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Theoretical evaluation of 1,4-dihydro-6-methyl-quinoxaline-2,3-dione (P2) as a corrosion inhibitor for mild steel in HCl solution)

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ABSTRACT

This paper describes the inhibitory effect of 1,4-dihydro-6-methyl-quinoxaline-2,3-dione(P2)on corrosion of mild steel in aqueous 1 M HCl .The inhibition behavior of P2 was investigated using different techniques (weight loss method, potentiodynamic polarisation technique and electrochemical impedance spectroscopy (EIS)).The nature of adsorption of compound P2 on mild steel surface is found to obey Langmuir adsorption isotherm. EIS measurement result is also correlated with the result of polarization. EIS plots exhibit individual capacitive loop. The presence of P2 in 1 M HCl solution increases charge transfer resistance, while it reduces double layer capacitance values. DFT study confirmed the adsorption of inhibitor molecules on mild steel surface.

Keywords: Mild steel; Acid corrosion; EIS; Corrosion inhibition; DFT.

INTRODUCTION

Quinoxalines are a versatile class of nitrogen containing heterocyclic compounds and they constitute useful intermediates in organic synthesis and medicinal chemistry. Quinoxaline derivatives possess a broad spectrum of biological activities including anti-bacterial, [1] anti-inflammatory, [2] anticancer, [3] and kinase inhibitors.[4] In addition, quinoxaline derivatives have been evaluated as anthelmintic agents, semiconductors, dyes and biocides [5,6]. (Figure 1).

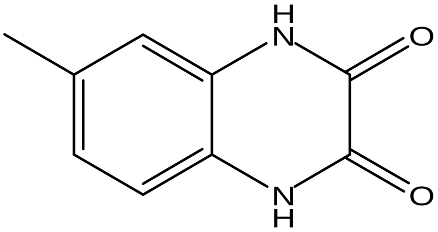
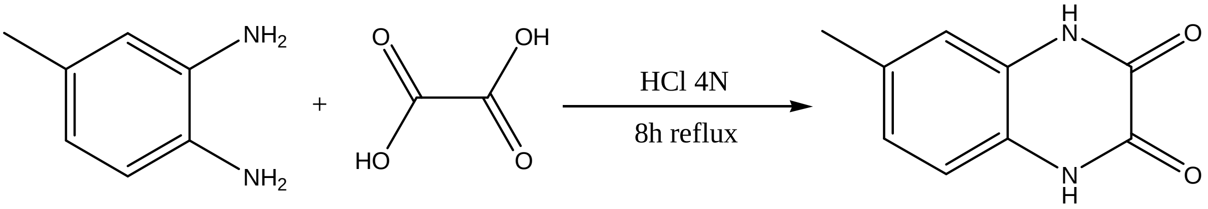


Figure 1: 1,4-dihydro-6-methyl-quinoxaline-2,3-dione (P2)

MATERIALS AND METHODS

2.1. Synthesis of inhibitor

1,4-dihydro-6-methyl-quinoxaline-2,3-dione was synthesized by the condensation of 18 mmol of 4-methyl-*o*-phenylenediamine with 20 mmol of oxalic acid by heating under reflux for 8 hours in 25 ml of hydrochloric acid solution (4N) (Scheme 1)



Scheme 1: Synthesis of 1,4-dihydro-6-methyl-quinoxaline-2,3-dione (P2)

2.2. Materials:

The mild steel strips having a composition (wt.%) of 0.09% P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance were mechanically cut into 1.5× 1.5 × 0.05 cm^3 dimensions for the electrochemical experiments. The surface of the specimens was abraded with emery paper grade 600 and 1200, which was then washed in deionized water, degreased ultrasonically in ethanol and acetone. The acid solutions (1.0 M HCl) were prepared by dilution of analytical reagent-grade 98 % HCl with double-distilled water. The range of concentration of P2 was 10^{-6} M to 10^{-3} M.

