Inhibition Of Corrosion Of Carbon Steel In Well Water By Natural Jeera Dye $-Zn^{2+}$ System

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ABSTRACT: The inhibition of corrosion behaviour of carbon steel in Well water has been studied by the anticorrosion behaviour of the natural Jeera dye (JD) and $ZnSO_4$ system. Results Obtained by Weight loss study shows 98 % Maximum Inhibition efficiency at 10 ml of Jeera dye Extract and 50ppm of $ZnSO_4$. Synergistic parameters suggest that a synergistic effect existing between Jeera dye extract and Zn^{2+}.Statistical study of "F" test also revealed this effect. The Surface analysis was performed by Scanning electron microscope technique (SEM)which was confirmed , the existence of an inhibitor molecules on the metal surface .FTIR Spectra revealed that the protective film consist of a complex formed between the active principle of the Jeera dye extract and Zn^{2+}.

Keywords: corrosion inhibition, carbon steel, weight loss study, F –Test, SEM, FTIR

1.INTRODUCTION

Corrosion is the deterioration of the metal by the chemical reaction when come in contact with the atmosphere or moisture[1] .The use of inhibitors is one of the best options of protecting metals against corrosion in various fields of application as acid pickling and acid descaling [2]. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. So the environmentally friendly inhibitors are chosen for their non-toxic, biodegradable and readily available in nature. Several investigations showed that different media for different metal using naturally occurring substances as corrosion inhibitors used. In those studies some of them found to inhibit corrosion in well water & sea water [3-5]as their medium. For example, Corrosion inhibition of Carbon steel in well water by vitexnegundo extract has been studied [6]. The Corrosion effects of Allium sativum (Garlic) extract have been reported [7]. Banana peel has been used as corrosion inhibitor for carbon steel in sea water [8]. The inhibition efficiency (IE) of an aqueous extract of Beetroot in controlling corrosion of carbon steel in well water has also been reported[9]. Pisonia Alba has been reported as corrosion inhibitor for carbon steel in well water[10]. The present study aimed to discuss the inhibitive performance of natural Jeera dye extract as eco-friendly corrosion inhibitor for carbon steel in well water by using weight-loss, syngeristic effect, and FTIR &SEM methods.

2. EXPERIMENTAL

2.1 Preparation of the Carbon steel specimens: Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, and 0.1% C and rest iron) of the dimensions 1.0 x 4.0 x 0.2 cm were polished to a mirror finish, degreased with trichloroethylene, and used for Weight-loss and surface examination studies.

2.2 Preparation of Jeera dye extract: 10gm of Jeera powder was weighed & boiled with double distilled water. The golden yellow colour dye of Jeera was filtered to remove suspended impurities & made up to 100ml. The Jeera Dye (JD) was used as corrosion inhibitor in the present study.

2.3 Weight –Loss method:

Determination of Surface area of the specimens: The length, breadth and the thickness of carbon steel specimens and the radius of the holes were determined with the help of vernier calipers of high precision and the surface areas of the specimens were calculated.

Weighing the specimens before and after Corrosion: All the weighing of the carbon steel specimens before and after corrosion was carried out using shimadzu balance –AY62.

Determination of corrosion rate : The weighed specimen in duplicate were suspended by means of glass hooks in 100ml beaker containing 100ml various test solutions and after 24 hours of immersion, the specimens were taken out, washed in running water, dried and weighed. From the change in weights of the specimen, corrosion rates were calculated using the following relationship.

$$\text{Corrosion Rate (mm /y)} = \frac{\text{Loss in weight (mg) x1000}}{\text{Surface area of the Specimen (dm}^2\text{)} \times \text{Period of immersion in days}} \times 0.0365/d$$

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

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

Where,

W_1 =Corrosion rate (mm /yr) in absence of inhibitor.

