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RESEARCH ARTICLE

Crossandra infundibuliformis Leaves as an Effective Inhibitor for Mild Steel Corrosion in 1 M HCl

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ABSTRACT:
Corrosion inhibition of mild steel in 1 M HCl was investigated in the absence and presence of different concentrations of extract of *Crossandra infundibuliformis* leaves. Weight loss measurements and electrochemical studies were employed. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive actions of plant extract are discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich, Frumkin, Flory-Huggins and the kinetic thermodynamic model were tested to clarify the nature of adsorption. Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency up to 97.41 % can be obtained. The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor.

KEYWORDS: Mild steel; Corrosion inhibitors; Adsorption isotherms; Inhibition efficiency.

INTRODUCTION:
Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting mild steel from corrosion is to use corrosion inhibitors[1]. Consequently, several authors conducted a lot of work to find effective inhibitors for mild steel in different media[2-22]. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products[23]. The recent trend is towards developing environmentally friendly inhibitors. Most of the natural products are non – toxic, bio – degradable and readily available in plenty. Various parts of plants – seeds, fruits, leaves, flowers etc., have been used as corrosion inhibitors[24]. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media[25-42]. Our previous work [43] reported a successful use of *Citrus aurantiifolia* leaves extract as corrosion inhibitor for mild steel in 1 M HCl.

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The present work is another trail to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel in HCl medium. For the present study, of extract of *Crossandra infundibuliformis* C.I.L is used as corrosion inhibitor for mild steel in 1 M HCl. The leaves were collected from a farm in Duraiyur, Trichy, Tamilnadu, India. The choice of the present inhibitor is based on the following considerations: less – expensive, non – toxic, possess no threat to the environment and easy availability.

2. MATERIAL AND METHODS:
2.1. Sample Preparation:
Mild steel specimens of composition (wt %): C - 0.0577, Mn - 0.1756, Si - 0.0722, P – 0.0168, S – 0.0165, Cr – 0.0096, Mo – 0.0015, Ni – 0.0041, V – 0.0004, Al – 0.0392, Cu – 0.0061, Ti – 0.0009, Nb – 0.0007, W – 0.0002, Ar – 0.0015, Pb – 0.0015, B – 0.0001, Sb – 0.0011, Bi – 0.0014, Ca – 0.0004, Zn – 0.0001, Ce – 0.0002 and Fe – 99.5904 were used for the experiment. The composition of the sample was analyzed using ARL 3460 Metal Analyzer, Optical Emission Spectrometer. Rectangular samples of area 5 x 1 cm^2 have been cut from a large sheet of mild steel. The samples were polished, drilled a hole at one end and numbered by punching. During the study, the samples were polished with 400 grade emery papers, degreased in a solution of non – toxic detergent, washed with distilled water, dried, weighed and stored in desiccators for further use.

2.2. Extraction of Plant material:
The leaves were collected, shade dried and powdered. The extract was prepared by refluxing 25 g of powdered dry leaves and seeds in 500 ml of 1 M HCl for 3 h and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 ml using the same acid and this was taken as stock solution.

2.3. Weight loss measurements:
Weighed samples in triplicate are immersed in 100 ml of 1 M HCl in absence and in presence of different concentrations of the inhibitor for various intervals of time. They are then taken out and immersed in saturated sodium bicarbonate solution to remove residual acids and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. The parameters used for the present study are

1. Time : ½ h, 1 h, 3 h, 7 h, 24 h, 48 h and 168 h
2. Concentration of the inhibitor: 0.005 %, 0.05 %, 0.15 %, 0.5 % and 2.5 % (V/V)
3. Temperature: (303, 313, 323, 333 and 343) ± 2 K

2.3.1 Determination of Corrosion rate:
The rate of dissolution of metal is calculated in terms of corrosion rate. The corrosion rate was calculated using the expression,

$$\text{Corrosion rate (C.R)} = \frac{534.\,W}{DAT}\ \text{mpy}$$

Where,
mpy = miles per year,
W = weight loss in mg,
D = density in g / cm^2 (7.9 g / cm^2),
A = area in square inch and
T = exposure time in hours.