2.2.1. Electrochemical measurements

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Before all experiments, the potential was stabilized at free potential during 30 min. The solution test is there after de-aerated by bubbling nitrogen. The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

RESULTS AND DISCUSSION

3.1. Corrosion performance

Electrochemical impedance spectroscopy (EIS) is commonly used technique in corrosion researches to explain the mechanisms and adsorption phenomena [7, 8]. Especially, in inhibition studies, a single semi-circular shape is observed for mild steel in acidic media [9–11]. As in previous studies [12], the parallel results were detected in EIS data. The EIS results and equivalent circuit were presented in Figures 1 and 2, respectively. In this equivalent circuit, Rs is the solution resistance; Rct presents charge transfer resistance. It is the diameter of Nyquist plot shows the difference in real impedance at lower and higher frequencies. The CPE is the constant phase element which is used in place of double layer capacitance (Cdl) to give non-ideal capacitive behavior [13].

In Figure 1, Nyquist plots for mild steel in 1 M HCl solution with, and without different concentrations of the P2 were seen. The Nyquist plots were detected as one part of a semicircle. The Rct increased with increasing P2 concentration. The maximum value was 100 Ωcm^2 in Table 1.

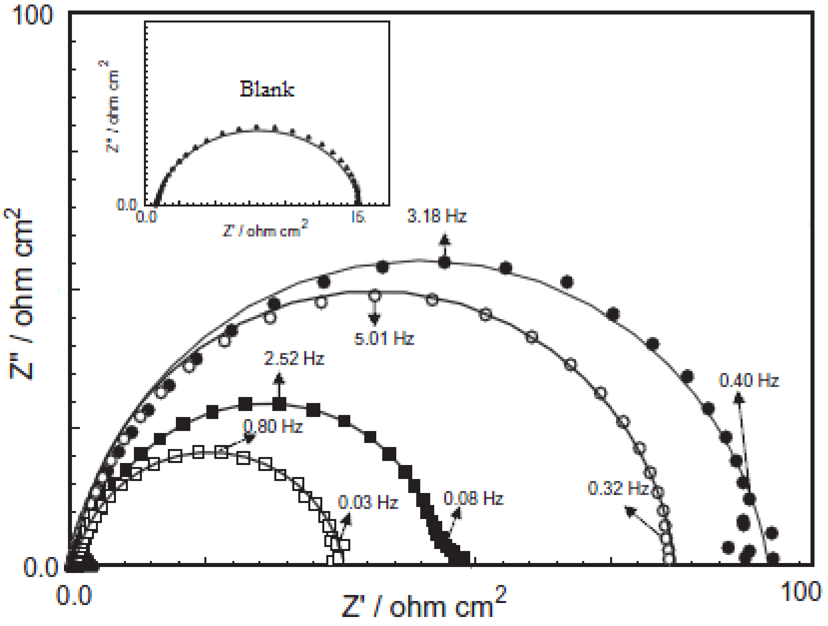


Figure 1. Nyquist plots of mild steel electrode obtained in 1 M HCl solution containing various concentrations of P1

Table 1. Electrochemical parameters for mild steel electrode corresponding to the EIS data in 1 M HCl solution in the absence and presence of various concentrations containing P2

Inhibitor	**Concentration** (M)	**R$_{ct}$** (Ω cm^2)	**CPE** /(µF/cm^2)	**n**	**E** (%)
HCl	**1**	12	891	0.86	--
P2	**10^{-6}**	65	216	0.89	89
	10^{-5}	87	130	0.90	90
	10^{-4}	92	78	0.90	90
	10^{-3}	100	67	0.91	91

In Table 1, the inhibition efficiency was symbolized as E and calculated by using the following equation [14]:

$$E\% = (R_{t(inh)} - R_{t(0)} / R_{t(inh)})*100 \qquad \textbf{(1)}$$

Where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively.

As seen from Table 1, E values increased and CPE decreased with increasing P2 concentration. The decrease in CPE depends on a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer [15]. The displacement occurs between P2 with water molecules during adsorption of P2 on mild steel surface, therefore electrical capacity decreases. As expected, the thickness of electrical double layer increases with increasing inhibitor molecule concentration [16].

Due to ensure and prove the Rct and E values. The maximum E was 91% for mild in 10^{-3} M P2 containing medium.

