

## EXPERIMENTAL AND QUANTUM CHEMICAL CALCULATIONS ON CORROSION INHIBITION OF MILD STEEL BY TWO FURAN DERIVATIVES

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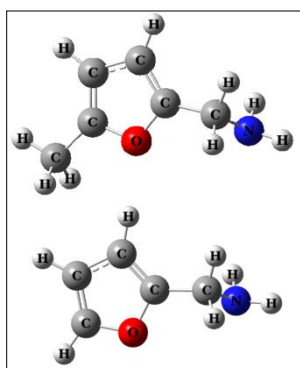
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### Graphical abstract



### Abstract

Two furan derivatives namely 5-methylfurfurylamine (MFA) and furfurylamine (FAM) were investigated as corrosion inhibitors for mild steel in 1 M HCl. The corrosion inhibition efficiencies (IE) were measured at 0.005M of the inhibitors using electrochemical potentiodynamic polarization measurements. The studied furan derivatives inhibit mild steel corrosion in acidic medium. The MFA shows higher inhibition efficiency of 84.77% compared to FAM of 41.75%. Quantum chemical calculations were performed at the B3LYP/6-311++G(d,p) level of density functional theory (DFT). Several quantum parameters were calculated to study the correlation between the molecular structures and the corrosion inhibition performance of the inhibitors. The MFA inhibitor shows higher HOMO energy, softness (S), fraction of electrons transferred ( $\Delta N$ ), and lower energy gap ( $\Delta E$ ) compared to the FAM. This result indicates a better corrosion inhibition performance of the MFA inhibitor. The results show that the calculated values of the quantum parameters using DFT calculations are consistent with the experimental findings.

Keywords: Polarization, DFT, corrosion inhibitors, acid corrosion

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## 1.0 INTRODUCTION

Metal corrosion is a serious issue because corrosion causes a waste of resources, reducing the equipment's lifetime and affecting the environment negatively [1-3]. Therefore, prevention of corrosion, or at least the reduction in the rate of corrosion, has been widely studied. Considerable effort has been given to studying iron and mild steel corrosion in acidic media [4-6]. Organic compounds with heteroatoms such as oxygen, nitrogen, sulfur and phosphorous, or compounds containing multiple bonds, are the most

reported inhibitors of metal corrosion. Organic inhibitors act by the adsorption onto the metal surface via lone pair and  $\pi$ -electrons donated by the heteroatoms and multiple bonds, forming a layer and decreasing the corrosion rate [7-9].

The corrosion inhibition efficiency of organic inhibitors is attributed to the electronic structures of inhibiting molecules, steric factor, aromaticity, electron density at the donor site, molecular area and molecular weight of the inhibitor. The higher number of lone pair and  $\pi$ -electrons increases the electron density on the molecule and causes a strong

interaction with the metal's surface [10, 11]. Furan compounds belong to heterocyclic five-membered aromatic compounds. The aromatic character of furan derivatives and the presence of oxygen atom with two pairs of free electrons in their molecules give them ability to act as efficient corrosion inhibitors [12].

Experimental and theoretical studies have been conducted to investigate the corrosion inhibition efficiency of different compound groups [13]. Experimental methods such as Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) are the most used approaches to investigate the inhibition performance of corrosion inhibitors. However, the experimental investigation of all expected inhibitors is costly and time-consuming. The use of theoretical and computational means in corrosion inhibition studies has become increasingly desirable since their use can overcome the disadvantages present when running experiments [14].

Computational methods have been applied to study, design and develop organic corrosion inhibitors [15]. Quantum chemical calculations are useful computational approaches to study the electronic parameter of the molecule using quantum chemistry [16]. Density functional theory (DFT) is a quantum chemical approach which is considered as a powerful tool with reasonable accuracy to calculate several quantum parameters of molecules. The quantum parameters are calculated to be used for theoretical investigations of corrosion inhibition properties [15, 16]. The properties of inhibitors activity involve the following parameters: geometry of the inhibitor in its ground state, the nature of the molecular orbitals, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The inhibition property of a molecule has been often correlated with HOMO energy, LUMO energy and energy gap between HOMO and LUMO [16].

