



INHIBITION OF CARBON STEEL CORROSION IN GROUND WATER BY POLYACRYLAMIDE

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ABSTRACT

The inhibition efficiency of Polyacrylamide (PAA) in controlling corrosion of carbon steel immersed in ground water has been evaluated in the absence and presence of Zn^{2+} . PAA has some inhibition efficiency. The inhibition efficiency increases in presence of Zn^{2+} . The synergistic effect exists between PAA and Zn^{2+} the maximum efficiency of 98% is obtained. The synergism parameters have been calculated. It is found that the synergistic effect exists between PAA and Zn^{2+} . The synergistic effect is statistically significant. This is proved by F-test. The mechanism of corrosion inhibition proposed based on AC impedance spectra. The productive film has been analyzed by SEM and AFM studies.

KEYWORDS: Corrosion inhibition, Carbon steel, Poly acrylamide, F-test, SEM Study, AFM Study.

1. INTRODUCTION

Corrosion can be defined as the destruction of metals and alloys by electrochemical reaction with its environment. The corrosion occurs because of the natural tendency of the metals to return back to their thermodynamically stable native state. It cannot be avoided, but it can be controlled and prevented by using appropriate preventive measures like cathodic protection, anodic protection, coating, alloying and using inhibitors, etc. Out of these methods, the inhibitors reduce the aggressiveness of the corrosive and harmful aqueous environment and preventing the metal and alloy by the formation of a protective layer on the metal surface. The applications of inhibitors are mostly find applications in cooling water system and boiler water system.^[1-2] The organic compounds containing hetero atoms like oxygen, nitrogen, phosphorus, halogen and sulphur, etc have been used as corrosion inhibitors to control the metals from corrosion.^[3-5] The compounds such as Gum Arabic and polyethylene glycol^[6], polyvinyl alcohol – sulphanic acid^[7] and halide ion – carboxymethyl cellulose^[8] have been used as corrosion inhibitors for mild steel in various aqueous environments. V. Srivastava et al. have been investigated that the corrosion behavior of carbon steel in presence of polyacrylamide.^[9] The corrosion inhibitive properties of polyacrylamide have been identified by S.A.Umoren et al.^[10]

The present work is undertaken:

- (i) To evaluate the inhibition efficiency(IE) of PAA in controlling corrosion of carbon steel in ground water which is collected from Yadava college which is located at Madurai, Tamil Nadu, India (Table 1)
- (ii) To examine the influence of immersion period (IP) on the IE of the PAA – Zn^{2+} system.
- (iii) To study the synergism using synergism parameters and analysis of variance.
- (iv) To understand the mechanistic aspects of corrosion inhibition and formation of protective film on the metal surface by AC impedance spectra.
- (v) To analyze the protective film formed on the metals surface by scanning electron microscopy(SEM) and atomic force microscopy(AFM)
- (vi) 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, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish and degreased with trichloroethylene and used for both weight-loss method and surface examination studies. The environment chosen is ground water and the physico-chemical parameter of ground water is given table in **Table 1**.

Table 1: Physico-Chemical Parameter of Ground Water.

Parameters	Value
pH	7.3
Total Hardness as CaCO ₃	460 ppm
Calcium	32 ppm
Magnesium	91 ppm
Nitrate	8 ppm
Chloride	270 ppm
Fluoride	0.8 ppm
Sulphate	100 ppm
Phosphate	0.46 ppm

2.2 Polyacrylamide solution

0.5gm polyacrylamide (PAA) was dissolved in double distilled water made up to 100ml in a SMF.

2.3 Weight- loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the ground water containing various concentrations of the inhibitor in the presence and absence of Zn²⁺ for 3, 5, 7 and 10 days. The corrosion product cleaned with Clark's solution.^[11] The weights of the specimens before and after immersion were determined using an analytical balance, Shimadzu AY210 model. Then the Inhibition efficiency (IE) was calculated using the equation (1).

$$IE = 100 [(W_2 / W_1)] \% \quad (1)$$

Where: W_1 = corrosion rate (mdd) in absence of inhibitor,

W_2 = corrosion rate (mdd) in presence of inhibitor.

