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Research Article

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Theoretical approach to the corrosion inhibition efficiency of some pyrimidine derivatives using DFT method of mild steel in HCl solution

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ABSTRACT

*The inhibition effect of new heterocyclic compounds, namely N-((3,5-dimethyl-1H-pyrazol-1-)methyl)pyrimidin-2-amine(**Pyrm1**);2-((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino) pyrimidine-4,6-diol (**Pyrm2**) and 2-(((3,5-dimethyl-1H-pyrazol-1-yl)methyl)amino)-6-methylpyrimidin-4-ol(**Pyrm3**) on mild steel corrosion in 1 M HCl has been studied by weight loss measurements, potentiodynamic polarisation and Electrochemical Impedance Spectroscopy (EIS) measurements. The results indicated that the inhibition efficiency depends on concentration and molecular structure of the investigated compounds. It is also found that the inhibition of Pyrm2 is greater than Pyrm3 and Ppyrm1. The molecular structure effect on the corrosion inhibition efficiency was investigated using DFT calculations. The structural and electronic parameters were calculated and discussed. The obtained results show that the experimental studies agree well and confirm that Pyrm2 is the better inhibitor.*

Keywords: Mild steel, Pyrimidine, HCl, Quantum chemical calculations, Corrosion inhibitors

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INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. Steel has found wide applications in a broad spectrum of industries and machinery; despite its tendency to corrosion. Corrosion inhibition of steel therefore is a matter of theoretical as well as practical importance [1-8]. Using inhibitors is one of the most practical methods for protecting metals against corrosion, especially in acidic media. Among numerous inhibitors, N-heterocyclic compounds are considered to be the most effective corrosion inhibitors [9]. Up to now, various N-heterocyclic compounds are reported as good corrosion inhibitors for steel in acidic media, such as pyrazine derivatives [10, 11], triazole derivatives [12-14], pyridine derivatives [15], diamine derivatives [16-18] , pyrazole derivatives [19-23], bipyrazole derivatives [23-26], pyridazine derivatives [27-31]. In a continuation of our program, the inhibition effect of three pyrimidine derivatives (Pyrm1, Pyrm2 and Pyrm3) on the corrosion of mild steel in 1.0 M HCl solution was studied using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. The adsorption isotherm of inhibitor on steel surface is obtained. Generally, N-heterocyclic compounds exert their inhibition by adsorption on the metal surface through N heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures. Furthermore, the adsorption of inhibitor on steel/solution interface is influenced by the chemical structure of inhibitor, the nature and charged surface of metal, the distribution of charge over the whole inhibitor molecule and the type of aggressive media. Generally, N-heterocyclic compounds exert their inhibition by adsorption on the metal surface through N heteroatom, as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures [30, 32, 33]. Furthermore, the adsorption of inhibitor on steel/solution interface is influenced by the chemical structure of inhibitor, the nature and charged surface of metal, the distribution of charge over the whole inhibitor molecule and the type of aggressive media.

The aim of the present investigation was to examine the corrosion inhibition effect of new pyrimidine derivatives for mild steel in 1 M HCl.

2.2. Inhibitors

Pyrm1, Pyrm2 and Pyrm3 were prepared by according to the literature procedure by condensation of one equivalent of 3,5-dimethyl-1H-pyrazol-1-yl)methanol with one equivalent of amine derivatives in acetonitril for 4 hours. The reaction was carried out at refluxed solvent under stiring. The tested compounds were characterized by IR, ^{1}H-NMR and ^{13}C-NMR and mass spectrometry. The procedure for synthesis of compounds will be sending for publication to Research on chemical intermediates and Arabian Journal of Chemistry. Fig. 1 shows all molecular structures used.

