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Influence of Al^{3+} on Corrosion Inhibition of Trisodium Citrate

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Abstract: The inhibition efficiency of trisodium citrate (TSC) in controlling corrosion of carbon steel immersed in well water in the absence of Al^{3+} has been evaluated by weight loss method. In presence of Al^{3+} Corrosion inhibition efficiency of TSC increases. A synergistic effect in observed between TSC and Al^{3+}. This effect is more pronounced in presence of 50 ppm of Al^{3+} than in presence of 25 ppm of Al^{3+} .This is supported by synergism parameter values. Polarization study reveals that TSC-Al^{3+} system control the cathodic reaction predominantly. It also indicates that formation of a protective film on a metal surface. The protective film has been analysed by FTIR spectra. FTIR spectra reveal that the protection film consists of Fe^{2+} - TSC complex, Al^{3+} -TSC complex and Al $(OH)_3$.

Keywords: Corrosion, Trisodium Citrate, Aluminium, carbon steel, well water.

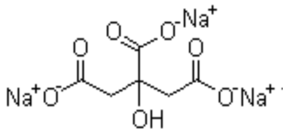
INTRODUCTION

Corrosion of a metal is a natural, spontaneous and thermodynamically favourable process. It is the expression of desire of the metal to go back its original state of ore. There are several methods to control the corrosion of metals. One such method is the use of corrosion inhibitors such as zinc salts[1,2], molybtadate[3,4], amines[5,6], phosphates[7,8] and extracts of natural products[9-15] have been used to control corrosion of metals. The present work is undertaken (i) to investigate the influence of Al^{3+} on the corrosion inhibition efficiency of Trisodium citrate (TSC) in controlling corrosion of carbon steel immersed in well water. The present work in undertaken

- To study the mechanistic aspects of corrosion inhibition by polarization study
- To analyse the protection film by FTIR spectra

EXPERIMENTAL

Metal specimens: Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, and 0.1 C 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 **scheme 1**.



Scheme-1: Structure of trisodium citrate

The inhibition efficiency of TSC-Al^{3+} system in controlling corrosion of mild steel in well water **(Table 1**) has been evaluated.

Table-1: Parameters of well water

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

Weight –Loss Method: Mild steel specimens in triplicate were immersed in 100 ml of well water containing various concentration of TSC in the presence and absence of Al^{3+} for three days. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution.The inhibition efficiency (IE,%) was then calculated using the equation: Corrosion

$$I.E = 100[1-(W_2/W_1)]\ \%$$

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 660A. A three-electrode cell assembly was used. The working electrode was mild steel. 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 Tafelslopes (anodic = b_a and cathodic = b_c) and Linear polarization resistance (LPR) were calculate.

Surface examination 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 surface of the metal specimens was analysed for surface analysis technique by FTIR spectra.

FTIR Spectra:FTIR spectra were recorded in a Perkin – Elmer1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

RESULTS AND DISCUSSION

Analysis of Results of Weight loss method: Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor trisodium citrate (TSC) are given in **Tables 2 to 4.** The inhibition efficiencies (IE) are also given in these tables. It is observed from **Table 2** that TSC shows some inhibition efficiencies. 50 ppm TSC has 13 percent IE. As the concentration of TSC increases, the IE increases. This is due to the fact that as the concentration of TSC increases, the protective film (probably iron TSC complex) formed on the metal surface is strengthened. More TSC is adsorbed on the metal surface.

Table-2: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.

TSC ppm	Al^{3+} 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

Inhibitor system: TSC-Al^{3+} (0 ppm)
Immersion period: 3 days

Influence of Al^{3+} on the inhibition efficiencies of TSC: Influence of Al^{3+} on the inhibition efficiencies of TSC is given in **Tables 3 and 4.**When 25 ppm of Al^{3+} is added, 50 ppm of TSC offers a maximum inhibition efficiency of 45%. But as the concentration of TSC increases, IE decreases. This is due to the fact, TSC combines with Al^{3+} and Al^{3+} TSC complex is precipitated in the bulk of the solution. TSC is not transported towards the metal surface. Hence the inhibition efficiency decreases. Similar observation is made when 50 ppm of Al^{3+} is added, however the formulation consisting of 50 ppm TSC and 50 ppm of Al^{3+} offers 85% IE, further addition of TSC lowers the IE of 85% to 61%.This is due to the precipitation as Al-TSC complex in the bulk of the solution. Similar observation has been made by Johnsirni et al while studying the inhibition efficiency of the - Zn^{2+} system[16]. The formulation consisting of 50 ppm Al^{3+} and 50 ppm of TSC offers 85%IE. A synergistic effect exists. In presence of Al^{3+} more amount of TSC is transported towards the metal surface.

