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PII: S0022-2860(20)30008-9

DOI: https://doi.org/10.1016/j.molstruc.2020.127685

Reference: MOLSTR 127685

To appear in: Journal of Molecular Structure

Received Date: 11 November 2019

Revised Date: 2 January 2020

Accepted Date: 3 January 2020

Please cite this article as: A. Singh, K.R. Ansari, M.A. Quraishi, S. Kaya, Theoretically and experimentally exploring the corrosion inhibition of N80 steel by pyrazol derivatives in simulated acidizing environment, *Journal of Molecular Structure* (2020), doi: https://doi.org/10.1016/j.molstruc.2020.127685.

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Theoretically and experimentally exploring the corrosion inhibition of N80 steel by Pyrazol derivatives in simulated acidizing environment

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Abstract

Acidizing is the important process used in petroleum industry for oil well stimulation. Here, we are exploring the green synthesis of 4,4'-((4-methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (PZ-1) and 4,4'-((4-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (PZ-2) under ultrasonic irradiation and its potential application for N80 steel corrosion mitigation in 15% HCl. The corrosion inhibition investigation was performed by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), linear polarization (LPR), potentiodynamic polarization (PDP), electrochemical frequency modulation (EFM), and electrochemical frequency modulation trend (EFMT), weight loss, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), density functional theory (DFT) and molecular dynamics (MD). The EIS and PDP results suggests an increased impedance in presence of PZs and mixed nature of inhibitor action respectively. The protection efficiency (η %) are 98.4% (PZ-1) and 94.3% (PZ-2). The results of EFMT provides the average decrease in corrosion rate and corrosion current density (i_{corr}). The surface analysis

suggests a protective layer of PZs. DFT analysis reveals that PZ-1 with lower value of ΔE acts as a better inhibitor compared to PZ-2. MD study supports a stronger binding and interaction ability of PZ-1 than PZ-2.

Keywords: N80 steel; Pyrazol; DFT; Corrosion; EFMT

1. Introduction

The application of N80 steel in petroleum industries as construction material for in transportation and casing pipes due to its cheap cost and easy availability [1]. Acidizing of an oil well is one of the most significant method to enhance oil recovery and usually carried out using 15-28% hydrochloric acid (HCl). The presence of the aggressive acidic environment leads to easy deterioration of the N80 steel surface. These deteriorated surfaces can give rise to accidents, failures, economic and human losses. Therefore, the corrosion of N80 steel in the oil well can possess serious threats causing complete stop to a working oil well. The protection of N80 steel from aggressive solution was reduced using inhibitors [2, 3].

Various organic inhibitors have been tested for N80 steel in acidic medium [4-7]. However, the problem with the available commercial inhibitors or synthesized inhibitors is that they are usually useful in high concentrations and toxicity is always a concern. Use of formulations to enhance the inhibition performance also increases the overall concentration. Therefore, it is very important to develop and test effective non-toxic inhibitors that can be used even at high acid concentration. The presence of heteroatoms and the benzene ring is an added advantage to any inhibitor, as they help in metal-solution interactions via adsorption. However, the detail mechanism of action is still unknown and choice of inhibitors is based on the number of heteroatoms, chemical, physical and macroscopic properties[8, 9]. The inhibitor namely 4,4'-((4-methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (PZ-1) and 4,4'-((4-

nitrophenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (PZ-2) was synthesized under ultrasonic irradiation following the green principles to get the non-toxic inhibitor which can be used at higher acid concentrations to mitigate corrosion of N80 steel.

2. Experimental procedures

2.1. Inhibitor

In a round bottom (RB) flask 4 mmol of ethyl acetoacetate and 4 mmol of phenyl hydrazine in a mixture of water/ethanol (10 mL/10 mL) ratio was taken and ultrasonically irradiated for 5 min. After this aldehyde (4-methoxy benzaldehyde and 4-nitro benzaldehyde) (2 mmol) was added into the RB and further irradiated for another 15-20 min. The scheme of synthesis is shown in Fig. 1 [10].

Appearance of precipitate represents the formation product. The compound was crystallized by ethanol. Molecular structure of inhibitor, melting points, ¹H NMR, and ¹³C NMR data are tabulated in Table S1. The ¹H NMR and ¹³C NMR spectra are shown in supplementary file (Fig. S1and S2) respectively.

4,4'-((4-methoxyphenyl)methylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) (PZ-1)

Melting point: 176-177 °C); ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.29 (s, 6H), 3.68 (s, 3H), 4.87 (s, 1H), 6.81 (d, 2H), 7.10 (d, 2H), 7.13-7.18 (m, 2H), 7.42 (t, 4H), 7.62-7.75 (m, 4H), 13.90 (s, 1H).

¹³C NMR (75 MHz, DMSO-*d*₆): δ 11.6, 32.4, 55.0, 113.5, 114.3, 118.3, 120.5, 125.5, 128.1, 128.7, 128.8, 128.9, 134.0, 136.8, 146.2, 157.5.

4,4'-((4-nitrophenyl)methylene)bis(3-methyl-1-phenyl-1*H*-pyrazol-5-ol) (PZ-2)

Melting point: 230-232 °C); ¹H NMR (300 MHz, DMSO-*d*₆): δ 2.35 (s, 6H), 5.13 (s, 1H), 7.26 (t, 2H), 7.45 (t, 4H), 7.52 (d, 2H), 7.71 (d, 4H), 8.18 (d, 2H), 13.86 (s, 1H, -OH);

¹³C NMR (75 MHz, DMSO-*d*₆): δ 12.1, 33.7, 104.4, 121.1, 123.8, 126.2, 129.1, 129.4, 137.7, 146.4, 146.8, 150.8.