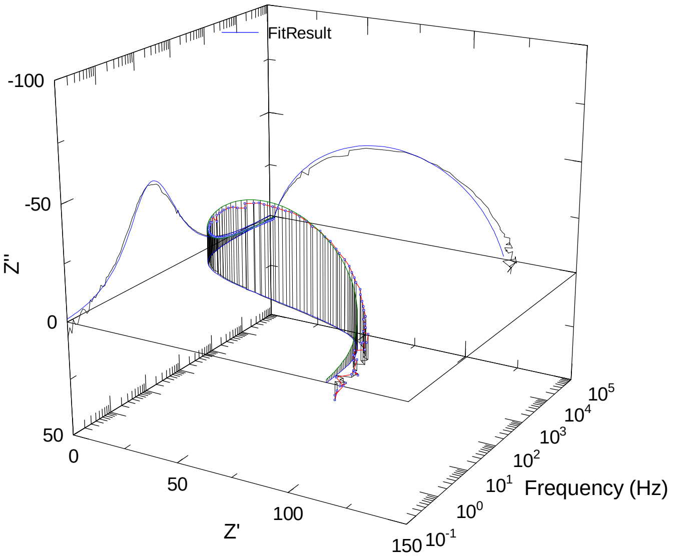


Figure 2. EIS Nyquist and Bode diagrams 3D for mild steel/1 M HCl + 10^{-3} M of P2 interface: (------) experimental; (------) fitted data.

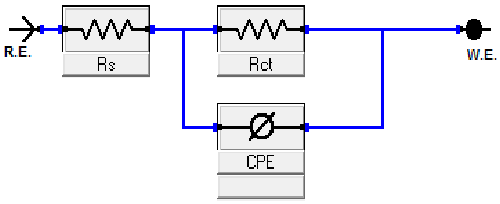


Figure 3. Electrical equivalent circuit model used for the modeling metal/solution

3.2. Adsorption isotherm

The interaction between the metal surface and the organic molecules is expressed by adsorption isotherms. Adsorption of organic molecules on a metal surface is a substitution process between the water molecules at the metal surface and P2 molecules in the electrolyte solution [17]. The adsorption of the inhibitors on the mild steel depends on the degree of surface coverage (θ). The degree of surface coverage (θ) at different concentrations of the inhibitors on the corrosion of mild steel was calculated from EIS results. The best fit among the tested various isotherms was obtained with the use of the Langmuir adsorption isotherms (Figure 4), which may be expressed by the following equation:

$$\frac{C}{\theta} = \frac{1}{k} + C \qquad \textbf{(2)}$$

Where C_{inh} is inhibitor concentration, and K_{ads} is equilibrium constant of adsorption.

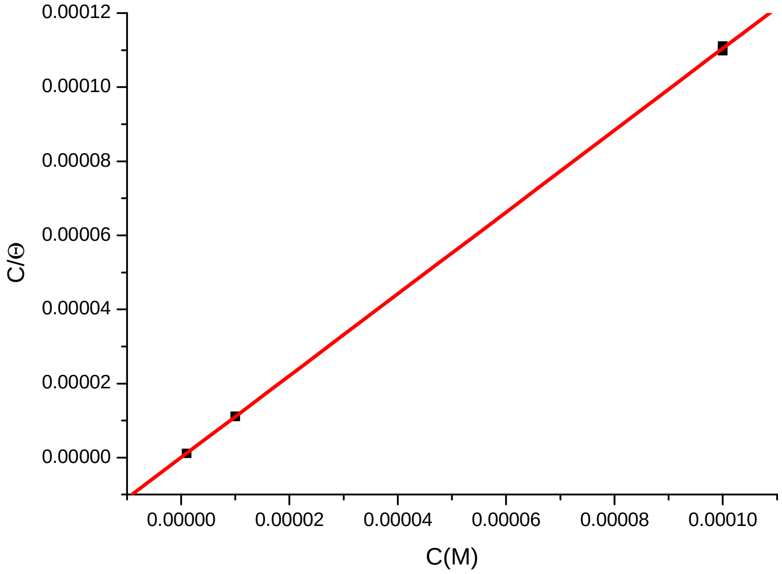


Figure 4. Langmuir adsorption plot for the mild steel electrode in 1 M HCl containing different concentrations of P2

The plots of C_{inh}/θ versus C_{inh} show the expected linear relationship for P2 in Figure 4. The K_{ads}, obtained from linear equation of the straight line is 2.44×10^7 for P2. The Langmuir isotherm indicates that one monolayer of P2 molecule is formed on the metal surface [18]. Based on the Langmuir isotherm, the standard free energy of adsorption ($\Delta G°_{ads}$) can be estimated by the following equation:

$$\Delta G_{ads} = -RT\ln(55,5K) \qquad \textbf{(3)}$$

Where R is the universal gas constant and T is the absolute temperature.