Table-3: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.

TSC ppm	Al^{3+} ppm	CR mdd	IE %
0	25	22.20	10
50	25	13.57	45
100	25	17.27	30
150	25	17.77	28
200	25	18.50	25
250	25	20.97	15

Inhibitor system: TSC - Al^{3+} (25 ppm)
Immersion period: 3 days

Table-4: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method.

TSC ppm	Al^{3+} ppm	CR mdd	IE %
0	50	24.67	15
50	50	37	85
100	50	4.93	80
150	50	6.41	74
200	50	7.15	71
250	50	9.62	61

Inhibitor system: TSC - Al^{3+} (50ppm)
Immersion period: 3 days

On the metal surface Fe- TSC complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH. This is controlled by the formation of $Al(OH)_3$ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Al^{3+} and TSC.

$$Fe \longrightarrow Fe^{2+} + 2e \text{ (Anodic reaction)}$$

$$Fe^{2+} + Al^{3+} \text{ - TSC complex} \longrightarrow Fe^{2+} \text{ - TSC complex} + Al^{3+}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4\,OH^- \text{ (Cathodic reaction)}$$

$$Al^{3+} + 3OH^- \longrightarrow Al(OH)_3\downarrow$$

The formulation of Al-TSC complex on the metal surface cannot be ruled out. Thus the protective film consists of Fe-TSC complex, Al – TSC complex and $Al(OH)_3$.

Table - 5: Inhibition efficiencies and synergism parameters for various concentrations of TSC -Al^{3+} (25 ppm) system, when carbon steel is immersed in well water.

TSC ppm	Inhibition efficiency IE(%)	IE / 100 Surface Coverage θ_1	Al^{3+} 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	45	0.45	1.39
100	20	0.20	25	10	0.10	30	0.30	1.03
150	25	0.25	25	10	0.10	28	0.28	0.94
200	26	0.26	25	10	0.10	25	0.25	0.88
250	30	0.30	25	10	0.10	15	0.15	0.06

Immersion period: 3days

Table - 6: Inhibition efficiencies and synergism parameters for various concentrations of TSC –Al^{3+} (50 ppm) system, when carbon steel is immersed in well water.

TSC ppm	**Inhibition efficiency IE (%)**	**IE / 100 Surface Coverage θ_1**	**Al^{3+} 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	85	0.85	4.93
100	20	0.20	50	15	0.15	80	0.80	3.4
150	25	0.25	50	15	0.15	74	0.74	2.45
200	26	0.26	50	15	0.15	71	0.71	2.16
250	30	0.30	50	15	0.15	61	0.61	1.53

Immersion period: 3 days

Synergism parameters (S_I): Synergism parameters (S_I) have been used to know the synergistic effect existing between two inhibitors [17-21]. Synergism parameters (S_I) can be calculated using the following relationship. Synergism parameters (S_I)= $\frac{1-\theta_{1-2}}{1-\theta_{1-2}}$ Where

$\theta_{1+2} = (\theta_1+\theta_2)-(\theta_1\theta_2)$
θ_1 = Surface coverage by TSC
θ_2 = Surface coverage by Al^{3+}

θ'_{1+2} = Surface coverage by both TSC and Al^{3+} Where θ = Surface coverage = $\frac{IE\%}{100}$

The synergism parameters of TSC – Al^{3+} system are given in **Tables 5 and 6,** 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 5 and 6,** 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 exist between TSC and Al^{3+}. Thus, the enhancement of the inhibition efficiency caused by the addition of Al^{3+} ions to TSC is due to the synergistic effect. It is observed that the synergistic effect is more pronounced in the case of 50 ppm of Al^{3+} than in the case of 25 ppm Al^{3+}.

Analysis of potentiodynamic polarization study: Polarization study has been used to know if a protective film is formed on the metal surface. If a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and corrosion current decreases [22-26].