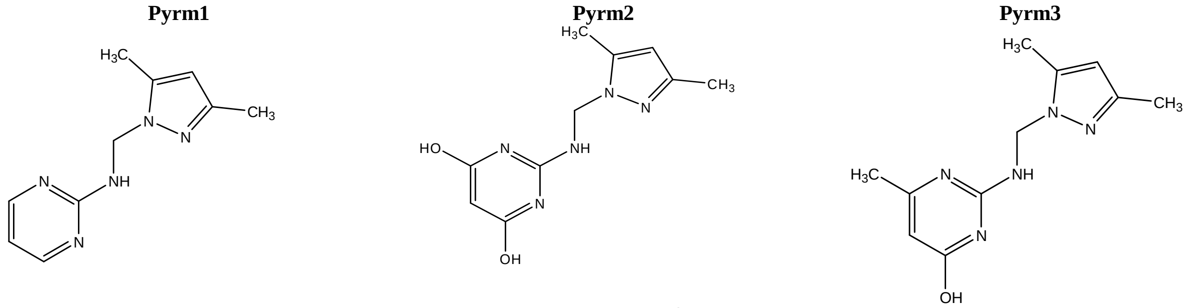


Fig.1. Chemical molecular structures of Pyrimidine derivatives

2.3. Solutions

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of inhibitors employed was 10^{-5} – 10^{3}(mol/l).

2.2. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition (0.09%P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm^3. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (**v**) is calculated using the following equation:

$$\mathbf{v = W / S}.t \tag{1}$$

where W is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (Ew) is determined as follows:

$$Ew\,\% = \frac{V0 - V}{V0}\ X\,100 \tag{2}$$

where $\mathbf{V_0}$ and **V** are the values of corrosion rate without and with inhibitor, respectively.

2.3. Electrochemical tests

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (Ep%) is defined as Equation3, where icorr(0) and icorr(inh) represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\mathrm{icor(0)} - \mathrm{icor(inh)}}{\mathrm{icor(0)}}\ \mathrm{x}\ 100 \tag{3}$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (E_R%) is estimated using the relation 4, where Rt(0) and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{Rt(inh) - Rt(0)}{Rt(inh)} x\ 100 \qquad (4)$$

2.4. Quantum chemical calculations

The quantum theoretical calculations were carried out with the Gaussian 03 program package [34-37]. The complete geometry optimization of the pyrimidine derivatives as corrosion inhibitor was carried out at DFT (Density Functional Theory) using the hybrid functional B3LYP level taking into account the exchange and the correlation with Beck's three parameters exchange functional along with Lee et al. non-local correlation functional [19,20]. All Calculations of DFT/B3LYP theory were done using 6-31G (d,p) basis set. The following quantum chemical indices were considered: the energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}), $\Delta E = E_{LUMO} - E_{HOMO}$, the dipole moment (μ) and total energy.

RESULTS AND DISCUSSION

3.1. Weight loss measurements

The weight loss method of monitoring inhibition efficiency is useful because of its simple application and reliability [21,22]. For the present study, the reproducibility of results obtained for both weight loss and percentage inhibition efficiency values for triplicate determination was very precise (±5%).

Table.1 illustrates the corrosion rate of mild steel in 1.0 M HCl at 35°C in the presence of different concentrations of pyrimidine derivatives. The corrosion rate reduces after addition of the selected three pyrimidine derivatives, and decreases with the inhibitor concentration due to the fact that the adsorption coverage increases, which shields the mild steel surface efficiently from the medium. At any given inhibitor concentration, the corrosion rate follows the order: v(Pyrm2) < v(Pyrm3) < v(Pyrm1), which indicates that Pyrm2 exhibits the best inhibitive performance among three pyrimidine compounds. E_w values of the examined pyrimidine derivatives follow the order:

Pyrm2 > Pyrm3 > Pyrm1

Table.1. Corrosion rate and inhibition efficiency in the absence and presence of Pyrimidine derivatives in 1.0 M HCl solution

Inhibitors	Concentration (M)	V ($mg.cm^{-2}\,h^{-1}$)	Ew (%)
1M HCl	-	0.82	---
Pyrm1	10^{-5}	0.41	50.00
	5.10^{-5}	0.35	57.32
	10^{-4}	0.31	62.20
	5.10^{-4}	0.23	71.95
	10^{-3}	0.14	82.93
Pyrm2	10^{-5}	0.19	76.83
	5.10^{-5}	0.15	81.71
	10^{-4}	0.11	86.59
	5.10^{-4}	0.08	90.24
	10^{-3}	0.03	96.34
Pyrm3	10^{-5}	0.29	64.63
	5.10^{-5}	0.22	73.17
	10^{-4}	0.18	78.05
	5.10^{-4}	0.13	84.15
	10^{-3}	0.1	87.80

3.1.3. Adsorption isotherm and standard adsorption free energy

Surface can be provided by adsorption isotherm. Several isotherms including Frumkin, Langmuir, Temkin isotherms are employed to fit the experimental data. It is found that the adsorption of studied inhibitors on steel surface obeys the Langmuir adsorption isotherm equation [2, 24, 35, 38, 39]:

$$\frac{C}{\theta}=\frac{1}{K}+C \qquad \textbf{(5)}$$

Where C is the concentration of inhibitor, K the adsorption equilibrium constant, and Θ is the surface coverage and expressed by the ration Ew%/100.

