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Studies on Mild Steel Corrosion Inhibition by *Millingtonia Hortensis* Extract in 1N Sulphuric Acid Medium

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Abstract

Efficiency of acid extracts of dry leaves of Millingtonia Hortensis(MH) as corrosion inhibitor for mild steel in H_2SO_4 medium is investigated in the present study by weight loss method and FT-IR Spectroscopy. The results indicate MH leaves to be good inhibitor having efficiency as high as 98.99% at 2% inhibitor concentration. Inhibitor efficiency increases with concentration of the extract. Temperature studies show that inhibition efficiency decreases with increase in temperature. Adsorption isotherms reveal that it obeys Langmuir isotherm.

Keywords: *FT-IR ; Mild steel; Weight loss method.*

1. INTRODUCTION

Corrosion is a naturally occurring phenomenon and commonly defined as the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention is more practical and achievable than complete elimination. It is a major destructive process affecting the performance of metals in their application in many construction and industrial sectors.Use of corrosion inhibitor is one of the methods to prevent corrosion. To protect materials from corrosion we use synthetic compounds like 2-aminopyrazine and 2-amino-5-bromopyrazine, 1-diethylthiocarbamoyldisulfanyl), N, Ndiethylmethanethioamide (disulfiram), tetradecylpyridinium bromide, p-substituted 4-(N,N-dimethyldodecylammonium bromide) benzylidene-benzene-2-yl-amine. (Deng *et al*. 2011; Singh *et al*. 2011; Li *et al*. 2011; Hegazy *et al*. 2011). In addition to the several synthetic organic compounds, large number of natural products like *Acacia Drepanolobium* and *Acacia Snegal*, *Terminaliacatappa*, *Bambusa Aruninacea phyllanthusamarus*, *Ferula assa–foetida* and *Doremaammoniacum*, *Rhizophoraapiculata*, *Justicagendarussa*, *GinkgoSpondiasmambin L. Dacryodisedulis, Uncariagambir, Naucielatifilia, Tinosporacripsa* (Buchweishaija *et al*. 2009; Vasudha *et al*.2011; Behpour *et al*.2011; Tan *et al*. 2011; Jothi and Ravichandran, 2013; Gunavathy and Murugavel, 2013) have been tried as mild steel corrosion inhibitors. In the present study the corrosion inhibitory effect of acid extract of leaves of MH have been investigated. Weight loss, and FT-IR studies were carried out.

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2. EXPERIMENTAL

2.1 Materials

Tests were performed on mild steel of the following composition (wt.%): 0.07%C, 0.3%Mn, 0.022%P, 0.01%S, 0.01%Si, 0.03%Al and remainder is Fe.Sheets of mild steel with 2mm thickness wereobtained locally and mechanically cut in to strips of 5x1 cm^2 size having a hole for the suspension. The strips were washed and polished with emery sheet of fine quality. To remove any oil and organic impurities strips were degreased with acetone and finally with de-ionised water dried and stored in a desiccator. Accurate weights of the samples were taken using electronic balance.

2.2 Inhibitor Material

The leaves of MH were collected, shade dried and powdered. The extract was prepared by refluxing 25g of powdered dry leaves with 1N H_2SO_4 for 3 hours. The refluxed solution was filtered and made up to 500 ml with 1N H_2SO_4 and this filtrate was taken as 5% stock solution. From this stock solution different concentration from 0.05% to 2 % v/v of the extract was prepared by further dilutions.

2.3 Weight loss method

The experimental solution, 1N H_2SO_4 with different concentrations of inhibitors was used. The pretreated specimens were immersed in the experimental solution with the help of glass hooks. The initial weight of the specimens was noted and it was immersed completely in to the experimental solution at 30 °C for different time duration. After the specified duration of immersion the specimens were taken out, washed thoroughly with distilled water, dried completely 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,

$$\text{Corrosion Rate (CR)} = (534 * W) / DAT \text{ (mpy)}$$

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.

$$\text{Inhibition Efficiency} = (W_B - W_I) / W_B \times 100$$

where W_B and W_I are weight loss per unit time in the absence and presence of inhibitors, respectively. The degree of surface coverage (θ) was calculated from the weight loss measurement results using the formula,

$$\text{Surface coverage } (\theta) = (W_B - W_I) / W_B$$

where W_B and W_I are weight loss in the absence and presence of inhibitors, respectively.

