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ORIGINAL PAPER

Experimental and theoretical study of the effect of some heterocyclic compounds on the corrosion of low carbon steel in 3.5% NaCl medium

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Abstract The efficiency of three heterocyclic compounds, 3-amino-1,2,4-triazole, 4-hydroxy-2H-1-benzopyran-2-one and 4-hydroxy-3-(1H-1,2,4-triazole-3-ylazo)-2H-1-benzopyran-2-one (abbreviated 3-ATA, 4-HQ and 3-ATA-Q, respectively) as steel corrosion inhibitors in 3.5% NaCl has been investigated by Tafel extrapolation and linear polarization methods. Corrosion parameters and adsorption isotherms were determined from current-potential curves. It was found that inhibition efficiencies (η%) and surface coverage (θ) increase with an increase in the concentration of 3-ATA and 3-ATA-Q. However, 4-HQ accelerates the corrosion rate as its concentration increases. The adsorption of 3-ATA and 3-ATA-Q on the steel surface obey Langmuir isotherm. A clear correlation was found between corrosion inhibition efficiency and theoretical parameters obtained by the density functional B3LYP/6-31g(d) method. The experimental results are supported by the theoretical data.

Keywords Steel · Corrosion · Inhibitor · Heterocyclic compounds · Theoretical calculations

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1 Introduction

Nitrogen-containing organic compounds have been found to serve as good inhibitors of corrosion and their inhibiting action has been explained in terms of the number of free electron pairs, the π-orbital character of free electrons and the electron density around the nitrogen atom [1–6].

There have been various studies on corrosion of steel which draw attention to the synergistic effect of enhanced inhibition efficiencies of 3-ATA and 4-HQ when they are used together [7–9]. However, there have been no studies in the literature that investigated the origins of the uniquely high inhibition efficiency of a new compound (3-ATA-Q) formed by linking of an inhibitor compound (3-ATA) with a corrosion accelerator compound (4-HQ).

In order to evaluate compounds as corrosion inhibitors and design novel inhibitors, the relationship between the structural properties of the molecules and their inhibition effects are being explored [10, 11]. Various organic compounds have been investigated for their inhibiting behaviour and their molecular structures have been also studied by quantum chemical methods in order to elucidate the origins of their inhibition effect [12].

The first objective of this work is to investigate the effect of three heterocyclic compounds, namely 3-ATA, 3-ATA-Q and 4-HQ on the corrosion of low carbon steel in 3.5% NaCl using Tafel extrapolation and linear polarization resistance. The second objective is to investigate the dependence of inhibition efficiency of these compounds on theoretical chemical parameters such as the energies of highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}), the energy difference (ΔE) between E_{HOMO} and E_{LUMO}; net atomic charges, dipole moments (μ), interaction energies (E_{int}) and total energies.

2 Experimental

The chemical structures, names and abbreviations of the heterocyclic compounds are given in Table 1. The composition of the steel used in experiments is shown in Table 2. Steel electrodes were of 4 mm diameter and embedded in polyester. Before the experiments, the sample surfaces were abraded with 1200 grade emery paper, washed with bidistilled water and then placed into the cell.

The experiments were carried out in a combined system which consisted of Wenking LB75L potentiostat, Wenking VSG72 voltage scanning generator, Yokogawa Technicorder Type 3077 recorder, Nüve B 101 thermostat and electromagnetic stirrer. The working electrode, a reference saturated calomel electrode (SCE) (inside a Luggin's capillary probe) and platinum counter electrode were placed inside a three compartment cell. All given potentials were referred to SCE. The potential scan rate chosen was 2.5 mVs^{-1}. Electrochemical experiments were carried out at room temperature (t = 25°C). The potential was started from the corrosion potential, E_{corr}, and scanning was carried out in the cathodic direction and subsequently in the anodic direction. Each experiment was repeated three times under the same conditions.