W_2 = Corrosion rate (mm /yr) in presence of inhibitor

d = Density of the metal

2.4 **Synergism parameters:** Synergism parameters are indication of synergistic effect existing between two inhibitors (1, 2).

Synergism Parameters were calculated using the relation

$$S_1 = (1-\Theta_{1+2} / 1-\Theta'_{1+2}) \quad \text{Where,}$$

$$\Theta_{1+2} = (\Theta_1 + \Theta_2) - (\Theta_1 \times \Theta_2)$$

Θ_1 = inhibition efficiency of substance 1

Θ_2 = inhibition efficiency of substance 2

Θ'_{1+2} = combined inhibition efficiency of substance 1& 2

2.5 F- test: F- test was carried out to investigate whether the synergistic effect existing between Jeera dyes extract and Zn^{2+} system statistically significant or not[11].

2.6 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 analysed by surface analysis technique, namely, infrared spectroscopy & SEM Analysis[10].

FTIR Spectra : These spectra were recorded with the Perkin – Elmer 1600 spectrophotometer. The FTIR spectrum of the protective film was recorded by ; carefully removing the film mixed it with KBr and making the pellet.

SEM Study: The surface morphology measurements of the carbon steel were examined by using JEOL JSM 6390 model. All SEM micrographs of carbon steel are taken at a magnification of X= 1000[11] .

3.RESULTS AND DISCUSSION

3.1 Analysis of the weight loss method :

The calculated inhibition efficiencies (IE) of jeera dye in controlling the corrosion of carbon steel immersed in well water both in the absence and presence of zinc ion have been tabulated in table 1 to 3. It is observed from table 1 shows the inhibition efficiency 46 % for 2ml of Jeera dye extract ,as the concentration of the inhibitor extract increases the inhibition efficiency also increases. The calculated values indicate the ability of jeera dye to be a good corrosion inhibitor. The inhibition efficiency is found to be enhanced in the presence of zinc ion. The formulation consisting of 10ml of JD & 50ppm of Zn^{2+} offers 98% inhibition efficiency.

Table 3.1.1: Corrosion rates (CR) of carbon steel in well water in the absence and presence of inhibitors and the inhibition efficiencies obtained by weight -loss method.

Inhibitor system: JD extract + Zn^{2+}(0ppm)

Period of immersion: 1 day

Jeera dye extract (ml)	Zn^{2+} (ppm)	CR (mm/y)	IE %
0	0	0.0695	-
2	0	0.0375	46
4	0	0.0319	54
6	0	0.0284	59
8	0	0.0271	61
10	0	0.0264	62

Table 3.1.2 :

Inhibitor system: Jeera Dye (JD)+Zn^{2+} (25ppm) Period of immersion: 1 day.

Jeera dye ml	Zn^{2+} ppm	CR mm/y	IE %
0	25	0.0556	20
2	25	0.0243	65
4	25	0.0201	71
6	25	0.0187	73
8	25	0.0173	75
10	25	0.0159	77

Jeera dye ml	Zn^{2+} ppm	CR mm/y	IE %
0	50	0.0417	40
2	50	0.0097	86
4	50	0.0076	89
6	50	0.0055	92
8	50	0.0027	96
10	50	0.0013	98

Table 3.1.3 : Inhibitor system: Jeera dye(JD) $+Zn^{2+}$ (50 ppm) Period of immersion: 1 day.

3.2 Influence of immersion period on the corrosion inhibition of carbon steel in well water by JD+Zn^{2+} system

The corrosion rates of carbon steel in the presence of the inhibitor system in well water for different durations of immersion are tabulated in table 3.2.1

The IE of 10 ml JD 50ppm Zn^{2+} system is found to decrease as the immersion period increases. 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 (665ppm) present in well water. There is competition on the anodic sites of the metal surface. A perusal of the results suggests that the formation of $FeCl_2$ is favoured when compared with the formation of Fe^{2+}-JD complex[12, 13.]

