



CORROSION INHIBITION OF CARBON STEEL IN WELL WATER BY TRISODIUM CITRATE – Cu^{2+} AS INHIBITOR

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ABSTRACT

The inhibition efficiency (IE) of Trisodium citrate- Cu^{2+} system in controlling of corrosion of carbon steel in well water has been determined by weight loss method. The experiment was carried out by varying the immersion period and concentration of the inhibitor at room temperature. A synergistic effect exists between TSC and Cu^{2+} ion. The inhibitor system TSC- Cu^{2+} consisting of 250ppm of TSC and 50ppm of Cu^{2+} ion showed 86% of IE. The FTIR spectra revealed the formation of the protective film on the metal surface consists of Fe^{2+} - TSC and $\text{Cu}(\text{OH})_2$. The formation of protective film was confirmed by the electrochemical studies such as polarization study, UV-Visible

spectra, AC impedance, SEM and AFM.

KEYWORDS: Corrosion, carbon steel, Trisodium citrate- Cu^{2+} , SEM, AFM, AC impedance.

1. INTRODUCTION

Corrosion is a major destructive phenomenon which occurs naturally. Corrosion is generally defined as the deterioration of metal surfaces due to the reaction between the metal and the environment.^[1] This destructive process can be controlled by using inhibitors. Corrosion inhibitors are the chemical substances which form a protective layer on the surface of metal and control the corrosion. Many of the inhibitors that are used for corrosion inhibition study are chemically hazardous.^[2] Therefore, the recent works are carried out by using, non-toxic,

low cost and eco-friendly inhibitors. Carbon steel is widely used for construction purpose, industries and engineering works due to its excellent mechanical properties and low cost. There are several methods including inhibitors are used to control corrosion. Some of the inhibitors are zinc salts, molybdates, amines, phosphates and some natural products have been used for inhibition study. The present work is undertaken,

- i) to investigate the inhibition efficiencies of Cu^{2+} ion and trisodium citrate system as inhibitor on carbon steel immersed in well water.
- ii) to study the mechanic aspect of corrosion inhibition by polarization study.
- iii) to analyse the protective film by FTIR, UV-Visible, SEM, AFM studies.

2. MATERIALS AND METHODS

Metal specimens

Carbon steel specimen used in the present study has the composition (wt%) of S-0.026, P-0.06, Mn- 0.4, C- 0.1 and balance iron. The dimension of the specimen was 1 x 4 x 0.2 cm. The molecular structure of trisodium citrate is shown in Fig. 1.

The inhibition efficiency of TSC- Cu^{2+} system against corrosion of mild steel in well water is determined. The parameter of well water is given in Table-1.

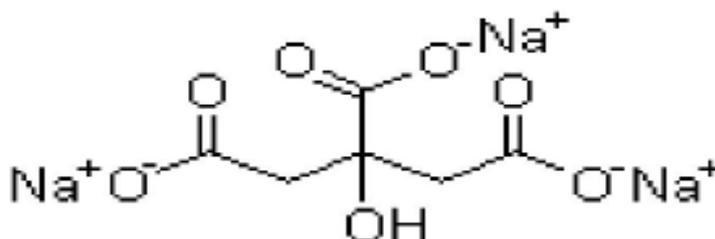


Fig. 1: Structure of Trisodium citrate.

Table. 1: Parameters of well water.

Parameters	Value
pH	8.38
Conductivity	3110 $\mu\Omega^{-1}\text{cm}^{-1}$
Chloride	665ppm
Sulphate	14ppm
TDS	2013ppm
Total Hardness	1100ppm

Weight-Loss Method: Carbon steel specimens in triplicate were immersed in 100ml of well water containing various concentration of TSC in the presence and absence of Cu^{2+} ion for

three days. The weight of the specimen metals before and after immersion were determined using a Shimadzu balance, model AY62. Then the corrosion products were cleansed with Clarke's solution.

The inhibition efficiency (IE %) was calculated by the following expression,

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

where, W_1 = Corrosion rate in the absence of the inhibitor

W_2 = Corrosion rate in the presence of the inhibitor

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 66A. A three electrode cell assembly was used in which the mild steel is the working electrode. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{Corr}), corrosion current (I_{corr}) and Tafel slopes (anodic= b_a , cathodic= b_c) and Linear polarization resistance (LPR) were calculated.

AC Impedance measurements

H and CH electrochemical impedance analyzer model CH1660 was used to record AC impedance measurements. The cell set setup was the same as the polarization technique. At a steady state potential, an AC potential of 10mV was superimposed at the varied AC frequency from 100 MHz to 100 KHz. For various frequencies the real part (z') and imaginary part (z'') of cell impedance were measured in ohms. The charge transfer resistance (R_t) and the double layer capacitance (C_{ds}) values were calculated. C_{dl} values can be calculated by the expression given below.

$$C_{\text{dl}} = \frac{I}{2 \times 3.14 \times R_t \times f_{\text{max}}}$$

UV-Visible Absorption Spectra

The possibility of the formation Zn-inhibitor complex and Fe-inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-Visible absorption spectra using Analytic-Jena Specord S-100, UV-Visible spectrophotometer.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. Then the specimen is taken out and dried. The nature of the film formed on the surface of the

metal specimens was analyzed for surface analysis techniques such as FTIR spectra, SEM, AFM studies.

FTIR Spectra: FTIR spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

Scanning Electron Microscopic Studies (SEM)

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of three days was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology by using Hitachi S-3000 H computer controlled scanning electron microscope.

Atomic Force Microscopy Characterization (AFM)

The carbon steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and subjected to the surface examination. The surface morphology measurements were determined by atomic force microscopy (AFM) using PicoSPM 2100 with the software version of Picoscan 5.4.

3. RESULT AND DISCUSSION

Analysis of results of weight loss method

Corrosion rates (CR) and inhibition efficiency (IE) of carbon steel immersed in well water in the absence and presence of various concentrations of inhibitor was determined by the weight loss method for three days. The results are given in the Table 2 and 3.

