SEBHA UNIVERSITY JOURNAL OF PURE & APPLIED SCIENCES VOL.20 NO. 2 2021
DOI: 10.51984/JOPAS.V20I2.1646

مجلة جامعة سبها للعلوم البحتة والتطبيقية
Sebha University Journal of Pure & Applied Sciences

Journal homepage: www.sebhau.edu.ly/journal/index.php/jopas

Corrosion Inhibition of Mild Steel in Acidic Media by Expired *Carbimazole* Drug

*Aisha A. AL-abbassi & Ibrahim E. Shana

Chemistry Department, Faculty of science/ Sebha University, Libya

Keywords:
Corrosion
Mild Steel
Acidic Medium
Weight Loss
Inhibition Efficiency
Expired Drug
DFT Calculation

ABSTRACT

The efficiency of the anti-thyroid, Carbimazole, expired drug, (CD), as corrosion inhibitor for mild steel in 0.5MHCl was investigated by weight loss method. Data obtained from weight loss measurement were analysed, and the results show that, the used Carbimazole drug was a good inhibitor. The inhibition efficiency increases with increasing the concentration of Carbimazole inhibitor and reached a maximum value of 84.95% at 30 OC and 100 ppm of the used inhibitor. The adsorption isotherm of Carbimazole obeyed Langmuir adsorption isotherm. Chemical calculations was established by density function theory, DFT, which were performed on Carbimazole drug. Many parameters such as EHOMO (the energy of the highest occupied molecular orbital) and ELUMO (the energy of the lowest unoccupied molecular orbital), gap energy (ΔE), dipole moment (μ), electronegativity ( ), electron affinity (A), global hardness (η), softness (σ) and ionization potential (I), were calculated and correlated to the experimental data.

تأكل الحديد الصلب في الوسط الحمضي باستخدام دواء الكاربيمازول المنتهي الصلاحية

عائشة العباسي و ابراهيم شنة

قسم الكيمياء، كلية العلوم، جامعة سبها ، ليبيا

الكلمات المفتاحية:
التآكل
الحديد الصلب
الاوساط الحمضية
فقدان الوزن
كفاءة تثبيط
نظرية الكثافة الالكترونية
الدواء المنتهي الصلاحية

الملخص

تم التحقق من فعالية عقار كاربيمازول (Carbimazole) كمثبط لتآكل الحديد لصلب في (0.5 M) حمض الهيدروكلوريك بواسطة طريقة فقدان الوزن. تم تحليل البيانات التي تم الحصول عليها من دراسات فقدان الوزن، وان النتائج تظهر أن الدواء المستخدم كان مثبط جيد لتآكل الحديد الصلب في (M0.5) حمض الهيدروكلوريك. كما أظهرت النتائج ان كفاءة التثبيط تزداد مع زيادة تركيز المثبط، وكفاءة تثبيط تصل إلى 84.95 % عند تركيز 100 جزء في المليون من المثبط المستخدم وعند درجة حرارة 30 درجة مئوية. وبدراسة منحنيات الإدمصاص تبين ان إدمصاص الدواء المثبط يخضع لمنحنى إدمصاص لانجمير (Langmuir). أجريت الحسابات الكيميائية الكمية لجزئية عقار Carbimazole (CD) على أساس نظرية الكثافة الالكترونية (DFT). وعلى هذا الاساس تم قياس طاقة كل من المدارات الجزئية الرابطة والغير رابطة (EHOMO & ELUMO) وفجوة الطاقة بين المدار الرابط والغير الرابط (ΔE) وعزم ثنائي القطب (μ) والسالبية الكهربائية ( ) والميل الإلكترون (A) والصلابة (η) ليونة (σ) وجهد التأين (I). وتم ربط نتائج الحسابات النظرية ومقارنتها وربطها بالبيانات التجريبية.

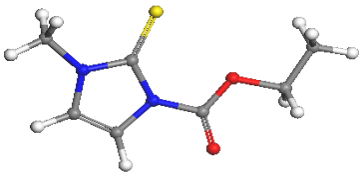
Introduction:

Corrosion is identified as the attack of metals or alloy by chemical or electrochemical reaction [1]. Steel alloys are the most widely used materials in variety of industries, frequently exposed to the acids action as acid cleaning, acid de-scaling [2-4]. Consequently, it needs to protect their structures against corrosion attack. Inhibitors are extensively used, especially in the acidic environments. An inhibitor is a chemical that diminishes the corrosion rate in a certain situation when supplied in modest amounts [5]. Acidic inhibitors are compounds which contained oxygen, sulfur and nitrogen [6-10].