All solutions were de-aerated in the cell by purging with pure nitrogen for 30 min prior to experiments. In order to remove traces of oxygen, nitrogen prior to being used in our experiments was thoroughly purified by passing through pyrogallol solution, vanadium chloride and hydrochloric acid, respectively. During each experiment, solutions were mixed with a magnetic stirrer. Bi-distilled water was used to prepare the solutions.

Table 2 The chemical composition (wt%) of steel used

Composition	C	Mn	P	S	Fe
Weight (%)	0.30	1.35	0.030	0.30	98.02

Theoretical calculations for the molecular parameters related to 3-ATA, 4-HQ and 3-ATA-Q were carried out using B3LYP/6-31g(d) method.

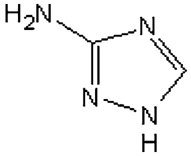
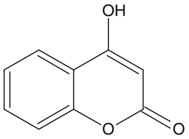
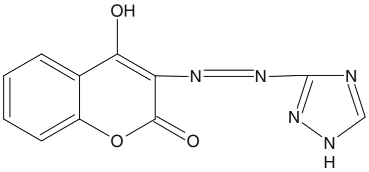
3 Results and discussion

3.1 Experimental results

Figure 1 shows the cathodic and anodic polarization curves of the steel in a blank solution of 3.5% NaCl and in the presence of different concentrations of 3-ATA (1×10^{-3} to 2×10^{-2} M).

Corrosion parameters, such as corrosion potentials, E_{corr}, anodic and cathodic Tafel slopes, β_a and β_c, corrosion current densities, i_{corr}, percentage inhibition efficiencies, $\eta\%$, and degrees of surface coverage, θ, for various concentrations of 3-ATA, 4-HQ and 3-ATA-Q in 3.5% NaCl are given in Table 3. According to the linear polarization

Table 1 The chemical structures, names and abbreviations of the compounds

Chemical structure	Name	Abbreviation
	3-amino 1,2,4 triazole	3-ATA
	4-hydroxy-2H-1-benzopyran-2-one (4-Hydroxycoumarin)	4-HQ
	4-hydroxy-3-(1H-1,2,4-triazole-3-ylazo)-2H-1-benzopyran-2-on	3-ATA-Q

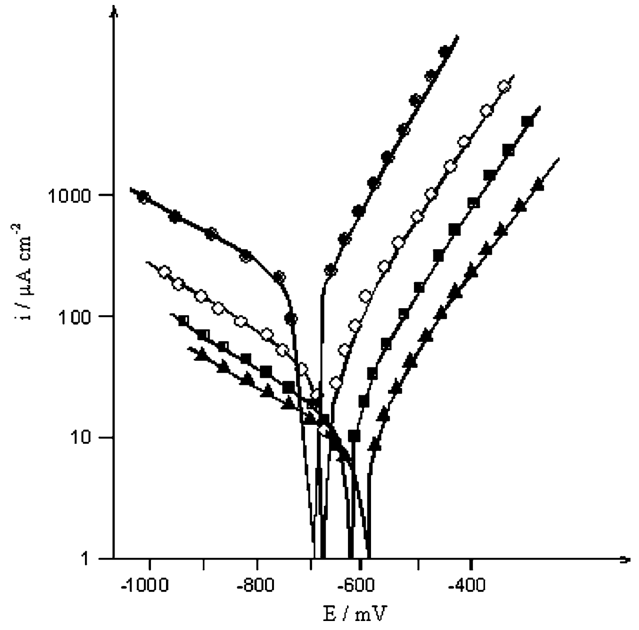


Fig. 1 The potentiodynamic polarization curves of steel for 3-ATA in 3.5% NaCl. (—●—) 3.5% NaCl, (—○—) 10^{-3} M, (—■—) 10^{-2} M, (—▲—) 2.10^{-2} M

method the same calculated parameters for these compounds are given in Table 4.