2.4 Synergism Parameter (SI)

Synergism parameters are indications of synergistic effect existing between the inhibitors. S_1 value is found to be greater than one suggesting that the synergistic effect between the inhibitors.^[12-13] The S_1 value can be calculated using the formula (2).

$$S_1 = 1 - \theta_{1+2} / 1 - \theta'_{1+2} \quad (2)$$

Where, $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$

θ_1 = Surface coverage of inhibitor PAA

θ_2 = Surface coverage of inhibitor Zn²⁺

θ'_{1+2} = Combined surface coverage of inhibitor polyacrylamide (PAA) and Zn²⁺.

2.5 Analysis of Variance (F-Test)

F-Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant.^[14] If F-value is above 4.96 for 1,10 degrees of freedom, it was proved to be at statistically significant. If it is below the value of 4.96 for 1,10 degrees of freedom, it was statistically insignificant at 0.05 level of significance confirmed.

2.6 AC impedance measurements

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 cm² 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 E_f (s) was zero and quiet time (s) was 2.

2.7 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).

2.7.1 Scanning Electron Microscopic studies (SEM)

The carbon steel immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of the carbon steel were examined using HITACHI S-3000 H computer controlled scanning electron microscope.

2.7.2 Atomic Force Microscopy characterization (AFM)

The carbon steel specimen immersed in blank and in the inhibitor for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried by atomic force microscopy (AFM) using SPM Veeco dilnnova with the software version V7.00 and scan rate of 0.7 Hz.

3. RESULTS AND DISCUSSION

3.1 Weight loss study

3.1.1 Influence of immersion period on the inhibition efficiency of the PAA (250 ppm)-Zn²⁺ (50 ppm) system

The influence of immersion period on the IE of PAA-Zn²⁺ system is given in Table 2. It is observed that as the immersion period increases, the IE decreases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl⁻ ion (270 ppm) present in ground water. There is a competition between the formation of FeCl₂ (and also FeCl₃) and iron - PAA complex (on the anodic sites of the metal surface). A perusal of the results suggests that the formation of FeCl₂ is favoured when compared with the formation of iron - PAA complex. Moreover, the iron - PAA 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. Similar observation has been made by Selvaraj *et al.* while studying corrosion protection of carbon steel by

polyvinyl pyrrolidone-Zn²⁺ system^[15] and also by Rajendran *et al.*, while investigating corrosion inhibition by sodium dodecyl sulphate.^[16]

Table 2: Influence of immersion period on the inhibition efficiency of the PAA (250 ppm) – Zn²⁺ (50 ppm).

System	Immersion period (days)			
	3	5	7	10
Ground Water, mdd	15.15	18.18	21.21	24.24
Ground Water + PAA (250 ppm) + Zn ²⁺ (ppm), mdd	0.30	2.18	5.09	7.99
IE%	98	88	76	67

3.2 Synergism parameters (S_I)

The synergism parameters of PAA- Zn²⁺ system are given in Tables 3. For different concentrations of inhibitors, S_I approaches 1 when no interaction between the inhibitor compounds exists. When S_I > 1, it points to synergistic effects. In the case of S_I < 1, it is an indication

that the synergistic effect is not significant. From Tables 3, it is observed that value of synergism parameters (S_I) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between PAA and Zn²⁺ ions.^[17]

Table 3: Inhibition efficiencies and synergism parameters for various concentrations of PAA-Zn²⁺ system, when carbon steel immersed in ground water.

Immersion period: 3 days

PAA ppm	Zn ²⁺ , ppm								
	0	5	S _I	10	S _I	25	S _I	50	S _I
0	0	7	--	10	--	12	--	15	--
25	5	55	1.96	40	1.43	80	4.18	50	1.62
50	18	65	2.18	60	1.85	82	4.01	65	1.99
75	25	70	2.33	76	2.81	84	4.13	76	2.66
100	35	75	2.42	80	2.93	88	4.76	88	4.60
125	42	85	3.60	82	2.90	90	5.10	90	4.93
250	48	86	3.69	88	3.90	94	7.63	98	22.1

3.3 Analysis of Variance (ANOVA)

To know whether the synergistic effect existing between PAA and Zn²⁺ is statistically significant or not, F-test was used.^[18] The results are given in Tables V.5.10 and V.5.13. It is observed that the calculated F-values 24.50,

15.73, 22.18 and 59.68 are greater than the table value 4.96 for 10 degrees of freedom at 0.05 level of significant. Therefore, it is concluded that the synergistic effect existing between PAA and Zn²⁺ (5, 10, 25 and 50 ppm) are statistically significant.