Although the large spectrum of chemical compounds accessible, the majority of studied inhibitors are both expensive and harmful. Nowadays, a big concern was directed to replace an environmental unsafe inhibitors with effective non-toxic alternatives. Expired drugs (non-toxic characteristics) were used to protect metals and their alloys. Thus, expired drugs which are of no use can be investigated as corrosion inhibition. So drugs represent a promising class of inhibitors [11-13]. In light of the above observation, we aimed to investigate the inhibition characteristics of expired drug namely

*Corresponding author:
E-mail addresses: ais.alabbasi@sebhau.edu.ly , (I. E. Shana) abra.shanah@fsc.sebhau.edu.ly
Article History : Received 06 December 2021 - Received in revised form 25 December 2021 - Accepted 27 December 2021

Carbimazole (**Scheme**. **1**) on steel in HCl solution, as part of undertaken investigation in our laboratory. *Carbimazole*, a drug used was selected as a corrosion inhibitor based on its molecular structure that has O, N and S active center atoms. The corrosion inhibition behaviour of *Carbimazole* and was studied using weight loss and DFT techniques.



Scheme 1. Inhibitor molecule of *Carbimazolen* (*CD*)

2. Experimental method

2.1. Material

The expired *Carbimazole* 5 mg tablets are round, white tablet Manufactured by Amdipharm UK Limited/ London/ UK. The tests were carried out on mild steel cylinders that had been freshly produced (specimens were collected from Musrata steel factory) . Specimens used in the weight loss experiment were mechanically cut into 4.0 cm length and 1cm diameter, then abraded with SiC abrasive papers 400-1200 grit, respectively, Before being used in corrosion tests, they were cleaned in 100% ethanol and acetone, dried at room temperature, and stored in desiccators prior to use.

2.2. Solutions

The aggressive HCl molar solution of 0.5 M were made by diluting analytical grade 37 percent HCl with distilled water. The concentration range of *Carbimazole* prepared and used in this study was 50 - 500 ppm. The inhibitor was prepared by dissolving the appropriate amount in distilled water.

2.4. Gravimetric measurements

In this study, weight loss technique was used to investigate the inhibition characteristic of *Carbimazole* drug. In an open beaker, a previously weighed mild steel coupon was immersed entirely in 50 mL of the test solution.. The beaker was placed in a water bath that was kept at 313 K. After a 90-minute delay, the coupons were retrieved, rinsed multiple times in deionized water, cleaned, dried in acetone, and re-weighed. By comparing the weight of mild steel coupons before and after immersion in various test solutions, the weight loss was estimated in milligrams. The corrosion rate in mg cm-2 min-1 was determined using the equation below. [14, 15]:

$$R\ (mg\ cm^{-2}min^{-1}) = \left(W / At \right) \qquad (1)$$

where W denotes the average weight loss of mild steel specimen; A is the entire area of one mild steel specimen; and t denotes the time spent immersed (90 min). Equations 2 and 3 were used to calculate the inhibitor efficiency (I %) and degree of surface coverage (Θ) based on the weight loss data.

$$I\% = \left(1 - \frac{R_{inh}}{R_0}\right) \times 100 \qquad (2)$$

$$\theta = \left(1 - \frac{R_{inh}}{R_0}\right) \qquad (3)$$

where R_{inh} and R_0 are the corrosion rate of mild steel in acidic solutions in the presence and absence of the inhibitor.

2.5. Details of the computational calculations

The molecular geometry, the orbitals energies of HOMO and LUMO, of the pharmacological inhibitor were computed using DMol^3 and the Materials Studio suite of programs at the DFT (Density Function Theory) level (version 5.5). To map the orbital structure of the complex, structure optimization calculations were done using a generalized gradient approximation (GGA) function [16, 17] and a hybrid exchange–correlation function (Becke-Lee-Yang-Parr) BLYP [18, 19] with a double numeric plus polarization (DNP) basis set.

