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Corrosion Inhibition of mild steel in 1N HCl media using Millingtonia Hortensis leaves extract

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Abstract: *Millingtonia Hortensis (MH) plant leaves extract is reported as corrosion inhibitor of mild steel in 1N HCl. Weight loss measurements, Tafel polarization and electrochemical impedance spectroscopy techniques are employed to analyze the effect on mild steel corrosion. It was found from the results of weight loss method that the inhibition efficiency increased with increase in MH extract upto 10 ppm. Electrochemical impedance spectroscopic measurements indicated that charge transfer resistance increases with increasing inhibitor concentration. Potentiodynamic polarization studies revealed that MH extracts act as mixed-type inhibitor. Scanning electron microscope (SEM) was used to analyze the surface adsorbed film.*

Keywords: *Mild steel, Millingtonia Hortensis, polarization, EIS.*

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I. Introduction

Economic importance of mild steel has increased due to its great demand in various industries. Inhibition of corrosion of mild steel has become very important. Use of hazardous chemical inhibitors is totally reduced because of environmental regulations. Chromates, Phosphates, Molybdates etc. and a variety of organic compounds containing hetero atom like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors[1-6]. There are some reports on the inhibition effects of non-toxic compounds on the corrosion of metals. The rare earth metals have been proposed as corrosion inhibitors [7, 8]. The inhibition effects of some non-toxic organic compounds have been also reported for steel corrosion [9, 10] but they are expensive.

Recently, new generation of corrosion inhibitors were extracted from plants [11-17]. These natural corrosion inhibitors are inexpensive, available from renewable resources, easily produced and considered as environmentally friendly compounds [18-21]. Furthermore, it solves the problem of using toxic compounds as corrosion inhibitors. The aim of this study is to investigate the inhibition effect of Millingtonia Hortensis leaves extract as a cheap, raw and non-toxic corrosion inhibitor on mild steel corrosion in 1N HCl. The electrochemical measurements were used to evaluate the inhibition efficiencies.

II. Materials And Methods

2.1 Preparation of Leaves Extract

The leaves of medicinal plant Millingtonia Hortensis collected were taken and cut into small pieces, and they were shade dried in room temperature for few days and ground well into powder. From this, 25 g of sample was refluxed in 200 ml distilled water for 3 hour and kept overnight. The refluxed was then filtered carefully, the filtrate volume was made up to 500 ml using double distilled water which was the stock solution, and the concentration of the stock solution was expressed in terms of ppm.

2.2 Preparation of Mild Steel Specimen

Mild steel strips containing the composition of (C-0.030%, S-0.029%, Cr-0.029%, Ni-0.030%, Mb-0.016%, Cu-0.017%), and the reminder Fe, were mechanically cut into 4 cm x 2 cm x 0.1cm and were used for weight loss studies. For electrochemical studies, the mild steel strips of the same composition but with an exposed area of 1cm^2 were used, subsequently degreased with acetone and finally washed with deionized water, and stored in the desiccators.

III. Methods

3.1 Weight Loss Method

Mild steel specimens were immersed in 200 ml of 1N HCl solution containing various concentration of the inhibitor in the absence and presence of mild steel for 24 hours. The weights of the specimens before and after immersion were determined using four digit model (shimadzu ay 220).

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$CR\ (mmpy) = \frac{K \times \text{Weight loss}}{D \times A \times t\ (\text{in hours})} \longrightarrow 1$$

Where, K = 8.76x10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.

The inhibition efficiency (%) was calculated using equation (2) respectively,

$$IE\% = \frac{W_0 - W_i}{W_0} X100 \longrightarrow 2$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor.

3.3 Potentiodynamic Polarization Method

Potentiodynamic polarization measurements were carried out using CHI660 E electrochemical work station analyzer. The polarization measurements were used to evaluate the corrosion current, corrosion potential and Tafel slopes. The experiments were carried out in conventional three electrode cell assembly with working electrode as mild steel specimen 1 cm^2. Platinum electrode was used as counter electrode and calomel electrode was used as reference electrode. A time interval of 10-15 minutes was given for each experiment to attain the study state open circuit potential. The polarization was carried out from cathodic potential to anodic potential at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula:

$$IE\% = \frac{I_{Corr} - I^*_{Corr}}{I_{Corr}} X100 \longrightarrow 3$$

Where I_{corr} and I^*_{corr} are corrosion current in the absence and presence of inhibitors.