The percentage inhibition efficiency, $\eta\%$, and the degree of surface coverage, θ, were calculated from the following equations:

$$\eta\% = \frac{i_0 - i_1}{i_0} \cdot 100 \tag{1a}$$

$$\theta = \frac{i_0 - i_1}{i_0} \tag{1b}$$

where i_0 and i_1 are the corrosion current densities in the absence and the presence of the inhibitor, respectively.

In the linear polarization method, the polarization resistance, R_p, was calculated from the Stern–Geary equation [13].

$$i_{corr} = \frac{\beta_a \cdot \beta_c}{2{,}303}(\beta_a + \beta_c)\frac{1}{R_p} = \frac{B}{R_p} \tag{2}$$

According to the polarization study 3-ATA acts as a mixed type inhibitor since E_{corr} values do not change significantly in the presence of 3-ATA, whereas cathodic Tafel slopes exhibit changes. The positive shift in the values of E_{corr} indicated that 3-ATA-Q acts as anodic inhibitor. As can be seen from Tables 3 and 4, the inhibition efficiencies and the degree of surface coverage increase with increasing concentrations of 3-ATA and 3-ATA-Q. However, in the case of 4-HQ, the corrosion current densities increase with increasing concentrations.

The adsorption of inhibitor molecules from an aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase, $Org_{(aq)}$, and water molecules at the electrode surface, $H_2O_{(s)}$:

$$Org_{(aq)} + xH_2O_{(s)} \rightleftarrows Org_{(s)} + xH_2O_{(aq)} \tag{3}$$

where x is the size ratio indicating the number of water molecules displaced by one molecule of organic inhibitor.

The adsorption isotherms provide important information for determining the mechanism of organo-electrochemical reactions. The most common isotherms are those developed by Langmuir, Frumkin, Hill de Boer, Parsons, Damaskin-Parsons, Temkin, Kastening Holleck, Flory-Huggins, Dhar-Flory Huggins, Bockris-Swinkels and El-Awady et al. [14].

Table 3 Corrosion parameters obtained by Tafel extrapolation for steel in 3.5% NaCl without and with inhibitors

Inhibitor	Conc./M × 10^3	E_{corr}/mV	β_a/mV dec^{-1}	β_c/mV dec^{-1}	i_{corr}/µA cm^{-2}	η/%	Coverage/θ
3-ATA	0	−650	69	146	790	–	–
	1	−655	68	137	410	48	0.48
	5	−648	61	136	316	60	0.60
	10	−643	64	123	221	72	0.72
	15	−640	60	110	172	78	0.78
	20	−635	56	109	141	82	0.82
4-HQ	0	−650	69	146	790	–	–
	1	−640	76	158	870	−10	−0.10
	20	−655	93	167	1470	−46	−0.46
3-ATA-Q	0	−650	69	146	790	–	–
	1	−608	56	122	180	77	0.77
	5	−604	62	117	140	82	0.82
	10	−592	60	109	106	86	0.86
	15	−580	54	110	86	89	0.89
	20	−570	48	100	45	94	0.94

Table 4 Corrosion parameters obtained by linear polarization method for steel in 3.5% NaCl without and with inhibitors

Inhibitor	Conc./M × 10^3	E_{corr}/mV	i_{corr}/μA cm^{-2}	$10^{-4}R_p/\Omega$	η/%	Coverage/θ
3-ATA	0	−650	790	1.950	–	–
	1	−655	419	3.679	47	0.47
	5	−648	292	5.270	63	0.63
	10	−643	205	7.500	74	0.74
	15	−640	166	9.285	79	0.79
	20	−635	134	11.470	83	0.83
4-HQ	0	−650	790	1.950	–	0
	1	−640	877	1.741	−11	−0.11
	20	−655	1386	1.112	−43	−0.43
3-ATA-Q	0	−650	790	1.950	–	–
	1	−608	198	7.800	75	0.75
	5	−604	134	11.470	83	0.83
	10	−592	95	16.250	88	0.88
	15	−580	71	22.840	91	0.91
	20	−570	55	27.857	93	0.93