Table 4: Distribution of F-value between the IE of various concentrations of PAA-Zn²⁺.

Zn ²⁺ (ppm)	SV	SS	DF	MS	F	LS
5	Between	5011.07	1	5011.07	24.50	P > 0.05
	Within	2045.1	10	204.51		
10	Between	4609.92	1	4609.92	15.73	P > 0.05
	Within	2929.8	10	292.98		
25	Between	6175.31	1	6175.31	22.18	P > 0.05
	Within	2784.6	10	278.46		
50	Between	9475.32	1	9475.32	59.68	P > 0.05
	Within	1587.8	10	158.78		

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

3.4 Analysis of AC impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance log (Z/ohm) value

increases. The AC impedance spectra of carbon steel immersed in ground water in the absence and presence of inhibitors (PAA-Zn²⁺) are shown in Figs.1 to 3. The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in Table 5. The impedance log (Z/ohm) values derived from Bode plots are also given in

Table 5. It is observed that when the inhibitors [PAA (250 ppm) + Zn²⁺ (50 ppm)] are added, the charge transfer resistance (R_t) increase from 1962.3 Ωcm^2 to 3236.6 Ωcm^2 . The C_{dl} value decreases from 2.5989×10^{-9}

F/cm^2 to $1.5757 \times 10^{-9} \text{F/cm}^2$. The impedance value [$\log(Z/\text{ohm})$] increases from 3.297 to 3.537. These results lead to the conclusion that a protective film is formed on the metal surface.^[19-21]

Table 5. Impedance parameters for corrosion of carbon steel immersed in ground water in the absence and presence of inhibitors obtained by AC impedance spectra.

System	Nyquist plot		Bode plot
	R_t $\Omega \text{ cm}^2$	C_{dl} F/cm^2	Impedance value $\log(z/\text{ohm})$
Ground Water	1962.3	2.5989×10^{-9}	3.297
Ground Water + PAA (250 ppm) + Zn ²⁺ (50 ppm)	3236.6	1.5757×10^{-9}	3.537

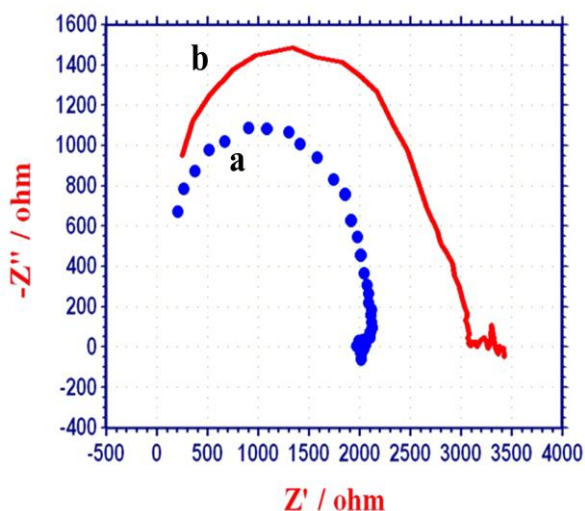


Fig 1: AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots).

