Evaluation of newly synthesized hydrazones as mild steel corrosion inhibitors by adsorption, electrochemical, quantum chemical and morphological studies

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ABSTRACT

Inhibition effect of newly synthesized heterocyclic aromatic compounds, 3-(cyano-dimethylmethyl)-benzoic acid thiophen-2-ylmethylene-hydrazide (CBTH) and 3-(cyano-dimethylmethyl)-benzoic acid furan-2-ylmethylene-hydrazide (CBFH) was studied on mild steel corrosion in hydrochloric acid medium by gravimetric, electrochemical and morphological techniques and correlated with quantum chemical indices of the respective molecules. At optimized concentration (2 mM), CBTH and CBFH showed the highest inhibition efficiency of 87.1% and 85.3%, respectively. Impedance study revealed that simultaneous increase in polarization resistance and decrease in double layer capacitance with increasing inhibitor concentration is due to adsorption phenomenon of hydrazones. Inhibitors shift the corrosion potential to less negative value which hinders dissolution of mild steel and evolution of hydrogen and it is more pronounced in anodic reaction. Corrosion current density decreased from 0.2 mA cm$^{-2}$ (blank) to 0.0177 and 0.026 mA cm$^{-2}$ and polarization resistance increased from 199 $\Omega$cm$^2$ to 1590 and 1552 $\Omega$cm$^2$ for CBTH and CBFH, respectively. Quantitative structure activity relationship (QSAR) results showed good correlations between a number of quantum chemical parameters and the experimentally determined inhibition efficiency. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses confirmed the formation of protective inhibitory film.

1. Introduction

The suffering of mild steel (MS) surface when exposed to various service environments containing hydrochloric acid and sulfuric acid due to corrosion is commonly observed in chemical processing, acid pickling, acid cleaning, ore production, petroleum production, oil well acidification and acid descaling. Mitigation of corrosion is usually done by either alloying the metal with other elements or protective film forming through chemical compounds (Kumar, Danaee, Avei, & Vijayan, 2015). Organic inhibitors are preferred for their high efficiency, ease of synthesis, less toxicity and cost-effective nature (Tourabi, Nohair, Traisnel, Jama, & Bentiss, 2013). Most commonly used corrosion inhibitors are organic compounds containing polar groups including nitrogen, sulfur, and/or oxygen atoms and heterocyclic compounds with polar functional groups and conjugated double bonds (Ansari, Quraishi, & Singh, 2017; Verma & Quraishi, 2017).

Hydrazones are close relatives of imines which exist as $R_1R_2C\equiv NNH_2$. Many researchers studied compounds containing $\equiv C\equiv N$ bond as corrosion inhibitors and obtained excellent results (Daoud, Douadi, Issaadi, & Chafaa, 2014; Saha, Dutta, Ghosh, Sukul, & Banerjee, 2015; Singh, 2012). Hydrazones have been much investigated owing to their wide range of properties including antibacterial (Khalil, Berghot, & Gouda, 2009), antitubercular (Telvekar, Belubbi, Bairwa, & Satardekar, 2012), antifungal (Secci et al., 2012) and antimalarial (Fattorusso et al., 2008) activities and recently reported corrosion inhibiting properties. Inhibition efficiency study of some water-soluble hydrazones for C-steel corrosion in hydrochloric acid has been done, and the maximum inhibition efficiency obtained was 95% (Moussa, El-Far, & El-Shafei, 2007). Corrosion inhibition efficiency of quinolinyl thipropano hydrazones was also tested and obtained excellent inhibition of 98% (Saliyan & Adhikari, 2009). Negm, Morsya, and Said (2005) studied some novel hydrazones as corrosion inhibitors.
inhibitors in NaCl medium containing 5% H₂S and obtained maximum inhibition efficiency up to 56% (Negm et al., 2005).