All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = KC \qquad (4)$$

where $f(\theta,x)$ is the configurational factor, which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the size ratio, a is the molecular interaction parameter, and K is the equilibrium constant of the adsorption process. The conventional form of the Langmuir adsorption isotherm is valid when $a = 0$ and $x = 1$. Starting with the conventional form of the Langmuir isotherm, that is

$$\frac{\theta}{1-\theta} = KC \qquad (5)$$

and rearranging gives:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

As can be seen from Fig. 2, the Langmuir isotherm is the best one which explains the experimental results.

3-ATA is chemisorbed at high coverage at the electrode surface via its amino group, which prevents the dissolution of iron and shows inhibition effect. Another possible explanation of the observed inhibition effect by 3-ATA is that it may act as a bidentate ligand for the compound transition metal cations forming insoluble complexes in solution, which adsorb at the steel surface and thereby inhibit corrosion. Moreover, 3-ATA-Q which is formed by the condensation of 3-ATA with 4-HQ acts as a tridentate ligand and may form insoluble complexes as in the case 3-ATA. In the structure of the steel Fe^{2+} and Mn^{2+} ions may form complexes with these ligands. In addition, the complexes formed due to the π-bonds in N=N and C=N moieties and other π-bonds in 3-ATA-Q, i.e., in the aromatic ring and in C=O, are strongly adsorbed on the steel surface and thus inhibit corrosion more than in the case of 3-ATA. On the other hand, 4-HQ is a ligand unable to form complexes. Since there is no amino group in its structure, its accelerating effect on the corrosion rate was unexpected.

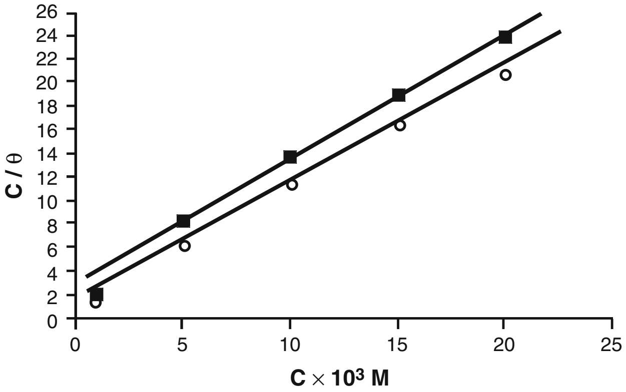


Fig. 2 Langmuir adsorption isotherm for the steel in 3.5% NaCl. (—○—) 3-ATA, (—■—) 3-ATA-Q

3.2 Theoretical calculations

The major thrust of quantum chemical research is to understand and explain the functions of these heterocyclic compounds in molecular terms. In order to support experimental data, theoretical calculations were conducted in order to provide molecular-level understanding of the observed experimental behaviour. Among quantum chemical methods for evaluation of corrosion inhibitors, DFT has shown significant promise [15] and appears to be adequate for pointing out the changes in electronic structure responsible for inhibitory action. In recent years, a hybrid version of DFT/HF methods, i.e., B3LYP has been applied successfully to model systems containing transition metal atoms [16]. Briefly, this method uses a Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) [17]. All calculations were carried on an Intel Pentium 4 2.8 GHz computer using HyperChem 7.52 package (evaluation version) [18]. The molecular structure in the most stable conformation found was optimized and the HOMO and the LUMO energies calculated employing B3LYP functional with the 6-31g(d) basis set. The optimized structures are shown in Fig. 3a, b and c.