2.3.2 Determination of Inhibition efficiency:
The effectiveness of the inhibitor in terms of efficiency is found by

$$\text{I.E (\%)} = \frac{\text{C.R (without inhibitor)} - \text{C.R (with inhibitor)}}{\text{C.R (without inhibitor)}}$$

Where,
I.E = Inhibition efficiency and
C.R = Corrosion Rate

2.3.3 Determination of Surface Coverage (θ):
Surface coverage of active sites by the inhibitor was determined by the relation,

$$\text{S.C }(\theta) = \frac{\text{C.R (without inhibitor)} - \text{C.R (with inhibitor)}}{\text{C.R (without inhibitor)}}$$

Where,
S.C (θ) = Surface Coverage

2.3.4 Determination of Activation energy:
The corrosion reaction can be regarded as an Arrhenius type process. The rate of which is given by

$$C.R = Ke^{-Ea/RT}$$

Where,
C.R is the corrosion rate,
E_a is the activation energy,
T is the absolute temperature,
K is the pre-exponential constant and
R is the Universal gas constant.

2.3.5 Determination of Free energy of adsorption:
The free energy of adsorption at different temperatures was calculated from the equation,

$$\Delta G^o_{ads} = 2.303\ RT\ (1.74 + \text{Log}\ (\theta/1-\theta-\text{Log}\ C))$$

Where,
ΔG^o_{ads} is the free energy of adsorption,
R is the gas constant,
T is the temperature in Kelvin,
θ is the degree of coverage on metal surface and
C is the concentration of inhibitor in %(V/V).

2.3.6 Determination of Free energy of enthalpy (ΔH°) and Free energy of entropy (ΔS°):
The free energy of enthalpy and free energy of entropy are calculated from the values of free energy of adsorption (ΔG^o_{ads}) by Gibbs Helmhotz relationship,

$$\Delta G^o_{ads} = \Delta H^o - T\Delta S^o$$

By plotting ΔG^o_{ads} vs. T, gives the slope, ΔS° and intercept, ΔH°

2.3.7 Adsorption Isotherms:
In the present study the values of surface coverage (θ) were evaluated using the values of inhibition efficiency at different immersion periods. Attempts were made to fit the θ values to various isotherms including Langmuir, Freundlich, Temkin, Frumkin and Flory-Huggins.

2.4 Potentiodynamic Polarization Measurements:
Potentiodynamic polarization studies were carried out using Solartron 1280 B. The cell of the polarization studies was a glass beaker containing the aerated unstirred test solution with a platinum electrode as the counter electrode, a saturated calomel electrode as reference electrode and the mild steel electrode as the working electrode.100 ml of 1 M HCl in absence and in presence of different concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode with an exposed area of 1 cm^2 was then introduced. The electrode was placed at -0.2 mv/sec towards the anodic direction in the Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current (I_{corr}).

TABLE -1: INHIBITION EFFICIENCY OF MILD STEEL IN 1 M HCl IN THE PRESENCE OF C.I.L AT 303 K

S. No	Conc. (% V/V)	½ h	1 h	3 h	7 h	24 h	48 h	168 h
1	0.005	37.96	15.38	24.89	47.23	70.98	69.11	71.18
2	0.05	45.56	34.54	54.69	71.86	90.52	82.28	90.29
3	0.15	53.39	46.85	55.83	77.79	93.64	88.39	92.20
4	0.5	68.55	60.39	73.47	82.70	94.81	91.52	95.33
5	2.5	72.29	69.09	76.24	86.63	96.08	93.34	96.27