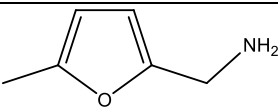
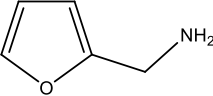
The aim of the present study is to investigate the inhibition efficiencies of two furan derivatives, i.e. 5-methylfurfurylamine (MFA) and furfurylamine (FAM), as corrosion inhibitors for mild steel in 1 M HCl. The measurements are to study the corrosion inhibition efficiency (*I<sub>E</sub>*) of the inhibitors experimentally using potentiodynamic polarization method (Tafel polarization). The study aims also to discuss the relationship between the quantum chemical calculation as a computational approach and the experimental inhibition efficiencies of the inhibitors. Several quantum chemical parameters were calculated such as the highest occupied molecular orbital energy (*E<sub>HOMO</sub>*), lowest unoccupied molecular orbital energy (*E<sub>LUMO</sub>*), the energy gap ( $\Delta E$ ), ionization potential (*I*), electron affinity (*A*), softness (*S*) and the fraction of electrons transferred ( $\Delta N$ ).

## 2.0 METHODOLOGY

### 2.1 Material Preparation and Inhibitors

The furan derivatives, MFA and FAM (Table 1), were obtained from Sigma-Aldrich and used as corrosion inhibitors of mild steel in 1 M HCl. The test solution (1 M HCl) was prepared from analytical grade hydrochloric acid (37 wt. %). The inhibited solution was 1 M HCl with the addition of 0.005M of the inhibitors. The experiments were carried out on mild steel specimens with a composition of (wt.%): 0.036 C, 0.172 Mn, 0.082 Cu, 0.108 Ni, 0.053 Cr, 0.035 Al, 0.146 Zr and Fe balance. The surface of the steel was abraded using 240, 320, 400, 600 and 1500 grades of sand paper. The specimens were well cleaned with deionized water and then again by acetone.

**Table 1** Names and structures of the furan derivatives used as corrosion inhibitors

No.	Compound	Abbreviation	Structure
1	5-Methylfurfurylamine	MFA	
2	Furfurylamine	FAM	

### 2.2 Potentiodynamic Polarization Measurements

Potentiodynamic polarization measurements were performed at room temperature ( $25 \pm 1^\circ\text{C}$ ) using 250 ml of the electrolyte (1 M HCl) with and without addition of 0.005M of the inhibitors. Before the polarization measurements, the mild steel electrode was immersed in the test solutions for 30 min to attain a steady state (stable OCP). Polarization curves were recorded at a scan rate of 10 mV/s with a scan range from  $-0.25$  and

$+0.25$  V with respect to open circuit potential (OCP). Potentiodynamic polarization measurements were carried out using Autolab Potentiostat/Galvanostat instrument. A three-electrode cell assembly that contained a 1 cm<sup>2</sup> coupon of mild steel embedded in a specimen holder was used. The mild steel specimen acted as working electrode (WE). A platinum electrode was used as a counter electrode (CE), and the reference electrode (RE) was a saturated calomel electrode (SCE).

### 2.3 Quantum Chemical Study

The geometry optimization and quantum chemical calculations of the studied inhibitors were performed at the B3LYP/6-311++G(d,p) level of DFT using Gaussian09 software. Several quantum chemical parameters were calculated such as  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ ,  $\Delta E$ ,  $I$ ,  $A$ , and  $S$ . All quantum chemical calculations were performed in a gas phase.

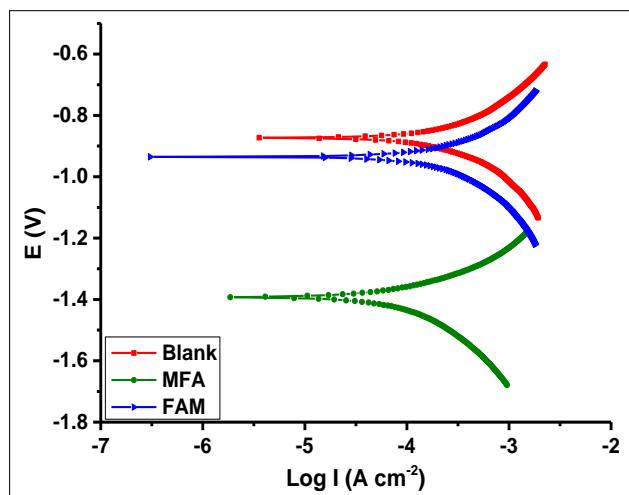
## 3.0 RESULTS AND DISCUSSION

### 3.1 Potentiodynamic Polarization Measurements

Figure 1 shows the cathodic and anodic Tafel polarization curves of mild steel in 1 M HCl without and with addition of the inhibitors. Tafel extrapolations of the anodic and cathodic lines of the polarization curves were used to determine various electrochemical parameters such as anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ), corrosion potential ( $E_{\text{corr}}$ ), and current density of corrosion ( $i_{\text{corr}}$ ). The corrosion inhibition efficiencies ( $IE$ ) were calculated using equation 1. The values of  $IE$  and the electrochemical parameters are given in Table 2.

