Understanding the Adsorption of Quinoxaline Derivatives as Corrosion Inhibitors for Mild Steel in Acidic Medium: Experimental, Theoretical and Molecular Dynamic Simulation Studies

Lgaz H1,2, Salghi R3, Jodeh S4, Ramli Y5, Larouj M6, Toumiat K7, Quraishi MA8, Oudda H1 and Jodeh W7

1Faculty of Science, University Ibn Tofail, Morocco
2Laboratory of Applied Chemistry and Environment, Ibn Zohr University, Morocco
3Department of Chemistry, An-Najah National University, Nablus, State of Palestine
4Medical and Pharmaceutical College, University Mohammed V, Morocco
5Department of Materials Sciences, Laghouat University, Algeria
6Department of Chemistry, Indian Institute of Technology, Uttar Pradesh, India
7Department of Human Medicine, An-Najah National University, Palestine

Abstract

The anti-corrosive properties of (E)-3-styrylquinoxalin-2(1H)-one (STQ), (E)-1-benzyl-3-(4-methoxystyryl) quinoxalin-2(1H)-one (BMQ) and (E)-3-(2-(furan-2-yl) vinyl) quinoxalin-2(1H)-one (FVQ) were analyzed by different techniques such as: potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), weight loss (WL) and molecular modeling by DFT method and Monte Carlo simulation studies. All quinoxaline derivatives showed appreciable inhibition efficiency. Among the quinoxaline derivatives studied, BMQ exhibited the best inhibition efficiency. The results from the experimental and theoretical investigations show that the order of inhibition efficiency by the quinoxaline derivatives follow the order BMQ > FVQ > STQ. The experimental results suggest that the three tested inhibitors function as mixed-type compounds and the inhibition efficiency increases with the increase in inhibitor concentration and decreased with temperature. Adsorption of the three compounds on mild steel (MS) surface obeys Langmuir’s isotherm model. The theoretical study by DFT method, Monte Carlo simulation and radial distribution function (RDF) provided strong evidence that the inhibition efficiency of quinoxaline derivatives is due to their ability to adsorb strongly at the MS surfaces, which is supportive of the obtained experimental results.

Keywords: Monte carlo; Quinoxaline; Mild steel; Corrosion inhibition; Fukui functions; DFT

Introduction

Mild steel is an iron-containing alloy, considered as one of the important constructional materials extensively used in different applications. Generally, acid solution (especially hydrochloric acid) plays a significant role in many fields of industry such as pickling, descaling and oil well acidification, its price is generally low and more consistent [1,2]. In the few last decades the use of chemical compounds as corrosion inhibitors is considered as one of the efficient and practical methods to protect the metals surfaces against aggressive mediums such as acidic solutions [3-5]. The effectiveness of these molecules is mainly from their ability to adhere to metal surfaces [6]. The use of synthetic inhibitors also appears to be economically viable and promising because of their simplicity in application, and they’re relatively cheaper. Meanwhile, the adsorption of these inhibitors produces a protective insoluble film on the MS surface, which reduces contact with the corrosive mediums and consequently the degree of metal attack [7-9]. The presence of N, O, S atoms and conjugates aromatic nucleus are responsible for their essential characteristics [10]. The quinoxaline is one of the important heterocyclic compounds; they have applications in many fields such as electroluminescent materials [11,12] and in the pharmacological industry [13,14] as well as in metallic industries [15,16], this indicates that the use of the quinoxaline derivatives as inhibitors is very interesting [17,18]. The high efficiency of these compounds against corrosion can be in their rich molecular structure, which explains the high capability of these molecules to overcome corrosion. Recently, in addition to experimental investigations, the evaluation of inhibition performance is also conducted theoretically by DFT calculation and molecular dynamic simulation studies for the understanding of some experimentally unknown properties, exploring and establishing relationships between inhibitor molecules and the metal surface [19,20]. N.A. Al-Mobarak et al. [21] have studied the corrosion inhibition of copper in 3.5% NaCl using new pyrimidine derivatives, namely, 2-mercapto-4-(p-methoxyphenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile (MPD) by Monte Carlo simulation and theoretical calculation, and all quantum analysis correlated well with electrochemical investigation. In addition, Youguo Yan et al. [22] have applied the DFT method using the GGA/PW91 functional with the double numerical plus d-functions basis set to investigate the adsorption behavior of three purine compounds, A, B and C on the Fe (0 0 1) surface. The theoretical results, including global molecular reactivity descriptors and active sites by Fukui functions analysis well support the order of the IE%.

*Corresponding author: Quraishi MA, Department of Chemistry, Indian Institute of Technology, B.H.U. Varanasi, Uttar Pradesh, India-221005, Tel: 9307025126; E-mail: maquraishi.apc@itbhu.ac.in

Received April 26, 2016; Accepted May 26, 2016; Published June 06, 2016

Citation: Lgaz H, Salghi R, Jodeh S, Ramli Y, Larouj M, et al (2016) Understanding the Adsorption of Quinoxaline Derivatives as Corrosion Inhibitors for Mild Steel in Acidic Medium: Experimental, Theoretical and Molecular Dynamic Simulation Studies. J Steel Struct Constr 2: 111. doi: 10.4172/2472-0437.1000111

Copyright: © 2016 Lgaz H, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
The quantum chemical parameters QCPs reveals that the electron donation and electron acceptance capability of 2-AB and 3-AB are in well accordance with experimental IE%. While, the MD simulation reveals that the distance between active sites and Fe (1 0 0) atoms are lying within a range of 3.5 Å, indicating that a chemical bonds are formed during the interaction of the inhibitors on the Fe (1 1 0) surface. Recently, Z. Zhang et al. [24] applied the radial distribution function (RDF) to study the mechanism of adsorption processes and the synergistic inhibition effect between indigo carmine and three cationic molecules on CS, in an acidic solution. The researchers reported that the bonding length of all heteroatoms-Fe and carbons-Fe are less than 3.5 Å, suggesting that the adsorption of indigo carmine and their cationic molecules occur mainly by these atoms. In addition, Si-Wei Xie et al. [25] also introduced the RDF accompanying with DFT and experimental studies to investigate the inhibitive performance of 3,5-dibromo salicylaldehyde Schiff’s base. The results obtained revealed that C, N, O and S atoms of three studied inhibitors are the most reactive sites responsible of efficiency of the tested compound. This work aims to evaluate the inhibitory properties and adsorption characteristics of three synthetic quinoxaline derivatives of the MS in 1.0 M HCl, using the weight loss (WL), electrochemical techniques (EIS and PDP) and surface examination by SEM. Quantum chemical parameters (QCPs) by DFT method and Monte Carlo simulation accompanying with radial distribution function (RDF) of the (E)-3-styrylquinoxalin-2(1H)-one (STQ), (E)-1-benzyl-3-(4-methoxystyryl) quinoxalin-2(1H)-one (BMQ) and (E)-3-(2-(furan-2-yl) vinyl) quinoxalin-2(1H)-one (FVQ) were calculated and discussed.

Data and Method

Inhibitors preparation

The tested inhibitors, namely (E)-3-styrylquinoxalin-2(1H)-one (STQ), (E)-1-benzyl-3-(4-methoxystyryl) quinoxalin-2(1H)-one (BMQ) and (E)-3-(2-(furan-2-yl) vinyl) quinoxalin-2(1H)-one (FVQ) were synthesized according to this experimental procedure:

The bibliography reports various methods to prepare styrylquinoxalines [26,27]. For our part, we suggested a different synthetic route which comprised reacting fusion 3-méthtylquinoxaline-2-one with aromatic aldehydes. This method was carried out in the absence of solvent. We had a possibility to isolate the desired product in a yield of around 80% (Scheme 1). Indeed, 6.25 mmol of 3-méthylquinoxalin-2(1H)-one was fused with 12.5 mmol of the furan-2-carbaldehyde for 2 h, at the boiling temperature of the latter. At the end of the reaction, the solid compound is allowed to cool and then heated to 100°C for 10 min in 50 ml of ethanol. The product was filtered hot and washed with ethanol (Scheme 3).

