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Synergistic effect of Fructose and Zn²⁺ in controlling corrosion of carbon steel

The inhibition efficiency of fructose (FR)-Zn²⁺ system in controlling corrosion of carbon steel in an aqueous environment has been evaluated by mass-loss method. The synergistic effect is noticed between fructose and Zn²⁺. The formulation consisting of 125 ppm of fructose and 50 ppm of Zn²⁺ shows 84% inhibition efficiency (IE). At lower and higher pH value IE decreases. Polarisation study reveals that FR-Zn²⁺ system functions as a mixed inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra, UV absorption spectra and SEM studies have been used to investigate into the nature of the thin protective film formed on the metal surface. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from mass loss study and surface analysis technique.

Key words: Corrosion inhibition, carbon steel, river water, synergistic effect

INTRODUCTION

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environments. Most of the corrosion inhibitors are synthetic chemicals, expensive, and very hazardous to environments. Therefore, it is desirable to source for environmentally safe inhibitors [1-3]. There are some reports on the inhibition effects of non-toxic compounds on the corrosion of metals. Gluconate and the gluconic acid are known to be effective non-toxic inhibitors for iron and mild steel in cooling water systems [4,5]. Sodium, calcium and zinc salts of gluconic acid have been reported to be successful inhibitors against the corrosion of tin, iron and of the mild steel in near neutral media [6].

Müller [7] has investigated the hydrogen corrosion of aluminium pigment can be inhibited with addition of the reducing saccharides fructose and mannose as well as with addition of the reducing ascorbic acid. Touir et al [8] have studied the effect of sodium gluconate anion (SG) on the corrosion and scale inhibition of ordinary steel in simulated cooling water. John Amalraj et al [9] have evaluated the inhibition efficiency of sodium gluconate (SG) in controlling corrosion of carbon steel immersed in the environment containing 60 ppm Cl⁻ in the presence and absence of Zn²⁺.

The aim of the present study is to evaluate, understand and discuss the mechanism of corrosion protection by fructose (FR) of ordinary steel in simulated cooling water using weight loss, polarisation curves and electrochemical impedance spectroscopy. The surface analysis was used to identify the compounds present on the inhibitive layer.

EXPERIMENTAL

Preparation of the carbon steel specimens:

Carbon steel specimens (0.026 % S, 0.06 % P, 0.40 % Mn, 0.10 % C, and the rest iron) of dimensions 1.0 × 4.0 × 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for mass-loss and surface examination studies.

Mass-loss method

The weighed specimens in duplicate were suspended by means of glass hooks in 100 ml beakers containing 100 ml of various test solutions. After 3 days of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimens, corrosion rates and I.E. were calculated.

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

Where:

W₁ = corrosion rate (mdd) in absence of inhibitor,
W₂ = corrosion rate (mdd) in presence of inhibitor.

Surface examination studies

The carbon steel specimens were immersed in various test solutions for a period of three days, the specimens were taken out, washed with distilled water and then dried. The nature of the film formed on the surface of metal specimens was analysed by the following techniques.

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FTIR spectra

The film was carefully removed with sharp edged glass rod, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded on a Perkin - Elmer 1600 spectrophotometer.

Potentiodynamic polarization study:

Potentiodynamic polarization studies were carried out using CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode (1 cm² area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

AC impedance measurements:

A CHI electrochemical impedance analyzer (model 660 A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open-circuit potential. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies (f). The values of the charge transfer resistance R_t and the double layer capacitance C_{dl} were calculated.

The UV-visible absorption spectra of solutions:

The possibility of the formation of Zn- inhibitor complex and also iron-inhibitor complex in solution was examined by mixing the respective solutions and recording their UV-visible absorption spectra using Lamda 35 UV-visible spectrophotometer 119 which is a PC controlled single beam scanning spectrophotometer. It covers a wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1nm.