According to Eq. (3), $\Delta G°_{ads}$ was calculated as −53.82 kJ mol^{-1} at 308 K, which suggested that the adsorption of inhibitor molecules is not merely physisorption and it may include a comprehensive adsorption (physical and chemical adsorption). However, the adsorption of inhibitor molecules on the metal surfaces cannot be accepted as completely physical or chemical phenomenon. In fact, there is no clear boundary between the physical and chemical adsorption. In general, physisorption is recognized as the first step of chemical adsorption [19]. Namely, besides physical adsorption, chemical adsorption can also be possible for adsorption of P2 molecules on mild steel surface. $\Delta G°_{ads}$ value obtained in this study indicates that the inhibitor adsorbs on the metal surface both physically and chemically, but physisorption is the predominant mode of adsorption [20–27].

3.3. Quantum chemical calculations

Quantum chemical calculations are used to correlate experimental data for inhibitors obtained from different techniques (viz., electrochemical and weight loss) and their structural and electronic properties. According to Koop man's theorem [28], E_{HOMO} and E_{LUMO} of the inhibitor molecule are related to the ionization potential (I) and the electron affinity (A), respectively. The absolute electronegativity (χ) and global hardness (η) of the inhibitor molecule are approximated as follows [29]:

$$\chi = \frac{I+A}{2}\ , \quad \chi = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \ \textbf{(4)}$$
$$\eta = \frac{I-A}{2}\ , \quad \eta = -\frac{1}{2}(E_{HOMO} - E_{LUMO}) \ \textbf{(5)}$$

Where I = $-E_{HOMO}$ and A= $-E_{LUMO}$ are the ionization potential and electron affinity, respectively.

The fraction of transferred electrons ΔN was calculated according to Pearson theory [30]. This parameter evaluates the electronic flow in a reaction of two systems with different electro negativities, in particular case; a metallic surface (Fe) and an inhibitor molecule. ΔN is given as follows:

$$\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})} \ \textbf{(6)}$$

Where χFe and χinh denote the absolute electronegativity of an iron atom (Fe) and the inhibitor molecule, respectively; ηFe and ηinh denote the absolute hardness of Fe atom and the inhibitor molecule, respectively. In order to apply the eq. 6 in the present study, a theoretical value for the electronegativity of bulk iron was used χFe = 7 eV and a global hardness of ηFe = 0, by assuming that for a metallic bulk I = A because they are softer than the neutral metallic atoms [31].

The electrophilicity introduced by Sastri et al [29], is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a compound within a relative scale. They have proposed the ω, as a measure of energy lowering owing to maximal electron flow between donor and acceptor, which defined as follows.

$$\omega = \frac{\chi^2}{2\eta} \quad (7)$$

The Softness σ is defined as the inverse of the η [32, 33]:

$$\sigma = \frac{1}{\eta} \quad (8)$$

3.4. Theoretical study

3.4.1. Quantum chemical calculations

In the last few years, the FMOs (HOMO and LUMO) are widely used for describing chemical reactivity. The HOMO containing electrons, represents the ability (E_{HOMO}) to donate an electron, whereas, LUMO haven't not electrons, as an electron acceptor represents the ability (E_{LUMO}) to obtain an electron. The energy gap between HOMO and LUMO determines the kinetic stability, chemical reactivity, optical polarizability and chemical hardness–softness of a compound [34].

