

Experimental and theoretical studies of benzoxazines corrosion inhibitors



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ABSTRACT

2-Methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1) and 3-amino-2-methylquinazolin-4(3H)-one (BZ2) were evaluated for their corrosion inhibition properties on mild steel (MS) in hydrochloric acid solution by weight loss technique and scanning electron microscopy. Results show the inhibition efficiency values depend on the amount of nitrogen in the inhibitor, the inhibitor concentration and the inhibitor molecular weight with maximum inhibition efficiency of 89% and 65% for BZ2 and BZ1 at highest concentration of the compounds.

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Introduction

Alloys such as mild steel are widely employed in numerous industries due to their acceptable mechanical characteristics and low cost [1], assumed considerable importance due to the efficiency of these molecules to inhibit corrosion in several corrosive solutions [2]. The inhibition ability of an organic molecules depends on their efficiencies to adsorb on the surface of the metals. Inhibitive impact organic molecules are usually be based on the substituent of H₂O molecules from the metal surface and formation of barrier film of the inhibitor compound on the surface of the metal [3,4]. Organic inhibitors mainly have heteroatoms, nitrogen, oxygen, sulfur, phosphorus, that are found to have higher basicity and electron density and thus act as corrosion inhibitors. [5]. O, N, S and P are active centers for the adsorption process on surface of the metal. The inhibition performance might follow the sequence O < N < S < P [6–13]. It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves

replacement of one or more water molecules adsorbed at the metal surface [14]. The inhibitor may then combine with freshly generated Fe²⁺ ions on the steel surface, forming metal inhibitor complexes [15–20]. To extend our previous work on designing novel inhibitor molecules [21–26], the benzoxazines 2-methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1) and 3-amino-2-methylquinazolin-4(3H)-one (BZ2), were synthesized. The molecular structures of these inhibitors are determined by CHN analysis, FTIR spectroscopy, and NMR spectroscopy. The abilities of these molecules to inhibit MS corrosion in an acidic solution are determined by the weight loss method and scanning electron microscopy (SEM).

Materials and methods

Inhibitor synthesis

All chemical compounds were purchased from Sigma-Aldrich/Malaysia. FTIR were recorded on a Shimadzu FTIR-8300 spectrometer. Elemental analyses were performed using a Carlo Erba 5500 CHN elemental analyzer. Nuclear magnetic resonance were obtained using a Bruker Spectrospin instrument equipped with 300 MHz UltraShield magnets. DMSO-*d*₆ and TMS were used as the solvent and internal standard, respectively.

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BZ1 and BZ2 syntheses

The inhibitors BZ1 and BZ2 were prepared according to literature methods [27]. The benzoxazines are synthesized from commercially available anthranilic acid according to the procedure illustrated in Fig. 1. The preparation has been done through condensation reaction refluxing anthranilic acid with acetic anhydride. The molecular weight of the synthesized corrosion inhibitor (C₉H₇NO₂) is calculated at 161 g/mol and it was supported by microelemental analysis. 2-methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1), could be dissolved in many solvents such as dimethylketone, CH₂Cl₂ (dichloromethane), DMF (dimethylformamide), DMSO (dimethylsulfoxide), methyl or ethyl alcohol. Based on the Carbon-Hydrogen-nitrogen (CHN) micro-elemental analysis for 2-methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1), the experimental values of the corrosion inhibitor of carbon 66.54 (67.07%), hydrogen 4.14 (4.38%), and nitrogen 8.97 (8.69%). The second compound is 3-amino-2-methylquinazolin-4(3H)-one (BZ2) which was synthesized through a reaction of 2-methyl-4H-benzo[d][1,3]oxazin-4-one with hydrazine. The molecular weight of the synthesized corrosion inhibitor BZ2 (C₉H₉N₃O) is 175.19 g/mol which was calculated directly from the molecular formula and is supported by microelemental analysis. 3-amino-2-methylquinazolin-4(3H)-one (BZ2). This inhibitor can be dissolved in many solvents such as dimethylketone, CH₂Cl₂ (dichloromethane), DMF (dimethylformamide), DMSO (dimethylsulfoxide), and methyl or ethyl alcohol. The micro-elemental analysis of Carbon-Hydrogen-nitrogen (CHN) micro-elemental analysis for 3-amino-2-methylquinazolin-4(3H)-one (BZ2) shows that the following contents: carbon 62.12 (61.70%), hydrogen 5.11 (5.18%), and nitrogen 24.27 (23.99%).

