

CORROSION KINETIC AND ADSORPTION THERMODYNAMIC ACTIVITY OF *Enicostemma littorale* (Indian Whitehead) FOR CARBON STEEL IN WELL WATER

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ABSTRACT

The inhibition actions of ethanolic extract of *Enicostemma littorale* (EL) leaves-Zn²⁺ for carbon steel (CS) surface in well water has been studied by mass-loss study, Tafel slopes, and Nyquist plots, Impacts of inhibitor concentration (100ppm-500ppm), temperatures (30°C-70°C), pH (3,8,12) and submersion period (1,3,7,12) were researched on the prevention capacity of the extract on CS submerged in well water. The adsorption of ethanolic extract of EL leaves onto the surface of CS pursued that as indicated by a Langmuir model. The *Enicostemma littorale* extract exposed a blended-type corrosion inhibitor in the considered environment as indicated by the electrochemical studies. Theoretical fittings for the corrosion kinetics and thermodynamic parameters have been determined to explain the method of adsorption of ethanolic extract of EL-Zn²⁺ on the CS surface. ΔG_{ads} values are less than -20KJ/mol. From these values, the adsorption of an inhibitor system is physisorption on the CS surface. Energy-dispersive X-ray technique was utilized to identify the elemental composition of the corrosion substances or potentially adsorbed inhibitor film on the CS. Scanning electron microscopy, atomic force microscopy and Fourier transfer infrared assessments affirm the development of a defensive layer by the ethanolic extract of *Enicostemma littorale* leaves on the CS surface in well-water.

Keywords: Carbon Steel Corrosion, Electrochemical Methods, Adsorption Isotherm, F-Test, Synergistic Effect, Surface Analysis.

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INTRODUCTION

Carbon steel (CS) was utilized for the treatment of salt, corrosive and acid combinations in chemical and associated industries. Theoretical and practical implications, research into corrosion protection of CS has always been vital. The presence of chloride, sulphate and nitrite particles in a wet environment bases high corrosion rates (CR).¹ The plant extract is one of the successful approaches to the counteraction of corrosion on the CS surface in well water. As a result, the plant extracts are nontoxic, eco-accommodating, biodegradable, and effectively possible for corrosion studies.²⁻³ Many research creativities are efficiently cultivated to set up these green inhibitors that are effective for corrosion avoidance on the various steels in the various medium solutions.⁴⁻⁸ The data of kinetic and thermodynamic studies associated with such inhibitors is vital for comprehension of their efficiency in the neutral medium at an expected temperature of the cycle. Corrosion kinetics and adsorption thermodynamic conduct of plant extracts on the metal surface in the various corrosive solutions is extensively informed.⁹⁻¹⁴ The heat of adsorption and free energy of adsorption values are negative in sign, these negative values reveal that an adsorption action of EL extract on the CS surface is spontaneous. When ΔG_{ads} values are less than -20KJ/mol, the inhibitor molecules adsorbed on the CS surface are physisorption. When ΔG_{ads} values are higher than -40KJ/mol, the inhibitor molecules adsorbed onto the CS surface are chemisorption.^{15,16,41} The present work is utilized to evaluate the corrosion kinetic and thermodynamic adsorption activity of *Enicostemma littorale* (EL) on the CS in well water by using activation energy (Ea), adsorption of enthalpy (ΔH), adsorption of entropy (ΔS), K_{ads} and ΔG_{ads} values. Lately, the approach in the use of corrosion inhibitors has shifted to obviously taking place and environmentally pleasant chemical materials, popularly called “green inhibitors”, because of the clean

accessibility and non-toxic effect such natural inhibitors have on both humans and the surroundings.⁵³ Ethanolic extract from one kind part of an *Enicostemma littorale* (EL) leaves is a correct example of an inexperienced inhibitor. Hence, in this study's work, the *Enicostemma littorale* extract might be investigated as a corrosion inhibitor, and its corrosion performance and adsorption conduct could be installed.

EXPERIMENTAL

Corrosion Test

An *Enicostemma littorale* (EL) leaves extract has been worked on the CS specimen with the chemical composition of 0.06 'percent' P, 0.4'percent' Mn, 0.3'percent' S, 0.1'percent' C, and the remainder Fe. Corrosion studies were carried out in well water (WW) on the CS surface by the ethanolic extract of EL leaves-Zn²⁺ ions (Combined inhibitor system).

Weight-Loss Assays

It was performed to calculate the IE, CR, and surface coverage^{17,18} for CS immersed in WW covering numerous concentrations (100ppm-500ppm) of EL extract. After various immersion periods, the CS was takeout, washed out in DD water, desiccated by a desiccator then weighted accurately. From these results, IE, CR, and surface coverage values for a tested inhibitor on the corrosion of CS is calculated using the following equation 1, 2, and 3.^{17-19,41}

$$IE \text{ ('per cent')} = \left(1 - \frac{\text{Weight loss (mg)}_{\text{Inhibitor}}}{\text{Weight loss (mg)}_{\text{Blank}}} \right) \times 100 \quad (1)$$

$$CR \text{ (mmpy)} = \frac{87.6 \times \text{Weight loss (mg)}}{\text{area(m}^2\text{)} \times \text{time(day)} \times \text{density(7.85gcm}^{-2}\text{)}} \quad (2)$$

$$\text{Surface coverage}(\theta) = \left(1 - \frac{WL \text{ (mg)}_{\text{Inhibitor}}}{WL \text{ (mg)}_{\text{Blank}}} \right) \quad (3)$$

Where WL is weight loss for the inhibitor and blank system.

