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# Journal of Chemical and Pharmaceutical Research, 2015, 7(9):158-167



**Research Article** 

## ISSN : 0975-7384 CODEN(USA) : JCPRC5

# Study on corrosion behaviour of mild steel in presence of acidic medium using natural products as inhibitors

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## ABSTRACT

The efficiency of the inhibitor (IE) of an aqueous extract medium of L. Acidissima and Tridax Procumben.L (TPL)in controlling and preventing the mild steel material have been studied and investigated using weight loss measurement in the absence and presence of corrosion inhibitor in 1M HCL acidic medium at room temperature. Further the rate of Corrosion and efficiency were studied by EIS, potentiodynamic polarization and surface morphological techniques. Potentiodynamic polarization studies have revealed that the compound L.Acidissima and TPL behave as mixed-type inhibitors. Changes in impedance parameters shows the adsorption of the compound present in the inhibitor over the metal surface. These studies have also shown that L.Acidissima and TPL acts as a good inhibitor for preventing mild steel in 1 M HCl acid solutions at room temperature in 2 hrs. On comparing the two natural inhibitor the inhibition efficiency was high for TPL when compared to L.Acidissima.

Keywords: Tridax Procumben. L, L. Acidissima, Langmuir, Corrosion inhibition, Mild steel, Environmental friendly inhibitor.

## INTRODUCTION

Corrosion is one of the most interesting fields of electrochemistry. The word Corrosion comes from the Latin word 'Corroder', which means gnaw away defined in many ways. For simplicity, it can be defined as "The spontaneous process of degradation and deterioration or destruction of metallic construction in the course of their chemical, biochemical or electrochemical interactions with the surroundings. According to the concept of corrosion the metastable condition of the metal to stable condition of its compound accompanied by the reduction in the free energy of the system [1-3]. Based on the literature there are plenty of methods to prevent corrosion one among the best method is mass loss method against both acidic and basic medium. Inhibitors are chemical substances which when added to corrosive environment reduce corrosion of large selection of organic compounds such as aldehydes, amines and sulphur compounds [4-6]. Inhibitors are mainly classified according to the chemical composition and structure. They are classified into chemical and electrochemical inhibitors. Electrochemical inhibitors are classified into cathodic, anodic or both the electrode process respectively. The majority of the

compounds or species used as inhibitors are organic in nature hence a distinction between organic and inorganic appends to rather useful [7]. Therefore in the present investigation the corrosion of mild steel was studied in absence and presence of natural inhibitors at room temperature.

### **EXPERIMENTAL SECTION**

#### 2.1 Preparations of Specimens:

All the test specimens of mild steel were cut to an overall apparent size of 5cm×1cm. The specimens were polished with different emery papers namely 150, 320, 400, 800, 1200 and 2000 and these specimens were degreased with trichloroethylene, dried and finally weighed. The elemental composition of the used mild steel specimen is presented in Table 1.

TABLE	1
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Elements	Chemical composition, (%)
Iron	99.686
Nickel	0.013
Molybdenum	0.015
Chromium	0.043
Sulphur	0014
Phosphorus	0.009
Silicon	0.007
Manganese	0.196
Carbon	0.17

## **2.2 Preparation of Inhibitors:**

## Inhibitor-I

Before extraction of the fruit (*L.Acidissima.*) were prepared by drying at room temperature (27  $^{\circ}$ C) followed by grinding. The dried material was extracted successively with methanol in Soxhlet extractor for 24 hours at 60 $^{\circ}$ C. The plant extract material was filtered and evaporated to 40 $^{\circ}$ C. The residue was dissolved in hot water and it was used as inhibitor.

