Pyrazoline derivatives as possible corrosion inhibitors for mild steel in acidic media: A combined experimental and theoretical approach

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Abstract: Various experimental and theoretical methods have been employed to study the effectiveness of two pyrazoline derivatives namely, 2-(4-(5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)phenoxy)acetic acid (P1) and 2-(4-(5-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenoxy)acetic acid (P2) as corrosion inhibitors for mild steel in 1.0 M HCl at 303 K. The inhibitors show high inhibition efficiency and their adsorption on mild steel surface was found to obey Langmuir adsorption isotherm. Potentiodynamic polarization results revealed that both compounds behaved as mixed-type inhibitors. The results from electrochemical impedance spectroscopy studies reveal an increase in polarization resistance. Density Functional Theory calculations and molecular dynamic simulations were used to give basic insights into the action mode of inhibitors as well as to substantiate the experimental results. The surface morphology of the mild steel surface was examined using Scanning Electron Microscopy and Atomic Force Microscopy.

Keywords: inhibitors; corrosion; pyrazoline; DFT; molecular dynamic simulation

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PUBLIC INTEREST STATEMENT
There are significant interest in the protection of metals against corrosion. Among many methods available to solve this problem, addition of inhibitors is one of the choice especially when the metal is exposed for large quantity of electrolyte medium. This paper explores the potential of the compounds synthesized for such applications. These compounds are synthetically scalable and chemically stable. These data presented may be useful for the practitioners of corrosion studies.
1. Introduction

Metal corrosion is the phenomenon that causes enormous economic costs, damage to the equipment, poses a serious threat to the environment and human health (Laabaissi et al., 2017; Salghi et al., 2017). Many methods and strategies to protect metals against corrosion are available at commercial level. Unfortunately, corrosion cannot be fully prevented, and corrosion control becomes an option which involve the slowing of the kinetics and/or altering the mechanism. Iron and its alloys are widely used in many industries due to their excellent combination of properties. However, when exposed to aggressive environments, such as the use of acid solutions for pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling, these processes usually lead to substantial loss of the metal due to corrosion (Aljourani, Raeissi, & Golozar, 2009; Machnikova, Whitmire, & Hackerman, 2008). Among the different methods of corrosion control and prevention, the use of corrosion inhibitors is one of the effective methods in combating corrosion (El Aoufir et al., 2017; El Azhar, Mernari, Traisnel, Bentiss, & Lagrenée, 2003; Kumar et al., 2017). The majority of highly effective inhibitors used in oil and gas industry are organic compounds containing one or more hetero atoms; such as oxygen, nitrogen, and sulfur atoms conjugated with multiple bonds within the molecular structure (Lgaz, Salghi, Jodeh, & Hammouti, 2017; Messali et al., 2017).

Pyrazoles and pyrazoline derivatives are well known for their biological activity. Their potential application range from antimicrobial, anti-inflammatory to anticancer activity. We have been working on such compounds for long time as part our structure property studies on antimicrobial activity and results show they are moderately active (Shubhalaxmi, Pathak, Ananda, & Bhat, 2016). Recently, there has been great interest in the field of organic corrosion inhibitors and obviously among them heterocyclic derivatives are the most common. Pyrazole derivatives are known corrosion inhibitors (Yadav, Sinha, Sarkar, & Tiwari, 2015). Pyrazoline derivatives synthesized by us expected to show good inhibitory potential because of the presence of heteroatoms like nitrogen and oxygen. An added advantage of these molecules is the presence of carboxylic acid group which may increase the solubility of compounds in aqueous medium. The present paper investigates the inhibitory effect of two such derivatives on the mild steel corrosion in aggressive hydrochloric acid solution using both chemical (i.e. gravimetric), electrochemical (Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS)). Further, to understand the inhibitive capabilities of these molecules, theoretical evaluation has been carried out by performing computational studies. The study leads to the determination of possible interaction and adsorption efficiencies of the inhibitor molecules on Fe. Previous research showed that density functional theory (DFT) along with Molecular dynamic simulations are powerful approaches for developing an understanding of the interaction between metal surfaces and inhibitor molecules (Awe, Idris, Abdulwahab, & Oguzie, 2015; Fouda, Elewady, Shalabi, & Abd El-Aziz, 2015; Lgaz, Subrahmanya Bhat, et al., 2017). The morphology of the corroding metal will be monitored, both in the absence and presence of inhibitors, with the aid of Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

2. Experimental

2.1. Inhibitors

The compounds P1 and P2 have been synthesized as per the details provided in our earlier publications (Ajees et al., 2017; Shubhalaxmi et al., 2016) (Table 1).