- a) Ground water
b) Ground water + PAA (250 ppm) + Zn²⁺ (50 ppm)

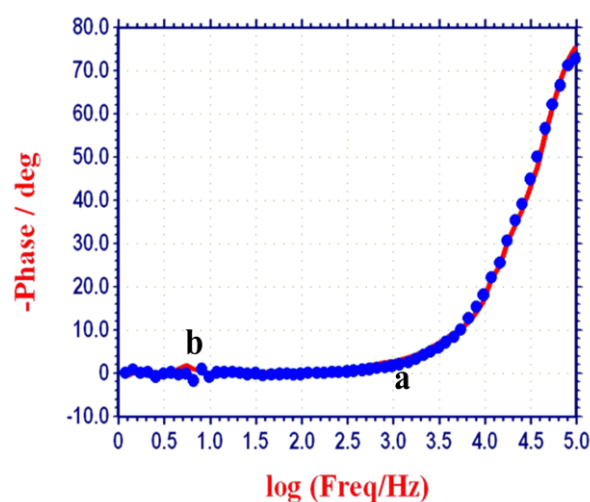


Fig 3: AC impedance spectra of carbon steel immersed in various test solutions (Phase-Bode plots).

- a) Ground water
b) Ground water + PAA (250 ppm) + Zn²⁺ (50 ppm)

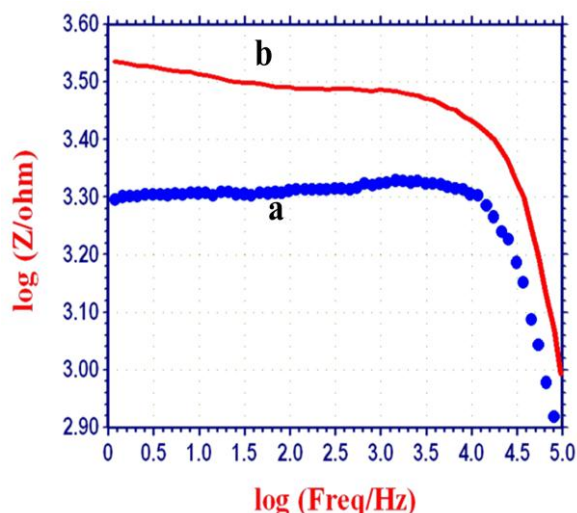


Fig 2: AC impedance spectra of carbon steel immersed in various test solutions (Bode plots).

- a) Ground water
b) Ground water + PAA (250 ppm) + Zn²⁺ (50 ppm)

3.5 Scanning Electron Microscopy (SEM)

SEM provides a pictorial representation of the 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.^[22] The SEM micrograph (X 500) 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 500) of carbon steel specimen immersed in the ground water for one day is shown in Fig. 4 (b) and (c) respectively. The SEM micrograph of carbon steel surface immersed in ground water in Fig. 4 (b) shows the roughness of the metal surface which indicates the corrosion of carbon steel in ground water. The Fig. 4 (c) indicates that in the presence of 250 ppm PAA and 50 ppm Zn²⁺ mixture in ground water, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface. In the presence of PAA and Zn²⁺, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of carbon steel.^[23]

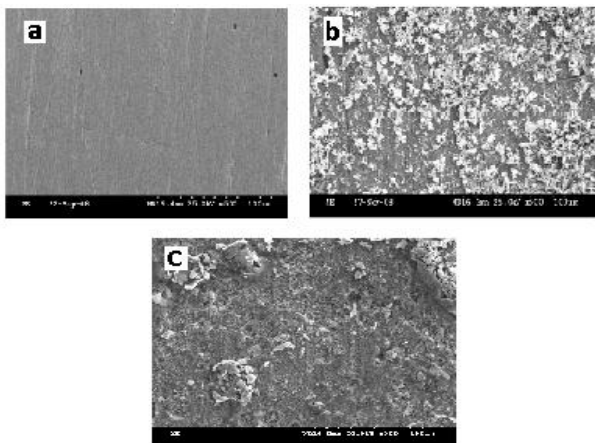


Fig. 4: SEM micrographs of carbon steel surface.

- Polished Carbon steel (control) Magnification X 500.
- Carbon steel immersed in ground water Magnification X 500.
- Carbon steel immersed in ground water containing PAA (250ppm) and Zn^{2+} (50ppm) Magnification X 500.

3.6 Atomic force Microscopy (AFM)

Atomic force microscopy is a powerful technique for the gathering of roughness statistics from a variety of surfaces. AFM is becoming an accepted method of roughness investigation.^[24-25]

All atomic force microscopy images were obtained in a SPM Veeco dilnnova lab incorporation AFM instrument operating in contact mode in air. The scan size of all the AFM images are $4.91 \mu m \times 4.91 \mu m$ 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 ground water (blank sample) and carbon steel surface immersed in ground water containing the formulation of PAA 250 ppm and 50 ppm of Zn^{2+} are shown in Fig. 5 (a, d, g), (b, e, h), (e, f, i) respectively.

