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Corrosion inhibition by an aqueous extract of Henna leaves (Lawsonia Inermis L)

An aqueous extract of plant material Henna (Lawsonia Inermis L) powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, by the mass loss method, in the absence and presence of Zn^{2+}. The main constituent of this plant extract is Lawsone. It has excellent inhibition efficiency (IE) and shows excellent IE at pH 6, 8 and 12. In the presence of Zn^{2+} there exists a synergistic effect. Synergism parameters have been calculated to evaluate the synergistic effect. Analysis of variance (F-test) reveals that the synergistic effect existing between henna extract and Zn^{2+} in statistically significant. The protective film has been analyzed using Fourier transform infrared (FTIR) spectroscopy. The film consists of Fe^{2+} - Lawsone complex and Zinc hydroxide [Zn $(OH)_2$]. It is found to be UV-fluorescent. Electro chemical studies such as potentiodynamic polarization and alternating current (AC) impedance have been used to find the mechanistic aspects of corrosion inhibition.

Key words: *Carbon steel, corrosion inhibition, Lawsone, Plant extract, Synergistic effect, ANOVA*

1. INTRODUCTION

Environmental friendly inhibitors have attracted several researchers. Nontoxic natural products have been widely used as corrosion inhibitors. Natural products such as tannins [1-3] have been used as inhibitors. Extracts of plants such as ceram petroselinum, Lupine, Doum and organge sheels have been used as corrosion and scale inhibitors[4]. Pomegranate [5], Swertia aungustitolia [6] and Azadiracta indica [7] have a good inhibitive property. The scale inhibition efficiencies of the aqueous extracts of plant materials, namely Cordia Latifolia, Eucalyptus and Jasmine auriculatum have been evaluated [8]. Caffeine has been used as inhibitor in controlling corrosion of mild steel immersed in an aqueous solution containing 60ppm of Cl^-[9]. Longo, et al [10], synthesized a number of different porphyrins and their metallo derivatives and used them as corrosion inhibitors for pure iron (Armco) and pure aluminium in 1% sodium chloride (NaCl) solution. Awad has used the extracts of the plants Calotropis procera and Diopyros mesipilioforms to control corrosion of mild steel in 0.1N hydrochloric acid (HCl) solutions, by adopting weight loss measurements and polarization studies [11].

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Aqueous extract of Rosamarinus officinalis L has been used as inhibitor for Al-Mg alloy corrosion in a 3% NaCl solution at 25°c. The results have been analyzed by polarization curves and impedance spectrum [12]. The inhibitive effects of aqueous extracts of eucalyptus (leaves), hibiscus (flower) and agaricus on the corrosion of mild steel for cooling water systems, using tap water have been investigated by means of the weight-loss and polarization method.

Rajendran, et al., have investigated the inhibitive property of an aqueous extract of Rhizome powder in controlling corrosion of carbon steel in an aqueous solution containing 60ppm of chloride ion [14].

The inhibition effect of Zenthoxylum alatum plant extract on the corrosion of mild steel in 20, 50 and 88% aqueous orthophosphoric acid (H_3PO_4) has been investigated by mass loss method and electrochemical impedance spectroscopy [15].

Corrosion inhibition of steel in hydrochloric acid (HCl) solution by Rosemary oil has been studied by Chaieb [16].

Naturally occurring henna (Lawsona inermis L) has anti-inflammatory, antipyretic and analgesic effect [17-18]. Henna has inhibitory action on aluminium and steel in aggressive solution [19]. Henna has been used as corrosion inhibitor for iron in hydrochloric acid [20].

The present work investigated the inhibition efficiency of an aqueous extract of plant material, Henna (Lawsonia inermis L) extract, in controlling corrosion of carbon steel (CS) immersed in an aqueous solution containing 60ppm of Cl^-, in the absence and presence of Zn^{2+}, using a mass loss study, examined the influence of pH on the inhibition efficiency of plant extract, analyzed the protective film by Fourier transform infrared (FTIR) spectroscopy and fluorescence spectroscopy, and proposed a suitable mechanism of corrosion inhibition, based on the results of the above studies and potentio -dynamic polarization and alternating current (AC) impedance spectra.