According to the frontier molecular orbital theory, the formation of a transition state is due to an interaction between frontier orbitals (HOMO and LUMO) of reacting species [19]. Thus, the treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions. It has been proved that the higher the HOMO energy (E_{HOMO}) level of the inhibitor is, the greater is the ease of offering electrons to the unoccupied d orbital of metallic iron and the greater is the inhibition efficiency of the inhibitor for iron [20–26]. The values of E_{HOMO}, E_{LUMO}, $\Delta E_{LUMO-HOMO}$ energy gap and the dipole moment (μ) are shown in Table 5. As can be seen from this table, the E_{HOMO} of these heterocyclic compounds increased in the following order: 3-ATA-Q > 3-ATA > 4-HQ.

If an inhibitor does not only offer electrons to the unoccupied d orbital of metallic iron but can also accept the electrons in the d-orbital of metallic iron by using their antibonding orbital to form a feedback bond, then it may be considered as an excellent inhibitor. It has been proved that the lower the LUMO energy (E_{LUMO}) level is, the easier is the acceptance of electrons of the d orbital of metallic iron [20–26]. The E_{LUMO} decreased in the following order: 4-HQ < 3-ATA < 3-ATA-Q. In this study, it is experimentally shown that 4-HQ accelerates the corrosion rate. This result is also supported by the calculated quantum chemical parameters since the lowest E_{HOMO} and the highest E_{LUMO} values were found for 4-HQ.

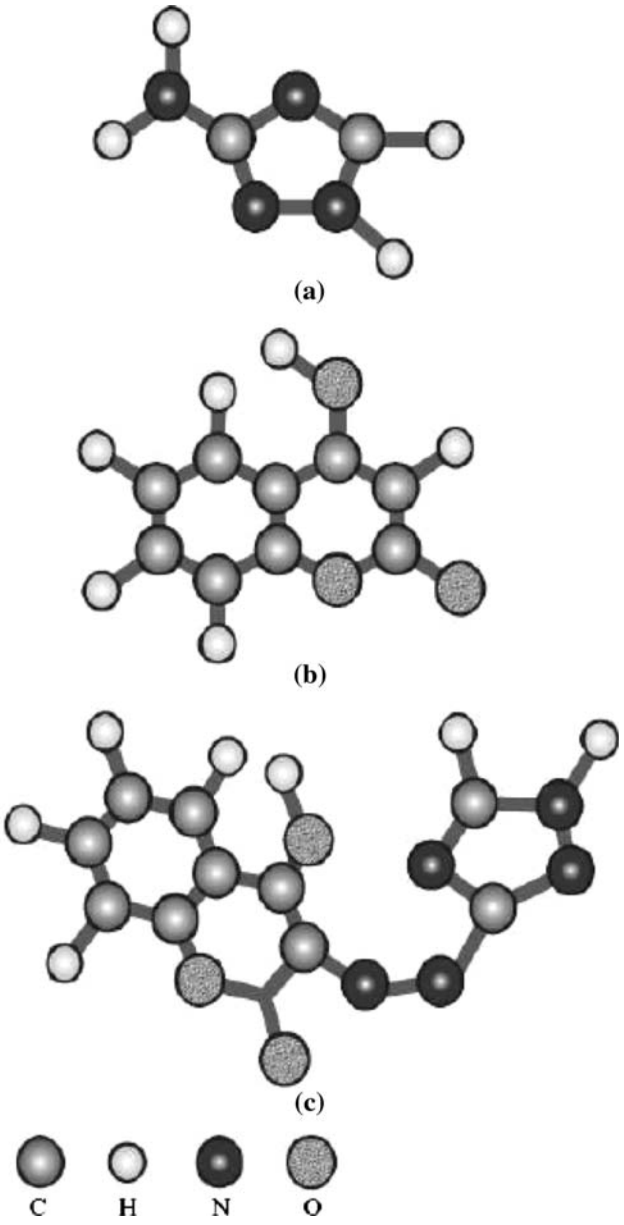


Fig. 3 Optimized structures of (**a**) 3-ATA, (**b**) 4-HQ and (**c**) 3-ATA-Q

Table 5 Calculated parameters for the compounds

Compound	E_{HOMO}/eV	E_{LUMO}/eV	$\Delta E(E_L - E_H)$/eV	μ/Debye
3-ATA	−10.265	−2.015	8.250	1.14
4-HQ	−11.239	−1.154	10.085	
3-ATA-Q	−9.034	−3.666	5.368	8.71