The energy gap between the HOMO and LUMO molecular orbitals, as well as the gap of energy (ΔE), are used to estimate molecule reactivity. The HOMO and LUMO energies are connected to the electron affinity, (A), the and ionization potential, (I), according to Koopman's theorem [20-22] by the following equations:

$$\Delta E = E_{HOMO} - E_{LUMO} \qquad (4)$$

$$I = -E_{HOMO} \qquad (5)$$

$$A = +E_{LUMO} \qquad (6)$$

Absolute electronegativity, (χ) and global hardness, (η), Softness, (σ), of the *Carbimazole* inhibitor are given by Pearson [22].

$$\chi = \frac{I + A}{2} \qquad (7)$$

$$\eta = \frac{I - A}{2} \qquad (8)$$

$$\sigma = \frac{1}{\eta} \qquad (9)$$

3. Results and discussion

The gravimetric method of inhibition testing is one of the most extensively employed. The Mass loss approach has become the standard method of measurement for many corrosion-monitoring systems because it is simple and reliable.

3.1. Inhibition characteristic of Carbimazole

The mass loss method was used to investigate the corrosion rate of steel in the presence and absence of *Carbimazole* at 303 K. The computed rates in mg $cm^{-2}min^{-1}$, and inhibition efficiency (I %) for steel dissolution in HCl (0.5 M) in the absence and the presence of expired *Carbimazole* drug are shown in **Table (1)** and **Fig. (1)**.

Table 1: Corrosion rate and inhibition efficiency of *Carbimazole* in the absence and presence of HCl at 30°C.

CD Conc. (ppm)	R x 10^{-2} (mg cm^{-2} min^{-1})	I%
100	0.001877	84.95
80	0.001976	84.12
70	0.002086	83.28
60	0.00225	81.96
50	0.002303	81.54
40	0.002642	78.82
20	0.004804	61.51
10	0.008612	30.96
0	0.012474	-

From the obtained data in **Table (1)**, it is apparent that, there is a decline in the rate of corrosion of steel in the presence of *Carbimazole*, when it was compared to the blank solution.

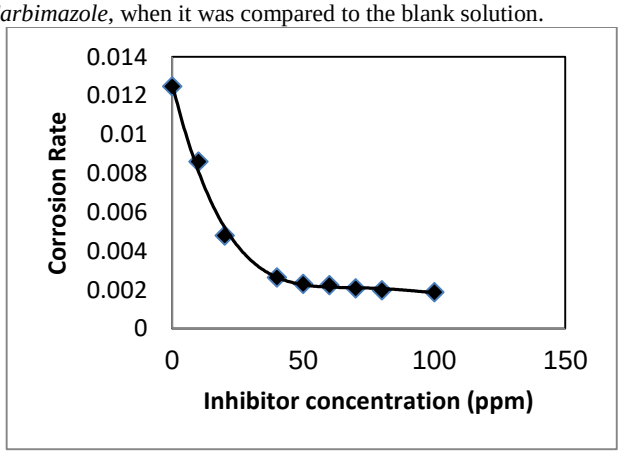


Fig. 1: The change of the *Carbimazole* concentration impact on the rate of steel corrosion of in HCl .

The rate steel corrosion (**Fig. (1)**) was decreased with an increase in the *Carbimazole* concentration. The last observation indicates that the presence of the *Carbimazole* in the solution will inhibit the steel corrosion in acid environment and that the level of inhibition will depend on the quantity of *Carbimazole* that present in investigated solution. Moreover, It has been revealed that as the concentration of

carbimazole increases the efficiency of inhibition increase as presented in **Fig. (2).**

