

Meloxiam as corrosion inhibitor for Aluminum in acid media Experimental and theoretical study

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Abstract

The effects of Meloxiam drug (MEL) on the corrosion of pure aluminum in 2 M HCl have been investigated using weight loss methods. The measurement showed that the inhibition efficiency increased with increase in the concentration of inhibitor. The adsorption of the inhibitors on the aluminum surface obeyed Langmuir adsorption isotherm and had a physical mechanism. The effect of temperature on the corrosion behavior in the presence of different concentration of the MEL inhibitors was studied in the temperature range of 25–65 °C. The associated activation energy of corrosion E_a and other thermodynamic parameters such as ΔH_{ads}^0 , ΔS_{ads}^0 , (K_{ads}) and ΔG_{ads}^0 were calculated to elaborate the mechanism of corrosion inhibition. Quantum chemical parameter such as HOMO, LUMO and Mulliken charge etc. have been calculated using DFT (B3LYP/ 6-311++G(d,p)). The results indicate that N and S atoms in the MEL structure was not effected in the adsorption of drug on the Al surface .

Key word: Corrosion inhibitors, Aluminium metal, Quantum chemical calculation

الخلاصة

تم فحص تأثير عقار الميل وكسام على تآكل الألمنيوم النقي في وسط حامضي من حامض الهيدروكلوريك بتركيز ٢ مولاري باستخدام طريقة فقدان الوزن. القياسات أظهرت ان كفاء التثبيط تزداد بزيادة تركيز المثبط. أثبتت الدراسة إن امتزاز MEL على سطح معدن الألمنيوم تتم بميكانيكية فيزيائية تخضع لمعادلة لانكمير للامتزاز الايزوثيرمي. كما درس تأثير مدى من درجات الحرارة (٢٥-٦٥ °م) على سلوك التآكل عند وجود تراكيز مختلفة من المثبط. كما تم حساب طاقة التنشيط المرافقة لعملية الامتزاز وكذلك الدوال الترموديناميكية لعملية الامتزاز مثل (الانثالبي والانتروبي وثابت التوازن وطاقة كس) بغية توضيح متقن لميكانيكية تثبيط التآكل. استخدمت طريقة DFT وعند مستوى B3LYP/6-311++G(d,p) لحساب HOMO, LUMO, ΔE وعزم ثنائي القطب وتوزيع الالكترونوني للشحنات على الذرات، دلت النتائج على ان ذرات النتروجين و ذرة الكبريت لا تشارك بصورة فعالة بعملية الامتزاز على سطح معدن الألمنيوم.

1-Introduction:

Among all the metals, aluminum has been one of the most common metals used for industrial and domestic purposes due to its excellent electrical conductivity, good forming properties, low cost and other relatively noble properties. It is a material commonly used in aerospace and household industries, and it is also used for reaction vessels, pipes, machinery and chemical batteries. A variety of environmental factors can easily cause corrosion of aluminum. Hydrochloric acid (HCl) solutions are used for pickling, chemical and electrochemical etching of Al. It is very important to add corrosion inhibitors to decrease the corrosion rate of Al in such solutions. Thus, aluminum corrosion and its inhibition have attracted the attention of a number of investigators [1–6].

A variety of organic compounds have been reported to be effective as corrosion inhibitors during acidization in industrial cleaning processes [7–11]. Unfortunately, most of the organic inhibitors used are very expensive and health hazards. Their toxic properties limit the field of their application. However, only a few non-toxic and eco-friendly compounds have been investigated as pickling inhibitors. Tryptamine [12], succinic acid [13], L – ascorbic acid [14] and sulfamethoxazole [15] were found to be effective inhibitors in acid environments. Among dithiobiurets (organic compounds containing N and S atoms have very low toxicity), Quraishi et al. [16] found that 1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB) exhibited the best performance towards the corrosion of mild steel in HCl solutions. The inhibitive action of four antibacterial drugs, namely, ampicillin (Amp),

cloxacillin (Clox), flucloxacillin (Fluclox) and amoxicillin (Amox) toward the corrosion of Al in HCl solution was investigated [17].