#### Inhibitor-II

The plant is collected, shade dried and powdered. By reducing the moisture content of the plant which will enrich the active principle in them, by reducing its moisture content. An aqueous extract of *Tridax Procumben.L* was prepared by boiling 20g of dried leaves with methanol in Soxhlet extractor for 24 hours at  $60^{\circ}$ C. The extracted plant material was filtered and methanol filtrate was evaporated to  $40^{\circ}$ C. The residue was dissolved in hot water and it was used as inhibitor with distilled water, and making up to 100 mL, after filtering the suspending impurities the solutions have been prepared for various milli molar concentrations.

#### 2.3 Preparation of Solutions:

The solutions required for carrying out the experiments were prepared as follows.

#### 2.3.1 Hydrochloric acid

1M Hydrochloric acid were prepared using double distilled water.

#### **2.4 Inhibitor Solution:**

Inhibitor solution of 1% *L.Acidissima* and TPL was prepared by dissolving 1gms of *L.Acidissima* and TPL powder separately in 100 ml of solution for different milli molar concentration were prepared

### 2.5 Weight loss measurement:

Mild steel specimens were immersed in 1 M HCl in two different inhibitors for 2 h at room temperature  $(28 \pm 2 \text{ °C})$  for each inhibitor concentration. Then the specimens were removed, rinsed in double distilled water, acetone and the loss in weight of the specimen was determined. From this, the inhibiton efficiency (IE %) was calculated using the formula,

Inhibition efficiency IE (%) = 
$$W_0 - W - X 100$$
  
 $W_0$ 

Where,

 $W_0$  - Weight loss without inhibitors in gm

W - Weight loss with inhibitors in gm

#### 2.6 Electrochemical measurements

Potentiodynamic measurement-Tafel polarization curves were recorded using electrochemical work station CHI 660 USA. In this setup a platinum electrode, calomel electrode and MS specimens were used as auxiliary, reference and working electrodes respectively which were immersed in acidic medium in the presence and absence of different concentration of the inhibitor.

The inhibitor efficiency was calculated using the following equation

$$IE\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

 $I_{corr}$  = Corrosion current density in the absence of inhibitor  $I_{corr(i)}$  = Corrosion current density in the presence of inhibitor.

### 2.7 Impedance spectroscopy:

A well polished mild steel electrode was introduced into 100ml of test solution and allowed to attain a steady potential value[8]. An A.C. signal of amplitude of 10mV was applied and the frequency was varied from 10 MHz to 10 KHz using electrochemical work station CHI 660 USA. The real and imaginary parts of the impedance were plotted in the form of Nyquist plots [9]. From the Nyquist plot, the charge transfer resistance ( $R_{cl}$ ) and double layer capacitance ( $C_{dl}$ ) values were calculated.

The charge transfer resistance values were obtained from the plots of Z' vs. Z". The values  $(R_s + R_{ct})$  correspond to the point where the plots cut Z' axis at low frequency and  $R_s$  corresponds to the point where the plots cut Z' axis at high frequency. The difference between  $R_{ct}$  and  $R_s$  values give the charge transfer resistance  $(R_{ct})$  values [10]. The  $C_{dl}$  values were obtained form the relationship

$$C_{dl} = \frac{1}{2\pi f_{\max} \times R_{ct}}$$

Where

 $C_{dl}$  = double layer capacitance  $R_{ct}$  = Charge transfer resistance  $f_{max}$  = frequency at Z'' value maximum.

The inhibition efficiencies were obtained from R<sub>ct</sub> values as follows

$$IE\% = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

Where  $R_{ct}$  = Charge transfer resistance in the absence of inhibitor  $R_{ct(i)}$  = Charge transfer resistance in the presence of inhibitor.

#### **RESULTS AND DISCUSSION**

#### **3.1 Weight Loss measurement:**

The comparison graph of corrosion behaviour and inhibitor efficiency of mild steel in 1 M HCl with *L. Acidissima* and TPL was shown in Figure 1(a). Inhibition Efficiency of *L. Acidissima and TPL* was given in Figure 1 (b) which was studied by weight loss method at 2 h at room temperatures. From the graph, it was experientially verified that the weight loss of mild steel in the acid decreases with increasing concentration of additives and the values were tabulated in Table 2 from which it clearly states that the corrosion rate has decreased with increasing concentration of the inhibitor. The inhibition

efficiency in 1 M HCl in TPL 70.37% and in *L.Acidissima* was 54.89% respectively at optimum concentration of the inhibitor solution for two hours at room temperature.