2. EXPERIMENTAL PROCEDURE

Preparation of plant extract

An aqueous extract was prepared by grinding 50g of dried Henna. (Lawsonia inermis L) leaves, filtering and making up to 500mL using double distilled water. It was used in the present study.

Mass Loss Measurements

Experiments were carried out using carbon steel (CS), in triplicate, in an aqueous environment containing 60 ppm of Cl^-. The CS sample was 1.0 cm by 4.0 cm by 0.2 cm (0.394 in. by 1.576 in. by 0.079 in) having the following composition(Wt %): 0.03% S, 0.04%, P,0.4% Mn, 0.15% C, and bal Fe. The CS samples were polished to mirror finish, degreased with trichloroethylene (C_2HCl_3) and immersed in 100 mL of solutions containing various concentrations of the inhibitors for a period of 1 day. The corrosion products were cleaned with Clarke's solution [21]. The mass of the specimens before and after immersion were determined. The inhibition efficiency (IE) was calculated using the relation.

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

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

Analysis of the protective film

The CS samples were immersed in various test solutions for a period of one day. After one day, the samples were taken out and dried. The film formed on the metal surface was carefully removed, mixed thoroughly with potassium bromide (KBr), and made as pellets. The FTIR spectra (KBr pe let) of the film formed on the CS samples were recorded with a Perkin Elmer 1600 spectrophotometer.

The fluorescence spectra of the film formed on the CS samples were recorded with a Hitachi F – 4500 fluorescence spectrophotometer.

Potentiodynamic Polarization study

Polarization study was carried out in an H & CH Electrochemical work station Impedance Analyzer Model CHI 660A provided with iR compensation facility, using a three electrode cell assembly. Carbon steel was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. After having done iR compensation, polarization study was carried out at a sweep rate of 0.01V/Sec. The corrosion parameters such as corrosion potential and Tafel slopes were measured.

Alternating Current Impedance Spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

3. RESULT AND DISCUSSION

Mass Loss Studies

An aqueous extract was prepared by grinding 50g of dried Henna leaves, filtering and making up to 500mL using double distilled water. It was used in the present study.

Table 1 shows the values of corrosion rates and inhibition efficiencies obtained from mass loss measurements of different concentrations of Henna extract (HE). 2mL of the HE offered 81% corrosion inhibition efficiency to carbon steel immersed in 100mL of an aqueous solution containing 60ppm of Cl^-. When the concentration of HE was increased the inhibition efficiency decreased. This is due to the fact that when higher concentrations of HE are added the protective film (Fe^{2+} - Lawsone complex) formed on the metal surface goes into solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken [22].

Table 1 - Corrosion Rates (CR) of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors and the inhibition efficiencies (IE) obtained by mass loss method.

Inhibitors: Henna extract (HE) + Zn^{2+}
Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	0	0	0.19484	--
2	60	2	0	0.03702	81
3	60	4	0	0.04676	76
4	60	6	0	0.060307	69
5	60	8	0	0.06434	67

Influence of Zn^{2+} on the inhibition efficiency of Henna extract

Tables 2 & 3, show the values of inhibition efficiencies from mass loss measurements for different concentrations of Henna extract and Zn^{2+}. 25 ppm of

Zn^{2+} had 5% of inhibition efficiency. However in combination with various concentrations of Henna extract, it showed good IE. This suggested a synergistic effect existing between the Henna extract and Zn^{2+}, for example 2mL of HE had 81% of IE, 25ppm of Zn^{2+} had 5% IE. Nevertheless their combination had 98% IE. Similarly 50 ppm of Zn^{2+} had 10% of IE. In combination with various concentration of HE, it showed good inhibition efficiency suggesting a synergistic effect between Zn^{2+} and HE. It must be recalled that curcumin also showed synergistic effect with Zn^{2+}, which plays the role of transformation the inhibitor towards the metal surface [14].