The under study anti-inflammatory drug 4-hydroxy-2-methyl-*N*-(5-methyl-1,3-thiazol-2-yl)-2-*H*-1,2-benzothiazine – 3 - carboxamide 1,1-dioxide (MEL) compound satisfy these requirements [18]. The compound have a large number of functional adsorption centers (e.g. –OH group, –SO₂–NH– group, S and/or N hetero atoms and aromatic rings). They are strongly basic, hence they can be readily soluble in the acid medium.

Recently, quantum chemical calculations have been widely used to study reaction mechanism. They have also proved to be a very important tool for studying corrosion inhibition mechanism [18,19]. In recent times, Density Functional Theory (DFT) has become an attractive theoretical method because it gives exact basic vital parameters for even huge complex molecules at low cost. Furthermore, by using sophisticated computational tools, [20]. Thus, the DFT has become a main source of connecting some traditional empirical concepts with quantum mechanics. Therefore, DFT is a very powerful technique to probe the inhibitor/surface interaction and to analyze experimental data.

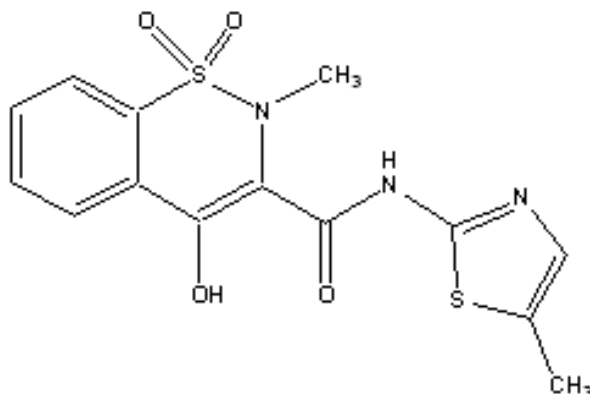
The aim of this work was to study the inhibition of Aluminum corrosion by MEL in 2 M HCl solutions in the temperature range of 25–65°C. The adsorption behavior of MEL was also analyzed in order to choose the appropriate adsorption isotherm.

2. Experimental

2.1. Inhibitor

MEL was purchased from medicine shop in Basrah as a trade name Meloxicam tablet and used with further Purification according [21,22] (m.p.= 463° K). Fig. 1 shows the molecular structure of MEL. MEL is a N-S heterocyclic

compound containing two nitrogen atoms which could be easily protonated in acid solution, and a great deal of p-electrons exists in this molecule. The concentrations range of the inhibitor used was (1×10^{-4} - 1×10^{-3} M).



4-hydroxy-2-methyl-N-(5-methyl-1,3-thiazol-2-yl)-2H-1,2-benzothiazine-3-carboxamide 1,1-dioxide

Fig .1: Shows the molecular structure of Meloxiam (MEL)[21]

2.2. Specimens preparation

Prior to all measurements, the rectangular pure aluminum 99.99 % (2.84 cm×1.13 cm × 0.23 cm) [from Ur State company for Engineering Industries-Aluminum production and manufacture factories in Nasiriah] were ground with different emery paper up to 1000 grade, washed thoroughly with bidistilled water, degreased and dried with acetone. The aggressive solution (2 M HCl) was prepared by dilution of analytical grade with bidistilled water. The solution volume was 100 cm³.