Results and Discussion

Weight loss measurement

Effect of concentration and temperature: The inhibitive efficiency calculated by the Eq. (1) of BMQ, FVQ and STQ in the corrosive medium of the MS was carried out after immersion for 6 h at 303 to 333 K, in all studied concentrations by weight loss measurements. The results are presented in Table 1 and Figure 1 (Similar plots obtained for 313-333 K, but not presented in this article).
is the change in enthalpy of activation, \( k \) is \( \frac{E_a}{R} \), which \( aH \) is the activation energy, \( n \) is the number of quinoxaline derivatives, while the range of studied temperature. Over temperature increase the \( \delta E \) percentage of our molecules is due to their adsorption on steel surface, which decreases the fatal effect of aggressive medium.

Activation parameters: The inhibitive mechanism can be understood based on the thermodynamic and activation parameters. From Table 1, it can be observed that \( C_{\text{inh}} \) depends on temperature for all inhibitor concentrations. The \( C_{\text{inh}} \) is related to the temperature by the following Eqs. (2,3) [39]:

\[
C_R = k \exp \left( -\frac{E_a}{RT} \right)
\]

\[
C_R = \frac{RT}{\Delta H_a} \exp \left( \frac{\Delta S_a}{RT} \right) \exp \left( -\frac{\Delta H_a}{RT} \right)
\]

where, \( E_a \) is the activation energy, \( \Delta S_a \) is the change in entropy of activation, \( \Delta H_a \) is the change in enthalpy of activation, \( k \) is the Arrhenius pre-exponential factor, \( h \) is Planck’s constant, \( N \) is Avogadro’s number, \( T \) is the absolute temperature and \( R \) is the universal gas constant.

Using Eq. (2) a plot of \( \ln C_R \) versus \( 1/T \) were drawn to get a straight line (Figure 2), from the values of slope and intercept, the values of \( E_a \) were calculated for three inhibitors at various concentrations. Using Eq. (3), another linear plot of \( \ln C_R \) versus \( 1/T \) was drawn (Figure 3) with slope \(-\frac{\Delta H_a}{R} \) and intercept \( \ln[R/N\Delta S_a/\Delta H_a] \), which were used for the calculation of \( \Delta H_a \) and \( \Delta S_a \). All the values are listed in Table 2. We can be find from Table 2 that the \( \Delta H_a \) (Inh) > \( \Delta H_a \) (Blank), which can be explained by the physical adsorption of quinoxaline molecules [40]. For three inhibitors, the value of the activation energy to take up higher maximum for the higher concentrations; and generally follows the order of \( \text{Ea (BMQ)} > \text{Ea (FVQ)} > \text{Ea (STQ)} \), this order is in good agreement with the order of inhibition efficiencies, that decreased with the increase of the temperature. In the same case, Saranya et al. [17] studied the inhibition effect of Acenaphtho[1,2-b]quinoxaline on the MS dissolution in acidic environment, the effect of temperature study reveals that the \( \delta E \) percentage decrease with the increase of the temperature and the \( E_I \) value decrease remarkably than the value obtained in blank solution, which in good correlation with our investigation (Figure 4).

The positive sign of the enthalpy (Table 2) reflects the endothermic nature of the MS dissolution process. While the higher values of \( \Delta S_a \) in presence of investigated compounds compared to those calculated from the uninhibited solution might be the result of the adsorption of quinoxaline derivatives from the aggressive solution, which could be regarded as a quasi-substitution process between inhibitor molecules in the aqueous phase and water molecules on the MS surface [41,42].

Adsortion isotherm and thermodynamic parameters

On the basis of evaluation of the interaction between the inhibitors and steel surface, it is important to consider the adsorption isotherms to analyze the mechanism and nature of the adsorption processes of chemicals species on the MS surface [43]. For additional information about the compounds tested, several types of adsorption isotherms carried out such as Frumkin (Eq. 4), Temkin (Eq. 5), Freundlich (Eq. 6) and Langmuir (Eq. 7) among which the Langmuir isotherm showed the best fit with regression coefficient \( R^2 \) values close to unity for all tested compounds. Considering a sufficient time for adsorption equilibrium, the fractional surface coverage \( \theta \) can be easily calculated by \( \eta_w (%) = 100 \).
Figure 2: Arrhenius plots for the MS in 1.0 M HCl in the absence and presence of different concentrations of (a) BMQ (b) FVQ and (c) STQ at different temperatures.

Figure 3: Transition state plots for the inhibition of corrosion of the MS in 1.0 M HCl in the absence and presence of different concentrations of (a) BMQ (b) FVQ and (c) STQ at different temperatures.
Where: C is the concentration of inhibitors in the electrolyte, K_{ads} is the equilibrium constant for the adsorption-desorption process, θ is the surface coverage and f is the molecular interaction constant. The values of K_{ads} can be calculated from the intercepts of the straight lines C/θ-axis. The K_{ads} related to the standard free energy of adsorption ΔG_{ads}° by following Eq. (8):

$$\Delta G_{ads}° = -RT \ln(C_{solvent} \times K_{ads})$$  \hspace{1cm} (8)

Where: C_{solvent} is the molar concentration of solvent (For H_2O is 55.5 mol L^{-1}), T is the absolute temperature. The K_{ads} values follow the order: K_{ads}(BMQ) > K_{ads}(FVQ) > K_{ads}(STQ). This further confirms that n_w(%) decreases with the increase in temperature and the better inhibitive performance of BMQ than the others compounds. The negative values of ΔG_{ads}° imply that the adsorption was spontaneous and the stability of the adsorbed film on the MS surface [45]. All the ΔG_{ads}° values are around -13 kJ/mol. normally; the physical adsorption is correlated with the absolute values of ΔG° around 20 kJ/mol or lower, and a value of ΔG_{ads}° up to 40 kJ/mol or more negative is an indication of the chemical adsorption [46,47]. The ΔG_{ads}° values in Table 3 indicate clearly the physical adsorption of tested compounds on the MS surface. In the literature, we can find in the investigation of Obot et al. [17] that the 2,3-Diphenylbenzoquinoxaline interact with the MS in the same way in sulphuric acid, the authors reported that the ΔG_{ads}° is -11.4 kJ mol^{-1}, which explained by the electrostatic interaction with tested quinoxaline derivative and the MS surface. The ΔH_{ads} and ΔS_{ads} calculated by the following Eq. (9):

$$\ln K_{ads} = \ln \frac{1}{55.5} - \frac{\Delta H_{ads}°}{RT} + \frac{\Delta S_{ads}°}{R}$$  \hspace{1cm} (9)
The values of \( \Delta H_{\text{ads}} \) and \( \Delta S_{\text{ads}} \) are collected in Table 3, more information of the corrosion process and nature of adsorption can be obtained on the basis of the values of \( \Delta H_{\text{ads}} \) of investigated compounds. The \( \Delta H_{\text{ads}} \) values of quinoxaline derivatives are negative, indicating the exothermic process of adsorption of studied inhibitors. The endothermic adsorption process \( \Delta H_{\text{ads}} > 0 \) is correlated to chemical adsorption, while the exothermic adsorption process \( \Delta H_{\text{ads}} < 0 \) is attributed to physical, chemical or mixture adsorption [48]. In an exothermic process, the physisorption process is correlated with the values of \( \Delta H_{\text{ads}} \) lower than 40 kJ mol\(^{-1}\). Whereas, chemical adsorption is values around 100 kJ mol\(^{-1}\). In this investigation, the derived parameters are presented in Figures 5a-5c and Table 4, indicating that before the adsorption of inhibitor’s molecules on the MS surface, inhibitor molecules might freely move in the bulk solution, but with the progress in the adsorption of BMQ, FVQ and STQ, inhibitors molecules were orderly adsorbed on the MS surface, as a result a decrease in entropy is observed [49]. Based on the thermodynamic principles, it can be noted that since the adsorption is an exothermic process, it must be accompanied by a decrease of entropy [50].

**Potentiodynamic polarization study**

The polarization experiments were undertaken to distinguish the behavior of the corrosion of the MS with and without studied concentrations of BMQ, FVQ and STQ at 303 K. The Tafel slopes and the derived parameters are presented in Figures 3a-3c and Table 4, respectively. The IE\% is calculated using the following Eq. (10) [51,52]:

\[
\eta_{\text{IE}}(\%) = \frac{I_{\text{corr}} - I_{\text{corr(i)}}}{I_{\text{corr}}} \times 100
\]

Where \( I_{\text{corr}} \) and \( I_{\text{corr(i)}} \) are the corrosion current densities for the tested compounds, respectively.

