Research Article

Millingtonia hortensis (Tree Jasmine) Leaves Extract as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid

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Abstract

Corrosion inhibition of mild steel in 1N HCl was studied in the absence and presence of different concentrations of extract of leaves of *Millingtonia hortensis* [MHL]. Results of weight loss studies and electrochemical impedance studies show that the inhibition increases with increase in concentration of the plant extract. Thermodynamic parameters calculated show that the adsorption of MHL extract on mild steel surface is spontaneous and found to be physisorbed.

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Keywords: corrosion inhibitor, potentiodynamic polarization, EIS, mild steel, Millingtonia hortensis

Introduction

The use of inhibitors is one of the best options of protecting metals against corrosion. Green inhibitors are used to prevent corrosion and they are eco friendly. Several synthetic inhibitors that are used are compounds having hetero atoms in their aromatic or long chain carbon compounds. Acid violet 6B[1], benzimidazole derivative[2], pyrazine derivative[3], hexamethylenetetramine[4], glycine derivative[5], disulfiram[6], tetradecylpyridinium bromide[7], 4-Amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol[8], sparfloxacin[9], 1-3 diamino propane [10]. Several natural products have been reported to be corrosion inhibitors for mild steel and other metals. *Musa species* [11], *Musa sapientum* [12], *Acacia seyal* var. seyal [13], beet root [14], *Citrus paradise* [15], *Oxandra asbeckii* [16] have been tried as mild steel corrosion inhibitors. The plant leaves contain phytochemicals like saponins, flavonoids, terpenoids, tannins, phlobatannins, glycoside, and alkaloid were reported [17, 18]. In the present study the corrosion inhibitory effect of acid extract of leaves of *Millingtonia hortensis* on mild steel in acid medium has been investigated. Weight loss, polarization and EIS studies were carried out.

Experimental

Material Preparation

Rectangular mild steel coupons of size 5x1cm and 2mm thickness, cut from a large sheet of mild steel were used in the present study. The plate was washed with distilled water, dried with acetone and polished successfully using emery sheets of 400mm, 600mm grades to remove adhering impurities. The plates were then kept in desiccator to avoid the absorption of moisture

Extract preparation

The leaves of *Millingtonia hortensis* were collected shade dried and made into powder. 25g of this powder was refluxed with 500ml of 5% HCl acid solution. The solution was refluxed for 3hours and left overnight. The refluxed solution was then filtered carefully and the filtrate volume was made up to 500ml. From this 5% stock solution, different dilutions ranging from 0.05% to 3.0%concentration v/v of the extract was prepared for the study.

Weight loss Method

The experimental solution 1N HCl with different concentrations of inhibitors was used. The pretreated specimens were immersed in the experimental solution with the help of the glass hooks. The initial weight of the specimens was noted and the steel strips were immersed completely in to the experimental solution for different time duration. After the specified duration of immersion the specimens were taken out, washed thoroughly with distilled water, rinsed completely and dried and their final weights were noted. From the initial and final weights of the specimen, the loss in weight was calculated and tabulated. The corrosion rate (mpy) and the efficiency of the inhibitors can be calculated using the formula,

Corrosion Rate (CR) = (534*W) / DAT (mpy)

where,

mpy = mils per year
W = loss in weight in milligrams
D = density in g/cm^2 (7.9 g/cm^2)
A = area in square inch
T = time in hours.

Inhibition Efficiency = $(W_B – W_I) / W_B$ x100

Where, W_B and W_I are weight loss per unit time in the absence and presence of inhibitors, respectively.

Effect of temperature:

The polished pre-weighed specimens were suspended in 100 ml of the test solution without and with the addition of different concentration of the leaves extract for 1 hour in the temperature range of 303K – 343K in a thermostat (Technico Serological digital Pit water bath – AI 209). The specimens were removed from the test solution after 1 hour and washed with distilled water, dried and weighed. The inhibition efficiency was then calculated from the weight loss

Potentiodynamic polarization studies

Potentiodynamic polarization studies were done using IVIUM make compact stat.e model analyzer. Before recording the polarization curves the mild steel rod as a working electrode was immersed in the test solution for 10 minutes to reach saturation. The potential was changed with the scan rate of 10 KHz to 0.01 Hz. From polarization measurement, the corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic (b_a) and cathodic (b_c) Tafel slopes were determined. The percentage inhibition efficiency (IE%) was calculated from,

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

Where, I_{corr} and I_{corr} (inh) are corrosion current density without and with inhibitor respectively.