Table 2 - Corrosion Rates (CR) of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors and the inhibition efficiencies (IE) obtained by mass loss method.

Inhibitors: Henna extract (HE) + Zn^{2+}
Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	0	25	0.18509	5
2	60	2	25	0.00389	98
3	60	4	25	0.03312	83
4	60	6	25	0.03312	83
5	60	8	25	0.03312	83

Table 3 - Corrosion Rates (CR) of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors and the inhibition efficiencies (IE) obtained by mass loss method.

Inhibitors: Henna extract (HE) + Zn^{2+}
Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	0	50	0.17535	10
2	60	2	50	0.00389	98
3	60	4	50	0.02338	88
4	60	6	50	0.02338	88
5	60	8	50	0.02338	88

Synergism parameters

Synergism parameters were calculated using the following relation

$$SI = /1-I_{1+2} \backslash 1-I'_{1+2}/$$

Where $I_{1+2} = (I_1 + I_2) - (I_1\ I_2)$, I_1 = inhibition efficiency of substance 1, I_2 = inhibition efficiency of substance 2, I'_{1+2} = combined inhibition efficiency of substance 1 and 2.

Synergism parameters are indication of synergistic effect existing between two inhibitors. The values of synergism parameters (Table 4 & 5) are greater than one, indicating synergistic effect existing between various volumes of henna extract and Zn^{2+}.

Table 4 - Synergism parameters derived from inhibition efficiencies of HE- Zn^{2+} system.

HE (mL)	Zn^{2+} 0 ppm	Zn^{2+} 25 ppm	S_I
0	0	5	-
2	81	98	3.30
4	76	83	3.66
6	69	83	3.32
8	67	83	3.22

Table 5 - Synergism parameters derived from inhibition efficiencies of HE- Zn^{2+} system.

HE (mL)	Zn^{2+} 0 ppm	Zn^{2+} 50 ppm	S_I
0	0	10	-
2	81	98	7.46
4	76	88	7.76
6	69	88	7.03
8	67	88	6.83

Synergism parameters as a function of various concentrations of HE are shown in Figure 1.

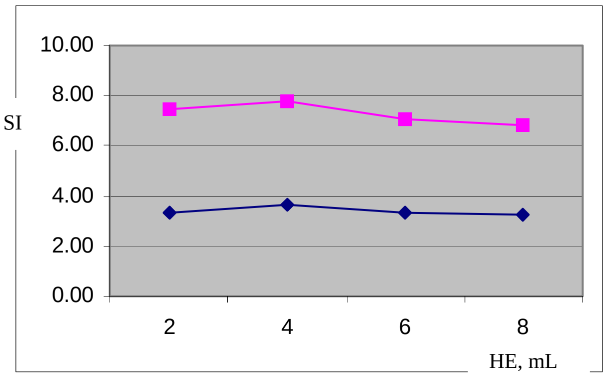


Figure 1 - Synergism Parameters as a function of various concentrartions of HE

Analysis of Variable (ANOVA)

To investigate whether, the influence of Zn^{2+} on the inhibition efficiencies of henna extract (HE) is statistically significant, usually, F-tests are carried out [24]. The results of these tests are given in table 6 and 7.

In table 6, the influence of 25ppm of Zn^{2+} on the inhibition efficiencies of 2, 4, 6 and 8 mL of HE is investigated. The obtained f-value 51.99 is statistically significant, since, it is greater than the critical F-value 5.99 for 1, 6 degrees of freedom at 0.05 level of significance. Therefore it is concluded that the influence of 25ppm of Zn^{2+} on the inhibition efficiencies of various concentrations of HE is statistically significant.

