Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 9, Page 2678-2685

http://www.jmaterenvironsci.com

Evaluation of 2-thiophene carbonitrile as Corrosion Inhibitor on Mild Steel in Acidic Media

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Received 13 Jan 2017,
Revised 14 Jul 2017,
Accepted 18 Jul 2017

Keywords
- ✓ Mild Steel;
- ✓ QSAR;
- ✓ Electrochemical;
- ✓ Corrosion;
- ✓ 2-thiophene carbonitrile

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Abstract

The inhibition effect of 2-thiophene carbonitrile (2TCN) on the corrosion of mild steel in 0.5M H_2SO_4 has been predicted using quantitative structure activity relationship (QSAR) and evaluated with quantum chemical calculations, weight loss and electrochemical methods such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). QSAR model shows that the percentage inhibition efficiency %IE of this compound is 60%. Effect of concentration on the corrosion inhibition was investigated by using potentiodyanamic polarization and weight loss and the result has confirmed that the predicted compound has potential to inhibit corrosion on mild steel. Microstructure of the mild steel surface were observed using Nikon microscope which shows improvement of the surface in the presence of 2TCN.

1. Introduction

Organic compounds containing heteroatoms are used as corrosion inhibitors to protected metal surface from being attacked by the aggressive media[1,2]. They usually act by adsorption on to the metal surface through the hetero atoms such as nitrogen, oxygen, phosphorous and sulphur, triple bonds or aromatic rings [3-5]. Therefore sulphur containing heteroatom compounds are found to be effective corrosion inhibitors because they offer strong affinity to prevent corrosion of metal in acidic solution [6,7]. In this study the corrosion inhibition efficiency of 2-thiophene carbonitrile on mild steel in 0.5M H_2SO_4 was predicted using QSAR model and supported by quantum chemical calculation to evaluate the model performance based on conventional method by quantum chemical descriptors. Finally the predictive model was validated using experimental results.

2. Computational Methods

2.1. QSAR

QSAR model was built by generating 2D structure and converted to 3D structure using ChemDraw. The descriptors were generated using Dragon software and the generated descriptors were uploaded into Matlab 7.9 as described elsewhere [8]

2.2. Quantum Chemical Calculation

Quantum chemical calculation was performed using density functional theory (DFT). The geometry optimisation of 2-thiophene carbonitrile were carried out using DFT at hybrid Beeck – three parameter and Lee –Yang- Parr (B3LYP) with the basis set 6-311G++(d,p) by using Gauss View 05 [9,10] and Guassian09 program package [11]. The optimized geometry was used to calculate the IR frequencies to check the stability of the studied compound. Besides, the cation and anion forms were also calculated to find the ionization

potential (IP) and electron affinity (EA). Some of the quantum chemical parameters such as E_{HUMO}, E_{LUMO}, Energy gap (E_{gap}), hardness (η), softness (S), dipole moment (μ), electronegativity (X), electron affinity (A), ionization energy (I) and total energy (TE) were calculated. The structure of 2TCN is presented in Figure 1**.**

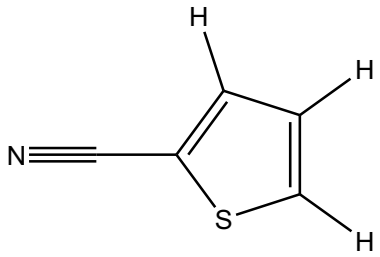

Figure 1: Molecular structure of thiophenecarbonitrile

2.3. *Experimental procedure*

2.3.1 Materials

The compositions of mild steel used in this study were obtained from Glow discharge spectroscopy

2.3.2 Solutions

The solutions of 0.5M H_2SO_4 was prepared by diluting 28 ml of H_2SO_4 with distilled water in a 1000ml volumetric flask. The stock solution of 2-thiophene carbonitrile was prepared by diluting 10^{-2}-10^{-6} M of TCN in 250 ml volumetric flask with 0.5M H_2SO_4respectively.