S.No	Conc. of inhibitor (mM)	Initial weight (g)	Final weight (g)	Difference in weight (g)	Corrosion Rate (mmpy)	Inhibition efficiency (%)	
			L.Ac	ridissima			
1	Blank	12.7271	12.7087	0.0184	20.5068		
2	7.12	12.8866	12.8727	0.0139	15.4916	24.45	
3	14.21	12.7856	12.7736	0.012	13.374	34.78	
4	21.11	12.1347	12.1237	0.011	12.2595	40.21	
5	28.23	12.1579	12.1482	0.0097	10.8106	47.28	
6	36.04	12.8292	12.8209	0.0083	9.2503	54.89	
TPL							
1	Blank	12.2102	12.0701	0.1401	156.1419		
2	7.14	12.9597	12.8733	0.0864	96.2931	38.32	
3	13.95	12.1286	12.0513	0.0773	86.1511	44.82	
4	22.02	12.5652	12.4984	0.0668	74.4488	52.31	
5	28.25	12.304	12.2536	0.0504	56.1709	64.02	
6	35.46	12.3598	12.3183	0.0415	46.3328	70.37	

Table 2- Corrosion parameters in absence and presence of various inhibitors in 1M HCl



Figure-1 (a): Comparison study of Corrosion Behavior on 1M HCl in LAcidissima and TPL



Figure-1 (b): Comparison study of Inhibiton Efficiency on 1M HCl in L.Acidissima and TPL

#### **3.2 Adsorption Isotherm:**

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either physical (electrostatic) adsorption or chemisorption with the metal [11]. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage  $\theta$  at different concentrations of inhibitors in 1M (HCl acid) solutions were determined by the weight loss measurements data using the formula,

$$(\theta) = \frac{Wo - Wi}{Wo}$$

Where, Wo and Wi are the values of corrosion current density of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1-\theta}$$

Where, c is the concentration of the inhibitor,  $\theta$  is the fractional surface coverage. The Langmuir isotherm, which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant *K* is related to the free energy of adsorption  $\Delta G_{ads}$  as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

Where,  $C_{solvent}$  represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm<sup>-3</sup>, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, It can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c$$

so that a linear-relationship can be obtained on plotting  $c/\theta$  as a function of c, with a slope of unity. The thermodynamic parameters K and  $\Delta G_{ads}$  for the adsorption of the studied inhibitors on mild steel obtained by Langmuir's adsorption isotherm are plotted in Figure 2 and the values obtained are given in Table 3. It was found that the linear correlation coefficients clearly prove that the adsorption of the *L.Acidissima* and TPL from 1M acid solutions on the mild steel corrosion obeys the Langmuir adsorption isotherm. The negative values of  $\Delta G_{ads}^0$  for the addition of inhibitors indicate that the processes of adsorption of studied inhibitors are spontaneous in nature. The free energy of adsorption of  $(\Delta G_{ads})$ , in 1M HCl was found to be -11.107kJmol<sup>-1</sup> in L.Acidissima while for TPL it was found to be -18.329 kJmol<sup>-</sup> respectively.

It is well known that the values of  $\Delta G_{ads}$  in the order of  $-20 \text{ kJ mol}^{-1}$  or lower indicate a physisorption while those about  $-40 \text{ kJ mol}^{-1}$  or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond.

