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Experimental studies on inhibition of mild steel corrosion by novel synthesized inhibitor complemented with quantum chemical calculations

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ABSTRACT

One of best method, which was used to prevent the mild steel from corrosion, was through employed natural or synthetic organic chemical compounds. Here in, we displayed a Schiff base derivative which has nitrogen, oxygen and sulfur atoms as corrosion inhibitor for MS "mild steel" in 1 M HCl "hydrochloric acid" solution. Synthesized inhibitor was characterized by using of FT-IR "Fourier transform infrared" and NMR "Nuclear magnetic resonance" spectroscopies in addition to CHN analysis technique. The weight loss and SEM "Scanning electron microscope" studies showed that inhibitor have the ability to prevent the alloy surface from corrosive solution by adsorbing on MS surface to form stable adsorbed layer that results in the higher inhibition efficiency. The inhibition influence of the synthesized inhibitor was increased parallel with increasing concentration and decrease with rising temperature degrees. Furthermore, DFT "Density function theory" has been employed to calculate quantum chemical parameters "Energy, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and electronegativity (χ)" which performed on synthesized corrosion inhibitor to determine the relationship between the structure of synthesized inhibitor molecule and inhibition performance.

Introduction

Mild steel "MS" is quite applied in considerable manufacturing applications such as Chemicals, pickling, acid cleaning, oil, gas, storage and pipeline transportation". MS seveir from corrosion due to corrosive solutions and lead to the degradation of the alloy, resulting in considerable economic losses for several industries. The degradation of MS is an effect of contact of MS with the acidic and/or basic solutions which were quite used in manufactures for diverse applications [1–6]. Schiff bases were quite significant class of molecules that synthesized from aromatic and/or aliphatic aldehydes or ketones, and amines [7–9]. In addition, the Schiff bases have the azomethane linkage (–C═N) which considered the essential structural requirement for different medicinal and pharmacological applications, including immunosuppressant activity [10], anti-malarial [11], anti-tubercular [12], anti-microbial and anti-cancer activities [13]. Quantum chemical calculations is nowadays employee in order to demonstrate the corrosion inhibition mechanism of the studied inhibitors such as DFT "Density function theory" [14–17]. Density function theory is proved a quite powerful tool for mechanism searching [18–20]. The aim of this paper is to study the dependence of inhibition performance of the studied molecule and inhibitory properties of new synthesized inhibitor, namely methyl "2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate" for the corrosion of mild steel in corrosive solution through gravimetric technique and quantum chemical calculations using DFT method. Theoretical calculations depending on the chemical parameters "highest occupied molecular orbital (EHOMO) and the lowest unoccupied molecular orbital (ELUMO), energy gap (ΔE), dipole moment (μ), electronegativity (χ), electron affinity (A), global hardness (η), softness (σ), ionization potential (I) and the global Electrophilicity (ω)". The chemical structure of the synthesized inhibitor was shown in Fig. 1.

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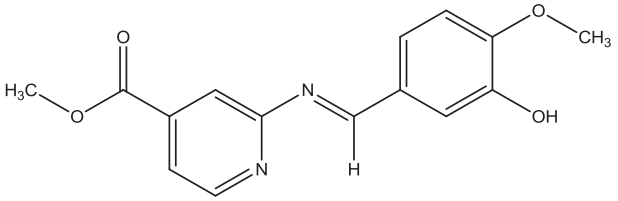

Fig. 1. The chemical structure of the studied inhibitor.