2.3.3 Weight Loss

Mild steel coupons of dimension (2cm x 2cm x 2cm) were cut and polished with abrasive paper of grade 240-1200 rinsed with methanol and dried in acetone and warm air. One side surface of the metal was covered with cello tape neglecting the thickness of the metal. The metal was weighed before immersion in to the test solution; mild steel coupons were immersed into 250ml beaker containing 200 ml of test solution with and without inhibitor and retrieved for 1hr interval at 30 ^{o}C and reweighed. The percentage inhibition efficiency %IE of the inhibitor was calculated by using equation (1).

$$\%IE = \frac{W_{un}-W_{in}}{W_{un}} \times 100 \quad (1)$$

$W_{un}$and W_{in} are the weight without and with inhibitor respectively and %IE is the inhibition efficiency percentage

Similarly the corrosion rate (CR) can be obtained theoretically from equation 2.

$$CR = \frac{\Delta m}{AT} \quad (2)$$

Where Δm is the Weight loss, A is the total surface area (cm^2) and T is the time of exposure in (hrs).The surface degree of coverage can be obtained from equation 3.

$$\Theta = \frac{W_{un}-W_{in}}{W_{un}} \quad (3)$$

2.3.4. Electrochemical Measurements

2.3.4.1Potentiodynamic polarization

Experimental apparatus used for electrochemical measurements were Autolab PGSTAT (30) model, monitored by PC computer and Princeton Applied Research (VersaSTAT 3.50). Three electrodes were assembled containing metal coupons of 2cm x 2cm x 2cm which is embedded in specimen holder as working electrode (WE). A large platinum mesh as counter electrode (CE) and a saturated calomel as reference electrode (RE) due to design of the electrochemical used [12].All electrochemical experiment was conducted at 30 °C using 250ml electrolyte (0.5M H_2SO_4 and 10^{-2}-10^{-6}M of TCN solution respectively) in a stationary condition. Before each potentiodynamic polarization (Tafel) experiment the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as function of time up to 15min. After this time a steady state OCP corresponding to the corrosion potential (E_{corr}) of the working electrode. The Tafel measurement was started from cathodic to the anodic direction E_{corr} = ±250 mVs^{-1} with scan rate of 5 mVs^{-1} which was carried out for all the inhibitor solution respectively. The inhibition efficiency was obtained from the relationship of current density of the metal with and without inhibitor given by equation 4.

$$\%IE = \frac{I_o - I}{I_o} \times 100 \quad (4)$$

Where I_o and I are the current density without and with inhibitor respectively.

2.3.4.2Electrochemical impedance spectroscopy

The Electrochemical impedance spectroscopy (EIS) measurements was carried out using electrochemical system (VersaSTAT 3.50) model as explained by [13, 14] . E_{corr} was obtained after immersion in solution without bubbling. Steady state current was obtained at potential sine wave voltage of 10mv peak to peak at a given frequency between 100 kHz-10 MHz, which are superimposed on the remaining potential**.** The measurements were performed in 30s at 303k for the remaining potential which was carried out at open circuit (OPC) which were control using Gemry automatic computer program and the impedance data were analyzed using ZSimpWimp3.10 . The impendence Nyquist diagrams are presented in Figure 2. The experiments were repeated three times in order to get good reproducibility. The inhibition efficiency was evaluated using equation 5:

$$\%IE = \frac{R_{ct} - R_{oct}}{R_{ct}} \times 100 \quad (5)$$

Where R_{ct} and R_{oct} are the charge transfer resistance in the presence and absence of 2TCN respectively.

2.3.4.3 Surface Analysis

Mild steel sample of dimension 2cm x 2cm x 2cm was prepared as described earlier. After immersion the sample in 0.5M H_2SO_4 solution in the absence and presence of 0.01 M 2TCN at 30^oC in 1hr, the sample was retrieved and clean with distilled water, dried with warm air and examine with Microscope Nikon FxL.