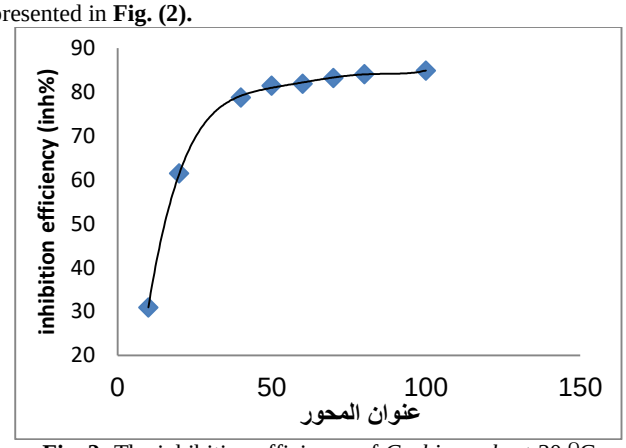


Fig. 2: The inhibition efficiency of *Carbimazole* at 30 ^{O}C

3.2. Adsorption isotherms

When there is not enough Fe-(Inh)$_{ads}$

The adsorption isotherm can display how the inhibitor interacts with the steel surface. The adsorbed layer prevents the acid solution from acting on the metal surface. When there aren't enough Fe-(Inh)$_{ads}$ to protect the metal surface (due to inactive adsorption or low inhibitor concentration), metal dissolution occurs at Fe-(Inh)$_{ads}$ sites on the steel surface. When sufficient inhibitor concentrations are present, a condensed and coherent inhibitor layer forms on the steel surface, preventing it from the chemical attack of the acid medium. Adsorption of an organic species on a metal surface is assumed to be a substitution process between the organic molecules Org$_{(aq)}$ in the aqueous phase and the water molecules adsorbed on the metal surface $H_2O_{(s)}$.

To derive the adsorption isotherm, Equation 3 was utilized to calculate the degree of surface covered (Θ) for various inhibitor amounts.

Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (10)$$

where k_{ads} denotes the equilibrium constant of the process of adsorption.

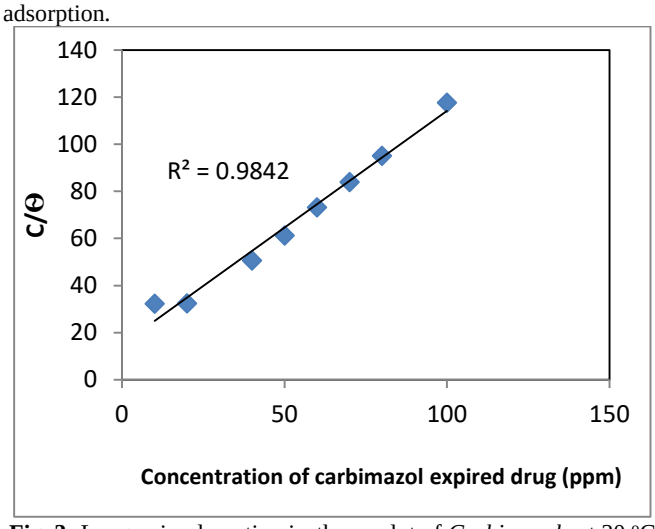


Fig. 3: Langmuir adsorption isotherm plot of *Carbimazole* at 30 ºC

Fig. (3) displays the curve of (C/Θ) against *Carbimazole* inhibitor concentration (C). Straight line plot with a 98.5 % correlation coefficient and a slope equal to unite were obtained . **Table 3** shows the Langmuir adsorption characteristics in HCl in the presence of *carbimazole*. The equilibrium constant for the adsorption process, which is related to the standard free energy of adsorption ΔG_{ads} by [23], is included in expressions of:

$$\Delta G^{o}_{ads} = -RT \ln(55.5 K_{ads}) \qquad (11)$$

where $-\Delta G^{o}_{ads}$, *R and T* donated to the adsorption free energy, the gas constant and the system temperature, respectively. In general, values up to −20 kJ mol^{-1} are consistent with the attractive forces between ionic species and charged metal (physisorption), whereas values larger than −40 kJ mol^{-1} involve the transfer of charged pairs or organic molecules onto the metal surface, forming a type of coordinated bond (chemical adsorption) [24, 25].

Table 2: Obtained parameters of thermodynamic–kinetic model and Langmuir isotherm for *Carbimazole* at 30 ºC

Parameter	K_{ads}	ΔG^{o}_{ads}
CD	0.066	-3.27 KJ/mol

The obtained data from this study was −3.27 kJ mol^{-1} for the *Carbimazole* which indicates that the mechanism of *Carbimazole* adsorption on steel in HCl environment at room temperatures is a physisorption.

3.3. Theoretical calculation

The structural characteristics that determine the *Carbimazole* inhibitor efficiency were investigated using quantum chemical simulations. The inhibitors' geometric and electronic structures were calculated by optimizing their energy, bond length, and angle. The computed bond lengths of *Carbimazole* molecules are in the typical range of single and double bond lengths, corresponding to the global minimum optimal structure in the neutral form (**Table (3)**). **Fig. (4)** shows the optimized molecular structures with the lowest energy obtained from DFT computations. The electronic density on the vacancy molecule is equally distributed in the figure.