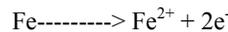
RESULTS AND DISCUSSION

Mass-loss method

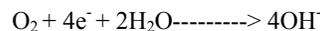
The corrosion inhibition efficiencies of fructose (FR)-Zn²⁺ systems, as determined by mass loss method, are given in Table 1. It is found from the table that FR is a poor inhibitor and 125 ppm of FR gives a maximum of 43 % IE. Perusal of the table reveals that a combination of Zn²⁺ and FR shows a better IE. For example, 50 ppm of Zn²⁺ gives an IE of 41 % and 125 ppm of FR gives 43 %, but their combination offers an IE of 84 %, which is found to be the maximum IE offered by the system. This suggests the existence of synergistic effect between Zn²⁺ and FR. The synergism may be due to the formation of complex between Zn²⁺ and FR. Because of the complex formation with Zn²⁺ the inhibitor molecules are readily transported from the bulk to the metal surface.

On the metal surface, Zn²⁺-FR complex is converted into Fe²⁺- FR complex on the anodic sites of the metal surface. Zn²⁺ is released. This combines with OH⁻ to

form Zn(OH)₂ on the cathodic sites of the metal surface. Thus both the anodic reaction



and cathodic reaction



are controlled effectively. This accounts for a synergistic effect between FR and Zn²⁺.

Table 1 - Inhibition efficiency of FR-Zn²⁺ system on the corrosion of carbon steel in river (cauvery) water. Immersion period: 3 days

FR, ppm	Zn ²⁺ , ppm				
	0	5	10	25	50
0	-	13	17	32	41
10	30	37	41	46	55
25	36	41	46	49	55
50	37	46	49	57	67
75	38	49	50	66	75
100	41	53	55	78	76
125	43	58	64	80	84

FTIR spectral analysis

The FTIR (KBr) spectrum of fructose(a) and the thin film formed on the surface of the metal after immersion in river water containing 50 ppm of Zn²⁺ and 125 ppm of fructose solution(b) are shown in Figure 1. The peak at 3367 cm⁻¹ is assigned to ν_{OH} stretching vibration. The peak at 1592 cm⁻¹ is due to the bending vibration of OH group. The bands at 1410.5 cm⁻¹ and 1348.5 cm⁻¹ are due to the coupling of OH inplane bending with the C-H wagging vibration. The band at 1252.4 cm⁻¹ is attributed to the symmetric stretching of ring breathing frequency. The band at 1060.4 cm⁻¹ is due to the asymmetric C-C-O stretching vibration. The peak at 977.63 cm⁻¹ is due to the asymmetric C-C-O ring stretching.

The IR spectrum of thin film formed on the metal surface after the immersion in Zn²⁺ and the fructose solution is shown in fig-1b. The ν_{OH} stretching frequency occurs at 3433.4 cm⁻¹. There is a band at 1632.2 cm⁻¹ which is characteristics of C=O stretching frequency. The band at 1021.4cm⁻¹ is assigned to the asymmetric C-C-O stretching. There is a broad band at 506.2 cm⁻¹ which may be assigned to M-O stretching frequency. The band at 3776.9 cm⁻¹ is due to the ν_{OH} stretching frequency of the OH group attached to a metal ion. The presence of ν_{C=O} stretching frequency at 1631.2 cm⁻¹, the absence of the ring frequency(1252 cm⁻¹ in the IR spectrum of fructose) and asymmetric C-C-O ring stretching(977 cm⁻¹ in the IR spectrum of fructose) shows that the C-O-C ring in the fructose is broken and C=O group exists in the fructose present in the film and also the shift in the ν_{OH} frequency from 3367.2 cm⁻¹(Figure 1a) to 3433.4 cm⁻¹ (Figure 1b) and in the asymmetric C-C-O stretching frequency from 1060.4 cm⁻¹ to 1021.4 cm⁻¹

clearly indicates that the hydroxyl group in the fructose forming a bond with metal ions. This is further confirmed by the presence of the characteristic ν_{M-O} ¹⁰ stretching frequency at 506.2 cm⁻¹. The presence of ν_{OH} frequency at 3776.9 cm⁻¹ shows that the hydroxyl group is attached to a metal ion [11]. The presence of Zn(OH)₂ in the film may be confirmed by the peaks at 3776.9 cm⁻¹ (ν_{OH}) frequency of M-OH, at 856.6 cm⁻¹ (ν_{Zn-O}) stretching and at 1352 cm⁻¹ (inplane bending vibration of OH).