2.2. Materials and specimens

The working electrodes of N80 steel were sealed using epoxy resin and let to dry overnight. Table 1 represents the composition of N80 steel. The electrode of 1 cm² area was abraded using SiC emery papers of different grades prior to all experiments. The newly abraded N80 steel electrodes were thoroughly rinsed using pure water, and then degreased using acetone followed by absolute ethyl alcohol solution in ultrasonic bath. Finally, the working electrode was dried at ambient temperature prior to experiment. Reagent grade hydrochloric acid (HCl) is used for the preparation of 15% HCl [11].

2.3. Weight loss measurements

In this experiment, inhibitor concentration used was in the range of 25 ppm-200 ppm. All the experiments were performed according to the American Society for Testing Material G1-03 [12, 13]. The tests were done in triplicate and the mean values are reported.

The calculation of corrosion rate (C_{Rcorr}) was done using equation 1:

$$C_{R} = \frac{8.76 \times 10^{4} \times \Delta m}{A \times t \times \rho} \tag{1}$$

where $C_{\rm R}$, Δm , ρ , A and t represents the corrosion rate (mm/y), weight loss (g), density (g/cm³), area (cm²) and exposure duration (h) respectively. The inhibition efficiency ($\eta_{\rm WL}$ %) and surface coverage (θ) were calculated as follows [13]:

$$\eta_{\rm WL} \% = \frac{C_{\rm R} - C_{\rm R(i)}}{C_{\rm R}} \times 100 \tag{2}$$

$$\theta = \frac{C_{\rm R} - C_{\rm R(i)}}{C_{\rm R}} \tag{3}$$

2.4. Electrochemical Experiments

The electrochemical experiments were performed by three-electrode Gamry workstation. The electrochemical setup consists of reference electrode (Ag/AgCl), counter electrode (graphite rod) and working electrode (N80 steel with an exposed area of 1 cm^2). The electrochemical tests were performed in the 15% HCl solution. Before starting the experiment an open circuit potential (OCP) was achieved by immersing the working electrode in the corrosive solution for 1 hour [14]. All experiments were reproduced, and repeated for three times at room temperature.

The applied frequency is in the range of 100 kHz to 10 mHz, with an amplitude of 10 mV/dec for EIS [15]. In PDP a potential range of -250 mV to +250 mV with the scanning rate of 1 mV/s was used for cathodic and anodic reaction area scanning [16]. Using the bellows equations the inhibition efficiency were calculated:

$$\eta_{\rm EIS} = \frac{R_{ct(\rm inh)} - R_{ct}}{R_{ct(\rm inh)}} \times 100 \tag{4}$$

$$\eta_{\rm PDP} = \frac{i_{\rm corr} - i_{\rm corr(inh)}}{i_{\rm corr}} \times 100$$
(5)

where $R_{ct(inh)}$ and R_{ct} are the resistance of charge transfer with and without PZs respectively. i_{corr} and $i_{corr(inh)}$ are the current density without and with PZs respectively.

Two frequencies i.e. 2 and 5 Hz were used for EFM measurements.. EFMT measurements were conducted to monitor the changes in corrosion rate and i_{corr} values for 1 hour. Both EFM and EFTM were analyzed at an amplitude of 10 mV and base frequency of 0.1 Hz.

2.5. Morphological study

For all surface morphology analysis, N80 steel coupons were immersed for 24 h in the corrosive solution without and with the addition of PZs at 308 K.

Ziess Evo 50 XVP instrument was used for SEM analysis, at the accelerating voltage of 5 kV and magnification of 5x.

AFM was analyzed by Dimension Icon Brock instrument. The 2D/3D images were developed by Nanoscope analysis software.

The metal samples after immersion of 6 hours in 15% HCl with and without inhibitors were exposed to XPS (Model: XSAM 800, Japan) instrument to sense the peaks formed during the corrosion process. Spectrum together with Fe 2p, O 1s, N 1s and C 1s regions, were recorded. XPS Peak-Fit 4.1 software was employed to fit the experimental data and then final regions were obtained by Shirley subtraction method.

2.6. Quantum chemical study

The optimization of the ground states of the synthesized inhibitors ware calculated at DFT/GGA level calculation and applying DNP basis set and BOP functional. All calculation were done using Materials Studio software package (version 6.0) [17]. The aqueous phase effect was control by COSMO [18].

2.7. MD simulations

The most stable and packed iron surface i.e. Fe (110) having a 5 Å slab was selected for MD simulation. The simulation box with the dimension of $24.82 \times 24.82 \times 35.69$ Å³ was selected that contains $491H_2O$, $9CI^-$, $9H_3O^+$ and one PZs molecule. The calculation were done using BIOVIA Materials Studio® software [17]. All MD simulations were done at 333 K temperature and maintained constant by the Andersen thermostat, a time step of 0.1 fs, NVT (fixed atom num- ber, system volume and temperature) ensemble and a simulation time of 20 0 0 ps to reach simulation system under an equilibrium state. The Condensed-phase Optimized Molecular

Potential for Atomistic Simulation Studies (COMPASS) force field was used for the optimization of inhibitor molecules [18].

3. Results and discussion

3. 1. Quantum Chemical Studies

3.1.1. Density functional theory (DFT)

Molecular level adsorption of PZs molecules was investigated using quantum chemical calculations. The optimized molecular structures of PZs, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown in Fig. 2.

