Thermodynamic Studies for the Corrosion Inhibition of Mild Steel by *Tectona Grandis* Leaves

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ABSTRACT

The corrosion inhibition of mild steel in 1 M HCl solution in the presence of Tectona Grandis Leaves (TGL) at temperature range of 30–70^{0}C was studied using weight loss and electrochemical methods namely potentiodynamic polarization and AC impedence method. The Tectona Grandis Leaves acts as an inhibitor in the acid environment. The inhibition efficiency (90.26%) increases with increase in inhibitor concentration (2.5%) but decreases with an increase in temperature. The inhibitive effect of the Tectona Grandis Leaves could be attributed to the presence of some phytochemical constituents in the Leaves which is adsorbed on the surface of the mild steel metal. The inhibition by Tectona Grandis Leaves was found to obey Langmuir, Frenudlich, Temkin adsorption isotherms. Phenomenon of physical adsorption is proposed from the activation parameters obtained. Polarization curves revealed that this inhibitor acta as a mixed type inhibitor. Thermodynamic parameters reveal that the adsorption process is spontaneous. The surface analysis study conforms the corrosion of mild steel and its inhibition by the inhibitor TGL.

Key Words: *Tectona Grandis* Leaves(TGL)*,* Mild steel, Adsorption isotherm, Thermodynamic parameters.

INTRODUCTION

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environment. Most of the corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. Therefore, it is desirable to source for environmentally safe inhibitors [1– 7] . It has been shown that natural products of plant origin contain different organic compounds (e.g. alkaloids, tannins, pigments, organic and amino acids, and most are known to have inhibitive action [8–15] . Other authors have also shown that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemicals present in the plant on the surface of the metal [16–19] , which blocks the metal surface and thus do not permit the corrosion process to take place. The wide use of this acid has led to the concentration of this study on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures [20-27]. The inhibition of mild steel corrosion by TGL was attributed to the presence of nerol, salicylic-acid, anthraquinone. since these compounds contain oxygen and nitrogen atoms which are the centers of adsorption. The encouraging results obtained by this research permit to test more plant materials. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the

corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

MATERIALS AND METHODS

Preparation of the specimen

The sheets of cold rolled mild steel, which is commercially available in the market, were machined into coupons of area 5 x 1 Cm^2. Holes were drilled on the center of one end of all the coupons for suspension and the coupons are numbered for identification. These coupons were degreased, cleaned with emery paper and washed with distilled water and stored in desiccators in the absence of moisture before their use for the investigation.

Preparation of the extract

The leaves *Tectona Grandis* of were shade dried and powered. The extract was prepared by refluxing 50g of powered dry leaves in 1000 ml of 1 M HCl for 3 hours and kept overnight. Then filtered and the volume of filtrate was made up to 1000 ml using the same acid. This solution was taken as the stock solution for further dilutions.

Weight loss measurement

Weighed samples are immersed in 100 mL of the acid (1 M HCl) without and with different concentrations of the inhibitor for a fixed immersion time ½ h. They are then taken out and immersed in saturated sodium bicarbonate solution to remove residual acids and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. The parameters used for the present study are given below

- Concnetration of the inhibitor: 0.005%, 0.01%. 0.05%, 0.10%, 0.15%, 0.2%, 0.5%, 1.0%, 1.5%, 2.5% (v/v)

- Temperatures: 303, 313, 323, 333, 343) ± 2 K

The percentage of inhibitor efficiency (IE %) for various concentrations of the inhibitor were calculated as
$$I E\% = \left[\frac{W_0 - W}{W_0} \right] \times 100$$

Where W_O and W are the corrosion rates of mild steel in 1 M HCl in the absence and presence of definite concentrations of the inhibitor.

Potentiodynamic Polarization technique

A frequency response analyzer 1284 (Solartron) and an IBM personal computer which automatically controls linear polarization and Tafel polarization was used for the polarization study. The data were analysed using computer software. The cell for the polarization studies was a glass beaker containing the aerated unstirred test solution was a glass beaker containing the aerated unstirred test solution with a platinum electrode as the counter electrode, a saturated calomel electrode as the reference electrode and mild steel as the working electrode. For potentiostatic polarization studies, mild steel strips of same composition (as in the weight loss method) coated with lacquer with an exposed area 1 Cm^2 was used.

AC impedance method

AC impendance measurements stated as soon as working temperature was achieved and

polarization has stopped. Applied sinusoidal signal amplitude was 10mV in the normal frequency range from 10 kHz to 0.02Hz. Combined frequency response analyzer and potentiostat (Solartron 1284) was used to make A.C impendance measurements under open circuit potential during the test. During each test the data were displayed as Nyquist plots (Z_{im} vs Z_{real}) via Z plot software.