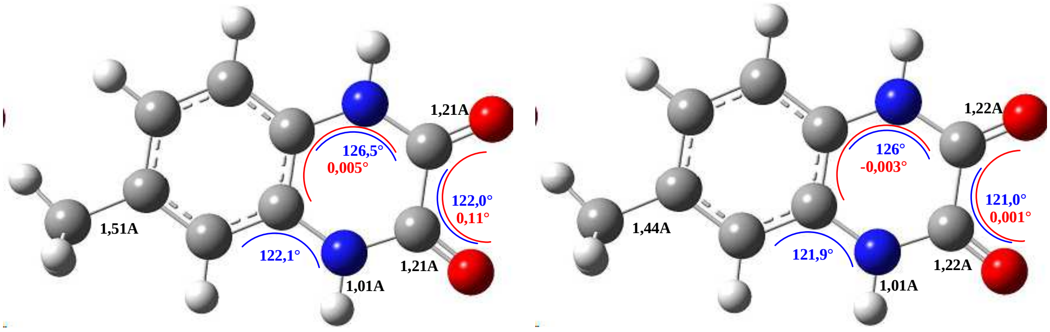
In this paper, we calculated the HOMO and LUMO orbital energies by using B3LYP method with 6-31G(d,p). All other calculations were performed using the results with some assumptions. The higher values of E_{HOMO} indicate an increase for the electron donor and this means a better inhibitory activity with increasing adsorption of the inhibitor on a metal surface, whereas E_{LUMO} indicates the ability to accept electron of the molecule. The adsorption ability of the inhibitor to the metal surface increases with increasing of E_{HOMO} and decreasing of E_{LUMO}.

High ionization energy (I= 6.67 eV, I= 3.46 eV in gas and aqueous phases respectively) indicates high stability [35-37], the number of electrons transferred (ΔN) was also calculated and tabulated in Table 2. The number of electrons transferred (ΔN) was also calculated and tabulated in Table 5. The ΔN(gas) < 3.6 and ΔN(aqueous) < 3.6 indicates the tendency of a molecule to donate electrons to the metal surface [38, 39].

Table 2. Quantum chemical descriptors of the studied inhibitor at B3LYP/6-31G(d,p) in gas, G and aqueous, A phases.

Prameters	Phase	
	Gas	Aqueous
Total Energy *TE* (eV)	-16537.6	-16538,2
E_{HOMO} (eV)	-6.7535	-6.7979
E_{LUMO} (eV)	-0.1924	-0.1023
Gap ΔE (eV)	6.5611	6.6956
Dipole moment μ (Debye)	6.6818	9.1042
Ionisation potential I (eV)	6.7535	6.7979
Electron affinity A	0.1924	0.1023
Electronegativity χ	3.4729	3.4501
Hardness η	3.2806	3.3478
Electrophilicity index ω	1.8383	1.7778
Softness σ	0.3048	0.2987
Fractions of electron transferred ΔN	0.5376	0.5302

The geometry of P2 in gas and aqueous phase (Figure 5) were fully optimized using DFT based on Beck's three parameter exchange functional and Lee–Yang–Parr nonlocal correlation functional (B3LYP) [31] and the 6–31G. The optimized molecular and selected angles, dihedral angles and bond lengths of P2 are given in figure 5. The optimized structure shows that the molecule P2 and have a non-planar structure. The HOMO and LUMO electrons density distributions of **P2** are given in Table 3.