2.3. Weight loss experiment

Pure aluminum specimens in triplicate for each inhibitor concentration were immersed in the acid solutions for

3 h at different temperature. The temperature was controlled by an aqueous thermostat. After that, the specimens were removed, rinsed in water and acetone, and dried in desiccator. Then the loss in weight was determined by analytical balance (±0.1mg). The corrosion rate (v) value of weight loss measurement was calculated from the following equation [23]:

$$v = \Delta W / St \quad \dots\dots\dots(1)$$

where ΔW is the average weight loss of three parallel Al sheets, S the total surface area of the specimen, and t is the immersion time (3 h). With the calculated corrosion rate, the inhibition

efficiency (I%) was calculated as follows [24]:

$$I\% = \frac{v_0 - v}{v} \times 100 \quad \dots\dots\dots(2)$$

where v_0 and v represent the values of the corrosion rate without and with addition of the inhibitor, respectively.

2.4. Quantum chemical study

The molecular structure of the MEL had been fully geometric optimize by DFT (B3LYP/ 6-311++G(d,p)) with Gaussian 03 software package [25], the quantum chemical indices such as the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), energy gap ($\Delta E = \text{HOMO} - \text{LUMO}$), and dipole moment (μ) were considered.

3. Result and Discussion

3.1 Corrosion rate and inhibition efficiency

The inhibiting effect of MEL on the corrosion of aluminium 2 M HCl was investigated using gravimetric technique. Fig.2 illustrates the variation of weight loss with time for aluminium corrosion in the absence and the presence of different concentrations of MEL at 35 °C. The plots show that MEL inhibits aluminium corrosion in the acidic environment. Corrosion rates in inhibited systems decreased with increasing concentration of MEL, suggesting that the inhibiting effect of the drug on aluminium corrosion in 2 M HCl is concentration dependent. Similar curve not shown have been obtained for the other temperatures under study.

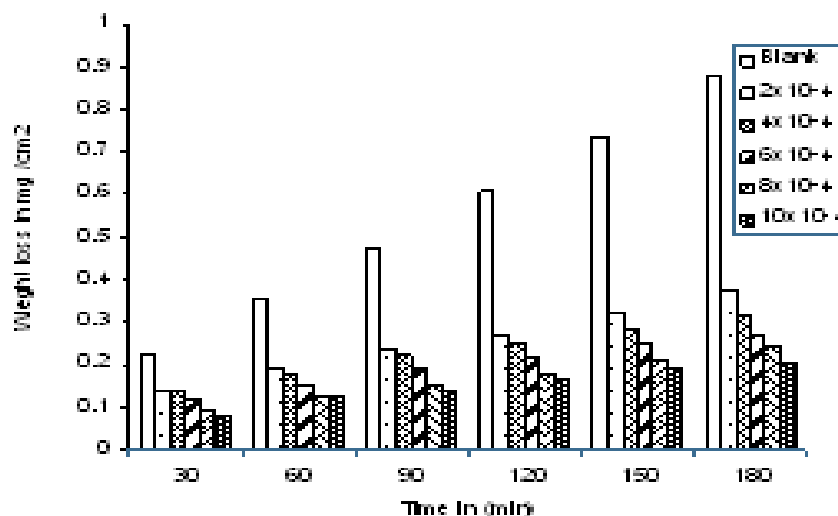


Fig.2: Weight loss-time curve for the corrosion of Al in 2M HCl in the absence and in the presence of different concentration of MEL at 35°C .

Fig. 3 compares the corrosion rates in the absence and presence of inhibitor at different temperatures after 3 h immersion period. The results indicate that introduction of MEL abridged aluminium dissolution at all temperatures studied and all

concentrations used in study. Corrosion rate decreased with increasing inhibitor concentration. This may be due to the adsorption of MEL at the Al surface also corrosion rates in inhibited as well as uninhibited systems increased with rise in temperature.