In continuation of our earlier work (Chaitra, Mohana, & Tandon, 2015; Gurudatt & Mohana, 2014; Kumar, Mohana, & Muralidhara, 2014), present paper reports the synthesis of 3-(cyano-dimethyl-methyl)-benzoic acid thiophen-2-ylmethylene-hydrazide (CBTH) and 3-(cyano-dimethyl-methyl)-benzoic acid furan-2-ylmethylene-hydrazide (CBFH) along with their characterization using FTIR, ¹H NMR and mass spectral studies and testing their corrosion inhibition properties using weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. The protective inhibitory film formed on the steel surface was studied by scanning electron microscope and energy dispersive X-ray analyses. In addition to this, quantum chemical calculations were done and obtained parameters were correlated with experimental findings.

2. Experimental

2.1. Materials and sample preparation

Mild steel specimen of dimension 2 cm × 2 cm × 0.1 cm and having composition (wt. %) of C = 0.051; Mn = 0.179; Si = 0.006; P = 0.005; S = 0.023; Cr = 0.051; Ni = 0.05; Mo = 0.013; Ti = 0.004; Al = 0.103; Cu = 0.050; Sn = 0.004; B = 0.00105; Co = 0.017; Nb = 0.012; Pb = 0.001, and the remainder being Fe was used in all experiments. Preparation of specimens and solutions were as reported earlier (Chaitra, Mohana, Gurudatt, & Tandon, 2016).

2.2. Synthesis of inhibitors

Scheme for the synthesis of CBTH and CBFH is outlined in Figure 1. Procedure for synthesis is given in section 1 of supporting data.

Figure 1. Scheme for the synthesis of inhibitors.

2.3. Weight loss measurements

Weight loss experiments were done as described by Chaitra et al. (2016).

2.4. Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) experiments were carried out using CHI660D electrochemical workstation. Electrochemical experiment was conducted as reported earlier (Chaitra et al., 2016). The electrochemical tests were performed using the synthesized hydrazones for concentrations of 0.5–2.0 mM at 303 K. Potentiodynamic polarization measurements were recorded by changing the electrode potential from −200 mV to +200 mV, related to the open circuit potential, with the scanning rate of 10 mV s⁻¹. EIS data were taken using AC sinusoidal signal in the frequency range of 0.1 to 100,000 Hz with amplitude 0.005 V. Simulation of EIS data and fitting of curves were done using Zsimpwin software.
2.5. Quantum chemical calculations

The geometrical optimization of the investigated molecules was done by Ab initio method at 6-31G** basis set for all atoms. The convergence limit at 1.0 and rms gradient at 1.0 kcal/A mol were kept for energy minimization. The Polak-Ribiere conjugate gradient algorithm which is quite fast and precise was used for optimization of geometry. The HYPERCHEM 7.52 (Hypercube Inc., Gainesville, FL, 2003) professional software was employed for all calculations.

2.6. Scanning electron microscopy and energy dispersive X-ray spectroscopy

The scanning electron microscopy (SEM) used was Zeiss electron microscope with the working voltage of 15 kV and the working distance of 10.5 mm. SEM images were taken of polished MS specimen and specimen immersed in acid solution with and without optimum concentration of inhibitors after 4 h of immersion. Energy dispersive X-ray spectroscopy (EDX) experiments were performed using FESEM Zeiss electron microscope with the working voltage of 15 kV and the working distance of 10.5 mm. SEM and EDX experiments were performed using FESEM quanta-200 FEI instrument.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

Gravimetric experiments were performed on MS in the temperature range of 303–333 K in 0.5 M HCl for both the hydrazones for 24 h of immersion. Following formulae was used for the calculation of corrosion rate (CR) and inhibition efficiency (IE) and results are tabulated (Table 1 of supporting data).

\[
CR = \frac{\Delta W}{St} \quad \text{(1)}
\]

\[
\text{IE (\%)} = \frac{(C_R)_a - (C_R)_b}{(C_R)_a} \times 100 \quad \text{(2)}
\]

where, \(\Delta W\) is the weight loss, \(s\) is the surface area of the specimen (cm\(^2\)), \(t\) is the immersion time (h), and \((C_R)_a\) and \((C_R)_b\) are corrosion rates in the absence and presence of the inhibitor, respectively.