3.4 Electrochemical Impedance Method

Experiments were carried out in three cells assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude 10 mV on the steady state open circuit potential. The real part (z') and the imaginary part (z'') were measured at various frequencies in the range of 100 kHz to 10 MHz. A plot of z' versus z'' was made. From the plot the charge transfer resistance (R_{ct}) was calculated and double layer capacitance (C_{dl}) was calculated using formula:

$$C_{dl} = 1/2\pi f_{max} Rct \longrightarrow 4$$

Where R_{ct} is charge transfer resistance and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

$$IE\% = \frac{R_{ct} - R^0_{ct}}{R_{ct}} X100 \longrightarrow 5$$

Where R_{ct} and R^0_{ct} are the charge resistance values in the inhibited and uninhibited solution respectively.

3.6. Effect of temperature

The polished and pre – weighed specimens were suspended in 100 ml of the test solution without and with the addition of various concentration of the MH extract for 1h in the temperature range of 303 – 323K using water thermostats. The specimens were removed from the test solution after 1 h and washed with distilled water, dried and weighed. The inhibition efficiency was calculated from the weight loss.

IV. Results And Discussion

4.1 FT-IR spectrum of MH

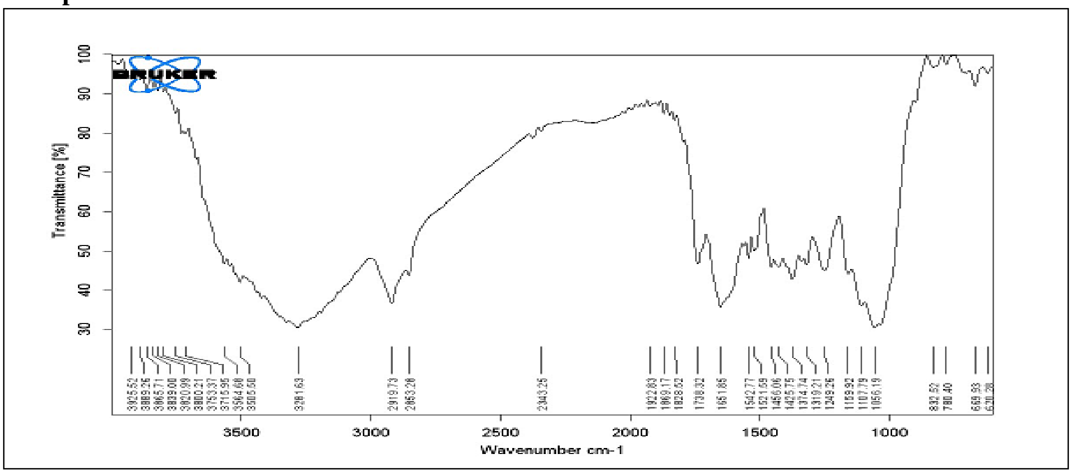

Figure 1. FT-IR spectrum of Millingtonia Hortensis leaves extract

FT-IR spectrum of MH leaves extract are recorded in order to confirm the presence of various compounds which contributed in effective working of the inhibitor are presented in Fig. 1. The Free O-H stretching was observed at 3500 to 3700 cm^{-1}.The broad peak obtained at 3281 cm^{-1} can be assigned to N-H or

O-H stretching. Another peak obtained at 2800 to 2900 cm^{-1} may be strong C-H stretching. Adsorption peak obtained at 1700 to 1900 cm^{-1} may be due to stretching of C=O. The peaks observed at 1000 to 1300 cm^{-1} may be C-O stretching vibration. Few peaks can also observed at 1542 cm^{-1}, 1456 cm^{-1}, 1374 cm^{-1}, which correspond to C=C stretching vibration.