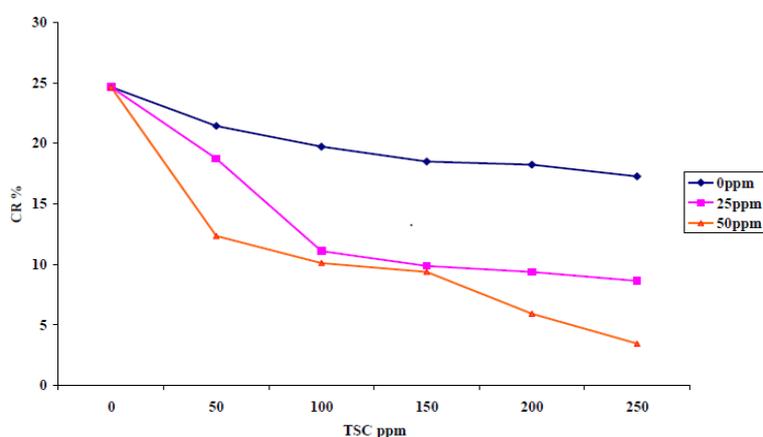


Fig. 2: Graph of inhibition efficiency (IE) of TSC-Cu²⁺ system in the corrosion of carbon steel immersed in well water.

Table. 2: Inhibition system: TSC- Cu²⁺ (0ppm) Immersion period: 3 days.

TSC ppm	Cu ²⁺ ppm	CR mdd	IE%
0	0	24.67	-
50	0	21.46	13
100	0	19.74	20
150	0	18.50	25
200	0	18.25	26
250	0	17.27	30

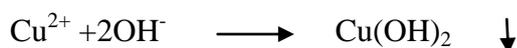
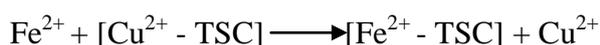
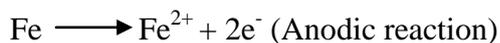
Table. 3: Inhibition system: TSC- Cu²⁺ (25ppm) Immersion period: 3 days.

TSC ppm	Cu ²⁺ ppm	CR mdd	IE%
0	25	24.67	10
50	25	18.75	24
100	25	11.10	55
150	25	9.87	60
200	25	9.37	62
250	25	8.63	65

Table. 4: Inhibition system: TSC- Cu²⁺ (50ppm) Immersion period: 3 days.

TSC ppm	Cu ²⁺ ppm	CR mdd	IE%
0	50	24.67	-
50	50	12.34	50
100	50	10.11	59
150	50	9.37	62
200	50	5.92	76
250	50	3.45	86

From Table-2 it is observed that the inhibitor TSC at 50ppm shows 13% of IE. As the concentration of TSC increases the value of IE also increases due to the stability of the protective film (Fe-TSC complex) on the metal surface. Table-3 explains the influence of Cu²⁺ ion on the inhibition efficiencies of TSC. The observed values clearly shows that as the given concentration of TSC increases the IE also increases. The combination of Cu²⁺ ion and TSC gives high IE at 25ppm of Cu²⁺ ion and 250ppm of TSC gives 65% of IE. Further, on increasing the concentration of Cu²⁺ ion ie) combination of 50ppm of Cu²⁺ and 250ppm of TSC gives a very high value of inhibition efficiency of 86% is given in Table-4. As the concentration of Cu²⁺ ion increases more amount of TSC is transported towards the metal surface. Fe-TSC complex is formed on the anodic sites of the metal surface and thus the anodic reaction is controlled. The formation of Cu(OH)₂ on the cathodic sites of the metal surface controls the cathodic reaction. As a result, there is a synergistic effect exists between Cu²⁺ ion and TSC.



Synergism Parameters (S_I)

The synergistic effect that exists between two inhibitors is determined by synergism parameter (S_I).^[3-8] S_I is calculated by the following expression.

$$\text{Synergism parameter } (S_I) = 1 - \theta_{1+2} / 1 - \theta'_{1+2}$$

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

θ_1 – Surface coverage by TSC

θ_2 – Surface coverage by Cu^{2+} ion

θ'_{1+2} - Surface coverage both TSC & Cu^{2+} ion

θ – Surface Coverage = IE% / 100

Table. 5: Inhibition efficiencies and synergism parameters for various concentrations of TSC- Cu^{2+} (25ppm) system for carbon steel in well water Immersion period: 3 days.

TSC ppm	Inhibition efficiency IE (%)	IE/100 Surface Coverage θ_1	Cu^{2+} ppm	Inhibition efficiency IE (%)	Surface Coverage θ_2	Combined IE% I'_{1+2}	Combined Surface Coverage θ'_{1+2}	Synergism parameters S_I
50	13	0.13	25	10	0.10	24	0.24	1.0
100	20	0.20	25	10	0.10	55	0.55	1.6
150	25	0.25	25	10	0.10	60	0.60	1.68
200	26	0.26	25	10	0.10	62	0.62	1.75
250	30	0.30	25	10	0.10	65	0.65	2.57

Table. 6: Inhibition efficiencies and synergism parameters for various concentrations of TSC- Cu^{2+} (50ppm) system for carbon steel in well water Immersion period: 3 days

TSC ppm	Inhibition efficiency IE (%)	IE/100 Surface Coverage θ_1	Cu^{2+} ppm	Inhibition efficiency IE (%)	Surface Coverage θ_2	Combined IE% I'_{1+2}	Combined Surface Coverage θ'_{1+2}	Synergism parameters S_I
50	13	0.13	50	15	0.15	50	0.50	1.48
100	20	0.20	50	15	0.15	59	0.59	1.66
150	25	0.25	50	15	0.15	62	0.62	1.68
200	26	0.26	50	15	0.15	76	0.76	2.62
250	30	0.30	50	15	0.15	86	0.86	4.25

From the Table (5) and Table (6) it is observed that there is a synergistic effect exists between TSC and Cu^{2+} . When S_I approaches 1 there no interaction between the inhibitor

compounds, if $S_I > 1$, then there is synergistic effect. If $S_I < 1$ it indicates that there is no significant synergistic effect.^[7] From the values calculated it is clear that the value of synergism parameters (S_I) were found to be one and greater than one.^[5,6,8] Thus the enhancement of IE by the addition of Cu^{2+} ions to TSC is due to synergistic effect.