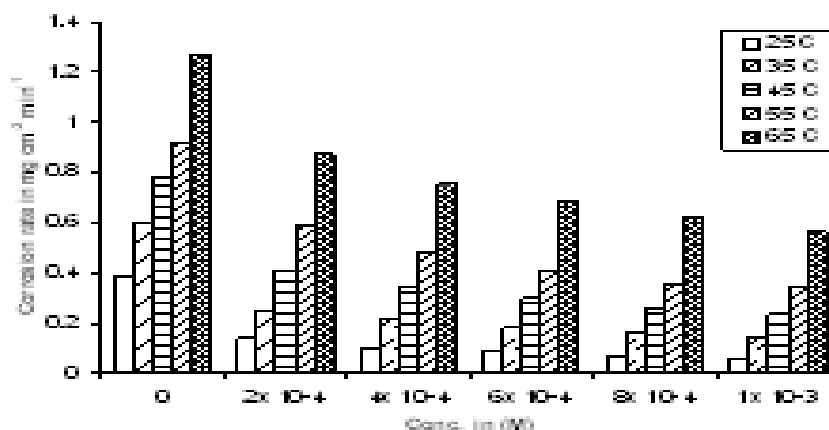


Fig .3: Variation of corrosion rate of Al at versus concentration of MEL drug

The corrosion behaviour of the aluminium specimen in the presence of MEL indicates that the drug molecules were adsorbed through nonbonding electron pairs present on nitrogen, sulfur and oxygen atoms as well as π -electrons [26] over the Al surface and that surface

coverage changed with temperature as well as concentration of the drug. As presented in Table 1, inhibition efficiency increased with MEL concentration at all temperatures. The trend of I% with temperature however follow a steady relationship.

Table 1: Corrosion parameters for Al 7075 in aqueous solution of 1M HCl in absence and presence of different concentrations of MEL from weight loss measurements at 35 °C for 3 h.

Concentration Temp. in °C	Inhibition Efficiency I %				
	25	35	45	55	65
2x 10 ⁻⁴	64.3	57.504	47.442	37.012	31.077
4x 10 ⁻⁴	73.491	64.249	56.138	47.835	40.755
6x 10 ⁻⁴	77.63	69.477	62.276	55.519	47.757
8x 10 ⁻⁴	81.57	72.344	67.263	59.74	51.14
1x 10 ⁻³	85.301	76.391	70.332	64.445	55.704

Maximum inhibition efficiency shown at 1×10^{-3} M concentration of the inhibitor in 2M HCl at 25°C (85.301), The high inhibitive performance of MEL suggests a higher bonding ability of inhibitor to the Al surface, which possess higher number of lone pairs on hetero atoms and p-orbitals.

The influence of solution temperature on inhibition efficiency is shown in fig.4 . It is observed that inhibition efficiency decreases with increase in temperature from 25 to 65°C . The decrease in inhibition efficiency with temperature may be

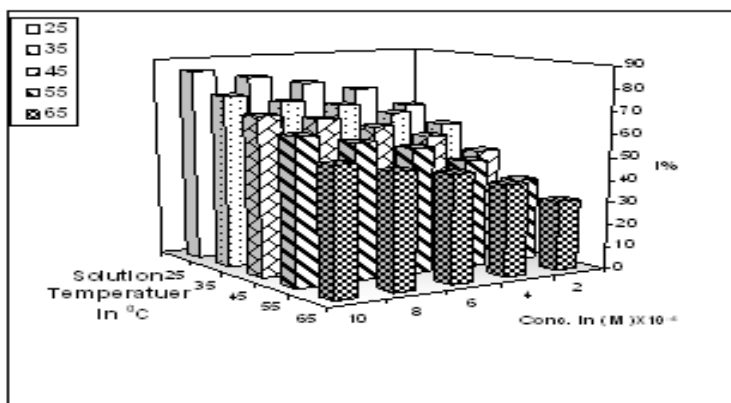
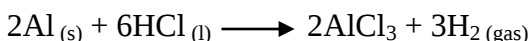


Fig. 4: Effect of different Conc. and temperature on the inhibition efficiency

attributed to desorption of the inhibitor molecule from metal surface at higher temperature [27]. Corrosion of Al in acidic environments is generally accompanied with hydrogen gas evolution and increase in temperature usually accelerates the evolution of hydrogen which results in higher dissolution rate of



the Al[28]. The decrease in inhibition efficiency may be probably due to increased rate of desorption at higher temperatures. also the increase in concentration of inhibitor lead to increase the inhibition efficiency at the same temperature.