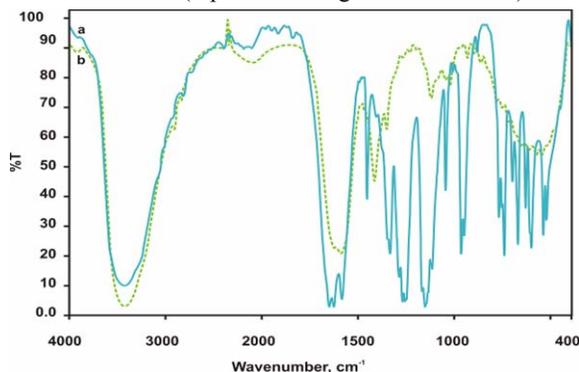


Figure 1 - FTIR spectra of (a) fructose and (b) Film formed on steel after immersion in river water containing 125 ppm FR & 50 ppm Zn²⁺

Analysis of the results of potentiodynamic polarization studies:

The potentiodynamic polarization curves of carbon steel immersed in river water in the presence and absence of Zn²⁺ and FR are given in Figure 2. The corrosion parameters of carbon steel immersed in river water in the presence and absence of 50 ppm of Zn²⁺ and 125 ppm of fructose are given in Table 2.

When carbon steel is immersed in river water, the corrosion potential (E_{corr}) is -463 mV vs SCE and the corrosion current is 1.556×10^{-5} A/cm². When 50 ppm of Zn²⁺ and 125 ppm of fructose are added to river water the corrosion potential is found to be -548 mV vs SCE. The corrosion current is 0.731×10^{-5} A/cm². The cathodic slope is found to change from 327 to 501 mV/decade and the anodic slope from 217 to 185 mV/decade. The linear polarization resistance has increased from 3.643×10^3 to 8.049×10^3 Ω cm². The shift in the value of b_c is considerably more than that of b_a . This shows that the formulation functions as cathodic inhibitor. The increase in LPR value and decrease in corrosion current indicate that a protective film is formed on the metal surface [13].

Table 2 - Corrosion parameters of carbon steel in river water (Cauvery) in the presence and absence of inhibitor obtained by potentiodynamic polarization

Environment	E_{corr} Mv vs SCE	b_c mv	b_a mv	LPR Ω Cm ²	I_{cor} A/cm ²
Cauvery water	-463	327	217	3.643×10^3	1.556×10^{-5}
Inhibitor system	-548	501	185	8.049×10^3	0.731×10^{-5}

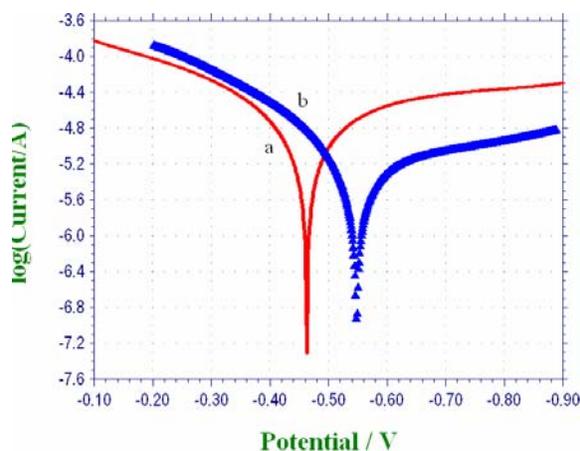


Figure 2 - Polarization curves of carbon steel immersion in river (cauvery) water and RW containing 125 ppm FR and 50 ppm Zn²⁺

Analysis of the results of AC impedance studies:

The AC impedance spectra of carbon steel immersed in various test solutions are shown in Figure 3.