Electrochemical Techniques

EIS and PDP measurements were directed in three-cathode electrochemical cell gathering by utilizing the model: 760D, CHI (electrochemical analyzer). A reference electrode operates as a saturated calomel electrode. The Counter electrode serves as a platinum (Pt) sheet. CS specimen behaves as a working electrode. IE was calculated using the following equation 4 and 5.²⁰

$$IE \text{ ('per cent')} = \left(1 - \frac{R_{ct} \text{ (Blank)}}{R_{ct} \text{ (Inhibitor)}} \right) \times 100 \quad (4)$$

Where R_{ct} is charge transfer resistance of blank and EL-Zn²⁺ system.

$$IE \text{ ('per cent')} = \left(1 - \frac{I_{\text{corrosion}} \text{ (Inhibitor)}}{I_{\text{corrosion}} \text{ (Blank)}} \right) \times 100 \quad (5)$$

Where ' $I_{\text{corrosion}}$ ' is the corrosion potential of the EL-Zn²⁺ and blank system.

Kinetic Study

Corrosion kinetic parameters (CKT) have been used to evaluate the corrosion process on the CS surface for EL leaves extracted with well water according to the Arrhenius equation-6.²⁰

$$\ln CR = \ln A - \frac{E_a}{RT} \quad (6)$$

Where, CR is the corrosion rate for the inhibitor system, A is the Arrhenius constant, R is 8.314KJ/mol and T is the temperature for the corrosion system.

Activation energy (E_a)²¹, and enthalpy change (ΔH)^{20,22,23} values were computed by equations 7 and 8.

$$E_a = \ln R \frac{CR_1(\text{lower temperature})}{CR_2(\text{higher temperature})} \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (7)$$

Where, CR_1 is the corrosion rate for a lower temperature (T_1) of the corrosion system, and CR_2 is the corrosion rate for a higher temperature (T_2) of the corrosion system.

$$\Delta H = E_a - RT \quad (8)$$

Where ' ΔH ' is the enthalpy change of the corrosion inhibition system.

Thermodynamic Study

Adsorption thermodynamic parameters (ATP) were calculated to determine the energy required for the heat involved and the mechanism^{22,23} of corrosion for EL leaves extract.

The free energy of adsorption (ΔG_{ads})^{20,24} heat of adsorption (q_{ads})¹⁷ are computed by equations 9 and 10.

The entropy of adsorption ΔS_{ads} is calculated from equation-9.¹⁸

$$\Delta G_{ads} = -RT \ln(K_{ads} 55.5) \quad (9)$$

Where, 55.5 is the concentration (molar) of water in a solution.

$$K_{ads} = \frac{\text{surface coverage}}{\text{Concentration}_{(inhibitor)} \times (1 - \text{surface coverage})}$$

$$q_{ads} = 2.303R \left[\log \frac{\theta_{T_2}}{1 - \theta_{T_2}} - \log \frac{\theta_{T_1}}{1 - \theta_{T_1}} \right] \left(\frac{T_1 T_2}{T_2 - T_1} \right) \quad (10)$$

θ_{T_1} is the surface coverage for a lower temperature (T_1) of the corrosion inhibition system. θ_{T_2} is the surface coverage for a higher temperature of the corrosion inhibition system.

$$\Delta S_{ads} = \frac{q_{ads} - \Delta G_{ads}}{T} \quad (11)$$

Synergistic Inhibition (SI) Parameters

The SI values are used to determine the synergistic inhibition action for EL leaves extract and Zn^{2+} .²⁵ SI values are calculated using the following equation-12.

$$SI = \frac{1 - \theta_{(a+b)}}{1 - \theta'_{(a+b)}} \quad (12)$$

$$\theta_{(a+b)} = (\theta_a + \theta_b) - (\theta_a \times \theta_b)$$

Where, θ_a and θ_b is surface coverage for the inhibitor and Zn^{2+} on the CS surface, θ_{a+b} is collective surface coverage for a combined inhibitor (EL- Zn^{2+}) system.

Adsorption isotherms model

The various isotherm models are performed to estimate the adsorption activity of an inhibitor as well as the best-fit adsorption isotherm model on the CS surface¹⁵ for EL leaves extract Zn^{2+} system in well water.

$$\text{Langmuir isotherm.}^{15,23,24,26,52} \frac{C_{Inhibitor}}{\theta} = C_{Inhibitor} + \frac{1}{K_{ads}} \quad (13)$$

Where C is the concentration of the inhibitor, K_{ads} is the equilibrium constant.

$$\text{EL-Awady isotherm}^{15}: \log \left(\frac{\theta}{1 - \theta} \right) = y \log C_{Inhibitor} + \log K_{ads} \quad (14)$$

Where y is the total number of inhibitor components inhabiting the CS surface.

$$\text{Flory-Huggins isotherm}^{15}: \log \frac{\theta}{C_{Inhibitor}} = b \log(1 - \theta) + \log K_{ads} \quad (15)$$

$$\text{Temkin isotherm}^{15}: \theta = \ln C_{Inhibitor} + K_{ads} \quad (16)$$

RESULTS AND DISCUSSION

Mass-loss (ML) Study

ML studies are used to calculate the IE, and CR from the various immersion period, temperatures, and pH on the CS surface in well-water with and without different concentration of EL leaves for identity the corrosion inhibition capacity of an inhibitor. A corrosion test is carried out on the CS immersed in well

water by using ethanolic extract of EL leaves with Zn^{2+} . Every inhibitor system has an individual IE that may be lower or higher IE. This is based on the number of molecules present in an inhibitor system. When the Zn^{2+} is added to the inhibitor system, the IE is increased to 95 ‘percent’ from 56 ‘percent’ for an optimum concentration of EL- Zn^{2+} (500ppm-30ppm) system. This result indicates the creation of a defensive complex of EL- Zn^{2+} and zinc hydroxide onto the oxidation and reduction region of the CS surface. Corrosion control takes place on both the anodic and cathodic sites.⁴⁵ The data of IE and CR is shown in Table-1. The effect of EL- Zn^{2+} concentration on IE is drawn in Fig.-1.