Experimental

Materials and chemical compounds

All the chemicals compounds and solvents that used in this study were purchased from Sigma Aldrich Chemicals/Malaysia. Shimadzu FTIR-8300 spectrometer was employee to obtained FT-IR "Fourier transform infrared" spectra. Carlo Erba 5500 elemental analysis was utilized to perform the CHN-Elemental analyses. NMR "Nuclear magnetic resonance" spectrum was recorded on a Bruker Spectrospin instrument at 300 nMHz UltraShield magnets. DMSO-d_6 "Dimethyl sulfoxide-d6" has been used as solvent and TMS "Tetramethylsilane" has been used as internal standard. The target inhibitor synthesized through condensation reaction of 3-hydroxy-4-methoxybenzaldehyde (0.005 mol) with methyl 2-aminoisonicotinate (0.005 mol) in ethanol (50 mL) and the mixture was refluxed with few drops of acetic acid for 5 h with stirring. TLC "Thin layer chromatography" has observed through the approach of reaction. The solid cooled, filtered, washed by ethanol and recrystallized from ethanol, yield 76%. M.P. 112–115 °C. The purity of synthesized compound was confirmed through TLC. IR: 3285.3 cm^{-1} (OH), 3051.5 cm^{-1} (aromatic group) 1711.8 cm^{-1} (carbonyl), 1629.7 cm^{-1} (C=N). ^{1}H NMR (DMSO-d_6); δ: 8.96 (d, 1H, H-C=N, pyridine), 8.29 (s, 1H, H-C=N), 6.88–7.81(s, 1H, aromatic benzene and pyridine rings), 5.31 (s, 1H, OH), 3.78 (s, 3H, OCH3 pyridine rings), 3.58 (s, 3H, OCH3 benzene rings). CHN analysis calculation (found) for $C_{15}H_{14}N_2O_4$: C 62.93 (62.13), H 4.93 (4.52), N 9.79 (9.21).

Corrosion studies

Mild steel "MS" coupons, which were applied as electrodes in our search, have been provided through the Company of Metal Samples. MS alloy composition of "99.21Fe, 0.21C, 0.38Si, 0.09P, 0.05S, 0.05Mn and 0.01Al"%. The efficient surface area was 4.5 cm^2 and it was cleaned approbate to the method ASTM G1-03 [21–23]. MS coupons were suspended duplicate in 0.2 L of 1 M hydrochloric acid solution in absence and presence of the target inhibitor. The concentrations of the inhibitor were 0.00, 0.05, 0.10, 0.15, 0.2.0, 0.25 and 0.50 g/L at five hours as an immersion time. Coupons were washed and dried then weighed accurately. CR "corrosion rate" and IE% "inhibition efficiency have been calculated as in Eqs. (1) and (2) respectively:

$$C_R = mg \times cm^2h^{-1} \tag{1}$$

$$IE = \left[1-\left(\frac{w_2}{w_2}\right)\right] \times 100 \tag{2}$$

Note: w_1 & w_2 are the MS coupons weight losses in presence and absence of the studied inhibitor respectively.

DFT calculations

The optimized Geometrical structures have been done without symmetry constraints employing "Gaussian 09, Revision A.02" [24]. The function B3LYP has been used for all optimized structures and energies such as EHOMO "Energy of highest occupied molecular orbital" and ELUMO "Energy of lowest unoccupied molecular orbital" calculations [25,26]. Inhibition mechanism of synthesized inhibitor derived from 3-hydroxy-4-methoxybenzaldehyde and methyl 2-aminoisonicotinate related quantum parameters that were indicated as in Eqs. (3)–(9) [27].