TABLE – 2: PROTECTION PERFORMANCE OF C.I.L ON MILD STEEL IN 1 M HCl (½ h) AT DIFFERENT TEMPERATURES

S. No	Conc. (% V/V)	303 K		313 K		323 K		333 K		343 K	
		CR (mpy)	I.E (%)	CR (mpy)	I.E (%)	CR (mpy)	I.E (%)	CR (mpy)	I.E (%)	CR (mpy)	I.E (%)
1	Blank	629.72	-	259.04	-	685.97	-	1031.80	-	4360.95	-
2	0.005	393.79	37.46	253.37	2.18	539.88	21.29	1048.80	1.64	1603.08	63.24
3	0.05	342.77	45.56	228.94	19.19	407.74	40.55	559.07	45.81	1160.01	73.40
4	0.15	293.49	53.39	190.66	22.92	343.20	49.96	501.75	51.37	783.69	82.02
5	0.5	197.98	68.55	164.84	36.36	279.53	59.24	484.50	57.18	636.26	85.41
6	2.5	174.43	72.29	131.70	49.15	126.46	81.56	278.22	73.04	411.23	90.57

TABLE – 3: ACTIVATION PARAMETERS FOR THE DISSOLUTION OF MILD STEEL IN THE PRESENCE OF C.I.L IN 1 M HCl

S. No	Conc. (% V/V)	$-E_a$ KJ /mole	$-\Delta H^0$ KJ /mole	ΔS^0 J / mole	$-\Delta G^0_{ads}$ (KJ) 303 K	313 K	323 K	333 K	343 K
1	Blank	50.79	-	-	-	-	-	-	-
2	0.005	57.84	-3.62	0.0549	22.15	20.79	21.47	14.42	28.08
3	0.05	41.02	32.74	0.157	17.19	14.48	17.77	18.92	22.86
4	0.15	43.17	36.10	0.1619	15.21	12.20	15.85	16.49	21.16
5	0.5	39.84	26.75	0.1266	13.80	10.77	13.62	14.16	18.44
6	2.5	33.53	36.08	0.1478	10.20	7.95	12.29	12.61	15.26

In anodic and cathodic plot, the slope of the linear portion gives Tafel constants, b_a and b_c respectively. According to the Stern – Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$I_{corr} = \frac{b_a \times b_c}{2.303\,(b_a + b_c)} \times \frac{1}{R_p}$$

Where, R_p is polarization resistance.

2.5 Surface Analysis:
Surface features of mild steel specimen were examined before and after exposed to 1 M HCl solution in absence and presence of a certain concentration of the studied extract. Optical microscope was used for this investigation.

3. RESULTS AND DISCUSSION:
3.1 Weight loss data:
The inhibitor was tested for six different concentrations and their corresponding weight loss data are presented in Table 1. The addition of inhibitor increases the inhibition efficiency, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface[44]. The inhibition efficiency is 96.27 % at a concentration of 2.5 % V/V. The results concerned with the effect of period of immersion at various concentration of the inhibitor on mild steel in 1 M HCl are also shown in Table 1. From the tabulated data, it is clear that for all concentrations of the inhibitor, inhibition efficiency increases from ½ h to 24 h period of immersion. The decrease in inhibition efficiency with time may be attributed to various factors such as an increase in the ferrous ion concentration[45 - 46].

3.2 Effect of Temperature:
The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations at different temperatures for a fixed immersion time of ½ h. The tabulated data (Table 2) reveal that as the concentration of the inhibitor increases, the corrosion rate has decreased at all temperatures. Though the corrosion rate has increased with temperature for a given concentration of the inhibitor, there is no regular trend in the change of inhibition efficiency. This may be explained on the basis of the time lag between the process of adsorption and desorption. However, the inhibitor of 2.5 % (V/V) at 343 K shows the better inhibition (I.E – 90.57 %) than the other concentrations at different temperatures.

3.3 Interpretation of Thermodynamic data:
Activation energy (Ea) and thermodynamic data, such as change in free energy (ΔG°_{ads}), enthalpy (ΔH°) and entropy (ΔS°) for mild steel in 1 M HCl in the absence and in the presence of the inhibitor was calculated and listed in Table 3. The activation energy at different concentrations of the inhibitor in HCl is calculated by plotting log C.R vs. 1/T (Fig 1). E_a values for inhibited systems are lower than those for uninhibited system indicating that the inhibitor exhibit high inhibition efficiency at elevated temperatures[47]. The negative values of suggest the strong interaction of the inhibitor molecules whereas low value of ΔG°_{ads} indicated spontaneous adsorption of inhibitor on mild steel surface [48].

