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Studies on Inhibition of Acid Corrosion of Mild Steel by *Terminalia catappa* (Tropical Almond) Leaves

V.G. VASUDHA[1] and R. SARATHA[2]

[1]Department of Chemistry, Nirmala College, Coimbatore, Tamilnadu (India).
[2]Department of Chemistry, Avinashilingam University for Women, Coimbatore (India).

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ABSTRACT

Acid extract of *Terminalia catappa* (Tropical almond / badam) leaves is investigated as a cheap and eco-friendly corrosion inhibitor for mild steel in 1N HCl medium by weight loss, polarization, FTIR and scanning electron microscope studies. Studies carried out using various concentrations of inhibitor for different immersion times indicate *Terminalia catappa* to be a good mixed type corrosion inhibitor for mild steel. The inhibition efficiency was found to increase with inhibitor concentration. Inhibition efficiency of 97% at 2% v/v inhibitor concentration was obtained.

Key words: Corrosion inhibition, Mild steel, Acid medium, *Terminalia catappa*.

INTRODUCTION

Acid corrosion inhibitors are used in industries where hydrochloric acid is used to remove scale and salts from steel surface. For pickling process, concentrated hydrochloric acid and sulphuric acid baths are used. During pickling along with the surface film some metal is also lost. A variety of compounds like azathiones[1], pyridine[2], thiazoles[3], schiff bases[4], dyes[5], triazoles[6] and various other heterocyclic compounds have been used as inhibitors to control this corrosion. Due to strict environment legislation the trend in recent years is to use natural products as corrosion inhibitors. The natural product inhibitors are not only environment friendly but also easily available. More than about eighty natural product materials like Aloe plants,[7] tea wastes[8], *Foenum graecum*[9] (fenugreek), *Embilica officianalis,* (Indian gooseberry), *Terminalia chebula*[10] (chebulic myrobalan), *Lawsonia inermis* (henna)[11], *Solanum verbascifolium*[12], *Pisum sativum*[13] etc. have been tried as mild steel corrosion inhibitors and proved to have good inhibition efficiency. In the present study the dried leaves of *Terminalia catappa* have been studied as mild steel corrosion inhibitors in 1N HCl medium by weight loss and polarization studies.

EXPERIMENTAL

weight loss method

Terminalia catappa leaves (TCL) were shade dried and powdered. 25 g of dry leaves powder were refluxed with 1N HCl for 3 hours. The refluxed solution was filtered and made up to 500ml with 1N HCl. From this stock solution further dilutions from 0.01% to 2% v/v were prepared.

From a big sheet of mild steel, specimens were cut to a uniform size of 5 x 1 cm^2 and provided with a hole for hanging in test solution. The specimens were polished with fine quality emery sheet, washed with distilled water and degreased with acetone. After drying they were weighed accurately and stored in desiccators. Pre-weighed mild steel specimens were immersed in the test solutions for different immersion times. After the immersion time, the specimens were removed, washed with sodium bicarbonate solution and with deionised water, dried and weighed. The loss in weight was determined in triplicate and the results were averaged. Parameters used for the study are different inhibitor concentrations and different time intervals.

Determination of corrosion rate

The rate of corrosion was calculated by using the formula

C.R (mpy) = 534 *W/DAT

where C.R is the corrosion rate in mils per year, W is the weight loss in mg, D is the density of mild steel, A is the exposed area of the specimen in square inches and T is the time in hours.

Potentiodynamic polarization method

The frequency response analyzer SOLARTRON 1280 B and an IBM personal computer which automatically controls and measures the linear polarization and Tafel polarization was used for the polarization measurements. The data were analyzed using computer software Experiments were carried out in the three electrode polarization cell containing platinum auxiliary electrode, saturated calomel reference electrode and polished mild steel specimen as working electrode..