$$IE\% = \frac{i_{\text{corr}}^{\circ} - i_{\text{corr}}}{i_{\text{corr}}^{\circ}} \times 100 \quad (1)$$

where  $i_{\text{corr}}^{\circ}$  and  $i_{\text{corr}}$  are corrosion current densities in the absence and presence of the inhibitors, respectively.



**Figure 1** Tafel polarization curves of mild steel in 1 M HCl without and with 0.005M of furan derivatives

Table 2 shows decreases in the values of corrosion current density ( $i_{\text{corr}}$ ) with the addition of the inhibitors. This result indicates that both inhibitors inhibit the corrosion of mild steel in the acidic medium. As shown in Figure 1, the addition of the inhibitors affects both the cathodic and anodic parts of the Tafel curves. The presence of the inhibitors changes the values of both

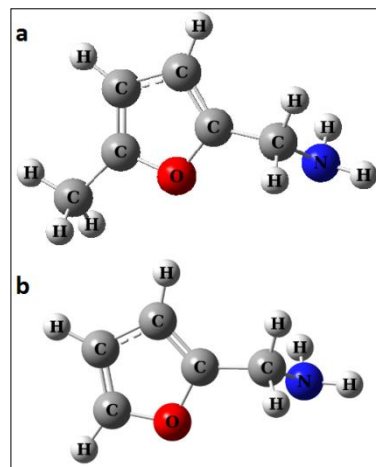
anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel slope constants (Table 2). Therefore, the presence of the inhibitors inhibits both hydrogen evolution and the anodic dissolution processes. The results indicate that the inhibitors act as mixed type corrosion inhibitors [6, 9, 17]. The MFA shows higher inhibition efficiency of 84.77% compared to FAM of 41.75%. The higher efficiency can be attributed to the substitute of hydrogen atom in furan ring by an alkyl group ( $-\text{CH}_3$ ). This group has an inductive effect (+I) which contributes to increase electron density and enhance the inhibition efficiency [10, 18].

**Table 2** Corrosion inhibition efficiency ( $IE$ ) and the electrochemical parameters obtained from Tafel polarization curves

Parameters	Blank (1 M HCl)	MFA	FAM
$b_a$ (mV dec <sup>-1</sup> )	424	138	245
$b_c$ (mV dec <sup>-1</sup> )	474	244	357
$E_{\text{corr}}$ (V)	-0.873	-1.392	-0.935
$i_{\text{corr}}$ ( $\mu\text{A cm}^{-2}$ )	655.10	99.77	381.60
$IE$ (%)	-	84.77	41.75

### 3.2 Quantum Chemical Study

The experimental corrosion inhibition efficiency of MFA of 84.77% is higher than that of FAM (41.75%). The quantum chemical calculations using DFT is to study the correlation between the quantum parameters with the experimental findings. The optimized molecular structures of the inhibitors are shown in Figure 2. The quantum chemical parameters values are listed in Table 3.



**Figure 2** The optimized molecular structures of (a) MFA and (b) FAM

The  $E_{HOMO}$  is associated with the ability of the molecule to donate electrons. Inhibitors with high  $E_{HOMO}$  value tend to donate electrons to vacant orbitals with lower energy of appropriate acceptor. The  $E_{LUMO}$  shows the capacity of the molecule to accept electrons. The lower  $E_{LUMO}$  indicates a better capacity of an inhibitor to accept electrons from the metal surface. The energy gap ( $\Delta E$ ) between HOMO and LUMO molecular orbitals is given by:  $\Delta E = E_{LUMO} - E_{HOMO}$ . The decrease in the  $\Delta E$  enhances the inhibition efficiency of the inhibitor [19].