3. Results and discussion

Molecular descriptors generated from Dragon software were used to build the QSAR model for corrosion inhibition prediction of 2TCN. The molecular descriptors performance was evaluated as presented in Table 1. From the calculated descriptors the positive values signifying positive contribution while the negative values represent less contribution of the descriptor. Therefore, both the descriptors presented in Table 1 as MATS4M and SpMax3_Bh3 (m) gives positive contribution to the model. The MATS4M descriptor is responsible for the information on the effect of branching, non-linearity and polarization whichindicates a tendency to donate electron to the metal atom by the inhibitor molecular 2TCNwith value of 1.329, while SpMax3_Bh3 (m) relates the size of the inhibitor atom and has higher positive value of 2.682 which make 2TCN to donate electron to the metal atom significantly and protect corrosion of mild steel. Hence this descriptor gives highest contribution in the model.

Table 1: Calculated Molecular Descriptors

Compound Name	MATS4M	SpMax3_Bh_3(m)
2-thiophene carbonitrile	1.329	2.682

The generated model is presented in equationn 6

$$\%IE = 135.541 + [-9.881(MATS4M) + [57.272\ (SPMax3\_Bh(m)] \quad (6)$$

$R^2 = 0.9295$, $R^2_{cv} = 0.8481$, $R^2_{pred} = 0.5144$

From the model %IE of 2TCN predicted is found to be 64.2%

3.1. **Quantum Chemical Calculations**

Quantum chemical calculation was carried out in order to investigate the effect of molecular structure on corrosion inhibition behaviour of 2- thiophenecarbonitrile with quantum chemical descriptors to support the model results. Table 2 and 3 shows the calculated quantum chemical descriptors at the level of B3LYP/6311G++(d,p) of the frontier molecular orbital such as highest occupied molecular orbital (E_{HOMO}), low unoccupied molecular orbital (E_{LUMO}), energy gap $\Delta E_{gap} = E_{LUMO}$-$E_{HOMO}$, dipole moment (μ), electronegativity (X), electron affinity (A), softness (S), ionization energy (I), hardness (η), and total energy (TE). The optimized structure of 2TCN is presented in Figure 2.

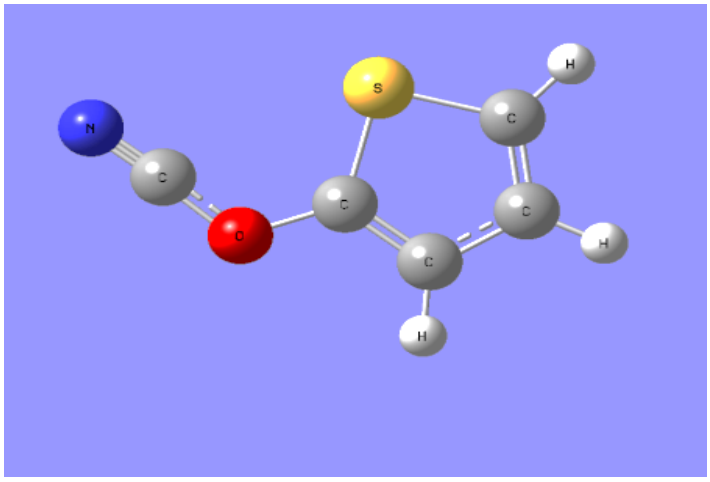

Figure 2: Optimized structure of 2-thiophene carbonitrile

Higher energy level of HUMO represents higher release of electron to the empty d-orbitals of the metal atom hence less value of ionization energy[15] . Energy gap (ΔE_{gap}) describes the molecular stability, higher energy gap indicates higher stability and the lower ΔE_{gap} the better the polarization of the molecule and the greater the adsorption on to the metal surface [16]. The higher energy of HUMO; lower energy of LUMO, ΔE_{gap}, and dipole moment (μ); the better the release of the electron and easier adsorbed on to metal surface which gives good inhibition efficiency as presented in Table 2

Table 2: Quantum chemical descriptors calculated using B3LYP/6-311G++(d,p)

E_{HUMO} (au)	E_{LUMO} (au)	ΔE_{gab}(au)	μ (debye)	%IE
-0.267	-0.108	0.159	4.608	60