It can be observed from Figures 5a-5c, that the addition of quinoxaline derivatives caused a decrease in the anodic and cathodic current densities with slight shifting of the corrosion potential (\( E_{\text{corr}} \)), indicating that the quinoxaline derivatives investigated are mixed type inhibitors [53,54]. The small change of the constant cathodic Tafel slope, \( \beta_c \), suggests that the mechanism of proton discharge reaction does not modify by addition of quinoxaline derivatives [55,56]. From Table 4, it can be found that the increase of the concentration of our molecules result in a considerable decrease of the \( I_{\text{corr}} \) values. In the same trend, a remarkable increase of the IE\% is observed when increasing the inhibitors concentration reaching a maximum value at 8 mM in the three quinoxaline derivatives studied. It is also evident that BMQ presents the better performance than other inhibitors, which can be correlated to the difference of the structure of the three inhibitors molecules (Figure 6).

**AC impedance study**

Nyquist plots of the MS in acidic solutions with and without various concentrations of STQ, FVQ and BMQ at 303 K after 30 min of immersion are given in Figures 7a-7c. Which a single capacitive loop is clearly observed over the frequency range studied [57,58]. Also appearing are depressed Nyquist plots into the real axis and imperfect semicircles, what can explained by the non-homogeneity and roughness of the MS surface [59]. As previously reported for steel/acid interface, the EIS data obtained was fitting used the R\( s \) (CPE/Rct) equivalent circuit (Figures 8 and 9) [60], where Rs is the solution resistance, R\( s \) denotes that the charge-transfer resistance and CPE is "constant phase element". The introduction of CPE was necessitated to compensate deviations from ideal capacitor due to distributed surface heterogeneity. The impedance of this element is frequency-dependent and can be calculated using the Eq. (11) [61,62]:

\[
\eta_{\text{ie}}(\%) = \frac{I_{\text{corr}} - I_{\text{corr(i)}}}{I_{\text{corr}}} \times 100
\]

| Inhibitor | Temperature (K) | \( K_{\text{ads}} \) (M\(^{-1}\)) | \( \Delta G_{\text{ads}} \) (kJ mol\(^{-1}\)) | \( \Delta H_{\text{ads}} \) (kJ mol\(^{-1}\)) | \( \Delta S_{\text{ads}} \) (J mol\(^{-1}\) K\(^{-1}\)) |
|-----------|----------------|-----------------|-----------------|-----------------|-----------------|
| BMQ       | 303            | 4.04            | -13.62          | -19.81          | -20.41          |
|           | 313            | 3.13            | -13.41          |                 |                 |
|           | 323            | 2.47            | -13.21          |                 |                 |
|           | 333            | 1.99            | -13.01          |                 |                 |
| FVQ       | 303            | 3.77            | -13.45          | -18.61          | -17.04          |
|           | 313            | 2.95            | -13.26          |                 |                 |
|           | 323            | 2.39            | -13.11          |                 |                 |
|           | 333            | 1.93            | -12.93          |                 |                 |
| STQ       | 303            | 3.61            | -13.34          | -18.59          | -17.81          |
|           | 313            | 2.85            | -13.17          |                 |                 |
|           | 323            | 2.30            | -13.01          |                 |                 |
|           | 333            | 1.84            | -12.80          |                 |                 |

**Table 3: Adsorption parameters of BMQ, FVQ and STQ for mild steel corrosion in 1.0 M HCl at different temperatures.**

| Inhibitor | Concentration (mM) | \( E_{\text{corr}} \) (mV/SCE) | \( \beta_c \) (mV dec\(^{-1}\)) | \( I_{\text{corr}} \) (\( \mu \)A cm\(^{-2}\)) | \( \eta_{\text{IE}} \) (\%) | \( \Theta \) |
|-----------|--------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----|
| Blank     | 1.0                | 496                         | 190.19                      | 564                        | 96.28                       | 0.9628 |
|           | 6                  | 499                         | 146.79                      | 20.98                      | 94.24                       | 0.9324 |
| BMQ       | 4                  | 525                         | 145.61                      | 38.12                      | 93.24                       | 0.9324 |
|           | 2                  | 539                         | 147.00                      | 68.04                      | 90.03                       | 0.9003 |
|           | 8                  | 513                         | 145.34                      | 30.08                      | 94.67                       | 0.9467 |
|           | 6                  | 530                         | 146.66                      | 50.67                      | 91.01                       | 0.9101 |
|           | 4                  | 544                         | 141.37                      | 71.59                      | 87.31                       | 0.8731 |
|           | 2                  | 557                         | 147.73                      | 85.18                      | 84.90                       | 0.8490 |
| STQ       | 8                  | 526                         | 135.19                      | 47.03                      | 91.66                       | 0.9166 |
|           | 6                  | 539                         | 134.24                      | 59.32                      | 89.48                       | 0.8948 |
|           | 4                  | 552                         | 137.27                      | 88.00                      | 84.40                       | 0.8440 |
|           | 2                  | 547                         | 139.13                      | 106.04                     | 81.20                       | 0.8120 |

**Table 4: Corrosion parameters for corrosion of MS with selected concentrations of the inhibitors in 1.0 M HCl by potentiodynamic polarization method at 303K.**
Figure 6: Polarisation curves of MS in 1.0 M HCl for various concentrations of the inhibitors: (a) BMQ, (b) FVQ and (c) STQ at 303K.

Figure 7: Nyquist curves for MS in 1.0 M HCl for selected concentrations of the inhibitors: (a) BMQ, (b) FVQ, and (c) STQ at 303K.
The inhibition efficiency values in the absence and presence of BMQ, FVQ and STQ yielded 96.53%, 94.98% and 93.73% in the highest concentrations, respectively with the following order: BMQ > FVQ > STQ. This order can be explained by the presence of a phenyl and (-OCH₃) in BMQ, which raised their reactivity.

**SEM analysis**

SEM photomicrographs of the surface of MS were immersed for 6 h in a corrosive medium with and without 8 mM of STQ, BMQ and FVQ. Results are displayed in Figures 10a-10e. In acidic environment, obvious dissolution can be observed without the presence of any inhibitors. In presence of BMQ, FVQ and STQ, it can be seen (Figures 10a-10c) that the surface of the MS was improved, smooth, and that less pits and less damage was observed. This demonstrates the formation of insoluble film, resulting from the adsorption of BMQ, FVQ and STQ on the MS surface. These observations support the high inhibition performance of the quinoxaline derivatives.

**Quantum chemical calculations**

**Global molecular reactivity:** We attempted to interpret the main factors responsible for the reactivity of the investigated quinoxaline derivatives and to analyse the capability of our molecules to donate and accept electrons to/from the MS surface. The optimized structures of the quinoxaline derivatives molecules were calculated and presented in Table 1. The QCPs such as $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E = (E_{\text{LUMO}} - E_{\text{HOMO}})$ total energy (TE), softness ($\sigma$), the fraction of electrons transferred ($\Delta N$) and dipole moment ($\mu$) were collected in Table 6. The $\%$ of BMQ, FVQ and STQ according to our experimental studies is:

- BMQ > FVQ > STQ

In Figure 11, The HOMO and LUMO orbitals are distributed over the entire quinoxaline molecules, resulting in the highest interaction of quinoxaline derivatives studied on the MS surface. This observation also suggests that the heteroatoms and the cycle rings containing $\pi$-bonds are the probable reactive sites for adsorption of inhibitors on the metal surface. Normally, $E_{\text{HOMO}}$ is often indicated the ability of a molecule to donate electrons; this ability becomes more considerable with a high value of $E_{\text{HOMO}}$. While, the lowering of $E_{\text{LUMO}}$ is often associated with the capability of an inhibitor to accept electrons [70,71]. The $\Delta E = (E_{\text{LUMO}} - E_{\text{HOMO}})$ was reported as a main chemical reactivity factor of an inhibitor from theoretical point of view [71]. According to these literature findings and the results from Table 6, it can be observed that our compounds have higher interactions with the steel surface. The reactivity of BMQ, FVQ and

**Table 5:** AC-impedance parameters for corrosion of MS for selected concentrations of the inhibitors in 1.0 M HCl at 303K.