In Table 7, the influence of 50ppm of Zn^{2+} on the inhibition efficiencies of 2, 4, 6 and 8 mL of HE is investigated the obtained f-value 107.26 is statistically significant, since it is greater than the critical F-value 5.99, for 1, 6 degrees of freedom at 0.05 level of significance. Therefore it is concluded that the influence of 50ppm of Zn^{2+} on the inhibition efficiencies of various concentrations of HE is statistically significant.

Table 6 - Distribution of F-value between the inhibition efficiencies of various concentration of extract of henna leaves (HE) (0ppm Zn^{2+}) and the inhibition efficiencies of HE in the presence of 25 ppm Zn^{2+}.

Source of variation	Sum of Squares	Degree of freedom	Mean square	F	Level of significance F
Between samples	364.5	1	364.5	51.99	p>0.05
With in samples	42.08	6	7.01		

Table 7 - Distribution of F-value between the inhibition efficiencies of various concentration of extract of henna leaves (HE) (0ppm Zn^{2+}) and the inhibition efficiencies of HE in the presence of 50 ppm Zn^{2+}

Source of variation	Sum of Squares	Degree of freedom	Mean square	F	Level of significance F
Between samples	595.12	1	595.12	107.26	p>0.05
With in samples	33.29	6	5.55		

Influence of pH on IE of HE-Zn^{2+} system

It is seen from Table 8, that at pH6, the HE (2mL) – Zn^{2+} (50 ppm) system has 98% IE. When pH is lowered to 4 by addition of dilute sulphuric acid the IE decreased to 75%. This is due to the fact that when the acid is added the protective film is broken by the aggressive H^+ ion present in the acid. When the pH is increased to 12 by addition of diluted sodium hydroxide solution, the IE is increased to 98%. This is due to the fact that the phenolic –OH groups would have been ionized to phenolate anion, $-O^-Na^+$. This helped the anchoring of phenolic O^- on the anodic sites of the metal surface effectively and hence IE increased at higher pH values. Similar observation has been observed in the case of corrosion inhibition by Curcumin extract. As the value of pH is increased the corrosion inhibition efficiency also increased [14].

Influence of immersion period on the inhibition efficiency of the HE-Zn^{2+} system

The influence of immersion period on the inhibition efficiency of the Henna extract is given in Table 9. As the period of immersion increases, the IE decreases. This is due to the fact that as the period of immersion increases the protective film formed on the metal surface is not able to withstand the attack of Cl^-, the film is broken and hence the IE decreases. Further, there is a competition between the formation of $FeCl_2$ (and also $FeCl_3$) and formation of iron-Lawsone complex. It seems that as the immersion period increases the formation of $FeCl_2$ is more favoured than the formation of iron-Lawsone complex at anodic sites of the metal. Hence a decrease in inhibition efficiency was noticed as the period of immersion increased. Similar observation was made with Fe^{2+} - Curcumin system [14].

Table 8 - Influence of pH on the Inhibition Efficiency of HE –Zn^{2+} system

Inhibitors: Henna extract (HE) + Zn^{2+}

Period of immersion: 1 day

Sl. No	pH	Cl- (ppm)	HE (mL)	Zn^{2+} (ppm)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
1	4	60	0	0	0.07422	-
	4	60	2	50	0.01856	75
2	6	60	0	0	0.19484	-
	6	60	2	50	0.00389	98
3	8	60	0	0	0.07886	-
	8	60	2	50	0.00394	95
4	12	60	0	0	0.04639	-
	12	60	2	50	0.00093	98

Table 9 - Influence of immersion period on the Inhibition Efficiency of HE –Zn^{2+} system

Inhibitors: Henna extract (HE) + Zn^{2+}

Period of immersion: 1,3,5,7 days

S.No	Immersion Period (day)	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	1	60	0	0	0.19484	--
	1	60	2	50	0.003897	98
2	3	60	0	0	0.31081	--
	3	60	2	50	0.02176	93
3	5	60	0	0	0.41287	--
	5	60	2	50	0.02890	93
4	7	60	0	0	0.62163	--
	7	60	2	50	0.04973	92

Influence of N-Cety1 - N, N, N – trimethyl ammonium bromide (CTAB) on the inhibition efficiency of the HE-Zn^{2+} system.