Quantum chemical descriptors such as electron affinity (A), ionization energy(I), softness (S) and Hardness (η) were obtained from Kopman's theory [10] as A= - HUMO, I= -LUMO, $\eta = \frac{I-A}{2}$, $S = \frac{2}{I-A} = \frac{1}{\eta}$. From the results presented in Table 3, electronegativity (X), electron affinity (A), ionization energy (I), softness (S) and hardness (η) and total energy (TE) were calculated as 0.242, 0.213,4.73, 0268, 0.108 and -.666.4au respectively. Therefore it has been established that higher of (X) and lower value (η) with higher value of (S) the better the inhibitor to release electron to the metal surface and lead to higher reactivity of the molecule with better corrosion inhibition efficiency. In addition higher value of (I) and (A) the better the tendency of the inhibitor to donate and accept electron by the inhibitor to the metal atoms.

Table 3: Quantum chemical descriptors calculated using B3LYP/6-311G++(d,p)

X (au)|	A (au)	I(au)	η(au)	S(au)	TE (au)
0.242	0.108	0.268	0.213	4.703	-666.4

3.2. Weightloss

The inhibition performance of different concentration of 2TCN on mild steel in 0.5M H_2SO_4 have been investigated by weight loss measurement at 30°C in 1hr. Table 4 presented the results of weight loss, surface coverage and percentage inhibition efficiency (%IE). From the results corrosion inhibition efficiency of 2TCN increases with increase in concentration due to increase in surface coverage which gives chance to the inhibitor to form a layer on the metal surface as presented in Table3.

Table 4: Weight loss measurement

C(M)	ΔW g	CR g/cm^{2}h	Θ	%IE
0.5	0.011	2.75x 10^{-2}	-	-
10^{-2}	0.0020	5.0x 10^{-4}	0.98	98
10^{-3}	0.0023	5.75x 10^{-4}	0.79	79
10^{-4}	0.0024	6.0x 10^{-4}	0.78	78
10^{-5}	0.0028	7.05x 10^{-4}	0.60	60

3.3. Potentiodynamic polarization

Cathodic and anodic polarizations scan was carried out at 30^{o}C in 0.5M H_2SO_4 with 0.01M concentration of different 2TCN. The polarization curve from tafel plot in the absence and presence of 0.01M 2TCN is presented in Figure 3.Corrosion parameters obtained from Figure 3 such as corrosion potential (E_{corr}), corrosion current density(I_{corr}), anodic Tafel slope (ba) and cathodicTafel slope (bc) and percentage corrosion inhibition efficiency (%IE) are presented in Table 5.

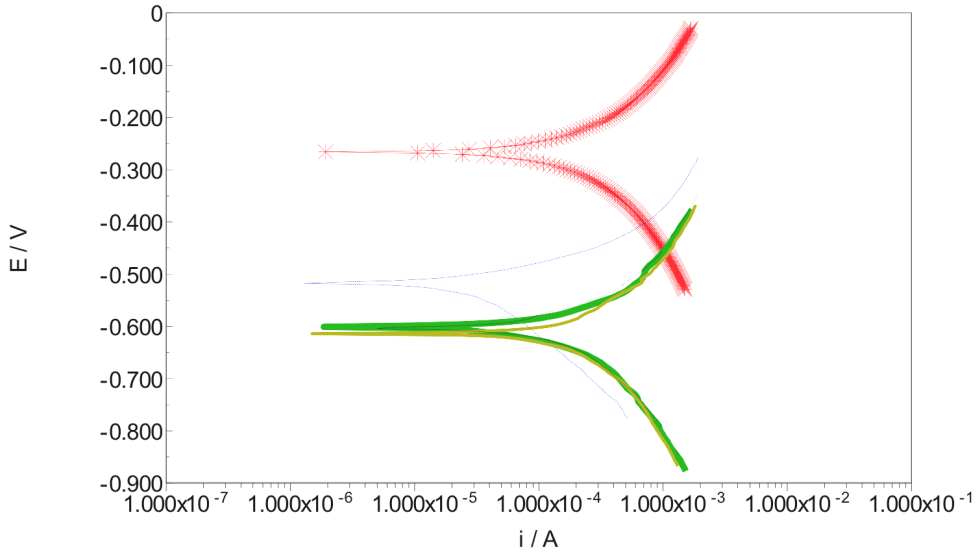

Figure 3: PDP curves for mild steel in the presence and absence of (1) Blank, (2) 10^{-2}M 2TCN, (3) 10^{-3}M 2TCN, (4) 10^{-4}M 2TCN, (5) 10^{-5}M 2TCN

