = Ax_jC_i + B \tag{8}$$

where A and B are constants obtained by regression analysis; x_j a quantum chemical index characteristic for the molecule j; C_i denotes the inhibitor concentration. Such linear approach was not found to be satisfactory for correlating the current data. A non-linear equation was used to correlate all quantum chemical parameters (E_{HOMO}, E_{LUMO}, ΔE, μ and ΔN) and inhibitor concentration (C_i) with experimental inhibition efficiencies. The non-linear model proposed by Lukovits _et al_. (2001) for the interaction of corrosion inhibitors with metal surface in acidic solutions has been used in this part of the study.

$$Eff_{cal}\% = \frac{(Ax_i + B)C_i}{1 + (Ax_i + B)C_i} \times 100 \tag{9}$$

The nonlinear estimation regression of equation 9 yields the following equation for Linalool (Eq. 9a) and Linalyl acetate (Eq. 9b):

$$Eff_{cal}\% = \frac{(33.77 - 7.42E_{HOMO} - 336.2E_{LUMO} + 7.67\Delta E - 200.4d - 211.67\Delta N)C_i}{1 + (33.77 - 7.42E_{HOMO} - 336.2E_{LUMO} + 7.67\Delta E - 200.4d - 211.67\Delta N)C_i} \times 100 \tag{9a}$$

$$Eff_{cal}\% = \frac{(51.6 - 7.88E_{HOMO} - 97.7E_{LUMO} - 24.57\Delta E + 42.06d - 304.4\Delta N)C_i}{1 + (51.6 - 7.88E_{HOMO} - 97.7E_{LUMO} - 24.57\Delta E + 42.06d - 304.4\Delta N)C_i} \times 100 \tag{9b}$$

The plots of the calculated and experimental inhibition efficiency of the selected CAL compounds are shown in Fig. 2. It can be seen that the relation between calculated and experimental efficiencies was not strong. This may be attributed to presence of components more than Linalool and Linalyl acetate that affect the protection mechanism.

Table 1: Quantum chemical parameters for most important components of CAL.

Component	E_{HOMO} (eV)	E_{LUMO} (eV)	IE	EA	χ	η	σ	ω	ΔN	ΔE (eV)	d (debye)
Linalool	-9.37	-0.38	9.37	0.38	4.875	4.495	0.22	2.64	0.24	8.99	1.22
Linalyl acetate	-9.42	-0.97	9.42	0.97	5.195	4.225	0.24	3.19	0.21	8.45	1.37

Table 2: Mulliken atomic charges for Linalool.

no	atom	charge	no	atom	charge
1	C	-0.226	16	H	0.120
2	C	-0.252	17	H	0.119
3	C	0.141	18	H	0.118
4	C	-0.319	19	H	0.111
5	C	-0.281	20	H	0.127
6	C	-0.231	21	H	0.107
7	C	-0.191	22	H	0.1428
8	C	-0.1153	23	H	0.1562
9	C	-0.275	24	H	0.1020
10	C	-0.287	25	H	0.1107
11	O	-0.312	26	H	0.106
12	H	0.159	27	H	0.102
13	H	0.117	28	H	0.1223
14	H	0.143	29	H	0.209
15	H	0.118	-		

Table 3: Mulliken atomic charges for Linalyl acetate.