Electrochemical impendance spectroscopy (EIS)

EIS study enables us to understand the various processes that take place on the metal- electrolyte solution interface, adsorption-desorption of the reaction intermediates. The Nyquist plots are obtained by measuring AC impedance and Tafel plot using polarization data. The EIS experiments were conducted using the same setup as used in the polarization method using frequency range 10 KHz to 10 mHz with AC amplitude of 10 mv. The real (Z’) and imaginary (Z'') impedance values were measured for various frequencies. The charge transfer resistance values (Rct) obtained by plotting Z' *vs*. Z'' were used to calculate the percentage inhibition efficiency from Rct

$$IE\% = \frac{R^{o}ct - Rct}{R^{o}ct} \times 100$$

Where, Rct and R^{o}ct are charge transfer resistance values with and without inhibitor.

Results and Discussions

Weight loss measurements: Effect of concentration and time

Corrosion parameters such as CR and IE, obtained by weight loss method for different concentrations of the inhibitor at various time intervals in 1N HCl are given in Table 1. The corrosion rate decreases with increase in concentration of the inhibitor and the percentage inhibition efficiency of the inhibitor increases with increase in inhibitor concentration. Maximum efficiency was achieved at 3 % v/v (89.38%). The decrease in corrosion rate and increase in inhibitor efficiency is attributed to the adsorption of plant constituents on the surface of mild steel which makes a barrier and protects further attack by the acid. It may be due to the presence of phytochemicals in the leaves extract which act as a barrier and prevent corrosion of mild steel. From the Table 1 it can be seen that at 24hours of immersion, corrosion rate is grossly reduced in presence of the inhibitor. In the presence of inhibitor IE was found to increase with increase in time from 1hour to 24 hours with the maximum of 99.04 % at 2% v/v for 24 hr immersion. This is due to the increase in the adsorption of phytochemicals present in the plant extract.

Table 1 CR of mild steel and IE of the inhibitor in 1 N HCl in presence and absence of MHL extract for different immersion times

conc	**1 hr**		**3 hrs**		**5 hrs**		**7 hrs**		**24hrs**	
(v/v%)	**CR(mpy)**	**IE%**	**CR(mpy)**	**IE%**	**CR(mpy)**	**IE%**	**CR(mpy)**	**IE%**	**CR(mpy)**	**IE%**
blank	492.79		420.11		477.97		418.66		1521.81	
0.01	331.44	32.74	116.29	72.32	93.33	80.47	80.99	80.65	56.87	96.26
0.05	252.94	48.67	94.49	77.51	68.03	85.77	77.88	81.4	33.07	97.83
0.10	148.27	69.91	91.58	78.2	50.59	89.42	74.76	82.14	27.07	98.22
0.50	117.75	76.11	79.95	80.97	40.12	91.61	62.92	84.97	18.72	98.77
1.00	109.03	77.88	72.68	82.7	39.25	91.79	44.23	89.43	17.08	98.88
1.50	87.22	82.3	66.87	84.08	34.02	92.88	32.4	92.26	15.99	98.95
2.00	78.5	84.07	53.79	87.2	30.53	93.61	29.28	93.01	14.54	99.04
2.50	65.42	86.73	34.89	91.7	27.91	94.16	22.43	94.64	17.08	98.88
3.00	52.33	89.38	27.62	93.43	20.93	95.62	15.58	96.28	18.17	98.81

Effect of temperature

To study the effect of temperature on the corrosion inhibition properties of MHL extract, experiments were carried out in absence and presence of varying concentration of the inhibitor in the temperature range from 303-343K. The results are summarized in Table 2. The data indicated that the MHL extract was effective up to 323K and slightly decreased thereafter. The maximum efficiency of 97.41% at 333K indicates that the inhibitor can be effectively used up to333K.

Thermodynamic parameters

The free energy of adsorption ΔG_{ads} was calculated using the following equation

$$\Delta G^o_{ads} = 2.303 \text{ x R x T } [1.74+\log\theta/c\ (1-\theta)]/1000$$

Where, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature.

Values of activation energy (Ea) for carbon steel in 1M HCl in absence and presence of different concentrations of the inhibitor were calculated from log CR and 1/T using the formula