$$\Delta E \text{ Energy gap} = E_{LUMO} - E_{HOMO} \tag{3}$$

$$X\text{""Electron affinity""} = -HOMO \tag{4}$$

$$I\text{""Ionization potential""} = -LUMO \tag{5}$$

$$\eta\text{""Global hardness""} = \frac{1}{2}(E_{HOMO} - E_{LUMO}) \tag{6}$$

$$S\text{""Chemical softness""} = \frac{1}{\eta} \tag{7}$$

$$\chi\text{""Electronegativity""} = \frac{1}{2}(E_{HOMO} + E_{LUMO}) \tag{8}$$

$$\omega\text{""electrophilicity index""} = \frac{\mu^2}{2\eta} \tag{9}$$

Results and discussion

Synthesis

To synthesize methyl 2-((3-hydroxy-4-methoxybenzylidene)amino) isonicotinate as a corrosion inhibitor, the sequence of the reaction outlined in Fig. 2, starting from the available commercial compounds methyl 2-aminoisonicotinate and 3-hydroxy-4-methoxybenzaldehyde. The synthesis have been done through the reflux of methyl 2-aminoisonicotinate in ethanol with 3-hydroxy-4-methoxybenzaldehyde. The target compound has molecular weight 286, that was estimated based on it formula ($C_{15}H_{14}N_2O_4$) which confirmed by CHN elemental analysis. The inhibitor methyl 2-((3-hydroxy-4-methoxybenzylidene) amino)isonicotinate can be dissolve in several polar solvents such as DMF, DMSO, dichloromethane, acetone and alcohol. The spectrum of FTIR for of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate show new absorption bands and disappeared of others absorption bands. The new band at 1611 cm^{-1} for azomethine group, and disappearance of the bands for amino and carbonyl groups at around 3350 cm^{-1} and 1700 cm^{-1} respectively. H NMR spectrum show singlet at 8.29 ppm due to the azomethine (H–C=N) proton.

Weight loss results

Corrosion inhibitors that were utilized in industries are the economical technique for efficiently protection of MS alloy surface [28].

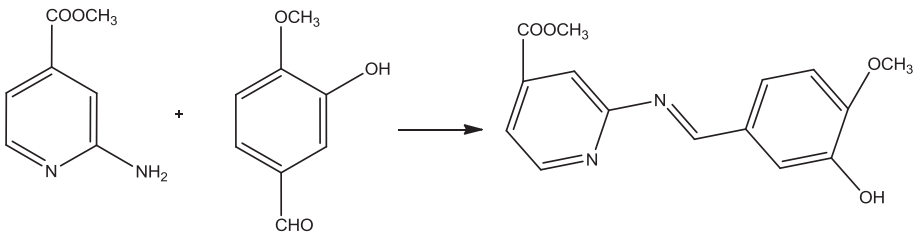

Fig. 2. The reaction sequence for synthesized of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino) isonicotinate.

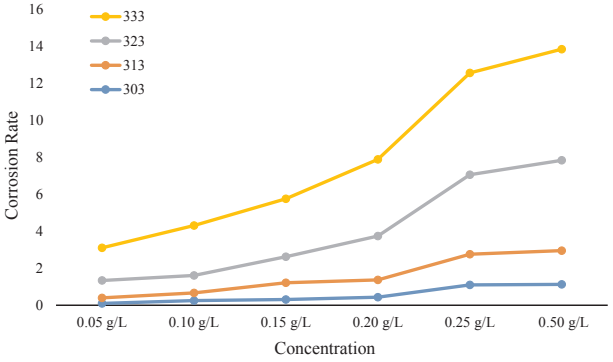

Fig. 3. Impact of concentrations on corrosion rate at 303–333 K.

Natural and/or synthetic organic inhibitors are the dominant compounds which were utilized in the oil manufacture due to formation of barrier film on the surface of MS vs acidic or basic media. Generality these inhibitors are often heterocyclic compounds, like thiadiazoles, oxadiazoles and triazoles [29–32]. The weight loss procedure was applied to calculate the inhibition competence of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate at the concentrations (0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 g/L) and at 303 K for MS in solution of 1 M of hydrochloric acid. Fig. 3, clarified the relation of concentrations of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate various CRs at deferent temperatures. CRs diminish based on inhibitor concentration rising in HCl solution. CR was slightly decreased in parallel with increasing of concentration.

The methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate results, that were demonstrate in Figs. 3 and 4, respectively, signalize that this inhibitor diminishes the corrosion on the surface of MS in HCl solution. The inhibition qualification was increased based on concentration increased and arrive to the extreme efficiency at the highest examined concentration.

To determine the impact of temperatures on the performance of the studied inhibitor, some experiments were done in presence and absence of methyl 2-((3-hydroxy-4 methoxybenzylidene)amino)isonicotinate at various temperatures (303, 313, 323 and 333 K). The inhibition achievement was promoting by concentration increase of the studied inhibitor and decreased with rising temperature. Fig. 4, displayed the temperature impact on the methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate inhibition performance.

The adsorption heat of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate on MS was negative, signalizing that process was exothermic, that clarify the decreasing in the inhibition efficiency with rising temperature.