2.2. Materials and inhibitors

The elemental composition of the mild steel specimens used for the experimental study was: 0.370% C, 0.230% Si, 0.680% Mn, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% Cu and balance Fe. The surface of mild steel was abraded and polished mechanically with 360–1,600 grade of emery paper (SiC). The working electrode was thereafter degreased with acetone, rinsed with bi-distilled water and then dried at room temperature before further use. The aggressive medium (1 M HCl) was prepared by diluting a reagent of analytical grade HCl 37% (from Sigma-Aldrich) with double-distilled water.
2.3. Weight loss tests and electrochemical measurements

The samples of mild steel used in the gravimetric method are in the form of a square of 
(1.8 × 1.8 × 0.06 cm³) dimension, were polished with 360–1,600 grits of emery paper and suspended 
for 6 h of immersion time with different concentrations of inhibitors, in absence of agitation main-
tained at a constant temperature (303 K). The exposed specimens were washed with distilled water, 
dried, and then weighed by using a Metler balance. The accuracy of the balance is 0.0001 g. The 
mean of weight loss values for three identical experiments was used to calculate the inhibition effi-
ciency of the inhibitor.

Three-electrode electrochemical glass cell consisting of a platinum (as counter electrode, CE), a 
saturated calomel electrode (ECS) (as reference electrode, RE), and mild steel (as working electrode, 
WE) with freshly pre-treated reactive surface area of 1 cm² was used for electrochemical studies. 
Electrochemical experiments were conducted using impedance equipment (Tacussel Radiometer 
PGZ 100) and controlled with Tacussel corrosion analysis software model VoltaMaster 4. The WE was 
left to undergo free corrosion in the test solution for 30 min, within which a stable open circuit po-
tential (OCP) was reached, and after which electrochemical perturbation was applied. For the Tafel 
polarization measurements, the potentials were swept between −800 to −200 mV at the scan rate 
of 1 mV/s relative to the corrosion potential (E_corr). For the EIS measurements, AC current signal was 
passed through the system within the frequency range of 10 mHz to 100 kHz at 10 mV amplitude.

2.4. DFT and Molecular dynamic simulations

The quantum-based calculations were conducted using Materials Studio software package (version 
6.0) at DFT/GGA level using BOP functional and DNP basis set on all atoms (Delley, 1990, 2000; 
Materials Studio, 2013). The calculations started without any geometry constraints until full geom-
etry optimizations. The COSMO (Mulliken, 1955) controls were used for solvation effects (aqueous 
phase). The ionization energy and the electronic affinity were determined by the values of the ener-
gies of the HOMO and LUMO orbital (Dewar & Thiel, 1977):

\[ I = -E_{\text{HOMO}} \]  \hspace{1cm} (1)

\[ A = -E_{\text{LUMO}} \]  \hspace{1cm} (2)

The values of \( I \) and \( A \) are exploited in order to find the values of the electronegativity and the 
global hardness of the inhibitory molecule (Pearson, 1990):

\[ \chi = \frac{I + A}{2} \]  \hspace{1cm} (3)

\[ \eta = \frac{I - A}{2} \]  \hspace{1cm} (4)

The fraction of electrons transferred (\( \Delta N \)) from inhibitor to metallic surface was calculated using 
the equation (Martinez, 2003):

Table 1. Names, molecular structure and abbreviation of tested compounds

| Names | Molecular structure | Abbreviation |
|-------|---------------------|--------------|
| 2-((4-(5-(p-tolyl)-4,5-dihydro-1H-pyrazol-3-yl)phenoxy)acetic acid | ![Molecular structure of P1](image) | P1 |
| 2-((4-(5-(4-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl)phenoxy)acetic acid | ![Molecular structure of P2](image) | P2 |
where $\phi$ is the work function used as the appropriate measure of electronegativity of iron, and $\eta_{Fe} = 0$. The value of $\phi = 4.82$ eV for Fe (110) surface which is reported to have higher stabilization energy (Kokalj, 2012; Pearson, 1988, 1989).