Oxidation reaction at anode site⁴⁵: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (17)

Reduction reaction at cathode site⁴⁵: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ (18)

Table-1: Mass-Loss Data for One Day Immersion Period

EL (ppm)	IE %				CR (mmpy)			
	Zn^{2+} (ppm)				Zn^{2+} (ppm)			
	0	10	20	30	0	10	20	30
0	-	10	12	28	0.1809	0.1628	0.1598	0.1302
100	25	36	39	41	0.1357	0.1158	0.1103	0.1067
200	37	49	54	62	0.1140	0.0922	0.0832	0.0687
300	44	56	65	73	0.1013	0.0795	0.0633	0.0488
400	49	63	69	81	0.0923	0.0669	0.0561	0.0344
500	56	74	79	95	0.0796	0.0470	0.0380	0.0090

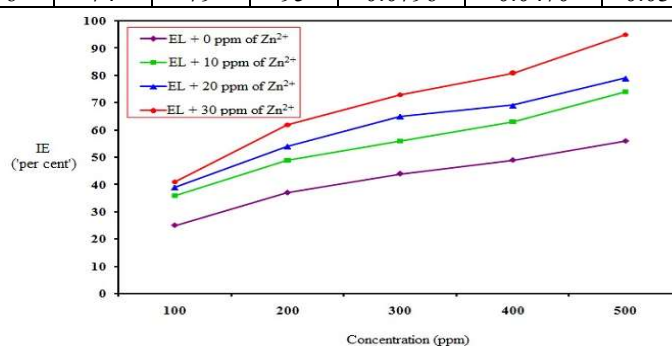


Fig.-1: Effect of Inhibitor Concentration on Percentage of IE

Effect of Immersion Period (EIP)

The EIP on the corrosion behavior of Ethanolic extract of EL leaves was investigated by the WL experiment. Fig.-2 and 3 depicted the impact of the immersion period (1,3,7 and 12) on the CR and IE. The data of EIP are shown in Table-2. The IE is found to be 95 ‘percent’, CR is 0.0090 at an optimum concentration of EL- Zn^{2+} (500ppm-30ppm) system.¹⁸ From this result, the two inhibitor combination has been stronger for obtained IE than a single inhibitor system.²⁷

Table-2: Immersion Period Data

Immersion Period (days)	CR (mmpy)		IE (‘percent’)
	Well water	EL- Zn^{2+} (500ppm-30ppm)	
1	0.1809	0.0090	95
3	0.2013	0.0262	87
5	0.2124	0.0425	80
7	0.2158	0.0626	71

Influence of Temperature (IT) on CR

The IT dependency of corrosion rates in inhibited and uninhibited solutions,^{41,46} ML measurement was performed in the temperature range from 30°C to 70°C by different concentrations of EL (100ppm-500ppm). The calculated CR and IE are given in Table-3. When the temperature is increased, CR is

increased and also IE is decreased for EL-Zn²⁺ System.^{41,46} This is due to the desorption process being increased on the CS surface at higher temperatures.⁴⁶ Therefore, this result indicates the adsorption of ethanolic extract of EL leaves is physisorption on the CS surface.^{41,46,43} The impact of temperature on CR and the percentage of IE is drawn in Fig.-4 and 5.

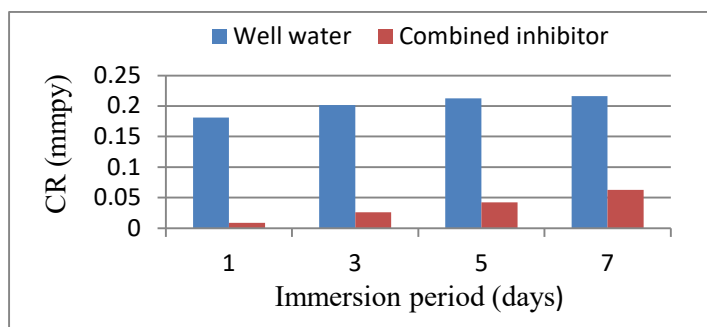


Fig.-2: Effect of Immersion Period on CR

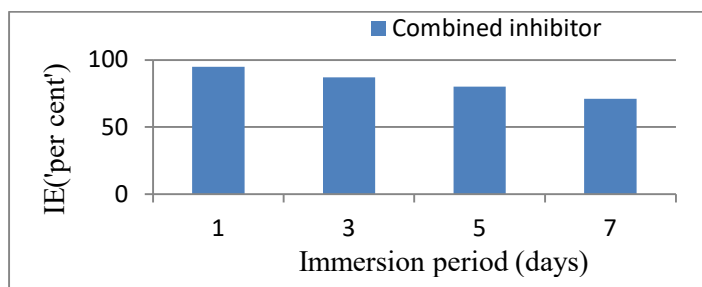


Fig.-3: Effect of Immersion Period on Percentage of IE

Table-3: Mass-Loss Data Using Various Temperatures

EL-Zn ²⁺ (ppm)	Temperature (Celsius)									
	30		40		50		60		70	
	IE ('percent') and CR (mmpy)									
Blank	-	0.1809	-	0.2248	-	0.2437	-	0.2728	-	0.3102
100	41	0.1067	38	0.1842	32	0.2001	27	0.2469	21	0.2762
200	62	0.0687	57	0.1528	51	0.1765	44	0.2036	38	0.2414
300	73	0.0488	68	0.1329	62	0.1596	56	0.1867	50	0.2033
400	81	0.0344	77	0.1199	71	0.1342	64	0.1629	59	0.1811
500	95	0.0090	91	0.0896	85	0.1032	78	0.1298	71	0.1533