$$Ea = -\text{slope}\times 2.303\times R$$

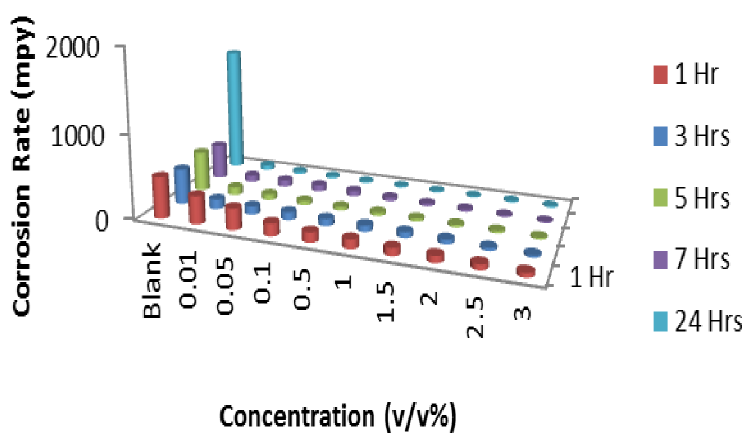

Figure 1 influence of immersion time on CR

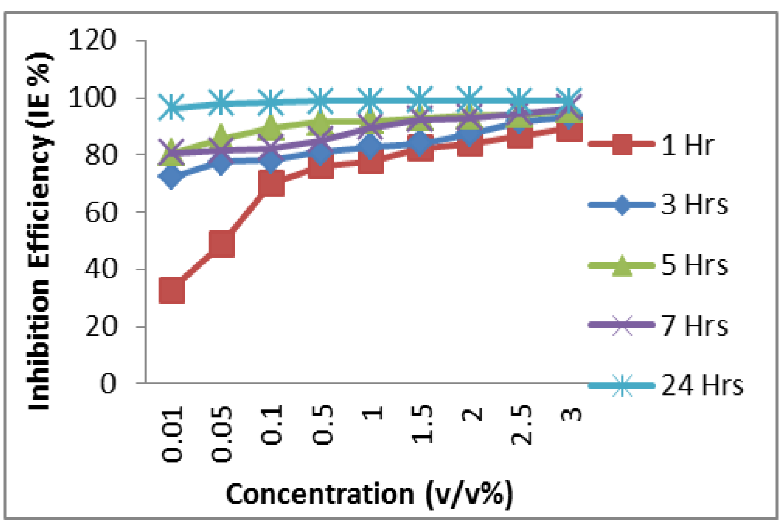

Figure 2 Influence of immersion time on IE

Table 2 Effect of temperature on CR of mild steel and IE the inhibitor in 1N HCl in absence and presence of MHL extract

Conc. (v/v%)	303 K CR	IE %	313 K CR	IE %	323 K CR	IE %	333 K CR	IE %	343 K CR	IE %	Ea (kJ/mol)
Blank	492.79	-	1011.75	-	6746.47	-	16022.31	-	9716.31	-	76197.26
0.05	252.94	48.67	492.79	51.29	689.04	89.79	11818.31	26.24	3759.18	61.31	74271.84
0.1	148.27	69.91	270.38	73.28	632.35	90.63	8503.95	46.92	2337.5	75.94	77864.40
0.5	117.75	76.10	392.49	61.21	623.62	90.76	985.59	93.85	915.81	90.57	44024.04
1.0	109.03	77.87	218.05	78.45	723.93	89.27	514.60	96.79	532.04	94.52	35520.60
1.5	87.22	82.30	100.30	90.09	279.10	95.86	741.37	95.37	523.32	94.61	48448.73
2.0	78.50	84.07	100.30	90.09	266.02	96.06	470.99	97.06	841.67	91.34	54241.52
2.5	65.42	86.70	143.91	85.78	440.46	93.47	414.30	97.41	693.4	92.86	50341.64
3.0	52.33	89.93	157.00	84.48	209.33	96.90	758.81	95.26	488.43	94.97	52687.40

Electrochemical method

Potentiodynamic polarization studies

The effect of the extract on the electrochemical behavior of mild steel was studied by carrying out cathodic and anodic polarization experiments. The potentiodynamic parameters of the inhibitor such as corrosion potential E_{corr}, corrosion current density I_{corr}, anodic and cathodic Tafel slopes, ba and bc, in absence and presence of inhibitor are listed in Table 4 and depicted in Figure 4. The result reveals that I_{corr} values of acid in presence of inhibitor are lower than that of acid in absence of inhibitor indicating that increase in inhibition property was due to adsorption of inhibitor molecules on the electrode surface.

The maximum inhibition efficiency of 58.33% was found at 2% v/v concentration of MHL extract. This shows that the leaves extract of *Millingtonia hortensis* in 1N HCl acts as very good corrosion inhibitor for mild steel. The steady value of E_{corr} suggests that the inhibitor is mixed type inhibitor and this infers that the inhibitor reduces the hydrogen evolution and anodic dissolution of mild steel.