The negative values of ΔH° indicate that the adsorption of inhibitor molecules is an exothermic reaction[49]. The change in entropy was found to be greater than zero. This indicates that the reaction is irreversible. It is clear that the complete desorption of the inhibitor is not possible.

Fig 1: ARRHENIUS PLOT FOR MILD STEEL DISSOLUTION PROCESS IN 1 M HCl

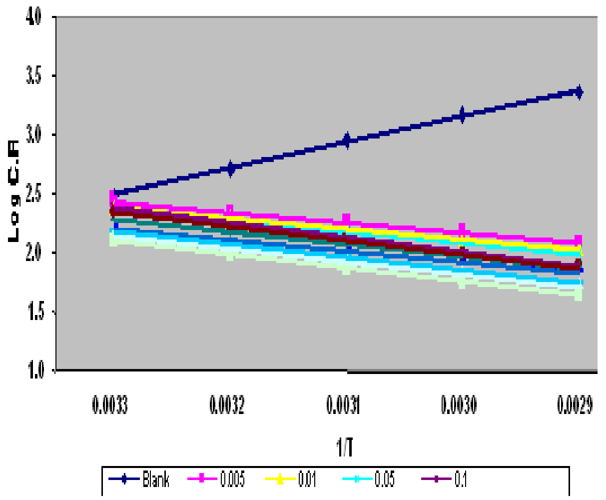
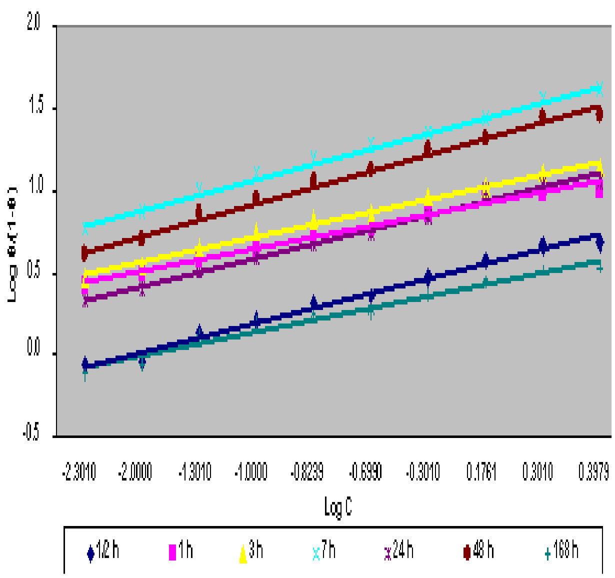


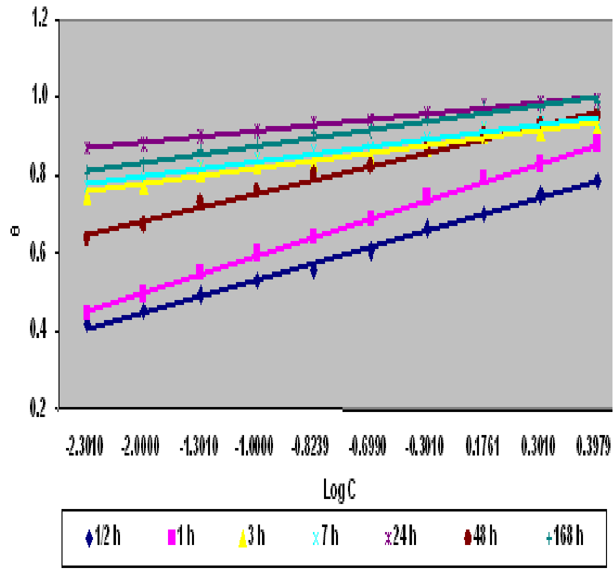
Fig 2: LANGMUIR ISOTHERM PLOT FOR THE ADSORPTION OF INHIBITOR IN 1 M HCl



3.4 Applicability of Adsorption Isotherms:

The surface coverage (θ) values for different concentrations of the inhibitor in HCl medium have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of log (θ/ (1-θ)) against log C (Fig 2) shows a straight line (R>0.9) indicating that adsorption from the acid follows the Langmuir adsorption isotherm. It is observed that although the plot is linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity[50]. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of (1/y). A straight line was obtained when the surface coverage (θ) was plotted against log C for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in Fig 3.

