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Journal of Chemical and Pharmaceutical Research, 2015, 7(10S):133-140

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Influence of malic acid-Zn^{2+} system on inhibition of corrosion of mild steel in simulated concrete pore solution prepared in well water

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ABSTRACT

The inhibition efficiency (IE) of Malic acid -Zn^{2+} system in controlling corrosion of mild steel in Simulated Concrete Pore Solution (SCPS) prepared in well water in the absence and presence of Zn^{2+} has been investigated by weight loss study. It is observed that the formulation consisting of 250 ppm of Malic acid and 50 ppm of Zn^{2+}provides 81% of inhibition efficiency. Inhibition was found to increases with an increasing concentration of Zn^{2+}. Polarization study confirms the formation of a protective film on the metal surface. AC impedance spectra also revealed that a protective film formed on the metal surface. The results obtained show that the Malic acid could serve as an effective inhibitor for the corrosion of mild steel in Simulated Concrete Pore Solution.

Key words: Concrete Corrosion, Simulated Concrete Pore Solution, Mild Steel, Malic acid, Well water.

INTRODUCTION

It is generally accepted that concrete is one of the most widely used engineering materials for constructions, and its durability is the major problem affecting the service life of the engineering structures. Corrosion of the steel reinforcement is one of the main reasons causing the premature deterioration of reinforced concrete [1-3] and leading to a significant economic loss.

Reinforced concrete is a versatile, economical and successful construction material. It is durable and strong, performing well throughout its service life. Conventional black steel reinforcements embedded in concrete are passive due to a protective, very thin oxide layer (about 10 nm) [2]that is formed on its surface in high alkaline media such as that the contained in the pores of the concrete (pH about 12.6) [4]. So, many authors have carried out the studies on steel corrosion in simulated concrete solution [56].Although the study is carried in the simulated solution, the results are still significant for the concrete. The simulated solution can not only reproduce the chemical environment in concrete but also shorten the experiment period. A saturated $Ca(OH)_2$ solution and a solution containing KOH, NaOH and $Ca(OH)_2$ are the most familiar solutions to simulate the alkalinity environment of the concrete pore solution [7].

In the present work, simulated concrete pore solution of $Ca(OH)_2$ is used. The study was conducted to examine the influence of Malic acid and Zn^{2+} ions on the corrosion resistance of mild steel immersed in SCPS prepared in well water. Corrosion resistance was measured by Weight loss method, polarization study, AC impedance spectra. The protective film was analyses by FTIR spectra.

EXPERIMENTAL SECTION

2.1 Preparation of simulated concrete pore solution (SCPS)

Simulated concrete pore solution is mainly consisted of Saturated $Ca(OH)_2$,KOH, NaOH with the pH-13.5 [8,9]. However in numerous studies of rebar corrosion saturated $Ca(OH)_2$ has been used a substitute for pore solution saturated calcium hydroxide solution is used in present study, as SCP solution with the pH-12.5.

2.2 Preparation of the specimens

Mild steel specimen was used in the present study. (Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2cm were polished to a mirror finish and degreased with acetone and used for the weight-loss method and surface examination studies. The environment chosen is well water and the physic-chemical parameter of well water is given in table 1.

Table–1 :Physico- Chemical Parameters of Well Water

PARAMETERS	VALUE
pH	8.38
Conductivity	$1770\mu\Omega^{-1}$cm-^{1}
Chloride	665 ppm
Sulphate	214 ppm
TDS	1100 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

2.3 Determination of Corrosion Rate

The weighed specimens in triplicate were suspended by means of glass hooks in 100ml SCPS prepared in well water containing various concentration of Malic acid in the presence and absence of Zn^{2+} for one day. The specimen were taken out, washed in running water, dried, and weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship:

CR = [(Weight loss in mg) / (Area of the specimens in dm^2 ×Immersion periods in days)] mdd. (1)

Corrosion inhibition efficiency (IE, %) was then calculated using the equation:

$I.E = 100[1-(W_2/W_1)]$ % (2)

Where, W_1 = corrosion rate in the absence of the inhibitor, and W_2 = corrosion rate in the presence of the inhibitor.