The local reactivity of inhibitor molecules (nucleophilic and electrophilic attacks) were obtained by condensed Fukui functions (Parr & Yang, 1984), using the following equations (Contreras, Fuentealba, Galván, & Pérez, 1999):

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

(5)

where $\phi$ is the work function used as the appropriate measure of electronegativity of iron, and $\eta_{Fe} = 0$. The value of $\phi = 4.82$ eV for Fe (110) surface which is reported to have higher stabilization energy (Kokalj, 2012; Pearson, 1988, 1989).

In simulation procedures, molecular dynamic (MD) simulations were carried out using Materials studio package (Bunte & Sun, 2000) in a 10 × 10 super cell using the COMPASS force field with a time step of 1 fs and simulation time of 500 ps (Bunte & Sun, 2000) in a simulation box of $(24.82 \times 24.82 \times 35.69 \text{ Å}^3)$. The Temperature was fixed at 303 K. The binding and interactions energies are estimated by using following equations (Zhang, Tian, Huang, Shang, & Wu, 2016):

$$
E_{\text{Interaction}} = E_{\text{Total}} - (E_{\text{Surface} + \text{Solution}} + E_{\text{Inhibitor}})
$$

(8)

and

$$
E_{\text{Binding}} = -E_{\text{Interaction}}
$$

(9)

where $E_{\text{Total}}$ is the total energy of the entire system $E_{\text{Surface} + \text{Solution}}$ referred to the total energy of Fe (110) surface and solution without the inhibitor and $E_{\text{Inhibitor}}$ represent the total energy of inhibitor.

### 2.5. Surface characterization

The surface characteristics of mild steel specimens after immersing in aggressive solution for 6 h without and with $5 \times 10^{-3}$ M of inhibitors were examined using scanning electron microscopy (SEM (Hitachi TM-1000)) and Atomic force microscopy (VEECO CPII atomic force microscope (MPP-11123)).

### 3. Results and discussion

#### 3.1. Weight loss tests

Table 2 presents the calculated values of corrosion rates $C_R$ and $\eta_w$ (%) at different concentrations of corrosion inhibitors. The Equations (1–2) were used to calculate the corrosion rates $C_R$ and the inhibition efficiency, $\eta_w$ (%) respectively:

$$
C_R = \frac{\Delta m}{S \times t}
$$

(10)

$$
\eta_w = \frac{C_R^0 - C_R}{C_R^0} \times 100
$$

(11)

where $C_R^0$ and $C_R$ are the weight losses of mild steel specimens in the absence and presence of inhibitors, respectively.
The results showed that \( \eta_W(\%) \) was increased by increasing the corrosion inhibitor concentration while the corrosion rate of the metal specimen in the solution without corrosion inhibitors is much higher than that with inhibitors. With increasing concentration of the corrosion inhibitors, the efficiency was increased and reached 96 and 93% for P2 and P1 respectively. These results indicate that more molecules of inhibitors are adsorbed on electrode surface which result a stable inhibitor film. The inhibitive action of these chemical compounds is mainly due to the presence of many reactive sites such as heteroatoms (N and O atoms), \( \pi \)-bonds and aromatic rings which play a crucial role during inhibition process via the interaction with metal surface (Verma, Quraishi, & Singh, 2015).

### 3.2. Tafel polarization curves

To further confirm the corrosion inhibition effect of tested inhibitors, potentiodynamic polarization experiments were performed at 303 K. Figure 1 shows the polarization curves of mild steel in the aggressive solutions containing different inhibitors, and the respective electrochemical parameters such as corrosion potential, anodic and cathodic Tafel slopes and corrosion current density extracted from the corresponding Tafel plots are given in Table 3. In the solutions without corrosion inhibitors, in the anodic branch, steel dissolution and in the cathodic branch, hydrogen evolution reaction was occurred. It can be seen that the presence of inhibitor molecules results in a marked shift in both cathodic and anodic branches of the polarization curves toward lower current densities.

