Inhibition of Corrosion of Carbon steel by Thiourea – Zn^{2+} System in Natural Sea Water

Manivannan M[1*], Rajendran S[2, 3] and A. Krishnaveni[4]

[1]Department of Chemistry, Chettinad College of Engineering and Technology, Karur 639 114, Tamil Nadu, INIDA
[2]Corrosion Research Centre, PG and Research Department of Chemistry, GTN Arts College,
Dindigul 624 005, Tamil Nadu, INDIA
[3]Department of Chemistry, RVS School of Engineering and Technology, Dindigul 624 005, Tamil Nadu, INDIA
[4]Department of Chemistry, Yadava College, Madurai 625 014, Tamil Nadu, INDIA

ABSTRACT

The inhibition efficiency (IE) of Thiourea (TU) in controlling corrosion of carbon steel in sea water in the absence and presence of Zn^{2+} has been evaluated by weight loss method. The formulation consisting of 200 ppm TU and 50 ppm Zn^{2+} has 95% IE. A synergistic effect exists between TU and Zn^{2+}. Synergism has been confirmed by Synergism parameter and F-Test. Influence of immersion period and pH on the IE of the inhibitor system has been investigated. AC Impedance study reveals that a protective film formed on the metal surface. The nature of the protective film has been characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Keywords – AFM, Carbon steel, F-Test, Sea water, TU

1. INTRODUCTION

Corrosion can be defined as the deterioration of material by reaction to its environment. The corrosion occurs because of the natural tendency for most metals to return to their natural state. It cannot be avoided, but it can be controlled and prevented using the suitable preventive measures such as alloying, cathodic protection, anodic protection, protective coating and application of inhibitiors, etc. Among all these techniques inhibitors reduce the aggressiveness of the corrosive environment and forming a protective layer on the metal surface thereby the metal and alloys are prevented from corrosion. Especially inhibitors find application in nuclear power plant and engine cooling systems [1,2]. The organic compounds containing hetero atoms like oxygen, nitrogen, phosphorus and sulphur,

etc have been employed as corrosion inhibitors to protect the metals from corrosion [3-7]. The corrosion inhibition of thiourea (TU) and its derivatives have been studied in various aqueous environments [8-12]. The presence of one sulphur and two nitrogen atoms containing lone pair of electrons in thiourea molecule makes it's as a very good corrosion inhibitor [13-15].

The present work is undertaken:

(i) to evaluate the inhibition efficiency (IE) of TU in controlling corrosion of carbon steel in sea water which is collected from Bay of Bengal at Marina Beach which is located at Chennai, Tamil Nadu, India (Table 1).

(i) to examine the influence of immersion period (IP) and pH on the IE of the TU – Zn^{2+} system.

(ii) to study the synergism using synergism parameters and analysis of variance.

(iii) to understand the mechanistic aspects of corrosion inhibition and formation of protective film on the metal surface by AC impedance spectra.

(iv) to analyze the protective film formed on the metals surface by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

(v) to propose a suitable mechanism for corrosion inhibition process.

2. EXPERIMENTAL

2.1. Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and rest iron) of the dimensions 1.0 X 4.0 X 0.2 cm were polished to a mirror finish and

degreased with trichloroethylene and used for the weight loss method and surface examination studies.

2.2. Weight loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the sea water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 1, 3, 5 and 7 days. The corrosion product cleaned with Clark's solution [16]. The parameter of the sea water is given in Table 1. The weights of the specimens before and after immersion were determined using an analytical balance, Shimadzu AY62 model. Then the Inhibition efficiency (IE) was calculated using the equation (1).

$$IE = 100 \left[1 - (W_2 / W_1) \right] \% \qquad (1)$$

Where W_1 and W_2 are corrosion rate in the absence and presence of the inhibitor respectively. The corrosion rate (CR) was calculated using the equation (2).

$$CR = \frac{87.6 \, W}{DAT} \, mm/y \qquad (2)$$

Table 1. Physico-Chemical Parameters of Sea Water

Parameters	Value
pH	7.66
Conductivity	44200 μmhos/cm
Chloride	16050 ppm
Sulphate	2616 ppm
TDS	30940 ppm
Total hardness	2800 ppm
Calcium	120 ppm
Sodium	6300 ppm
Magnesium	600 ppm
Potassium	400 ppm

Where W = weight loss in mg, D = density of carbon steel, 7.87 g/cm^3, A = surface area of the specimen (10 cm^2) and   T = immersion period in hrs.