Variations in \(C_R\) with the change in temperature and concentration are depicted in Figure 2. \(C_R\) decreased considerably with increase in concentration of both the hydrazones, but the extent of inhibition offered by CBTH was higher compared to CBFH. The increase in inhibition efficiencies with increase in concentration is due to increased surface coverage caused by adsorption of inhibitors. The maximum inhibition efficiencies exhibited were 87.1% and 85.3% by CBTH and CBFH, respectively. The protective property of hydrazones may be due to the interaction between \(\pi\)-electrons and lone pair of electrons present on oxygen, nitrogen and sulphur with charged steel surface. Presence of nitrile group attached to two electron donating methyl groups also contributes to the inhibition efficiency because the electron density is more towards nitrile group. As a result, the net negative charge developed on the nitrile group resulting in good inhibition effect (Gurudatt & Mohana, 2014). In the presence of hydrochloric acid, protonation can occur on carbonyl oxygen atom or nitrogen atom. When the protonation occurs, solubility of the inhibitor increases. This has positive effect on inhibition efficiency. The general trend reported in the inhibition efficiencies of molecules containing heteroatoms is in the order \(O < N < S < P\) (Obot & Obi-Egbedi, 2011). The higher inhibition efficiency shown by CBTH compared to CBFH is due to better electron donating capacity due to the presence of sulphur instead of oxygen atom.

3.1.2. Activation and thermodynamic parameters

Corrosion rate for both CBTH and CBFH increased with increasing solution temperature and maximum efficiency was obtained at 303 K. This can be attributed to the quick desorption of adsorbed inhibitor molecules from the surface in addition to the decomposition of these molecules at elevated temperatures (Aljourani, Raeissi, & Golozar, 2008). Activation thermodynamic parameters were calculated using Arrhenius equation and its alternative form given as equations (3) and (4), respectively.

\[
C_R = k \exp \left( -\frac{E_a^*}{RT} \right) \quad \text{(3)}
\]

\[
C_R = \frac{RT}{Nh} \exp \left( \frac{\Delta S_a^*}{R} \right) \exp \left( -\frac{\Delta H_a^*}{RT} \right) \quad \text{(4)}
\]

where, \(E_a^*\) is activation energy, \(\Delta S_a^*\) is the entropy of activation, \(\Delta H_a^*\) is the enthalpy of activation, \(k\) is 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. Plot of \(C_R\) vs 1/T gave the values \(E_a^*\) and \(k\) whereas \(\ln C_R/T\) vs 1/T gave \(\Delta H_a^*\) and \(\Delta S_a^*\) (Figure 1 and Figure 2 of
supporting data). All parameters involved in Arrhenius equation were calculated and listed in Table 2 of supporting data. It was found that \(E_a\) values for systems containing CBTH (27.6 to 33.3 kJ mol\(^{-1}\)) and CBFH (ranged from 33.2 to 34.9 kJ mol\(^{-1}\)) were higher as compared to inhibitor free acid solution (23.9 kJ mol\(^{-1}\)). Increase in \(E_a\) value after the addition of hydrazones indicates the reduction in the ease for charge and mass transfer due to the formation of energy barrier. It is reported that if inhibition efficiency decreases with an increase in temperature, then \(E_a\) (inhibited solution) > \(E_a\) (uninhibited solution) (Singh, 2010). Results obtained in the present study justify this statement. Positive values of \(DHa\) which varied between 24.9 and 32.2 kJ mol\(^{-1}\) show that MS dissolution is endothermic. Negative values of \(Ds\) which varied from 159.8 and 174.4 JK\(^{-1}\) mol\(^{-1}\) in the presence of inhibitors suggests that formation of the activated complex in the rate determining step is association rather than dissociation leading to decrease in randomness (Ghareba & Omanovic, 2011). Movement from reactant to activated complex state is accompanied with change in activation entropy due to complex adsorption and desorption between hydrazones and water molecules on the metal surface which is referred to as quasi substitution. Negative value of activation entropy indicates the decrease in randomness due to increase in solute entropy due to adsorption of hydrazones.