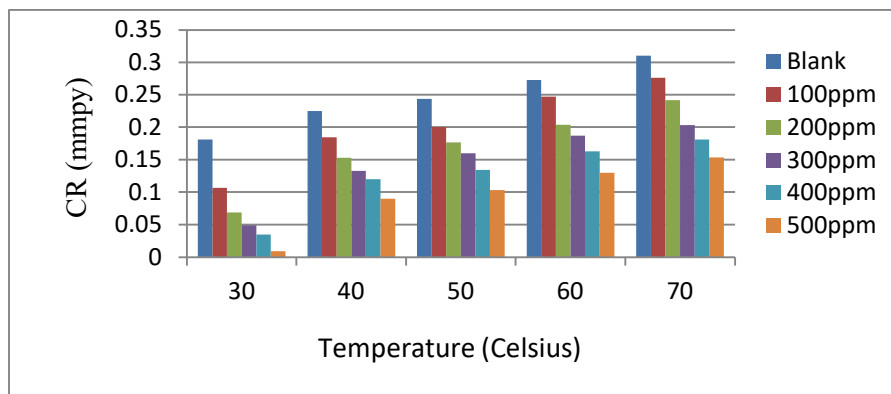


Fig.-4: Effect of Temperature on CR

Effect of pH

The CR and IE were obtained from immersion tests as a function of well-water and an optimum concentration of ethanolic extract of EL leaves on the CS surface at three pH values (3, 8, and 12). This result is given in Table-4. In the pH 8 region, the corrosion rate remained constant approximately. When the pH value is reduced to 3 by the addition of HCl, the corrosion rate is increased from 0.0090 to 0.0682. This is due to the HCl being added to an inhibitor system (pH 8), a defensive layer damaged by the intense attack of H^+ ions.³³

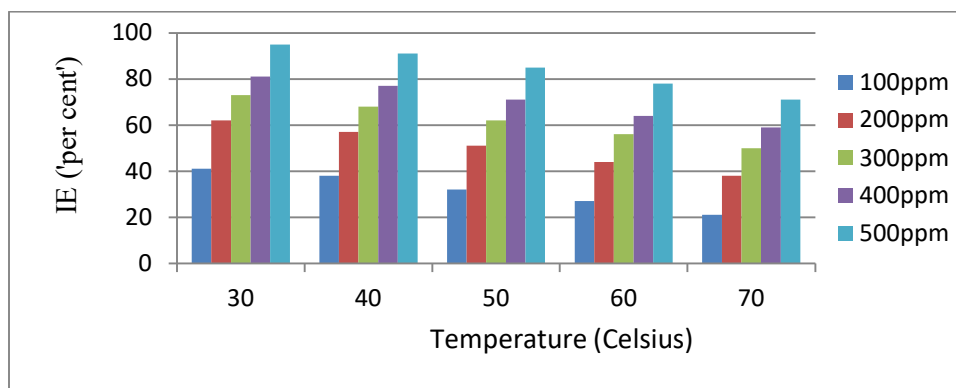


Fig.-5: Effect of Temperature on Percentage of IE

The pH value is increased to 12 by the addition of NaOH, and CR is decreased to 0.0249 from 0.0682, because of a statement that Zn^{2+} in a bulk of the solution is precipitated as $Zn(OH)_2$.²⁸ The influence of pH on CR and the percentage of IE is drawn in Fig.-6 and 7.

Table-4: Mass-Loss Data Using Different the pH Level

pH	CR (mmpy)		IE ('percent')
	Well water	EL- Zn^{2+} (500-30ppm) system	
3	0.2067	0.0682	67
8	0.1809	0.0090	95
12	0.1912	0.0249	87

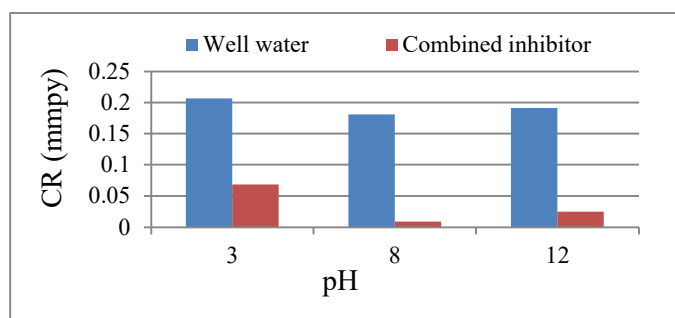


Fig.-6: Effect of pH On CR

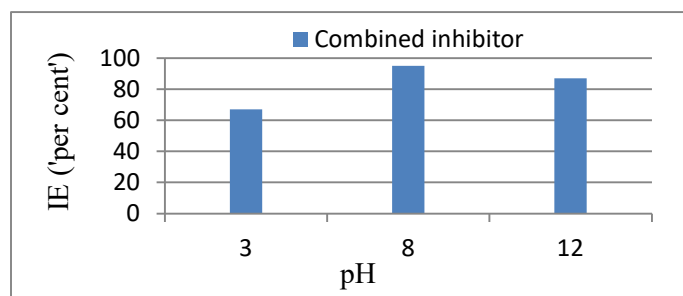


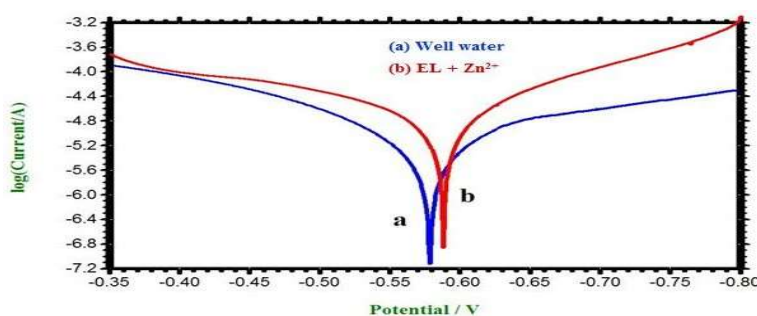
Fig.-7: Effect of pH on The Percentage of IE

Potentiodynamic Polarization (PDP) Study

The PDP curves obtained for CS submerged in well-water and EL leaves extract are drawn in Fig.- 8. The polarization curves are utilized to compute the corrosion potential ($E_{\text{corrosion}}$), corrosion current ($I_{\text{corrosion}}$), anodic incline (b_a), and cathodic incline values (b_c).^{51,52} These results are shown in Table-5. $E_{\text{corrosion}}$ is -580mV SCE, when CS is submerged in a blank system. When the CS submerged in a blank system with an optimum concentration of EL-Zn²⁺ (500ppm-30ppm) system, the $E_{\text{corrosion}}$ value is shifted into -589mV vs SCE (positive side) from -580mV vs SCE. The maximum displacement in $E_{\text{corrosion}}$ value is found to be < -10mV. Therefore, in this work, the EL leaves extract behaves as a blend-type inhibition on the CS surface.^{51,52,55} This is due to a change in $E_{\text{corrosion}}$ value is less than 85mV in presence of an inhibitor.⁵² Linear polarization resistance (LPR) value is increased and C_{dl} is also decreased^{46,52} when 500ppm of EL and 30ppm of Zn²⁺ are added to a blank system. These results appearances the formation of a defensive layer on the surface of CS.^{46,51,52}