The electron donation and electron acceptation tendency of molecules are described by highest occupied molecular orbital (E_{HOMO}) and energy of lowest unoccupied molecular orbital (E_{LUMO}) [19,20]. The energy gap i.e. $\Delta E = (E_{LUMO}-E_{HOMO})$ that provides the adsorption reactiveness of PZs molecules over the N80 steel surface [21]. The calculated parameters are tabulated in Table 7. According to Table 7, PZ-1 has higher value of E_{HOMO} as well as lower value of E_{LUMO} , which reveals its higher tendency to donate and accept electrons respectively. Because of this reason, PZ-1 is more effective corrosion inhibitor than PZ-2. The presence of electron donating functional group i.e. OCH3 in PZ-1 causes to increase its electron donation ability while in PZ-2 electron withdrawing NO2 causes to reduce the electron donating ability. In addition to this, the adsorption ability of PZ-1 is better than PZ-2, because of the lower value of ΔE . The obtained results from this study supports the results obtained by experiments

3.1.2. Molecular Dynamics (MD)

Theoretical prediction methods including molecular dynamics simulations cannot yet replace traditional experimental assays, but there is no doubt that they can provide useful information in corrosion research [22]. Based on this information and in an attempt to further

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probe the relationship between the effectiveness of inhibitors and their molecular structures, we propose that the MD simulations can be used to achieve better results [23,24]. The equilibrium configurations adsorption of PZs are shown in Fig. 3a, b respectively.

Understanding the factors that enhance the corrosion inhibition efficiency of an organic compound is paramount to design and efficiently apply any preventive control. In our simulations, we observed that all tested compounds adsorbed in a horizontal manner over the Fe (110) surface. In this situation, it is possible that the interaction between inhibitor molecules and iron surface could provide the means necessary for corrosion mitigation. This can be achieved in several ways, such as via electron donation, electron acceptation, back-donation, etc. Heteroatoms greatly enhance the adsorption ability of the corrosion inhibitors. The exposed part of iron surface can be successfully reduced by the covering of the entire molecular structure of inhibitors, thus preventing the metal surface from the corrosion attack which is the case in our study. Importantly, the adsorption profile of both neutral and protonated forms of PZs are almost having the same conformation that indicates their strong influence on the inhibition process.

The binding (E_{binding}) and interaction ($E_{\text{interaction}}$) energies of PZs molecules are tabulated in Table 8. According to Table 8, binding energy of PZ-1 is higher than PZ-2. This suggests the stronger adsorption ability of PZ-1 than PZ-2 over the N80 steel surface [25,26]. This finding is in accordance with those of the experimental results.

3.2. X-Ray photoelectron spectroscopy (XPS)

The analyses of N80 steel surface by XPS are shown in Fig. 4. Measurements were performed on steel coupons exposed to solution without and with inhibitors. Binding energies were revised using the C 1s peak at 284.8 eV. Fig. 4a shows the C 1s spectrum for all samples that can be deconvoluted in two components. The first component situated at 284.8 eV has the major

influence and is endorsed to the C-H of aromatic bonds, C-C, or C=C [36,27]. The carbon atom of the C–O bond may be ascribed by the peak at 289.0 eV [28]. After immersion in PZs, the deconvoluted C 1s spectrum for steel depicts three components demonstrating three dissimilar carbon interactions, as shown in Fig. 4b, 4c. The presence of C-N bonds in PZs are confirmed by third peak at 286.3 eV and that may arise due to the presence of amino groups or C-O bond in the inhibitors [29]. Fe 2p3/2 peak is differentiated into oxide and hydroxide forms with 711.2 eV and 724.9 eV binding energies respectively along with the elemental peak at 717.8 eV. The peak at 711.2 eV confirms the presence of complexes of ferric ions such as Fe₂O₃, FeOOH. The presence of hydroxides of Fe⁺³ is confirmed by second peak at 724.9 eV. The appearance of peak at a 717.8 eV is accredited to Fe(III) satellite forms of iron (Fig. 4d, 4e, and 4f) [30].

Fig.e 4g, 4h represents the O 1s peak determined into oxide and hydroxide with values of 530.2 and 531.8 eV respectively. The first peak at 530.2 eV may arise due to the presence of oxygen (O^{2-}) bonded to iron (Fe^{3+}) like FeO, Fe₂O₃ and/or Fe₃O₄. The appearance of second peak at 531.8 eV corresponds to OH⁻, and it could be related to oxides of hydrous iron, like FeOOH [31]. Adsorption of PZs of N80 steel surface can be elucidated by the presence of the N1s peak which is absent in blank sample. The peak is at about 399.9 eV as shown in figure 4i, 4j [32]. The performed XPS studies give sufficient suggestion of PZs adsorption over the N80 steel surface.

3.3. Weight loss experiment

The N80 steel samples were immersed in 15% HCl at 308 K temperature for 6 h without and with PZs. Fig. 5a,b, represents the variation of inhibition efficiency (η_{WL} %) and corrosion rate (C_R) at different PZs concentration. The inspection of figure demonstrate that the values of inhibition efficiency and corrosion rates were increased and decreased respectively with increased in the concentrations of PZs. This phenomenon is due to the adsorbing nature of PZs molecules over the metal surface.

3.4. Electrochemical analysis

3.4.1. Electrochemical impedance spectroscopy (EIS)

EIS study was carried out without and with different concentration of PZs in acidic solution at 308K temperature. Open circuit potential (OCP) for PZ-1 and PZ-2 was carried out after an immersion time of 30 minutes for 1000 seconds and are represented in Fig. S3a, b.