| Inhibitor | Conc (M) | $R_c$ (Ω cm$^2$) | $n$ | $Q$×10$^4$ (aF cm$^2$) | $C_a$ (μF cm$^2$) | $\eta_\text{IE}$ (%) | $\Theta$ |
|-----------|----------|------------------|-----|-----------------------|-------------------|---------------------|--------|
| Blank     | 1.0      | 29.35            | 0.88| 1.7610                | 85.89             | -                   | -      |
| BMQ       | 8        | 847.1            | 0.92| 0.2139                | 15.09             | 96.53               | 0.9653 |
|           | 6        | 515.2            | 0.89| 0.2870                | 17.05             | 94.30               | 0.9430 |
|           | 4        | 301.3            | 0.91| 0.3354                | 21.29             | 90.25               | 0.9025 |
|           | 2        | 231.1            | 0.93| 0.4121                | 28.86             | 87.29               | 0.8729 |
|           | 8        | 585.2            | 0.92| 0.2655                | 18.48             | 94.98               | 0.9498 |
| FVQ       | 6        | 353.4            | 0.92| 0.2889                | 19.39             | 91.69               | 0.9169 |
|           | 4        | 273.3            | 0.93| 0.3702                | 26.20             | 89.26               | 0.8926 |
|           | 2        | 203.3            | 0.91| 0.4812                | 30.45             | 85.56               | 0.8556 |
| STQ       | 8        | 468.8            | 0.93| 0.2911                | 21.07             | 93.73               | 0.9373 |
|           | 6        | 280.7            | 0.91| 0.3546                | 22.48             | 89.54               | 0.8954 |
|           | 4        | 192.2            | 0.93| 0.4132                | 27.14             | 84.73               | 0.8473 |
|           | 2        | 156.2            | 0.91| 0.5170                | 32.10             | 81.20               | 0.8120 |

**Figure 8:** EIS Nyquist plots for carbon steel in 1.0 M HCl with 6 mM of inhibitors interface: dotted lines experimental data; dashed line calculated.

**Figure 9:** Equivalent electrical circuit corresponding to the corrosion process on the MS in hydrochloric acid.

$$Z_{\text{CPE}} = \frac{1}{Q[jo]^n}$$ \hspace{1cm} (11)

Where $Q$ is the CPE constant (in $\Omega^{-1}$ $s^{-n}$), $\omega$ is the angular frequency (in rad $s^{-1}$), $j = -1$ is the imaginary number and $n$ is a CPE exponent which can be used as a gauge for the heterogeneity or roughness of the surface [63]. The electrochemical parameters derived from the fitting of impedance spectra are collected in Table 5. The $\%$ was calculated by the Eq. (12):

$$\eta_\text{IE} \% = \left(\frac{R_c - R_c^*}{R_c})\right) \times 100$$ \hspace{1cm} (12)

Where: $R_c^*$ and $R_c$ are the charge transfer resistances without and with various concentrations of inhibitors respectively. According to the values of $R_c$ displayed in Table 5, the $R_c$ value increase considerably with rising in inhibitors concentration (from 231.1 to 847.1 $\Omega$ for BMQ) resulting in a slower corrosion of steel due to the adsorption of quinoxaline derivatives on metal surface [64,65]. Regarding, the double layer capacitances, $C_{dl}$ is associated with a CPE by the following Eq.(13) [66]:

$$C_{dl} = \left(Q(R_c^{1-n})\right)^{1/n} \hspace{1cm} (13)$$

The $C_{dl}$ values were decreased, so that the $C_{dl}$ values reached 15.09 $\mu$F cm$^{-2}$ for BMQ, 18.48 $\mu$F cm$^{-2}$ for FVQ and 21.07 $\mu$F cm$^{-2}$ for STQ considering 85.89 $\mu$F cm$^{-2}$ for the uninhibited solution. On the other side, the values of the proportional factor $Q$ of CPE increase when decreasing the concentration of the quinoxaline derivatives. These results are probably correlated with the adsorption of the three inhibitors on steel surface [66,67]. Accordingly, the values of $n$ lies between 0.89 and 0.92 for inhibited solutions, the addition of quinoxaline derivatives increased $n$ values, indicating the increase in in-homogeneity of the MS surface, due to the adsorption of the our inhibitors [68,69].
STQ can be classified by the following order:

BMQ > FVQ > STQ

Recently, Olasunkanmi et al. [14] employed four quinoxaline derivatives, noted Me-4-PQPB, Mt-4-PQPB, Mt-3-PQPB and Oxo-1,3-PQPB to study the corrosion inhibition of MS in hydrochloric acid medium, the authors reported that the \( \text{IE}\% \) values at optimum concentration are 80.42\%, 72.01\%, 69.66\% and 68.41\% respectively. While, in the theoretical calculations the \( \Delta E \) values are found to be 3.55, 3.93, 3.93 and 3.67, these results further support the inhibitive performance of our compounds.

The absolute electronegativity (\( \chi \)) and global hardness (\( \eta \)) of the inhibitors molecule are approximated as follows [72,73]:

\[
\chi = \frac{I + A}{2} \\
\eta = \frac{I - A}{2}
\]

(14)

(15)

Where: \( I = -E_{\text{HOMO}} \) and \( A = -E_{\text{LUMO}} \)

Thus the fraction of electrons transferred from the inhibitor to metallic surface, \( \Delta N \), is given by [74]:

\[
\Delta N = \frac{X_{Fe} - X_{inh}}{2(\eta_{Fe} + \eta_{inh})}
\]

(16)
• The theoretical values of $\chi_{Fe}$ (4.06 eV mol$^{-1}$) and of $\eta_{Fe}$ (0 eV mol$^{-1}$) are used to calculate $\Delta N$ [75,76]. The results from Table 6, show that the order of electron transfer is such that BMQ > FVQ > STQ which also confirms that BMQ has the highest tendency to donate electrons and therefore the highest tendency to bind onto the metal surface [76,77].

The hard-soft-acid-base (HSAB) theory introduced by Pearson [78] can be used in correlation with the FMO theory to understanding the tendencies of the inhibitors to bonding towards the MS atoms [79]. According to HSAB theory, hard acids prefer to co-ordinate to hard bases to give ionic complexes and soft acids prefer binding to soft bases to give covalent complexes. On the other hand, metal atoms are definite as soft acids. Hard molecules have a high value of $\Delta E_{HOMO-LUMO}$. In contrast, soft molecules have a small $\Delta E_{HOMO-LUMO}$ [80]. Thus soft base compounds are the most capable to bind with metal atoms. So, the BMQ compound which has the lowest $\Delta E_{HOMO-LUMO}$ and the highest softness has mostly been confirmed by calculating the softness, $\sigma$, to measures the reactivity of a molecule: $\sigma = 1/ \eta$, (Table 6). It was observed that BMQ compounds have the highest $\sigma$ value and the order at which softness increases, so that the reactivity will be:

BMQ > FVQ > STQ

Figure 11 shows the relationship between the FMO of quinoxaline compounds studied and their energy gap $\Delta E_{g}$. BMQ, FVQ and STQ have low energy gap, which facilitate their adsorption. The order of the reactivity of tested molecules is clearly observed from this figure by considering a small difference between the energy of HOMO and LUMO [81,82].

Actives sites: To investigate reactive sites in the tested inhibitors, molecular electrostatic potential (MESP) provides a visual method to understand the region of the electrophilic attack, nucleophilic attack and the electrostatic potential zero regions [83]. The total electron density surface mapped with molecular electrostatic potential (MEP) and contour representation of electrostatic potential of BMQ, FVQ and STQ are collected in Figures 13a-13b, respectively. In these maps, different values of the MESP were demonstrated with the help of different colors, which are red, yellow, green, light blue and blue. The
red and yellow colors suitable for the negative parts of the MEP are linked to electrophilic reactivity, blue colors suitable for the positive parts to the nucleophilicity and the green color represents the ESP zero region. In Figures 13a-13c, the red and yellow sites are mainly observed over the benzene ring, the heteroatoms (N13, N14, and Oxygen atoms) and the conjugated double bonds, the blue and light blue sites are mainly localized around the second atom of nitrogen and benzene ring. The green regions stand for the zero electrostatic potential.

These remarks confirmed by the Mulliken charges of the inhibitor atoms as can be seen in Figure 13c [84]. As noticed that the MS acting as an electrophilic, and the nucleophilic centers are heteroatoms with free electron pairs and π-systems in the conjugated double bonds. The inhibitors can promote formation of a chelate on the MS surface by transferring electrons from tested molecules to Fe-atoms (d-orbital) and forming a coordinate covalent bond through the adsorption process [85].