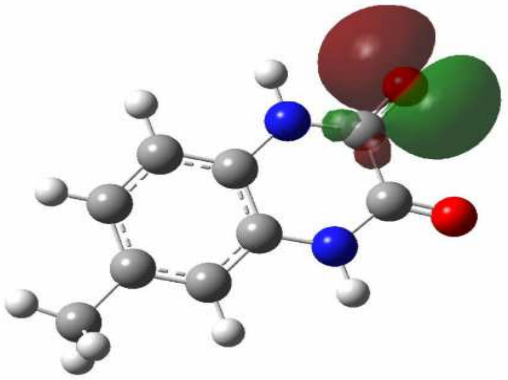
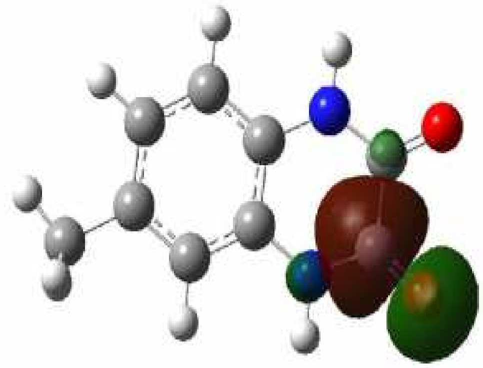
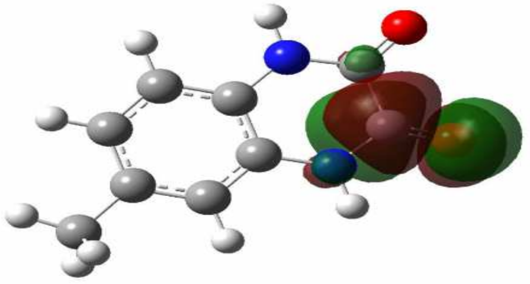
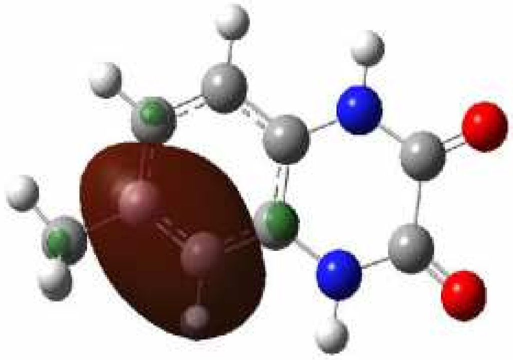


(P2) Gas phase **(P2) Aqueous phase**

Figure 5. Optimized molecular structures and selected dihedral angles (red), angles (blue) and bond lengths (black) of the studied inhibitors calculated in gas and aqueous phase with the DFT at the B3LYP/6-31G level

After the analysis of the theoretical results obtained, we can say that the molecule **P2** have a non-planar structure.

Table 3 : The HOMO and the LUMO electrons density distributions of the studied inhibitors computed at B3LYP/6-31G (d,p) level in gas and aqueous phases

	P2 Gas phase	**P2** Aqueous phase
HOMO		
LUMO		

The inhibition efficiency afforded by the quinoline derivative P2 may be attributed to the presence of electron rich O.

CONCLUSION

The inhibition behavior of P2 on mild steel in 1 M HCl was investigated using different techniques. The following points can be highlighted;

- The obtained results indicate that,P2 performs excellent inhibition activity against the corrosion of mild steel in 1 M HCl solution. The determined high inhibition efficiency is attributed to the adherent adsorption of compound P2.
- EIS plots exhibit individual capacitive loop. The presence of P2 in 1 M HCl solution increases charge transfer resistance, while it reduces double layer capacitance values.
- The adsorption of P2 molecules on the metal surface obeys Langmuir adsorption isotherm in 1 M HCl solution. The high adsorption equilibrium constant suggests strongly adsorbed P2 molecules on the mild steel surface.

- The theoretical calculations show that there is a correlation between quantum and experimental parameters.