Plots of C/θ against c yield straight lines as shown in Fig. 2, and the corresponding linear regression parameters are listed in Table 2. Both linear correlation coefficient (r) and slope are close to 1, indicating the adsorption of three pyrimidine inhibitors on steel surface obeys Langmuir adsorption isotherm. Also, K follows the order: Pyrm2 > Pyrm3 > Pyrm1. Generally, large value of K means better inhibition performance of a given inhibitor. This is in good agreement with the values of Ew obtained fromTable.1.

The adsorption equilibrium constant (K) is related to the standard adsorption free energy (ΔG^0) as shown the following equation [32]:

$$K=\frac{1}{55.5}\exp\left(\frac{\Delta G^0}{RT}\right) \qquad \textbf{(6)}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature(K), and the value 55.5 is the concentration of water in the solution.

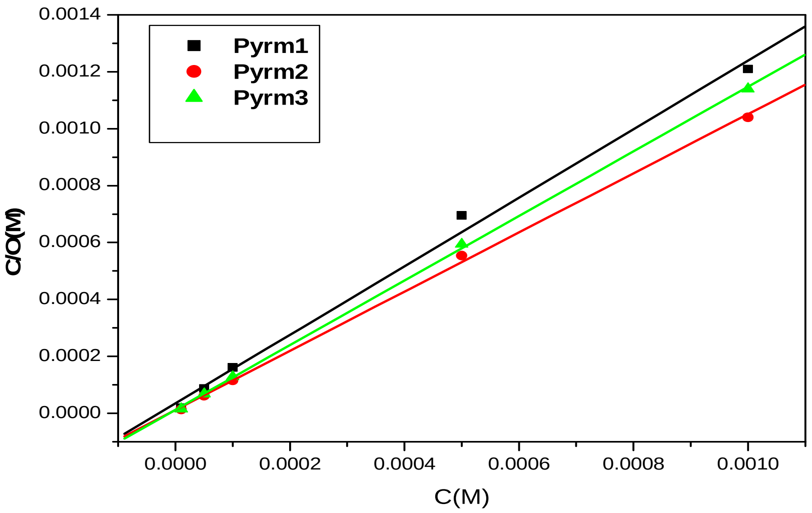


Fig.2. Langmuir isotherm adsorption of Pyrm1, Pyrm2 and Pyrm3 on the mild steel surface in 1.0 M HCl at 35°C

Table.2. Parameters of the straight lines of c/θ–c and adsorption free energy (ΔG^0) in 1.0 M HCl at 35°C (Weight loss method, immersion time is 6 h)

Inhibitors	Linear correlation coefficient (*r*)	Slope	K (M^{-1})	ΔG^0 (kJ mol^{-1})
Pyrm1	0.9975	1.20	2.87×10^4	-36.56
Pyrm2	0.9995	1.03	8.71×10^4	-39.41
Pyrm3	0.9998	1.13	8.05×10^4	-39.24

The negative values of (ΔG^0_{ads}) suggest that the Pyrimidine inhibitor was spontaneously adsorbed on mild steel–electrolyte interface. It has been reported that values of ΔG^0_{ads} up to -20 kJ/mol are consistent with the physisorption; those around -40 kJ/mol or higher are consistent with chemisorptions [27]. In the present study, the value of ΔG^0 is found to be within the range from -39.41 to -36.56 kJ mol^{-1}, probably means that the adsorption of each Pyrimidine inhibitor on the steel surface exhibits both physical adsorption and chemical adsorption.

3.1. Potentiodynamic polarization curves

Fig. 3 presents potentiodynamic polarization curves for mild steel in 1 M HCl containing different concentrations of Pyrm1; Pyrm2 and Pyrm3. It can be remarked that the cathodic branches exhibit well defined Tafel region. It is seen also that the inhibitors addition hindered the acid attack on mild steel. Indeed, an increase in their concentrations gives a decrease in current densities [40].