BZ1 was obtained by refluxing anthranilic acid with acetic anhydride and was subsequently reacted with hydrazine hydrate to yield BZ2.

Corrosion tests

Mild steel specimens obtained from the Metal Samples Company were used as working electrodes throughout this study, each

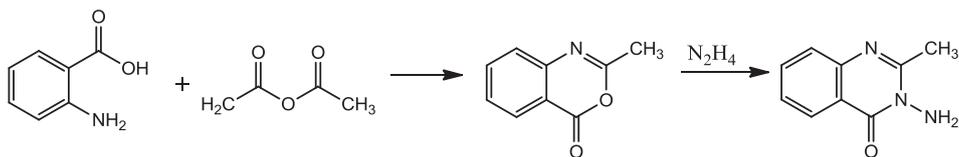


Fig. 1. Inhibitor synthesis procedure.

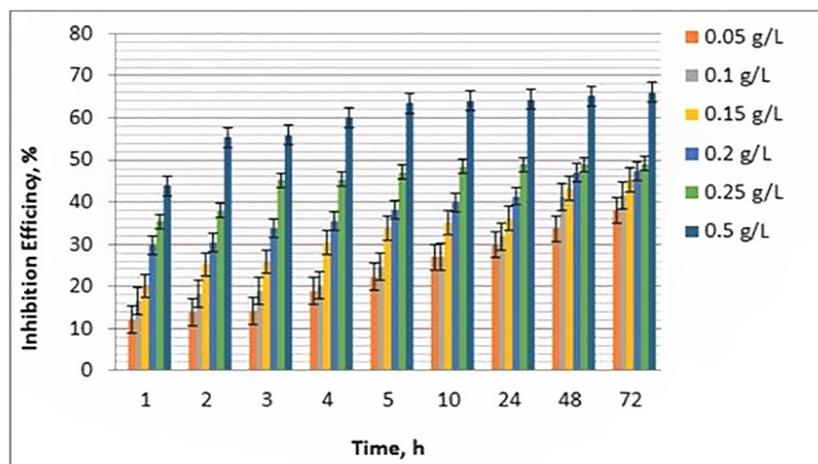


Fig. 2. BZ1 inhibition efficiency for MS as a function of time at various inhibitor concentrations and 303 K.

with an active surface area of 4.5 cm². The MS composition was 99.21% Fe, 0.21% C, 0.38% Si, 0.09% P, 0.05% S, 0.05% Mn and 0.01% Al. surface was cleaned according to ASTM G1-03 [28]. In a typical procedure, an MS sample was suspended (in duplicate) in 200 mL of a corrosive solution with or without inhibitor BZ1 or BZ2. The inhibitor concentrations studied were 0.001, 0.05, 0.10, 0.15, 0.2.0, 0.25 and 0.50 g/L. After a given amount of time 1, 2, 3, 4, 5, 10, 24, 48 or 72 h, the sample was washed, dried, and weighed. The inhibition efficiencies (IEs, %) were calculated using Eq. (1):

$$IE (\%) = \left(1 - \frac{W_2}{W_1} \right) \times 100, \quad (1)$$

where W_1 and W_2 are the weight losses of the MS specimens in the absence and presence of an inhibitor, respectively.