The AC impedance parameters namely charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) are given in Table 3.

Table 3 - Impedance parameters of carbon steel in river water in the absence and presence of inhibitor obtained by AC impedance spectra

Environment	R_t Ω cm ²	C_{dl} μ F/cm ²
River water	1102	8.2187×10^{-9}
River water+ 50 ppm Zn ²⁺ +125 ppm FR	1206	7.5141×10^{-9}

When carbon steel is immersed in river water the R_t value is found to be 1102 Ω cm². The C_{dl} value is 8.2187×10^{-9} F/cm². When 50 ppm of Zn²⁺ and 125 ppm of fructose are added the R_t value has increased from 1102 to 1206 Ω cm² and the C_{dl} value has decreased from 8.2187×10^{-9} to 7.5141×10^{-9} F/cm². The increase in R_t values and decrease in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in river water .

This behaviour means that the film obtained acts as a barrier to the corrosion process that clearly proves the formation of the film [14].

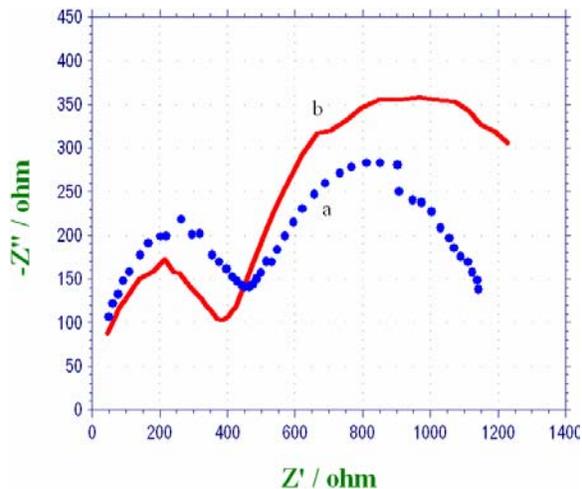
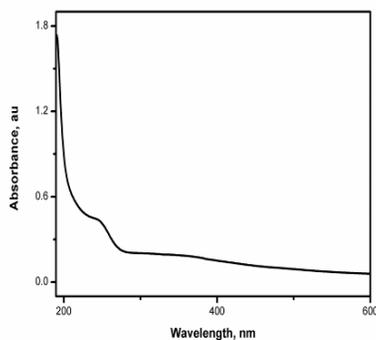


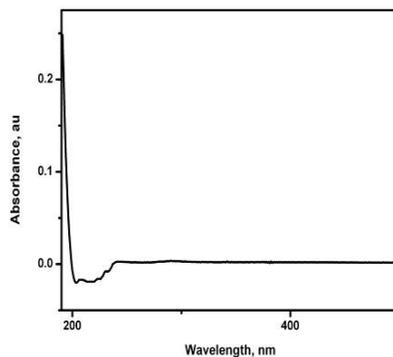
Figure 3 - AC impedance spectra of carbon steel immersed in various test solutions a) River water, b) River water + 50 ppm FR + 50 ppm Zn²⁺