As shown in Table 3, the  $E_{HOMO}$  values of MFA and FAM are  $-5.9798\text{eV}$  and  $-6.3110\text{eV}$ , respectively. The MFA inhibitor has the higher  $E_{HOMO}$  value, indicating its better ability to donate electrons to vacant orbitals of the acceptors. The  $E_{LUMO}$  values of MFA and FAM are  $-0.4054\text{eV}$  and  $-0.4721\text{eV}$ , respectively. The FAM inhibitor has lower  $E_{LUMO}$  value. This result indicates a better capacity of FAM to accept electrons from the mild steel surface. The consideration of  $E_{LUMO}$  only is not enough to estimate the inhibition performance of the inhibitors. The inhibition performance of an inhibitor can be estimated based on the values of several quantum parameters. The MFA shows lower  $\Delta E$  of  $5.5743\text{eV}$  than that of FAM ( $5.8388\text{eV}$ ). The higher value of  $E_{HOMO}$  and lower value of  $\Delta E$  obtained for MFA indicate its higher inhibition efficiency compared to FAM inhibitor. This result matches the experimental corrosion inhibition efficiencies.

The values of electronegativity ( $\chi$ ) and hardness ( $\eta$ ) of an inhibitor molecule are calculated as follows [20]:

$$\chi = \frac{I + A}{2} \text{ and } \eta = \frac{I - A}{2}, \text{ respectively. The softness (S) is}$$

the inverse of the hardness:  $S = \frac{1}{\eta}$ . According to

previous studies, adsorption probably occurs at the site of the molecule where  $S$  has the highest value to facilitate the transfer of the electrons [8, 21]. The MFA has higher value of softness ( $S$ ) of  $0.3587\text{eV}$  compared to FAM of  $0.3425\text{eV}$ . This result indicates that MFA is more efficient inhibitor compared to FAM [21].

The fraction of electrons transferred ( $\Delta N$ ) was calculated as follows [22]:  $\Delta N = \frac{\chi_{Fe} - \chi_{inh}}{2(\eta_{Fe} + \eta_{inh})}$  using the

values of the  $\chi$  and  $\eta$  of the inhibitor molecules and the reported theoretical values for iron,  $\chi_{Fe} = 7.09\text{eV}$  and  $\eta_{Fe} = 0\text{eV}$ . The value of  $\Delta N$  is related to the inhibition efficiency obtained by donating electrons. According to Lukovits *et al.* [23], if  $\Delta N < 3.6$ , the inhibition efficiency increases with the increase of the ability to donate electrons to a metal surface. As shown in Table 3,  $\Delta N$  values are in agreement with Lukovits' study, and MFA shows higher  $\Delta N$  value of  $0.6991\text{eV}$  compared to  $0.6334\text{eV}$  for FAM inhibitor. This result

indicates higher inhibition efficiency of MFA inhibitor [19].

Based on the above discussion, the results obtained from quantum study suggest MFA as a better corrosion inhibitor than FAM. This conclusion is consistent with the experimental results.

**Table 3** Quantum chemical parameters of the inhibitors calculated at the B3LYP/6-311++G(d,p) level of DFT

Quantum parameter	MFA	FAM
$E_{HOMO}$ (eV)	-5.9798	-6.3110
$E_{LUMO}$ (eV)	-0.4054	-0.4721
$\Delta E$ (eV)	5.5743	5.8388
$I$ (eV)	5.9798	6.3110
$A$ (eV)	0.4054	0.4721
$\chi$ (eV)	3.1926	3.3915
$\eta$ (eV)	2.7871	2.9194
$S$	0.3587	0.3425
$\Delta N$	0.6991	0.6334
IE (%)	84.77	41.75

## 4.0 CONCLUSION

Corrosion inhibition efficiencies of two furan derivatives (i.e. MFA and FAM) for mild steel in 1 M HCl were investigated experimentally using potentiodynamic polarization measurements. The MFA shows higher inhibition efficiency of 84.77% compared to 41.75% obtained for FAM inhibitor. The quantum chemical calculations at the B3LYP/6-311++G(d,p) level of DFT was applied to suggest a theoretical description for the inhibition behavior of the inhibitors. The MFA shows lower value of energy gap, and higher values of HOMO energy, softness ( $S$ ), and fraction of electrons transferred ( $\Delta N$ ). The results obtained by the quantum calculations suggest better corrosion inhibition performance of MFA compared to that of FAM. The obtained values of the quantum parameters are in agreement with the experimental results.

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