The observed potential after 1000 seconds show a stable nature. In the Nyquist plots (Fig. 6a, b), a depressed semi-circle and an inductive loop towards inward is observed with different concentrations of PZs. Although, the semicircular shape of the Nyquist plots for N80 steel is similar due to similar reaction mechanism in acidic solution for different concentration of the PZs. The semi-circle is usually attributed to resistance of charge transfer [33]. This is because after corrosion the metal surface becomes inhomogeneous and rough. Although the addition of PZs causes to increase the size of the depressed semi-circle and this increment is more pronounced at the higher PZs concentration. This phenomenon suggest that the charge transfer resistance (R_{ct}) values are higher in presence of PZs which provides a better protection of the N80 steel surface [34, 35].

In the bode plots (Fig. S4a, b), the increment of slope values occurs with the addition of PZs (Table 2). This corresponds towards the inhibition action of PZs on N80 steel surfaces. At the intermediate frequency in the phase angle plots, the values of the phase angle increases as the PZs concentration increases (Fig. S4a, b). This is an indication of the formation of protective barrier that isolate the N80 steel surface from the aggressive solution [36]. Thus, in other words adsorption of the PZs molecules over the metal plays the significant part, which ultimately

increased its corrosion resistance property. The magnitude of the phase angle and slope values are tabulated in Table 2.

The fitted experimental results of the impedance parameters are given in Table 3.

The equivalent circuits used for fitting is shown in (Fig. 7a, b). The equivalent circuit model contains *CPE*, charge transfer resistance (R_{ct}) and Inductance (L). The frequency dependent distribution of the current density along the N80 steel surface can be compensated by using the *CPE* in place of pure capacitor [37, 38]. The *CPE* impedance (ZCPE) was calculated using the below equation:

$$Z_{\rm CPE} = Y_0 [j\omega^{\alpha}]^{-1} \tag{9}$$

where *j* represent an imaginary number $(j = \sqrt{-1})$, Y_o is the admittance and it is the constant for *CPE*, ω is the angular frequency in rad/s and α , is the phase shift [39]. The adsorption of inhibitor molecules at the metal solution interface causes the modification of the capacitance values. Thus, it become important to calculate the values of double layer capacitance (C_{dl}) because the representation of C_{dl} by *CPE* and Y_o is not accurate when the values of α is less than 1. The accurate relationship between the C_{dl} and *CPE* can be calculated using the equation [40]:

$$C_{\rm dl} = Y_{\rm o}^{1/\alpha} \left[\frac{1}{R_{\rm s}} + \frac{1}{R_{\rm ct}} \right]^{(\alpha-1)/\alpha}$$
(6)

According to the Table 3, the addition of PZs causes the increment in the values of the R_{ct} and diminution of C_{dl} . This can be ascribed to the molecular adsorption of PZs over the metal surface and decreases direct contact between metal and aggressive solution [41].

3.4.2. Electrochemical Frequency Modulation (EFM)

The EFM in an importance technique that gives the corrosion current values without calculating Tafel constants [42]. The intermodulation and wave form spectra are shown in Fig. S5a-c.

The EFM parameters are tabulated in Table 4. The adsorption of the PZs molecules over the metal surface causes to reduce the corrosion current with increasing the inhibitor concentrations. The closeness of the casuality factors (Table 4) with that of the theoretically obtained values supports the accuracy of the EFM technique [43]. The evaluation of the inhibition efficiency (η_{EFM} %) was done as per equation 7:

$$\eta_{\rm EFM} \% = \left(1 - \frac{i^{\rm inh}}{i^{\rm blank}}_{\rm corr}\right) \times 100$$
(7)

where $i^{\text{blank}}_{\text{corr}}$ and $i^{\text{inh}}_{\text{corr}}$ are the corrosion current without and with PZs respectively. According to Table 4, the casuality factors values are of noble eminence and close to the standard values i.e. 2 and 3.

Although electrochemical frequency modulation is a nice technique for measuring instantaneous corrosion rate but it provides data for a short period of time. However, a new technique known as electrochemical frequency modulation trend (EFMT) can monitor the inhibitor and metal interaction and provide the corrosion rate for longer time period i.e. 1 hour. The EFMT shows the higher corrosion rate and i_{corr} values for N80 steel in absence of PZs while it is much lower in presence of PZs as shown in Fig. 8a-c. Table 5 shows the average decrease in corrosion rate and corrosion current (i_{corr}) after the addition of PZs with respect to time. In the due course of time, the inhibitors form a protective barrier over the metal surface that hindered the corrosive solution to interact with the metal. This vindicates the good inhibition efficiency of the PZs inhibitor.

3.4.3. Potentiodynamic polarization (PDP)

The obtained PDP curve without and with different concentration of PZs in acidic solution at room temperature are shown in Fig. 9a, b. The analyses of curve generate some parameters that

are presented in Table 6. The decrease in the i_{corr} values (Table 6) with the addition of PZs is due to the adsorption of the PZs molecules over the metal surface, which make the metal to act an insulator for the aggressive solution. In addition to this, with increasing the concentration of PZs the E_{corr} values are shifting towards the cathodic region (more negative) as compared to the blank (without PZs). This clearly shows that the PZs has predominant influence on the cathodic reaction than the anodic [44,45]. Although, both the Tafel curve branches i.e. anodic and cathodic are migrating in the direction of smaller current density. This suggests towards the retardation of metal dissolution (anodic) and hydrogen evolution (cathodic). Thus, the action of inhibitor could be classified in the category of mixed type [46]. The magnitude of both Tafel slopes i.e. cathodic (β_c) and anodic (β_c) are almost same without and with PZs, which suggests that the adding PZs does not causes any corrosion reaction modification [47]. Although, the values of cathodic Tafel constants shows more displacement as compared to the anodic Tafel constant. This further supports predominance nature of cathodic reaction [48].