Surface analysis

Surface features of mild steel specimen were examined before and after exposure to 1M HCl solution in the absence and presence of certain concentration of the extract. Optical microscope (NIKON-model EPI-PHOT) was used for this investigation.

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RESULT AND DISCUSSION

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Effect of temperature

The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations at different temperatures (303, 313, 323, 333 and 343) $\pm$ 2 K for a fixed immersion time ½ h. The tabulated data (Table 1) reveal that, as the concentration of the inhibitor increases the corrosion rate has decreased at all temperatures.There is no regular trend in the change of inhibition efficiency. This may be explained on the basis of the time lag between the process of adsorption and desorption. However, the inhibitor could be effectively used at 323K and maximum efficiency being 90.26%.

Table1 Protection performance of TGL on mild steel in 1 M HCl ($^1/_2$ h) at different temperatures

CONC(%) (v/v)	Inhibition Efficiency %				
	303	313	323	333	343
Blank	-	-	-	-	-
0.005	43.1	44.24	50.15	45.86	41.08
0.010	48.1	50.63	58.35	52.14	50.48
0.050	62.1	65.37	71.24	57.75	60.4
0.100	74.3	77.02	77.26	73.53	72.72
0.150	74.7	77.32	77.90	75.75	73.71
0.200	75.5	77.58	78.72	76.88	76.15
0.500	77.9	81.37	84.47	77.72	81.62
1.500	79.8	83.40	86.54	84.88	82.94
2.000	82.0	84.99	89.49	86.99	84.71
2.500	83.7	85.73	90.26	89.55	86.44

Interpretation of thermodynamic data

Activation energy (E_a) and thermodynamic data, such as change in free energy (ΔG_{ads}), enthalpy (ΔH) and entropy (ΔS) for mild steel in 1 M HCl in the absence and in the presence of the inhibitor was calculated and listed in Table 2.The activation energy at different concentration of the inhibitor in 1 M HCl is calculated by plotting Log C.R vs. 1/T (Fig.1). E_a values for inhibited systems are

lower than those for uninhibited system indicating that all the inhibitors exhibit high I.E at elevated temperatures. The range of E_a is 33.05 – 44.46 kJ/mol for TGL in 1 M HCl. The low and negative values of ΔG_{ads} (12.27- 25.88 kJ) suggest the strong interaction of the inhibitor molecules whereas low value of ΔG_{ads} indicated spontaneous adsorption of inhibitors on mild steel surface. The ΔH values of (0.029 - 1.128 kJ/mol) at all concentrations are found to be below 10 kJ/mol which indicate physical adsorption over the surface of mild steel. The change in entropy was found to be greater than zero (0.049-0.078 J/deg/mol). This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible.

Table 2. Activation parameters for the dissolution of MS in the presence of TGL in 1 M HCl

Conc (%)(v/v)	Activation energy	Free energy of adsorption (-ΔG)					Heat of adsorption(ΔH)	Entropy changes
		303	313	323	333	343K		
Blank	33.05	-	-	-	-	-	-	-
0.005	43.59	22.99	23.72	24.44	25.16	25.88	1.128	0.072
0.010	47.01	21.78	22.56	23.35	24.13	24.91	0.064	0.078
0.050	49.86	19.30	19.79	20.29	20.78	21.28	0.029	0.049
0.100	50.20	18.86	19.38	19.89	20.41	20.93	0.037	0.052
0.150	51.09	17.88	18.41	18.93	19.47	19.99	0.039	0.053
0.200	49.72	17.19	17.76	18.33	18.90	19.47	0.047	0.057
0.500	48.31	15.43	16.00	16.57	17.14	17.76	0.036	0.056
1.500	46.28	13.08	13.65	14.21	14.78	15.35	0.029	0.056