Analysis of potentiodynamic polarization study

Polarisation study has been used to confirm the formation of the protective film on the metal surface. When the linear potential resistance (LPR) value increases and the corrosion current decreases indicates the formation of the protective film. Fig.3 shows the potentiodynamic polarization curves of mild steel immersed in various test solutions. the corrosion parameters namely corrosion potential (E_{Corr}), Tafel slopes ($b_c = \text{cathodic}$, $b_a = \text{anodic}$), linear potential resistance (LPR) and corrosion current (I_{Corr}) are given in Table (7). When the mild steel is immersed in well water the corrosion potential is -630mV vs SCE. The LPR value is 7799.9 ohm cm^2 . The corrosion current is $5.537 \times 10^{-6} \text{ Acm}^{-2}$. When inhibitors (TSC $250\text{ppm} + \text{Cu}^{2+} 50\text{ppm}$) are added to the system, the LPR value increases from 7799.9 to 21999ohm cm^2 . Increase in the LPR value indicates the formation of protective film on the metal surface.^[9-11] Simultaneously there is a decrease in the corrosion current value from 5.537×10^{-6} to $1.960 \times 10^{-6} \text{ Acm}^{-2}$. In the presence of inhibitors the E_{Corr} has shifted to cathodic side (-630 to -651 mV) and suggests that the cathodic reaction predominantly controlled.

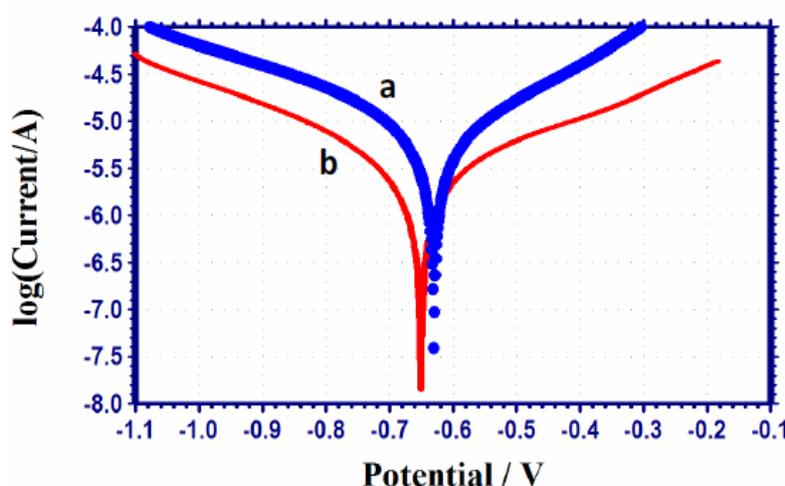


Fig. 3. Polarization curves of mild steel immersed in various test solutions.

a) well water (Blank).

b) well water + TSC (250 ppm) + Cu^{2+} (50 ppm).

Table. 7: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study.

System	E_{corr} % mVE vs SCE	b_c mV/decade	b_a mV/decade	I_{corr} A/cm ²	LPR ohm cm ²
Well water	-630	202	194	5.537×10^{-6}	7799.9
Well water TSC(250ppm) + Cu ²⁺ (50ppm)	-651	187	212	1.960×10^{-6}	21999

Thus by the increase in LPR value from 7799.9ohm cm⁻² to 21999ohm cm⁻², the corrosion current decreases from 5.537×10^{-2} A/c cm⁻² to 1.960×10^{-2} A/c cm⁻². Thus the polarization study confirms the formation of the protective film on the metal surface.

Analysis of AC impedance spectra

AC impedance spectra is used to confirm the formation of the protective film on the metal surface. If a protective film is formed on the metal surface, charge transfer resistance (C_{dl}) decreases and the impedance log (z/ohm) value increases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 4(a,b) –Nyquist plots and in Fig.5(a,b) – Bode plots. Table-8 explains charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots. The impedance log (z/ohm) values derived from Bode plots are also given in Table-8. It is observed when the inhibitors TSC (250 ppm) + Cu²⁺ (50 ppm) are added, the R_t increases.

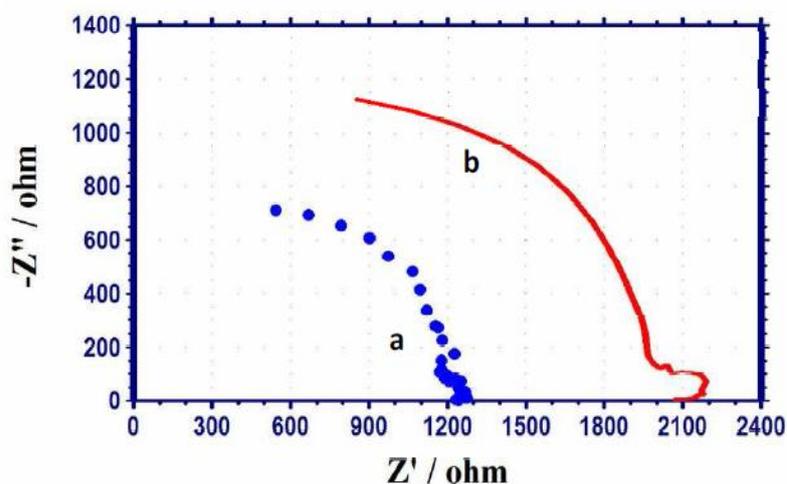


Fig. 4. AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plot).