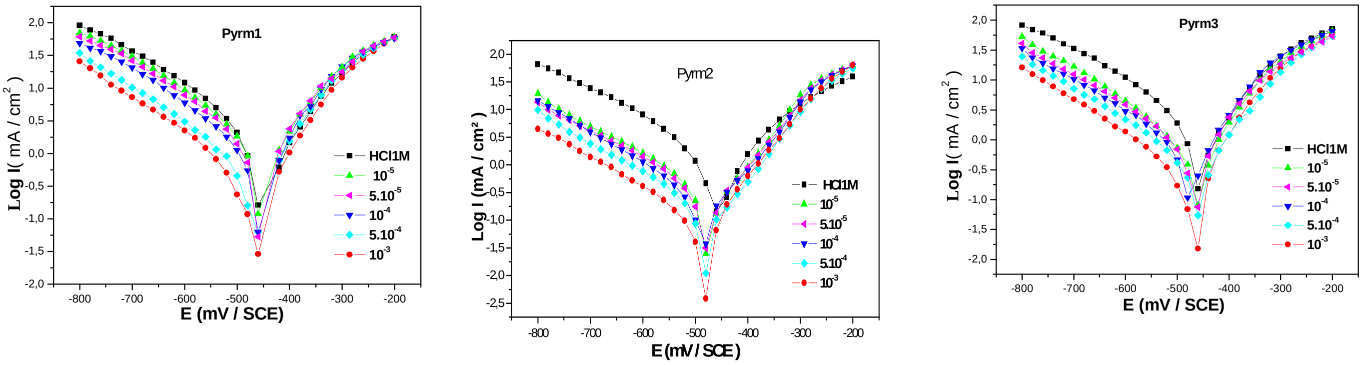


Fig.3. Potentiodynamic polarization curves of mild steel in 1 M HCl at various concentration of Pyrm1; Pyrm2 and Pyrm3

Table.3. Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of Pyrimidine derivatives at 35°C

Inhibitors	**Concentration** (M)	**-E$_{corr}$** **(mV/SCE)**	**I$_{corr}$** **(µA/cm^2)**	**-βc**	**βa**	**E** **(%)**
1M HCl	-	455	600	173	113	--
Pyrm1	**10^{-5}**	461	392	112	81	34.67
	5.10^{-5}	463	283	113	89	52.83
	10^{-4}	462	219	157	88	63.50
	5.10^{-4}	457	177	117	84	70.50
	10^{-3}	457	121	114	80	79.83
Pyrm2	**10^{-5}**	456	115	155	108	80.83
	5.10^{-5}	457	113	150	113	81.17
	10^{-4}	462	94	168	102	84.33
	5.10^{-4}	459	62	112	85	89.67
	10^{-3}	470	27	82	84	95.50
Pyrm3	**10^{-5}**	455	271	171	100	54.83
	5.10^{-5}	457	206	177	103	65.67
	10^{-4}	456	196	185	110	67.33
	5.10^{-4}	461	94	157	94	84.33
	10^{-3}	458	79	165	89	86.83

As it is shown in Fig.3 and Table 3, cathodic polarisation curves rise to parallel Tafel lines, indicating that the hydrogen evolution reaction is activation controlled. Thus, the presence of pyrimidine compounds does not affect the mechanism of this process. The addition of molecules tested causes a decrease of the current density.

The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration to attain 96% at 10^{-3} M and 87% at 10^{-3} M for Pyrm2 and Pyrm3, respectively. This result indicates that Pyrimidine derivatives act as cathodic inhibitors.

3.2. Electrochemical impedance spectroscopy

In order to confirm the results extracted from polarization curve and to acquire more information about corrosion mechanisms, EIS measurements were carried out at corrosion potential. The obtained results after immersion in 1 M HCl with and without Pyrm1, Pyrm2 or Pyrm3 at different for 1/2 h are presented in Fig.4.