3.5. Surface analysis

3.5.1. Scanning electron microscopy (SEM)

The morphological texture of N80 steel without and with the addition of PZs (200 ppm) are depicted in Fig. S6a-c.

Surface property of the steel without adding PZs is very rough with the presence of large amount of corrosion products because of the uncontrolled dissolution and corrosion (Fig. S6a). Although, introduction of PZs molecules to the aggressive medium makes steel surface very smooth (Fig. S6b, c). This observation suggests that in presence of inhibitor (PZs) the rate of corrosion process is reduced due to the adsorption and formation of a protective layer of PZs molecules over metal surface [35,31].

3.5.2. Atomic force microscope (AFM)

Surface microstructural images of N80 steel are depicted in Fig. S7a-c. The severe damage of steel surface without adding PZs are shown in Fig. S7a. However, the roughness property of the steel surface was relatively reduced with the addition of the PZs molecules (Fig. S7b, c). This anticorrosive property of the inhibitor is certainly due to their adsorption onto the metal surface.

4. Conclusions

The corrosion inhibition performance of PZs increases as the concentration of PZs increases and achieved maximum values of 98.4% (PZ-1) and 94.3% (PZ-2) at 200 mg/L. The results of EIS reveals that R_{ct} values increase as PZs concentration increases. PDP studies suggest that PZs are mixed type inhibitor with predominantly cathodic in nature. EFM and EFMT results indicated the good inhibitive action of PZs in the acidic solution. SEM and AFM analysis reveals that less corrosion occurs with the addition of PZs, which is due to the formation of inhibitor film. XPS result suggests that PZs molecules forms a film over the metal surface. DFT analysis reveals that PZ-1 with lower value of ΔE acts as a better inhibitor compared to PZ-2. MD study supports a stronger binding and interaction ability of PZ-1 than PZ-2.

Acknowledgment

KRA and MAQ thankfully acknowledge the financial support provided by the King Fahd University of Petroleum and Minerals (KFUPM), Kingdom of Saudi Arabia under the Deanship of Scientific Research (DSR) project number DF181007. KRA is thankful to KFUPM for the Post-Doctoral Fellowship. AS is thankful to the Sichuan 1000 Talent Fund, financial assistance provided by the Youth Scientific and Innovation Research Team for Advanced Surface Functional Materials, Southwest Petroleum University number-2018CXTD06 and open fund project number-X151517KCL42.

References

[1] Y. Qiang, S. Zhang, L. Guo, X. Zheng, B. Xiang, S. Chen, Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid, Corrosion Science, 119 (2017) 68-78.

[2] M.B.P. Mihajlović, M.B. Radovanović, Ž.Z. Tasić, M.M. Antonijević, Imidazole based compounds as copper corrosion inhibitors in seawater, Journal of Molecular Liquids, 225 (2017) 127-136.

[3] M. Mousavi, T. Baghgoli, Application of interaction energy in quantitative structure-inhibition relationship study of some benzenethiol derivatives on copper corrosion, Corrosion Science, 105 (2016) 170-176.

[4] G. Quartarone, M. Battilana, L. Bonaldo, T. Tortato, Investigation of the inhibition effect of indole-3-carboxylic acid on the copper corrosion in 0.5 M H2SO4, Corrosion Science, 50 (2008) 3467-3474.
[5] B. Tan, S. Zhang, Y. Qiang, L. Feng, C. Liao, Y. Xu, S. Chen, Investigation of the inhibition effect of

Montelukast Sodium on the copper corrosion in 0.5 mol/L H2SO4, Journal of Molecular Liquids, 248 (2017) 902-910.

[6] H. Nady, Tricine [N-(Tri (hydroxymethyl) methyl) glycine]–A novel green inhibitor for the corrosion inhibition of zinc in neutral aerated sodium chloride solution, Egyptian Journal of Petroleum, 26 (2017) 905-913.

[7] X.G. Zhang, Corrosion and electrochemistry of zinc, Springer Science & Business Media, 2013.
[8] Y. Qiang, S. Zhang, L. Guo, S. Xu, L. Feng, I.B. Obot, S. Chen, Sodium dodecyl benzene sulfonate as a sustainable inhibitor for zinc corrosion in 26% NH4Cl solution, Journal of cleaner production, 152 (2017) 17-25.

[9] A. Singh, K. Ansari, A. Kumar, W. Liu, C. Songsong, Y. Lin, Electrochemical, surface and quantum chemical studies of novel imidazole derivatives as corrosion inhibitors for J55 steel in sweet corrosive environment, Journal of Alloys and Compounds, 712 (2017) 121-133.

[10] A. Hasaninejed, M.R. Kazerooni, A. Zare, Room-temperature, catalyst-free, one-pot pseudo-fivecomponent synthesis of 4, 4-(arylmethylene) bis (3-methyl-1-phenyl-1H-pyrazol-5-ol) s under ultrasonic irradiation, ACS Sustainable Chemistry & Engineering, 1 (2013) 679-684.

[11] A. Singh, K. Ansari, J. Haque, P. Dohare, H. Lgaz, R. Salghi, M. Quraishi, Effect of electron donating functional groups on corrosion inhibition of mild steel in hydrochloric acid: Experimental and quantum chemical study, Journal of the Taiwan Institute of Chemical Engineers, 82 (2018) 233-251.

[12] A.C.G.-o.C.o. Metals, Standard practice for preparing, cleaning, and evaluating corrosion test specimens, ASTM international, 2017.

[13] A. Singh, K. Ansari, X. Xu, Z. Sun, A. Kumar, Y. Lin, An impending inhibitor useful for the oil and gas production industry: Weight loss, electrochemical, surface and quantum chemical calculation, Scientific reports, 7 (2017) 14904.