Table 3: Thermodynamic parameters for the adsorption of LAcidissima in various acids (1M HCl) on the mild steel (2 hrs)

ĺ	Name of the Acid	Concentration in (mM)	acentration in (mM) Surface coverage (0)		K x 10 <sup>-2</sup>
ſ	L.Acidissima	36.04	0.5489	-11.107	1.79
ľ	TPL	35.46	0.7673	-18.329	1.79



Figure 2- Langmuir isotherm for adsorption of L.Acidissima and TPL on mild steel surface studied at 1M HCl

## 3.3 Potentiodynamic polarization studies:

Potentiodynamic polarization results obtained for the inhibitory effect of *L.Acidissima* and TPL on mild steel corrosion in 1M HCl are depicted clearly in Figure 3. The various polarization parameters such as corrosion current (Icorr), corrosion potential (Ecorr), anodic and cathodic Tafel slopes ( $-\beta a$  and  $-\beta c$ ) were derived from potentiodynamic polarization studies on mild steel in both acid media[12,13].



Figure 3 -Potentiodynamic polarization curves of mild steel in 1M HCl in the absence and presence of the inhibitors

The influence of various inhibitors on the polarization behaviour of mild steel in 1M HCl is shown in Figure.3. The corrosion current density of anodic and cathodic region decreased considerably. The more shift in the cathodic current density was observed when compared to anodic current density. This clearly revealed that all the studied inhibitors act as mixed type inhibitors and predominantly controls the cathodic reaction. The corresponding Tafel parameters are summarized in Table 4.

S.NO	Inhibitors	$\beta_c$ (V dec <sup>-1</sup> )	$\frac{\beta_a}{(V dec^{-1})}$	E <sub>Corr</sub> (V)	I <sub>Corr</sub> x10 <sup>-4</sup> (A)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
1	Blank	5.026	10.632	-0.493	3.913	18.81	
2	L.Acidissima	5.182	9.062	-0.515	1.448	6.96	62.99
3	TPL	7.595	15.685	-0.505	1.261	6.058	67.77

Table 4: Polarization parameters of mild steel electrode immersed in 1M HCl in the absence and presence of the inhibitors

From the Potentiodynamic polarization curves, TPL shows the maximum inhibition efficiency (67.77 %). The Inhibiton efficiency follows the order TPL > L.Acidissima. This result suggests that the addition of inhibitors retards the hydrogen evolution reaction. It tends to found that these two inhibitors are found to be cathodic type inhibitors when compared to blank.

### 3.4 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 1M HCl solution in the absence and presence of various studied inhibitors like TPL and L.Acidissima were investigated by EIS measurement at open circuit potential condition [14]. Nyquist plots for mild steel obtained at the interface of electrode and electrolyte in the absence and presence of optimum concentration of inhibitors is given in Figure-4. The Nyquist diagram obtained with 1M HCl shows only one capacitive loop and the diameter of the semicircle increases on the increasing the electrostatic attraction of the inhibitor suggesting that the formed inhibitive film was strengthened by the addition of such inhibitors. All the obtained plots show only one semicircle and they were fitted using one time constant equivalent model (Randle's model) with capacitance(C) and charge transfer resistance ( $R_{ct}$ ) [15]. The main parameters deduced from the impedance technique are given Table 5.

The lower double layer capacitance ( $C_{dl}$ ) value for 1M HCl medium indicates that the homogeneity of the surface of the mild steel roughened due to corrosion. The double layer capacitance  $C_{dl}$  values decreased on the effective addition of different inhibitors at the optimum concentration. All the studied system indicating that the reduction of charge accumulated in the double layer due to formation of adsorbed inhibitor layer. The inhibiting efficiencies show that the inhibitory actions may be due to the adsorption of the inhibitors on mild steel surface.