Jeera dye ml	Zn^{2+} ppm	Immersion Period Days	Corrosion Rate mm/y	Inhibition Efficiency %

Table 3.2.1: **Influence of immersion period on the inhibition efficiency of the JD (10 ml) –Zn^{2+} (50ppm).**

Corrosion rates (CR) of carbon steel in well In the absence and presence of inhibitor system and the inhibition efficiencies obtained by the mass - loss method.

Inhibitor system: JD (10 ml) +Zn^{2+} (50ppm).

0	0	1	0.0695	-
10	50	1	0.0013	98
0	0	3	0.2318	-
10	50	3	0.0649	72
0	0	5	0.1252	-
10	50	5	0.0375	70
0	0	7	0.4823	-
10	50	7	0.2507	48

3.3 Influence of pH on inhibition efficiency of Jeera dye +Zn^{2+} system.

Corrosion rates of carbon steel in well water in the presence of the inhibitor system at different pH and the IE are tabulated in table 3.3.1

At pH 8, the IE of JD Zn^{2+} system is 67 %.when the pH is lowered to 6 (by the addition of dil .H_2SO_4).The IE decreases to 80 due to the attack of H^+ ion present in the acid. On protective film formed on the metal surface. When the pH decreased from 8 to 7. The IE decreases from 67 to 61. This is due to the fact that the protective film formed on the metal surface is broken by the attack of H^+ ion [14-17].

Table 3.3.1: Influence of pH on the inhibition efficiency of JD (10ml) -Zn^{2+} (50 ppm).

Corrosion rates of carbon steel in well at different pH and the inhibition efficiencies obtained by the mass loss method.

Inhibitor system: JD (10ml) -Zn^{2+} (50 ppm).

Immersion period: 1 day.

Jeera	Zn^{2+}		Corrosion	IE

dye ml	ppm	pH	Rate mm/y	%
0	0	7	0.1808	-
10	50	7	0.0705	61
0	0	8	0.1716	-
10	50	8	0.0566	67
0	0	6	0.1205	-
10	50	6	0.0241	80

3.4 Synergism parameters

Synergism parameters have been calculated to evaluate the synergistic effect existing between two inhibitors[18,19].when the value of synergism parameter is greater than 1 synergistic effect exists. synergistic effect can be calculated using the following equation.

$$\text{Synergism parameters } (S_1) = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}$$

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

θ_1 = inhibition efficiency of substance1.

θ_2 = inhibition efficiency of substance 2.

Θ'_{1+2} = inhibition efficiency of combined substance 1 & 2.

Where, θ = surface coverage = IE% / 100

The synergism parameters are given in table IV.6. It is observed that the value of synergism parameter is greater than1.This suggests that a synergistic effect exists between JD and Zn^{2+} indicating synergistic effect existing between various volumes of JD and Zn^{2+}.It is also interesting to note that the values of S_1 are slightly smaller in the case of 50 ppm of Zn^{2+}. When compared with 25 ppm of $Zn2^{+}$.This is in agreement with inhibition efficiencies obtained by weight loss method. Thus the values of synergism parameter give a synergism existing between two inhibitors.

Table 3.4.1: Synergism parameters derived from inhibition efficiencies of JD - Zn^{2+} (25 ppm) and (50 ppm) system.

Jeera dye ml	Zn^{2+}		S_1
	0 ppm	25 ppm	
0	-	20	-
2	46	65	1.2342
4	54	71	1.2689
6	59	73	1.2148
8	61	75	1.2480
10	62	77	1.3217

Jeera dye ml	Zn^{2+}		S_1
	0 ppm	50 ppm	
0	-	40	-
2	46	86	2.3142
4	54	89	2.5090
6	59	92	3.075
8	61	96	5.85
10	62	98	11.4

3.5 F-Test

It is observed from the table that the calculated F value 19.0578 is greater than the table value 5.32 for 8 degree of freedom at 0.05 level of significance. Hence it is concluded that the synergistic effect existing between jeera dye extract and 50 ppm of Zn^{2+} is statistically significant.[11]

Table 3.5.1: Distribution of F-Value between the inhibition efficiencies of various concentrations of JD (0ppm of Zn^{2+}) and the inhibition efficiencies of JD in the presence of 25ppm of Zn^{2+} and 50ppm of Zn^{2+}.