The values of the polarization resistance were calculated by subtracting the high frequency intersection from the low frequency intersection [2, 33, 41]. Double layer capacitance values were obtained at maximum frequency (f_m), at which the imaginary component of the Nyquist plot is maximum, and calculated using the following equation.

$$C_{dl}=1/2\pi f_m R_t \qquad \textbf{(7)}$$

with C_{dl} Double layer capacitance (µF.cm^{-2}); f_m: maximum frequency (Hz) and R_t: charge transfer resistance (Ω.cm2). The impedance parameters derived from these investigations are listed in Table 3. From Fig.5, the obtained impedance diagrams (consist of one large capacitive loop), indicates that a charge transfer process mainly controls the corrosion of steel [2, 42-44]. The general shape of the curves is very similar for all samples; the shape is maintained throughout the whole concentration, indicating that almost no change in the corrosion mechanism occurred due to the inhibitor addition[33]. The R_t values increased with the increase of the concentration of pyrimidine compounds. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in the values of Cdl follows the order similar to that obtained for Icorr in this study. The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.

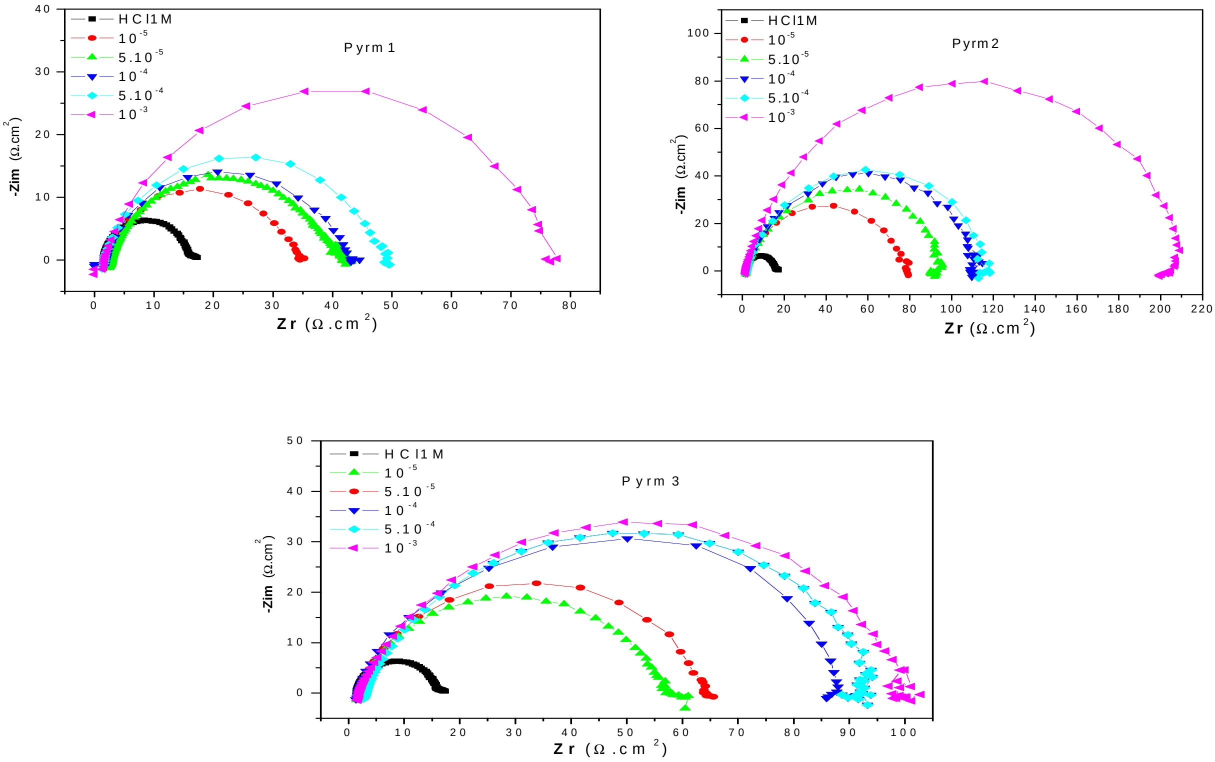


Fig.4. Nyquist plots for mild steel in 1 M HCl at various concentrations of Pyrm1; Pyrm2 and Pyrm3

