Crossandra Infundibuliformis Leaves as Corrosion Inhibitor for Mild Steel in 1 M HcI and 0.5 M H$_2$SO$_4$ - A Compartive Study

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Abstract

The inhibition effect of Crossandra infundibuliformis leaves (C.I.L) on the corrosion of mild steel in 1.0 M HCl and 0.5 M H$_2$SO$_4$ solutions was studied by weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy. The corrosion rate of mild steel and inhibition efficiencies were calculated. The results obtained show that the inhibition was found to increase with increasing concentration of the plant extract. Polarization curves revealed that C.I.L inhibitor acts as mixed type inhibitor and inhibition efficiency follows the order: H$_2$SO$_4$>HCl.

Keywords: Acid Corrosion; Corrosion inhibitors; Mild steel; Weight loss method .

1. INTRODUCTION

Acids are used to remove oxides, shop-soil and other contaminants from metal surfaces. Acids are also used for derusting and pickling, the cleaning of refinery equipment, and the removal of calcareous deposits from boilers, radiators of vehicles, pipelines carrying water or petroleum products, heat exchangers etc., Both HCl and H$_2$SO$_4$ are frequently used in the above industrial activities. Inhibitors are generally used in these processes to control the metal dissolution as well as acid consumption. Use of inhibitors is an important task in the protecting of metals from corrosion. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products (Abdel- Gader *et al.* 2006; Gunavathy and Murugavel, 2013; Jothi and Ravichandran, 2013). The recent trend is towards developing environment 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 (Rajendran *et al.* 2005). Our previous works (Saratha *et al.* 2009) reported a successful use of natural product as corrosion inhibitor for mild steel in acidic medium. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

2. EXPERIMENTAL

Rectangular samples of area 5x1 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.

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For the present study, natural product of *Crossandra infundibuliformis* leaves (C.I.L) is used as corrosion inhibitor for mild steel in 1 M HCl and 0.5 M H_2SO_4. The leaves were collected from a farm in Duraiyur, Trichy. The leaves were collected, shade dried and powdered. 5% extract was prepared by refluxing 25 g of powdered dry leaves and seeds in 1 M HCl and 0.5 M H_2SO_4 for 3 hours and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 ml using the same acid.

2.1 Weight loss measurements

Weighed samples in triplicate are immersed in 100 ml of 1 M HCl and 0.5 M H_2SO_4 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 hr, 1 hr, 3 hr, 7 hr, 24 hr, 48 hr and 168hr
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

2.2 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 and 0.5 M H_2SO_4 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}). In anodic and cathodic plot, 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.

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

where, R_p is polarization resistance.

3. RESULTS & DISCUSSIONS

3.1 Weight loss data

The inhibitor was tested for five 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. The inhibition efficiency is 96.27 % and 99.06 % for 1 M HCl and 0.5 M H_2SO_4 respectively 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 and 0.5 M H_2SO_4 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 7h and 24 h period of immersion for 1 M HCl and 0.5 M H_2SO_4 respectively. The decrease in inhibition efficiency with time may be attributed to various factors such as an increase in the ferrous ion concentration (Quraishi *et al.* 2006).

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 hr. Table 2 reveals 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 and 323 K for 1 M HCl and 0.5 M H_2SO_4 respectively shows the better inhibition (I.E – 90.57 % and 92.43 % for 1 M HCl and 0.5M H_2SO_4 respectively) 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 and 0.5 M H_2SO_4 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 1 M HCl and 0.5 M H_2SO_4 is calculated by plotting log C.R vs 1/T. E_a values for inhibited systems are lower than those for uninhibited system indicating

that the inhibitor exhibit high inhibition efficiency at elevated temperatures (Putilova *et al.* 1960). The negative values suggest the strong interaction of the inhibitor molecules whereas low value of ΔG°_{ads} indicated spontaneous adsorption of inhibitor on mild steel surface (Quraishi *et al.* 2003). The negative values of ΔH° indicate that the adsorption of inhibitor molecules is an exothermic reaction. 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.

3.4 Potentiondynamic Polarisation results

The various electrochemical parameters calculated from Tafel plot Fig 1 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. 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 1. Inhibition Efficiency of Mild Steel in 1 M HCL and 0.5 H_2SO_4 in the presence of C.I.L at 303 K

Conc. (%v/v)	½h 1M HCl	½h 0.5M H₂SO₄	1h 1M HCl	1h 0.5M H₂SO₄	3h 1M HCl	3h 0.5M H₂SO₄	7h 1M HCl	7h 0.5M H₂SO₄	24h 1M HCl	24h 0.5M H₂SO₄	48h 1M HCl	48h 0.5M H₂SO₄	168h 1M HCl	168h 0.5M H₂SO₄
0.005	37.96	62.77	15.38	62.61	24.89	78.26	47.23	92.23	70.98	72.57	69.11	22.79	71.18	11.69
0.05	45.56	74.26	34.54	80.30	54.69	89.77	71.86	96.71	90.52	91.51	82.28	80.96	90.29	44.13
0.15	53.39	80.65	46.85	84.24	55.83	92.13	77.79	97.75	93.64	94.70	88.39	87.53	92.20	63.40
0.5	68.55	83.59	60.39	85.82	73.47	94.14	82.70	98.07	94.81	96.63	91.52	91.83	95.33	74.02
2.5	72.29	85.61	69.09	90.61	76.24	96.77	86.63	**99.06**	96.08	98.01	93.34	96.58	**96.27**	91.33