The influence of CTAB on the inhibition efficiency of the HE-Zn^{2+} system is given in Table 10. As the concentration of CTAB increases the IE remains constant. CTAB has biocidal effect [25, 26]. So the formulation consisting of Henna extract. Zn^{2+} and CTAB will have excellent corrosion inhibition efficiency and excellent biocidal efficiency. This formulation may find application in cooling water systems, provided the experiments are carried out at high temperature and dynamic condition.

Table 10 - Influence of CTAB of the Inhibition Efficiency of HE –Zn^{2+} system

Inhibitors: Henna extract (HE) + Zn^{2+} CTAB

Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	CTAB (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	2	50	0	0.00386	98
2	60	2	50	50	0.00389	98
3	60	2	50	100	0.00387	98
4	60	2	50	150	0.00388	98
5	60	2	50	200	0.00385	98
6	60	2	50	250	0.00389	98

Influence of Sodiumdodecylsulphate (SDS) on the inhibition efficiency of the HE – Zn^{2+} system

The influence of SDS on the inhibition efficiency of the HE-Zn^{2+} is given in Table 11. As the concentration of SDS increases the IE remains constant. The biocidal effects of SDS are under investigation [27]. If it is established on the formulation may find application in cooling water systems.

Table 11 - Influence of SDS of the Inhibition Efficiency of HE –Zn^{2+} system

Inhibitors: Henna extract (HE) + Zn^{2+} + SDS

Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	SDS (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	2	50	0	0.00390	98
2	60	2	50	50	0.00389	98
3	60	2	50	100	0.00388	98
4	60	2	50	150	0.00386	98
5	60	2	50	200	0.00387	98
6	60	2	50	250	0.00385	98

Influence of Sodium Sulphite (Na_2SO_3) on the inhibition efficiency of the HE-Zn^{2+} system.

The influence of Na_2SO_3 on the inhibition efficiency of the HE-Zn^{2+} is given in Table 12. As the concentration of Na_2SO_3 increases the IE remains constant. This may be explained by the fact that removal of oxygen in water by Na_2SO_3, and oxygen scavenger has no role to play in this system. Similar result has been observed in the case of caffeine – Zn^{2+} system[28]. But removal of oxygen had a major role in the curcumin Na_2SO_3 system, where it was noticed that an increase in the concentration of Na_2SO_3 improved the inhibition efficiency of curcumin [14].

Table 12 - Influence of Na_2SO_3 of the Inhibition Efficiency of HE –Zn^{2+} system

Inhibitors: Henna extract (HE) + Zn^{2+} + Na_2SO_3

Period of immersion: 1 day

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	Na_2SO_3 (ppm)	Corrosion Rate (mm/y)	Inhibition efficiency (%)
1	60	2	50	0	0.00385	98
2	60	2	50	50	0.00389	98
3	60	2	50	100	0.00388	98
4	60	2	50	150	0.00386	98
5	60	2	50	200	0.00387	98
6	60	2	50	250	0.00390	98

Analysis of Polarization curves

The polarization curves of carbon steel immersed in various solutions are shown in Figure 2. The corrosion parameters are given in Table 13. When carbon steel is immersed in an aqueous solution, the corrosion potential is –444 mV_{SCE}. When 2 mL of HE is added, the corrosion potential is shifted towards the onodic side, (-362$mVsc_E$) indicating that the HE controls the anodic reaction predominatly by forming Fe^{2+} - Lawsone complex on the anodic sites of the metal surface. when 2 mL of the HE and 50 ppm of Zn^{2+} are added to the chloride environment, the corrosion potential is shifted to cathodic side (-542 mV_{SCE}). This is due to the fact that in the presence of Zn^{2+}, cathodic reaction is also controlled by the formation of Zn $(OH)_2$ on the cathodic sites of the metal surface.