Table.4. Impedance parameter values for the corrosion of mild steel in 1M HCl

Inhibitor	**Concentration** (M)	**R_t (Ω.cm^2)**	**R_b (Ω.cm^2)**	**f_{max} (Htz)**	**C_{dl} (μf/cm^2)**	**E (%)**
1M HCl	-	14.57	1.37	54.64	200	--
Pyrm1	10^{-5}	34.66	1.8	34.26	134.1	57.96
	5.10^{-5}	42.1	2.22	31.16	121.4	65.39
	10^{-4}	43.12	1.81	31.83	116	66.21
	5.10^{-4}	49.31	1.52	33.54	96.28	70.45
	10^{-3}	76.84	1.75	24.46	84.71	81.04
Pyrm2	10^{-5}	78.76	1.67	15.53	130.2	81.50
	5.10^{-5}	95.44	1.58	18.20	91.65	84.73
	10^{-4}	110	1.42	16.77	86.3	86.75
	5.10^{-4}	116.5	1.9	16.18	84.49	87.49
	10^{-3}	211.7	1.63	20.02	37.58	93.12
Pyrm3	10^{-5}	56.90	1.74	30.75	91.02	74.39
	5.10^{-5}	65.58	1.75	23.88	101.7	77.78
	10^{-4}	85.84	1.94	26.49	70.03	83.03
	5.10^{-4}	97.37	2.63	23.56	69.41	85.04
	10^{-3}	100	2.18	24.41	65.23	85.43

3.6. Quantum chemical calculations

Quantum chemical methods have already proven to be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [36, 37]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. Fig.5 shows full geometry optimization of the inhibitor molecules. The Frontier molecular orbital density distributions of all pyrimidines are presented in Fig.6.

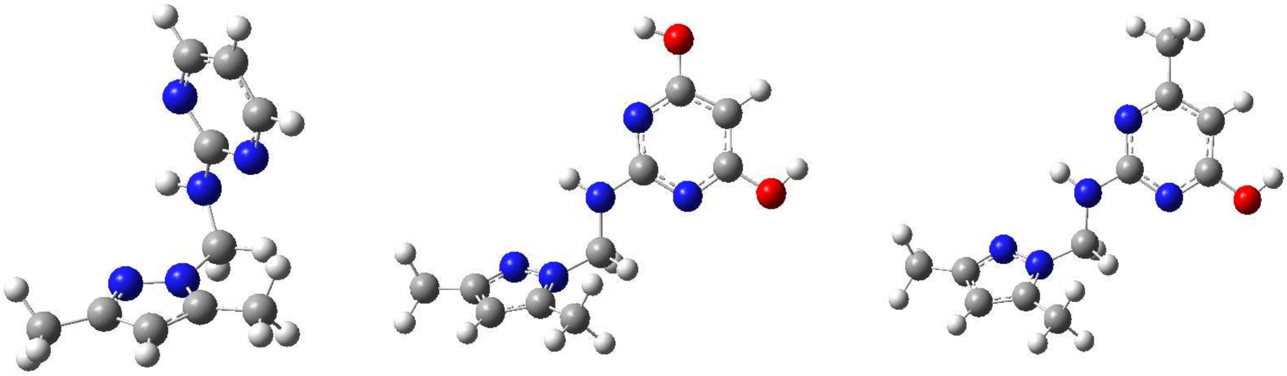
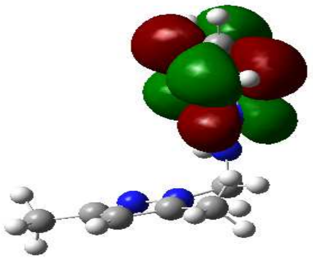
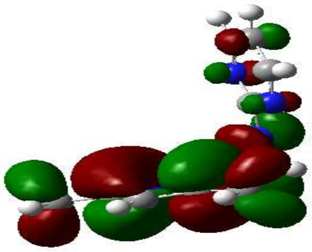
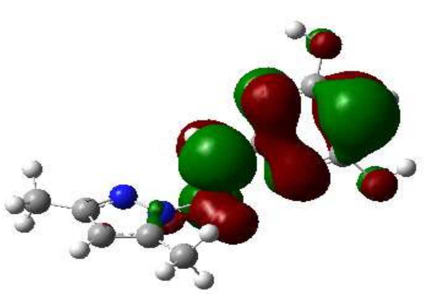
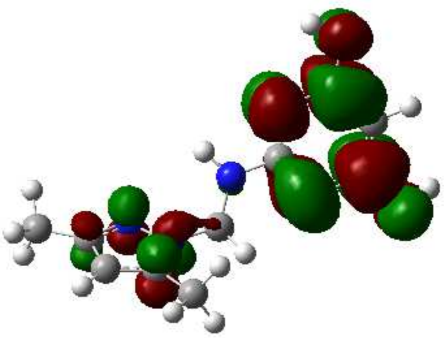