With increasing the concentration of corrosion inhibitors, the corrosion current density was reduced. Adding inhibitors prevent the acid attack to the steel’s surface. Comparing the anodic and cathodic branches of the curves indicates that by increasing the corrosion inhibitor concentration, the current density in both anodic and cathodic branches were reduced which indicates that the corrosion inhibitors worked as mixed type on mild steel in this solution. These changes are increased by increasing the concentration of corrosion inhibitors and this behavior indicates the corrosion inhibitors adsorption on the metal’s surface and protective effect on the transfer of electrical charges and ions in the anodic and cathodic reactions (Lgaz, Salghi, et al., 2017; Lgaz, Subrahmanya Bhat, et al., 2017). What’s more, as seen from Table 3, the Tafel slopes of anodic and cathodic curves almost unchanged, indicating the inhibitor molecules act as adsorptive inhibitor (Salarvand, Amirnasr, Talebian, Raeissi, & Meghdadi, 2017). Since the current density in the existence of the P2 was lower than that of P1, this means the corrosion inhibition performance of P2 excels P1. This observation is in consistence with the results of weight loss measurements.

### 3.3. Electrochemical impedance spectroscopy measurements

For more information about the corrosion inhibitor performance and the authentication of the obtained data of the potentiodynamic polarization tests, the electrochemical impedance spectroscopy is done on steel specimens. EIS is a powerful method to study the corrosion mechanism (Singh, Kumar, Udayabhanu, & John, 2016). Graphical presentations of the Nyquist plots performed in 1 M HCl and in
the presence of P1 and P2 at 303 K are presented in Figure 2. As can be seen from Figure 2, all the impedance spectra in EIS tests show depressed semicircles, and the deviation to a perfect semicircle may be attributed to inhomogeneity and roughness of the electrode surface (Lgaz, Subrahmanya

Table 3. The PDP parameters and inhibition efficiency of mild steel at different concentrations of pyrazoline derivatives in 1 M HCl at 303 K

| Inhibitors | Concentration (M) | $-E_{corr}$ (mV/SCE) | $-\beta_c$ (mV/dec) | $\beta_a$ (mV/dec) | $i_{corr}$ (μA/cm$^2$) | $\eta_{PDP}$ (%) |
|------------|-------------------|----------------------|---------------------|---------------------|-------------------------|-----------------|
| Blank      | 1.0               | 496                  | 162                 | 132.2               | 564                     | –               |
| P1         | $5 \times 10^{-3}$ | 487                  | 151                 | 111                 | 58                      | 89              |
|            | $1 \times 10^{-3}$ | 484                  | 150                 | 108                 | 70                      | 87              |
|            | $5 \times 10^{-4}$ | 473                  | 149                 | 103                 | 88                      | 84              |
|            | $1 \times 10^{-4}$ | 486                  | 149                 | 113                 | 105                     | 81              |
| P2         | $5 \times 10^{-3}$ | 502                  | 157                 | 105                 | 46                      | 92              |
|            | $1 \times 10^{-3}$ | 490                  | 155                 | 107                 | 61                      | 89              |
|            | $5 \times 10^{-4}$ | 495                  | 155                 | 104                 | 80                      | 85              |
|            | $1 \times 10^{-4}$ | 484                  | 153                 | 105                 | 98                      | 82              |
Bhat, et al., 2017). An increased diameter of the impedance plot in the presence of inhibitors suggests the enhanced inhibition performances.

Relating the impedance curve to an equivalent electrical circuit, leads to the confirmation of a mechanism for the system. Such relation leads to the calculation of the numeric value associated with the physical or chemical properties (Yadav, Gope, Kumari, & Yadav, 2016; Yadav, Sinha, Sarkar, Bahadur, & Ebenso, 2015). The equivalent circuit shown in the Figure 3 has been used for EIS data fitting. $R_s$ is the solution resistance, $R_p$ is related to the polarization resistance, and CPE is the constant phase element. The impedance of CPE ($Z_{CPE}$) represented by following equation (Lgaz, Subrahmanya Bhat, et al., 2017):

$$Z_{CPE} = \frac{1}{Q(j\omega)^n}$$

(12)

where $Q$ is the CPE coefficient, $n$ the CPE exponent (phase shift) which can be used as a measure of surface inhomogeneity (Chen et al., 2013), $\omega$ the angular frequency and $j$ stands for the imaginary unit. The interfacial capacitance $C_{dl}$ can be calculated using the expression (Olasunkanmi, Obot, & Ebenso, 2016):

$$C_{dl} = \sqrt{Q \times R_p^{1-n}}$$

(13)
Table 4 lists the values of EIS parameters obtained by fitting the EIS spectra together with the values of the inhibition efficiency calculated by the following equation (Gholami, Danaee, Maddahy, & RashvandAvei, 2013):

\[
\eta_{EIS}(\%) = \left(\frac{R_{p(inh)} - R_p}{R_{p(inh)}}\right) \times 100
\]

where \( R_{p(inh)} \) and \( R_p \) are polarization resistances with and without inhibitors, respectively.