UV-Visible spectral study

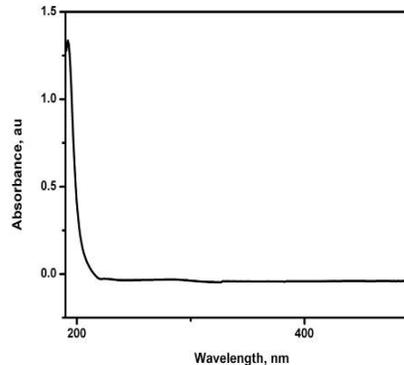
The UV -visible spectrum of Zn²⁺, Fe²⁺ ion, FR, Zn²⁺- FR and Fe²⁺-FR in distilled water are given in figure 4a-e. From Figure 4a, it is noted that 50 ppm of Zn²⁺ gives an absorbance of 0.1640 at 190 nm and the absorbance falls sharply and reaches 0.0155 at 300 nm, then changes gradually and reaches 0.0755 at 600 nm. UV-visible spectrum of Fe²⁺ (Figure 4b) in river water shows two small peaks at 207.6 (abs-0.1013) and 240.01 (abs-0.1052) nm. These peaks have disappeared in the spectrum of Fe²⁺ + FR in RW (Figure 4e). The UV spectrum of fructose (Figure 4c) shows 3 peaks at 290.04 nm (0.0035), 243.96 nm (0.0026) and 208.04 nm (0.0170). In the UV spectrum of FR-Zn²⁺ and FR-Fe²⁺ (Fig-4d,e) the peaks at 208.04 nm (0.0170) and 243.96 nm (0.0026) disappeared and the peak at 290.04 nm (0.0035) is shifted to 280.87 nm (0.0319) and 293.86 nm (0.2399) respectively. This is a clear proof that fructose has strong interaction with Zn²⁺ and Fe²⁺ ions.



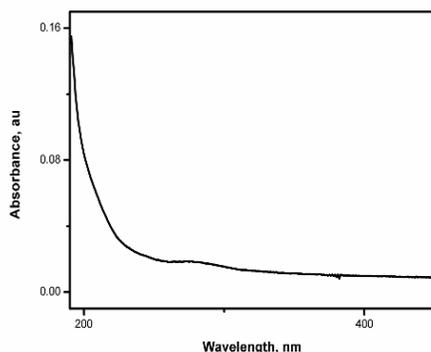
b) Fe²⁺ ions



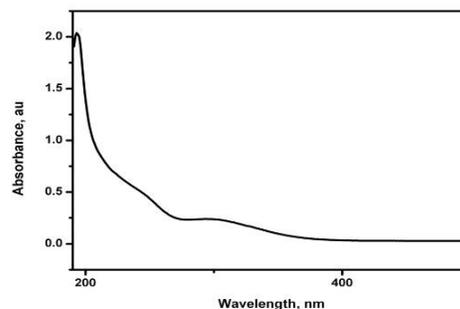
c) FR



d) FR and Zn²⁺ ions



a) Zn²⁺ ions



e) FR and Fe²⁺ ions

Figure 4 - UV-Visible absorption spectra of the test solutions in river water

SEM analysis

The SEM micrographs of polished carbon steel surface (Figure 5a) shows smooth surface. This shows the absence of any corrosion products on the metal surface. Bits are seen (Figure 5b) in the SEM micrographs of polished carbon steel immersed in river water.