2.4 Potentiodynamic Polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three electrode assembly is shown in Fig-1. 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 Tafel slopes (anodic = *b*a and cathodic =*b*c) and Linear polarization resistance (*LPR*) were calculated. The scan rate *(V/S)* was 0.01.Hold time at (Efcs) was zero and quit time(s) was two.

2.5 AC impedance spectra

AC impedance spectral 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. The real part (Z’) and imaginary part (Z”) of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculate.

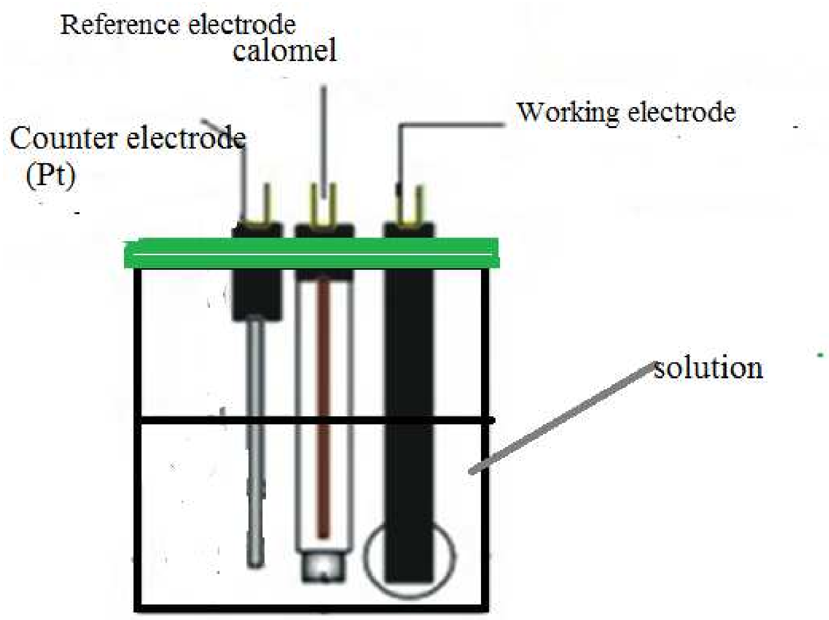

Figure-1 **Circuit diagram of three- electrode cell assembly**

2.6 Fourier Transform Infrared Spectra

These spectra were recorded in a Perkin-Elmer -1600 spectrometer using KBr pellet. The spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

RESULTS AND DISCUSSION

3.1 Analysis of Weight loss Study

Corrosion rates (CR) of carbon steel immersed in SCPS prepared in well water the absence and presence of inhibitors (Malic acid and Zn^{2+} system). The calculated corrosion inhibition efficiency (IE) and corrosion rates (CR) of citric acid in controlling corrosion of SCPS in well water, for a period of one day in absence and presence of zinc ion are given in Table 1.It is observed from the Table 2 that Malic acid is a good inhibitor. The IE is found to be enhanced in the presence of Zn^{2+} ion. Malic acid alone shows some inhibition efficiencies. The formulation consisting of 250 ppm of Malic acid and 50 ppm of Zn^{2+} shows 81% of inhibition efficiency. Weight loss study reveals that citric acid and Zn^{2+} individually showed some IE, but exhibited better IE when applied in combination. This suggests that CA and Zn^{2+} exhibit synergistic behavior [10-13].