In order to analyze the active sites of BMQ, FVQ and STQ, Fukui indices was used to measure the local reactivity of the inhibitors molecules and indicate their chemical reactivity for nucleophilic and electrophilic nature. The condensed Fukui functions can be computed unambiguously using a scheme of finite difference approximations such as [86]:

\[
f_{k}^{+} = P_{k}^{+} (N+1) - P_{k} (N)
\]

\[
f_{k}^{-} = P_{k} ^{-} (N) - P_{k} (N-1)
\]

where \( P_{k}^{+} \), \( P_{k} \), \( P_{k}^{-} \) represent charge values of atom k for anion, neutral, and cation, respectively.

Generally, the high value of \( f_{k}^{+} \) is the preferred site for nucleophilic attack, while the sites with a high value of \( f_{k}^{-} \) are preferred for electrophilic attack. The Fukui indices for BMQ, FVQ and STQ are present in Tables 7-9. In BMQ atoms C1(0.09169), C5(0.08025), N14(0.18102), C32(0.09582), in FVQ atoms C1(0.08292), C15(0.10027), C22(0.09368), C26(0.10635) and in STQ atoms C1(0.07165), N13(0.10305), C17(0.13096), presented the highest values of \( f_{k}^{+} \) regarding the most susceptible sites for nucleophilic attacks. On the other hand, in BMQ atoms C12(0.1312), N14(0.11428), N15(0.09401), C32(0.0813), in FVQ atoms C11(0.10201), N13(0.10542), C17(0.12482), C22(0.08514) and in STQ atoms C1(0.07756), N13(0.06573), C15(0.09977), C26(0.06255) are the preferable sites for electrophilic attacks and consequently donating charges to the MS surface, as they presented the highest values of \( f_{k}^{-} \). Based on these findings, the distribution of the active sites is quite different. This implies the highest capacity of adsorption of BMQ, FVQ and

![Figure 13: Quantum chemical results of inhibitors molecules: (a) total electron density surface mapped with electrostatic potential (b) contour representation of electrostatic potential (c) optimized structures with Mulliken charges values.](image-url)
suitable configuration for adsorption of quinoxaline derivatives on Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation. The total energy, average total energy, van der Waals energy, and intramolecular energy for Fe (1 1 0) substrates obtained by Monte Carlo simulation.

**Monte Carlo (Molecular dynamic) simulation**

Molecular dynamics (MD) simulation provides considerable information about the physical movements of atoms and molecules, which gives a view of the motion of the atoms after interaction at a certain time. Figure 14 represents the top and side views of the most

### Table 8: Natural population and Fukui functions of FVQ calculated at B3LYP/31G (d, p) in gas phase.

| Atom  | P<sub>i</sub>(N) | P<sub>i</sub>(N−1) | f<sub>i</sub> | f<sub>i</sub>^+ |
|-------|-----------------|-----------------|---------|---------|
| C1    | 6.21617         | 6.13325         | 6.28993 | 0.08292 | 0.07376 |
| C2    | 6.2738          | 6.27643         | 6.29536 | -0.00263 | 0.02156 |
| C3    | 5.93805         | 5.97178         | 5.86767 | 0.04727 | 0.03862 |
| C4    | 5.88888         | 5.86003         | 5.86956 | -0.03995 | -0.01948 |
| C5    | 6.2058          | 6.17683         | 6.259   | 0.02897 | 0.05352 |
| C6    | 6.23611         | 6.36265         | 6.27016 | 0.02213 | 0.01151 |
| H7    | 0.75304         | 0.72666         | 0.78621 | 0.02844 | 0.03117 |
| H8    | 0.75914         | 0.73335         | 0.76838 | 0.02579 | 0.02724 |
| H9    | 0.74663         | 0.72829         | 0.76772 | 0.01834 | 0.02109 |
| H10   | 0.75481         | 0.72733         | 0.78374 | 0.02748 | 0.02893 |
| C11   | 8.4971          | 8.77975         | 8.59172 | -0.02842 | 0.10201 |
| C12   | 6.37612         | 6.35734         | 6.36266 | -0.00662 | -0.00052 |
| C13   | 7.59209         | 7.36143         | 7.53541 | 0.06766 | 0.10542 |
| C14   | 6.26023         | 6.15996         | 6.25541 | 0.01027 | -0.00482 |
| C15   | 0.73282         | 0.71214         | 0.75768 | 0.02068 | 0.02486 |
| C16   | 6.21247         | 6.16189         | 6.33729 | 0.05058 | 0.12482 |
| H17   | 0.74159         | 0.71956         | 0.76004 | 0.02203 | 0.01845 |
| H18   | 0.56136         | 0.53755         | 0.58985 | 0.02381 | 0.02849 |
| O2    | 6.81062         | 6.548           | 6.69652 | 0.06262 | 0.0589 |
| C21   | 5.73382         | 5.70826         | 5.70547 | 0.02556 | -0.00265 |
| C22   | 6.28375         | 6.19007         | 6.38899 | 0.09368 | 0.08514 |
| C23   | 8.44743         | 8.46819         | 8.46959 | 0.00124 | 0.01916 |
| C24   | 6.33764         | 6.31054         | 6.34671 | 0.0271 | 0.00907 |
| H25   | 0.74659         | 0.71959         | 0.76898 | 0.027 | 0.02329 |
| C26   | 5.88059         | 5.77442         | 5.92162 | 0.10635 | 0.07157 |
| H27   | 0.74063         | 0.71232         | 0.77442 | 0.03374 | 0.02834 |
| H28   | 0.76826         | 0.73585         | 0.79574 | 0.03268 | 0.02748 |

**STQ on the MS surface**: these results are in good correlation with the experimental IE%.

**Monte Carlo (Molecular dynamic) simulation**

Molecular dynamics (MD) simulation provides considerable information about the physical movements of atoms and molecules, which gives a view of the motion of the atoms after interaction at a certain time. Figure 14 represents the top and side views of the most
Figure 14: The side and top views of the most stable low energy configuration for the adsorption of the inhibitors on Fe (1 1 0) surface obtained through the Monte Carlo simulation. (a) BMQ, (b) FVQ, and (c) STQ.

Figure 15: A typical energy profile for the adsorption progress of BMQ on Fe (110) surface using the Monte Carlo sampling procedure.

exist at around 2 Å – 3.5 Å. The pair correlation function, $g(r)$, of C, N, and O of quinoxaline derivatives atoms and surface atoms was depicted in Figure 16. Generally, the chemical bonds can be formatted in correlation with the peak within 3.5 Å, while the Van der Waals force or Coulomb force interactions are correlated with the peak outside of 3.5 Å. We will consider the distribution of heteroatoms according to their importance on the adsorption process of chemical compounds on the metal surface, while, the carbons atoms reactivity can be obtained from π-system. For STQ, the highest peaks of the pair correlation function curve of O, C and N atoms appear at 3.43 Å, and the interactive force of these atoms on the Fe (1 1 0) surface follow the same trend. For BMQ, the highest peaks of the pair correlation function curve of C, N, and O atoms appear at 2.55 Å, 2.85 Å, and 2.55 Å, respectively, and the interactive force of these atoms during the interaction with the Fe(1 1 0) surface follow the order of $F(O) > F(C) > F(N)$. For FVQ, the highest peaks of the pair correlation function curve of C, N, and O atoms appear at 2.85 Å, 3.15 Å, and 2.85 Å, respectively, and the interactive force of C, N, and O atoms occur during interaction with the Fe (1 1 0) surface following the order of $F(C) = F(O) > F(N)$. Overall, the pair correlation function curves of C, N, and O of quinoxaline derivatives and the Fe (1 1 0) surface show that the highest peak of all interaction appeared within 3.5 Å. This indicates that chemical bonds can be formed between active centers of investigated compounds and Fe (1 1 0) atoms, confirming the high inhibition efficiency of tested inhibitors.