The potentiodynamic polarization curves of mild steel immersed in various test solutions are shown in **Figure 1**.The corrosion parameters namely, corrosion potential (E_{corr}), Tafelslopes (b_c= cathodic,b_a =anodic), linear polarization resistance (*LPR*) and corrosion current (I_{corr}) are given in **Table.7.** When mild steel is immersed in well water the corrosion potential is -630 mV vs SCE. The *LPR* value is 7799.9 ohmcm^2. The corrosion current is 5.537x10^{-6} Acm^{-2}. When inhibitors (TSC50 ppm +Al^{3+} 50 ppm) are introduced into the system, the *LPR* value increases tremendously from 7799.9 to 19902 ohm cm^2. Increases in LPR value is an indication of formation of protective film formed on the metal surface .This is also supported that by the fact that there is a sharp decrease in the corrosion current value, the corrosion current decreases from 5.537x10^{-6} A cm^{-2} to 2.058x10^{-6} A cm^{-2}. It is observed that the corrosion potential has shifted to the cathodic side (-630 to -662mV vs SCE), in presence of inhibitors. This suggests that the cathodic reaction is controlled predominantly in presence of inhibitor system. The LPR value increases from 7799.9 ohm cm^2 to 19902 ohm cm^2; the corrosion current decreases from 5.537x10^{-6} A/cm^2 to 2.058x10^{-6} A/cm^2. Thus polarization study confirms the formation of a protective film on the metal surface.

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} mV vs SCE	b_c mV /decade	b_a mV/decade	I_{corr} A/cm^2	LPR ohm cm^2
Well water	-630	203	194	5.537X10^{-6}	7799.9
Well water TSC (50ppm) + Al^{3+} (50 ppm)	-662	194	182	2.058x10^{-6}	19902

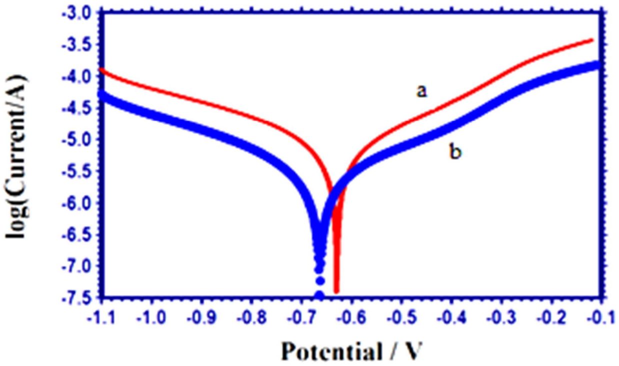


Figure.1: Polarization curves of mild steel immersed in various test solutions (a) Well water (blank) (b) well water + TSC (50ppm) + Al^{3+}(50ppm)

Analysis of FTIR spectra: FTIR spectroscopy has been used to analyse the protective film formed on the metal surface [27-29].The FTIR spectrum of pure TSC is shown in **Figure 2(a).** The >C=O stretching frequency of the carboxyl group appears that 1647cm^{-1}. The -OH stretching frequency appears that 3432 cm^{-1}. The FTIR spectrum of the film formed on mild steel surface after immersion in the solution containing 50 ppm of TSC and 50 ppm of Al^{3+} is shown in **Figure.2 (b).** It is observed that the >C=O stretching frequency has shifted from 1647cm^{-1} to 1625 cm^{-1}. The -OH stretching frequency shifted from 3432 cm^{-1} to 3424 cm^{-1}.This indicates that the oxygen atoms of the carboxyl group and -OH have coordinate with Fe^{2+} resulting in the formation of Fe^{2+}-TSC complex formed on the anodic sites of the metal surface. The peaks at 1433 cm^{-1} and 618cm^{-1} are due to Al-O bond. The –OH stretching frequency appears at 3424cm^{-1}.These observation suggest that Al $(OH)_3$ is formed on the cathodic sites of the metal surface. Similar observation has been made by Manivannan et al while studying the Succinic- Zn^{2+} system is controlling corrosion of carbon steel in sea water. The protective film consisted of Fe^{2+} - Succinic acid complex and Zn $(OH)_2$ [30].