REFERENCES

[1] J. P Dirlam, J. E. Presslitz, *Journal of Med. Chem*, **1978**, 21, 483-48.
[2] Y.B Ki, Y.H. Kim, J.Y. Park, S.K. Kim, *Bio org. Med. Chem. Lett*, **2004**, 14, 541- 544:.
[3] G. Aguirre, H.Cerecetto, R. Di Maio, M. Gonzalez, M.E.M. Alfaro, A. Jaso, B. Zarranz, M.A.Ortega, I . Aldana, A.Monge-Vega, *Bioorg. Med. Chem. Lett*, **2004**, 14, 3835-3839.
[4] H.Elmsellem, A.Aouniti, Y. Toubi, H. Steli, M. Elazzouzi, S. Radi, B. Elmahi, Y. El Ouadi, A. Chetouani, B. Hammouti, *Der Pharma Chemica*, **2015**, 7(7), 353-364.
[5] H Elmsellem., H. Bendaha, A. Aouniti, A. Chetouani, M. Mimouni, A. Bouyanzer, *Mor. J. Chem*, **2014**, 2 (1), 1-9.
[6] H. Elmsellem, A. Elyoussfi, H. Steli, N. K. Sebbar, E. M. Essassi, M. Dahmani, Y. El Ouadi, A. Aouniti, B. El Mahi, B. Hammouti, *Der Pharma Chemica*, **2016**, 8(1), 248-256.
[7] H. Elmsellem, M. H. Youssouf, A. Aouniti, T. Ben Hadd, A. Chetouani, B. Hammouti, *Russian, Journal of Applied Chemistry*, **2014**,87(6), 744−753.
[8] M. Y. Hjouji, M. Djedid, H. Elmsellem, Y. Kandri Rodi, M. Benalia, H. Steli, Y. Ouzidan, F. Ouazzani Chahdi, E. M. Essassi, B. Hammouti, *Der Pharma Chemica*, **2016**, 8(4), 85-95.
[9] H. Elmsellem, T. Harit, A. Aouniti, F.Malek, A. Chetouani, B. Hammouti, *Protection of Metals and Physical Chemistry of Surfaces*, A, **2015**, 51(5), 873–884.
[10] N. K. Sebbar, H. Elmsellem, M. Boudalia, S. lahmidi, A. Belleaouchou , A. Guenbour, E. M. Essassi, H. Steli, A. Aouniti, *J. Mater. Environ. Sci*, **2015**, 6 (11), 3034-3044.
[11] S. Bahri , M. Belayachi, H. Zarok, A. Shaim, M. Galai, A. Zarrouk, A. El Midaoui, M. Ebn Touhami, B. Lakhrissi, H. Oudda, *Der Pharma Chemica*, **2014**, 6(3):110-118.
[12] H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat, R. Touzani, M. Elazzouzi, *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(4), 1216-1224.
[13] H. Elmsellem, H. Nacer, F. Halaimia, A. Aouniti, I. Lakehal, A. Chetouani, S. S. Al-Deyab, I. Warad, R.Touzani, B. Hammouti, *Int. J. Electrochem. Sci*, **2014**, 9, 5328.
[14] H. Elmsellem, N. Basbas, A. Chetouani, A. Aouniti, S. Radi, M. Messali, B. Hammouti, *Portugaliae. Electrochimica. Acta*, **2014**, 2, 77.
[15] Y. Filali Baba, H. Elmsellem, Y. Kandri Rodi, H. Steli, C. AD, Y. Ouzidan, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, B. Hammouti, *Der Pharma Chemica*, **2016**, 8(4), 159-169.
[16] M. Ellouz, H. Elmsellem, N. K. Sebbar, H. Steli, K. Al Mamari, A. Nadeem, Y. Ouzidan, E. M. Essassi, I. Abdel-Rahaman, P. Hristov, *J. Mater. Environ. Sci*, **2016**, 7(7), 2482-2497.
[17] M. Sikine, Y. Kandri Rodi, H. Elmsellem, O. Krim, H. Steli, Y. Ouzidan, A. Kandri Rodi, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, *J. Mater. Environ. Sci*, **2016**, 7 (4), 1386-1395.
[18] M. Y. Hjouji, M. Djedid, H. Elmsellem, Y.Kandri Rodi, Y. Ouzidan, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, I. Abdel-Rahman, B. Hammouti, *J. Mater. Environ. Sci*, **2016**, 7(4), 1425-1435.
[19] I. Chakib, H. Elmsellem, N. K. Sebbar, S. Lahmidi, A. Nadeem, E. M. Essassi, Y. Ouzidan, I. Abdel-Rahman, F. Bentiss, B. Hammouti., *J. Mater. Environ. Sci*, **2016**, 7(6), 1866-1881.
[20] Y. Filali Baba, H. Elmsellem, Y. Kandri Rodi, H. Steli, F. Ouazzani Chahdi, Y. Ouzidan, N. K. Sebbar, E. M. Essassi, K. Cherrak., *J. Mater. Environ. Sci*, **2016**,7 (7), 2424-2434.
[21] M. El Azzouzi · A. Aouniti · S. Tighadouin · H Elmsellem · S. Radi ·B. Hammouti · A. El Assyry ·F. Bentiss · A. Zarrouk. **2016**, DOI: 10.1016/j.molliq.2016.06.007.
[22] A. L. Essaghouani, H. Elmsellem, M. Ellouz, M. El Hafi, M. Boulhaoua, N. K. Sebbar, E. M. Essassi, M. Bouabdellaoui, A. Aouniti and B. Hammouti, *Der Pharma Chemica*, **2016**, 8(2), 297-305.
[23] I. El Mounsi, H. Elmsellem, A. Aouniti, H. Bendaha, M. Mimouni, T. Benhadda, R. Mouhoub, B. El Mahi, A. Salhi and B. Hammouti. *Der Pharma Chemica*, **2015**, 7(10),350-356.
[24] N. K. Sebbar, H. Elmsellem, M. Ellouz, S. Lahmidi, E. M. Essassi, I. Fichtali, M. Ramdani, A. Aouniti, A. Brahimi and B. Hammouti. *Der Pharma Chemica*, **2015**, 7(9), 33-42.
[25] F. Yousfi, M. El Azzouzi, M. Ramdani, H. Elmsellem, A. Aouniti, N. Saidi, B. El Mahi, A. Chetouani and B. Hammouti, *Der Pharma Chemica*, **2015**, 7(7), 377-388.
[26] M. Ramdani, H. Elmsellem, N. Elkhiati, B. Haloui, A. Aouniti, M. Ramdani, Z. Ghazi, A. Chetouani and B. Hammouti, *Der Pharma Chemica*, **2015**, 7(2), 67-76.
[27] N. Saidi, H. Elmsellem, M. Ramdani, A. Chetouani, K. Azzaoui, F. Yousfi, A. Aounitia and B. Hammouti, *Der Pharma Chemica*, **2015**, 7(5), 87-94.
[28] R.G.Pearson, *Inorg. Chem*, **1988**, 27, 734–740.
[29] V.S.Sastri, J.R.Perumareddi, *Corrosion*, **1997**, 53, 617–622.
[30] H. Elmsellem, H. Nacer, F. Halaimia, A. Aouniti, I. Lakehal, A. Chetouani, S. S. Al-Deyab, I. Warad, R.Touzani, B. Hammouti, *Int. J. Electrochem. Sci*, **2014**, 9, 5328.