3.1.3. Adsorption isotherm

Adsorption of organic molecule occurs because the interaction energy between the metal surface and the inhibitor is higher than the interaction energy between the metal surface and the water molecules (El-Maksoud, 2008). Attempts were made to fit the data to various isotherms like Langmuir, Freundlich, Temkin and other isotherms among which Langmuir isotherm was formed to be most suitable. The regression co-efficient \((R^2)\) for three of the studied isotherms is included in the Table 3 of supporting data. The equation for Langmuir isotherm is

\[ \frac{C}{\theta} = \frac{1}{K_{ads}} + C \]  

(5)

where, \(\theta\) is the surface coverage and \(C\) is the concentration of the inhibitor. A plot of \(C/\theta\) versus \(C\) gave straight line (Figure 3) using which different adsorption parameters were calculated and listed in Table 1. Regression co-efficient and slope for CBTH and CBFH are around 0.99 and 1, respectively which confirms the validity of Langmuir isotherm model for adsorption. Free energy of adsorption can be calculated from \(K_{ads}\) using the equation,

\[ \Delta G^o_{ads} = -RT\ln(55.5K_{ads}) \]  

(6)

where, \(R\) is gas constant and \(T\) is the absolute temperature of the experiment and the constant value 55.5 is the concentration of water in solution in mol dm\(^{-3}\). The negative value obtained for \(\Delta G^o_{ads}\) indicates that the adsorption process onto the metal surface is spontaneous and the adsorbed layer is stable (Scendo & Trela, 2013). The interaction between hydrazones with the MS could be described by physisorption, chemisorption or by complexation which are influenced by the nature and charge of the metal, the type of electrolyte and the chemical structure of the inhibitor. (Yang, Li, & Mu, 2006). The value of \(\Delta G^o_{ads}\) for studied inhibitors varies between −31.6 kJ mol\(^{-1}\) and −33.9 kJ mol\(^{-1}\), so the kind of adsorption cannot be completely either physisorption or chemisorption, but it is a complex and comprehensive adsorption involving both (Singh, Gopal, Prakash, Ebenso, & Singh, 2013). Entropy of adsorption and enthalpy of adsorption process is calculated using the following thermodynamic equation.

\[ \Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \]  

(7)

A graph of \(\Delta G^o_{ads}\) vs \(T\) gives straight line with slope \(-\Delta S^o_{ads}\) and intercept \(\Delta H^o_{ads}\) (Figure 4).

The gain in entropy is attributed to the increase in solvent entropy. That is, hydrazones get adsorbed on to the MS surface as soon as water molecules get desorbed. It is reported that endothermic adsorption

![Figure 3. Langmuir isotherm for the adsorption of (a) CBTH and (b) CBFH on MS in 0.5 M HCl at different temperatures.](image-url)
Table 1. Adsorption thermodynamic parameters in the absence and presence of various temperatures.