Results and discussion

Concentration effect

The results acquired from weight loss technique are displayed in Figs. 2 and 3, at room temperature. The corrosion efficiency increased with raising concentration of BZ1 and BZ2. The superior inhibition efficiencies reach 89% and 65% were observed for BZ2 and BZ1, respectively at optimum an inhibitor concentration of 0.5 g/L. Examination of the results demonstrate that inhibition effectiveness of the investigated molecules BZ1 and BZ2 increases with raising of concentrations. It is imputing due to increase in the efficient surface of the metal. The highest value of inhibition efficiency, was 89% was acquired at 0.5 gL⁻¹ concentration for BZ2. Further, raise in the concentrations would not give any considerable shift or variation in the inhibition efficiencies signaling that 0.5 gL⁻¹ was the optimum concentration. The inhibition efficiencies of the investigated compounds follow the order: BZ2 > BZ1. This arrangement of inhibition efficiencies would be illustrated by means of amino group moiety attached to the nitrogen of heterocyclic ring. The higher inhibition activity of the BZ2 as compared to BZ1 is impute to presence of electron releasing amino

group (in BZ2) substituents at the position of the heterocyclic ring and also presence of nitrogen atom. These electron releasing nitrogen atom and amino group in BZ2 increase the electron donating capability of BZ2 molecule toward the surface of mild steel by increasing conjugation system and the resonance owing to presence of unshared electron pairs on the nitrogen atoms and hence improve the inhibition efficiencies [29–31]. The weight loss method was used to calculate the inhibition efficiencies of 65% or 89% were achieved with BZ1 or BZ2, respectively at concentrations of 0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 g/L for time intervals of 1, 2, 3, 4, 5, 10, 24, 48 and 72 h, and temperature of 303 K for MS in corrosive media. The BZ1 and BZ2, results, which are shown in Figs. 2 and 3, respectively, indicate that these inhibitors reduced MS corrosion in corrosive media. For all the inhibitors, the inhibition efficiency increased with increasing concentration, reaching a maximum at the highest tested concentration.

Effect of temperature

The decreasing inhibition performance on raising temperature of solution may be due to increasing of the inhibitor molecules mobility that lead decreasing the interaction between inhibitor molecules and mild steel surface [29]. Also, desorption of the adsorbed molecules (BZ1 and BZ2) at higher temperature could also reduce the inhibition efficiencies [31]. Inhibition efficiencies of the BZ1 and BZ2 as investigated at concentrations between 0.05 g/L and 0.5 g/L in corrosive solutions and various tempera-

tures degrees of 303, 313, 323 and 333 K, indicate that efficiencies are decreasing with raising temperatures. Figs. 4 and 5 refer to the changing effects in temperatures degrees regarding to inhibition efficiencies of both inhibitors BZ1 and BZ2.

Arrhenius equation could be utilized to demonstrate the impact of temperatures on the inhibition efficiencies of investigated molecules, as in Eq. (2) [32].

$$\log(C_R) = \frac{-E_a}{2.303RT} + \log A \quad (2)$$

where, C_R is the corrosion rate ($\text{mg}/\text{cm}^2\cdot\text{h}$), A is the Arrhenius factor, E_a is the activation energy, whereas R is the gas constant and T is the temperature.

The activation energies for the absence and presence of the studied compounds BZ1 and BZ2 have been evaluated from Eq. (3) in Fig. 6.

$$\text{Slope} = \frac{-\Delta E_a}{2.303R} \quad (3)$$

The activation energies of the in presence of studied compounds BZ1 and BZ2 were 72.94 and 84.63 kJ/mol respectively. It can be shown from these values were higher than the blank ($29.17 \text{ kJ mol}^{-1}$) that obviously signalize that in presence of BZ1 and BZ2 molecules more energy barrier were accomplished for surface of the mild steel corrosion due to the figuration of inhibitors protective film, that lastly decreases the corrosion rate (Table 1) [33].