Conclusion

The synthesized quinoxaline derivatives act as good corrosion inhibitors for the MS in 1.0 M HCl solution and the inhibiting performance of BMQ is better than FVQ and STQ. Polarization results
Figure 16: The pair correlation function of C, N, and O atoms from three quinoxaline derivatives with Fe atoms from Fe (1 1 0) surface.

| Atom | $P_1 (N)$ | $P_2 (N-1)$ | $P_3 (N+1)$ | $f_i^+$ | $f_i^-$ |
|------|-----------|-------------|-------------|--------|--------|
| C1   | 6.21773   | 6.14017    | 6.28938     | 0.07165 | 0.07756 |
| C2   | 6.27371   | 6.27612    | 6.29525     | 0.02154 | -0.00241 |
| C3   | 5.84047   | 5.79659    | 5.86754     | 0.02707 | 0.04388 |
| C4   | 5.88828   | 5.85992    | 5.86958     | -0.0187 | 0.02836 |
| C5   | 6.20657   | 6.1783     | 6.25852     | 0.05195 | 0.02827 |
| C6   | 6.2587    | 6.23972    | 6.26991     | 0.01121 | 0.01898 |
| H7   | 0.75553   | 0.72885    | 0.7859      | 0.03037 | 0.02668 |
| H8   | 0.75969   | 0.73561    | 0.78621     | 0.02652 | 0.02408 |
| H9   | 0.74683   | 0.73023    | 0.76739     | 0.02056 | 0.0166 |
| H10  | 0.75531   | 0.72967    | 0.78345     | 0.02814 | 0.02564 |
| C11  | 5.84455   | 5.87515    | 5.9476      | 0.10305 | -0.0306 |
| C12  | 5.36739   | 5.37412    | 5.36706     | 0.00047 | -0.00673 |
| N13  | 7.43082   | 7.36509    | 7.53289     | 0.10207 | 0.06573 |
| N14  | 7.59265   | 7.56719    | 7.62214     | 0.02949 | 0.02546 |
| C15  | 6.2723    | 6.17253    | 6.26119     | -0.01111 | 0.09977 |
| H16  | 0.74831   | 0.72885    | 0.77186     | 0.02355 | 0.01846 |
| C17  | 6.15179   | 6.1024     | 6.26275     | 0.13096 | 0.04939 |
| H18  | 0.7553    | 0.7344     | 0.7717      | 0.0164  | 0.0209 |
| C19  | 6.108     | 6.0772     | 6.07915     | -0.02885 | 0.0308 |
| C20  | 6.18418   | 6.14051    | 6.22587     | 0.04169 | 0.04367 |
| C21  | 6.18885   | 6.16303    | 6.22418     | 0.03533 | 0.02582 |
| C22  | 6.32592   | 6.30241    | 6.33193     | 0.00601 | 0.02351 |
| H23  | 0.75973   | 0.73896    | 0.77395     | 0.01422 | 0.02077 |
| C24  | 6.27262   | 6.25183    | 6.28159     | 0.00897 | 0.02079 |
showed that all tested inhibitors are of mixed type in nature. In the presence of all inhibitors, charge transfer resistance increases and double layer capacitance decreases due to adsorption of the inhibitors’ molecules on the MS surface. The experimental results showed that the quinoxaline derivatives adsorb spontaneously on the MS surface and conform to the Langmuir adsorption isotherm. The adsorption process involves physical adsorption. DFT calculations, Monte Carlo simulation and RDF were performed to identify the reactivity of these molecules towards corrosion inhibition, and the results are in good agreement with the experimental investigations. Both experimental and quantum chemical results showed that the order of inhibition efficiency, for the studied compounds is as follows: BMQ > FVQ > STQ.

References

1. Anejjar A, Salghi R, Zarrouk A (2014) Inhibition of carbon steel corrosion in 1M HCl medium by potassium thiooctyanate. Journal of the Association of Arab Universities for Basic and Applied Sciences 15: 21-27.

2. Bammou L, Belkhouda M, Salghi R, Benali O, Zarrouk A, et al. (2014) Corrosion inhibition of steel in sulfuric acid solution by the chenopodium ambrosioides extracts. Journal of the Association of Arab Universities for Basic and Applied Sciences 16: 83-90.

3. Bazzi L, Salghi R, Zine E (2002) Inhibition de la corrosion de l’alliage BMQ.

4. Bazzi L, Salghi R, Zine E (2003) Inhibition effect on the electrochemical and quantum chemical studies of copper corrosion inhibitors in sulfuric acid medium. Journal of Molecular Liquids 121: 168-186.

5. Bazzi L, Salghi R, Zine E (2004) Synergistic effect of potassium iodide with (E)-3-(4-methoxystyryl) quinolin-2(1H)-one on the corrosion inhibition of carbon steel in 1.0 M HCl. Der Pharma Chemica 7: 36-45.

6. Anupama KK, Ramya K, Joseph A (2016) Electrochemical and computational aspects of surface interaction and corrosion inhibition of mild steel in hydrochloric acid by Phyllanthus amarus leaf extract (PAE). Journal of Molecular Liquids 216: 146-155.

7. Farag AA, Ismail AS, Megahed M (2015) Inhibition of carbon steel corrosion in acidic solution using some newly polyester derivatives. Journal of Molecular Liquids 211: 915-923.

8. Gupta NK, Verma C, Quaisa MI, Mukherjee AK (2016) Schiff’s bases derived from Hysine and aromatic aldehydes as green corrosion inhibitors for mild steel: Experimental and theoretical studies. Journal of Molecular Liquids 215: 47-57.

9. Murulana LC, Kabanda MM, Ebensho EE (2016) Investigation of the adsorption characteristics of some selected sulphonamide derivatives as corrosion inhibitors at mild steel/hydrochloric acid interface: Experimental, quantum chemical and QSAR studies. Journal of Molecular Liquids 215: 763-779.

10. Ramesh Kumar S, Danee I, Rashvand Aei A, Vijayan M (2015) Quantum chemical and experimental investigations on equipotent effects of (+) R and (+) S enantiomers of racemic amisulpride as eco-friendly corrosion inhibitors for mild steel in acidic solution. Journal of Molecular Liquids 212: 168-186.

11. Sharma G, Raisinghani P, Abraham I, Pardasani RT, Mukherjee T (2009) Synthesis of quinoxaline quinones and regio-selectivity in their Dils-Alder cycloadditions. Indian Journal of Chemistry (Section B) 48: 1590-1596.

12. Thomas KJR, Velusamy M, Lin JT, Chuen CR, Tao YT (2005) Chromophore-labeled quinoxaline derivatives as efficient electroluminescent materials. Chemistry of Materials 17: 1860-1866.

13. Aguirre G, Cerretetto H, Maio DR, Gonzalez M, Alfaro ME, et al. (2004) Quinoxaline N, N’-dioxide derivatives and related compounds as growth inhibitors of Trypanosoma cruzi. Structure-activity relationships. Bioorganic and Medicinal Chemistry Letters 14: 3835-3839.

14. Oulasunkanni LO, Kabanda MM, Ebenso EO (2016) Quinoxaline derivatives as corrosion inhibitors for mild steel in hydrochloric acid medium: Electrochemical and quantum chemical studies. Physica E: Low-dimensional Systems and Nanostructures 76: 109-126.

15. Obot IB, Obi-Egbedo NO, Odozi NW (2010) Acenaphtho[1,2-b] quinoline as a novel corrosion inhibitor for mild steel in 0.5 MH 2 SO 4. Corrosion Science 52: 923-926.

16. Saranya J, Sounthari P, Parameswari K, Chitra S (2016) Acenaphtho[1,2-b] quinoline and acenaphtho[1,2-b]pyrazine as corrosion inhibitors for mild steel in acid medium. Measurement 77: 175-186.

17. Obot IB, Obi-Egbedo NO (2010) 2, 3-Diphenylbenzoquinoline: A new corrosion inhibitor for mild steel in sulphuric acid. Corrosion Science 52: 282-285.

18. Laskhri M, Arshadi MR (2004) DFT studies of pyridine corrosion inhibitors in electrical double layer: solvent, substrate, and electric field effects. Chemical physics 299: 131-137.

19. Verma C, Ebenso EE, Bahadur I, Obot IB, Qaisah MA (2015) 5-(Phenylthio)-3H-pyrrole-4-carbonitriles as effective corrosion inhibitors for mild steel in 1M HCl: Experimental and theoretical investigation. Journal of Molecular Liquids 212: 209-218.

20. Al-Mobarak N, Khaleed K, Hamed MNH, Abdel-Azimb KM, Abdelshafibet NS (2010) Corrosion inhibition of copper in chloride media by 2-mercapto-4-(p-methoxyphenyl)-6-oxo-1,6-dihydropyrimidine-5-carbonitrile: Electrochemical and theoretical study. Arabian Journal of Chemistry 3: 233-242.