2.3 Synergism parameter

Synergism parameters are indications of synergistic effect existing between the inhibitors. S_I value is found to be greater than one suggesting that the existence of synergistic effect between the inhibitors [17-20]. The S_I value can be calculated using the formula (3).

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \qquad (3)$$

Where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \, \theta_2)$, θ = IE/100, θ_1 = Surface coverage of inhibitor TU, θ_2 = Surface coverage of inhibitor Zn^{2+} and θ'_{1+2} = Combined inhibition efficiency of inhibitor TU and Zn^{2+}.

2.4 Analysis of Variance (F – Test)

F – Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [21,22]. If F – value is above 5.32 for 1, 8 degrees of freedom, it was proved to be at statistically significant. If it is below the value of 5.32 for 1, 8 degrees of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

2.5 AC Impedance Spectra

AC Impedance study was carried out in Electrochemical Impedance Analyzer model CHI 660A using a three electrode cell assembly. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. AC impedance spectra were recorded after doing iR compensation. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms for various frequencies. The corrosion parameters such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated. During the AC impedance spectra, the scan rate (V/s) was 0.005; Hold time at Ef (s) was zero and quiet time (s) was 2.

2.6 Surface Characterization Study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day the specimens were taken out and dried. The nature of the film formed on the metal surface was analyzed by surface characterization studies such as scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2.6.1 Scanning Electron Microscopy (SEM)

The carbon steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by scanning electron microscopy (SEM) using HITACHI S-3000H SEM.

2.6.2 Atomic Force Microscopy (AFM)

The carbon steel specimens immersed in various test solutions for one day were taken out, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out by atomic force microscopy (AFM) using SPM Veeco diInnova connected with the software version V7.00 and the scan rate of 0.7Hz.

3. RESULTS AND DISCUSSION

3.1 Weight loss study

3.1.1. Influence of Immersion period on the IE of TU-Zn^{2+} system

The influence of immersion period on the IE of TU (200 ppm) – Zn^{2+} (50 ppm) system is given in Table 2. It is found that as the immersion period increases, the inhibition efficiency decreases. This is due to the fact that as the immersion period increases the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as chloride (16050 ppm) present in sea water. There is a competition between two processes, namely, formation of $FeCl_2$ (and also $FeCl_3$) and iron – TU complex on the anodic sites of the metal surface.

It appears that the formation of iron chlorides is more favoured than the formation of iron - TU complex. Moreover, the iron - TU complex film formed on the metal surface is converted into iron chlorides which go into solution and hence, the IE decreases as the immersion period increases [23-24].

Table 2. Influence of immersion period on the inhibition efficiency of TU (200 ppm) and Zn^{2+} (50 ppm) system

System	Immersion Period (Days)			
	1	3	5	7
Sea water CR (mm/y)	0.1030	0.1124	0.1197	0.1247
Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)	0.0030	0.0056	0.0083	0.0099
IE%	97	95	93	92

3.1.2. Influence of pH on the IE of TU-Zn^{2+} system

The influence of pH on inhibition efficiency of TU (200 ppm) – Zn^{2+} (50 ppm) system is given in Table 3. It is found that at (pH 8) the IE is 96 percent. When acid (dil H_2SO_4) is added to attain pH 6, the IE decreases to 94 percent. When NaOH solution is added to the boost the pH, (pH 10) IE decreases to 95 percent.

Table 3. Influence of pH on the inhibition efficiency of TU (200 ppm) and Zn^{2+} (50 ppm) system

Immersion Period: 3 days

System	pH			
	6	8	10	12
Sea water CR (mm/y)	0.1065	0.1035	0.1104	0.0978
Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)	0.0063	0.0041	0.0055	0.0029
IE%	94	96	95	97

When NaOH is added further (pH 12) IE increases to 97 percent. It is found that at pH 8 the IE was 96 percent, when acid was added (pH 6), IE decreased. The protective film was brokened by H^+ ions of the acid. When NaOH was added further (pH 12) $Zn(OH)_2$ was solubilized as sodium zincate Na_2ZnO_2. Now TU was transported towards the metal surface. Hence IE increased [23-25].

3.2 Synergism Parameters (S_I)

The values of synergism parameters are given in Table 4 and 5. Here the values of S_I are greater than one, suggesting a synergistic effect. S_I approaches 1 when no interaction exists between the inhibitor compounds. When $S_I > 1$, this points to synergistic effects. In the case of $S_I < 1$, the negative interaction of inhibitors prevails (i.e. corrosion rate increases).