3.1 Thermodynamic parameters and adsorption isotherm

It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal surface and the

adsorption depends on the molecule's chemical composition. Basic information on the adsorption of inhibitor on metals surface can be provided by adsorption isotherm. Attempts were made to fit the experimental data to various isotherms including Frumkin, Langmuir, Temkin, Freundlich , Bockris–Swinkels and Flory–Huggins isotherms. By far the results were best fitted by Langmuir adsorption isotherm equation [29]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \dots\dots\dots(3)$$

where c is the concentration of inhibitor, K_{ads} the adsorptive equilibrium constant, and θ represents the Surface coverage values for the inhibitor were obtained from the $\theta = I\% / 100$ for various concentrations at the studies range temperatures.

The best fitted straight line is obtained for the plot of C/θ versus C , from the intercepts of the straight lines

on the C/θ -axis, K_{ads} values can be calculated as shown in Fig. 5. The strong correlation (R^2) as shown in Table 2 . are almost nears one, suggests that

the adsorption of MEL inhibitor on the metal surface obeyed to the Langmuir's adsorption isotherm [30] , also from table 2 indicates

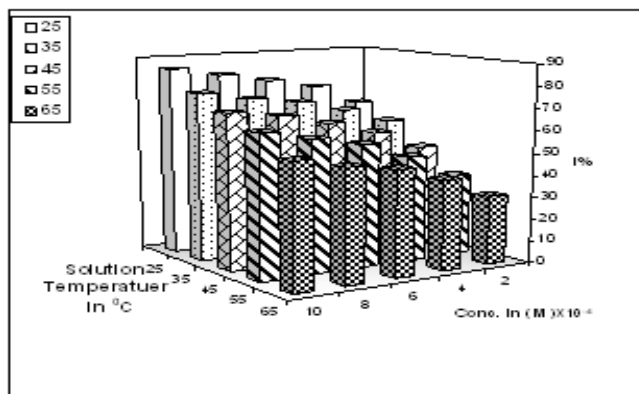


Fig. 5: Langmuir isotherm adsorption model of MEL at different Conc. on the aluminium surface.

that the adsorptive equilibrium constant K_{ads} values decrease with the increase of temperature . Large values of K_{ads} mean

better inhibition efficiency of a given inhibitor and it is in good agreement with the previous work [31].

Table 2: Adsorption parameters deduced from Langmuir adsorption isotherms

Temperature in °C	Slope	R^2	$K(M^{-1})$
25	1.12	0.998	10526.31
35	1.025	0.9979	8333.33
45	1.125	0.997	5000
55	1.05	0.9968	3125
65	1.69	0.997	2777.22

Standard free energy of adsorption, ΔG_{ads}^0 relate the K_{ads} as given by the following equation [32]:

$$\Delta G_{ads}^0 = -2.303RT \log (55.5 K_{ads})..... (4)$$

The calculated free energies (ΔG_{ads}^0) are given in Table 3; the negative values of ΔG_{ads}^0 indicate spontaneous adsorption of MEL on the Al surface as well as a strong interaction between the inhibitor molecules and the metal surface[33]. Generally, values of ΔG_{ads}^0 up to -20 kJ/mol are consistent with physisorption,

While those around -40 kJ/mol or higher are associated with chemisorptions as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate [34].