2.4 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 303 K – 343K in the water thermostat (Technico Serological digital Pit water bath – AI 209). The specimens were removed from the test solution after 1 hr and washed with distilled water, dried and weighed. The inhibition efficiency was then calculated from the weight loss.

2.5 Adsorption isotherm

Since corrosion inhibition is a surface phenomena involving adsorption of the inhibitor on the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can be understood with adsorption isotherms.

3. RESULTS & DISCUSSIONS

3.1 Weight loss measurements: Effect of concentration

Corrosion parameters such as corrosion rate and IE obtained by weight loss method for different inhibitor concentrations at various time intervals in

1 N H_2SO_4 are given in Tables 1 and Table 2. The corrosion rate of mild steel decreases with increase in concentration of the inhibitor. The percentage inhibition efficiency of the inhibitor increases with increase inhibitor concentration. Maximum efficiency was achieved at 2 % v/v (98.8%)at room temperature.The decrease in corrosion rate and increase in inhibitor efficiency is usually 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 like saponins, flavonoids and terpenoids which act as a barrier and prevent corrosion of mild steel. The corrosion rate of mild steel increases as the immersion period increases as shown in Fig. 1 and inhibition effeciency of the inhibitor increases as shown in Fig. 2. This is due to the presence of the inhibitor in acid solution. The effect of temperature study indicates both CR and IE found to be increased at different temperatures. The calculated CR and IE values are listed in Table 3 and Table 4. Fig. 3 and Fig. 4 shows the CR and IE respectively.

3.2 Adsorption isotherm

The decrease in inhibition efficiency with increasing time may be due to the shift in adsorption and desorption equilibria which takes place simultaneously on prolonged exposure to the corrosive media. These results suggest that the adsorption model arrangement and orientation of the constituents present in the plantextract on the surface of mild steel may change with time. The phytoconstituents present in the plant extract prevent the corrosion of mild steel. At higher concentration of inhibitor, more number of inhibitor molecules gets absorbed on the surface of mild steel.The effect of temperature was studied by varying the temperature from 30º - 70ºC. The activation energy

Table 1. Corrosion Rate of mild steel in 1N H_2SO_4 in presence and absence of MH leaves extract at different immersion times

Concentration of MH (%)v/v	Corrosion Rate (mpy)					
	1hr	3hrs	5hrs	7hrs	12hrs	24hrs
Blank	1731.32	1987.16	2387.21	2599.78	2882.26	3006.73
0.05	257.3	356.15	478.84	701.5	623.26	623.44
0.10	191.88	255.85	185.78	158.87	160.63	73.59
0.50	91.58	114.84	110.77	85.97	94.49	64.32
1.00	61.05	75.59	80.24	91.58	118.47	53.24
1.50	17.44	71.23	89.84	111.52	42.88	45.06
2.00	17.44	47.97	49.72	112.76	49.42	36.16