Table 4. Synergism parameters (SI) for carbon steel immersed in sea water in the absence and presence of inhibitor

Inhibitor system: $TU + Zn^{2+}$ **IP:** 3 days

TU ppm	θ_1	θ_2 (Zn^{2+} = 25 ppm)	θ_{1+2}	θ'_{1+2}	S_I
50	0.10	0.12	0.20	0.30	1.13
100	0.16	0.12	0.18	0.45	1.47
150	0.34	0.12	0.41	0.64	1.61
200	0.50	0.12	0.56	0.80	2.20
250	0.62	0.12	0.66	0.75	1.33

From Table 4 and 5, it can be seen that the values of S_I are greater than unity, suggesting that the phenomenon of synergism existing between TU and Zn^{2+}. Also the synergism parameter (S_I) for the formulation consisting of 200 ppm of TU and 50 ppm of Zn^{2+} is 8.3, which is greater than one. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} to TU is only due to the synergistic effect.

Table 5. Synergism parameters (SI) for carbon steel immersed in sea water in the absence and presence of inhibitor

Inhibitor system: $TU + Zn^{2+}$ **IP:** 3 days

TU ppm	θ_1	θ_2 (Zn^{2+} = 50 ppm)	θ_{1+2}	θ'_{1+2}	S_I
50	0.10	0.17	0.25	0.42	1.28
100	0.16	0.17	0.30	0.65	1.99
150	0.34	0.17	0.45	0.80	2.73
200	0.50	0.17	0.58	0.95	8.30
250	0.62	0.17	0.68	0.85	2.10

3.3 Analysis of Variance (ANOVA)

To investigate whether, the influence of Zn^{2+} on the inhibition efficiencies of TU is statistically significant, F – test was carried out. The results are given in Table 6. The results of Analysis of Variance (ANOVA) shows the influence of 25 ppm and 50 ppm of Zn^{2+} on the inhibition efficiencies of 50 ppm, 100 ppm, 150 ppm, 200 ppm and 250 ppm of TU. The obtained F – value 3.13 for 25 ppm of Zn^{2+}, is not statistically significant, since it is less than the critical F – value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance.

Table 6. Distribution of F - value between the IE of various concentrations of TU-Zn^{2+} system.

Zn^{2+} (ppm)	SV	SS	DF	MS	F	LS
25	Between	288	1	288	3.13	$p < 0.05$
	Within	740	8	92		
50	Between	761	1	761	8.36	$p > 0.05$
	Within	728	8	91		

SV – Sources of Variance; SS – Sum of Squares DF – Degrees of Freedom; MS – Mean Square; LS – Level of Significance of F.

Therefore, it is concluded that the influence of 25 ppm of Zn^{2+} on the inhibition efficiencies of various concentrations of TU is not statistically significant. The obtained F – value 8.36 for 50 ppm of Zn^{2+}, is statistically significant, since it is greater than the critical F – value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it is concluded that the influence of 50 ppm of Zn^{2+} on the inhibition efficiencies of various concentration of TU is statistically significant.

3.4 Analysis of AC Impedance spectra

The AC impedance spectra of carbon steel immersed in sea water in the absence and presence inhibitors are shown in Fig. 1 to 3. The AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and impedance value [log (z/ohm)] are given in Table7. When carbon steel is immersed in sea water the corrosion potential is -731 mV vs saturated calomel electrode (SCE). The R_t value is 83.63 Ω cm^2 and C_{dl} value is 7.7500 x 10^{-6} μF/cm^2. When TU and Zn^{2+} are added to sea water, R_t value increases from 83.63 Ω cm^2 To 99.32 Ω cm^2. The C_{dl} value decreases from 7.7500 x 10^{-6} μF/cm^2 to 6.5273 x 10^{-6} μF/cm^2. This confirms that the formation of protective film on the metal surface. This accounts for the very high IE of TU – Zn^{2+} system. This is further supported by the increase in impedance value [log (z/ohm)] from 2.011 to 2.050 [26-29].

Table 7. Impedance parameters for corrosion of carbon steel immersed in sea water in the absence and presence of inhibitors obtained by AC impedance spectra.