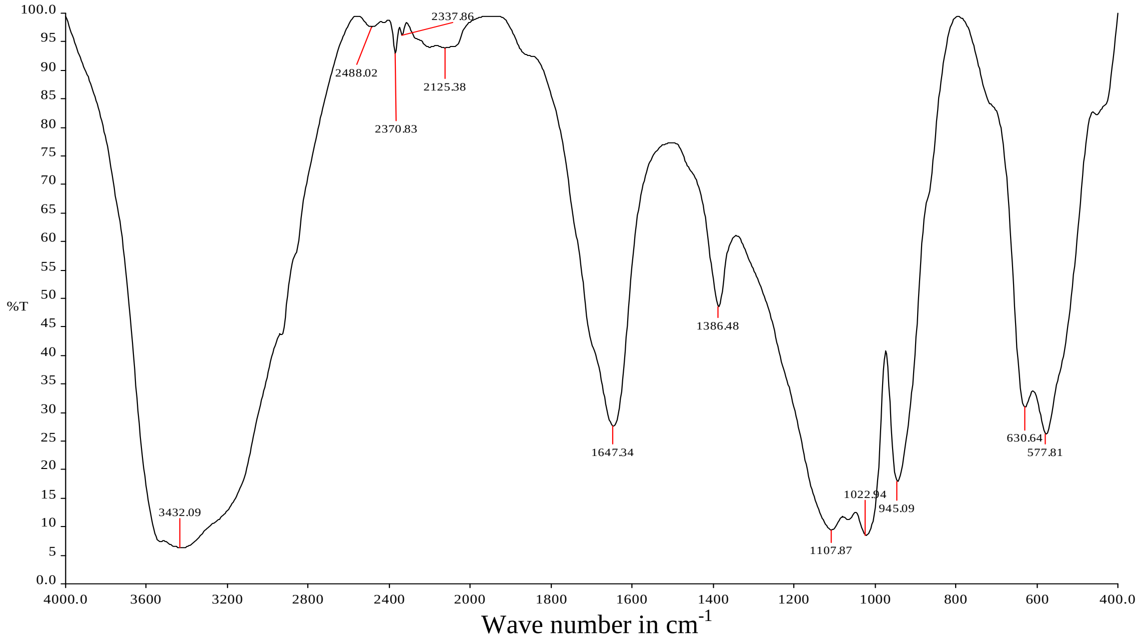


Figure.2 (a): FTIR spectra of Pure TSC

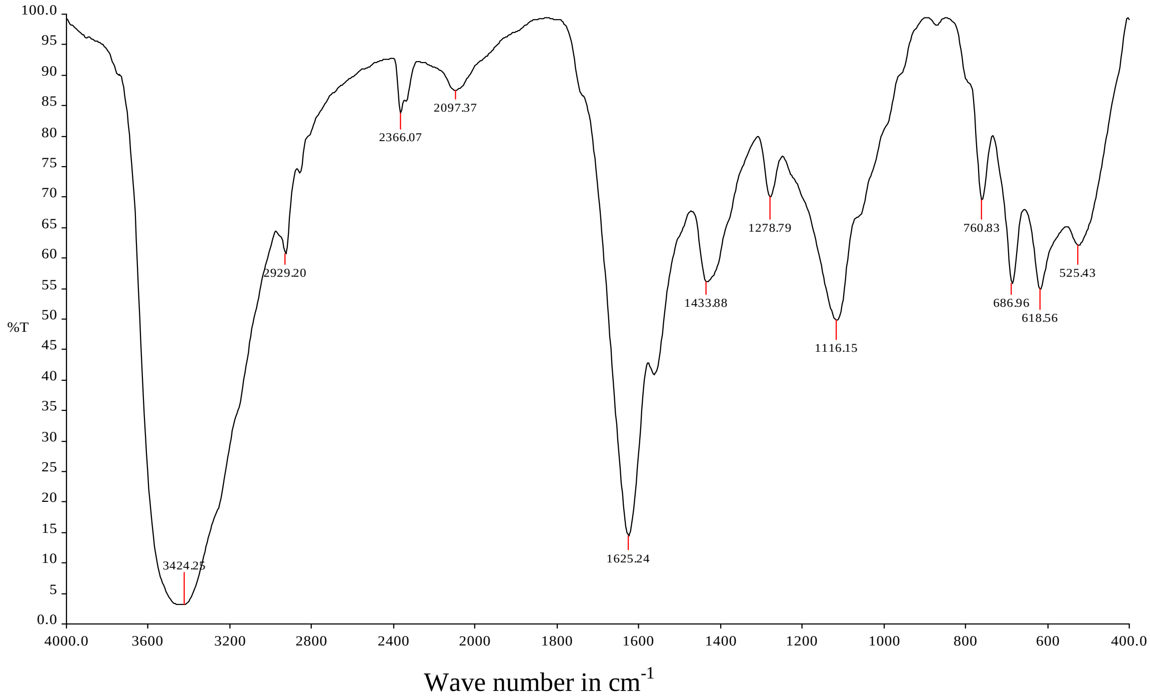


Figure.2 (b): Film formed on the metal surface after immersion in solution containing 50 ppm of TSC and 50 ppm Al^{3+}

CONCLUSIONS

The present study leads to the following conclusions:

- The inhibition efficiency (IE) of trisodium citrate(TSC)- Al^{3+} system is Controlling corrosion of Carbon steel in well water has been evaluated by weight loss method.
- The formulation consisting of 50 ppm of TSC and 50 ppm of Al^{3+} offers 85% IE to Carbon steel immersed in well water.
- Polarization study reveals that TSC –Al^{3+} system controls the cathodic reaction predominantly.
- FTIR spectra reveal that the protective film consists of TSC-Fe^{2+} complex and $Zn(OH)_2$.

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