Table 2. Protection performance of C.I.L on mild steel in 1 M HCL and 0.5 M H_2SO_4 (½ H) at different temperatures

Acid solution	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 M HCl	Blank	629.72	-	259.04	-	685.97	-	1031.80	-	4360.95	-
	0.005	393.79	37.46	253.37	2.18	539.88	21.29	1048.80	1.64	1603.08	63.24
	0.05	342.77	45.56	228.94	19.19	407.74	40.55	559.07	45.81	1160.01	73.40
	0.15	293.49	53.39	190.66	22.92	343.20	49.96	501.75	51.37	783.69	82.02
	0.5	197.98	68.55	164.84	36.36	279.53	59.24	484.50	57.18	636.26	85.41
	2.5	174.43	72.29	131.70	49.15	126.46	81.56	278.22	73.04	411.23	90.57
0.5 M H_2SO_4	Blank	948.94	-	358.90	-	2266.38	-	2807.14	-	6638.93	-
	0.005	353.23	62.77	313.11	12.75	488.86	78.42	2492.28	11.21	3693.28	44.36
	0.05	244.21	74.26	230.69	35.72	361.95	84.02	712.57	74.61	1539.41	76.81
	0.15	183.39	80.65	198.48	44.69	296.61	86.91	580.83	79.30	1344.04	79.75
	0.5	155.68	83.59	181.41	49.45	236.36	89.57	477.08	83.00	988.19	85.11
	2.5	136.49	85.61	139.98	60.99	171.38	92.43	307.44	89.04	660.68	90.04

Table 3. Activation parameters for the dissolution of mild steel in the presence of C.I.L. in 1 M HCl and 0.5 M H_2SO_4

Acid solution	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 M HCl	Blank	50.79	-	-	-	-	-	-	-
	0.005	57.84	-3.62	0.0549	22.15	20.79	21.47	14.42	28.08
	0.05	41.02	32.74	0.157	17.19	14.48	17.77	18.92	22.86
	0.15	43.17	36.10	0.1619	15.21	12.20	15.85	16.49	21.16
	0.5	39.84	26.75	0.1266	13.80	10.77	13.62	14.16	18.44
	2.5	33.53	36.08	0.1478	10.20	7.95	12.29	12.61	15.26
0.5 M H_2SO_4	Blank	50.79	-	-	-	-	-	-	-
	0.005	57.84	-13.69	0.0308	24.76	19.21	28.45	20.03	25.89
	0.05	41.02	17.00	0.1182	20.31	16.69	23.26	22.37	23.38
	0.15	43.17	12.67	0.0980	18.47	14.81	20.94	20.06	20.74
	0.5	39.84	16.15	0.1009	15.94	12.17	18.39	17.40	18.37
	2.5	33.53	21.62	0.1078	12.27	9.20	15.02	14.35	15.09

Table 4. Electro chemical parameters for mild steel in 1 M HCl and 0.5 M H₂SO₄ with various concentrations of C.I.I.

S.No	Conc (%V/V)	$-E_{corr}$ mV		I_{corr} µAcm^{-2}		b_a mV/dec		b_c mV/dec		I.E (%)	
		1M HCl	0.5M H₂SO₄	1M HCl	0.5M H₂SO₄	1M HCl	0.5M H₂SO₄	1M HCl	0.5M H₂SO₄	1M HCl	0.5M H₂SO₄
1	Blank	520.81	551.39	4.523	7.274	179.05	394.07	127.98	257.46	-	-
2	0.005	516.53	546.64	6.281	3.859	225.8	302.38	150.74	179.65	-38.86	46.94
3	0.05	518.13	526.90	1.345	0.733	138.36	159.64	104.37	98.91	70.26	89.92
4	0.15	517.13	519.25	0.777	0.059	145.04	73.54	102.05	58.79	82.80	99.18
5	0.5	510.28	514.69	0.323	0.266	144.95	171.99	88.32	81.58	92.84	96.34
6	2.5	516.71	512.13	0.117	0.016	143.15	75.12	87.90	1034.6	97.41	99.78

Table 5. Impedence parameters for the corrosion of mild steel in 1 M HCl and 0.5 M H₂SO₄ containing different concentration of C.I.I.