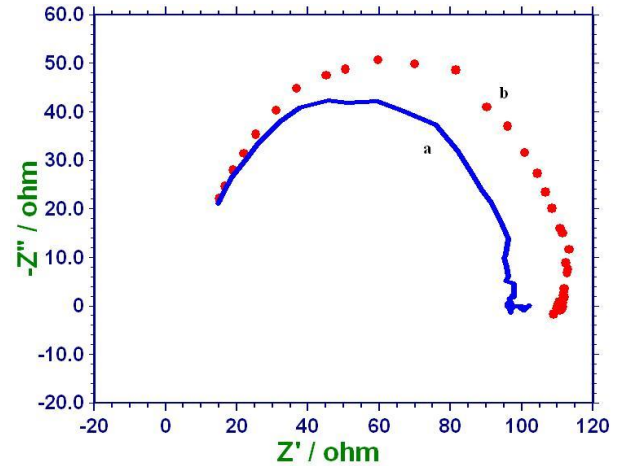| System	R_t Ω cm^2	C_{dl} μF/cm^2	log (z/ohm)
Sea water	83.63	7.7500 x 10^{-6}	2.011
Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)	99.32	6.5273 x 10^{-6}	2.050

Fig. 1. AC Impedance spectra of carbon steel immersed in various test solutions (Nyquist plots).

(a) Sea water
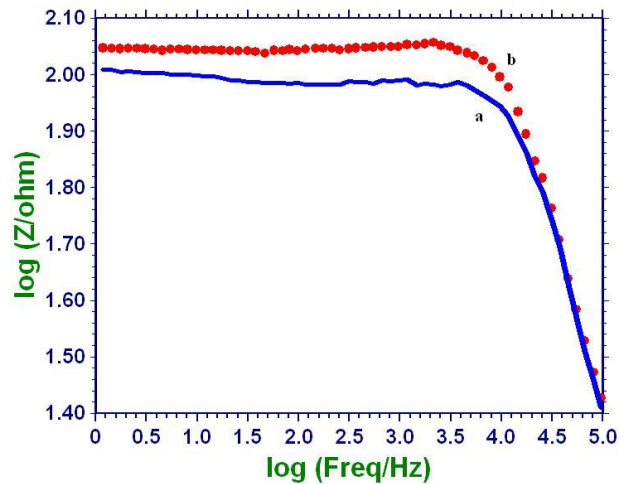(b) Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)

Fig. 2. AC Impedance spectra of carbon steel immersed in various test solutions (Frequency Bode plots).

(a) Sea water
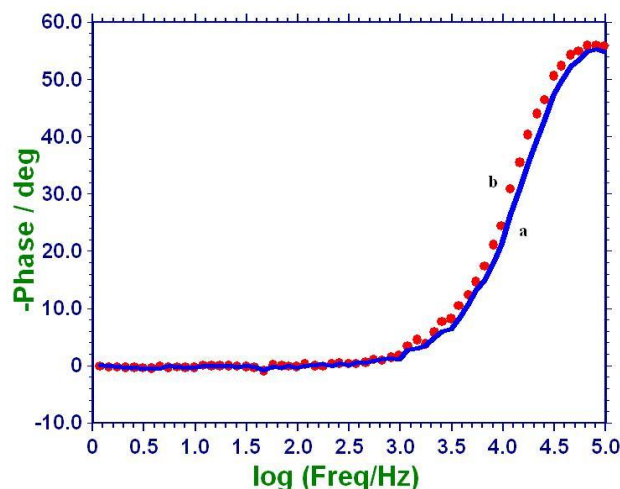(b) Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)

Fig. 3. AC Impedance spectra of carbon steel immersed in various test solutions (Phase Bode plots)

(a) Sea water
(b) Sea water + TU (200 ppm) + Zn^{2+} (50 ppm)

3.5 Scanning Electron Microscopy (SEM)

SEM provides a pictorial representation of the metal surface. To understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined. The SEM micrograph (X 1000) of a polished carbon steel surface (control) in Fig. 4. (a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The SEM micrograph (X 1000) of carbon steel specimen immersed in the sea water for one day in the absence and presence of inhibitor system is shown in Fig. 4. (b) and (c) respectively.