Table 3: Thermodynamic parameters of adsorption of MEL on the Al surface

Temperature in °C	ΔG_{ads}^0 (kJmol ⁻¹)	ΔH (kJmol ⁻¹)	ΔS (kJmol ⁻¹)
25	-32.9	-36.581	-0.123
35	-33.4	-36.581	-0.0103
45	-33.14	-36.581	-0.0108
55	32.82	-36.581	-0.0112
65	-33.57	-36.581	-0.0089

The values of ΔG_{ads}^0 in our measurement was less than -40kJ/mol ,suggesting that MEL strong physisorped on aluminium surface .

Thermodynamically, ΔG_{ads}^0 is related to the standard enthalpy and entropy of the adsorption process, ΔH_{ads}^0 and ΔS_{ads}^0 , respectively, via Eq. (5):

$$\Delta G_{ads}^0 = \Delta H_{ads}^0 - T\Delta S_{ads}^0 \dots\dots\dots (5)$$

and the standard enthalpy of adsorption (ΔH_{ads}^0) can be calculated according to the van't Hoff equation [35]:

$$\ln K_{ads} = \frac{-\Delta H_{ads}^0}{RT} + Const. \dots\dots\dots(6)$$

A plot of $\ln K_{ads}$ versus $1/T$ gives a straight line, as shown in Fig. 6. The slope of the straight line is $-\Delta H_{ads}^0/R$. The value of ΔH_{ads}^0 is given in Table 3. Since the ΔH_{ads}^0 value is negative, the adsorption of inhibitor molecules onto the Al surface is an exothermic process. In an exothermic process, chemisorption is distinguished from physisorption by considering the absolute value of ΔH_{ads}^0 ; for the chemisorption process, it approaches 100 kJ/mol, while for the physisorption process , it is less than 40 kJ /mol [36]. In the present study, the ΔH_{ads}^0 (physical adsorption heat)value is slightly small, once again implying that physical adsorption is taking place.

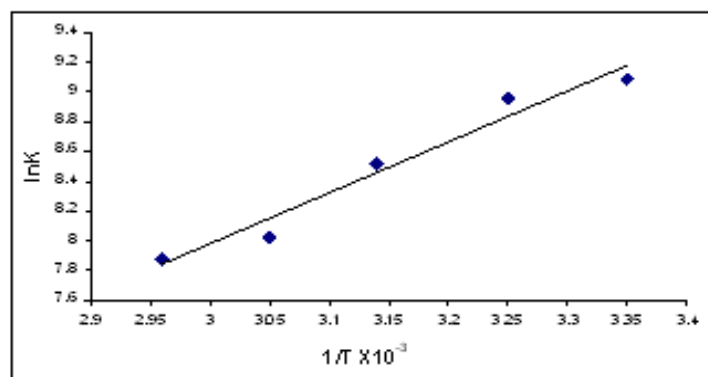


Fig.6: Plots of $\ln k(\text{equilibrium constant})$ versus $1/T \times 10^3$

The standard entropy of inhibitor adsorption, ΔS_{ads}^0 , can be calculated from Eq. (5). The calculated values of ΔS_{ads}^0 are recorded in Table 3. It is obvious that the values of ΔS_{ads}^0 are negative, as inhibitor molecules move freely in the bulk solution (are chaotic) before adsorption, while as adsorption progresses, the inhibitor molecules adsorbed onto the Al surface become more orderly, resulting in a decrease in entropy [37].

Plots of $\ln v$ vs. $1/T$ for pure aluminum in 2 M HCl in absence and presence of various concentrations of MEL are shown in fig.7 .As shown a straight line

were obtained according to Arrhenius – type equation:

$$v = A \exp\left(-\frac{E_a}{RT}\right) \dots\dots\dots(7)$$

Where v is the corrosion rate in $\text{mg cm}^2 \text{min}^{-1}$, A is constant depends on a metal type and electrolyte, E_a is the apparent activation energy, R is gas constant and is the absolute temperature. Values of E_a were determined in the presence and absence of MEL . The E_a in free acid solution is equal to 29.098 kJmol^{-1} which is of the same order of magnitude as those observed by Ashassi et al [38]