Table 5: Polarization data of mild steel in 0.5MH_2S0_4 with and without addition of inhibitor at 303k for 2-thiophene carbonitrile

Compound	C(M)	E_{corr} (mAcm^{-2})	-ba (mVdec)	-bc/mVdec.	C.R (mm/year)	I_{corr}(μA/cm^2)	%IE
Blank	0.5	-0.453	0.427	0.443	9.098	783.3	-
TCN	10^{-2}	-0.253	0.060	0.113	2.71	190.0	76
	10^{-3}	-0.600	0.147	0.296	2.58	222.3	72
	10^{-4}	-0.620	0.253	0.270	3.49	300.1	62
	10^{-5}	-0.614	0.235	0.603	5.08	436.3	44

c b a

The %IE was calculated from the relationship in equation 5. From the result in Table 5 the corrosion current density (I_{corr}) decreases with addition of 2TCN as corrosion inhibitor which shows lower I_{corr}then the solution without inhibitor. From figure 3 the inhibitory effect of 2TCN is clearly explained by the tafel plot the site change of cathodic and anodic plot shows a kind of reduction in both side which shows the presence of inhibitor that behave as mixed inhibitor. This is behaviour is due to addition of 2TCN which decreases the current density of both cathodic and anadic hence move the corrosion potential towards negative values wich act on metal dissolution reaction . Therefore inhibition efficiency (%IE) increases with the increases in concentration of 2TCN as 76 % in 0.01M.

The corrosion inhibition performance of 2TCN was also evaluated using EIS at 30^{o}C for 0.01M concentration of the inhibitor in 0.5MH_2S0_4. The equivalent circuit used to fit the impedance data is shown in Figure 4. The results are presented in Table 6. The resistance charge transfer (Rct) was found to decrease with increase in capacitance double (C_{dl}) which resulted in decrease in dielectric constant with increase in double layer thickness, this probably due to the action of the inhibitor which is adsorbed on to the metal surface to form a double layer as shown in equation 7 and 8 [17]. The Nyquist diagram for 2TCN is shown in Figure 5. From the impedance diagram it can be noticed that the semicircle is complete hence charge transfer process is controlling the corrosion of mild steel. The above explanation can also be supported by Bode plots in Figure 6.