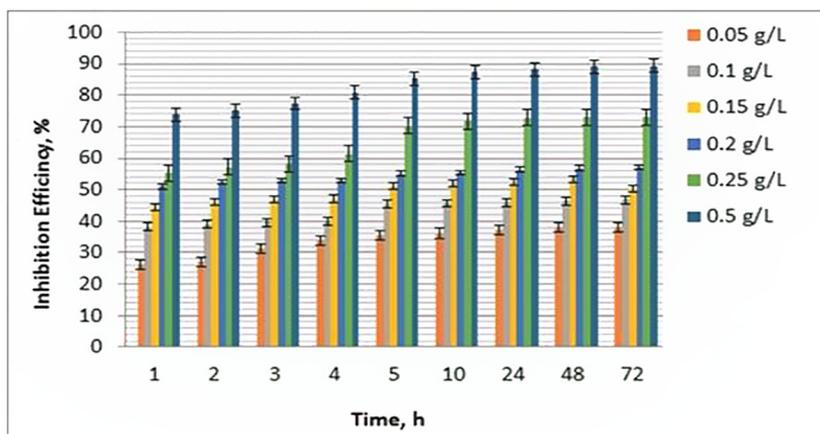


Fig. 3. BZ2 inhibition efficiency for MS as a function of time at various inhibitor concentrations and 303 K.

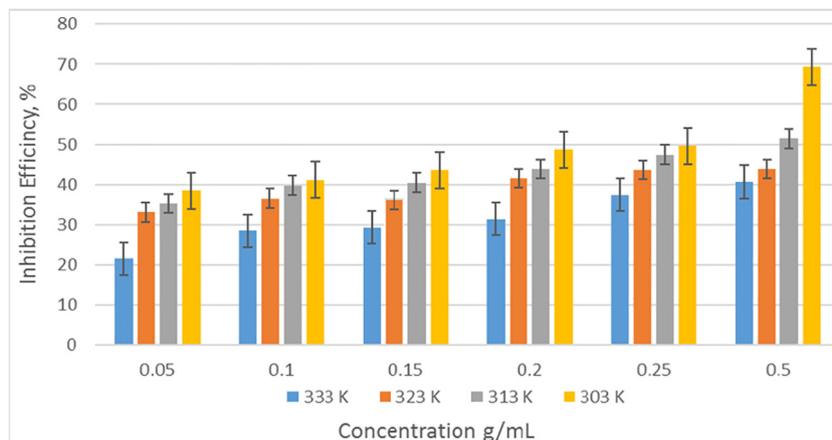


Fig. 4. Effect of temperature on inhibition efficiencies of 2-methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1).

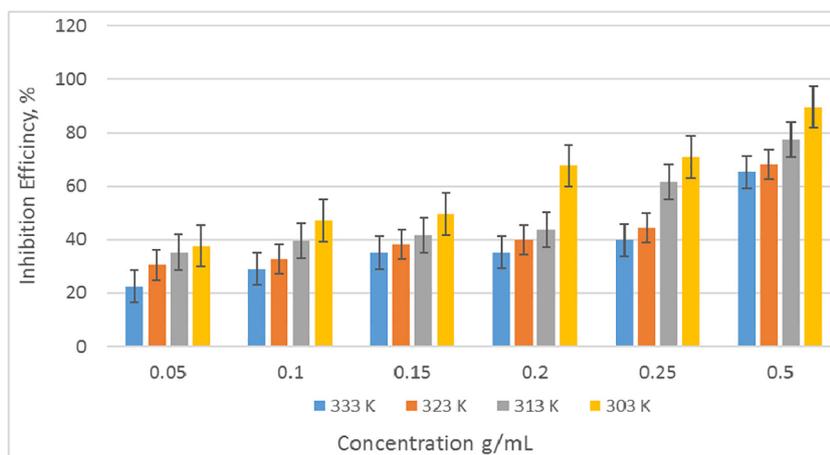


Fig. 5. Effect of temperature on inhibition efficiencies 3-amino-2-methylquinazolin-4(3H)-one (BZ2).