It is clarified that the inhibition percentage was diminish at studied temperatures which were 303 K to 333, at the concentrations 0.05–0.5 g/L; while the inhibition efficiency quite increased at 303 K.

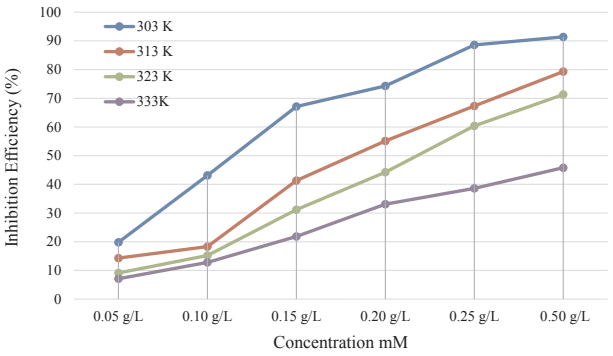

Fig. 4. Effect of inhibitor concentrations on inhibition efficiencies at various temperatures.

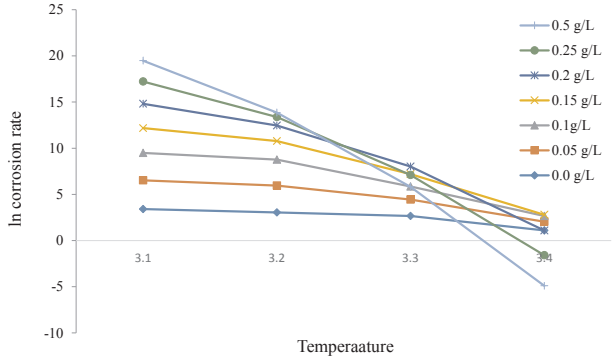

Fig. 5. The temperature impacts on the CR according to Arrhenius plot of for MS in HCl solution.

Assessment of our results show that the inhibition efficiency of the methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate increased in parallel with increasing concentration. The highest value of inhibition efficiency was 91.4% which at 0.5 g/L as concentration for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate. Moreover, the best concentration for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate was 0.5 g/L, and the reason was no significant changes in inhibition efficiency at higher concentration. The Arrhenius equation "Eq. (10)" was applied to demonstrate the temperature effects on the inhibition efficiency of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate as studied inhibitor [33,34].

$$\ln C_R = \frac{-E_a(\text{activation energy})}{R(\text{gas constant})T(\text{temperature})} + \ln A(\text{Arrhenius factor}) \quad (10)$$

The energy without and with methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate are calculated as in Eq. (11) and Arrhenius plots that displayed in Fig. 5.

$$\text{Slope} = -\frac{\Delta E_a}{2.303R(\text{gas constant})} \quad (11)$$

The E_a value was 89.7 kJ mol^{-1} for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate, which indicate the important of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate in HCl media that could be compared with the value of E_a in absence of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate and this result refer to that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules forming protective film on coupon surface [33].

Proposed inhibition mechanism

The inhibition performance of the target inhibitor methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate might depend on one of the major parameters that were atomic charges and/or molecular weights, and minor parameter which was the stability of complex that depend on the linkage nature between the inhibitor and the metal. Fig. 6 displayed formation of complex between the atoms at the surface of MS and the studied inhibitor molecules.

The mechanism for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate can be clarified based on VBT "valence bond theory". The electron configuration of iron ion + +, is [Ar]3d6. The 3d orbitals mix with the unoccupied 4 s and 4p orbitals to form sp3 or d2sp3 hybrid orbitals that may be oriented appropriately across the azomethine group and/or non-bonding electrons pairs of oxygen atoms in molecules of studied inhibitor. Orbitals overlap of iron ions and methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate, complex with form with, tetrahedral, square planar or octahedral geometry that the metal orbital loaded and formation of valence shell. The mechanism of inhibition may have clarified in other theories