4.2 Weight Loss Method

Weight loss method was done for mild steel in 1N HCl with various concentrations of MH extract ranging from 5 to 25 ppm and the corresponding values of inhibition efficiency and corrosion rate are given in Table 1. It was observed from the table that the corrosion rate decreased and thus the inhibition efficiency increases with increasing concentration of MH extract (5 to 25 ppm). The maximum inhibition efficiency of about 91.21% was achieved at 10 ppm of MH extraction. This result indicated that MH extract could act as an excellent corrosion inhibitor.

Table1. Data from Weight Loss Method for MS corroding in 1N HCl solutions at various concentrations of MH extract

Conc. of MH Extract (ppm)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
blank	0.0330	*
5	0.0124	53.33
10	0.0081	91.21
15	0.0075	86.18
20	0.0110	77.93
25	0.0104	76.60

4.3 Potentiodynamic polarization Studies

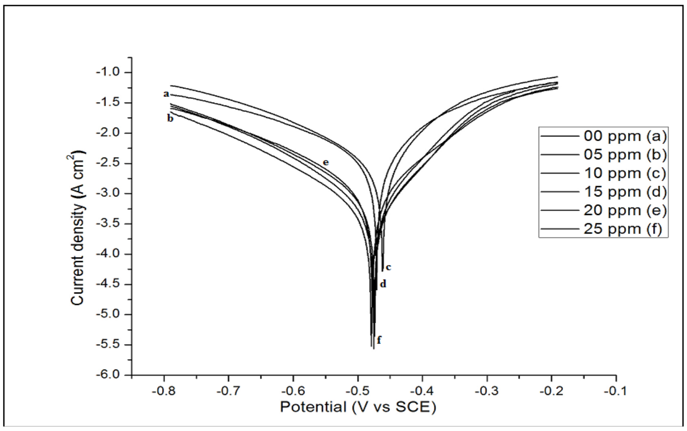

Figure 2. Potentiodynamic polarization curves for mild steel in 1N HCl solution in the absence and presence of different concentrations of MH leaves extract

The polarization measurements were made to evaluate the corrosion current, corrosion potential and Tafel slopes. The potentiodynamic polarization curves for mild steel in 1N HCl with and without inhibitor (extract) are shown in Figure 2. It is evident from the Figure 2 that the anodic and cathodic curves for mild steel inhibited with extract were shifted towards positive potential region compared to the blank metal immersed in 1N HCl. The corrosion parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}), obtained from Tafel plots are given in Table 2. From the table, it is observed that the I_{corr} values are found to decrease with increase in the inhibitor concentrations, ranging from 5 to 25 ppm. The maximum inhibition efficiency of 92.20 % was achieved at 10 ppm. However, the shift in the values of corrosion potential (E_{corr}) for MH extract is not significant. This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors.

Table 2. Potentiodynamic polarization parameter for mild steel in 1N HCl solution containing various concentrations of MH leaves extract.

Conc. of MH (ppm)	E_{corr} (mV) vs. SCE	I_{corr} ($mAcm^{-2}$)	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
0	-471	4.706	0.0264	208	162	*
5	-479	0.450	0.0097	153	84	90.43
10	-462	0.367	0.0065	178	128	92.20

15	-474	0.738	0.0060	156	87	84.17
20	-477	1.087	0.0088	163	122	76.90
25	-472	1.145	0.0084	168	111	75.66

4.4 Electrochemical Impedance spectroscopy (EIS) Studies

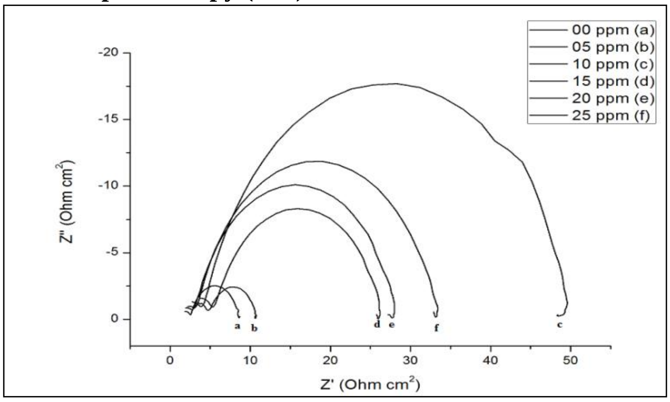

Figure 3. Nyquist plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of MH leaves extract

The shape of impedance gives mechanistic information. Nyquist plots of mild steel in uninhibited and inhibited acid solution containing various concentrations of MH extract are presented in Figure 3 and the parameters are given in table 3. It is followed from Figure. 3 that the impedance of the mild steel increases with increase in the inhibitor concentration..The presence of a single semi-circle in the blank and for different concentrations of the inhibitor systems corresponds to the single charge transfer mechanism during dissolution of mild steel, which is unaltered by the presence of inhibitor components.