The value of \( R_{ct} \) increases while the \( C_{dl} \) decreases with increasing the concentration of inhibitors within the range of \( 1 \times 10^{-4} \) to \( 5 \times 10^{-3} \) M. The higher \( R_p \) value (631 \( \Omega \) cm\(^2\) for P2; 352 \( \Omega \) cm\(^2\) for P1) has been found at optimum inhibitors concentration of \( 5 \times 10^{-3} \) M, and the best inhibition efficiency \( (\eta_{EIS}(\%)) \) for P1 and P2 are 91 and 95%, respectively. The increase of \( R_p \) indicates the increase of inhibitor molecules adsorbed on the steel surface (Murulana, Kabanda, & Ebenso, 2016; Yadav, Sinha, Kumar, Bahadur, & Ebenso, 2015), and the decrease in \( C_{dl} \) can be attributed to the decrease in local dielectric constant and/or the increase in the thickness of the double layer. Hence, these results may be attributable to the adsorption of inhibitors forming protective adsorption layers on the steel surface (Lgaz, Salghi, et al., 2017; Lgaz, Subrahmanya Bhat, et al., 2017; Messali et al., 2017).

### 3.4. Adsorption isotherm

Interactions between inhibitor molecules and mild steel surface can be recognized by considering the adsorption isotherm, which usually reflected by the relationship between surface coverage values, \( \theta \), and inhibitor concentration, \( C \). The different relationships basically can be divided in to several serials, including Langmuir, Temkin, Frumkin and Flory–Huggins. In this manuscript, the Langmuir isotherm model was applied to fit the adsorption behavior of inhibitors on mild steel surface in 1 M HCl at 303 K. For Langmuir isotherm, the correlation between \( C/\theta \) and \( C \) can be represented by the following equation (Kumar et al., 2017):

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]
where \( K_{ads} \) is the adsorption equilibrium constant. The involved experiment data are derived from weight loss measurements. The Langmuir isotherm fitting straight lines are showed in Figure 4. The slopes of the fitting lines in Figure 4 approximately equal to 1 and the strong correlation \( (R^2 > 0.99) \) indicates that the adsorption of inhibitors on mild steel surface obeys to Langmuir isotherm which was finally chosen for further study the mechanism of corrosion inhibition for tested inhibitors. The intercept was applied to calculate the \( K_{ads} \), and the adsorption free energy \( \Delta G_{ads}^\circ \) was estimated from the follow equation:

\[
\Delta G_{ads}^\circ = -RT \ln(K_{ads} \times 55.5)
\]

Generally, the negative value of free energy means that the adsorption process occurs spontaneously, and the values of adsorption free energy \( \Delta G_{ads}^\circ \) up to \(-20\) kJ/mol or less negative usually correspond to physical adsorption while those more negative than \(-40\) kJ/mol are assigned to chemisorption (Lgaz, Salghi, Jodeh, et al., 2016; Toumiat et al., 2016). Therefore, the interaction of tested inhibitors with the steel surface takes place mainly through physical and chemical adsorption (Lgaz et al., 2017), with \( \Delta G_{ads}^\circ \) values between \(-36\) and \(-37\) kJ/mol shown in Table 5. As compared with P1, the more negative value of \( \Delta G_{ads}^\circ \) of P2 and the higher value of the adsorption equilibrium constant \( K_{ads} \) in aqueous 1 M HCl with P2 indicates that this compound exhibits a slightly stronger tendency to be adsorbed on the steel surface, and consequently provides a higher corrosion inhibiting efficiency.