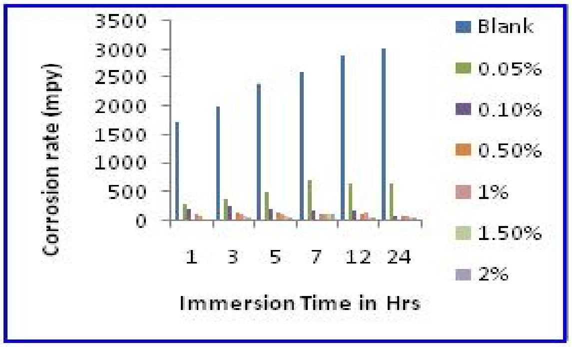

Fig. 1: Influence of immersion time on CR

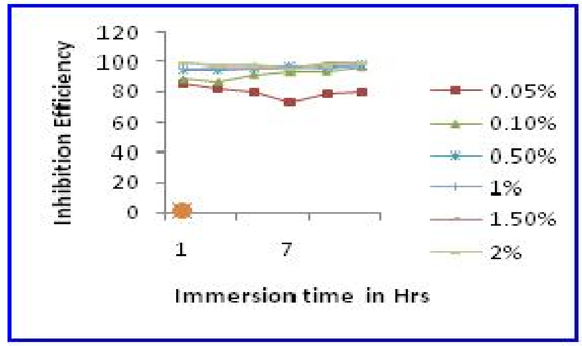

Fig. 2: Influence of immersion time on IE

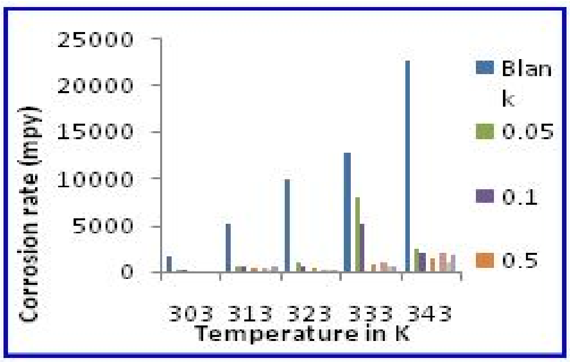

Fig. 3: Influence of temperature on CR

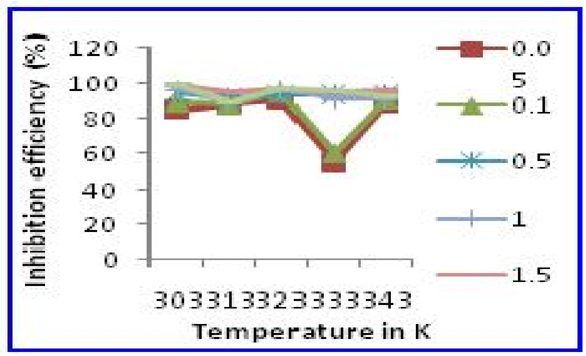

Fig. 4: Influence of temperature on IE

Table 2. Inhibition Efficiency of inhibitor in 1N H_2SO_4 in presenceand absence of MH leaves extractat different immersion periods

Concentration of the plant extract(%)v/v	Inhibition Efficiency (%)					
	1hr	3hrs	5hrs	7hrs	12hrs	24hrs
0.05	85.14	82.08	79.94	73.02	78.38	79.27
0.10	88.92	87.13	92.22	93.89	94.43	97.55
0.50	94.71	94.22	95.36	96.69	96.72	97.86
1.00	96.47	96.2	96.64	96.48	95.89	98.23
1.50	98.99	96.42	96.24	95.71	98.51	98.5
2.00	98.99	97.59	97.92	95.66	98.29	98.8

Table 3. Effect of temperature on corrosion rate of the inhibitor - MH leaves extract in 1 N H_2SO_4

Concentration v/v(%)	Inhibition Efficiency (%)				
	303K	313K	323K	333K	343K
0.05	85.14	88.08	90.28	54.21	88.72
0.10	88.92	87.58	94.42	60.15	90.65
0.50	94.71	91.23	93.89	93.35	93.50
1.00	96.47	89.16	96.39	90.99	90.92
1.50	98.99	94.12	96.83	94.51	95.23
2.00	98.99	88.66	97.10	95.02	92.00

Table 4. Effect of temperature on IE of inhibitor in1 N H_2SO_4in presence and absence of MH leaves extract

Concentration of MH extract(%)v/v	Corrosion Rate (mpy)				
	303 K	313 K	323 K	333 K	343 K
Blank	1731.32	5268.09	9916.91	12782.09	22664.12
0.05	257.3	627.98	963.78	8032.96	2555.55
0.10	191.88	654.15	553.85	5093.65	2119.45
0.50	91.58	462.27	606.18	850.40	1474.02
1.00	61.05	571.29	357.60	1151.30	2058.39
1.50	17.44	309.63	313.99	702.12	1081.53
2.00	17.44	597.46	287.83	636.71	1814.18

(E_a) and free energy of adsorption (ΔG^0_{ads}-)were calculated for inhibited and uninhibited systems. The calculated values were found to obey Langmuir adsorption.