3.6.1 Root – mean-square roughness, average roughness and peak-to-valley value

AFM image 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 five adjoining sampling heights). R_q is much more sensitive than R_a to large and small heights deviations from the mean.^[26-29] Table 6 is summary of the average roughness (R_a), rms roughness (R_q) maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments.

Table 6: AFM data for carbon steel surface immersed in inhibited and uninhibited environments.

Samples	RMS(R_q) Roughness (nm)	Average (R_a) Roughness (nm)	Maximum peak-to-valley height (nm)
Polished carbon steel (control)	4.3	5.7	9.71
Carbon steel immersed in ground water	26.0	21.1	120.0
Carbon steel immersed in ground water + PVA (250 ppm) + Zn^{2+} (50 ppm)	15.2	12.0	48.1

The value of R_{RMS} , R_a and P-V height for the polished carbon steel surface (reference sample) are 4.3 nm, 5.7 nm, and 9.71 nm respectively, which shows a more homogeneous surface, with some places in where the height is lower than the average depth. Fig. 5 (a, d, g) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmosphere corrosion. The rms roughness, average roughness and P-V height values for the carbon steel surface immersed in ground water are 26.0 nm, 21.1 nm and 120.0 nm respectively. These data suggest that carbon steel surface immersed in ground water as a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and is due to the corrosion of the carbon steel in ground water. Fig 5 (b, e, h) displays corroded metal surface with few pits. The presence of 250 ppm of PAA and 50 ppm of Zn^{2+} in ground water reduces the R_q by a factor of 15.2 nm from 26 nm and

the average roughness is significantly reduced to 12.0 nm when compared with 21.1 nm of carbon steel surface immersed in ground water. The maximum peak-to-valley height also was reduced to 48.1 nm from 120 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+} - PAA complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel. Also the above parameters 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.^[30]

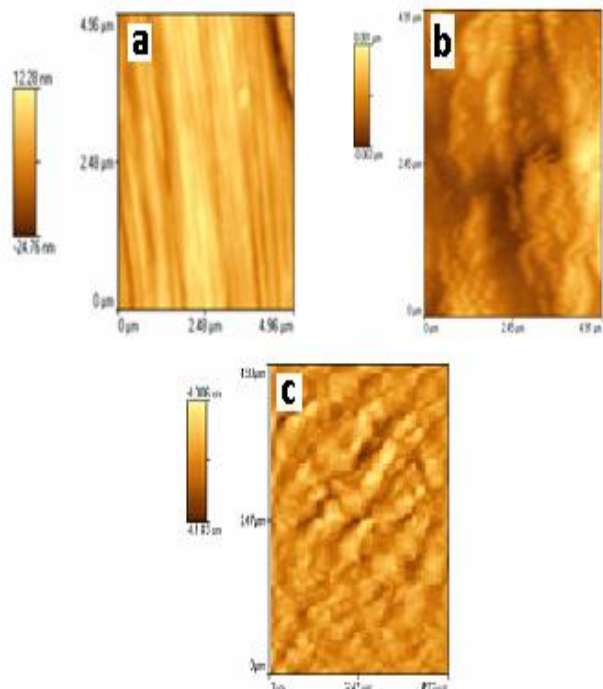


Fig. 5: 2D AFM images of carbon surface.