As can be seen from Table 5, 3-ATA-Q has the highest HOMO energy (E_{HOMO}) and the lowest LUMO energy (E_{LUMO}) among these three organic heterocyclic compounds. Therefore, 3-ATA-Q has the strongest interaction with iron and has the best inhibitory effect on corrosion of iron in this chloride solution. Another point to be considered is the HOMO–LUMO gap (ΔE), i.e., the difference between the HOMO and LUMO energies for the compounds. This is an important stability index and the concept of HOMO–LUMO energy gap is used to develop theoretical models which are qualitatively capable of explaining the structure and conformation barriers in many molecular systems. The smaller is the value of HOMO–LUMO energy gap, the more probable it is that the compound has inhibition efficiency [20–23]. 3-ATA-Q has the smaller HOMO–LUMO gap as compared to 3-ATA.

The dipole moment (μ) is another indicator of the electronic distribution in a molecule and is one of the properties used to discuss and to rationalize the structure [27]. Since 4-HQ increases the corrosion rate, the value of the dipole moment for this compound is not considered (Table 5), whereas only the values of dipole moment of the inhibitory compounds, 3-ATA and 3-ATA-Q, are calculated. The higher value of μ for 3-ATA-Q corresponds to the higher inhibition efficiency of this compound as compared with 3-ATA. Although there is a lack of agreement in the literature on the correlation between the dipole moment and inhibition efficiency [21, 28], many researchers proposed that the adsorption of polar compounds possessing high dipole moments on the metal surfaces is enhanced, which contributes to their high inhibition efficiency [27, 29]. According to our experimental and theoretical results, the inhibition efficiency of 3-ATA-Q is the highest due to strong adsorption on the metal surface and a higher value of dipole moment than in the case of 3-ATA. Consequently, our findings support the assumption that the compound with a higher value of dipole moment is expected to have higher inhibition efficiency.

The computed values of the net atomic charge for inhibitor compounds are presented in Table 6. For simplicity, only net atomic charges over the carbon (C), nitrogen (N) and oxygen (O) atoms are shown. As can be seen from Table 6, the negative charge on nitrogen atom for 3-ATA-Q is higher than for 3-ATA. Additionally, another possible adsorption center in the structure of 3-ATA-Q is the oxygen atom which has more negative atomic charge value than the nitrogen atom. The inhibition effect of inhibitor compounds is usually ascribed to adsorption of those molecules on steel surface. There can be physical adsorption (physisorption) and chemical adsorption (chemisorption) depending on the adsorption strength. Adsorption caused by van der Waals and Coulombic interactions are described as physisorption, whereas that resulted from interaction between the π-electrons of organic molecules and d-orbital of metal correspond to chemisorption. Physical adsorption inevitably precedes chemisorption. After physical adsorption inhibitor compounds are chemisorped subsequently on metal surface.

Table 6 Calculated net atomic charges of the inhibitor compounds

Compound	Atom	Net atomic charge
3-ATA	C	−0.039
	N	−0.198
3-ATA-Q	C	−0.029
	N	−0.216
	O	−0.609

Since the binding energy of the inhibitor molecule to an iron site is an important consideration [30], in order to investigate the interaction between the inhibitory compounds and the iron atom, it is appropriate to calculate the interaction energy by:

$$E_{int} = E_{(Fe-Xn)} - (E_X + E_{Fe}) \quad (7)$$

where E_{Fe} is the total energy of the iron atom and E_X is the total energy of inhibitory compound. When the adsorption occurs between the compound and the iron atom, the energy of the new system is expressed as $E_{(Fe-Xn)}$. Here, n (n = 1,...,5) is the position number of the nitrogen atoms (Fig. 4) that are the possible adsorption sites for iron on the compounds.