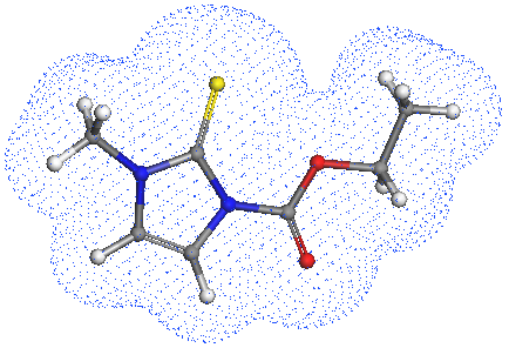


Fig. 4: Optimized molecular structure and electron density of *Carbimazole* drug

The centers of adsorption of the inhibitor molecule was predicted using the highest occupied HOMO, and lowest unoccupied LUMO orbitals as presented in **Fig. (5)**. The HOMO and the LUMO were being used to estimate the adsorption active site of the inhibitor molecules LUMO. According to the theory of the frontier molecular orbital, the generation of a chemical inhibitor transition state is attributable to a collision between the interacting inhibitor's HOMO and LUMO [26-30]. The establishment of a chemical inhibitor transition state is influenced by the interactions of the active inhibitor's HOMO and LUMO. The HOMO energy reflects a molecule's capability to donate electrons and its susceptibility to be attacked by electrophiles. The high value of E_{HOMO}, (-4.799 eV), suggests that the molecules prefer to donate electrons to acceptor molecules with low energy orbitals or unoccupied electron orbitals [26, 29].

In contrast, the LUMO energy describes the ability of molecules to accept electrons including its accessibility to nucleophilic attack. E_{LUMO} of 1.81- eV has a low value, indicating that an inhibitor molecule can accept electrons [26].

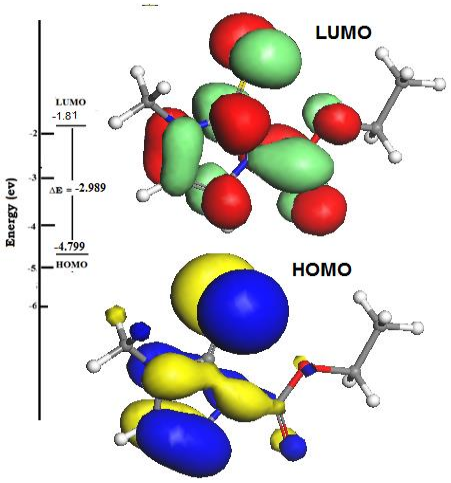


Fig. 5: HOMO and LUMO of the *Carbimazole* molecule

Table 4: Chemical reactivity parameters of *Carbimazole* molecule

Parameters	quantities
E_{HOMO}	-4.799
E_{LUMO}	-1.81
Energy band gap (ΔE)	2.989
Ionization potential (I)	4.799
Electroaffinity (A)	-1.81
Electronegativity (χ)	1.4945
Global hardness(η)	2.203
global softness (σ)	0.454

Carbimazole inhibitor adsorption at iron alloy surfaces occurs via electro transfer, which involves the π-electrons of aromatic rings, or by non-bonded electrons of hetero-atoms as O, N and/or S which interacting with the unoccupied d-orbitals of metal surface atoms [31]. *Carbimazole* molecules possibly will be adsorbed on metal surfaces through the physiosorption mechanism, which includes the water molecules displacement from the iron surface and interfaces between sulphur, oxygen, nitrogen, and Fe atoms. (**Fig. (6**)).

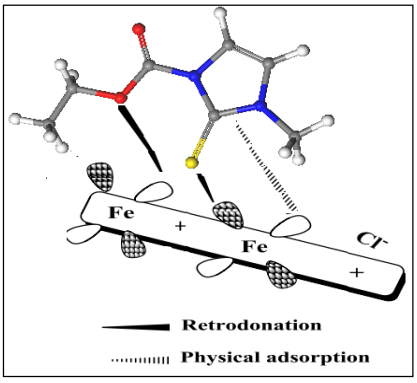


Fig. 6: Suggested adsorption mechanism of *Carbimazole* expired drug on the iron surface

4. **Conclusion**

The *carbimazole* drug (CD) was revealed to be a mild steel corrosion inhibitor in an HCl environment. *Carbimazole* concentration improved the effectiveness of inhibition. To fit the *Carbimazole* adsorption, the Langmuir and adsorption isotherms can be utilized. *Carbimazole* adsorption on mild steel in HCl solution is a physisorption process at the temperatures investigated. According to evidence generated from quantum chemical studies using DFT, LUMO and HOMO are distributed throughout the length of drug molecules.