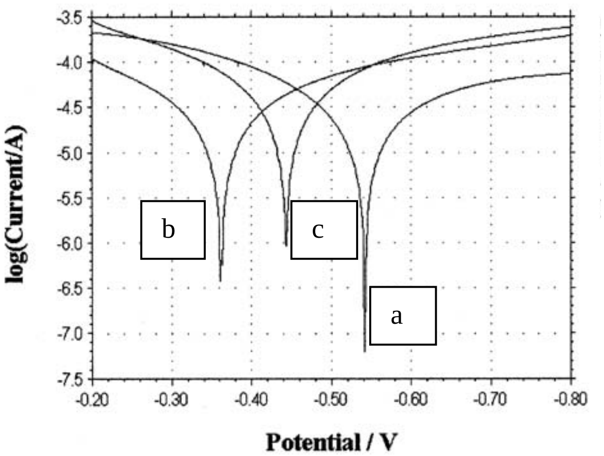


Figure 2 - Polarisation Curves of Carbon Steel immersed in various test solutions. (a) Cl^- 60ppm; (b) Cl^- 60ppm +HE 2mL; (c) Cl^- 60ppm +HE 2mL+Zn^{2+} 50ppm

Table 13 - Corrosion parameters of carbon steel immersed in various test solutions

Inhibitors: (HE) - Zn^{2+}

S.No	Cl- (ppm)	Henna extract (mL)	Zn2+ (ppm)	Ecorr (mVSCE)	ba (mV)	bc (mV)	I corr (A/cm2)
1	60	0	0	-444	89.47	84.21	1.2100x10-5
2	60	2	0	-362	31.58	47.37	0.39628x10-5
3	60	2	50	-542	42.10	47.37	0.33954x10-5

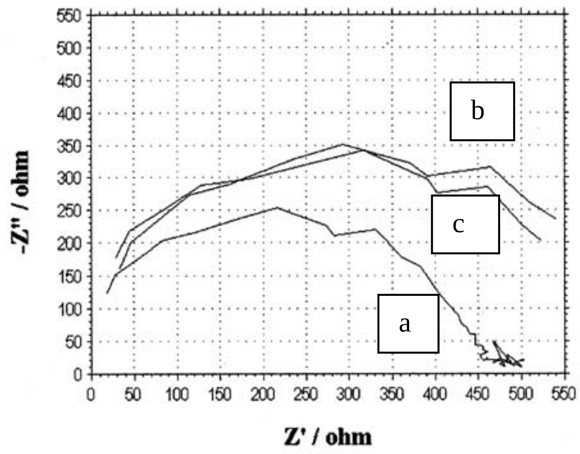


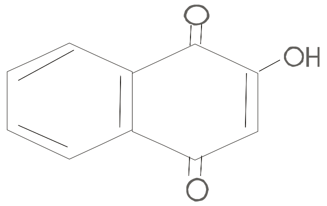
Figure 3 : AC Impedance Parameters of Carbon Steel immersed in various test solutions: (a) Cl^- 60ppm, (b) Cl^- 60ppm +HE 2mL, (c) Cl^- 60ppm +HE 2mL+Zn^{2+} 50ppm

Table 14 - Alternating Current Impedance parameters of carbon steel immersed in various solutions

Inhibitors: (HE) - Zn^{2+}

S.No	Cl^- (ppm)	Henna extract (mL)	Zn^{2+} (ppm)	R_t (Ωcm^2)	C_{dl} ($\mu F/cm^2$)
1	60	0	0	437.02	$1.4351x10^{-8}$
2	60	2	0	570.50	$0.89317x10^{-8}$
3	60	2	50	593.35	$0.85877x10^{-8}$

Fourier Transform Infrared Spectra



2–hydroxy–1,4- naphthaquinone

Scheme 1 : Lawsone

The main constituent of Henna extract is Lawsone. The structure of Lawsone is shown in scheme 1. It contains benzene unit, p-benzoquinone unit and phenolic group.