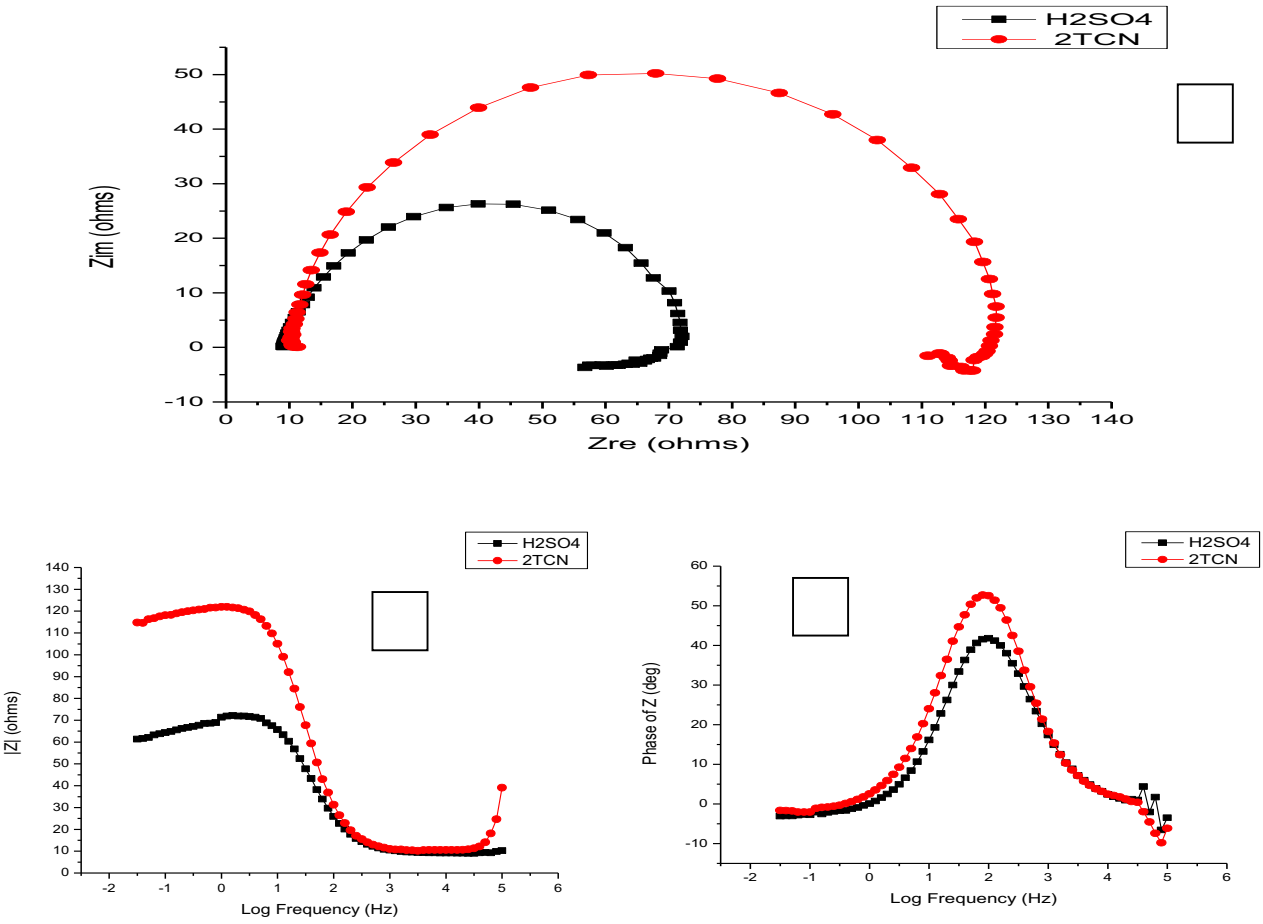

Figure 5: Nyquist plot (a) and Bode plots (b) and (c) for mild steel in 0.5M H_2SO_4solution in the absence and the presence of 2TCN

It can be observed that there is no significant difference between the shape of the impedance plot with and without inhibitor. This confirmed that the presence of inhibitor (2TCN) which increases the charge transfer and double layer impedance due to the formation of protective layer on the metals surface without changing the mechanism of the corrosion. This is in agreement with the result from potentiodynamic polarization. The %IE was calculated usingequation 7:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (7)$$

Helmholtz model in (equ (8)) relate the C_{dl}value in terms of double layer thickness

$$C_{dl} = \frac{\varepsilon\varepsilon_o A}{d} \quad (8)$$

ε is the dielectric constant of the medium, $\varepsilon_o$the vacuum permittivity, A is the expose area of the electrode and d is the thickness of the layer formed to protect the metal.