Fig 3: TEMKIN ISOTHERM ADSORPTION MODEL FOR INHIBITOR IN 1 M HCl ON THE SURFACE OF MILD STEEL



The plot of log θ Vs log C is shown in Fig 4. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm. The plot of Inhibition Efficiency (IE) against log C is shown in Fig 5. The sigmoidal shape shows that the adsorption of the inhibitor on mild steel surface in 1 M HCl follows Frumkin isotherm[51]. The equation of Flory Huggins Isotherm is

$$\log \theta / C = \log XK + X \log (1-\theta)$$

Where, θ is the degree of coverage.

X is the number of active sites occupied by one inhibitor molecule or number of water molecules replaced by one molecule of the adsorbate. The value of X>1, implied that one inhibitor molecule replaces more than one water molecule. The plots of log (θ/C) against log (1-θ) are shown in Fig 6.

Fig 4: FREUNDLICH ISOTHERM ADSORPTION MODEL OF INHIBITOR ON MILD STEEL IN 1 M HCl

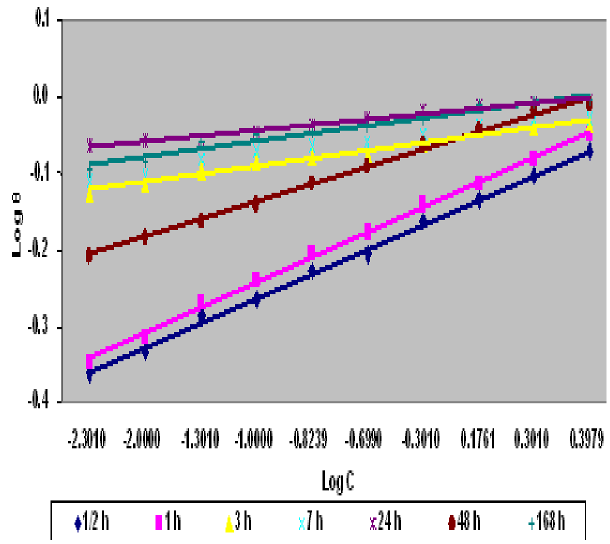


Fig 5: FRUMKIN ADSORPTION ISOTHERM MODEL OF INHIBITOR ON THE SURFACE OF MILD STEEL IN 1 M HCl

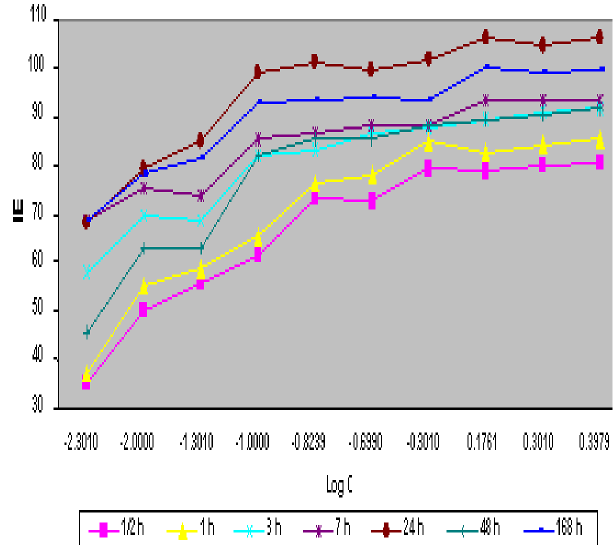


Fig 6: CURVE FITTING OF THE CORROSION DATA OF MILD STEEL IN THE PRESENCE OF INHIBITOR IN 1 M HCl TO FLORY-HUGGINS ISOTHERM