The Henna extract was evaporated to dryness to get a solid mass. Its FTIR spectrum is shown in Figure 4a. The phenolic O-H stretch appeared at $3437cm^{-1}$. The aromatic C=C stretching frequency appeared at 1514 cm^{-1} The C=0 stretching frequency appeared at 1624 cm^{-1}. Thus lawsone was characterized by IR spectroscopy [29].

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the solution containing 60 ppm of Cl^-, 50 ppm of Zn^{2+} and 2mL of HE is shown in Figure 4b. It is found that the phenolic O-H stretch has shifted from 3437 cm^{-1} to 3346 cm^{-1}. the aromatic C=Cstretching frequency has shifted from 1514 cm^{-1} to 1504 cm^{-1}. The c=0 stretching frequency has shifted from 1624 cm^{-1} to $1655cm^{-1}$. It was inferred that Lawsone has coordinated with Fe^{2+} through the phenolic oxygen, aromatic ring and C=0 group of the p-benzo quinone resulting in the formation of Fe^{2+} - Lawsone complex on the anodic sites of the metal surface. The bund at 1350 cm^{-1} due to the Zn $(OH)_2$ formed on the cathodic sites of the metal surface. Thus FTIR spectral study leads to the conclusion that the protective film consists of Fe^{2+} - Lawsone complex and Zn $(OH)_2$ [30,31].

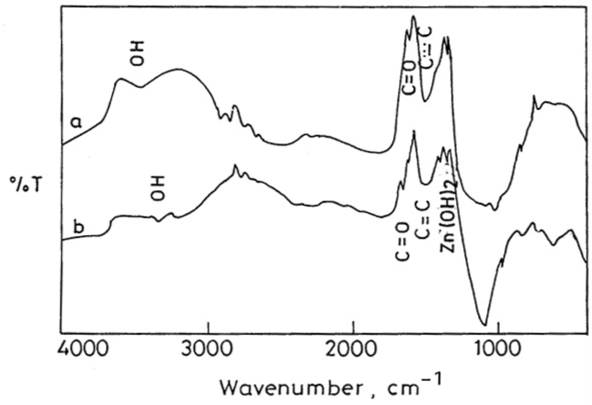


Figure 4 - FTIR Spectra: (a) HE evaporated to dryness (Lawsone); (b) Film formed on metal surface after immersion in the solution containing 60ppm Cl^- +2mL of HE+50ppm of Zn^{2+}

Fluorescence spectra

The aqueous extract of Henna (Lawsone) was evaporated to dryness to get a solid mass. It emission spectrum (λ em = 527 nm) is shown in Figure 5a. Peaks appeared at 426, 484, 527 and 670 nm. The corresponding excitation spectrum (λ ex = 387 nm) is shown in Figure 5d. Peaks appeared at 235, 256 and 386 nm. The emission spectrum (λ em = 527 nm) of solid Fe^{2+} - Lawsone complex prepared by mixing Fe^{2+} and aqueous extract of Lawsone is shown in Figure 5b. Peaks appeared at 126, 488 and 527 nm. The corresponding excitation spectrum (λex=387nm) is shown in Figure 5e. Peaks appeared at 235, 254 and 384 nm.

The fluorescence spectrum (λem = 527 nm) of the film formed on the surface of the metal after immersion in the solution containing 60 ppm of Cl^-, 50ppm of Zn^{2+} and 2ml of Henna extract is shown in Figure 5c. The peaks appeared at 425, 489, 527 nm confirming the presence of Fe^{2+} - Lawsone complex formed on the metal surface. The corresponding excitation spectrum (λex = 387 nm) is shown in Figure 5f.