The SEM micrograph of carbon steel surface immersed in sea water in Fig. 4. (b) shows the roughness of the metal surface which indicates the corrosion of carbon steel in sea water. The Fig.4. (c) indicates that in the presence of 200 ppm TU and 50 ppm Zn^{2+} mixture in sea water, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface. In the presence of TU and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel [12, 30-32].
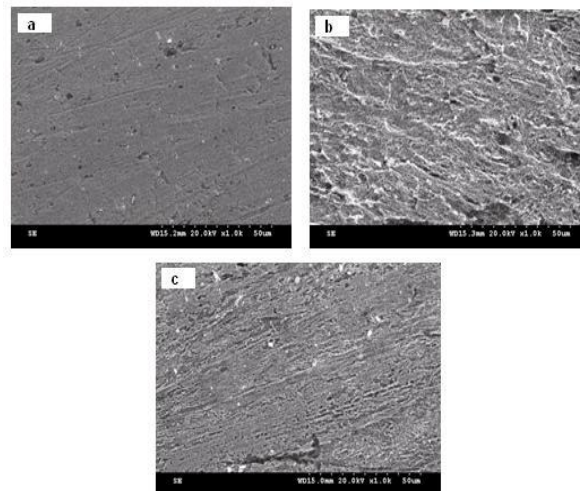

Fig. 4. SEM micrographs of carbon steel surface

(a) Polished carbon steel (control)
(b) Carbon steel immersed in sea water
(c) Carbon steel immersed in sea water containing TU   (200 ppm) and Zn^{2+} (50 ppm)

3.6 Atomic Force Microscopy (AFM)

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces [33,34]. AFM is becoming an accepted method of roughness investigation [35-39]. All AFM images were obtained using SPM Veeco diInnova AFM instrument operating in contact mode in air. The scan size of all the AFM images is 4.91 μm x 4.91 μm areas at a scan rate of 0.7 Hz. The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank) and carbon steel surface immersed in sea water containing the formulation of 200 ppm of TU and 50 ppm of Zn^{2+} are shown in Fig. 5. (a, d, g), (b, e, h), (c, f, i) respectively.

3.7.1   Root-mean-square   roughness,   average roughness and peak-to-valley height

AFM images analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R_q (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V)

height values (largest single peak-to-valley height in five adjoining sampling heights) [40]. R_q is much more sensitive than R_a to large and small height deviations from the mean [41]. The summary of the average roughness (R_a), rms roughness (R_{RMS}) and maximum peak-to-valley height (P-V) value for carbon steel surface immersed in various test solutions are given in Table 8.

Table 8. AFM data for carbon steel surface immersed in inhibited and uninhibited environments

Samples	(R_a) Average Roughness (nm)	(R_q) RMS Roughness (nm)	Maximum peak-to-valley (P-V) height (nm)
Polished carbon steel (control)	5.6241	8.1069	44.40
Carbon steel immersed in sea water	32.9000	40.2000	140.60
Carbon steel immersed in sea water containing TU (200 ppm) and Zn^{2+} (50 ppm)	9.0758	12.0118	67.29

The value of R_a, R_q and P-V for the polished carbon steel surface (reference sample) are 5.6241 nm, 8.1069 nm and 44.40 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth [42]. The Fig. 5 (a, d, g) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The average roughness, root-mean-square roughness and P-V height values for the carbon steel

surface immersed in sea water are 32.9000 nm, 40.2000 nm and 140.60 nm respectively. These data suggests that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in sea water. The Fig. 5 (b, e, h) displays corroded metal surface with few pits.

The presence of 200 ppm of Thiourea and 50 ppm of Zn^{2+} in sea water reduced the R_{RMS} by a factor of 3.34 (12.0118 nm) from 40.2000 nm and the average roughness is significantly reduced to 9.0758 nm when compared with 32.9000 nm of carbon steel surface immersed in sea water. The maximum peak-to-valley height also was reduced to 67.29 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - TU complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel. Also the above parameter observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.
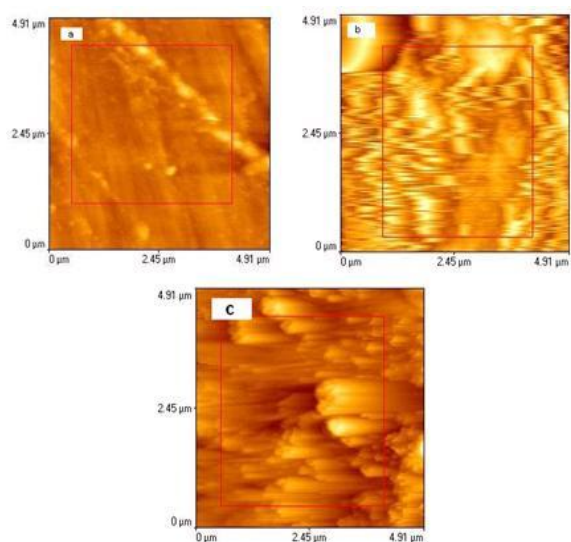