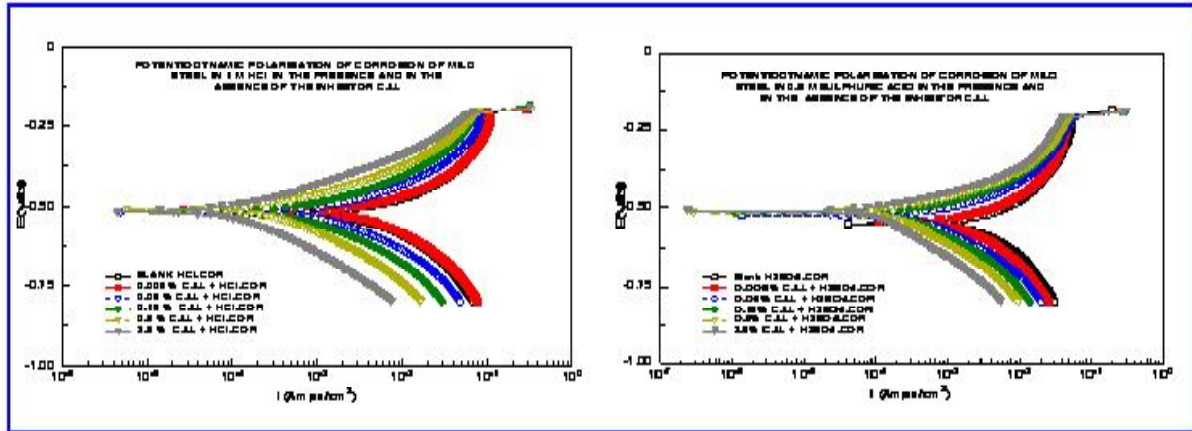| S. No	Conc (% V/V)	R_{ct} (Ω cm^2)		C_{dl} (µ Fcm^{-2})		I.E (%)	
		1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄	1 M HCl	0.5 M H₂SO₄
1	Blank	19.66	20.84	150.01	99.01	-	-
2	0.005	18.15	37.33	222.58	71.48	-8.30	44.17
3	0.05	62.05	77.80	108.42	66.09	68.31	73.21
4	0.15	171.05	90.30	78.94	54.82	88.50	76.92
5	0.5	246.54	123.97	67.69	36.48	92.02	83.18
6	2.5	386.60	244.36	54.76	25.39	94.91	91.47

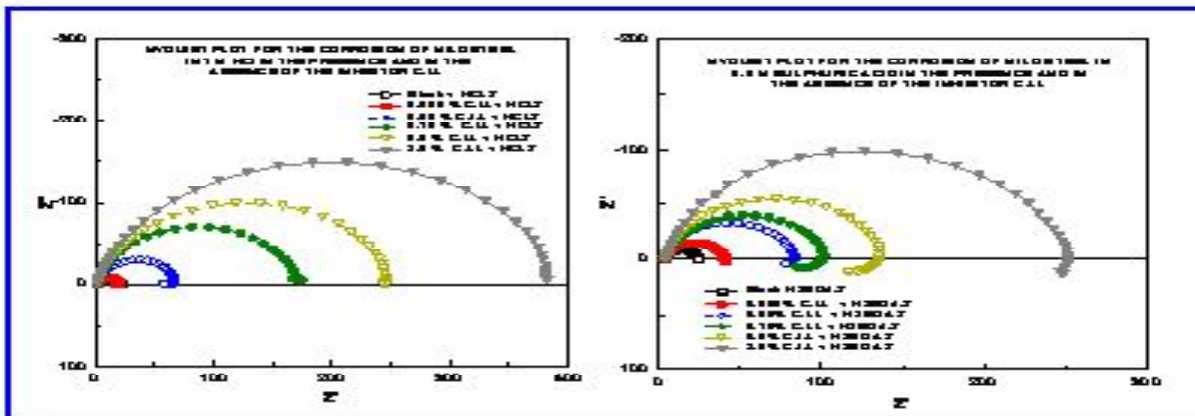**Fig. 1: Tafel plots for the corrosion inhibition of MS with and without C.I.L**

Fig. 2: Nyquist plots for the corrosion inhibition of MS with and without C.I.L different concentrations of C

3.5 Electrochemical impedance spectroscopy Results

Impedance diagram (Nyquist plot) obtained for mild steel in 1 M HCl and 0.5 M H_2SO_4 in the presence of various concentrations of the inhibitor is depicted in Fig. 2. They are perfect semicircles and this was attributed to charge transfer reaction.

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.

4. CONCLUSIONS

The natural extract of the inhibitor was found to be effective inhibitor in the acidic medium giving up

to 96.27 % and 99.06 % for 1 M HCl and 0.5 M H_2SO_4 efficiency. The extract under study resists corrosion at higher temperature in acidic medium. The optimum temperature was found to be 343 K for 1 M HCl and 323 K for 0.5 M H_2SO_4. The results obtained from the polarization study revealed that the extract under study behaved as a mixed type of inhibitor. From the comparative studies it is concluded that the inhibition efficiency is better in H_2SO_4 than in HCl, because sulphuric acid is a dibasic acid, so it stimulated the corrosion rate of mild steel.

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