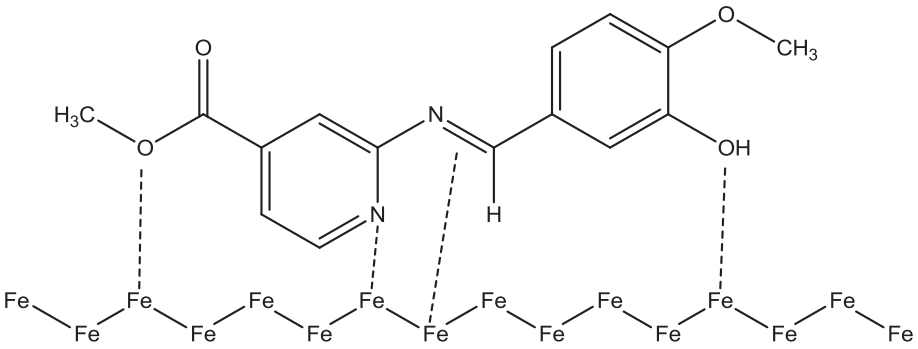

Fig. 6. The proposed mechanism.

namely CFT "crystal field theory" or MOT "molecular orbital theory". The complexation between the iron and inhibitor molecules, coordination bonds form via transfer electron from the nitrogen and oxygen atoms to the d orbitals of iron.

Scanning electron microscopy

MS coupons surfaces have been characterized via SEM before and after coupons immersion in corrosive solution at 30 °C without the inhibitor and with the inhibitor at the concentration of 0.5 g/L for three hours, as displayed in Fig. 7. Coupon surface have been damaged in absence of inhibitor because of high dissolution rate of iron in HCl solution. On the other hand, a film has been observed on coupon surface in presence of the studied inhibitor. This result indicate that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules adsorbed on the coupon surface as barrier film against corrosive solution.

Quantum calculations

The inhibitor methyl 2-((3-hydroxy-4-methoxybenzylidene)amino) isonicotinate molecules have various atoms such as oxygen and nitrogen with azomethine group in addition to aromatic rings that having resonance effect, through the linkage between azomethine group, phenyl and pyridine rings together to form molecule with significant properties due to inductive and resonance effects. It is clear from geometrical structure of methyl 2-((3-hydroxy-4-methoxybenzylidene) amino)isonicotinate, the optimized structure is planar due to the aromaticity. Electronic structures of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate were find using of DFT-B3LYP/6-311G. EHOMO "highest occupied molecular orbital energy" and ELUMO "lowest unoccupied molecular orbital energy" studied for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate and shown as in Fig. 8. Factors such as ΔE, μ and χ have been displayed as in Table 1. EHOMO demonstrate the electron ability of the methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate with electron susceptibility as comparing to other searched natural or synthetic organic

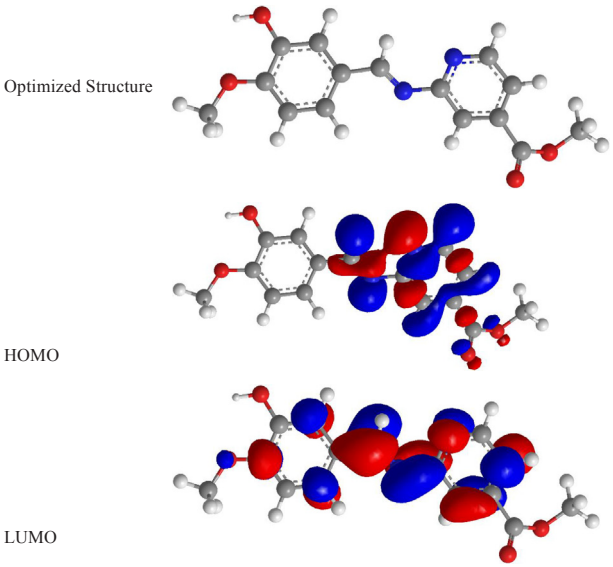

Fig. 8. Electronic structures of methyl 2-((3-hydroxy-4-methoxybenzylidene) amino)isonicotinate.