| Inhibitor | T (K) | $R^2$ | Slope | $K_{ads}$ (L mol$^{-1}$) | $\Delta H_{ads}$ (kJ mol$^{-1}$) | $\Delta S_{ads}$ (J mol$^{-1}$ K$^{-1}$) | $\Delta G_{ads}$ (kJ mol$^{-1}$) |
|-----------|-------|-------|-------|--------------------------|---------------------------------|-------------------------------------|---------------------------------|
| CBTH      | 303   | 0.9965| 1.0679| 5042                     | $-31.6$                         | 76.1                                 | $-8.68$                         |
|           | 313   | 0.9983| 1.0975| 5195                     | $-32.7$                         |                                     |                                 |
|           | 323   | 0.9931| 1.0990| 4243                     | $-33.2$                         |                                     |                                 |
|           | 333   | 0.9912| 1.0961| 3832                     | $-33.9$                         |                                     |                                 |
| CBFH      | 303   | 0.9995| 1.0855| 5449                     | $-31.7$                         | 47.2                                 | $-17.6$                         |
|           | 313   | 0.9966| 1.0987| 4677                     | $-32.4$                         |                                     |                                 |
|           | 323   | 0.9974| 1.0903| 3565                     | $-32.7$                         |                                     |                                 |
|           | 333   | 0.9998| 1.0987| 2978                     | $-33.2$                         |                                     |                                 |

Figure 4. Plot of $\Delta G_{ads}$ vs. $T$ for CBTH and CBFH.

3.2. Electrochemical impedance spectroscopy

EIS determines different impedance parameters between MS-hydrochloric acid interface in the absence and presence of optimum concentration of two hydrazones, and results are presented in Table 2. Detailed information about the EIS experiments is presented in Table 4, Figures 3, 4(a–c), 5(a–c) of supporting data. Open circuit potential vs time, Nyquist, bode and phase angle plots for CBTH and CBFH are presented in Figure 5(a–d). Nyquist plots exhibit single semicircle whose diameter increases with increase in the concentration whereas shapes of the curves remains the same after the addition of hydrazones. Nyquist plots are explained based on equivalent electrical circuit consisting of polarization resistance ($R_p$) parallel with constant phase element (CPE) both in series with solution resistance ($R_s$) Figure 5(b). Inhibition efficiency can be calculated by $R_p$ using the following formula,

$$IE\% = \left(\frac{(R_p)_a - (R_p)_b}{(R_p)_a}\right) \times 100$$  (8)

where, $(R_p)_a$ and $(R_p)_b$ are the polarization resistance in the absence and presence of inhibitor, respectively. $R_p$ increases with increase in the concentration and reaches maximum value of 1590 and 1522 $\Omega\text{cm}^2$ at optimum concentration of 2 mM for CBTH and CBFH, respectively. The increase in $R_p$ could raise the tendency of the current to pass through the capacitance in the circuit.

CPE can be expressed as

$$Z_{CPE} = Y_o^{-1}e^{-j\omega t}$$  (9)

where, $Y_o$ is the magnitude of CPE, $\omega$ is the angular frequency (in rad s$^{-1}$), $t^2 = -1$ is the imaginary number. The double layer capacitance ($C_{dl}$) can be calculated from CPE parameters using the equation,

$$C_{dl} = (Y_oR_p)^{-1-n}/n$$  (10)

Here $n = \alpha/(\pi/2)$ in which $\alpha$ is the phase angle of CPE. “n” is fractional exponent for solid electrodes/solution interfaces and its value is $-1 \leq n \leq 1$ (Chaitra et al., 2016). Depending on the value of $n$, CPE can represent resistance ($n = 0$, $Y_o = R$), capacitance ($n = 1$, $Y_o = C$), inductance ($n = -1$, $Y_o = L$) or Warburg impedance ($n = 0.5$, $Y_o = W$) (Murulana, Kabanda, & Ebenso, 2015). In the present study, value of $n$ for blank 0.76 increases in case of both hydrazones (varying between 0.78 and 0.85) represents deviation from the ideal behaviour (where $n = 1$). Generally, high value of $n$ is associated with low surface roughness and high surface coverage (Verma, Ebenso, Bahadur, Obot, & Quraishi, 2015). Increase in the value of $n$ shows that after the adsorption of inhibitor the surface becomes more homogeneous, also there is increase in surface coverage of MS by CBTH and CBFH that leads to increase in capacitative behavior.