(a) well water (Blank).

(b) well water + TSC (250 ppm) + Cu²⁺(50 ppm).

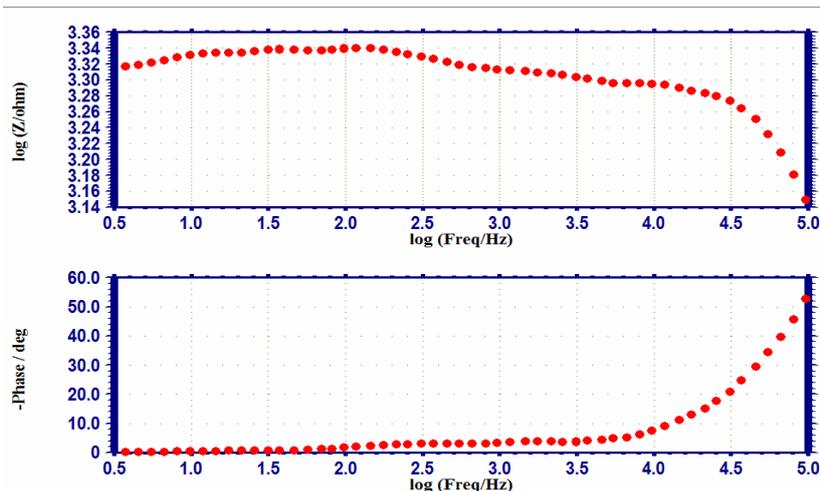


Fig. 5: AC impedance spectra of carbon steel immersed in various test solutions (Bode plot).

(a) well water (Blank).

(b) well water + TSC (250 ppm) + Cu²⁺(50 ppm).

Analysis of UV-Visible absorption spectra: The UV-Visible absorption spectra of an aqueous solution containing TSC is shown in Fig.(6a) in which a peak is observed at 340 nm. A peak appears at 940 nm when Fe²⁺ (FeSO₄·7H₂O) is added. The peak at 796 nm indicates the decrease in intensity is due to the formation of TSC- Fe²⁺-Cu²⁺ complex in solution. This indicates the formation of complex between TSC and Cu²⁺.^[12-13]

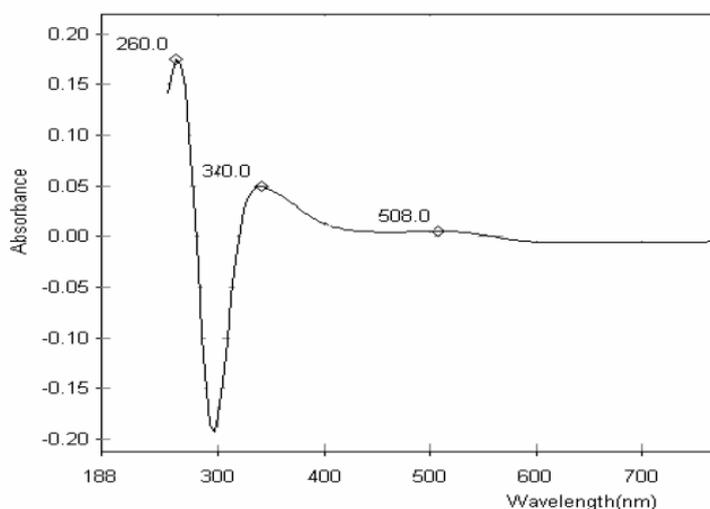


Fig.(6): UV absorption spectrum of solution containing.

a) TSC.

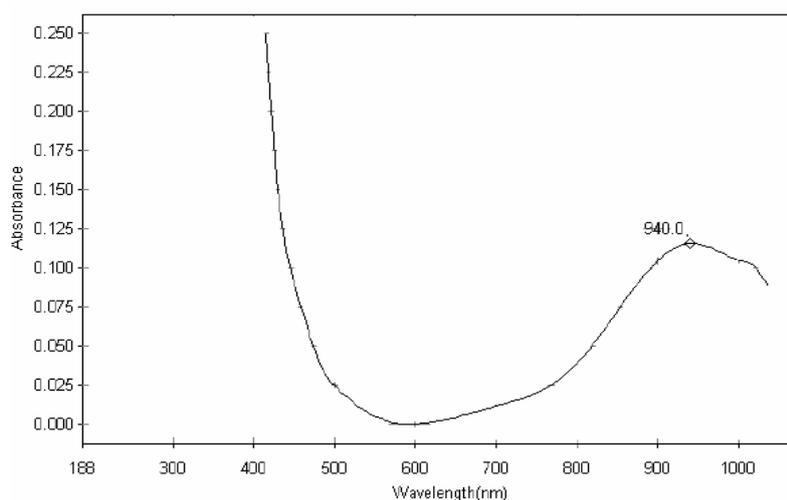


Fig. (6): UV absorption spectrum of solution containing.

b) TSC + Fe²⁺ complex in solution.

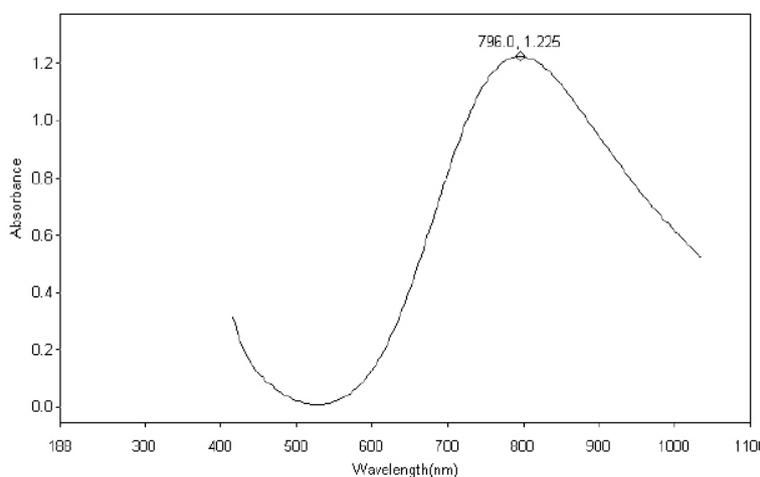


Fig. (6): UV absorption spectrum of solution containing.

c) TSC + Fe²⁺ + Cu²⁺ complex in solution.