[14] J. Zhao, N. Zhang, C. Qu, X. Wu, J. Zhang, X. Zhang, Cigarette butts and their application in corrosion inhibition for N80 steel at 90 C in a hydrochloric acid solution, Industrial & Engineering Chemistry Research, 49 (2010) 3986-3991.

[15] R. Sabzi, R. Arefinia, Investigation of zinc as a scale and corrosion inhibitor of carbon steel in artificial seawater, Corrosion Science, 153 (2019) 292-300.

[16] A. Singh, K. Ansari, M. Quraishi, H. Lgaz, Y. Lin, Synthesis and investigation of pyran derivatives as acidizing corrosion inhibitors for N80 steel in hydrochloric acid: Theoretical and experimental approaches, Journal of Alloys and Compounds, 762 (2018) 347-362.

[17] Materials Studio, Revision 6.0, Accelrys Inc., San Diego, USA, (2013).

[18] H. Sun, COMPASS: an ab initio force-field optimized for condensed-phase applications overview with details on alkane and benzene compounds, The Journal of Physical Chemistry B, 102 (1998) 7338-7364.

[19] J. Haque, K. Ansari, V. Srivastava, M. Quraishi, I. Obot, Pyrimidine derivatives as novel acidizing corrosion inhibitors for N80 steel useful for petroleum industry: a combined experimental and theoretical approach, Journal of Industrial and Engineering Chemistry, 49 (2017) 176-188.

[20] K. Ansari, M. Quraishi, Experimental and computational studies of naphthyridine derivatives as corrosion inhibitor for N80 steel in 15% hydrochloric acid, Physica E: Low-dimensional Systems and Nanostructures, 69 (2015) 322-331.

[21] A. K. Singh, B. Chugh, S. K. Saha, P. Banerjee, E. E. Ebenso, S. Thakur, B. Pani, Evaluation of anticorrosion performance of an expired semi synthetic antibiotic cefdinir for mild steel in 1M HCl medium: An experimental and theoretical study, Results in Physics 14 (2019) 102383

[22] D. Rapaport, R. Blumberg, S. McKay, W. Christian, others. The Art of Molecular Dynamics Simulation, Comput. Phys, 10 (1996) 456-456.

[23] H. Lgaz, K.S. Bhat, R. Salghi, S. Jodeh, M. Algarra, B. Hammouti, I.H. Ali, A. Essamri, Insights into corrosion inhibition behavior of three chalcone derivatives for mild steel in hydrochloric acid solution, Journal of Molecular Liquids, 238 (2017) 71-83.

[24] R. Kumar, S. Chahal, S. Kumar, S. Lata, H. Lgaz, R. Salghi, S. Jodeh, Corrosion inhibition performance of chromone-3-acrylic acid derivatives for low alloy steel with theoretical modeling and experimental aspects, Journal of Molecular Liquids, 243 (2017) 439-450.

[25] K. Ansari, M. Quraishi, A. Singh, S. Ramkumar, I.B. Obote, Corrosion inhibition of N80 steel in 15% HCl by pyrazolone derivatives: electrochemical, surface and quantum chemical studies, RSC Advances, 6 (2016) 24130-24141.

[26] A. Singh, K. Ansari, M. Quraishi, H. Lgaz, Effect of electron donating functional groups on corrosion inhibition of J55 steel in a sweet corrosive environment: experimental, density functional theory, and molecular dynamic simulation, Materials, 12 (2019) 17.

[27] J. Castle, Practical surface analysis by Auger and X - ray photoelectron spectroscopy. D. Briggs and MP Seah (Editors). John Wiley and Sons Ltd, Chichester, 1983, 533 pp.,£ 44.50, Surface and Interface Analysis, 6 (1984) 302-302.

[28] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy; Chastain, J, Perkin-Elmer Corp., Eden Prairie, MN, (1992).

[29] M. Outirite, M. Lagrenée, M. Lebrini, M. Traisnel, C. Jama, H. Vezin, F. Bentiss, ac impedance, X-ray photoelectron spectroscopy and density functional theory studies of 3, 5-bis (n-pyridyl)-1, 2, 4-oxadiazoles as efficient corrosion inhibitors for carbon steel surface in hydrochloric acid solution, Electrochimica Acta, 55 (2010) 1670-1681.

[30] F. Bentiss, C. Jama, B. Mernari, H. El Attari, L. El Kadi, M. Lebrini, M. Traisnel, M. Lagrenée, Corrosion control of mild steel using 3, 5-bis (4-methoxyphenyl)-4-amino-1, 2, 4-triazole in normal hydrochloric acid medium, Corrosion Science, 51 (2009) 1628-1635.

[31] M. Bouanis, M. Tourabi, A. Nyassi, A. Zarrouk, C. Jama, F. Bentiss, Corrosion inhibition performance of 2, 5-bis (4-dimethylaminophenyl)-1, 3, 4-oxadiazole for carbon steel in HCl solution: Gravimetric, electrochemical and XPS studies, Applied Surface Science, 389 (2016) 952-966.

[32] M. Tourabi, K. Nohair, M. Traisnel, C. Jama, F. Bentiss, Electrochemical and XPS studies of the corrosion inhibition of carbon steel in hydrochloric acid pickling solutions by 3, 5-bis (2-thienylmethyl)-4-amino-1, 2, 4-triazole, Corrosion Science, 75 (2013) 123-133.