21. Yan Y, Wang X, Zhang Y, Wang P, Zhang J (2013) Theoretical evaluation of inhibition performance of purine corrosion inhibitors. Molecular Simulation 39: 1034-1041.

22. Saha SK, Banerjee P (2015) A theoretical approach to understand the inhibition mechanism of steel corrosion with two aminobenzonitrile inhibitors. RSC Advances 5: 71120-71130.

23. Zhang Z, Tian NC, Huang XD, Shah W, Wu L (2016) Synergistic inhibition of carbon steel corrosion in 0.5 M HCl solution by indigo Carmine and some cationic organic compounds: experimental and theoretical studies. RSC Advances 6: 22250-22268.

24. Xie SW, Liu Z, Han GC, Li W, Liu J, et al. (2015) Molecular dynamics simulation of inhibition mechanism of 3, 5-dibromo salicylaldehyde Schiff’s base. Computational and Theoretical Chemistry 1033: 50-62.

25. Lanquist J, Stacey G (1953) 568. Quinoxaline N-oxides. Part II. Oxides of Pyridine. J Am Chem Soc 75: 2830.

26. Ried W, Hinsching S (1956) Synthese heterocyclisch substituierter Äthylene cycloadditions. Indian Journal of Chemistry (Section B) 48: 1590-1596.

27. Anupama KK, Ramya K, Joseph A, Al-Salghi R, Benali O, et al. (2014) Corrosion inhibition of steel in sulfuric acid solution by the chenopodium ambrosioides extracts. Journal of the Association of Arab Universities for Basic and Applied Sciences 15: 21-27.

28. Bammou L, Belkhouda M, Salghi R, Benali O, Zarrouk A, et al. (2014) Corrosion inhibition of steel in sulfuric acid solution by the chenopodium ambrosioides extracts. Journal of the Association of Arab Universities for Basic and Applied Sciences 16: 83-90.

29. Bazzi L, Salghi R, Zine E (2002) Inhibition de la corrosion de l’alliage BMQ.

30. Bazzi L, Salghi R, Zine E (2003) Inhibition effect on the electrochemical and quantum chemical studies of copper corrosion inhibitors in sulfuric acid medium. Journal of Molecular Liquids 121: 168-186.

31. Bazzi L, Salghi R, Zine E (2004) Synergistic effect of potassium iodide with (E)-3-(4-methoxystyryl) quinolin-2(1H)-one on the corrosion inhibition of carbon steel in 1.0 M HCl. Der Pharma Chemica 7: 36-45.

32. Anupama KK, Ramya K, Joseph A (2016) Electrochemical and computational aspects of surface interaction and corrosion inhibition of mild steel in hydrochloric acid by Phyllanthus amarus leaf extract (PAE). Journal of Molecular Liquids 216: 146-155.

33. Farag AA, Ismail AS, Megahed M (2015) Inhibition of carbon steel corrosion in acidic solution using some newly polyester derivatives. Journal of Molecular Liquids 211: 915-923.

34. Gupta NK, Verma C, Quaisa MI, Mukherjee AK (2016) Schiff’s bases derived from Hysine and aromatic aldehydes as green corrosion inhibitors for mild steel: Experimental and theoretical studies. Journal of Molecular Liquids 215: 47-57.

35. Murulana LC, Kabanda MM, Ebensho EE (2016) Investigation of the adsorption characteristics of some selected sulphonamide derivatives as corrosion inhibitors at mild steel/hydrochloric acid interface: Experimental, quantum chemical and QSAR studies. Journal of Molecular Liquids 215: 763-779.
27. Adarrou K, Tour R, Ramli Y, Essassi EM (2013) Comparative inhibition study of mild steel corrosion in hydrochloric acid by new class synthesized quinoxaline derivatives: part I. Research on Chemical Intermediates 39: 1843-1855.

28. Ramli Y, Slimani R, Zouhri H, Lazzer S, Essassi EM (2010) 2-Methyl-3-(n-octylsulfanyl)quinoxaline. Acta Crystallographica Section E 66: 6992.

29. Lazg H, Belkhaouda M, Larouj M, Salghi R, Jodeh S, et al. (2016) Corrosion protection of carbon steel in acidic solution by using ylang-ylang oil as green inhibitor. Moroccan Journal of Chemistry 4: 101-111.

30. Larouj M, Belkhaouda M, Lazg H, Salghi R, Jodeh S, et al. (2016) Experimental and theoretical study of new synthesized organic compounds on corrosion behaviour and the inhibition of carbon steel in hydrochloric acid solution. Der Pharma Chemica 8: 114-133.

31. Becke AD (1992) Density-functional thermochemistry. I. The effect of the exchange-only gradient correction. The Journal of Chemical Physics 96: 2155-2160.

32. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. The Journal of Chemical Physics 98: 5648-5652.

33. Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Physical Review B 37: 785-789.

34. Frisch M, Trucks G, Schlegel H (2003) Gaussian 03, revision B.05. Gaussian, Inc., Pittsburgh PA.

35. Materials Studio (2013) Revision 6.0. Accelrys Inc., San Diego, USA.

36. Sasakiyama A, Akeunale A, Olasunkanni L, Bahadur I, Baskar R, et al. (2015) Experimental, chemical and Monte Carlo simulation studies on the corrosion inhibition of some alkyl imidazolium ionic liquids containing tetrafluoroborate anion on mild steel in acidic medium. Journal of Molecular Liquids 211: 105-118.

37. Elvani AR, Zhou J, Duszczyk J (2012) A new approach to incorporating the effect of nano-sized dispersoids on recrystallization inhibition into Monte Carlo simulation. Computational Materials Science 54: 370-377.

38. Solzam R, Kardas G, Cilula M, Yazici B, Ezri M (2008) Investigation of adsorption and inhibitive effect of 2-mercaptothiazoline on corrosion of mild steel in hydrochloric acid media. Electrochimica Acta 53: 5941-5952.

39. Singh DK, Kumar S, Udayabhanu G, John RP (2016) (N, N-dimethylamino) benzaldehyde nicotinic hydrazone as corrosion inhibitor for mild steel in 1M HCl solution: An experimental and theoretical study. Journal of Molecular Liquids 216: 738-746.

40. Singh P, Srivastava V, Quraishi MA (2016) Novel quinoline derivatives as green corrosion inhibitors for mild steel in acidic medium: Electrochemical, SEM, AFM, and XPS studies. Journal of Molecular Liquids 216: 164-173.

41. Moura P, Singh P, Tewari A, Rastogi RB, Singh MM, et al. (2015) Relationship between structure and inhibition behaviour of quinolinium salts for mild steel corrosion: experimental and theoretical approach. Corrosion Science 95: 71-87.

42. Bayol E, Gürtler AA, Dursun M, Kayacikaz K (2008) Adsorption Behavior and inhibition corrosion effect of sodium carboxymethyl cellulose on mild steel in acidic medium. Acta Physico-Chimica Sinica 24: 2236-2243.

43. Avci Ö (2008) Inhibitor effect of N,N'-methyleneacrylamidylcarbonyl on corrosion behavior of mild steel in 0.5 M HCl. Materials Chemistry and Physics 112: 234-238.

44. Yuço AO, Solzam R, Kardas G (2012) Investigation of inhibition effect of rhodamine-N-acetic acid on mild steel corrosion in HCl solution. Materials Chemistry and Physics 131: 615-620.

45. Yang Z, Zhan F, Pan Y, Lü Z, Han C, et al. (2015) Structure of a novel Benzyl Quinolinium Chloride derivative and its effective corrosion inhibition in 15 wt.% hydrochloric acid. Corrosion Science 99: 281-294.

46. Hameed RSA (2011) Aminolysis of polyethylene terephthalate waste as green corrosion inhibitor for carbon steel in HCl corrosive medium. Electrochimica Acta 56: 2844-2857.

47. Bentiss F, Lebrini M, Lagrenée M (2005) Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/2, 5-bis (n-thienyl)-1, 3, 4-thiadiazoles/hydrochloric acid system. Corrosion Science 47: 2915-2931.

48. Mu G, Li X, Liu G (2005) Synergistic inhibition between tween 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid. Corrosion Science 47: 1932-1952.

49. Thomas JM, Thomas WJ, Salzberg H (1967) Introduction to the principles of heterogeneous catalysis. Journal of The Electrochemical Society 114: 279C-297C.