Double layer capacitance is calculated from thickness of the double layer ($d$) by the following equation,

$$C_{dl} = A\varepsilon\varepsilon_0/d$$  (11)

where, $\varepsilon$ is the dielectric constant of the protective layer, $\varepsilon_0$ is the permittivity of the free space and $A$ is the area of the working electrode. In the present study, decrease in $C_{dl}$ after the addition of hydrazones is due to increase in thickness of the protective film which results in decrease in local di-electric constant (Verma, Singh, & Quraishi, 2016). The single
peak obtained in Bode plots for both CBTH and CBTH indicates that the electrochemical impedance measurements fit well in the one-time constant equivalent model. In the present study, phase angle value close to 70° has been obtained whereas an ideal capacitor is characterized by slope value of 90°.

3.3. Potentiodynamic polarization

Tafel curves for MS in the absence and presence of optimum concentrations of CBTH and CBFH in 0.5 M HCl at 303 K are presented in Figure 5(e). The corrosion kinetic parameters such as corrosion potential

| Inhibitor | $R_p$ (Ω cm$^2$) | $Y_0$ (μΩ cm$^{-1}$ s$^1$) | $n$ | $C_{dl}$ (μF cm$^{-2}$) | $\Delta E$ (%) | $E_{corr}$ (mV) | $i_{corr}$ (mA cm$^{-2}$) | $b_a$ (mV dec$^{-1}$) | $b_c$ (mV dec$^{-1}$) | $IE$ (%) |
|-----------|-----------------|-----------------|------|-----------------|-----------|----------------|-----------------|-----------------|-----------------|---------|
| Blank     | 198.9           | 356.5           | 0.7631 | 132.8           | –         | –502           | 0.2000          | 220             | 376             | –       |
| CBTH      | 1590            | 68.7            | 0.8563 | 14.0            | 87.8      | –498           | 0.5277          | 79.3            | 106             | 91.2    |
| CBFH      | 1552            | 71.2            | 0.8513 | 14.2            | 85.1      | –440           | 0.0265          | 69.9            | 162             | 86.7    |

Table 2. Impedance and polarization parameters for the corrosion of MS in 0.5 M HCl in absence and presence of optimum concentration of inhibitors at 303 K.

Figure 5. (a) Open circuit potential versus time (b) Nyquist (c) Bode (d) Phase angle (e) Tafel plots in the absence and presence of different concentrations of CBTH and CBFH.
Table 3. List of quantum chemical parameters for CBTH and CBFH.

| Quantum chemical parameters | CBTH | CBFH | CBTH (Protonated) | CBFH (Protonated) |
|-----------------------------|------|------|--------------------|-------------------|
| Total Energy (kJ mol⁻¹)     | -3265108 | -2421885 | -3284628 | -2435933 |
| Dipole (Debye)              | 6.2875 | 5.6444 | 6.8650 | 6.5201 |
| EHOMO (eV)                  | -9.0228 | -8.8556 | -9.3422 | -7.4542 |
| ELUMO (eV)                  | 1.6668 | 1.8809 | 2.9564 | 3.3280 |
| ΔE = ELUMO - EHOMO (eV)     | 10.689 | 10.736 | 12.2986 | 10.7822 |
| ΔE² = ELUMO of acid − EHOMO of base (eV) | 8.8228 | 8.6556 | 9.1422 | 7.2542 |
| Ionization potential, l = −EHO MO | 9.0228 | 8.8556 | 9.3422 | 7.4542 |
| Electron affinity, E = −ELUMO | -1.6668 | -1.8809 | -2.9564 | -3.3280 |
| Electronegativity (χ) = (I + E)/2 | 3.678 | 3.4873 | 3.6774 | 2.0631 |
| Hardness of the molecule (η) = (I − E)/2 | 5.3348 | 5.3682 | 6.1493 | 5.3911 |
| Softness (σ)                | 0.1874 | 0.1862 | 0.1626 | 0.1854 |

(\(E_{corr}\)), corrosion current density (\(i_{corr}\)), cathodic Tafel slope (\(b_c\)), anodic Tafel slope (\(b_a\)) and percentage inhibition were derived from the curves and are recorded in Table 2. Detailed information on polarization measurement is included in the Figure 6 and Table 5 of supporting data.