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[33] K. Ansari, M. Quraishi, A. Singh, Schiff's base of pyridyl substituted triazoles as new and effective corrosion inhibitors for mild steel in hydrochloric acid solution, Corrosion Science, 79 (2014) 5-15.
[34] A. Singh, K. Ansari, Y. Lin, M. Quraishi, H. Lgaz, I.-M. Chung, Corrosion inhibition performance of imidazolidine derivatives for J55 pipeline steel in acidic oilfield formation water: Electrochemical, surface and theoretical studies, Journal of the Taiwan Institute of Chemical Engineers, 95 (2019) 341-356.
[35] K. Ansari, M. Quraishi, A. Singh, Pyridine derivatives as corrosion inhibitors for N80 steel in 15% HCI: Electrochemical, surface and quantum chemical studies, Measurement, 76 (2015) 136-147.

[36] A. Singh, Y. Lin, I. Obot, E.E. Ebenso, K. Ansari, M. Quraishi, Corrosion mitigation of J55 steel in 3.5% NaCl solution by a macrocyclic inhibitor, Applied Surface Science, 356 (2015) 341-347.

[37] R. De Levie, The influence of surface roughness of solid electrodes on electrochemical measurements, Electrochimica Acta, 10 (1965) 113-130.

[38] H. Keleş, D.M. Emir, M. Keleş, A comparative study of the corrosion inhibition of low carbon steel in HCl solution by an imine compound and its cobalt complex, corrosion science, 101 (2015) 19-31.

[39] A. Singh, I. Ahamad, V. Singh, M.A. Quraishi, Inhibition effect of environmentally benign Karanj (Pongamia pinnata) seed extract on corrosion of mild steel in hydrochloric acid solution, Journal of Solid State Electrochemistry, 15 (2011) 1087-1097.

[40] G. Brug, AlG van den eeden, m. Sluyters-rehabach, JH Sluyters, J. Electroanal. Chem, 176 (1984) 275-295.

[41] L. Jiang, Y. Qiang, Z. Lei, J. Wang, Z. Qin, B. Xiang, Excellent corrosion inhibition performance of novel quinoline derivatives on mild steel in HCl media: experimental and computational investigations, Journal of Molecular Liquids, 255 (2018) 53-63.

[42] K. Khaled, Application of electrochemical frequency modulation for monitoring corrosion and corrosion inhibition of iron by some indole derivatives in molar hydrochloric acid, Materials chemistry and physics, 112 (2008) 290-300.

[43] I. Obot, I.B. Onyeachu, Electrochemical frequency modulation (EFM) technique: theory and recent practical applications in corrosion research, Journal of Molecular Liquids, 249 (2018) 83-96.

[44] S. Pareek, D. Jain, S. Hussain, A. Biswas, R. Shrivastava, S.K. Parida, H.K. Kisan, H. Lgaz, I.-M. Chung, D. Behera, A new insight into corrosion inhibition mechanism of copper in aerated 3.5 wt.% NaCl solution by eco-friendly Imidazopyrimidine Dye: experimental and theoretical approach, Chemical Engineering Journal, 358 (2019) 725-742.

[45] D.K. Yadav, M. Quraishi, B. Maiti, Inhibition effect of some benzylidenes on mild steel in 1 M HCl: an experimental and theoretical correlation, Corrosion Science, 55 (2012) 254-266.

[46] P.M. Krishnegowda, V.T. Venkatesha, P.K.M. Krishnegowda, S.B. Shivayogiraju, Acalypha torta leaf extract as green corrosion inhibitor for mild steel in hydrochloric acid solution, Industrial & Engineering Chemistry Research, 52 (2013) 722-728.

[47] A. Kahyarian, A. Schumaker, B. Brown, S. Nesic, Acidic corrosion of mild steel in the presence of acetic acid: Mechanism and prediction, Electrochimica Acta, 258 (2017) 639-652.

[48] T. Pojtanabuntoeng, M. Salasi, An electrochemical study of carbon steel CO2 corrosion in the presence of monoethylene glycol: The effects of pH and hydrodynamic conditions, Electrochimica Acta, 258 (2017) 442-452.

Table 1:	Composition	of N80 steel	in wt.	(%).
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N80 steel								
С	Si	Mn	Р	S	Cr	Fe		
0.31	0.19	0.92	0.010	0.008	0.2	98.362		

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Table 2: The slopes of the Bode impedance magnitude plots at intermediate frequencies (*S*) and the maximum phase angles (α) for N80 steel in 15% HCl without and with different concentration of the inhibitors.

	PZ-1		PZ-2	0
С (ррт)	- <i>S</i>	α°	- <i>S</i>	a°
15% HCl	0.456	42.3	0.456	42.3
25 ppm	0.554	55.7	0.481	65.2
50 ppm	0.581	66.3	0.503	65.6
100 ppm	0.644	67.8	0.545	66.2
200 ppm	0.711	69.1	0.604	66.9

C _{inh} (mg/L)	R _s (Ω)	$\frac{R_{\rm ct}}{(\Omega \ \rm cm^2)}$	Y ₀ (μF/cm ²)	α (H	L [cm ²)	C_{dl} μ F/cm ²	η _{EIS} (%)
15% HCl	8.2	9.7±0.329	398	0.528		256.7	
PZ-1							
25	7.8	45.9±0.817	241	0.767	18	99.1	79.0±0.244
50	7.6	163.8±0.524	123	0.779	26	55.4	94.0±0.097
100	5.9	194.2±0.736	78	0.872	56	44.7	95.0±0.203
200	7.5	615.3±0.697	64	0.880	31	27.6	98.4±0.184
PZ-2							
25	9.43	61.7±0.555	225	0.711	3	103.2	84.2±0.113
50	8.63	103.4±0.282	142	0.722	29	74.7	91.0±0.023
100	8.99	119.6±1.049	109	0.846	37	66.5	92.0±0.383
200	7.11	171.3±0.880	105	0.860	11	53.7	94.3±0.299

Table 3: Electrochemical impedance parameters of N80 steel in 15% HCl at differentconcentration of PZs.