The mild steel specimen was lacquered so as to expose 1 sq. cm area. 100 ml of acid was taken in the electrochemical cell. The polished electrode was then introduced and held for 5 minutes to attain a constant potential. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of 2mV/s in the potential range from -0.2 V to -1 V relative to the corrosion potential. Inhibition efficiency (IE%) was calculated as follows

Tafel method

$$IE\ \% = [\{I_{corr}(blank) - I_{corr}(additive)\}/ I_{corr}(blank)] \times 100$$

where I_{corr}(additive) and I_{corr}(blank) are the corrosion currents with and without the inhibitors respectively

LPR method

$$IE\ \% = [\{R_p(additive) - R_p(blank)\}/ R_p(additive)] \times 100$$

where R_p(additive) and R_p(blank) are the resistance polarizations with and without the inhibitor respectively.

AC Impedance method

Impedance spectra were recorded at E_{corr} in the frequency range 0.1 to 20000Hz. Impedance parameters R_{ct} and C_{dl} were computed using EIS software

RESULTS AND DISCUSSION

weight loss method

Corrosion rate (CR) and Inhibition efficiency (IE) calculated from weight loss measurements of mild steel samples immersed for different time intervals in 1N HCl in the absence and presence of different concentrations of the plant extract are given in the Table 1.

As the extract concentration increases, CR is found to decrease. At lower concentrations the inhibition efficiency (IE %) increases invariably with increase of inhibitor concentration. This is associated with increase of surface coverage by the constituents present in the extracts, which retards the corrosion of mild steel and hence IE increases. The rate of increase of IE with concentration of the extract is appreciable at lower concentration range and at higher concentrations around 1%, the change in IE is not much. The maximum inhibition efficiency for TCL at 2% concentration is 91% for 1 hour immersion period and 97% for 24h immersion. Thus the plant extract is found to be a good inhibitor for mild steel corrosion in HCl medium.

TCL extract shows decrease in IE with increasing immersion time for lower concentrations of plant extract. The changes in IE with immersion time can be explained as due to changes in adsorption – desorption equilibrium. The extract shows maximum inhibition efficiency at 24h immersion time. Prolonged immersion of the sample in the medium with plant extract leads to greater adsorption of plant constituents.

Electrochemical measurements

Potentiodynamic polarization method

The Tafel polarization results at different concentrations of the inhibitor in 1N HCl is presented in Table 2 and the corresponding Tafel plots in fig. 1.

Table 1: CR of mild steel and IE (%) of TCL in 1N HCl at different concentrations and different immersion periods

Conc. of	1h		3h		5h		7h		12h		24h	
plant extract {%v/v}	C.R (mpy)	IE (%)	C.R (mpy)	IE (%)	C.R (mpy)	IE (%)	C.R (mpy)	IE (%)	C.R (mpy)	IE (%)	C.R (mpy)	IE (%)
Blank	894	-	901	-	994	-	1109	-	1103	-	1795	-
0.01	544	39	730	19	903	9	965	13	944	14	1561	13
0.05	513	59	420	53	564	43	674	39	654	41	1123	37
0.1	327	74	232	74	355	64	383	65	338	69	641	64
0.5	185	85	69	92	101	90	84	92	175	84	70	96
1	125	90	53	94	55	95	48	96	44	96	74	96
1.5	111	91	47	95	46	95	43	96	44	96	63	96
2	101	91	57	94	44	96	35	97	46	96	52	97

Table 2: Tafel polarisation parameters for mild steel in 1N HCl in the presence of TCL

Conc. (%)	$-E_{corr}$ mV	I_{corr} µA cm^{-2}	b_a mV/dec	b_c mV/dec	I.E (%)	R_p (Ω/cm^{-2})	I.E (%)
Blank	505	5.98	167	130	-	5.40	-
0.01	507	4.63	171	121	22	6.61	19
0.05	509	3.05	159	117	49	9.68	44
0.1	504	1.28	148	95	78	19.02	72
0.5	495	0.37	97	70	93	29.09	81

Table 3: Impedance parameters for mild steel in HCl in the presence of TCL

Conc. (%)	Rct ((Ω)	Cdl (µF cm^{-2})	I.E (%) from Rct	I.E (%) from Cdl
Blank	37.34	488.57	-	-
0.01	47.19	263.18	20.88	46.14
0.05	66.44	141.19	43.80	71.09
0.1	106.64	121.82	64.98	75.00
0.5	264.98	120.93	85.90	75.25