Table-5: Polarization Parameters

System	$E_{\text{corrosion}}$ (mV)	b_a (mV/decade)	b_c (mV/decade)	LPR ($\Omega \text{ cm}^2$)	$I_{\text{corrosion}}$ ($\mu\text{A}/\text{cm}^2$)	IE ('percent')
Well water (Blank)	-580	116.23	110.88	963	5.5431	-
EL-Zn ²⁺ (500:30ppm)	-589	146.35	160.24	3604	0.1329	97.61

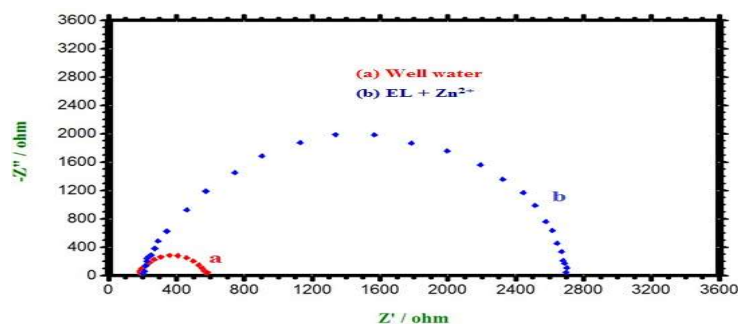
Fig.-8: Tafel Curves for Well Water and EL-Zn²⁺ System

AC Impedance Spectroscopy (EIS) Test

EIS study is performed to calculate the values of charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) from Nyquist curves in well-water with an optimum concentration of EL-Zn²⁺ (500ppm-30ppm) system to determine the activity of adsorption for an inhibitor over the CS surface.^{45,46,51} The data of EIS parameters are given in Table-6. Electrochemical impedance spectra appear that the diameter of Nyquist curves is raised on the cumulative concentration of EL leaves extract demonstrating reinforcement of the protective film²⁹ over the CS surface. The Nyquist plot comprises of a depressed semicircle which is an attribute of the solid electrode that demonstrates the frequency dispersion of impedance data, due to surface inhomogeneity and roughness of CS electrodes. An inductive curve in the lesser-frequency region (LFR) and a down capacitance curve in the higher-frequency region (HFR) were observed in the Nyquist plots. The HFR capacitance curve is due to the R_{ct} reaction and time constant of the C_{dl} to the CS surface irregularity of structural or interfacial sources in adsorption processes.^{30,31} The R_{ct} value has increased and also C_{dl} value is reduced, when the 500ppm of EL extract, 30ppm of Zn²⁺ is added to the blank system. This result shows that the creation of a defensive layer on the surface of CS.^{45,46,51} Nyquist plots exist shown in Fig.-9.

Table-6: EIS Parameters

System	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE ('percent')
Well water (Blank)	599	1.3137	-
EL- Zn ²⁺ (500ppm-30 ppm)	2700	0.03171	77.81

Fig.-9: Nyquist Plots for Well Water and EL-Zn²⁺ System

Synergistic Inhibition (SI) Effect

SI effect was used to calculate the SI parameters for determining the synergistic inhibition effect existing between the ethanolic extract of EL leaves and Zn²⁺ ions.⁵¹ Data of the SI effect are given in Table-7. If the value of SI is less than one, this inhibitor system has a negative SI effect existing between EL extract and Zn²⁺ ions. If the value of SI is equal to one⁵¹, this inhibitor system has no SI effect existing between EL extract and Zn²⁺ ions. If the value of SI is greater than one, this inhibitor system has a good SI effect existing between EL extract and Zn²⁺ ions.⁵¹ Therefore, the 100ppm of EL extract and 30ppm of Zn²⁺ system have a negative SI effect between EL extract and Zn²⁺. From the 200ppm to 500ppm of EL extract and 30ppm of Zn²⁺ systems have an effective SI effect between EL extract and Zn²⁺. This is due to the SI value is greater than one in a higher concentration of EL extract.⁵¹

Table-7: Synergism Parameters

EL (ppm)	Zn ²⁺ (ppm)	θ_1	θ_2	θ'_{1+2}	SI	IE ('percent')
100	30	0.25	0.28	0.41	0.9295	41
200	30	0.37	0.28	0.62	1.1937	62
300	30	0.44	0.28	0.73	1.4933	73
400	30	0.49	0.28	0.81	1.9326	81
500	30	0.56	0.28	0.95	6.3360	95

F-Test

F-study was performed to evaluate whether the EL-Zn²⁺ system was statistically significant or not by the SI effect between ethanolic extract of EL and Zn²⁺ ions.³² These results are displayed in Table-8. The computed F values of 10 and 20ppm of Zn²⁺ are 0.95 and 4.04. These inhibitor systems are not statistically significant, since these F values are smaller than the critical F value of 5.32 for 1.8 degrees of freedom on 0.05level of significance.³² The calculated F value for 30ppm of Zn²⁺ is 7.16. This inhibitor system has a statistically significant, due to the F-value being higher than the critical F value of 5.32 for 1.8 degrees of freedom on 0.05level of significance.³²

Table-8: F-study Data

Zn ²⁺ (ppm)	Level of Significance of F	Source of variance	Sum of squares	Degree of freedom	Mean square	F
10	P > 0.05	Between	448.9	1	448.9	2.59
		Within	1384	8	173	
20	P > 0.05	Between	903.1	1	903.1	4.82
		Within	1499	8	187.4	
30	P > 0.05	Between	1988.1	1	1988.1	7.16
		Within	2222	8	277.8	