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Solution	i _{corr}	β_{a}	- β _c	CF-2	CF-3	$\eta_{ m EFM}$
	$(\mu A/cm^2)$	(mV/dec)	(mV/dec)			(%)
15% HCl	966.1±1.239	87.0	132.0	1.940	2.786	
PZ-1	59.2±0.736	108.0	162.2	2.051	2.901	94.0±0.251
PZ-2	84.9±0.817	50.4	95.9	1.977	2.839	91.2±0.211
					0	

Table 4: Electrochemical frequency modulation parameters for N80 Steel in 15% M HCl in absence and presence of optimum concentration of inhibitors at 308K.

Table 5: Electrochemical frequency modulation trend parameters for N80 Steel in 15% M HCl in absence and presence of optimum concentration of inhibitors at 308K after 1 hour.

i _{corr}	Corrosion rate	$\eta_{ m EFMT}$
$(\mu A/cm^2)$	(mpy)	(%)
37.07±0.788	16.06	<u> </u>
10.6±0.410	04.6	71.4±0.189
14.9±1.239	06.4	60.0±0.225
	<i>i</i> _{corr} (μA/cm ²) 37.07±0.788 10.6±0.410 14.9±1.239	i_{corr} Corrosion rate $(\mu A/cm^2)$ (mpy) 37.07 ± 0.788 16.06 10.6 ± 0.410 04.6 14.9 ± 1.239 06.4

Inhibitor (mg/L)	<i>E</i> _{corr} (mV/SCE)	$i_{\rm corr}$ (μ A/cm ²)	β _a (mV/dec)	- β _c (mV/dec)	η _{PDP} (%)
15% HCl	-435±0.816	129.7±1.020	115	86	
PZ-1					
25	-406±0.816	49.4±0.997	90	122	62.0±0.011
50	-410±0.408	18.3±0.697	55	79	86.0±0.161
100	-422±0.408	11.8±0.524	87	92	91.0±0.248
200	-427±0.235	7.1±0.402	54	33	95.0±0.309
PZ-2					
25	-411±0.816	52.7±0.555	98	95	59.3±0.232
50	-436±1.699	37.6±0.410	83	135	71.0±0.305
100	-442±0.432	21.2±0.736	79	107	84.0±0.142
200	-415±0.736	12.9±0.920	62	96	90.0±0.050

Table 6: Potentiodynamic polarization parameters of N80 steel in 15% HCl at different concentration of PZs.

Table 7. Orbital energy parameters obtained from DFT calculation.

	Neutral form				Protonate	d form
System	E _{HOMO} (kJ/mol)	E _{LUMO} (kJ/mol)	ΔΕ	E _{HOMO} (kJ/mol)	E _{LUMO} (kJ/mol)	ΔE
PZ-1	-4.906	-1.305	3.601	-6.760	-3.014	3.746
PZ-2	-6.33	-2.358	3.972	-8.748	-4.122	4.626

	Neutral fo	orm	Protonated form		
System	$E_{ m interaction}$	E _{binding}	$E_{\rm interaction}$	E _{binding}	
	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	
Fe + PZ-1	- 631.22	631.22	- 598.91	598.91	
Fe + PZ-2	- 301.15	301.15	- 258.59	258.59	

Table 8. Selected energy parameters obtained from MD simulations for adsorption of inhibitors on Fe (110) surface.





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Figure 2: DFT images for (a) Optimized structures of PZ-1 and PZ-2 (b) HOMO structures for PZ-1 and PZ-2, and (c) LUMO structures for PZ-1 and PZ-2.

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(a)



(b)

Figure 3: Molecular dynamic simulation images for (a) PZ-1 and PZ-2 in neutral form (b) PZ-1 and PZ-2 in protonated form.

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(a)

(b)



Figure 4: XPS images (a) Carbon for Blank (b) Carbon for PZ-1 (c) Carbon for PZ-2, (d) Fe for Blank (e) Fe for PZ-1 (f) Fe for PZ-2, (g) Oxygen for PZ-1 (h) Oxygen for PZ-2, (i) Nitrogen for PZ-1 and (j) Nitrogen for PZ-2 of N80 steel in 15% HCl with and without inhibitors.



Figure 5: (a) Inhibition efficiency (b) corrosion rate vs. concentration graphs for PZ-1 and PZ-2 inhibitors





Figure 6: Nyquist graphs for N80 steel in 15% HCl with (a) PZ-1 and (b) PZ-2 inhibitors.



Figure 7: Corresponding circuits used for fitting the data obtained from impedance spectroscopy.





Figure 8: Electrochemical frequency modulation trend (EFMT) graphs for N80 steel immersed in (a) 15% HCl (b) PZ-1 and (c) PZ-2 inhibitors.



Figure 9: Polarization graphs for N80 steel immersed in 15% HCl with (a) PZ-1 and (b) PZ-2 inhibitors.

Highlights

- PZs exhibited max IE of 98.4% at 200 mg/L in 15% HCl.
- PDP study suggests the mixed mode of inhibition by PZs
- SEM, AFM and XPS analysis supports the formation of inhibitor film on metal surface.
- EFMT provides the average decrease in corrosion rate and corrosion current density
- Inhibitor-metal interaction was studied using MD

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dr. K. R. Ansari (corresponding author)

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