It is observed from Table 2 that the I_{corr} values decrease in the presence of inhibitors. This suggests that the adsorption of the inhibitor molecules on the metal surface reduces the uncovered surface area for the anodic as well as cathodic reactions. This is also seen from the increase in the R_p values. The fact that there is no significant change in the E_{corr} values suggests that the inhibitor functions as a mixed type of inhibitor. In all concentrations b_c is greater than b_a suggesting that though the inhibition is mixed control the effect of the inhibitor on the cathodic polarization is more pronounced than on the anodic polarization. Polarisation plots reveal that the presence of the extract shifts the anodic curves towards the more positive potential direction and the cathodic curves towards the negative direction. This behaviour confirms the inhibitive effect of the additive.

AC Impedance method

Impedance parameters derived from Nyquist plot are given in Table 3 and the Nyquist plot is shown in Figure 2.

Nyquist plots show that the mild steel-inhibitor system is under charge transfer resistance control without any loops that could indicate inductive behaviour in the low frequency region. Thus it may be inferred that the inhibitor is selectively adsorbed in specific places on the mild steel surface. It can

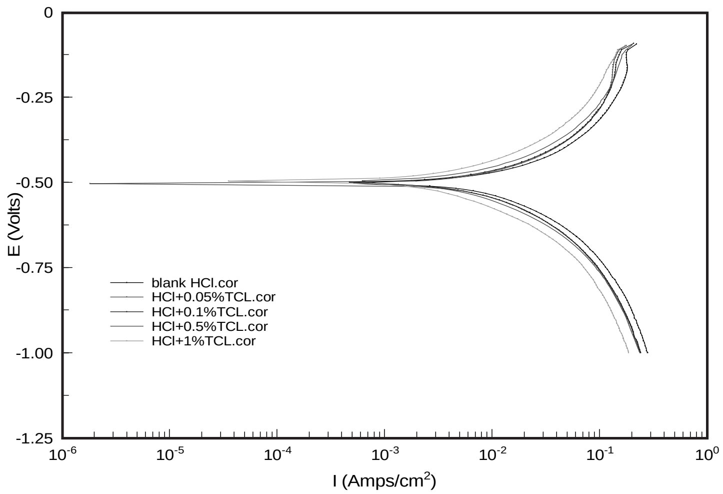


Fig. 1: Potentiodynamic polarization of mild steel in 1N HCl in the absence and presence of TCl