Acknowledgment

The authors wish to acknowledge chemistry department - Sebha University for providing the necessary facilities to carry out the studies.

References

[1]- D. A. Jones, *Principles and Prevention of Corrosion*. Prentice Hall, 1996.

[2]- B. Sanyal, "Organic compounds as corrosion inhibitors in different environments: A review," *Progress in Organic Coatings*, vol. 9, no. 2, pp. 165-236, 1981, doi: http://dx.doi.org/10.1016/0033-0655(81)80009-X.

[3]- E. Ghali, V. S. Sastri, and M. Elboujdaini, *Corrosion Prevention and Protection: Practical Solutions*. Wiley, 2007.

[4]- P. Marcus, *Corrosion Mechanisms in Theory and Practice, Third Edition*. Taylor & Francis, 2011.

[5]- S. A. Abd El–Maksoud, "The Effect of Organic Compounds on the Electrochemical Behaviour of Steel in Acidic Media. A review," *Int. J. Electrochem. Sci.,*, vol. 3, pp. 528-555, 2008.

[6]- K. F. Khaled and N. Hackerman, "Investigation of the inhibitive effect of ortho-substituted anilines on corrosion of iron in 1 M HCl solutions," *Electrochimica Acta*, vol. 48, no. 19, pp. 2715-2723, 2003, doi: http://dx.doi.org/10.1016/S0013-4686(03)00318-9.

[7]- M. J. Bahrami, S. M. A. Hosseini, and P. Pilvar, "Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium," *Corros Sci*, vol. 52, 2010, doi: 10.1016/j.corsci.2010.04.024.

[8]- C. M. Goulart, A. Esteves-Souza, C. A. Martinez-Huitle, C. J. F. Rodrigues, M. A. M. Maciel, and A. Echevarria, "Experimental and theoretical evaluation of semicarbazones and thiosemicarbazones as organic corrosion inhibitors," *Corrosion Science*, vol. 67, pp. 281-291, 2012, doi: http://dx.doi.org/10.1016/j.corsci.2012.10.029.

[9]- M. S. Suliman, Al-abbasi A., "The Synergistic effect of halide ions and organic nitrogen containing compounds on the inhibition of mild steel corrosion in hydrochloric acid solution," in *The 6th Libyan corrosion conference 2007*, Tripoli. Libya` 2007, vol. 6.

[10]- M. Yadav, S. Kumar, R. R. Sinha, I. Bahadur, and E. E. Ebenso, "New pyrimidine derivatives as efficient organic inhibitors on mild steel corrosion in acidic medium: Electrochemical, SEM, EDX, AFM and DFT studies," *Journal of Molecular Liquids*, vol. 211, pp. 135-145, 2015, doi: http://dx.doi.org/10.1016/j.molliq.2015.06.063.

[11]- G. k. Gece, "Drugs: A review of promising novel corrosion inhibitors," *Corrosion Science*, vol. 53, no. 12, pp. 3873-3898, 2011, doi: http://dx.doi.org/10.1016/j.corsci.2011.08.006.

[12]- S. Karthikeyan, "Drugs/Antibiotics as potential corrosion inhibitors for Metals - A Review," *International Journal of ChemTech Research*, vol. 9, pp. 251-259, 2016.

[13]- G. T. A. AL-abbassi, E. Matrood, A. Dnkm, A. Sallh, R. Izrik, M. Suliman, "Study of the Behavior of Sodium Diclofenac Expired Drug as an Corrosion Inhibitor of Iron in Sulfuric Acid Using UV-VIS Spectrophotometry," *International Journal of Scientific Research in Science, Engineering and Technology*, vol. 7, no. 2, pp. 233-242, 2020.

[14]- A. AL-Abbasi, "Study of corrosion inhibition kinetics of steel by using some organic compounds," MSc, CHEMISTRY DEPARTMENT, Sebha University, Sebha, 2006.