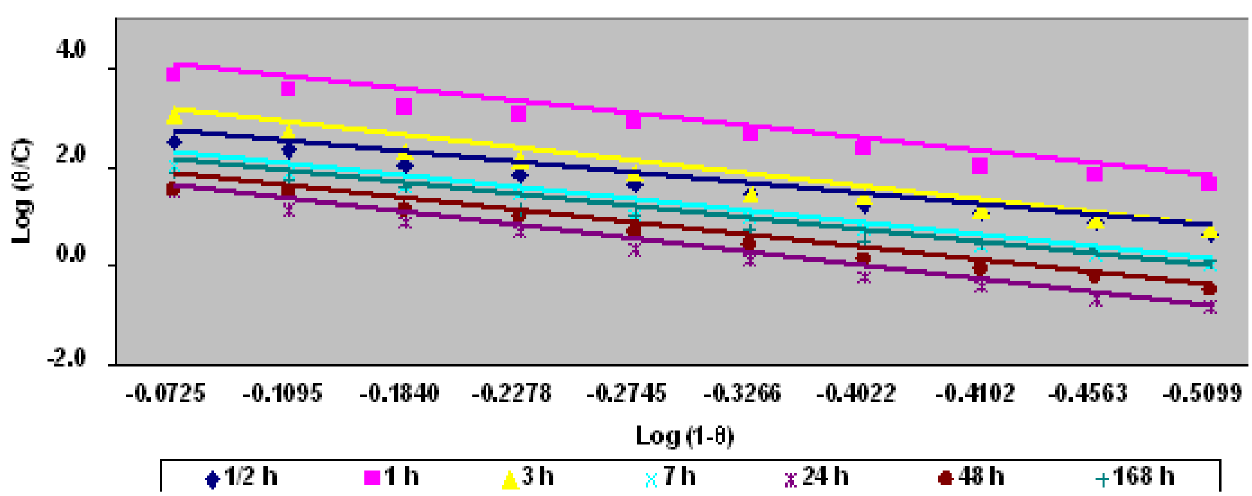
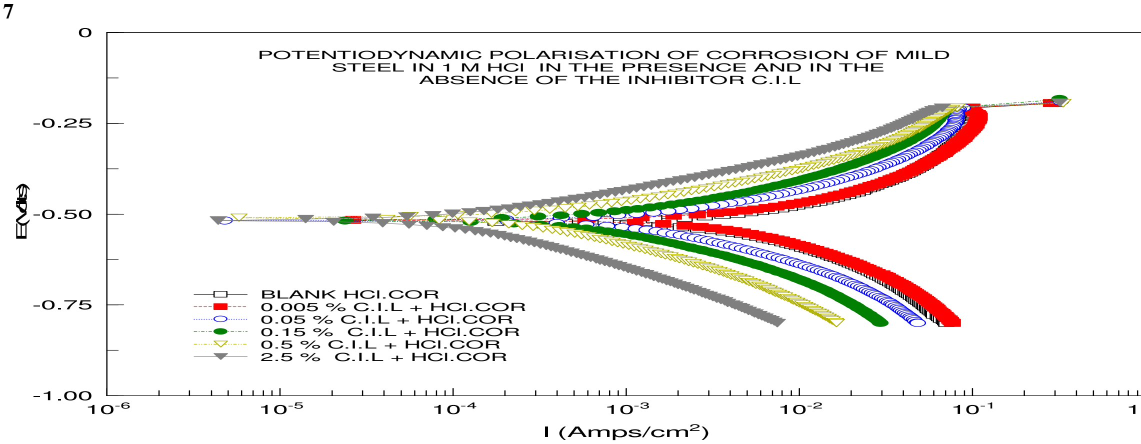