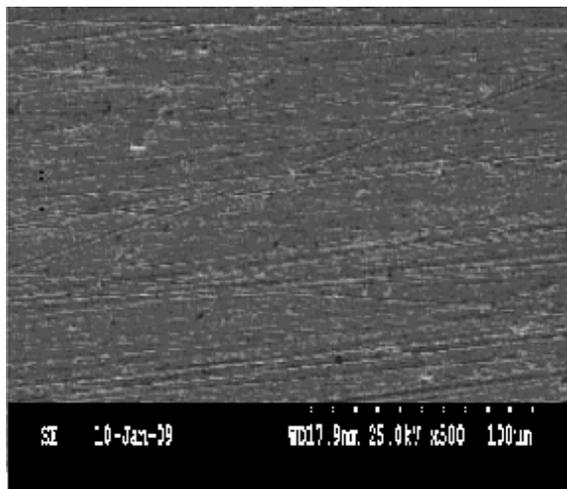


Figure 5a - Scanning electron micrograph of carbon steel

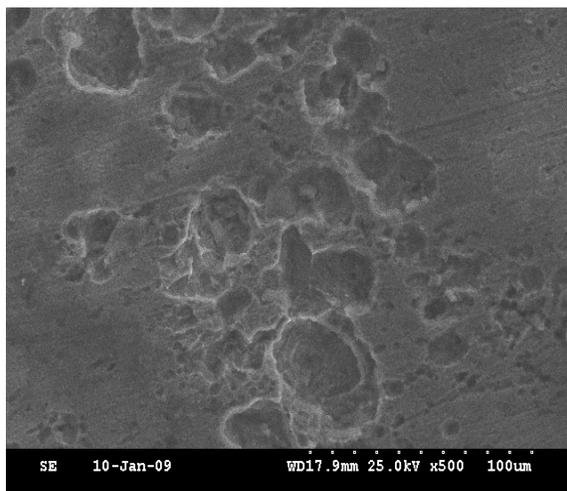


Figure 5b - Scanning electron carbon micrograph of carbon steel in river water

The SEM micrographs of the metal immersed in river water containing 50 ppm of Zn^{2+} and 50 ppm of fructose (Figure 5c) shows that a surface film of inhibitor system is formed more uniformly on the carbon steel surface. The film formed on the metal surface is found to be more compact and could inhibit the corrosion of carbon steel. This revealed that the compounds 50 ppm Zn^{2+} and 125 ppm fructose interacts more effectively with anodic and cathodic sites of carbon steel and binds strongly on the metal surface.

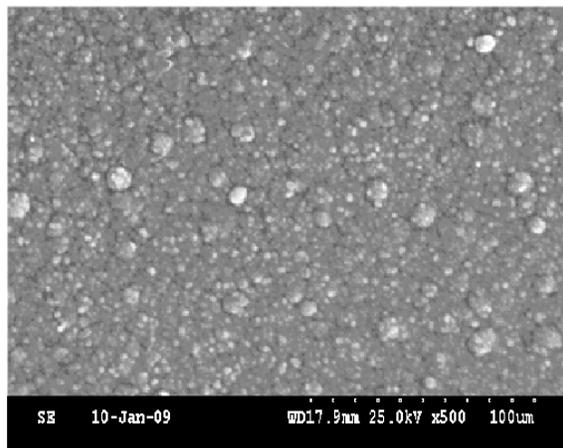


Figure 5c - Scanning electron micrograph of carbon steel in the presence of 50 ppm of Zn^{2+} and 125 ppm of fructose

Mechanism of corrosion inhibition:

- ❖ The analysis of the results of the mass-loss method shows that the formulation consisting of 125 ppm of fructose and 50 ppm of Zn^{2+} offers maximum IE of 84%.
- ❖ The AC impedance spectral studies reveal the formation of a film with higher resistance than that of the river water alone.
- ❖ Results of polarization study show that this formulation functions as a cathodic inhibitor.
- ❖ The UV – visible absorption spectra indicate the possibility of formation of iron- FR complex and also Zn^{2+} - FR complex in solution.
- ❖ The FTIR spectra confirm the formation of film consisting of iron - FR complex and $Zn(OH)_2$ [14].

Based on the above facts the following mechanism is proposed:

- ❖ In river (cauvery) water containing 50ppm of Zn^{2+} and 125 ppm of fructose, a sort of complex is formed between Zn^{2+} and fructose.
 - ❖ When the metal is immersed in this environment, this complex diffuses from the bulk of the solution to the surface of the metal.
 - ❖ On the surface of the metal, Zn complex is converted into the iron complex at the local anodic sites, as the latter is more stable than the former.
- $$Zn\text{-Complex} + Iron \rightarrow Iron\text{-Complex} + Zn^{2+}$$
- ❖ The released Zn^{2+} ions will form $Zn(OH)_2$ in the local cathodic regions.
 - ❖ The protective film consists of iron-complex and $Zn(OH)_2$ [15,16].

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