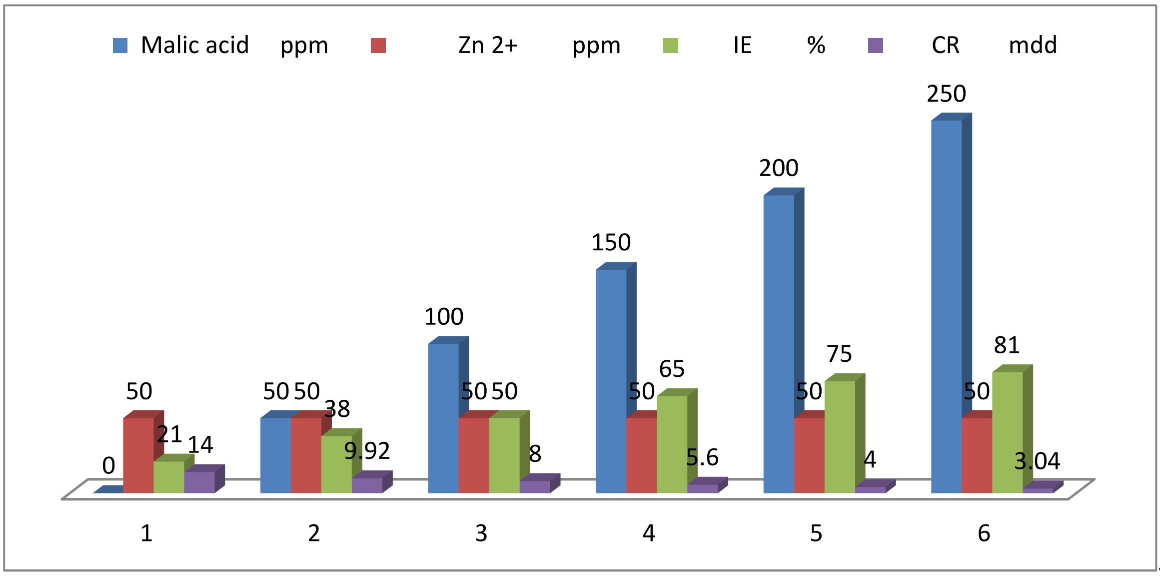

Figure 2 **Effect of Malic acid+50ppm Zn^{2+} system**

Table 2:Corrosion rates (*CR*) of mild steel immersed in Simulated Concrete Pore Solution (SCPS) prepared in well water in the presence and absence of Malic acid Zn^{2+} in the inhibition efficiency (IE) obtained by weight loss method

Malic Acid (ppm)	Zn^{2+} (ppm)					
	0		25		50	
	IE %	CR mdd	IE %	CR mdd	IE %	CR mdd
0	-	16	17	13.2	21	14.0
50	12	14.08	31	11.04	38	9.92
100	19	12.96	38	9.92	50	8.00
150	25	12.00	40	9.60	65	5.60
200	31	11.04	63	5.92	75	4.00
250	44	8.96	39	4.96	81	3.04

3.2 Analysis of Polarization Curves

When mild steel is immersed in simulated concrete pore solution prepared in well water the corrosion potential was -842 mV vs SCE (saturated calomel electrode). When Malic acid (250 ppm) and Zn $^{2+}$(50 ppm) were added to the above system the corrosion potential shifted to the anodic side -835 mV vs SCE; that is noble side. This indicates that the MA- Zn^{2+} system controls anodic reaction predominantly. This indicates that the passive film is formed on the metal surface in presence of inhibitor. The shifting of corrosion potential towards anodic side in presence of inhibitors has been reported by several researchers [13-17].