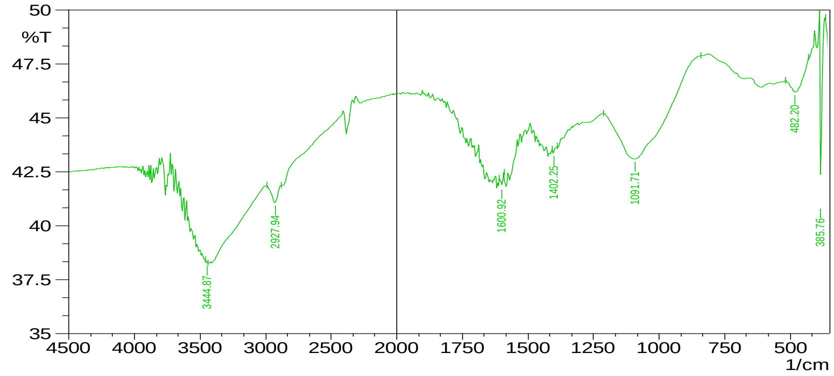
Zn^{2+} (ppm)	Source of variance	Sum of squares	Degree of freedom	Mean square	F-Value	Level of significance
0	Between	125	1	125		
25	Within	258	8	32.25	3.8759	$p<0.05$
0	Between	640.82	1	640.82		
50	Within	269	8	33.625	19.0578	$p>0.05$

3.6 Analysis of FTIR spectra:

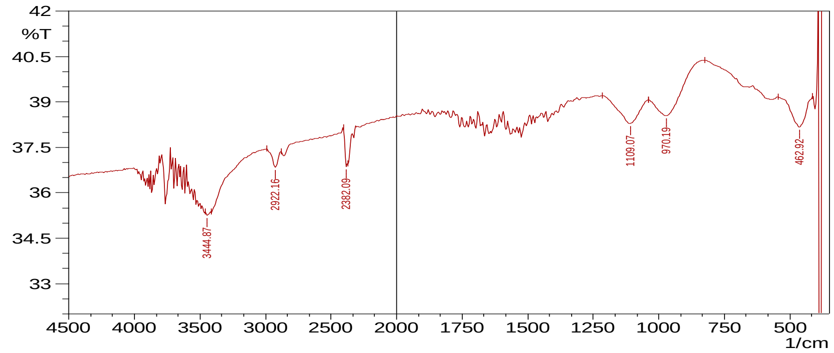
The active principle in an aqueous extract of Jeera dye is cuminaldehyde. The golden yellow colour of the extract is due to cuminaldehyde. The main constituent of Jeera powder is cuminaldehyde[20]. The structure of cuminaldehyde is shown in figure1.The cuminaldehyde extract was evaporated to dryness to set a solid mass. FTIR spectrum is shown in fig.3.6 a. Suggest, the C=O stretching frequency appears at 1600.92 cm^{-1}.

The FTIR spectrum of the protective film formed on the surface of the metal after immersed in the solution containing 50ppm of $Zn^{2+}$and 10ml of JD shown in fig.3.6.b. The C=O stretching .Frequency has decreased from 1600.92 Cm^{-1} to 1109.07 Cm^{-1}.The -OH stretching Frequency appears at 3444.87Cm^{-1}.The ring oxygen appeared at 970.19Cm^{-1}.It has coordinated Fe^{2+} to form protective film on metal surface. The peak at 1360Cm^{-1} is due to Zn-O stretching. Peak at 3444.87Cm^{-1} is due to –OH stretching. So it is concluded that $Zn(OH)_2$ is formed on cathodic sites of the metal surface[21-23.]