Fig 7



3.5 Potentiondynamic Polarisation results:

The various electrochemical parameters calculated from Tafel plot (Fig 7) are given in Table 4. The lower corrosion current density (I_{corr}) values in the presence of inhibitor without causing significant changes in corrosion potential (E_{corr}) suggests that the compound is mixed type inhibitor (i.e., inhibit both the anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction[52]. In all concentrations, b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

TABLE – 4: ELECTROCHEMICAL PARAMETERS FOR MILD STEEL IN 1 M HCl WITH VARIOUS CONCENTRATIONS OF C.I.L

S. No	Conc (%V/V)	$-E_{corr}$ mV	I_{corr} μAcm^{-2}	b_a mV/dec	b_c mV/dec	I.E (%)
1	Blank	520.81	4.523	179.05	127.98	-
2	0.005	516.53	6.281	225.8	150.74	-38.86
3	0.05	518.13	1.345	138.36	104.37	70.26
4	0.15	517.13	0.777	145.04	102.05	82.80
5	0.5	510.28	0.323	144.95	88.32	92.84
6	2.5	516.71	0.117	143.15	87.90	97.41

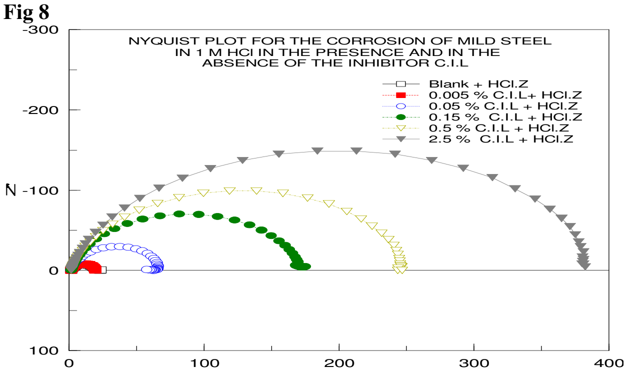
3.6 Electrochemical impedance spectroscopy results:

Impedance diagram (Nyquist plot) obtained for mild steel in 1 M HCl in the presence of various concentrations of the inhibitor is depicted in Fig 8. They are perfect semicircles and this was attributed to charge transfer reaction[53]. Impedance parameters derived from Nyquist plots are tabulated in Table 5. It can be seen that as the concentration of inhibitor increases, C_{dl} values decrease. Decrease in C_{dl}, which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecule function by adsorption at the metal-solution interface[54].

TABLE – 5: IMPEDANCE PARAMETERS FOR THE CORROSION OF MILD STEEL IN 1 M HCl CONTAINING DIFFERENT CONCENTRATIONS OF C.I.L

S. No	Conc (%V/V)	R_{ct} (Ω cm^2)	C_{dl} (μ Fcm^{-2})	I.E (%)
1	Blank	19.66	150.01	-
2	0.005	18.15	222.58	-8.30
3	0.05	62.05	108.42	68.31
4	0.15	171.05	78.94	88.50
5	0.5	246.54	67.69	92.02
6	2.5	386.60	54.76	94.91

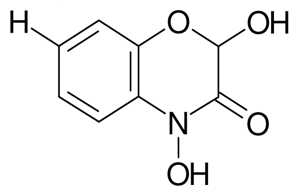
Fig 8



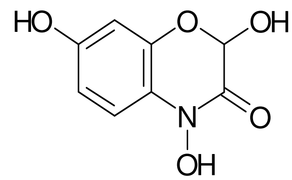
3.7 Mechanism of Inhibition:

The constituents present in C.I.L are

DIBOA



7-HYDROXY DIBOA



The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the extract. The inhibition may be due to the adsorption of phytochemical constituents present in the extract through oxygen atoms on to the surface of the metal.