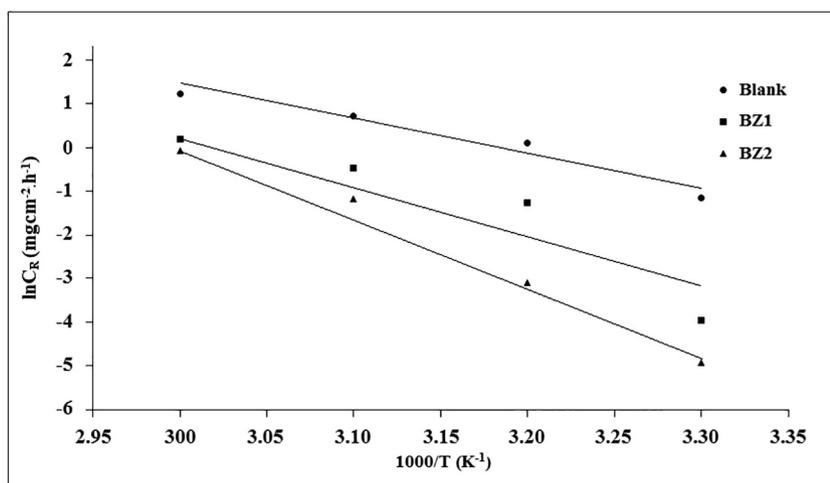


Fig. 6. Arrhenius plots for mild steel in 1 M HCl in presence and absence of the BZ1 and BZ2 as corrosion.

Table 1
The Corrosion rates (CR) ($\text{mg cm}^{-2} \text{h}^{-1}$) and Inhibition efficiencies in absence and presence of highest utilized concentration of BZ1 and BZ2 at various temperature degrees.

Comp.		Temperatures in K			
		303	313	323	333
Blank	C_R	10.84	15.13	16.22	20.24
	E%	65	51.39	42.73	37.35
BZ1	C_R	0.69	2.36	4.24	7.59
	E%	89	79.28	74.18	61.21
BZ2	C_R	0.55	1.97	3.17	6.17
	E%	89	79.28	74.18	61.21

Proposed inhibition mechanism

The mechanism of inhibition in acidic solutions are demonstrate regarding to the adsorption of molecules with organic structures onto the surface of the mild steel. The inhibition performance of the inhibitors are concerning to considerable factors including type of the metal surface, acidic solution, size of the inhibitor molecules, adsorption centers, structure of the inhibitor molecules, chemical characteristics of the of the inhibitor molecules and the nature of interactions the inhibitor molecules with the surface of the metal [34].

BZ1 or BZ2, adsorbed on MS, form a barrier and thus prevent cathodic or anodic reactions from occurring at the MS surface. These inhibitors might react with the metal atoms at the surface

to form stable, insoluble complexes, blocking the metal surface sites [35]. The efficiencies of the tested inhibitors might depend on their charge or molecular weight, the bonding nature of the metal, and its ability to form complexes. Fig. 7 shows the proposed complexes formed between the metal surface atoms and the tested inhibitors.

The inhibition mechanism of the tested inhibitors can be explained by valence bond theory (VBT). The Fe^{2+} electron configuration is $[\text{Ar}]3d^6$. The 3d orbitals mix with the unoccupied 4s and 4p orbitals to form sp^3 or d^2sp^3 hybrid orbitals that might be suitably oriented toward the nitrogen or oxygen non-bonding electron pairs in the inhibitors. When these Fe and inhibitor orbitals overlap, tetrahedral, square planar or octahedral complexes in which the metal has a filled valence shell are formed. The inhibition