Applicability of adsorption isotherms

The surface coverage (Θ) values for different concentrations of the inhibitor in 1 M HCl have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of Log ($\Theta/1-\Theta$) against Log C (Fig. 2) shows a straight line (R>0.9) indicating that adsorption follows the Langmuir adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of (1/y). A straight line was obtained when the surface coverage was plotted against Log C for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in Fig.3.The plots of Log Θ vs. Log C are shown in Figure 4. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm.
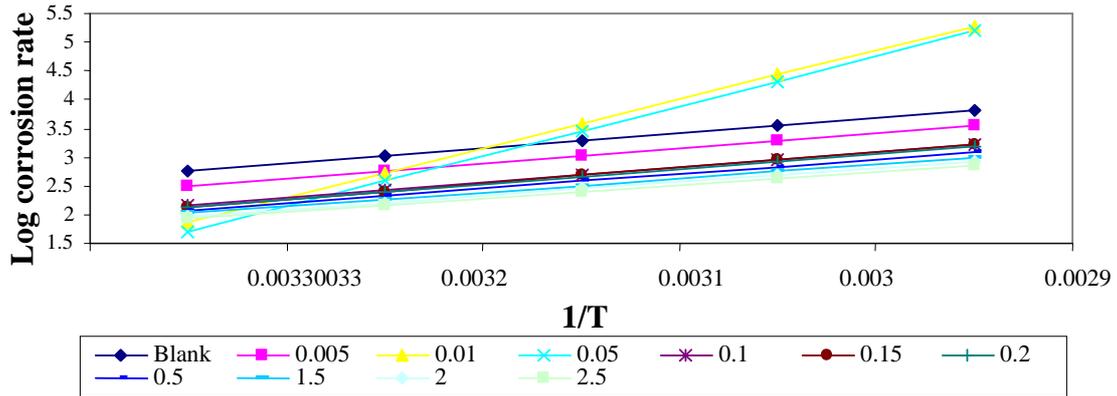
Figure 1. Arrhenius plots for mild steel dissolution process in 1 M HCl
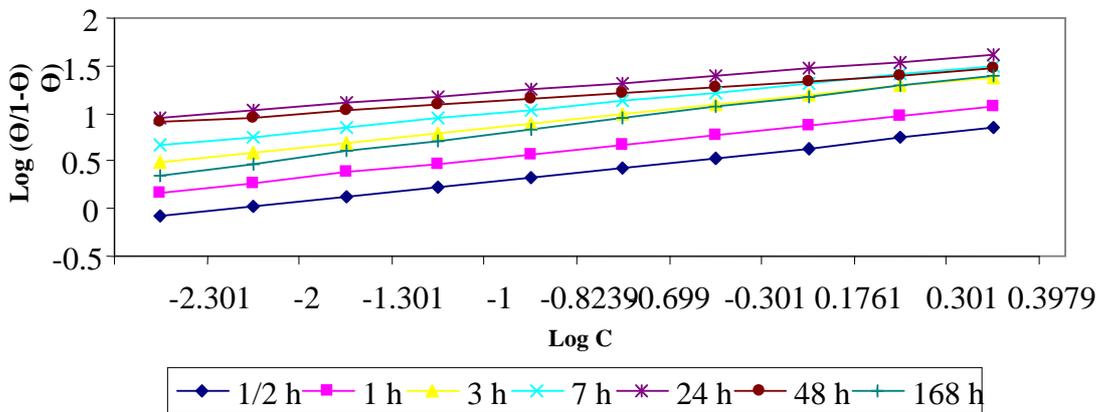
Figure 2. Langmuir isotherm plots for the adsorption of TGL in 1 M HCl
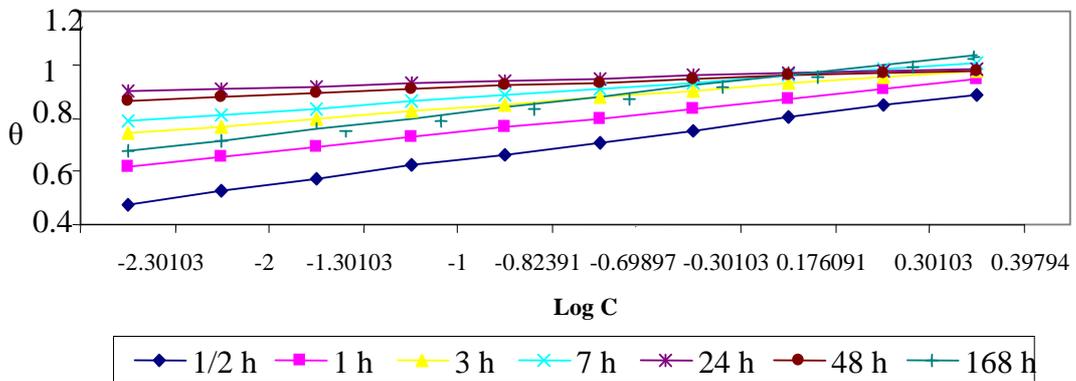
Figure 3. Temkin isotherm plots for the adsorption of TGL in 1 M HCl
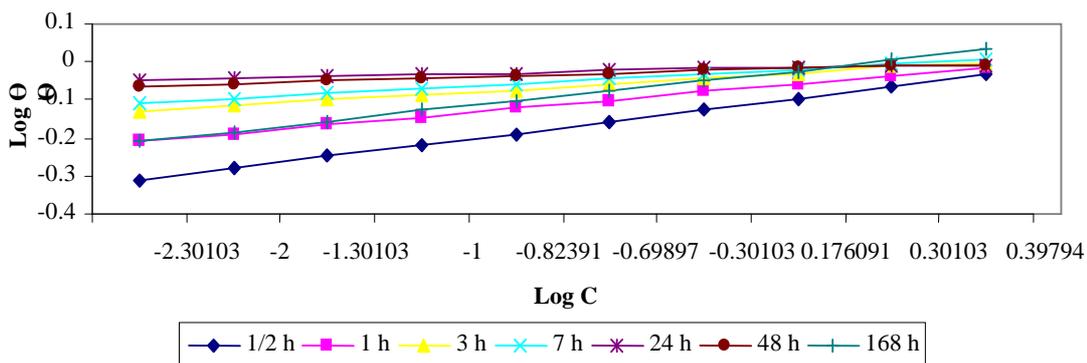
Figure 4. Freundlich isotherm plots for the adsorption of TGL in 1 M HCl