3.8 Surface Analysis:

The polished specimen and the test specimens are immersed in the blank (1 M HCl) and in the inhibitor for 168 h, were observed under a Metallurgical Microscope and photomicrographs are shown in the Plates 1 to 4. Plate 1 shows the polished mild steel surface before exposure to the corrosion solution, which is associated with polishing scratches. It is clear from the Plate 2, the surface of the mild steel was heavily corroded in 1 M HCl, whereas in the presence of inhibitor in 1 M HCl, the surface condition was comparatively better (Plates 3 and 4) depends on the concentration of the inhibitor solution suggesting the presence of a protective adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

PHOTOMICROGRAPHS OF MILD STEEL SAMPLES IN THE ABSENCE AND IN THE PRESENCE OF C.I.L IN 1 M HCl

Plate 1: Polished Sample

Plate 2: Sample Immersed in 1 M HCl

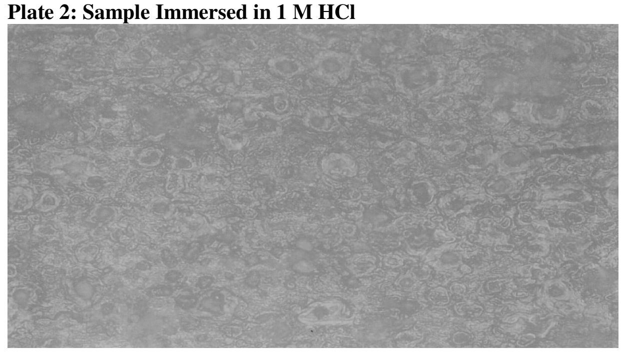


Plate 3: Sample Immersed in 0.2% V/V Inhibitor solution

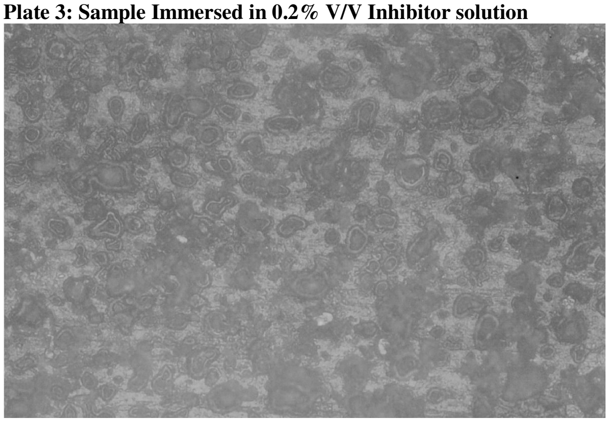
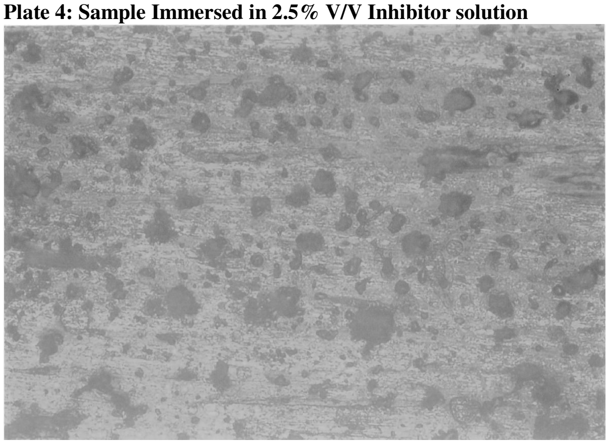


Plate 4: Sample Immersed in 2.5% V/V Inhibitor solution



4. CONCLUSION:

The principal conclusions are

1. The natural extract of the inhibitor was found to be effective inhibitor in the acidic medium giving up to 96.27 % efficiency. The extract under study resists corrosion at higher temperature in 1 M HCl. The optimum temperature was found to be 343 K.
2. Adsorption models –Langmuir, Temkin, Freundlich, Frumkin and Flory – Huggins isotherm fit well as evident from the correlation coefficient values ($R \approx 1$ in all cases). This proves the applicability of all the models to the process.
3. The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor, C.I.L.
4. The results obtained from the polarization study revealed that the extract under study behaved as a mixed type of inhibitor.
5. The inhibitor can be adsorbed on the metal surface through their oxygen atom of the constituents present in the extract.

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