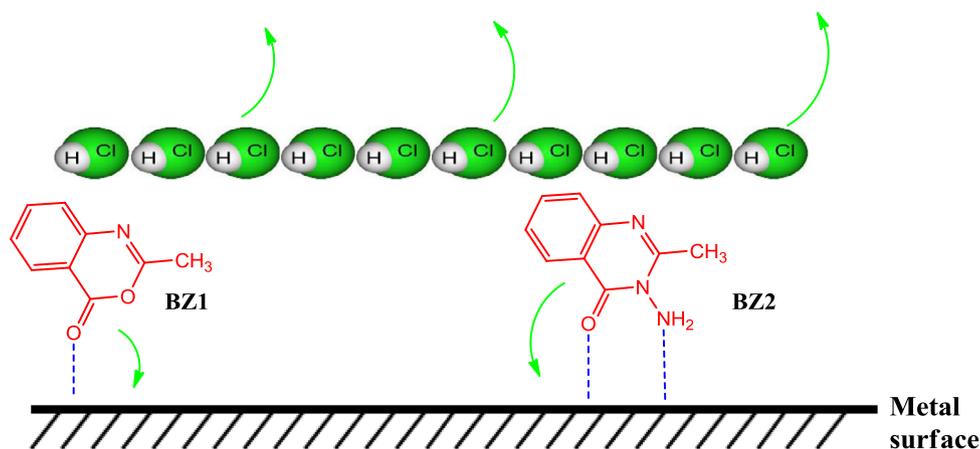


Fig. 7. Inhibition mechanism.

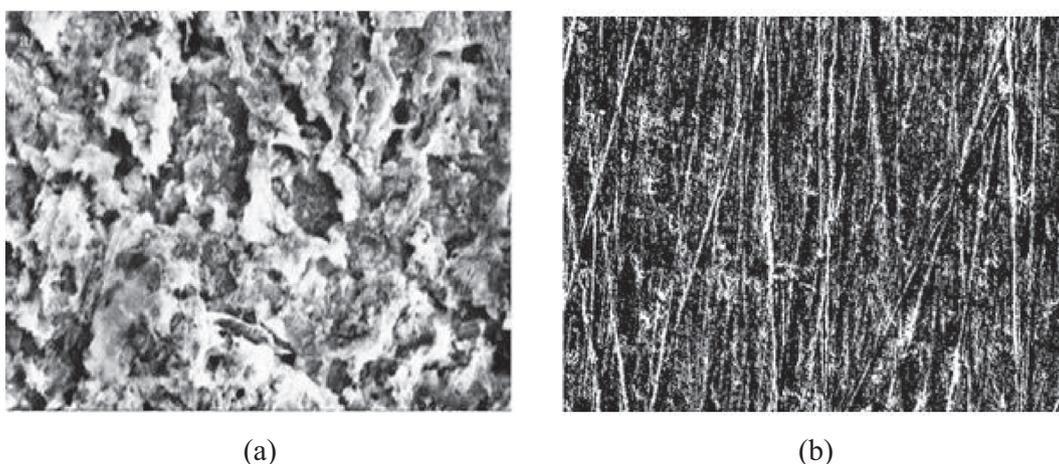


Fig. 8. SEM images of MS after immersion in a 1.0 M HCl solution (a) without and (b) with BZ2 at 30 °C.

mechanism can also be explained in terms of crystal field theory (CFT) or molecular orbital theory (MOT).

Scanning electron microscopy

Scanning electron microscopy (SEM) was a general wide utilized and excellent analytic surface technique for characterization of the surface. Generally, SEM analysis gives images for the metal surface with high resolution. The MS surface, shown in Fig. 8a, was analyzed by SEM after immersion in 1.0 M HCl without 0.5 g/L BZ1 or BZ2 for 3 h at 30 °C. The SEM images of uninhibited and inhibited mild steel surface were provided in Figs. 8a and 7b. The SEM image Fig. 8a of uninhibited surface demonstrated highly damaged and corroded area due to cracks that were attributed due to corrosive solution attack of mild steel surface. The surface appeared to be damaged due to the high iron dissolution rate in corrosive media. However, SEM image Fig. 8b of the inhibited mild steel surface were smoothed. The mild steel surface with smoothed area with corrosion inhibitor BZ2 molecules was attributed because of the adsorption on the mild steel surface. A barrier was observed on the MS surface when BZ2 was added to the solution as shown in Fig. 8b. This result shows that BZ2 adsorbed on the MS surface, protecting it from corrosion by hydrochloric acid.