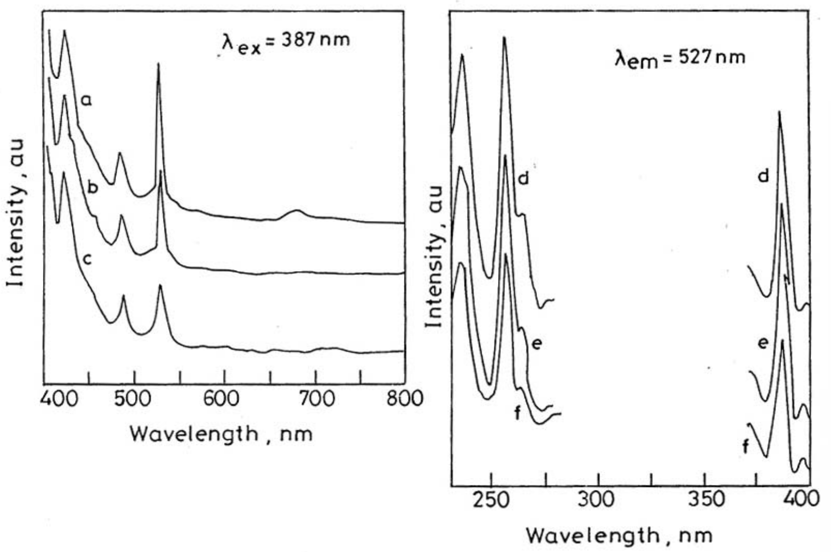


Figure 5 - Fluorescence Spectra: (a) and (d) Emission and Excitation spectrum of solid mass obtained by evaporating the HE (Lawsone); (b) and (e) Emission and Excitation spectrum of solid Fe^{2+}- Lawsone Complex prepared; (c) and (f) film formed on the surface of Carbon Steel after immersion in the solution containing 60ppm of Cl^- +2mL of HE+ 50ppm of Zn^{2+}

Mechanism of Corrosion inhibition

The formulation consisting of 60 ppm of Cl^-, 50ppm of Zn^{2+} and 2 mL of HE has 98% IE. Based on the results of mass loss study, FTIR spectral study, fluorescence spectral study, polarization and AC impedarance studies the following mechanism of corrosion inhibition is proposed.

1. When the environment consisting of 60 ppm of Cl^-, 50 ppm of Zn^{2+} and 2mL of Henna extract is prepared, there is formation of Zn^{2+} - Lowsone complex in solution.
2. When carbon steel specimen is introduced in this solution, Zn^{2+} - Lawsone complex diffuses from the bulk of the solution toward the metal surface.
3. On the metal surface, Zn^{2+} - Lawsone complex is converted into Fe^{2+} - Lawsone complex on the anodic sites of the metal surface, Zn^{2+} ion is released Zn^{2+} - Lawsone + $Fe^{2+} \rightarrow Fe^{2+}$ -Lawsone+Zn^{2+}
4. The released Zn^{2+} combines with OH^- to form Zn $(OH)_2$ on the cathodic sites of the metal surface.
5. Thus the protective film consists of Fe^{2+} - Lawsone complex and Zn $(OH)_2$.
6. This film is found to be UV-fluorescent.

CONCLUSION

- The main constituent of the aqueous extract of Henna is Lawsone.
- An aqueous extract of Henna has excellent IE in controlling corrosion of Carbon steel in an aqueous solution containing 60 ppm of Cl^-.
- It has excellent, IE at pH 6, 8 and 12; it shows good IE at pH 4.
- The IE of Lawsone increases when mixed with Zn^{2+} ion.
- A synergistic effect exists between Zn^{2+} and Lawsone
- The protective film consists of Fe^{2+} - Lawsone complex and Zn $(OH)_2$
- It is found to be UV – fluorescent.
- The HE – Zn^{2+} formulation controlls the cathodic reaction predominantly.
- The excellent inhibition efficiency of HE – Zn^{2+} system remains constant in the presence of CTAB, SDS and Na_2 So_3.
- The IE decreases, when period of immersion increases.

Scope for further research

There is vast scope for using henna extract under various conditions

- Experiments may be carried out at high temperature and under dynamic condition.
- Experiments may be carried out under deaesated conditions
- The biocidal influence of SDS may be established
- The biocidal influence of HE may be established

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