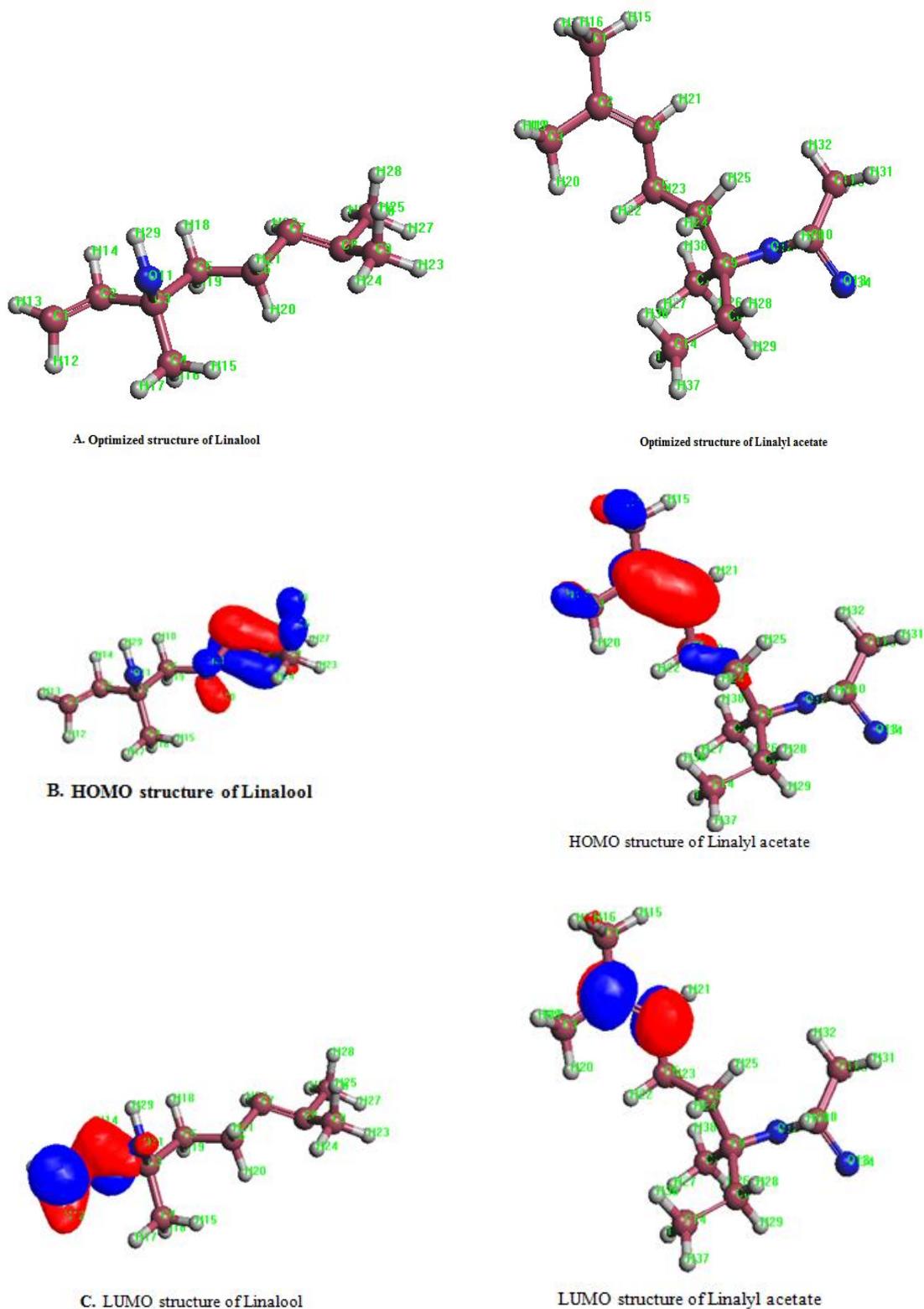| no	atom	charge	no	atom	charge
1	C	-0.262	20	H	0.108
2	C	-0.135	21	H	0.186
3	C	-0.266	22	H	0.124
4	C	-0.242	23	H	0.137
5	C	-0.201	24	H	0.128
6	C	-0.269	25	H	0.131
7	C	-0.337	26	H	0.128
8	C	-0.281	27	H	0.119
9	C	0.131	28	H	0.125
10	C	0.142	29	H	0.146
11	C	-0.366	30	H	0.129
12	O	-0.303	31	H	0.123
13	O	-0.351	32	H	0.119
14	C	-0.308	33	H	0.121
15	H	0.108	34	H	0.227
16	H	0.111	35	H	0.105
17	H	0.110	36	H	0.106
18	H	0.113	37	H	0.111
19	H	0.114	38	H	0.117

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Fig. 1: A: Optimized geometry of Linalool and Linalyl acetate , B: HOMO distribution, C: LUMO distribution.
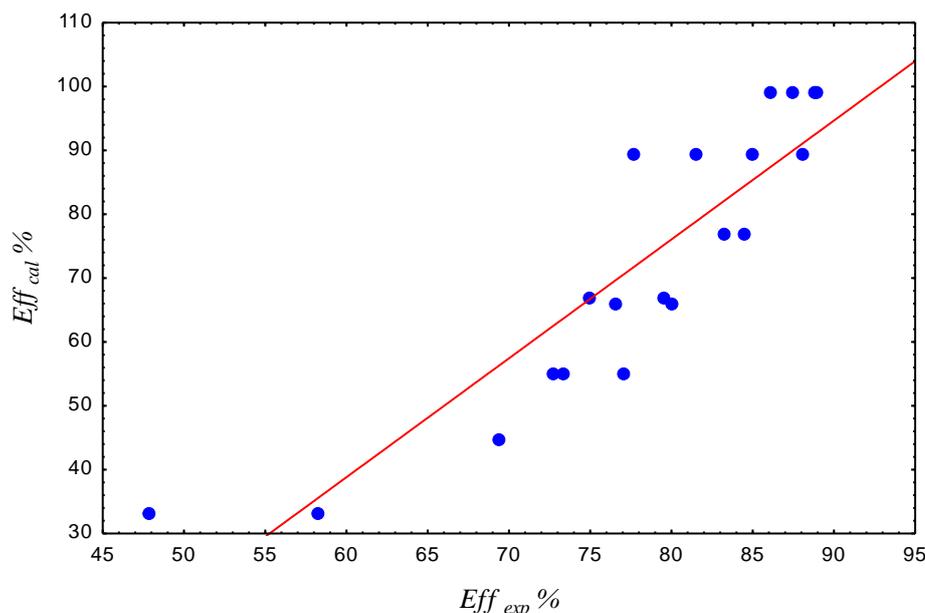
Fig. 2 Calculated inhibitor efficiency aganist experimental one.

Conclusion:

In our previous experimental work, the acid extract of citrus aurantium acts as good and efficient inhibitor for the corrosion of steel in H_2SO_4 medium. Inhibition efficiency increases with inhibitor concentration and decreased with temperature. Present work was an attempted to application of quantum chemical theoretical calculations. Experimental work and literature survey shown that Linalool and Linalyl acetate is the most components in citrus aurantium leaves. Theoretical calculations proved that there are an electron transfer between these material and steel surface. Calculated inhibitors efficiency was not very close to experimental one, which attributed to presence of multi components in citrus aurantium leaves that affect its efficiency.

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