50. Odewunmi NA, Umoren SA, Gasem ZM (2015) Watermelon waste products as green corrosion inhibitors for mild steel in HCl solution. Journal of Environmental Chemical Engineering 3: 286-296.

51. Eddy NO, Momoh-Yahaya H, Oguzie EE (2015) Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. Journal of Applied Research 6: 203-217.

52. Zhang D, Tang Y, Qi S, Donga D, Cang H, et al. (2016) The inhibition performance of long-chain alkyl-substituted benzimidazole derivatives for corrosion of mild steel in HCl. Corrosion Science 102: 517-522.

53. Hussin MH, Rahim AA, Ibrahim MM, Bross NE (2016) The capability of ultrafiltrated alkaline and organosolv oil palm (Elaeis guineensis) fronds lignin as green corrosion inhibitor for mild steel in 0.5 M HCl solution. Measurement 78: 90-103.

54. Zhang Q, Hua YX (2009) Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. Electrochimica Acta 54: 1881-1887.

55. Ramya K, Anupama KK, Shainy KM, Joseph A (2016) Synergistic and hydrogen bonded interaction of alkyl benzimidazolates and urea pair on mild steel in hydrochloric acid: Adsorption, electroanalytical and theoretical studies. Journal of the Taiwan Institute of Chemical Engineers 58: 517-527.

56. Khadiri A, Sadik R, Bekkouche K, Aounibil A, Hammoudi B, et al. (2016) Gravitricimetric, electrochemical and quantum chemical studies of some pyridazine derivatives as corrosion inhibitors for mild steel in 1 M HCl solution. Journal of the Taiwan Institute of Chemical Engineers 58: 552-564.

57. Odewunmi NA, Umoren SA, Gasem ZM, Ganiyu SA, Muhammad Q (2015) L-Citrulline: An active corrosion inhibitor component of watermelon rind extract for mild steel in HCl medium. Journal of the Taiwan Institute of Chemical Engineers 51: 177-185.

58. Shahraji M, Dehdab M, Etili S (2016) Theoretical studies on the corrosion inhibition performance of three amine derivatives on carbon steel: Molecular dynamics simulation and density functional theory approaches. Journal of the Taiwan Institute of Chemical Engineers 62: 313-321.

59. Verma CB, Quraishi M, Singh A (2015) 2-Aminobenzene-1, 3-dicarbonylitrone as green corrosion inhibitor for mild steel in 1 M HCl. Electrochemical, thermodynamic, surface and quantum chemical investigation. Journal of the Taiwan Institute of Chemical Engineers 49: 229-239.

60. Verma C, Quraishi M, Singh A (2016) A thermodynamical, electrochemical, theoretical and surface investigation of dietheroaryliothio ethers as effective corrosion inhibitors for mild steel in 1 M HCl. Journal of the Taiwan Institute of Chemical Engineers 58: 127-140.

61. Xu B, Gong W, Zhang K, Chen Y, et al. (2015) Theoretical prediction and experimental study of 1-Butyl-2-(4-methylphenyl)benzimidazole as a novel corrosion inhibitor for mild steel in hydrochloric acid. Journal of the Taiwan Institute of Chemical Engineers 51: 193-200.

62. Xu Z, Yuan S-L, Yan H, Liu C-B (2011) Adsorption of histidine and histidine-containing peptides on Au (111): a molecular dynamics study. Colloids and Surfaces A: Physicochemical and Engineering Aspects 380: 135-142.

63. Zhang K, Yang W, Xu B, Liu Y, Yina X, et al. (2015) Corrosion inhibition of mild steel by bromide-substituted imidazoline in hydrochloric acid. Journal of the Taiwan Institute of Chemical Engineers 56: 167-174.

64. Hegazy M, Abdallah M, Awad M, Rezk M (2014) Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part I: experimental results. Corrosion Science 81: 54-64.

65. Quraishi MA (2014) 2-Amino-3, 5-dicarboxylic acid as corrosion inhibitors for mild steel in 1 M HCl. Industrial & Engineering Chemistry Research 53: 2851-2859.

66. Hegazy M, Abdallah M, Awad M, Rezk M (2014) Three novel di-quaternary ammonium salts as corrosion inhibitors for API X65 steel pipeline in acidic solution. Part II: theoretical results. Corrosion Science 81: 54-64.

67. McCafferty E (2010) Introduction to corrosion science. Springer Science & Business Media.

68. Khalil N (2003) Quantum chemical approach of corrosion inhibition. Electrochimica Acta 48: 2635-2640.
69. Sastri VS, Perumareddi JR (1997) Molecular orbital theoretical studies of some organic corrosion inhibitors. Corrosion 53: 617-622.

70. Pearson RG (1988) Absolute electronegativity and hardness: application to inorganic chemistry. Inorganic Chemistry 27: 734-740.

71. Martínez S (2003) Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms. Materials Chemistry and Physics 77: 97-102.

72. Lukovits I, Kalman E, Zucchi F (2001) Corrosion inhibitors-correlation between electronic structure and efficiency. Corrosion 57: 3-8.

73. Rodríguez-Valdez LM, Villamisar W, Casales M (2006) Computational simulations of the molecular structure and corrosion properties of amidoethyl, aminoethyl and hydroxyethyl imidazolines inhibitors. Corrosion Science 48: 4053-4064.

74. Li X, Deng S, Fu H, Li T (2009) Adsorption and inhibition effect of 6-benzylaminopurine on cold rolled steel in 1.0 M HCl. Electrochimica Acta 54: 4089-4098.

75. Pearson RG (1988) Chemical hardness and bond dissociation energies. Journal of the American Chemical Society 110: 7684-7690.

76. Koch E (2005) Acid-Base interactions in energetic materials: I. the hard and soft acids and bases (HSAB) Principle—Insights to Reactivity and Sensitivity of Energetic Materials. Propellants, Explosives, Pyrotechnics 30: 5-16.

77. Zhou Z, Parr RG (1990) Activation hardness: new index for describing the orientation of electrophilic aromatic substitution. Journal of the American Chemical Society 112: 5720-5724.

78. Gece G (2008) The use of quantum chemical methods in corrosion inhibitor studies. Corrosion Science 50: 2981-2992.

79. Okulik N, Jubert AH (2005) Theoretical analysis of the reactive sites of non-steroidal anti-inflammatory drugs. Internet Electronic Journal of Molecular Design 4: 17-30.

80. Daoud D, Douadi T, Hamani H (2015) Corrosion inhibition of mild steel by two new 5-heterocyclic compounds in 1 M HCl: Experimental and computational study. Corrosion Science 94: 21-37.

81. Tian H, Li W, Cao K, Hou B (2013) Potent inhibition of copper corrosion in neutral chloride media by novel non-toxic thiadiazole derivatives. Corrosion Science 73: 281-291.

82. Terrones RR, Fuentesbalba P, Galván M, Pérez P (1999) A direct evaluation of regional Fukui functions in molecules. Chemical Physics Letters 304: 405-413.

83. Contreras RR, Fuentesbalba P, Galván M, Pérez P (1999) A direct evaluation of regional Fukui functions in molecules. Chemical Physics Letters 304: 405-413.

84. Kaya S, Kaya C, Guo L, Kandemirli F, Türün B, et al. (2016) Quantum chemical and molecular dynamics simulation studies on inhibition performances of some thiazole and thiazole derivatives against corrosion of iron. Journal of Molecular Liquids 219: 497-504.

85. Verma C, Olasunmikan LO, Obot IB, Ebenso EE, Guraishi MA (2016) 5-Arylpyrimido-[4,5-b]quinoline-diones as new and sustainable corrosion inhibitors for mild steel in 1 M HCl: a combined experimental and theoretical approach. RSC Adv 6: 15639-15654.

86. Khaled K, El-Maghraby A (2014) Experimental, Monte Carlo and molecular dynamics simulations to investigate corrosion inhibition of mild steel in hydrochloric acid solutions. Arabian Journal of Chemistry 7: 319-326.

87. Kühlke A (2009) Self-assembly of organic molecules at metal surfaces. Current Opinion in Colloid and Interface Science 14: 157-168.

88. Shi WY, Ding C, Yan JL, Hanb XY, Lva ZM, et al. (2012) Molecular dynamics simulation for interaction of PESA and acrylic copolymers with calcite crystal surfaces. Desalination 291: 8-14.