The charge transfer resistance (R_{ct}) value calculated for blank mild steel exhibited 6.787 Ωcm^2 and the double layer capacitance (C_{dl}) was $9.857x10^{-3}$ $\mu F/cm^2$. The higher R_{ct} value obtained for higher inhibitor concentration suggests that a protective film is formed on the surface of the metal. The decreased in the C_{dl} values results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface. Further, the adsorption may also due to the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface. All the electrochemical parameters clearly proposed that the corrosion control depends on the concentration of the inhibitor.

Table 3. The electrochemical parameters (EIS) for mild steel corrosion rate in 1N HCl solution in different concentrations of MH leaves extract

Conc. of MH (ppm)	**Cdl ($\mu F\ cm^{-2}$)**	**b_c (mV/dec)**	**b_a (mV/dec)**	**Rct ($\Omega\ cm^2$)**	**IE (%)**
0	$9.857x10^{-3}$	208	162	6.787	-
5	$1.842x10^{-4}$	153	84	49.226	86.21
10	$9.663x10^{-4}$	178	128	86.235	92.12
15	$5.867x10^{-4}$	156	87	26.948	74.81
20	$8.530x10^{-4}$	163	122	22.306	74.05
25	9.374×10^{-4}	168	111	21.471	68.38

4.5 Bode Plot

Bode plots of mild steel in uninhibited and inhibited acid solution containing various concentrations of MH extract are presented in Figure. 4. It is apparent that the mild steel specimens with MH extract showed increase in maximal phase angle value, which indicated an inhibition property on the surface mild steel. The linear portion observed in the low frequency region indicated that the diffusion process controlled the metal dissolution rate at the surface of mild steel.

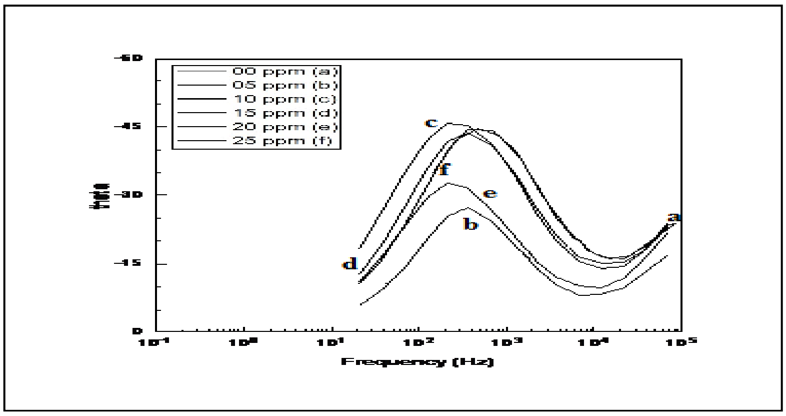

Figure 4. Bode plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of MH leaves extract