- (a) Polished carbon steel (control)
 (b) Carbon steel immersed in ground water (blank)
 (c) Carbon steel immersed in ground water containing PAA (250 ppm) and Zn^{2+} (50 ppm)

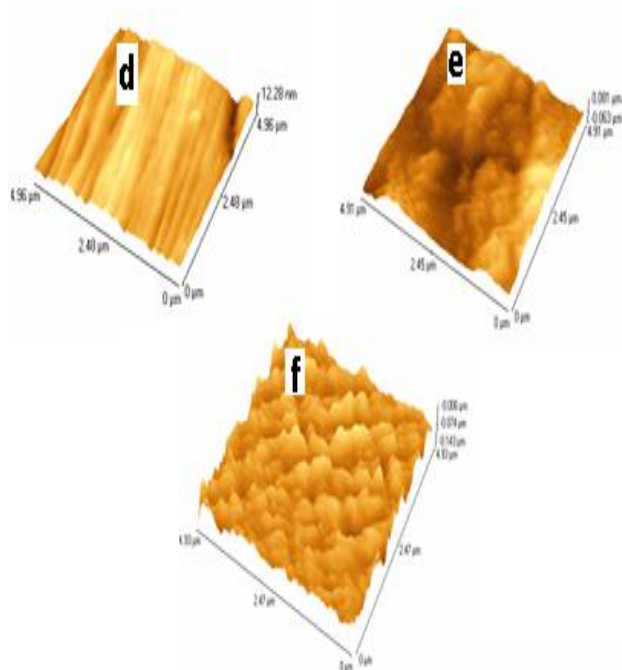


Fig. 5: 3D AFM images of carbon steel surface

- (d) Polished carbon steel (control)
 (e) Carbon steel immersed in ground water (blank)
 (f) Carbon steel immersed in ground water containing PAA (250 ppm) and Zn^{2+} (50 ppm)

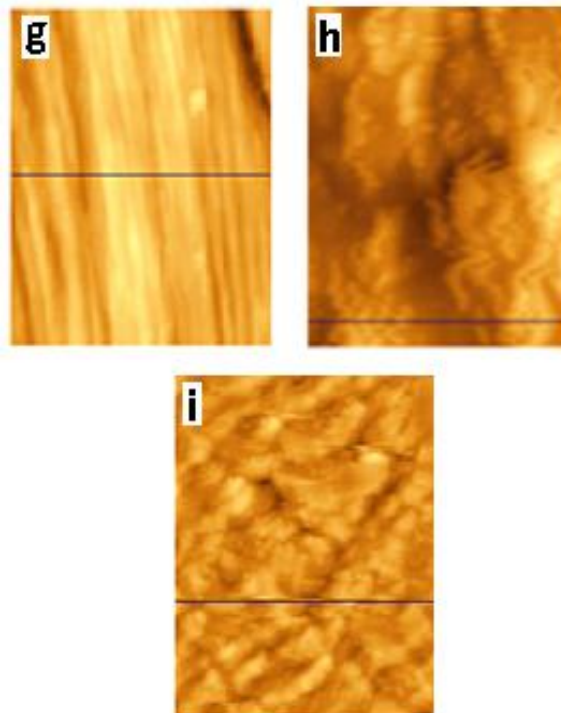


Fig.5: The cross sectional profiles which are corresponding to as shown broken lines (black colour) in AFM images of carbon steel surface.

- (g) Polished carbon steel (control)
 (h) Carbon steel immersed in ground water (blank)
 (i) Carbon steel immersed in ground water containing PAA (250 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) $Zn^{2+} - PAA + Fe^{2+} \rightarrow Fe^{2+} - PAA + Zn^{2+}$
 (ii) $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$
 (iii) Protective film consists of $Fe^{2+} - PAA$ complex and $Zn(OH)_2$
 (iv) At anode: $Fe \rightarrow Fe^{2+} + 2e^-$
 At cathode: $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2 OH^-$
 $Fe^{2+} - PAA \rightarrow PAA \text{ complex}$
 $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$
 (v) It accounts for the synergism of PAA – Zn^{2+}

5. CONCLUSIONS

The present study leads to the following conclusions:

- (i) The formulation consisting of 250 ppm of PAA and 50 ppm of Zn^{2+} offers 98% IE to carbon steel immersed in ground water.
 (ii) Synergistic effect of exists between PAA and Zn^{2+} .
 (iii) AC impedance spectra reveal that the formation of protective film on the metal surface.
 (iv) FTIR spectra reveal that the protective film consists of $Fe^{2+} - PAA$ complex and $Zn(OH)_2$.
 (v) The SEM micrographs confirm the formation of protective layer on the metal surface.

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