Analysis of FTIR spectra

The protective film that has been formed on the metal surface was analyzed by the FTIR spectroscopy.^[14,15,16] The FTIR of the pure TC is shown in Fig.(7a). The stretching frequency obtained at 1647 cm⁻¹ indicates the presence of carboxylic group (>C=O). A peak observed at the stretching frequency 3432 cm⁻¹ indicates the presence of -OH group. The FTIR spectrum of the film that has been formed on the metal surface after immersed in the solution containing 250ppm of TSC and 50ppm of Copper is shown in Fig.(7b). It is observed that >C=O stretching frequency has shifted to lower frequency (1647 cm⁻¹ to 1641 cm⁻¹). Similarly the -OH stretching frequency shifted from 3432 cm⁻¹ to 3430 cm⁻¹. This indicates

that the oxygen atoms of the carboxyl group and $-OH$ have coordinated with Fe^{2+} resulting the formation of Fe^{2+} -TSC complex formed on the anodic sites of the metal surface. The peaks at 1077 cm^{-1} and 525 cm^{-1} are due to $Cu-O$ bond. The $-OH$ stretching frequency appears at 3430 cm^{-1} . These observation suggest that $Cu(OH)_2$ is formed on the cathodic sites of the metal surface.

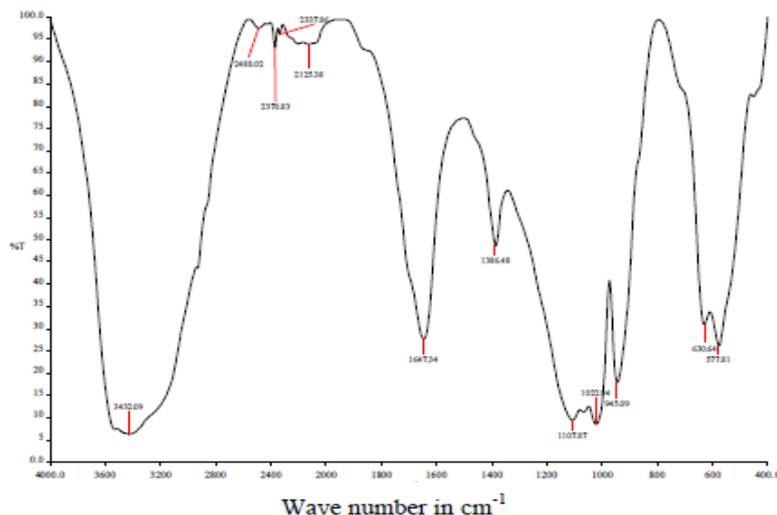


Fig. 7(a): FTIR spectra of pure TSC.

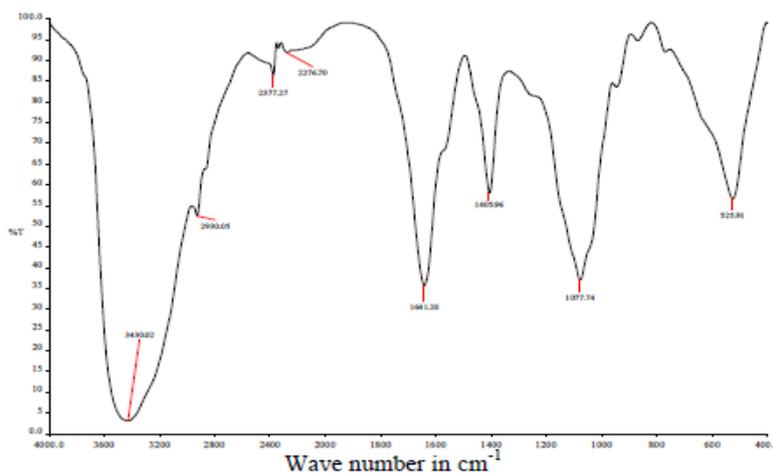


Fig. 7(b): FTIR spectra of pure TSC + Cu^{2+} .

SEM analysis of metal surface

SEM is a surface examination which provides a pictorial representation film formed on the surface. The protective film formed on the surface of the metal in the absence and presence and the corrosion extent of carbon steel were examined by the SEM micrographs. The SEM images of the carbon steel specimen with different magnification(X500/X1000) which were immersed in the well water for 3 days in the absence and presence of inhibitor system are

shown in Fig.8(a,b). Clearly shows the smooth surface of the metal which indicates the presence of the inhibitor complex as film on the surface. The SEM micrograph of carbon steel immersed in well water in figure shows the roughness of the metal surface indicates the highly corroded region of the metal surface. The SEM images of carbon steel immersed in blank is shown in Fig.8(c,d) and in the presence of the inhibitor 250ppm of TSC and 50ppm of Cu^{2+} ion is shown in Fig.8(e,f). The suppression of corrosion rate is confirmed by the decrease of corrosion area. Thus the formation of the insoluble complex $[\text{TSC-Cu}^{2+}]$ on the surface of the metal effectively controls the dissolution of carbon steel.