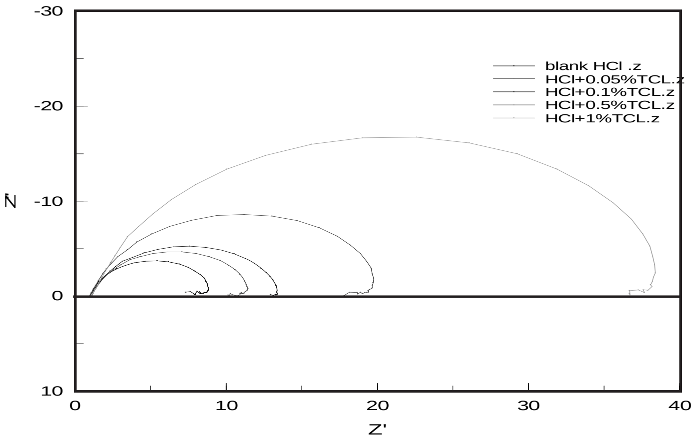


Fig. 2: Nyquist plot - mild steel in 1n HCL in the absence and presence of TCL

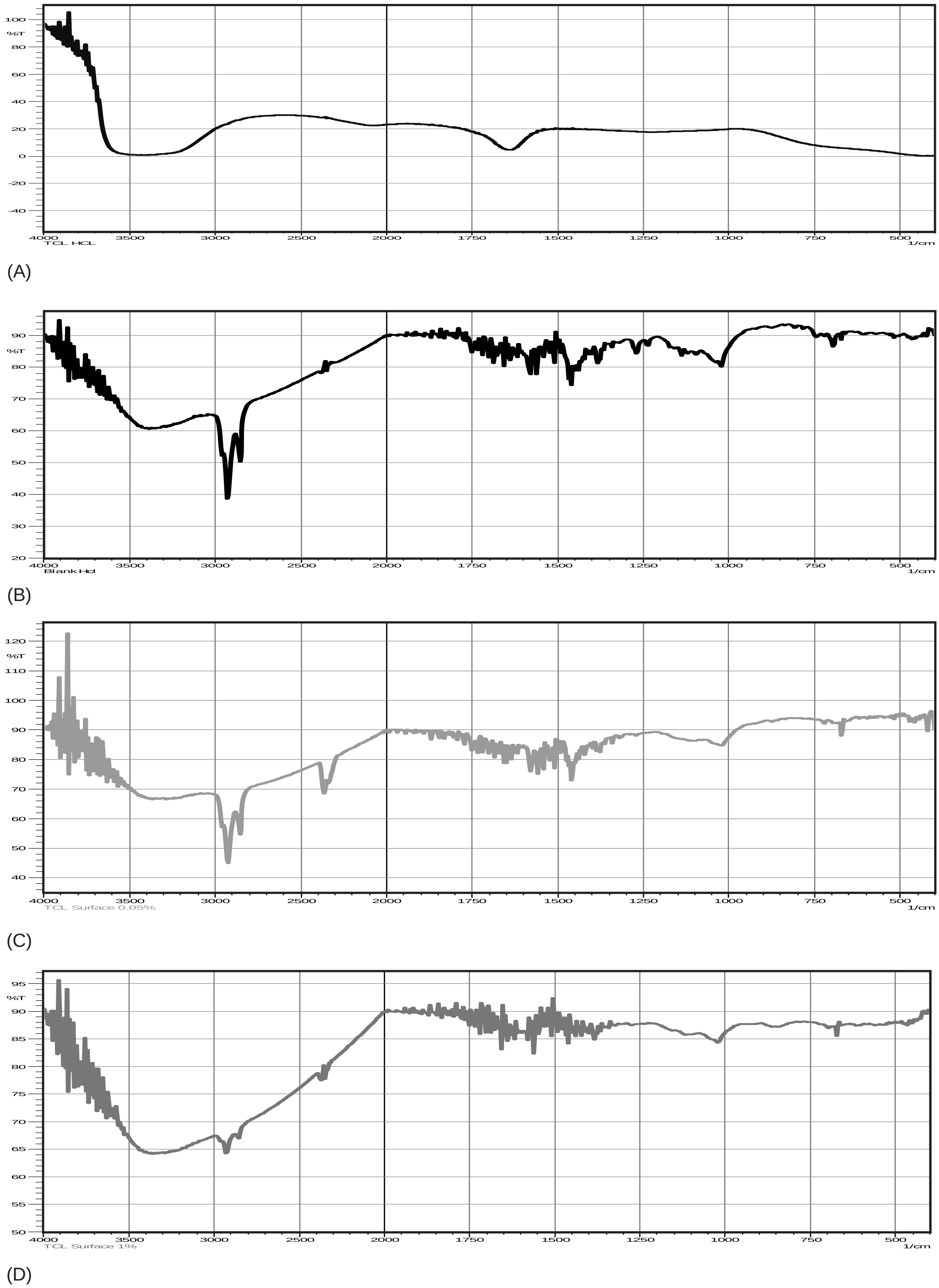


Fig. 3: FTIR spectra of (a) TCL extract (b) corrosion product of ms in 1N HCl (c) corrosion product of ms in 1N HCl with .05% TCL extract (d) corrosion product of ms in 1N HCl with 1% TCL extract

be seen from Table 3 that the presence of the inhibitor enhances the value of R_{ct} and reduces the C_{dl} values. The decrease in C_{dl} may be due to the adsorption of the inhibitor to form an adherent film on the metal surface and suggest that the coverage of the metal surface with this film decreases the double layer thickness