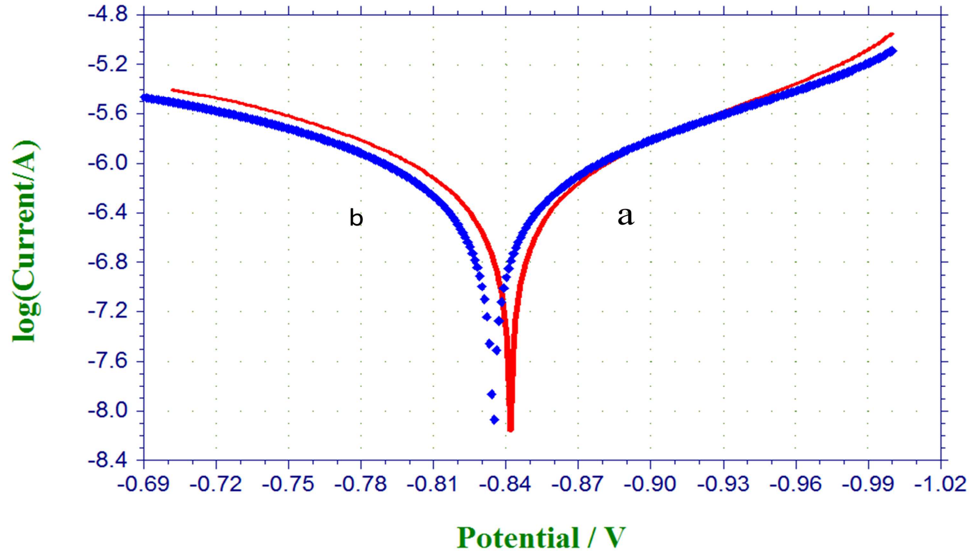

***Figure 3*:Polarization curves of mild steel immersed in various test solution**
a) SCPS b) Malic acid 250 ppm+ Zn^{2+} 50 ppm

Table-3 Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from Potentiodynamic Polarization Study

System	E_{corr} mVvs SCE	b_c mV/decade	b_a mV/decade	LPR Ohm cm^2	I_{corr} A/cm^2
SCPS	-842	131	145	41473	$7.237x10^{-7}$
SCPS+Malicacid 250ppm+zn^{2+} 50ppm	-835	149	167	45428	$6.530x10^{-7}$

Further, the *LPR* value increases from 41473 ohm cm^2 to 45428 ohm cm^2; the corrosion current decreases from $7.237x10^{-7}$A/cm^2 to $6.530x10^{-7}$A/cm^2 .When a passive film formed on mild steel surface, in presence of inhibitor system the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

3.3 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 decreases and the impedance log (z/ohm) value increases[19-23]. The AC impedance spectra of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitors (MA- $Zn^{2+)}$ are shown in Fig 4. (Nyquist plots) and Figures 4 and 5. (Bode plots). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in table 4.The impedance log (z/ohm) values derived from Bode plots are also given in table 4.

Table-4 Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from AC impedance spectra

System	Nyquist plot		Bode plot
	R_t, Ohm cm^2	C_{dl} F/cm^2	Impedance value log z/ohm
SCPS	566	$9.013x10^{-9}$	2.86
SCPS+Malicacid250ppm+Zn^{2+} 50ppm	1162	$4.388x10^{-9}$	3.16

It is observed that when the inhibitors Malic acid (250ppm) + Zn^{2+} (50 ppm) are added to SCPS the charge transfer resistance (R_t) increases from 566 ohm cm^2 to1162 ohm cm^2. The C_{dl} value decreases from 9.013x 10^{-9} F /cm^2 to 4.388 x 10^{-9} F /cm^2. The impedance values [log (z/ohm)] increases from 2.86 Z/ohm to 3.16 Z/ohm. These results lead to the conclusion that a protective film is formed on the metal surface.

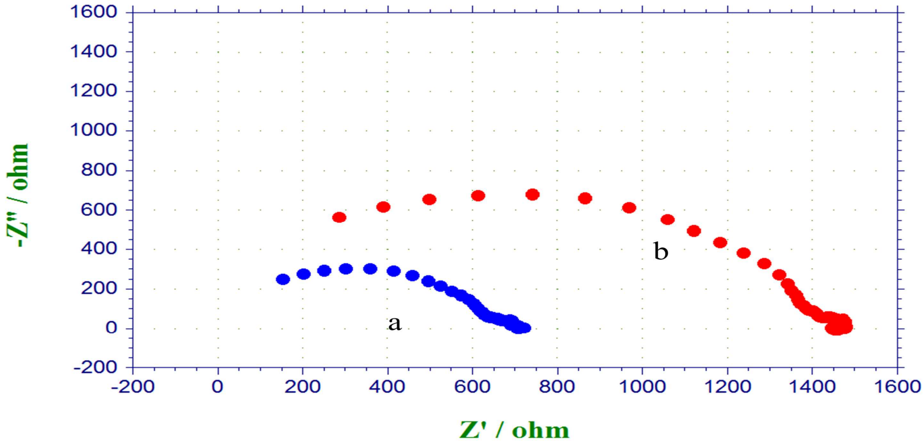

***Figure 4*:AC Impendence curves of mild steel immersed in various test solution (Nyquist plots)**
a) SCPS b) SCPS +Malic acid 250 ppm+ Zn^{2+} 50 ppm