[31] A. Aouniti, H. Elmsellem, S.Tighadouini, M. Elazzouzi, S. Radi, A. Chetouani, B. Hammouti, A. Zarrouk, Journal of Taibah University for Science, **2015**, http://dx.doi.org/10.1016/j.jtusci.2015.11.008.
[32] N. K. Sebbar, H. Elmsellem,M. Ellouz, S. Lahmidi, A.L. Essaghouani, E. M. Essassi,M.
Ramdani, A. Aouniti1, B. El Mahi and B. Hammouti. *Der Pharma Chemica*, 2015, 7(10):579-587.
[33] P. Udhayakala, T. V. Rajendiran, S. Gunasekaran, *Journal of Chemical, Biological and Physical Sciences A*, **2012**, 2(3), 1151-1165.
[34] M. Govindarajan, M. Karabacak, *Spectrochim Acta Part A Mol Biomol Spectrosc*, **2012**, 85, 251–260.
[35] K.F. Khaled, N.S. Abdelshafi, A. El-Maghraby, N. Al-Mobarak, *J. Mater. Environ. Sci*, **2011**, 2, 166.
[36] H. Elmsellem, K. Karrouchi, A. Aouniti, B. Hammouti, S. Radi, J. Taoufik, M. Ansar, M. Dahmani, H. Steli, B. El Mahi, *Der Pharma Chemica*, **2015**, 7(10), 237-245.
[37] A. Elyoussfi, H. Elmsellem, A. Dafali, K. Cherrak, N. K. Sebbar, A. Zarrouk, E. M. Essassi, A. Aouniti, B. El Mahi and B. Hammouti, *Der Pharma Chemica*, **2015**, 7(10), 284-291.
[38] I. Lukovits, E. Kalman, F. Zucchi, *Corrosion*, **2001**, 57, 3-7.
[39] H. Elmsellem, K. Karrouchi, A. Aouniti, B. Hammouti, S. Radi, J. Taoufik, M. Ansar, M. Dahmani, H. Steli, B. El Mahi, *Der Pharma Chemica*, **2015**, 7(10), 237-245.