Table 3 Thermodynamic parameters of adsorption on mild steel surface in 1M HCl containing different concentrations of the inhibitor

Conc(C)	-ΔG_{ads}(kJ/mol) 303K	313K	323K	333K	343K	Δsads (j/mol K)	ΔHads (kJ/mol)
0.05	17.54199	18.32919	24.70887	21.30897	22.6972	0.132902	-22.0101
0.1	18.03119	19.00973	23.15981	21.37734	22.75153	0.118083	-17.2749
0.5	14.74549	13.39625	18.83701	21.44407	22.80484	0.241665	-59.8123
1-0	13.28372	13.72213	16.37661	21.50923	22.85718	0.269340	-69.4471
1.5	12.89373	15.09142	18.20799	21.57289	22.90857	0.265112	-67.4961
2.0	12.52637	14.34266	17.4353	21.63512	22.95905	0.281578	-73.1701
2.5	12.57572	12.76779	15.24761	21.69598	23.00866	0.297941	-79.1757
3.0	12.86282	11.88446	17.14678	21.75553	23.05741	0.302603	-80.3992

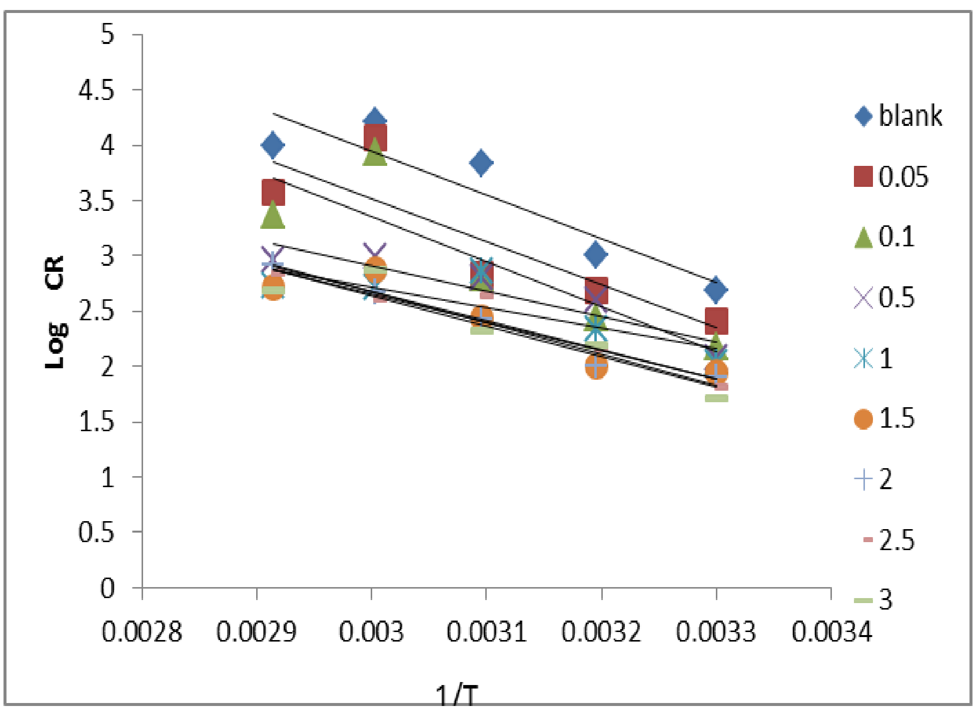

Figure 3 Arrhenius plots for mild steel in 1N HCl in the absence and presence of inhibitor.

Table 4 Potentiodynamic polarization parameters for mild steel in 1N HCl in the absence and presence of MHL extract

cocentration (v/v%)	b_c V/dec	b_a V/dec	$i_{cor.}$ A	$E._{corr}$ V	R_p Ohm	IE% TAFEL	IE% LPR
blank	0.146	0.076	0.0001244	-0.4906	174.6		
0.05	0.130	0.06	0.0000686	-0.4593	259.5	42.83	32.71
1.00	0.184	0.063	0.0000638	-0.4307	319.1	46.83	45.28
2.00	0.180	0.064	0.0000507	-0.4163	403.3	58.33	56.70
3.00	0.178	0.07	0.0000758	-0.4285	287	36.83	39.16