Fig. 5. 2D AFM images of carbon steel surface

(a) Polished carbon steel (control)
(b) Carbon steel immersed in sea water (blank)
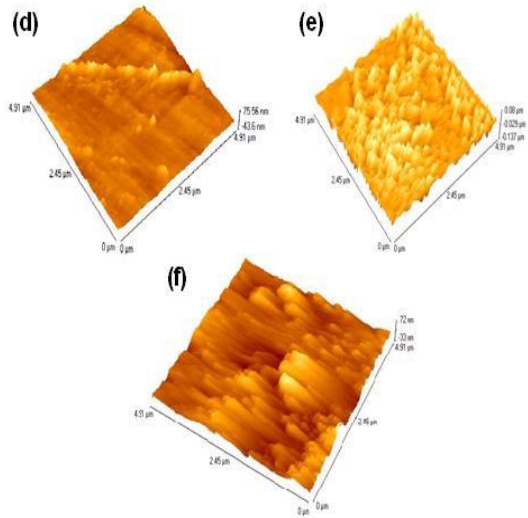**(c) Carbon steel immersed in sea water containing TU (200 ppm) and Zn^{2+} (50 ppm)**

Fig. 5. 3D AFM images of carbon steel surface

(d) Polished carbon steel (control)
(e) Carbon steel immersed in sea water (blank)
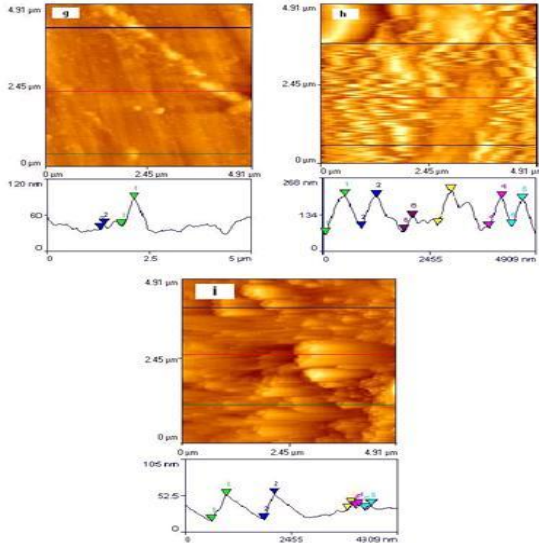(f) Carbon steel immersed in sea water containing TU (200 ppm) and Zn^{2+} (50 ppm)

Fig. 5. The cross-sectional profiles which are corresponding to as Shown broken lines (black colour) in AFM images of carbon steel surface.

(g) Polished carbon steel (control)
(h) Carbon steel immersed in sea water (blank)
(i) Carbon steel immersed in sea water containing TU (200 ppm) and Zn^{2+} (50 ppm)

4. MECHANISM OF CORROSION INHIBITION

Based on the above studies the following mechanism can be proposed for corrosion inhibition process.

(i) $Zn^{2+} - TU + Fe^{2+} \rightarrow Fe^{2+} - TU + Zn^{2+}$

(ii) $Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \downarrow$

(iii)   Protective film consists of Fe^{2+} - TU complex and $Zn(OH)_2$

(iv)   At anode: $Fe \rightarrow Fe^{2+} + 2\,e^-$
At cathode: $H_2O + \frac{1}{2} O_2 + 2\,e^- \rightarrow 2\,OH^-$
$Fe^{2+} + TU \rightarrow Fe^{2+} - TU$ complex
$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \downarrow$

(v)   It accounts for the synergism of TU-Zn^{2+}.

5. CONCLUSION

The present study leads to the following conclusions:

(i)   The formulation consisting of 200 ppm of TU and 50 pm of Zn^{2+} offers 95% IE to carbon steel immersed in sea water.
(ii)   Synergistic effect exists between TU and Zn^{2+}.
(iii)   AC impedance spectra reveal that the formation of protective film on the metal surface.
(iv)   SEM and AFM studies confirm the formation of protective film on the metal surface and hence the corrosion process is inhibited.

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