The data presented in Table 7 were used to compare the energetic behaviour of these two heterocyclic compounds. The values of E_{int} are all negative, which means that the adsorption can occur spontaneously. The lower the value of E_{int}, the more stable the formed complex is, and the compound has a higher inhibition efficiency [24, 31]. A comparison of the energies of the two compounds studied (Table 7) reveals that 3-ATA-Q is a better corrosion

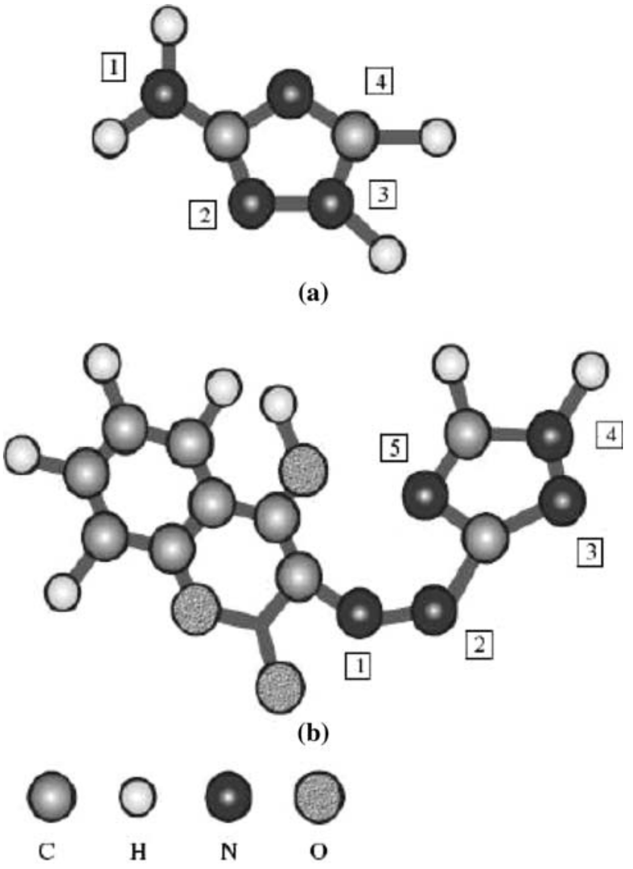


Fig. 4 Possible adsorption position numbers of nitrogen atoms with iron atom for (**a**) 3-ATA and (**b**) 3-ATA-Q

Table 7 The energetic data for 3-ATA and 3-ATA-Q

Compound	E_X/au	n	$E_{(Fe-Xn)}$/au	E_{int}/au
3-ATA	−1.589	1	−9.390	−0.313
		2	−9.084	−0.007
		3	−9.082	−0.075
		4	−9.081	−0.004
4-ATA-Q	−3.890	1	−12.187	−0.809
		2	−12.356	−0.978
		3	−11.490	−0.112
		4	−11.855	−0.477
		5	−11.588	−0.210
Fe	−7.488			

inhibitor for iron than 3-ATA, which is in excellent agreement with the experimental results.

4 Conclusions

The following conclusions can be drawn from this study:

1. Inhibition efficiency increases with increasing concentration of 3-ATA and 3-ATA-Q.
2. Corrosion current densities increase with increasing concentration of 4-HQ.
3. In determining the corrosion rates Tafel extrapolation and linear polarization methods give similar results.
4. Adsorption of 3-ATA and 3-ATA-Q on the steel surface obeys the Langmuir isotherm.
5. Calculated theoretical parameters support the relative inhibition efficiencies of 3-ATA and 3-ATA-Q.

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