inhibitors [35,36]. The releasing electronic ring pyridine bonded to phenyl group via azomethine in methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate increase the electron donating abilities of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules as in Fig. 8. Energies of HOMO may be consider as the affinity of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules. ΔE is first factor that depict the bond of coupon MS surface and methyl 2-((3-hydroxy-4-methoxybenzylidene)amino) isonicotinate molecules. The searched inhibitor methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate has energy gap equal to 5.349 eV as showed in Fig. 8 and Table 1. Generally, the searched inhibitor with minimum χ indicate higher electron propensity demonstrate higher inhibition efficiency. χ quite support our results. The

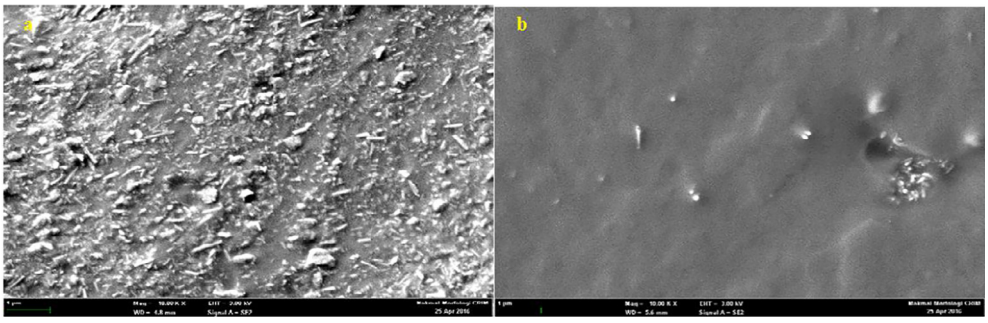

Fig. 7. The SEM images of MS coupons surface in HCl in the absence (a) and presence (b) of inhibitor.

Table 1
Electronic parameters for methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate.

Parameters	Inhibitor
HOMO [eV]	−9.726
LUMO [eV]	−4.377
ΔE = ELUMO − EHOMO [eV]	5.349
Dipole moment μ	4.113
Electron affinity A	9.726
Ionization potential (I)	4.377
Electronegativity $\chi\left[\chi=\frac{I+A}{2}\right]$	7.051
Global hardness $\left[\eta=\frac{I-A}{2}\right]$	2.674
Chemical softness $\left[S=\frac{1}{\eta}\right]$	0.373
Electrophilicity index $\left[\omega=\frac{\mu^2}{2\eta}\right]$	3.163

dipole moment with high value refer to superior corrosion inhibitor. Best on our research, the value of dipole moment of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate was 4.113 that refer to methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules have superior inhibition performance. From table 1 the μ of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules have higher value than that of water molecules and this indicating that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules have higher abilities to react physically or chemically with coupons MS surface. Hence we can conclude that, methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules may be adsorbed on the MS surface by removing of war molecules [37–39].

The hardness and softness were utilized to evaluate the activity and stability of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecules. Hardness displayed resistance against the electron polarization. Hard molecule has large energy gap while soft molecule has moderate energy gap [40]. Methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecule has global hardness equal to 2.674 and it was proved that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecule that has hardness with small value was refer to excellent inhibitor. Electron transfer need chemical softness with maximum value [41]. Methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate molecule has chemical softness equal to 0.373 eV so, it has the excellent inhibition efficiencies.

Conclusion

The inhibition effects of the studied inhibitor methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate on MS coupon surface in HCl solution have been searched using weight loss and SEM techniques. DFT have been applied to confirm the methodological findings. The weight loss results demonstrate that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate inhibit the HCl media and the inhibition efficiencies increase in parallel with rising of concentration. The inhibition performance was 91.4% that demonstrate the superior protection versus hydrochloric acid. The molecules of methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate inhibit the corrosion at MS coupon surface in HCl by adsorbing on the surface of coupon and form protective barrier through physisorption or chemisorption SEM pictures indicate that methyl 2-((3-hydroxy-4-methoxybenzylidene)amino)isonicotinate adsorbed on coupon surface and shield the surface from HCl.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2018.06.019.

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