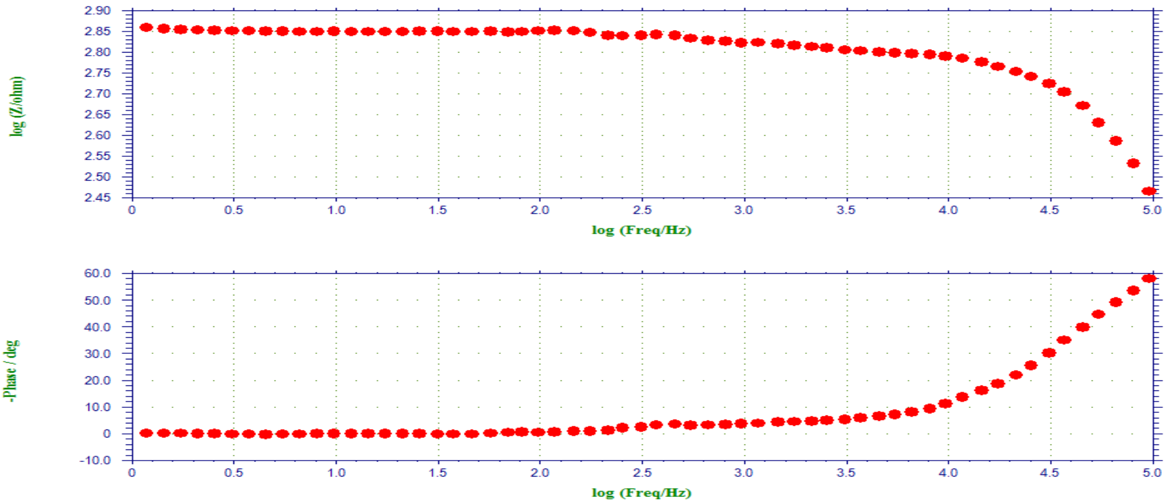

***Figure 5(a):*AC impendance spectra of mild steel immersed in SCPS(Bode plots)**

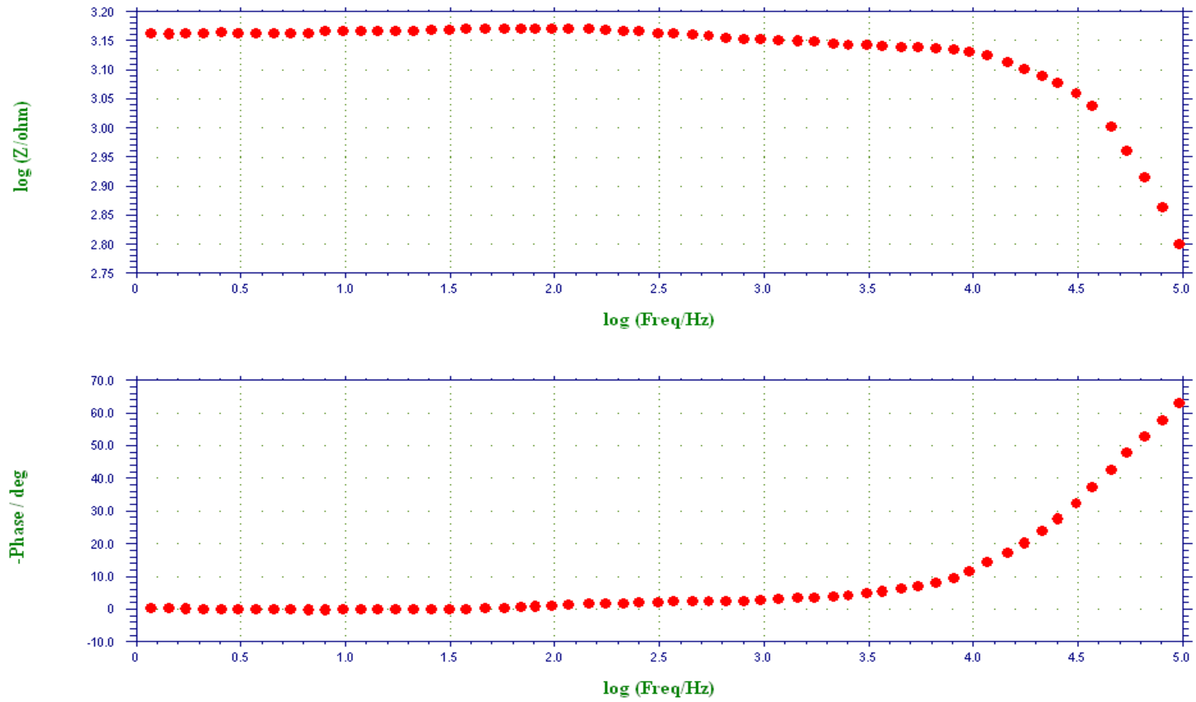

Figure 5(b):**AC impendance spectrum of mild steel immersed in SCPS+ 250 ppm Malic acid+50ppm Zn^{2+} system (Bode plots).**

3.4 Analysis of FTIR spectra

The FTIR spectra were used to analyze the inhibitor film formed on mild steel.The FTIR spectrum of the pure Malic acid (Fig 6 a) is compared with the FTIR spectrum of film formed on the metal surface after immersion in SCPS prepared in well water containing 250 ppm of Malic acid and 50 ppm of Zn^{2+} (Fig6b) .The results showed that the OH stretching frequency of pure Malic acid appears at 3122cm^{-1} where as in the SCPS containing 250 ppm of Malic acid and 50 ppm of Zn^{2+} system, the stretching frequency has shifted from 3122 cm^{-1} to 3630 cm^{-1}. In case of C=O, the stretching frequency which appeared at 1603 cm^{-1} for Malic acid has disappeared for the SCPS system containing 250 ppm of Malic acid and 50 ppm of Zn^{2+} system. This confirms that the oxygen atom of carboxyl group has coordinated with Fe^{2+} resulting in the formation of Fe^{2+} -Malic acid complex formed on the metal surface. And also, the peak appearing at 1566, 1324 and 816 cm^{-1} confirmed the presence of calcium carbonate, calcium oxide and calcium hydroxide formed on the metal surface.[24-30].