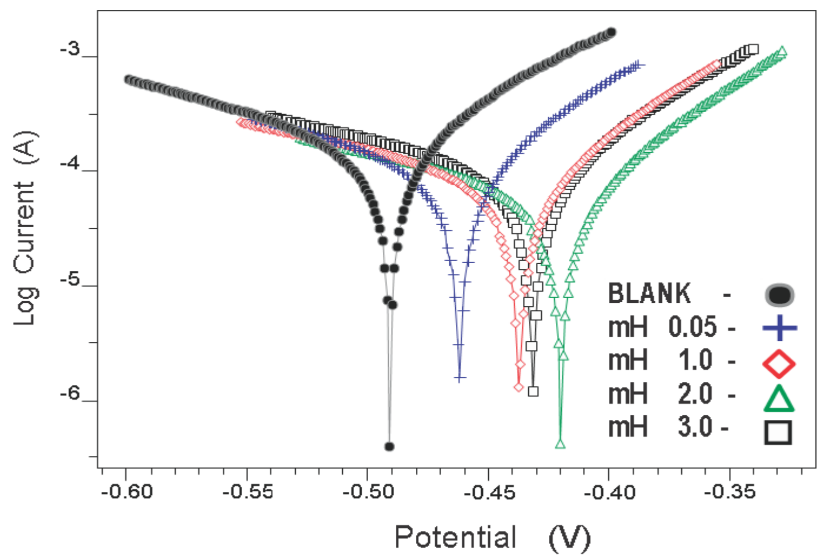

Figure 4 Potentiodynamic polarization curves for mild steel in 1N HCl without and with different concentrations of MHL extract

Electrochemical Impedance studies (EIS)

The corrosion behavior of mild steel in 1 N HCl in presence of MHL was also studied using EIS at 30°C. The charge transfer resistance (R_{ct}) and the corresponding inhibition efficiency are determined. It is clear from the Table 5 and Figure 5 that R_{ct} values increase with increase in the concentration of the inhibitor which is in accordance with the results obtained by weight loss method.

Conclusion

The inhibition efficiency of the plant extract on mild steel in 1N HCl was studied using weight loss and polarization and impedance methods. The following were the conclusions drawn from the studies.

1. The leaves extract of *Millingtonia hortensis* was found to be effective inhibitor at concentration of 2% v/v in 1 N HCl solution.
2. The inhibition efficiency of mild steel in 1N HCl increases with increase in concentration of MHL extract. The performance of the extract as corrosion inhibitor was maintained even at higher temperature.
3. The activation energy E_a is higher for the test solution in the presence of the extract showing that there is an inhibition of corrosion reaction.

4. The investigated inhibitors were suggested to be physisorbed on the electrode surface on the basis of the low values of the free energy of adsorption ΔG ranging from 11.88 kJ/mol – 24.71kJ/mol.
5. AC impendence plots of mild steel in the acid medium show that charge transfer resistance increases with the increase of extract concentration. The results indicate that inhibition effect of the plant extract was due to physical adsorption of the phytochemicals present in the extract onto the active sites on the surface of the metal.
6. Potentiodynamic polarization curves revealed that MHL extract is a mixed-type inhibitor.

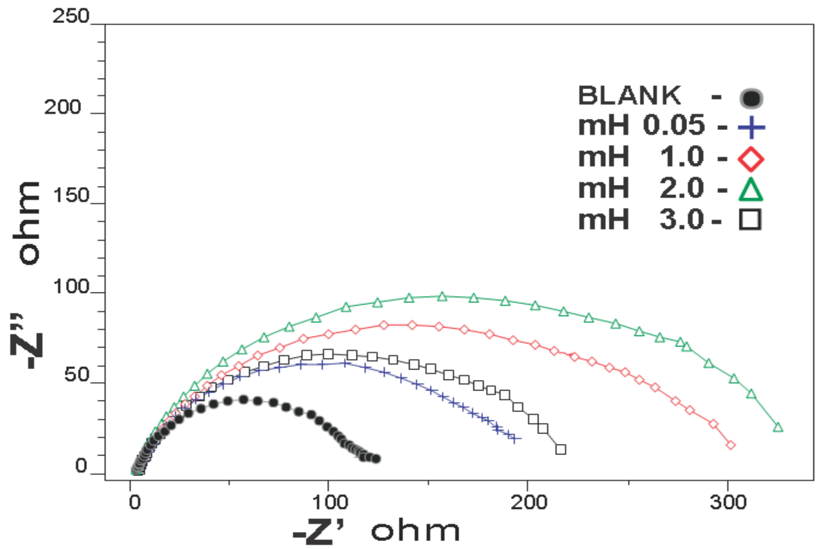

Figure 5 Impedance plots recorded for mild steel in 1 N HCl solutions without and with various concentrations of MHL extract

Table 5 EIS parameters for the IE of the inhibitor in 1 N HCl containing MHL extract at 30°C

Concentration (v/v%)	Rct Ohm cm^2	IE% (Rct)
blank	89.9	
0.05	144	37.57
1	209	56.99
2	242	62.85
3	158	43.1

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Publication History
Received 20th Sep 2013
Revised 30th Oct 2013
Accepted 05th Nov 2013
Online 10th Jan 2014