Inhibition efficiency (IE %) values were derived from corrosion current density (\(i_{corr}\)) were calculated by the Tafel plot,

\[ IE (\%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \]  (12)

where, \(i^0_{corr}\) and \(i_{corr}\) are the uninhibited and inhibited corrosion current densities, respectively. It is evident from Figure 5(e) that both hydrogen evolution and metal dissolution reactions were retarded after the addition of hydrazones. Corrosion current density values decreased on increasing concentration of inhibitors indicating that inhibitors bring down electrochemical reaction. The corrosion current density which was 0.2 mA cm⁻² for blank decreased to 0.0177 mA cm⁻² and 0.02654 mA cm⁻², respectively for CBTH and CBFH at optimum concentration. The variations in the values of both \(b_c\) and \(b_a\) signify the influence of CBTH and CBFH on both anodic and cathodic reactions and its irregularities indicate that some mechanisms are involved. The corrosion potentials for inhibitors are slightly anodically displaced with respect to the bare MS in solution without an inhibitor. This shows the predominant hindrance of MS dissolution compared to hydrogen evolution. According to the literature, when \(E_{corr}\) is displaced more than ±85 mV relating to potential of the blank, the inhibitor can be considered as either cathodic or anodic type (Chaubey, Savita, Singh, & Quraishi, 2017). In the present investigation, the shift in \(E_{corr}\) is 47 mV and 62 mV towards anodic for CBTH and CBFH, respectively. Therefore, the studied inhibitors are neither anodic nor cathodic, but are of mixed type.

3.4. Quantum chemical calculations

Quantum chemical methods are useful in elucidating the electronic structure and reactivity which could be helpful in designing high-efficiency inhibitors by quantitative structure–activity relationship (QSAR) method (Zhang & Musgrave, 2007). The structures of CBTH and CBFH were first optimized and the simulated to calculate the electronic parameters. Various quantum chemical parameters such as \(E_{HOMO}\) Energy of highest occupied molecular orbital, \(E_{LUMO}\) Energy of lowest unoccupied molecular orbital, \(\Delta E\) Energy gap \((\Delta E)\), dipole moment \((\mu)\), ionization potential \((I)\), electronegativity \((\chi)\), hardness \((\eta)\) and softness \((\sigma)\) were calculated for inhibitors and their protonated forms and these are listed in Table 3. Following equations are used for the calculation of quantum chemical parameters:

\[ I = \frac{-E_{HOMO}}{2} \]  (13)
\[ A = \frac{-E_{LUMO}}{2} \]  (14)
\[ \chi = \frac{I + A}{2} \]  (15)
\[ \eta = \frac{I - A}{2} \]  (16)
\[ \sigma = \frac{1}{\eta} \]  (17)

Difference in the energy between inhibitor molecules and their protonated forms (energy of protonation) is calculated and found to be −19,520 kJ mol⁻¹ for CBTH and −14,048 kJ mol⁻¹ for CBFH. From electrostatic potential map of CBTH and CBFH, negative charge is accumulated near oxygen atom (indicated by red color lines) so protonation on oxygen atom is most favorable. After protonation, nitrogen atom becomes negative therefore the adsorption of hydrazones occurs mainly through interaction between nitrogen atom and MS surface. From Table 4, HOMO and LUMO orbitals of CBTH is mainly distributed around nitrogen atoms, CO–NH–NH₂ group and thiazole ring, whereas in CBFH they are distributed mainly around CO–NH–NH₂ so these act as active adsorption centers. A good correlation was found between \(E_{LUMO}\) and dipole moment with experimentally determined inhibition efficiency. Higher HOMO energy results in more reactivity towards electrophiles and lower LUMO energy results in higher reactivity towards nucleophiles (Rauk, 2001). As the energy required to remove the last occupied orbital
will be low, lower values of energy gap will have good inhibition efficiency (Obot, Obi-Egbedi, & Umoren, 2009). The present study showed lower $E_{\text{LUMO}}$ for CBTH, thereby implying better electronic interaction with the metal surface. Hence it has better inhibitor property compared to CBFH.