FI-IR Spectroscopy

It is utilized to characterize and detect the various functional atoms existing in the ethanolic extract of EL leaves. FITR spectra of dried EL extract and EL-Zn²⁺ system are depicted in Fig.-10. From Fig.-10a, the broad peak attained at 3407 cm⁻¹ (O-H) indicates an alcohol/phenol functional group.³³ The C-O stretching vibration obtained at 1170cm⁻¹.³³ Fig.-10b shows the broad peak obtained at 3259cm⁻¹(O-H) suggests an alcohol/phenol functional group.³³ The peak around 1177cm⁻¹ indicates C-O stretching

vibration.³³ The peak was obtained at 619cm^{-1} , indicating a Zn-O group. Therefore, it is concluded that the formation of EL-Zn²⁺ complex protects to anode side corrosion, and also Zn(OH)₂ protects to cathode side corrosion on the CS surface.

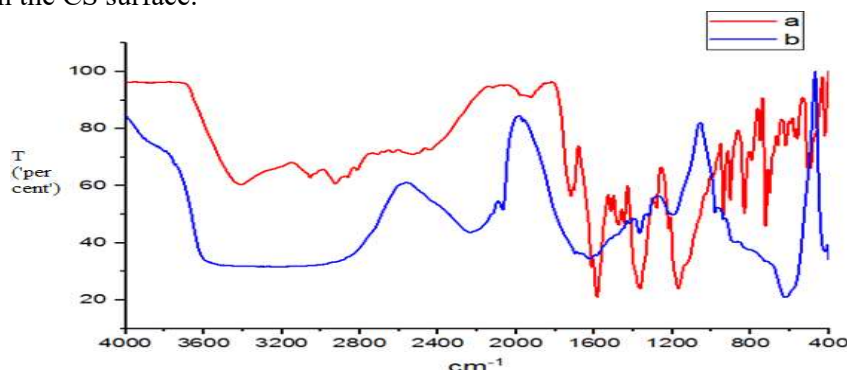


Fig.-10: FT-IR Spectra for Well Water (a) and EL-Zn²⁺ (b) System

Corrosion Kinetic Studies

Temperature can affect CS corrosion in a blank system (well water) as well as the ethanolic extract of EL leaves. To compute the kinetic variables such as activation energy (E_a) and the enthalpy change (ΔH) for evaluating the mode of reaction and adsorption process taking place on the CS surface. The data of corrosion kinetic variables are given in Table-9. E_a values are increases when the concentration of EL leaves extract is increased, this result exposes the adsorption activity existing over the CS surface.^{21,46} The values of enthalpy change (ΔH) are positive in sign. The positive data of ΔH suggest that the creation of strong adsorption on the CS surface is an endothermic reaction.^{22,34} The Arrhenius plots for the effect of temperature are drawn in Fig.-11.

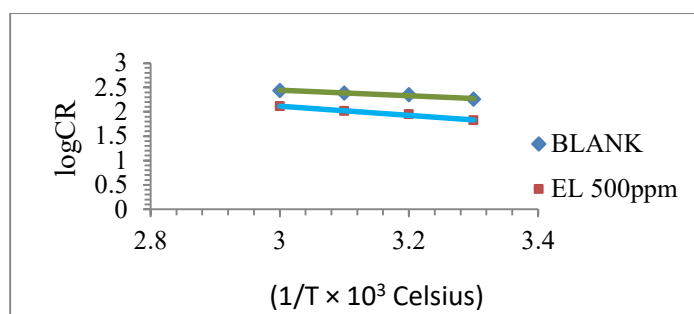


Fig.-11: Arrhenius Plots

Table-9: Kinetic Variables

EL-Zn ²⁺ (ppm)	E_a (KJ/mol)	ΔH (KJ/mol)
Blank	17.1	14.6
100	43.0	40.5
200	63.0	60.5
300	79.0	76.5
400	98.5	95.9
500	181.2	178.7

Adsorption Thermodynamic (AT) studies

AT parameters are used to identify the mechanism of the corrosion protection process^{36,37} on the CS surface using an optimum concentration of ethanolic extract of EL leaves-Zn²⁺ (500ppm-30ppm). ATP results are shown in Table-10. Gibb's free energy of adsorption (ΔG_{ads}) and heat of adsorption (q_{ads}) values are negative in sign. The ΔG_{ads} values are less than -20KJ/mol. Therefore, the adsorption of EL leaves extract on the CS surface is physisorption due to the electrostatic contact among the inhibitor

molecules and the charged CS.^{22,23,34,38,39} These values (ΔG_{ads} and q_{ads}) supported the spontaneous and a stable physical adsorption mechanism of ethanolic extract of EL leaves on the CS surface in well water.^{35-37,46} The negative values for the entropy of adsorption (ΔS) proposed to the creation of an activated complex among the adsorbate and adsorbent, the absorption activity also indicates an associative mechanism on the CS surface.^{23,36,37}

Table-10: Thermodynamic Parameters

EL-Zn ²⁺ (500ppm-30ppm) system				
Temperature (Celsius)	ΔG_{ads} (KJ/mol)	q_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol)	K_{ads}
30	-19.3	-49.8	-0.228	38
40	-18.3	-48.7	-0.214	20.2
50	-17.3	-41.9	-0.184	11.3
60	-16.6	-35.2	-0.155	7.1

The Adsorption Isotherm Models

Adsorption isotherm model provides the fundamental information on the interaction between the ethanolic extract of EL leaves and the CS surface.⁴¹ Hence, the surface coverage values for the various concentrations of EL leaves extract in well-water at the temperature range from 303K to 343K have been explained using the best-fit isotherm to identify the adsorption process.⁴⁰ The Regression coefficient (R^2) values obtained for the Langmuir model at various temperatures (303K-343K) are quiet when compared with that from the three isotherm models (EL- Awady, Temkin, and Flory-Huggins). From the results in Figures (Fig.-11, 12, 13, and 14), the R^2 value of the Langmuir model is close to the unit^{40,41,53}, the C is linearly related to the C/θ .⁴⁶ Therefore, the adsorption of EL leaves extract is followed by the Langmuir isotherm model.^{41,52,53} Equilibrium constant (K_{ads}) values are utilized to determine the strength between adsorbate and adsorbent⁴¹. The K_{ads} values are reduced when the temperature is increased (30° C -70° C). This result shows that a defensive layer is broken from the surface of CS, due to the desorption process taking place on the CS surface. From the calculated K_{ads} values, the adsorption of ethanolic extract of EL leaves on the CS surface is physisorption.