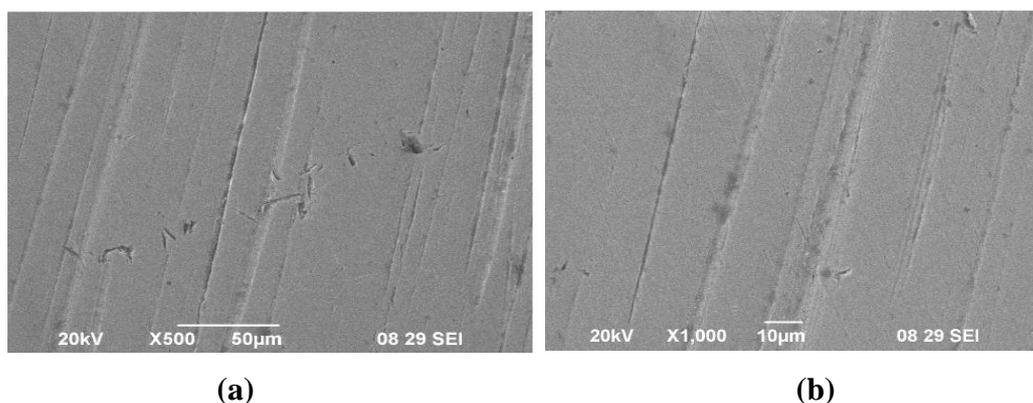
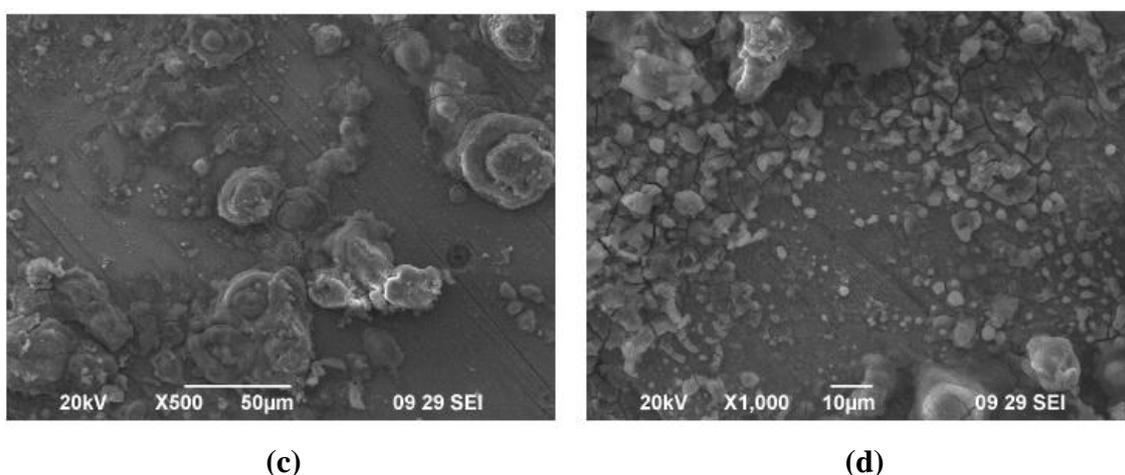


Fig. 8: SEM analysis of

(a) Carbon steel magnification X 500 (Control).

(b) Carbon steel magnification X 1000 (Control).



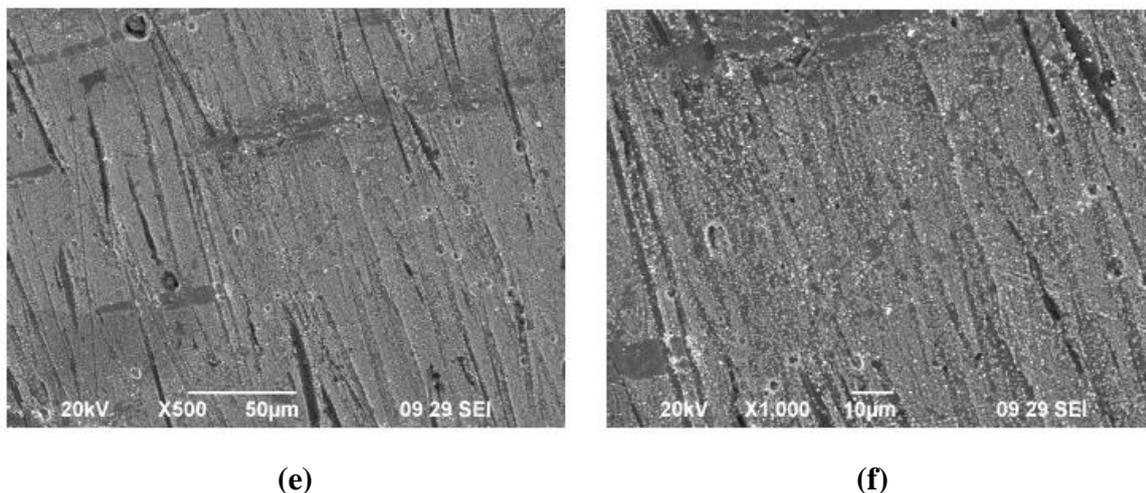


Fig. 8: SEM analysis of

- (c) Carbon steel immersed in well water, magnification X 500 (Blank).**
- (d) Carbon steel immersed in well water, magnification X 500 (Blank).**
- (e) Carbon steel immersed in well water + 250 ppm of TSC + 50 ppm of Cu^{2+} magnification X 500.**
- (f) Carbon steel immersed in well water + 250 ppm of TSC + 50 ppm of Cu^{2+} magnification X 1000.**

Atomic Force Microscopy Characterization

Atomic force microscopy is a technique used for the gathering of roughness statistics from a variety of surfaces.^[17-19] All the AFM images were obtained in VEECO lab incorporation. The AFM instrument was operated in the contact mode in air. The scan sizes of all the AFM images are 05m X 05m are as at a scan rate of 6.68m/second. The two dimensional (2D) and three dimensional(3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel (reference), carbon steel immersed in well water(blank sample) and the carbon steel surface immersed in well water containing 50ppm of TSC and 25ppm of Cu^{2+} are shown in Fig. (a, d, g), (b,e,h), (c,f,i) respectively.