Z'/ohm

Figure-4. A.C. Impedance curves of mild steel electrode immersed in 1M HCl in the absence and presence of the inhibitors

Table 5: A.C. Impedance parameters of mild steel electrode immersed in 1M HCl in the absence and presence of the inhibitors

	Parameters					
Inhibitors	R <sub>ct</sub> (ohm cm <sup>2</sup> )	C <sub>dl</sub> (µF X10 <sup>-5</sup> )	Inhibition Efficiency (%)			
Blank	71.81	4.378	-			
TPL	189.54	1.455	67.78			
L.Acidissima	205.54	1.441	68.92			

Among the compound investigated *LAcidissima* has been found to give an excellent inhibition due to the interaction of the molecule present in the inhibitor. This leads to the strong electrostatic attraction of LAcidissima on the metal surface thereby resulting in the high inhibition efficiency. Generally on the metal side, electrons control the charge distribution whereas on the solution side is controlled by ions. Since ions are much larger than the electrons, the equivalent ions to the charge on the metal will occupy quite a large volume on the solution side of the double layer. It can be obtained from Table 5 that, the capacitance of the electrical double layer (Cdl) decreases in the presence of the inhibitors. Decrease in the  $(C_{dl})$  which can result from a decrease in local dielectric constant and / or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecule may act by adsorption at the metal/solution interface.

#### 3.5 SEM Analysis:

The specimens used for surface morphology examination were immersed in 1M hydrochloric acid without and with milli molar concentrations of inhibitors LAcidissima and TPL for 48 h. Then, they were removed, rinsed quickly with rectified spirit and dried. The analysis was performed on HITACHI - model S - 3000 H Scanning Electron Microscope. The SEM images of the mild steel surfaces in the absence and presence of L.Acidissima and TPL were taken after the weight loss measurement. From the micrographs Figure 5 it can be seen that a number of pits occurred due to the attack of aggressive medium on the mild steel surface.

Figure 5 (A) shows an SEM image of mild steel surface after immersion in 1M HCl solution for 48 h. The micrograph reveals that the surface is highly damaged in absence of the inhibitor. Figure 5 (B and C) shows the image of another mild steel surface immersed in1M HCl solution for the same period in the presence of various inhibitors like LAcidissima and TPL. From this micrograph, it is obvious that all the studied inhibitors exhibit a good protective film on mild steel surface. This is attributed to the involvement of the compounds in the interaction with the active sites of metal surface. This results in enhanced surface coverage of the metal so that there is a decrease in the contact between metal and the aggressive medium.

Blank



L.ACIDISSIMA





TRIDAX PROCUMBEN.L (TPL)

Figure 5. SEM images obtained for the mild steel surfaces immersed for 48 h in 1M HCl A) Freshly polished surface dipped in blank acid solution, B) 1M HCl with 36.04mM of *L.ACIDISSIMA*, C) 1M HCl with 35.46mM of TPL

#### CONCLUSION

The present study leads to the following conclusions in controlling the corrosion of mild steel by *L.Acidissima* and TPL in 1M HCl.

1. L.Acidissima and TPL was found to be an effective inhibitor in the acidic medium giving

inhibition efficiency upto 70.37 % in 1M HCl and 54.89 % in 1M HCl respectively.

2. The adsorption of the compound investigated follows the Langmuir isotherm and the adsorption is physical in nature.

3. Polarization measurements demonstrate that the compound under investigation of the inhibitor both anodic and cathodic reaction and hence it act as mixed type inhibitor.

4. Impendance measurements indicate that, the presence of electron donating group on the inhibitor increase the charge transfer resistance and decreasing the double layer capacitance. The type of the substitutents group and the type of the functional atoms of the inhibitor molecule are found to play an important role in the inhibition process.

5. Results obtained from weight loss measurements and electrochemical measurements are in good agreement.

6. The morphological investigation also confirms the effective protection of mild steel, through the less damaged and minimum pits found in the inhibited surface.

7. This investigation gave an overview on material science in relation with physical and chemical science background and the nature of the metal was studied. For further conclusion of corrosion rate the same work can be carried out in microorganism mediated corrosion.

### Acknowledgement

We thankful to AMET University and Mahendra Engineering College (Autonomous) for providing Lab Facilities to bring out this work.

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