### 3.5. Surface characterization

SEM micrographs of the mild steel have been carried out without and with \( 5 \times 10^{-3}\) M of P2. Figure 5(a) represents the SEM image of the uninhibited metallic specimen which is drastically damaged and corroded due to free acid attack in the absence of inhibitors. However, in the presence of P2 at \( 5 \times 10^{-3}\) M, the surface morphology of the metallic specimens (Figure 5(b)) was remarkably improved, due to the formation of the protective film by inhibitor molecules on the metallic surface.

Atomic Force Microscopy images of mild steel surface in 1 M HCl and containing \( 5 \times 10^{-3}\) M of P2 were shown in Figure 5(c)–(d). The surface roughness value of the corroded steel surface (Figure 5(c)) was 779 nm, while the specimen immersed in 1 M HCl with presence of inhibitor at \( 5 \times 10^{-3}\) M of P2 (Figure 5(d)) reached 76.8 nm indicating that the formation of the adsorbed layer of inhibitor restrained effectively the corrosion of metal.
3.6. DFT calculations

3.6.1. Global reactivity descriptors
The interaction of corrosion inhibitors and metal surfaces depend on their electronic properties such as frontier molecular orbitals, electronegativity and electronic energy (Jafari, Danaee, Eskandari, & RashvandAvei, 2014; Singh, Kumar, Tiwari, & Rawat, 2013). Quantum chemical calculations were used in this study to elucidate the corrosion inhibition mechanism in terms of electronic and molecular structure properties. The optimized molecular structure and the electron density iso-surfaces of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) for P1 and P2 are depicted in Figure 6. It is clear from the respective figure that the electron densities of these molecules lie in the vicinity of unsaturation (double bond and aromatic rings) as well as in the environment of hetero atoms.

The HOMO and LUMO of P1 is distributed over the entire molecule which includes O-atoms, π-electrons of phenyl rings, and the N-atoms of pyrazoline ring. The LUMO of P2 is located around the phenyl ring and nitro group while The HOMO is spread over entire molecule except of phenyl ring and its attached nitro. These observations suggest that the inhibitor molecules with their orbitals having surplus electrons can interact with the empty d-orbital of the metal surface mainly through π-electrons, heteroatoms, nitro and acid acetic functional groups.

The quantum chemical calculations parameters such as $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, $\Delta E$ and $\Delta N$ are represented in Table 6. The HOMO energy (EHOMO) is a measure of a molecule’s ability to give electron to an

| Inhibitor | Slope | $K_{\text{ads}}$ (M$^{-1}$) | $R^2$ | $\Delta G_{\text{ads}}^\circ$ (kJ/mol) |
|-----------|-------|----------------------------|-------|-------------------------------------|
| P1        | 1.03  | 33,332                     | 0.9999| −36                                 |
| P2        | 1.04  | 36,536                     | 0.9999| −37                                 |

3.6.2. Adsorption parameters

Figure 5. 3D AFM and SEM images of (a and c) uninhibited mild steel and (b and d) inhibited solution ($5 \times 10^{-3}$ of P1).
acceptor, while the LUMO energy (ELUMO) is a measure of a molecule’s proclivity to receive electron from donor species (Messali et al., 2017). The higher the EHOMO the better the tendency of electron donation by a molecule and vice versa (Messali et al., 2017). Lower ELUMO suggests better propensity of a molecule to receive electron and vice versa. Therefore, higher EHOMO and/or lower ELUMO favor(s) higher corrosion inhibition strength (Messali et al., 2017). It is observed from Table 6 that the P1 has highest value of EHOMO indicating that it has the highest tendency of donating electrons to the empty orbital of metal surface. P2 has the lowest value of ELUMO indicating its maximal capability for accepting electrons. The results listed in the Table 6 suggest that EHOMO decrease in the order of P1 > P2 indicating that the binding tendency on the metal surface decreases in the similar order which does not follow the order of inhibition efficiency. This result may be an indication of the presence of complex interactions perhaps playing the crucial role in the adsorption process (Saha, Dutta, Ghosh, Sukul, & Banerjee, 2016). The smaller value of ∆E, the greater the reactivity of a molecule (Wazzan, 2015). High reactivity means that the molecule has a greater chance to interact with the metal surface. P2 has the lowest value of ∆E, indicating its maximal ability to inhibit the corrosion of iron which is in agreement with the order of experimental inhibition activities of tested molecules. However, the study of quantum chemical parameters is only complete with the calculation of the electron transfer value, ∆N. ∆N value indicates the ability of tested inhibitors to transfer its electrons to metal if ∆N > 0 and vice versa if ∆N < 0 (Kokalj, 2010; Kovačević & Kokalj, 2011). According to this criterion, it is obvious from results in Table 6 that both compounds have higher tendency to donate electrons to a metal surface.