[15]- S. M. M. M. Al-abbasi A., "The Synergistic Effects of Iodide Ions on the Corrosion Inhibition of Mild Steel in H2SO4 Using phenyl Benzoylthiourea," presented at the The first International Conference on Science and Technology, Sebha / Libya, 2.017.

[16]- J. P. Perdew, K. Burke, and Y. Wang, "Generalized gradient approximation for the exchange-correlation hole of a many-electron system," *Physical Review B*, vol. 54, no. 23, p. 16533, 1996.

[17]- B. Jon, K. Alain, and D. Bernard, *The generation and use of delocalized internal coordinates in geometry optimization*. AIP, 1996, pp. 192-212.

[18]- A. D. Becke, "Density-functional exchange-energy approximation with correct asymptotic behavior," *Physical Review A*, vol. 38, no. 6, p. 3098, 1988.

[19]- C. Lee, W. Yang, and R. G. Parr, "Development of the Colle-Salvetti correlation-energy formula into a functional of the

electron density," *Physical Review B*, vol. 37, no. 2, p. 785, 1988.

[20]- Y. S. Kara, S. G. Sagdinc, and A. Esme, "Theoretical study on the relationship between the molecular structure and corrosion inhibition efficiency of long alkyl side chain acetamide and isoxazolidine derivatives," *Protection of Metals and Physical Chemistry of Surfaces*, journal article vol. 48, no. 6, pp. 710-721, 2012, doi: 10.1134/s2070205112060056.

[21]- V. S. Sastri and J. R. Perumareddi, "Selection of Corrosion Inhibitors for Use in Sour Media," *CORROSION*, vol. 50, no. 6, pp. 432-437, 1994, doi: doi:10.5006/1.3293521.

[22]- R. G. Pearson, "Absolute electronegativity and hardness: application to inorganic chemistry," *Inorganic Chemistry*, vol. 27, no. 4, pp. 734-740, 1988, doi: 10.1021/ic00277a030.

[23]- A. A. EL-Awady, Abd EL-Nabey, B. A., Aziz, S. G. , "Kinetic-Thermodynamic and Adsorption Isotherms Analyses for the Inhibition of the Acid Corrosion of Steel by Cyclic and Open-Chain Amines," *J. Electrochem. Soc.*, vol. 139, pp. 2149-2154, 1992.

[24]- I. B. Obot and N. O. Obi-Egbedi, "Anti-corrosive properties of xanthone on mild steel corrosion in sulphuric acid: experimental and theoretical investigations," *Curr Appl Phys*, vol. 11, 2010, doi: 10.1016/j.cap.2010.08.007.

[25]- F. M. Donahue, . and Nobe K., "Theory of Organic Corrosion Inhibitors: Adsorption and Linear Free Energy Relationships," *The Electrochemical Society*, vol. 112, no. 9, pp. 886-891, 1965.

[26]- J. M. Costa and J. M. Lluch, "The use of quantum mechanics calculations for the study of corrosion inhibitors," *Corros Sci*, vol. 24, 1984, doi: 10.1016/0010-938x(84)90113-6.

[27]- G. Gece, "The use of quantum chemical methods in corrosion inhibitor studies," *Corros Sci*, vol. 50, 2008, doi: 10.1016/j.corsci.2008.08.043.

[28]- E. E. Ebenso, D. A. Isabirye, and N. O. Eddy, "Adsorption and quantum chemical studies on the inhibition potentials of some thiosemicarbazides for the corrosion of mild steel in acidic medium," *Int J Mol Sci*, vol. 11, 2010, doi: 10.3390/ijms11062473.

[29]- N. A. Wazzan, "DFT calculations of thiosemicarbazide, arylisothiocynates, and 1-aryl-2,5-dithiohydrazodicarbonamides as corrosion inhibitors of copper in an aqueous chloride solution," *Journal of Industrial and Engineering Chemistry*, vol. 26, pp. 291-308, 2014, doi: http://dx.doi.org/10.1016/j.jiec.2014.11.043.

[30]- S. Martinez, "Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms," *Materials Chemistry and Physics*, vol. 77, no. 1, pp. 97-102, 2003, doi: http://dx.doi.org/10.1016/S0254-0584(01)00569-7.

[31]- R. Agrawal, Namboodhiri, TKG. , "The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas," *Corros. Sci.*, vol. 30 pp. 37-52, 1990.