Quantum chemical calculations

The studied molecules BZ1 and BZ2 varied from each other by the heteroatoms (oxygen or nitrogen) and substituted amine that

attached to the nitrogen atom of the quinazolin moiety. From the results of geometrical optimization process we may conclude that the structure of studied molecules was planar. The electronic characteristics of the molecules change due to amino group. The electronic characteristics of the BZ1 and BZ2 have been calculated employing the method DFT/B3LYP with the basis set 6-311G. HOMO and LUMO (highest occupied molecular orbital and lowest unoccupied molecular orbital) investigated for BZ1 and BZ2 as corrosion inhibitors molecules and were shown in Fig. 9. The parameters such as energy of frontier molecular electrons, energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$), dipole moment (μ) and electronegativity (χ) are demonstrated in Table 2. E_{HOMO} indicates electron donating ability of the corrosion inhibitor molecules, and in this investigation they have the order: $-9.60\text{BZ2} > -10.84\text{BZ1}$. It obviously indicates that BZ2 molecule has more electron donating susceptibility comparing with that of BZ1 [36,37]. The tendency of values of EHOMO spotted for investigated inhibitor molecules quite support the experimental results of inhibition efficiencies. The electron releasing group that was amino group in BZ1 increase the electron donating susceptibility of inhibitor molecules.

In inequality to HOMO energy, energy value of LUMO can be defined as the measure of electron affinity of the molecules [68,69]. In this investigation the values of energy of LUMO was not offer any systematic trends. In addition, ΔE is second significant parameter that describe the interaction of molecules and the surface of the metal. Generally, the lower value ΔE of inhibitor molecules are consisted with reactivity and associated with higher inhibition effectiveness comparing with inhibitors molecules that with high

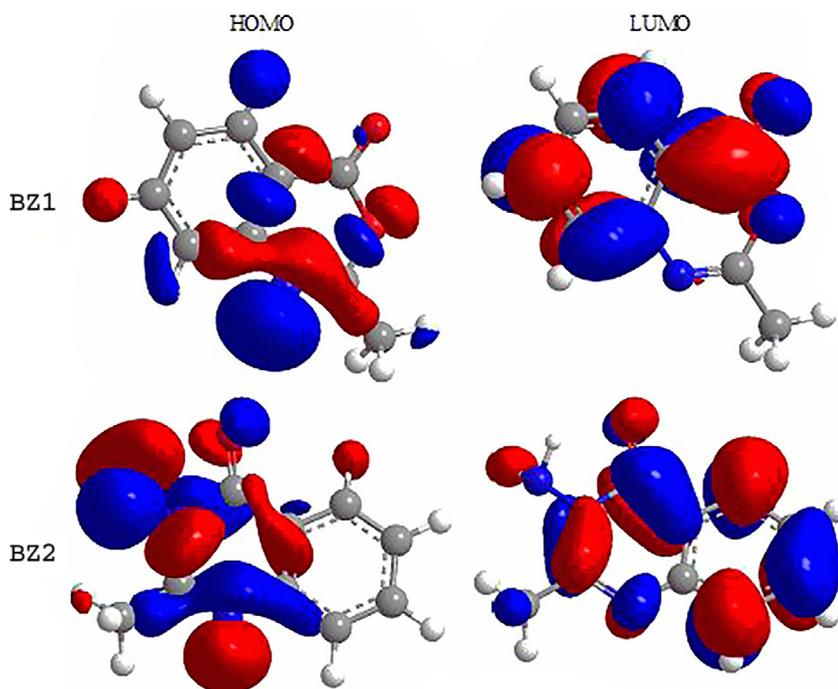


Fig. 9. Structures of the HOMO and LUMO orbitals for molecules in employing DFT methodology.

Table 2

Electronic parameters for BZ1 and BZ2 molecules employing DFT methodology.