4.6 Scanning Electron Microscopy (SEM)

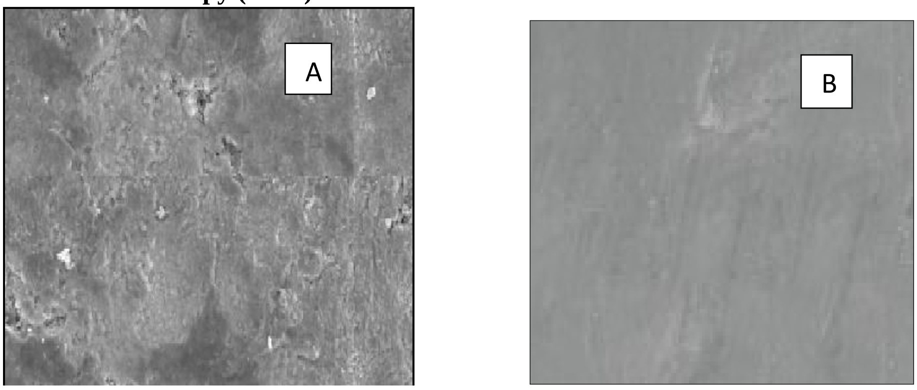

Figure 5. SEM image of the surface of mild steel after immersion for 24 hrs in 1N HCl solution. (A) in the absence of inhibitor (B) in the presence of 20 ppm MH leaves extract

SEM images for the mild steel specimens exposed to 1N HCl in the absence and presence of MH extract are shown in Figure. 5 (A and B). From SEM images, It can be concluded that MH leaves extract inhibited mild steel dissolution in acid by covering the surface area with protective film which has found absent in case of acid interaction with mild steel. Examination of Figure. 5A revealed that the specimen immersed in 1N HCl was rough and highly damaged due to the attack of aggressive acids. Figure. 5B clearly showed that the mild steel surface was covered with the protective layer formed by inhibitor which prevents the metal from further attack of acid medium thus inhibiting corrosion.

4.7 Phytochemical Screening

Phytochemical screening of the aerial parts of plant's powder (alcoholic) extract was tested in order to find the presence of various chemical constituent included Alkaloids, Carbohydrates, Proteins, Saponins, Triterpenoids the results are listed in Table 4.

Table 4. Phytochemical screening of leaves extract of MH.

S.No	Phytochemical Test	Alcoholic extract of MH
1	Alkaloids	+
2	Carbohydrates	+
3	Proteins	+
4	Saponins	+
5	Triterpenoids	+

+ is Present **- is Absent**

4.8. Effect of temperature

The effect of temperature on the corrosion inhibition properties of leaves extract was studied by exposing the mild steel to 1 N HCl containing 5, 10, 15, 20, 25 ppm of the leaves extract in the temperature range of 303-323K. The data in table 5 indicated that the leaves extract is effective as inhibitor for mild steel in 1N HCl upto 303K and decrease thereafter. The inhibition showed a maximum of 62.10% at 303K of leaves extract in 1N HCl.

Table. 5 IE at various Temperature

Concentration of solution (ppm)	IE (%)		
	303K	**313K**	**323K**
5	34.74	31.57	28.21
10	42.25	36.31	32.67
15	57.31	47.89	44.45
20	61.43	53.68	54.45
25	62.10	57.89	56.35

4.9. Adsorption isotherms

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and its characteristics of inhibitor on the metal surface. In our present study the Tempkin adsorption isotherm is investigated. The straight line in Fig. 6 clearly indicated that the inhibitor obey Tempkin adsorption isotherm.

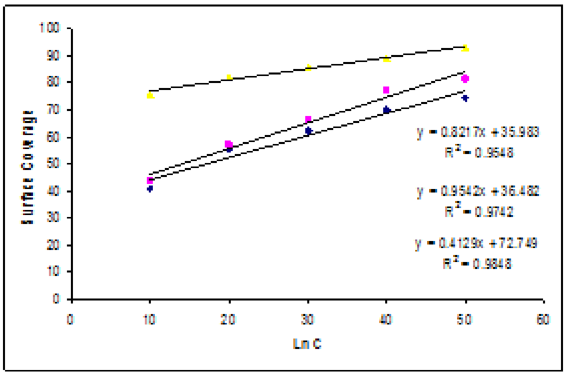

Figure. 6. Temkin Isotherm of Millingtonia Hortensis leaves extract

V. Conclusion

In this study, the aqueous extract of Millingtonia Hortensis leaves as inhibitor was tested for mild steel in 1N HCl. Present study showed that the investigated ecofriendly inhibitor had a high inhibitory effect to corrosion process of mild steel. The inhibition efficiency increased with increase in inhibitor concentration. E_{Corr} values shifted to more positive potential direction. SEM study clearly explained the strong adsorption of the inhibitor. The adsorption of Millingtonia Hortensisleaves extract on mild steel obeys Temkin adsorption isotherm.

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