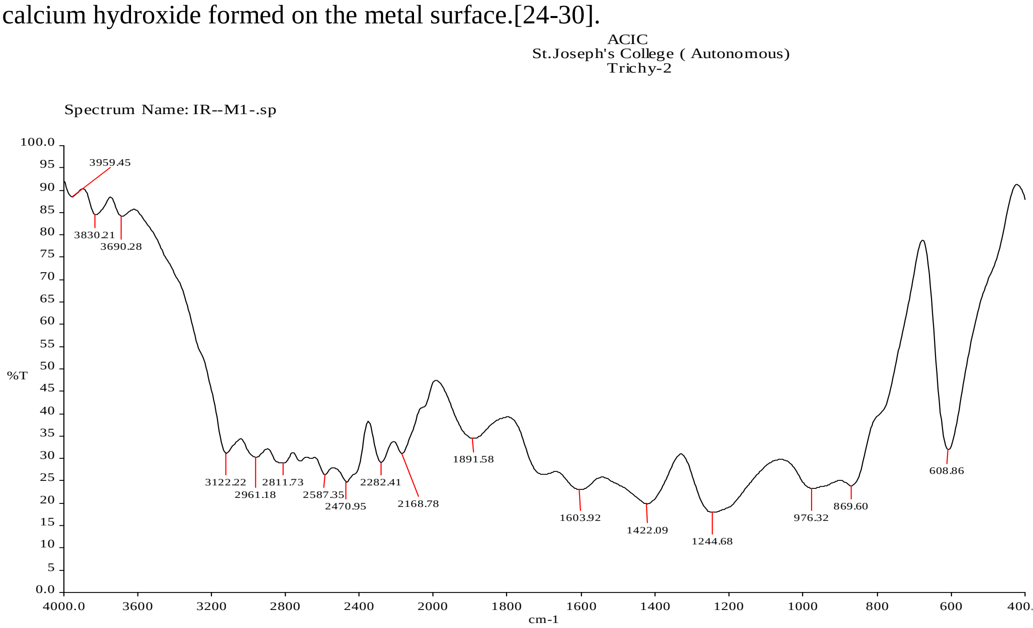

Figure 6(a): **FTIR spectrum of Pure Malic acid**

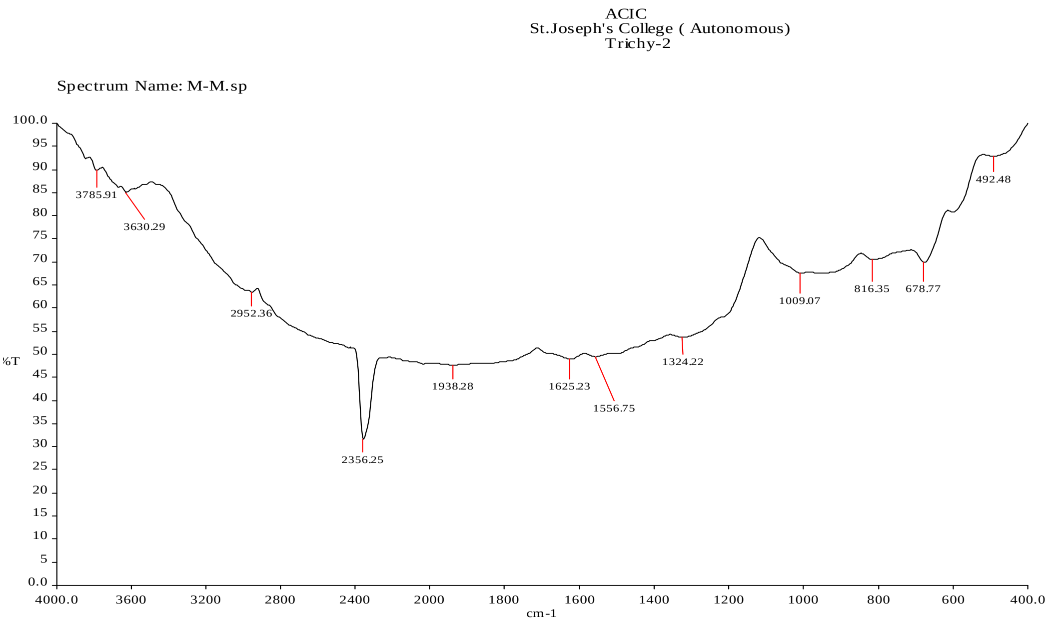

Figure 6(b) **:FTIR spectrum of inhibitor film formed on the mild steel after immersion in SCPS prepared in well water containing of 250 ppm Malic acid and 50 ppm of Zn^{2+}**

CONCLUSION

The present study leads to the following conclusions:
i. The formulation consisting of 250ppm of Malic acid and 50 ppm of Zn^{2+} offers 81% IE to mild steel immersed in simulated concrete pore solution prepared in well water.
ii. Polarization study reveals that Malic acid system controls the anodic reaction predominantly.
iii. AC impedance spectra reveal that the formation of protective film on the metal surface.
v. FTIR spectra reveals that the inhibitive film consists of Fe^{2+}-Malic acid complex, calcium carbonate, calcium oxide and calcium hydroxide.

Acknowledgement
The authors are thankful to their respective management and University Grants Commission, New Delhi

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