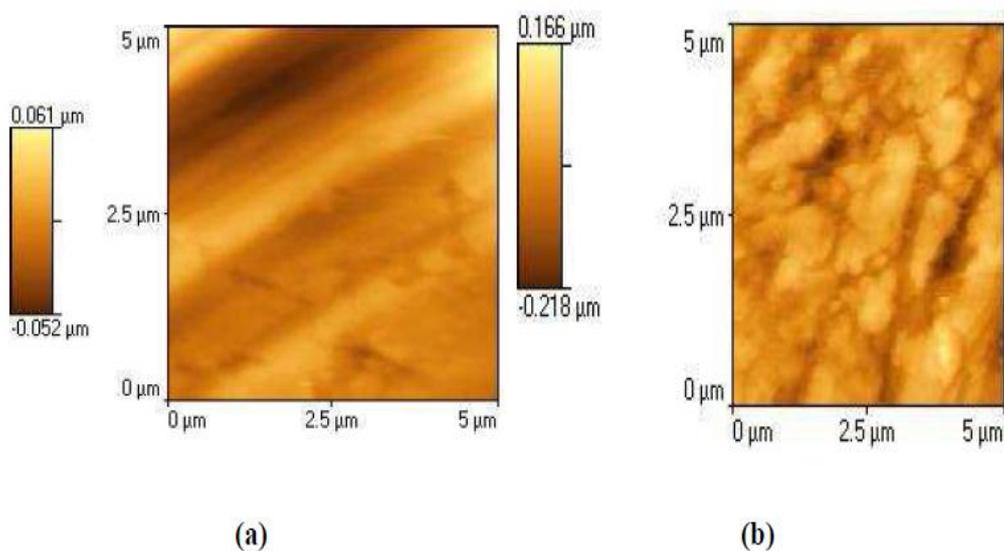
Root mean square roughness, average roughness, peak-to-valley value

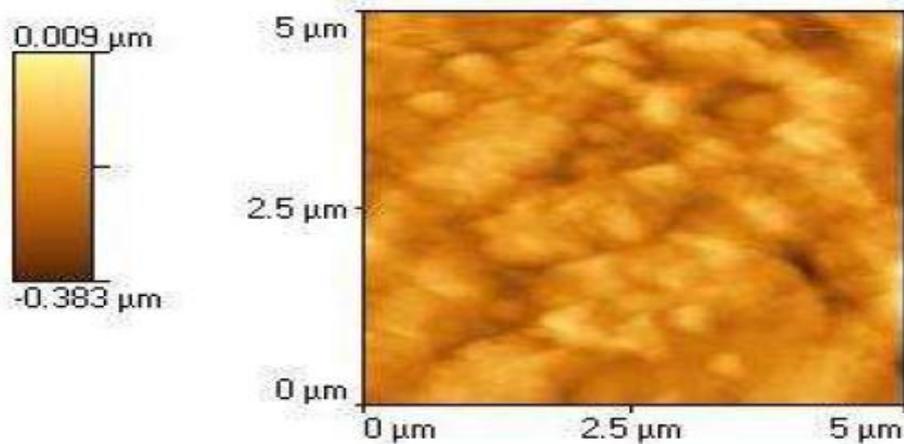
AFM image analysis is used to determine the average roughness R_a , root-mean-square roughness, R_q and the maximum peak-to-valley(p-v) height values.^[20] R_q is much more sensitive than R_a to large and small height deviations from the mean.^[21] Table-9 explains the average value of the above mentioned parameters for the carbon steel surface immersed in different environments. The value of R_{RMS} , R_a and p-v height for the polished carbon steel surface(reference sample) are 19.1 nm, 14.6 nm and 21.91 nm respectively, which shows

more homogeneous surface, with some places in where the height is lower than the average depth.^[22] Fig.9 (a,d,g) displays the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The rms roughness, average roughness and p-v height values for the carbon steel immersed in well water are 74.6 nm, 62 nm and 162.5 nm respectively. As the result, the carbon steel surface immersed in well water has a greater surface roughness than the polished metal surface. Fig. 9(b,e,h) shows the corroded metal surface with few pits. The formulation of 250 ppm of TSC and 50 ppm of Cu^{2+} in well water reduces the R_q by a factor of 46.2 nm from 74.6nm and the average roughness is significantly reduced to 37.3 nm when compared with 62 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also was reduced to 63.5 nm from 162.5 nm. Thus the surface is smoother and it is due to the formation of a protective film consisting of Fe^{2+} -TSC complex and $\text{Cu}(\text{OH})_2$ on the metal surface.^[23]

Table. 9: AFM data for carbon steel surface immersed in inhibited and uninhibited environments.

Samples	RMS (R_q) Roughness (nm)	Average (R_q) Roughness (nm)	Maximum peak to valley height (nm)
Polished carbon steel (Control)	19.1	14.6	21.91
Carbon steel immersed in well water (Blank)	74.6	62	162.5
Carbon steel immersed in well water containing TSC (250 ppm) + Cu^{2+} (50 ppm)	46.2	37.3	63.5





(c)

Fig. 9: 2D AFM Images of the surface of

- (a) Polished carbon steel (Control).
- (b) Carbon steel immersed in well water (Blank).
- (c) Carbon steel immersed in well water containing TSC (250 ppm) + Cu^{2+} (50 ppm).