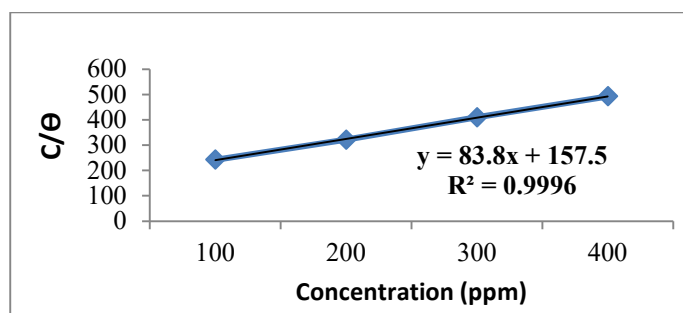


Fig.-11: Langmuir Adsorption Isotherm at 30° C

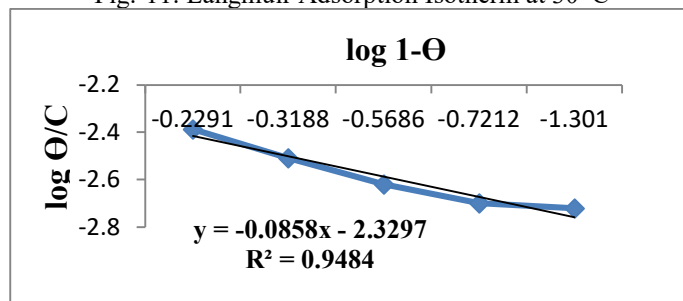


Fig.-12: Flory-Huggins Adsorption Isotherm at 30° C

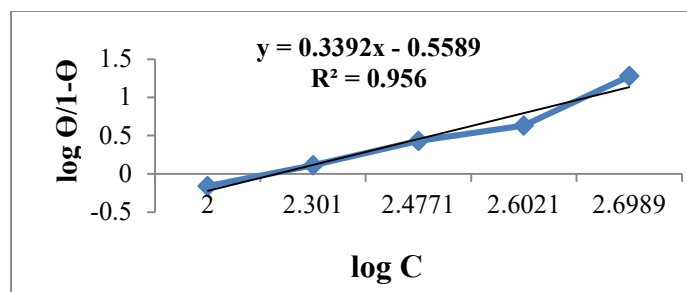


Fig.-13: El-Awady Adsorption Isotherm at 30° C

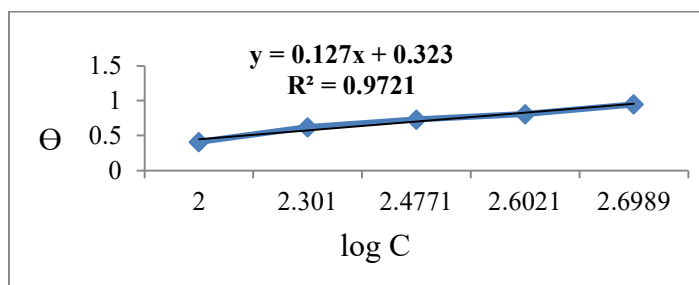


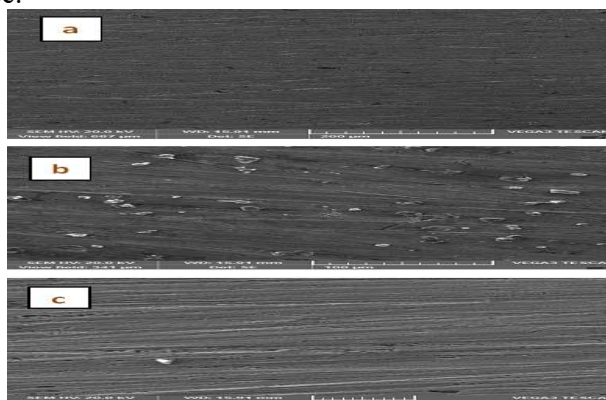
Fig.-14: Temkin Adsorption Isotherm at 30° C

Table-11: Adsorption Isotherm Parameters

Adsorption isotherm	R ²	Slope	Intercept
Langmuir	0.999	83.8	157.5
Flory-Huggins	0.948	0.0858	-2.329
EL-Awady	0.956	0.3392	-0.558
Temkin	0.972	0.127	0.323

Scanning Electron Microscope (SEM) Technique

SEM study is utilized broadly to consider the surface morphology of CS.^{42,43} Fig.-15 shows the SEM result. From Fig.-15a, The polished CS coupons show the nonappearance of corrosion product and have a smooth surface.^{44-46,51,54} Fig.-15b indicates the appearance of corrosion product and has highly damaged part.^{44-46,51,54} When the 500ppm of EL leaves extract is added to a blank system, the CS surface is smoother and has no corrosion product.^{44-46,51,54} Therefore, the SEM images confirmed the creation of a safe layer on the CS surface.^{51,54,55}

Fig.-15: SEM Images for Polished CS (a), Well Water (b) and EL-Zn²⁺ (c) System

Energy Dispersive X-ray (EDX) Test

EDX study is performed to identify the composition of elements of an inhibitor molecule on the CS surface. EDX spectra (Fig.-16) show the various elements present when CS is submersed in a blank system in the presence of EL leaves extract. The EDX spectrum for a polished CS indicates that the Fe,

small amounts of C and O elements are present on the CS surface (Fig.-16a). The CS immersed in well-water without inhibitor concentration indicated that the Fe, C, O, and Cl elements were present on the CS surface (Fig.-16b). From Fig.-16c, the EDX spectrum for CS immersed in well-water with the ethanolic extract of EL leaves-Zn²⁺ has a strongly coordinated with ferric/ferrous ion available on the CS surface, indicating that the CS corrosion is controlled through the creation of a defensive layer of EL leaves extract.^{47,48}