Parameters	BZ1	BZ2
HOMO [eV]	−10.843	−9.60
LUMO [eV]	−3.905	−3.107
$\Delta E = ELUMO - EHOMO$ [eV]	6.938	6.493
Dipole moment [D]	3.83	5.69
Electron affinity (A)	10.843	9.60
Ionization potential (I)	3.905	3.107
Electronegativity χ [$\chi = \frac{I+A}{2}$]	7.374	6.3535
Global hardness [$\eta = \frac{I-A}{2}$]	3.469	3.2465
Chemical softness [$S = \frac{1}{\eta}$]	0.288	0.308

value of ΔE . The studied inhibitors BZ1 and BZ2 have small difference's of energy gap and that was of 6.493 eV and 6.938 eV respectively. The relative electron donating capability of the investigated inhibitors could be supported by the electronegativity (χ). Generally, the molecule that has the lowest χ is related with higher electron donating tendency thus displayed higher inhibition efficiency comparing with molecule with higher value of (χ). In this investigation the values of (χ) have the sort: BZ1 > BZ2, that completely support our methodology results. The dipole moment is a significant character that could be utilized to linked the proportional interaction of inhibitor molecules with the surface of the metal. In general, inhibitor molecule that has high value of dipole moment is linked with high polarizability value and good effective surface area and hence could be perfect corrosion inhibitor comparing with inhibitor with low dipole moment value. In this investigation, dipole moment values of synthesized inhibitor molecules have the order: BZ2 > BZ1, that implies BZ1 have excellent inhibition effective surface area and have excellent efficiency compare with that of BZ2. In addition, from Table 2 we can conclude that the dipole moment for BZ2 and BZ1 as investigated corrosion inhibitors have higher values from that of water and this referring that BZ2 and BZ1 have more efficiency to react (physically or chemically) with the surface of the metal. From this results we can say that BZ2 and BZ1 might adsorbed on the studied surface of mild

steel through substituent H_2O molecules [38–40]. Results of HOMO and LUMO that calculated theoretically for the studied molecules BZ1 and BZ2, it can be shown that the HOMO orbital have been created through the same active center. The LUMO orbitals for BZ1 have been shifted to the benzene. The LUMO orbitals of the BZ2 molecule was located at the skeleton of the whole molecule.

Chemical hardness and softness were the requisite chemical significance, called global or universal reactivity descriptors that were theoretically justified through the domain of DFT (density functional theory) [41]. These are the significant characteristics to evaluate the stability and reactivity of molecules. It is clear that the hardness mainly indicates the impedance towards the polarization of the electron can of the atom, ion or molecule under small disruption of chemical reaction. Hard molecules have great energy gap and soft molecules have good energy gaps [42]. In our present study BZ1 and BZ2 with hardness value 3.2465 eV and 3.2465 eV respectively and usually, the inhibitor with the minimum value of hardness was predictable to has the superior inhibition efficiency [43]. For the easy transfer of electron, adsorption may exist at the side of molecule where S, has a maximum value [44]. BZ2 and BZ1 with the softness value of 0.308 eV and 0.288 eV respectively have the maximum inhibition efficiencies.

Conclusions

MS corrosion inhibitors were synthesized and their structures were fully characterized by spectroscopic techniques. Their abilities to inhibit MS corrosion in a 1.0 M HCl solution at 303, 313, 323 and 333 K were subsequently studied. The inhibitors, namely 2-methyl-4H-benzo[d][1,3]oxazin-4-one (BZ1) and 3-amino-2-methylquinazolin-4(3H)-one (BZ2), exhibited excellent corrosion inhibition performances. The maximum inhibition efficiencies of 89% and 65% were observed for BZ2 and BZ1, respectively at an inhibitor concentration. The inhibition efficiency increased with increasing inhibitor concentration, whereas it decreased with increasing temperature. The SEM images show that BZ1 and BZ2 might form a protective film on the MS surface.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.rinp.2017.10.027>.

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