Table 6: Electrochemical impedance parameters for corrosion inhibition of mild steel in 0.5M H_2SO

C(M)	$R_{s\ \Omega cm^2}$	$R^o_{ct\ \Omega cm^2}$	CdlμF/cm^2	%IE
0.5	5.04	11.4	755	-
10^{-2}	15.4.	103.5	650.2	89

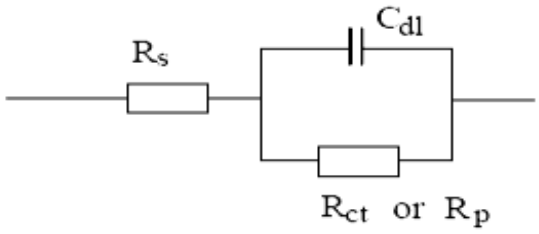

Figure 6: Equivalent circuit used to check the impedance spectra

Surface Analysis

The surface morphology and microstructure of the mild steel in the absence and presence of 2TCN were obtained using Nikon model microscopes. The mild steel surface was immersed in 0.5M H_2SO_4 solution in the absence and presence of 0.01M 2TCN as shown in figure 6(a,b). Figure 6a shows the surface of the metal was strongly damage due to the nature of acid attack in the absence of inhibitor. The image in Figure 6b shows more smooth surface of the mild steel which has less damaged compared to Figure 6a which indicated that the metal adsorbed 2TCN which act as inhibitive layer and reduce the corrosion on to the metal surface**.**

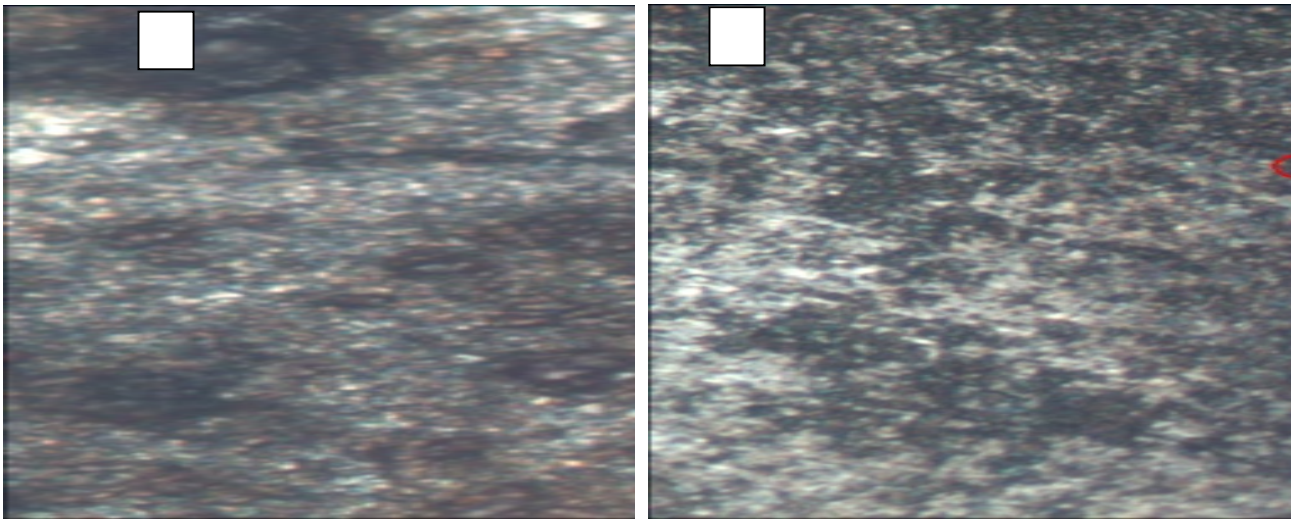

Figure 6a, b: Surface morphology and microstructure of the mild steel in the absence and presence of 2TCN

Conclusion

QSAR model have proven to be a good tool in searching for corrosion inhibitors using descriptors from the Dragon software before experimental evaluation. Quantum chemical calculation also confirmed that the model has predictive power. Weight loss shows that the inhibitor is a good inhibitor due to its good %IE. Potentiodynamic polarization shows that the inhibitor is a mixed inhibitor. EIS shows the mechanism of inhibition through double layer and charge transfer impedance. Microstructure analysis have shown the formation of protective layers on the metal surface by the inhibitor when compared with the metal surface without inhibitor.

Acknowledgment-The authors thank Research Management Centre (RMC) Vot No. 4F 257, and Computational Chemistry Laboratory, Universiti Teknologi Malaysia. Also the support of Bayero University, Kano, Nigeria and McArthur foundationis highly acknowledged

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