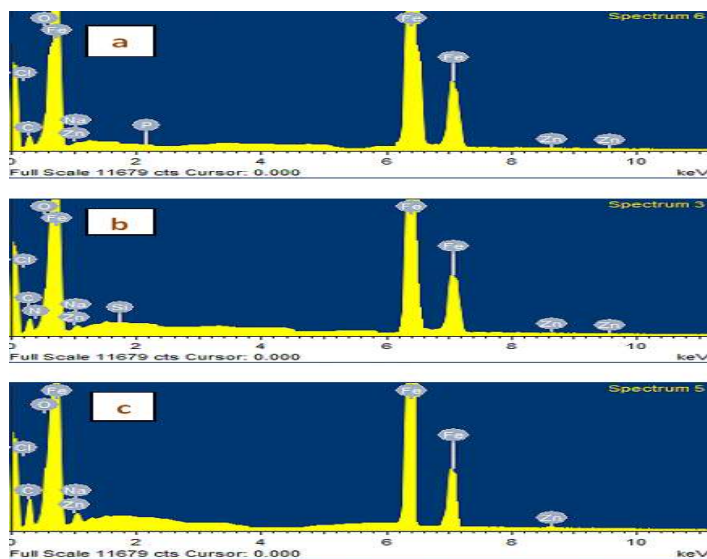


Fig.-16: EDX Spectra for Polished CS (a), Well Water (b) and EL-Zn²⁺ (c) System

Atomic Force Microscope (AFM) Technique

AFM surface topography is performed to compute the surface roughness of the CS specimen.^{49,51,52} AFM spectra for polished CS and CS submersed in well water containing EL leaves extract-Zn²⁺ are shown in Fig.-17.

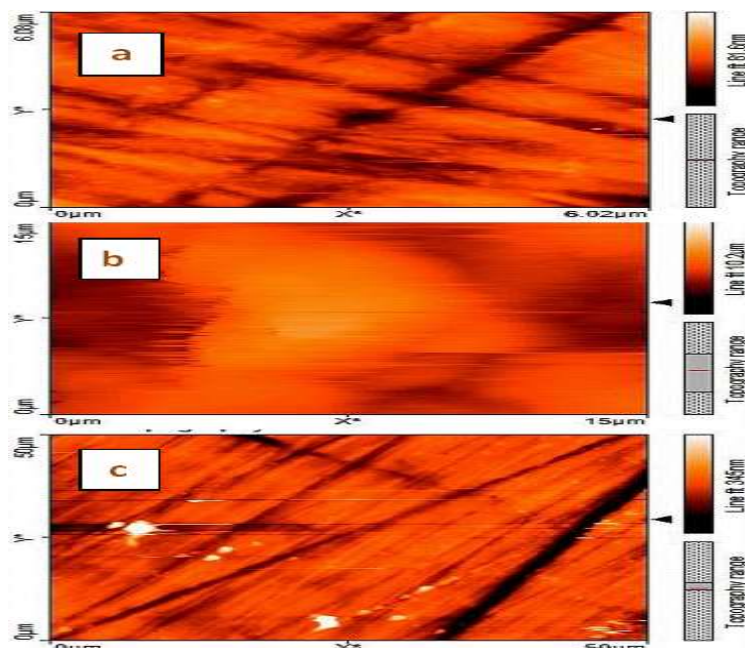


Fig.-17: AFM 2D Images for Polished CS (a), Well Water (b) and EL-Zn²⁺ (c) System

When CS is submersed in well water, the surface roughness is higher than the polished CS roughness^{51,52}, due to a safe layer being harshly broken on the CS surface by uniform corrosion.^{49,51,52} The 500ppm of EL leaves extract and 30ppm of Zn²⁺ are added to a blank system. The average roughness, root mean square,

and maximum peak- to- valley height roughness (R_a , R_{rms} P-V) are reduced to 25.07nm from 1317.08, 1476.12 to 33.95 and 3791 to 248.29nm. AFM roughness values affirm that the CS surface is protected from corrosion activity.^{49,51,52} The perfection of the surface is because of the development of a solid defensive layer of EL leaves extract- Zn^{2+} on the CS surface,^{49,51,52} thereby preventing the corrosion of CS.^{50,52}

Table-12: 2D AFM Parameters

Parameters (nm)	CS-Polished	Well water (Blank)	EL- Zn^{2+} (500ppm-30ppm) System
R_a	5.66	1317.08	25.07
R_{rms}	6.25	1476.12	33.95
P-V	24.14	3791	248.29

CONCLUSION

The current work infers that ethanolic extract of *Enicostemma littorale* (EL) leaves is an intense natural harmless corrosion inhibitor for CS in well water. The external corrosion inhibitory of ethanolic extract of EL leaves- Zn^{2+} at the optimum concentration (500ppm-30ppm) was observed to be 95 ‘percent’ in one day submersion period at 30°C. Corrosion kinetic activity (E_a , ΔH) and adsorption thermodynamic parameters (ΔG_{ads} , q_{ads} , ΔS_{ads}) show a physisorption behaviour on the CS surface. As indicated by the R^2 values, adsorption of EL leaves extract is followed by the Langmuir isotherm model. The EL extract has a synergistic restraint impact with Zn^{2+} . The Tafel curves uncover that the inhibitor proceeds as a blended kind of inhibitor over the CS surface. FT-IR spectra propose that the Fe^{2+} -EL complex and $Zn(OH)_2$ formed onto the CS specimen in well water. The SEM and AFM microscopy investigation affirmed the arrangement of a defensive film of EL extract onto the CS surface. EDX spectra additionally demonstrated the adsorption of EL leaves extract on the CS surface.

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