Table 4: Values of the activation energy and regression between $\ln k$ and

Conc. (M)	$E_a(kJmol^{-1})$	R^2
0	29.098	0.9805
2×10^{-4}	33.256	0.9927
4×10^{-4}	37.413	0.9847
6×10^{-4}	37.413	0.9807
8×10^{-4}	39.419	0.9813
1×10^{-3}	43.648	0.9872

Generally one can say the nature and the concentration of electrolyte affect greatly the activation energy for the corrosion process, also the relative small values of activation energy of the inhibited corrosion reaction indicate a physical adsorption takes place in the first stage. This behaviour is due to an increase in surface area of metal covered by MEL [39].

MEL planer molecules. The binding capability of a molecule depend on the

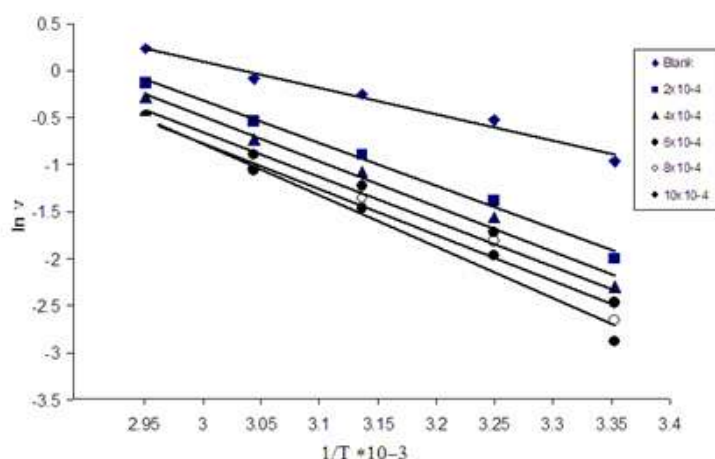


Fig.7: Plots of $\ln(\text{corrosion rate})$ versus $1/T \times 10^{-3}$ for different Concentration.

3.3 Quantum calculation

In order to obtain more information about the electronic structure and the inhibitory action of the MEL compound, Density function theory (DFT) calculations were performed using DFT(B3LYP / 6-311++G(d, p)) methods. Fig. 8a shows a full geometry optimization of the MEL molecules. It shows that the thiazol ring and substitution $-NH$ group are in the same one plane with benzene ring so the

electronic charge on the chelating atom. thus, the values were obtained by the Mulliken population analysis. Fig.8b presents Mulliken charge of the atoms in MEL molecule.