The activation energy (E_a) values were calculated from Arrhenius plot Fig.5 for different inhibitor concentrations at various temperatures. The values of E_a and ΔG^0_{ads} for corrosion of mild steel using leaf inhibitors in 1N H_2SO_4 is given in the Table 5. The apparent E_a values calculated showed that there is an increase in activation energy. This suggests that the presence of reactive centers on the inhibitor, block the active sites for corrosion resulting in the decrease incorrsion with increase in the activation energy. The lessnegative value of free energy of adsorption ΔG^0_{ads}Table. 5 with increase in temperature indicates the physical adsorption of inhibitor molecule on the

Table 5 Thermodynamic paramers in 1N 1 N H_2SO_4 in presence of MH leaves extract

Conc. % v/v	$-\Delta G_{ads}$ (KJ/mol)					ΔH_{ads} (KJ/mol)	ΔS_{ads} (KJ/mol)	E_a (KJ/mol)
	303 K	313 K	323 K	333 K	343 K			
0.05	22.03	23.43	24.79	17.93	25.85	439.81	-5.781	-62.28
0.10	21.14	21.5	24.54	18.61	24.47	411.792	-4.6362	-59.68
0.50	19.11	18.33	19.96	20.33	21.01	432.62	-5.0872	-53.82
1.00	18.1	15.91	19.59	17.5	18	368.995	-2.4938	-67.28
1.50	20.65	16.59	18.86	17.85	18.81	416.791	-4.3366	-79.48

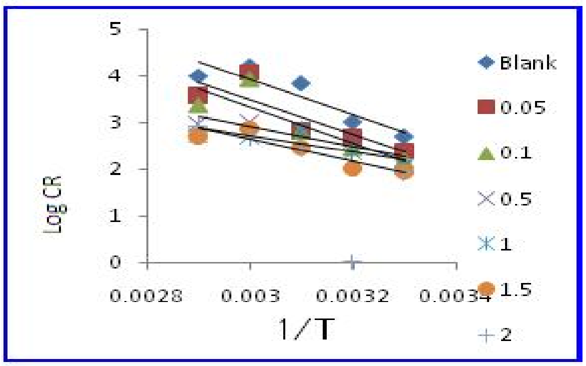

Fig. 5: Arrhenius plot of mild steel in 1N H_2SO_4 at different concentration of leaves of MH

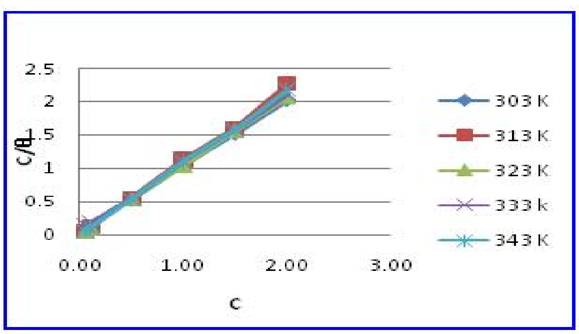

Fig. 6: Langmuir plot of mild steel in 1N H_2SO_4 at different concentration of leaves of MH

metal surface. In the presence of the extract the Ea for the process is more showing the corrosion reaction is more. As the concentration increases E_a value increases progressively.

3.3 Fourier Transform Infrared Spectroscopy

The FT IR spectra of the plant extract and the corrosion products in the absence and presence of inhibitor. From the spectra it can be noted that peaks in the frequency range 1500 - 1750cm^{-1}in the extract spectrum are altered / missing in the corrosion productsspectrum. This may be because the groups absorbing in that range are involved in the adsorption process. This has to be further confirmed by other surface analysis studies.

4. CONCLUSION

The inhibition efficiency of the plant extract on mild steel in 1N H_2SO_4 was studied using weight loss and FTIR technique. The following were the conclusions drawn from the studies. The inhibition efficiency of the plant extract increases with increase in inhibitor concentration but decreased with temperature. From weight loss method the maximum efficiency of 98.99% at 2% inhibitor concentration was found. The adsorption of the plant extract on to the surface follows the Langmuir isotherm. The activation energy E_a is higher for the test solution in the presence of the extract showingthat there is inhibition of corrosion reaction. The negative value of ΔG_{ads} indicates that the inhibition by the adsorption of the plant constituents is a spontaneous process and the value of ΔG ranges from 17 – 25.85 KJ/molindicating physical adsorption.

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