FTIR studies

FTIR spectra of the film carefully scratched from the surface of the mild steel immersed for 3 hours in 1N HCl acid in the absence and presence of plant extracts and that of the plant extract have been recorded in the region 400 – 4000cm^{-1}. The spectra are shown in Fig. 3

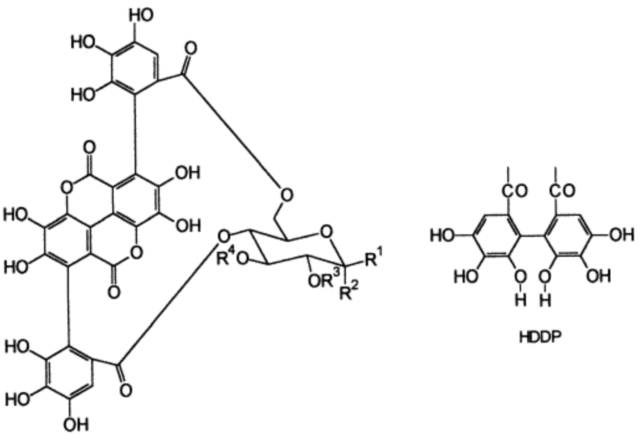
The broad envelope between 3300 – 3600 cm^{-1} is assigned to the O-H stretch of water The broadening shows the formation of H-bonded O-H stretch and confirms the presence of layer of water over the metal surface. The peak around 1640 cm^{-1} is assigned to OH_2 bending vibration and C=C stretching vibration[14]. The peak around 1000cm^{-1} is due to Fe-O-Fe stretching vibration. The peak at 698 cm^{-1} is attributed to γ OH and the band at 450- 700 cm^{-1} is due to the presence of g Fe_2O_3[15]. The peak around 1640 cm^{-1} in the extract spectra is missing in the spectra of mild steel surface immersed in acid containing extract indicating that there is interaction between the extract and Fe in mild steel. The peak at 2923 cm^{-1} shows the presence of adsorbed plant extract on the surface of steel.

Terminalia catappa belongs to the combretaceae family and its common name is Indian almond. Phytochemical studies of *Terminalia Catappa* leaves[16] reveal the presence of following constituents:

1-Degalloyl Eugenin	-	195 Ppm
Hexahydroxy diphenoyl glucose	-	625 Ppm
Chebulagic acid		
Gentisic acid		
Granatin – B	-	282 Ppm
Punicalagin	-	
4812.5Ppm		
Punicalin	-	550 ppm
Quercetin		
Tercatain		
Terflavin – A	-	399 Ppm

Punicalin and Punicalagin are the ellagitannins having the structure.

1. Punicalin a
2. Punicalin b
3. Punicalagin a
4. Punicalagin b



1 $R^1 = H$; $R^2 = OH$; $R^3 = R^4 = H$

2 $R^1 = OH$; $R^2 = H$; $R^3 = R^4 = H$

3 $R^1 = H$; $R^2 = OH$; R^3 ; R^4 = HDDP

4 $R^1 = OH$; $R^2 = H$; R^3 ; R^4 = HDDP

Fig. 4:

The main components of TCL are the Tannins, hexahydroxy compound and Terflavin. The inhibitive action of tannin has been attributed to the formation of a passive layer of tannates on the metal surface[17]. The layer must have formed primarily by an adsorption of the inhibitive species present in the extract consisting of organic molecules having hetero atoms like N, O, etc.

CONCLUSION

From the experimental results the following conclusions can be made

´ The acid extract of *Terminalia catappa* leaves show good inhibition efficiency of mild steel in 1N HCl medium as revealed by both weight loss and polarization studies.

´ Inhibition efficiency increases with inhibitor concentration and reaches a maximum of 97% for 2% v/v inhibitor concentration.

´ From the polarization studies the inhibitor is found to be of a mixed type inhibiting both anodic and cathodic corrosion reactions.

´ The mechanism of inhibition may be due to the adsorption of the plant constituents on the metal surface.

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