FTIR SPECTRA:



3.6(a)Pure JD



3.6 (b) Film formed on metal surface after immersion in well water containing 10ml of JD - 50ppm of Zn^{2+}.

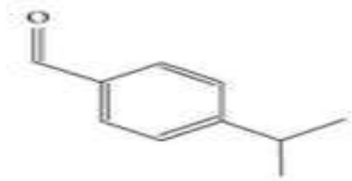


Fig.1 structure of Cuminaldehyde

3.7 SEM analysis of metal surface

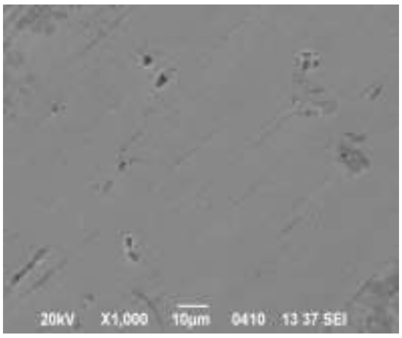
SEM provides a pictorial representation of the surface to understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined[24].

The SEM image of different magnifications (X 1000) of carbon steel specimen and carbon steel specimen immersed in well water for 1 day in the absence and presence of inhibitor system are shown in fig 3.7 as images (a ,b, and c) respectively.

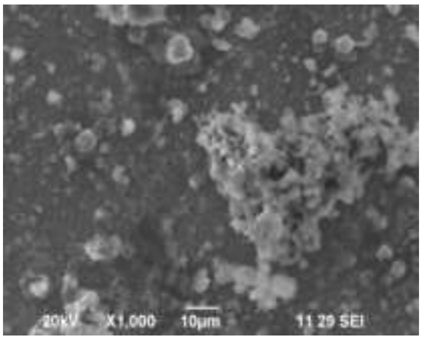
The micrograph of polished carbon steel surface (control) in fig.3.7 images (a) illustrates the smooth surface of the metal. These shows the absence of any corrosion products formed on the metal surface.

The image 3.7(b) denotes the SEM micrographs of carbon steel surface immersed in well water. These show the type of rough surface characteristic of the uniform corrosion of the metal surface in well water, indicating in an inhibitor free solution, the surface is highly corroded.

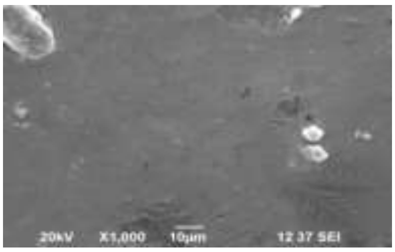
The image 3.7 (c) confirms that in the presence of 10 ml of JD & 50 ppm of Zn^{2+} mixture in well water, the rate of corrosion is suppressed ,as can be seen from the decrease in corroded areas. This is due to the formation of insoluble complex (JD-Zn^{2+} inhibitor complex) formed on the metal surface of the carbon steel[25]



3.7.a) Polished Carbon steel



3.7.b) Carbon steel immersed in well water



3.7.c) Carbon steel immersed in well water containing 10 ml of JD- 50ppm of Zn^{2+}.

4. CONCLUSION

The inhibition efficiency (IE) of Jeera Dye –Zn^{2+} system in controlling corrosion of carbon steel in an aqueous solution containing 665 ppm of Cl^- has been evaluated by mass loss method. The present study leads to the following conclusion.

- Weight loss study reveals that the formulation consisting of 10mL of JD and 50ppm of Zn^{2+} has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in an aqueous solution containing 665ppm of Cl^-.
- Synergistic parameters suggest that a synergistic effect exists between JD and Zn^{2+}.
- The FTIR spectra reveal that the protective film consists of Fe^{2+}-JD complex.
- The SEM micrograph confirms the formation of protective layer formed on the metal surface.

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