### 3.6.2. Fukui indices

The Fukui indices are used to evaluate the probable active atomic sites of the inhibitor molecules that can interact with the atoms present on the metal surface (Lgaz, Benali, et al., 2016). The atomic site on which an electron surplus exists and that a deficient radical species can attack is predicted by the Fukui indices \( f^+ \) and \( f^- \), respectively (Lgaz, Benali, et al., 2016). Table 7 reports the estimated condensed Fukui indices for inhibitors.

The preferred site for nucleophilic attack (shown by the highest value of \( f^+ \)) is on N (2), C (15) and C (16) for P1 and on N (1), O (39) and O (40) for P2. While the highest values of \( f^- \) are on N (1), C (9) and C (10) for P1 and on N (1), C (3) and O (18) for P2. The results obtained from these regions are in agreement with analysis from LUMO and LUMO orbitals because the same predictions from the site with most electron deficient. The results obtained for these regions in nucleophilic and electrophilic attacks support the high capability of tested compounds to react with surface of metal through donor-acceptor interactions between most reactive sites of our inhibitor and mild steel surface.
3.7. Molecular dynamic simulations

For the quantification of the interaction between each inhibitor molecules and the metal surface, Molecular dynamic (MD) simulations were used to investigate the inhibition action of tested inhibitors (Xie et al., 2015; Zhang et al., 2016). The most stable adsorption configuration of P1 and P2 molecules onto Fe (110) obtained by discover module are presented in Figure 7. Both of the studied molecules prefer planar adsorption onto the studied surface in each case with the heteroatoms pointing toward the surface. This orientation leads to maximum surface coverage of Fe (110) by the inhibitor molecules. The binding and interaction energies of the adsorbed inhibitors have been approximated when the simulation system reached their equilibrium state (Lgaz, Salghi, et al., 2017). Table 8 presents the binding and interaction energies distribution of the P1 and P2 molecules on Fe (110), respectively. The interaction energy of P1 is −893.65 kJ/mol, whereas the interaction energy for P2 reaches −975.44 kJ/mol. These relatively large negative values for both molecules reflect their strong adsorption on the studied surfaces (Lgaz et al., 2017; Lgaz, Salghi et al., 2017). It can be also seen from the data in Table 8 that the binding energies of the adsorption of inhibitors on Fe (110) surface are positive and of high magnitude suggesting the high stability of the adsorbed inhibitors (Lgaz et al., 2017; Lgaz, Salghi, et al., 2017). The inhibitor molecules avoid intimate contact with the Fe atoms on the surface that would result from significant covalent bonding. This orientation maximizes contact between inhibitor and Fe (110) surface improving the adsorption strength. These

| Atom  | P1 f⁺ | P1 f⁻ | P2 f⁺ | P2 f⁻ |
|-------|-------|-------|-------|-------|
| N (1) | 0.018 | 0.081 | 0.061 | 0.110 |
| N (2) | 0.064 | 0.033 | 0.036 | 0.054 |
| C (3) | 0.024 | 0.052 | 0.033 | 0.069 |
| C (4) | −0.008| −0.016| −0.011| −0.045|
| C (5) | 0.025 | −0.050| −0.013| −0.010|
| C (6) | 0.020 | 0.021 | 0.016 | −0.011|
| C (7) | −0.017| 0.014 | −0.002| −0.002|
| C (8) | 0.029 | 0.021 | 0.017 | 0.026 |
| C (9) | 0.012 | 0.071 | 0.013 | 0.017 |
| C (10)| 0.022 | 0.084 | 0.027 | 0.028 |
| C (11)| 0.011 | 0.022 | 0.015 | 0.027 |
| C (12)| 0.014 | 0.015 | 0.015 | 0.035 |
| C (13)| −0.039| 0.072 | 0.008 | −0.007|
| C (14)| −0.055| 0.079 | 0.024 | 0.017 |
| C (15)| 0.077 | −0.040| 0.003 | 0.014 |
| C (16)| 0.321 | −0.057| 0.027 | 0.005 |
| C (17)| 0.018 | 0.008 | 0.012 | 0.020 |
| O (18)| 0.015 | 0.039 | 0.027 | 0.066 |
| C (19)| −0.015| −0.015| −0.013| −0.028|
| C (20)| 0.008 | −0.008| 0.000 | 0.005 |
| O (21)| 0.021 | 0.031 | 0.027 | 0.041 |
| O (22)| 0.000 | −0.005| 0.014 | 0.028 |
| C (38)| −0.057 | 0.052 | 0.045 | 0.006 |
| O (39) | | | 0.109 | 0.035 |
| O (40) | | | 0.106 | 0.028 |
results are in good agreement with experimental and DFT studies which have shown that both compounds act as good corrosion inhibitors of mild steel.