Fig.5. Optimized structures of Pyrm1, Pyrm2 and Pyrm3

The calculated quantum chemical parameters related to the inhibition efficiency of the studied molecules, such as the energies (E_{HOMO}, E_{LUMO}), the gap energy (ΔE) and the dipole moment (μ) from the inhibitor molecules to iron, are collected in Table 5. It is seen that the highest E_{HOMO} is obtained for Pyrm2, this result is not sufficient to conclude that Pyrm2 is more efficient than Pyrm3 and Pyrm1. Therefore, the high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low empty molecular orbital. Indeed, the excellent corrosion inhibitors are usually the organic compounds which not only give electrons to the unoccupied orbital of metal, but also to accept free electrons from it [2, 34, 37].

Table.5. Calculated quantum chemical parameters of the studied compounds

Quantum parameters	**Pyrm1**	**Pyrm2**	**Pyrm3**
E_{HOMO} (eV)	-0.330	-0.311	-0.312
E_{LUMO} (eV)	-0.197	-0.135	-0.160
ΔEgap (eV)	0.133	0.176	0.152
μ (debye)	2.5417	1.3422	2.4772
TE (u.a.)	0.18273211	0.05503130	0.11541051

Inhibitors	**HOMO**	**LUMO**
Pyrm1		
Pyrm2		

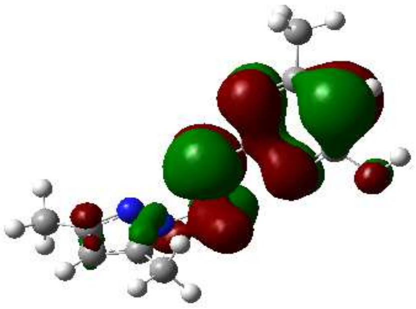
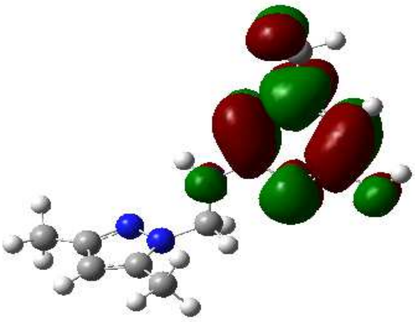
Pyrm3		

Fig.6. The frontier molecular orbital density distribution of three Pyrimidine derivatives

The dipole moment (μ) provides information on the polarity of the whole molecule. High dipole moment values are reported to facilitate adsorption by influencing the transport process through the adsorbed layer. Several authors have stated that the inhibition efficiency increases with dipole moments values. On the other hand, literature survey reveals that many irregularities appear in the correlation of dipole moments with inhibition efficiency [36, 45-47].

CONCLUSION

The inhibition efficiency of mild steel corrosion in 1 M HCl by pyrimidine derivatives has been investigated using electrochemical measurement, weight loss measurements and quantum chemical calculations. The following conclusions were drawn from this study:

1. Reasonably good agreement was observed between potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss techniques.
2. The corrosion inhibition efficiency decreased in the order of pyrimidine derivatives Pyrm2 > Pyrm3 > Pyrm1. Their corrosion inhibition efficiencies increased with increasing inhibitor concentration.
3. A good correlation was found between the quantum chemical parameter E_{HOMO} and inhibition efficiency. This can be explained by the fact that Pyrm2 compound can give and receive electrons from the metal and these processes reinforce the adsorption of Pyrm2 molecules on metallic surface.
4. Pyrimidine compounds were found to be cathodic-type inhibitors.
5. The density distributions of the frontier molecular orbital (HOMO and LUMO) show that Pyrm1, Pyrm2 and Pyrm3 adsorb through the actives centres nitrogen and π electrons of the Pyrimidine ring.
6. Both physisorption and chemisorptions seemed to contribute to the adsorptive behaviour of the inhibitor and Adsorption process obeyed Langmuir adsorption isotherm.

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