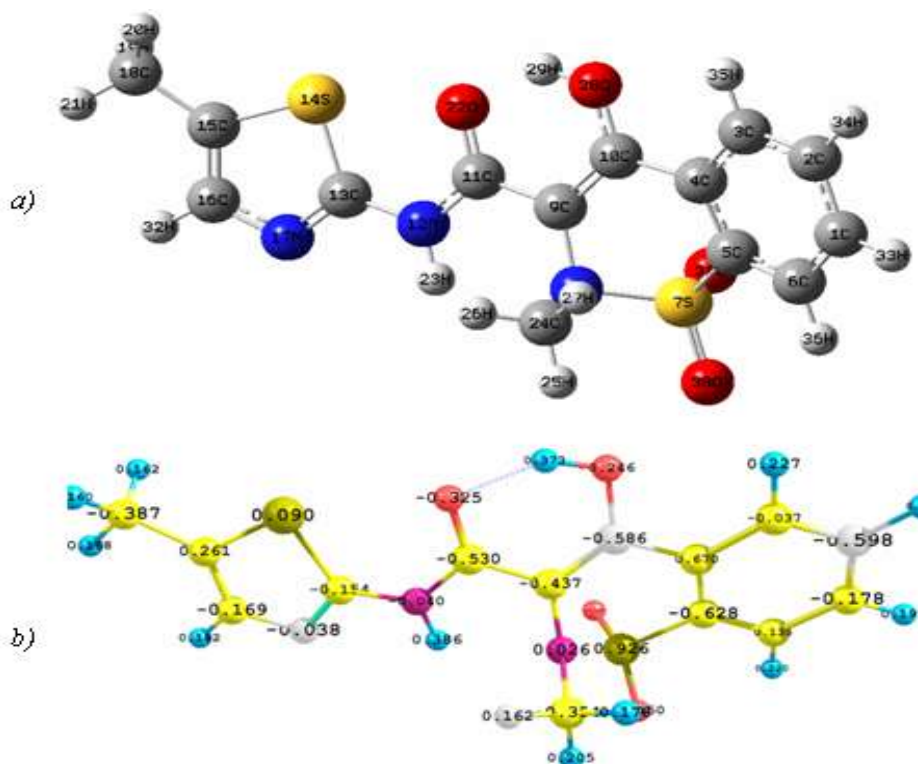


Fig.8 : Explain a)The optimization molecular structure of MEL and b) Mulliken charges of the atoms in MEL molecule

By careful examination of the values of Mulliken charges, the larger negative charge of atoms are found in (C9,C10,C11,O22 , O28, and ,C1 ,C2, C5 at the phenyl ring also C13 and C16 in the thiazol five member ring) which connect to the donating electrons, and could donate its lone electron pair to the unfilled orbital of the metal atom, the MEL molecule can be adsorbed on the metal surfaces by the above atoms .

The quantum chemical indices energies E_{HOMO} , E_{LUMO} , and ΔE have been calculated, were ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) is the gap between E_{HOMO} and E_{LUMO} . The smaller energy gap (ΔE) obtained (3.595 eV) to MEL can be interpreted by a stronger adsorption bond and perhaps greater inhibitor efficiency [40]. As

E_{HOMO} is often associated with the electron donating ability of molecule, high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy, empty molecular orbitals. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [41]. E_{LUMO} , the energy of the lowest unoccupied molecular orbital indicates the ability of the molecules to accept electrons. The lower value of E_{LUMO} , the more probable , it is that the molecule would accept electrons [41] . The obtained E_{HOMO} (-6.268 eV) which it high comparing with Lie at [42] and Yan at[43] *also the E_{LUMO} value is -2.673 eV which it small than the results given by above researcher . This may*

explain the good inhibition efficiency of MEL molecule is due to increasing energy of the HOMO and the decreasing

energy of the LUMO. Fig.9 shows the frontier orbital density distribution of HOMO and LUMO.

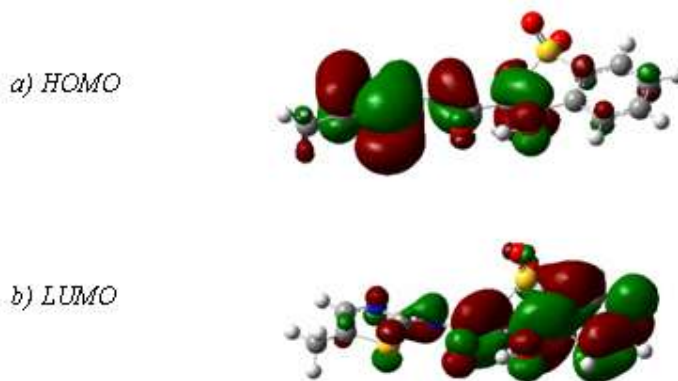


Fig.9: Three dimensions pictures of frontier orbital density distribution
a) HOMO and b) LUMO

The dipole moment (μ) is another indicator of the electronic distribution in a molecule and is one of the properties used to discuss and to rationalize the structure [44].The high value of dipole moment probably increases the inhibitor adsorption and increase of inhibition efficiency [41] the dipole moment of the MEL is 4.3523 Debye which relatively agreement to the literature including the correlation between the dipole moment and inhibition efficiency[40,45].

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