3.8. Mechanism of adsorption and inhibition

Using corrosion inhibitors is one of the most efficient and economical method for protection of the metals and their alloys against corrosion, especially in acidic media. Usually, heterocyclic organic compounds with N, O or S atoms, as well as π-electrons, are proved as the most effective corrosion inhibitors. The reason why corrosion inhibitors can reduce the corrosion rate usually is ascribed to its adsorption to the metal and alloy surface. In this study, the effects of nitro and methyl groups present in pyrazoline derivatives on their inhibition potentials have been studied and discussed using experimental, surface examination, theoretical and MD simulations. The results obtained from experimental and computational methods indicate that the pyrazoline derivatives tested in this study inhibit effectively the mild steel corrosion which is not very surprising because the nitro-group containing compounds are found to be efficient corrosion inhibitors in different corrosive mediums.

Table 8. Interaction and binding energies obtained from MD simulations for the most stable configurations adsorption of pyrazoline derivatives on iron surface

| System                        | $E_{\text{Interaction}}$ (kJ/mol) | $E_{\text{Binding}}$ (kJ/mol) |
|-------------------------------|-----------------------------------|-----------------------------|
| Fe + P1/491H$_2$O, 9Cl$^-$ and 9H$_3$O$^+$ | -893.65                           | 893.65                      |
| Fe + P2/491H$_2$O, 9Cl$^-$ and 9H$_3$O$^+$ | -975.44                           | 975.44                      |
(Wang et al., 2015). In the light of the present findings, we hypothesized that the mechanism of adsorption of tested pyrazoline derivatives can be explained by one and/or more of the following ways (Gupta, Verma, Quraishi, & Mukherjee, 2016; Verma, Ebeno, Bahadur, Obot, & Quraishi, 2015; Yadav, Sinha, Sarkar, & Tiwari, 2015).

(1) In a strong acid solutions such as hydrochloric acid solution (1 M HCl), the pyrazoline derivatives are expected to be protonated which will be in equilibrium with the corresponding neutral form by the following equation (Singh, Srivastava, & Quraishi, 2016):

\[ PS + H^+ \rightleftharpoons (PSH)^+ \]

The protonated forms of the pyrazoline derivatives get adsorbed onto the negatively charged mild steel surface (due to the presence of hydrated chloride ions) via electrostatic interaction (physisorption).

(2) The pyrazoline derivatives can be adsorbed on the mild steel surface through the donor-acceptor interaction between free electron pairs of heteroatoms as well as \( \pi \)-electron system from the aromatic rings and vacant \( d \)-orbital of the MS.

(3) Donor-acceptor interactions between the anti-bonding molecular orbitals of the pyrazoline derivatives and the \( d \)-electrons of surface Fe-atoms (The electron transfer results in the accumulation of the negative charge on the mild steel surface).

4. Conclusion

In summary, novel chemical compounds derived from pyrazoline were used as corrosion inhibitors for mild steel in 1.0 M HCl. The study was carried out using several methods which include weight loss, electrochemical analysis, SEM, AFM and computational calculations. The inhibitors show good inhibition performances. The study reveals that both compounds are mixed-typed inhibitors following Langmuir adsorption model. SEM and AFM analyses revealed that tested compounds protect the surface of mild steel in the tested acid. The experimental results were very well supported by quantum chemical calculations and MD simulations.

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