Dipole moment is the measure of polarity in a bond and is related to the distribution of electrons in a molecule (Gece, 2008). As the energy of deformability increases with increase in dipole moment, high value of dipole moment increases the adsorption between chemical compound and metal surface. There is increase in dipole moment after protonation for both CBTH and CBFH indicating ease of interaction with the metal surface. Higher value of dipole moment for CBTH as compared to that of CBFH helps the former to strongly adhere on MS surface. Chemical hardness is defined as the resistance offered towards the deformation of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction (Zarrok et al., 2012). For the simple transfer of electron, adsorption could occur on the part of the molecule where softness ($\sigma$), which is a local property, is maximum (Hasanov, Sadikoglu, & Bilgic, 2007). Since iron is a soft acid it is more likely to react with soft bases. The quantum chemical study results show good correlation with experimental values.

### 3.5. Scanning electron microscopy

To confirm the presence of protective inhibitory film, SEM images were taken with and without CBTH and CBFH at optimum concentration (Figure 6(a–d)) at 303 K. In the absence of inhibitors, MS surface exhibited increased pitting. But, in the presence of both the inhibitors the surface showed great improvement without the formation of any pits.
3.6. Energy dispersive X-ray analyses

Energy dispersive X-ray analysis was done to get information about the composition of MS in 0.5 M HCl in the absence and presence of inhibitors. EDX spectra of CBTH and CBFH are given in Figure 7 of supporting data. Table 5 presents weights of elements in uninhibited and inhibited MS samples. The weight percent of Fe considerably decreased by the addition of inhibitors. The decrease in percent weight of Fe from 56.95 to 22.95 and 8.5, respectively after the addition of CBTH and CBFH. The peaks of other elements such as nitrogen, oxygen, carbon and sulphur were also appearing in inhibited EDX spectra. This clearly proves the adsorption of inhibitors on to the Fe surface.

3.7. Mechanism of inhibition

Inhibition effect of hydrazones on mild steel can be explained on the basis of the mode of interaction with the metal surface. Studied hydrazones contain nitrogen atoms as well as the carbonyl both of which can undergo protonation. From electrostatic potential map (Table 4), carbonyl group has more negative charge compared to nitrogen atom so carbonyl group predominantly undergoes protonation. The protonated form of hydrazones physically adsorbs on the positively charged mild steel surface through chloride irons (Cl⁻). On the other hand, direct adsorption takes place by donor-acceptor interactions between lone pair of electrons on nitrogen, oxygen and sulphur atoms and pi-electrons of benzene and heterocyclic rings and vacant d-orbitals of Fe atom. Among CBTH and CBFH, sulphur bearing CBTH shows better inhibition efficiency compared to oxygen bearing CBFH because oxygen is more electronegative compared to sulphur.

4. Conclusion

Synthesized hydrazone derivatives showed good inhibition property against MS corrosion in 0.5 M HCl medium. Hydrazones proved efficient at lower
temperatures than higher temperature. The adsorption behavior of both hydrazones followed Langmuir isotherm. Polarization study revealed that the hydrazones acted as cathodic and anodic inhibitors. Nyquist plots, Bode plots and morphological studies (SEM and EDX) confirmed the presence of protective inhibitory film. Quantum chemical studies proved that electronic interaction of CBTH is better than that of CBFH.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
One of the authors (T. K. C) received meritorious fellowship (RFMS) from University Grants Commission, New Delhi (Order No. MGC/003/2015-16 dated 04/08/2015) and this is gratefully acknowledged.

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