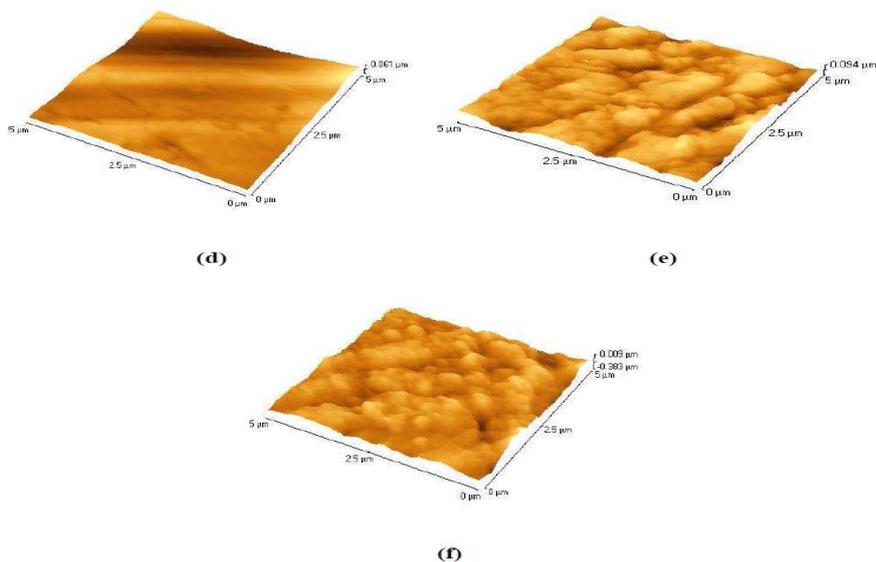


Fig. 9: 3D AFM Images of the surface of

- (d) Polished carbon steel (Control).
- (e) Carbon steel immersed in well water (Blank).
- (f) Carbon steel immersed in well water containing TSC (250 ppm) + Cu^{2+} (50 ppm).

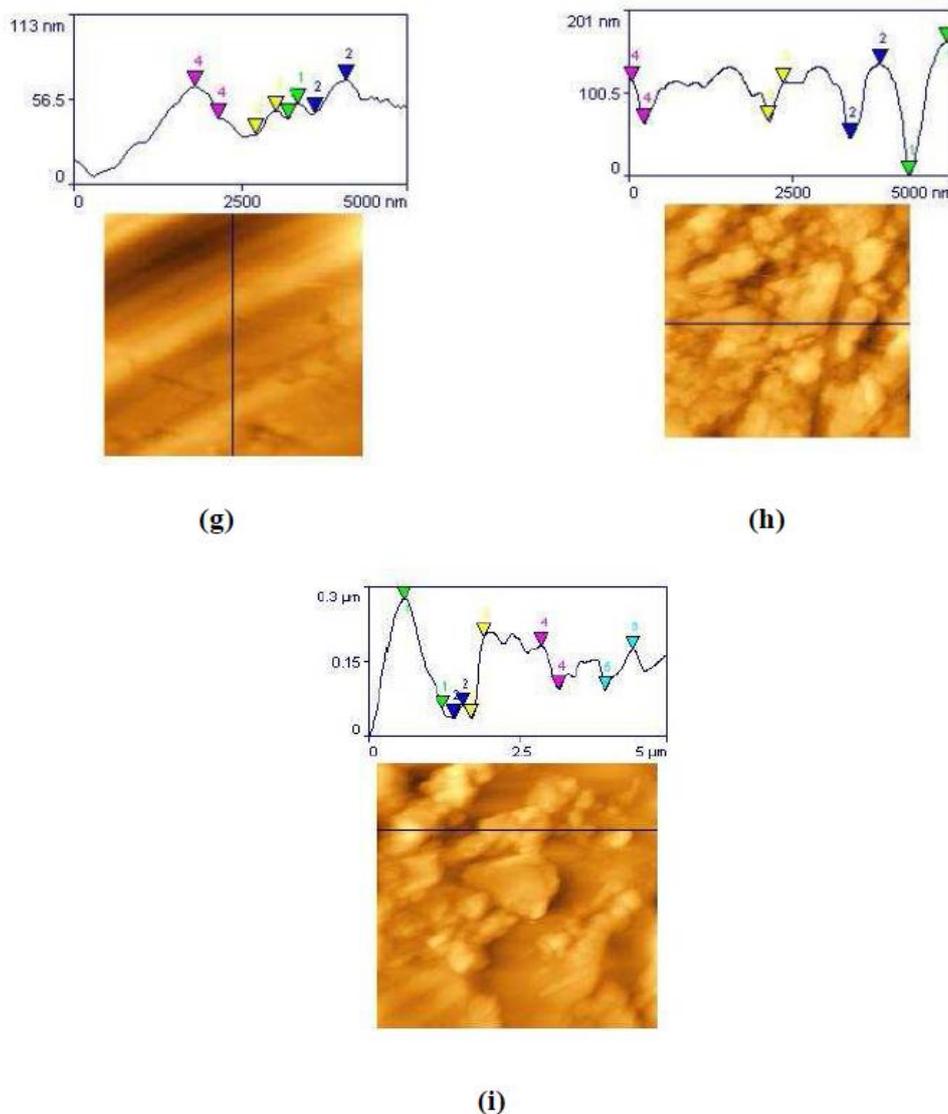


Fig.9: The cross section profile which are corresponding to as shown broken lines in AFM Images of the surface of

(g) Polished carbon steel (Control).

(h) Carbon steel immersed in well water (Blank).

(i) Carbon steel immersed in well water containing TSC (250 ppm) + Cu²⁺ (50 ppm).

CONCLUSION

The present work concludes that,

- The inhibition efficiency (IE) of Trisodium citrate (TSC)- Cu²⁺ system on controlling the corrosion of carbon steel in well water has been determined by weight loss method.
- The inhibitor system consisting of 50ppm of Cu²⁺ and 250ppm of TSC gives 86% of IE to carbon steel immersed in well water.

- Polarisation study reveals that the TSC-Cu²⁺ system controls the cathodic reaction predominantly.
- AC impedance spectra reveals the formation of the protective film on the metal surface.
- UV-Visible and FTIR spectra reveals that the protective film consists of TSC-Fe²⁺ complex and Cu(OH)₂.
- The SEM micrographs and AFM images confirms the formation of protective layer consists of TSC-Fe²⁺ complex and Cu(OH)₂ on the metal surface.

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