Potentiodynamic Polarization Studies

The values of various electrochemical parameters are presented in the Table 3 and corresponding Tafel plot in Figure 5. It is observed from the table that the I_{corr} values decrease in the presence of the inhibitor. These suggest that the adsorption of the inhibitor molecules on the metal surface reduces the uncorved surface area for the anodic as well as cathodic reactions. This is also seen from the increase in the Rp values. The fact there is no significant change in the E_{corr} values 523.69 mV to 535.90 suggests that the inhibitor function asa mixed type. In all concemtrations b_a greater than b_c suggesting that though the inhibition is under mixed control the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.
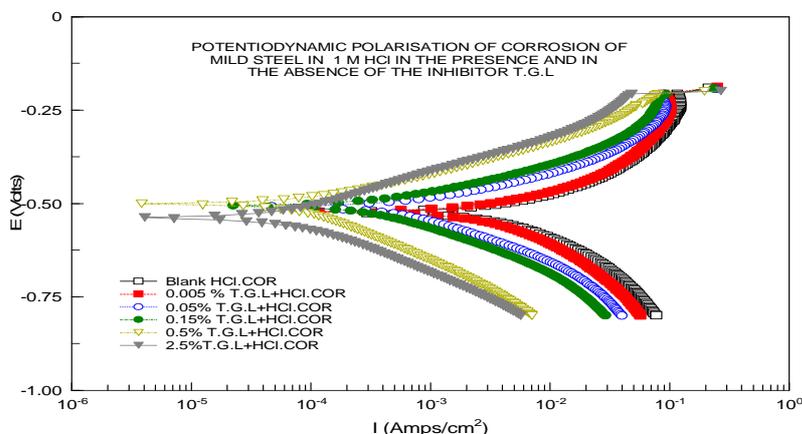
Figure 5. Potentiodynamic polarization curves for mild steel in 1 M HCl in the presence of different concentrations of the extract at room temperature.

Table 3 Electrochemical parameters for mild in 1 M HCl with various concentrations of the extract

Conc (%) (v/v)	$-E_{corr}$ mV	I_{corr} $\mu A\ cm^{-2}$	b_a mV/dec	b_c mV/dec	I.E (%)	Rp ($\Omega\ cm^2$)	I.E (%)
Blank	523.69	6.0740	212.70	146.7	-	6.25	-
0.005	520.75	2.7800	159.50	107.18	54.23	8.16	23.41
0.05	509.20	0.0729	131.60	84.18	98.80	29.86	79.07
0.15	504.24	0.0348	123.00	76.80	99.43	54.54	88.54
0.5	499.46	0.0065	124.16	69.59	99.89	217.90	97.13
2.5	535.90	0.0058	117.47	98.46	99.90	341.70	98.17

Impendance Measurements

Impedance diagrams (Nyquist plots) obtained for mild steel in 1 M HCl in the presence of various concentrations of the inhibitor is depicted in the Figure 6. It is seen from these figure that the inpedence diagram for the inhibitor is not perfect semicircle. The difference has been attributed to the frequency dispersion.
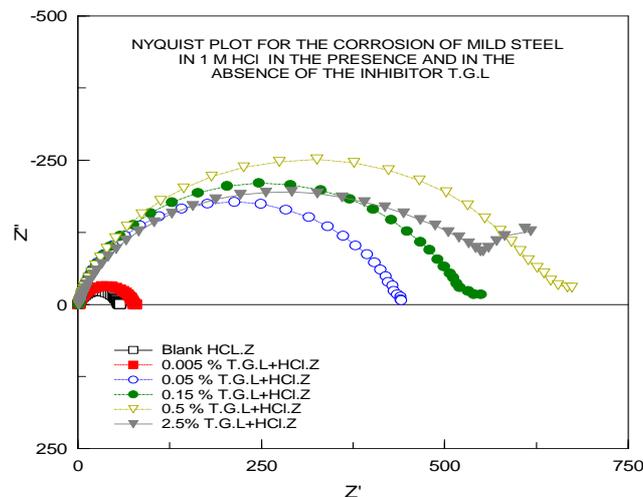
Figure 6. Nyquist plot for mild steel in 1 M HCl in the presence of different concentrations of the extract at room temperature.

Impedance parameters derived from Nuquist plots are tabulated in table 4. It can be seen that the presence of the inihibitor enhances the values of R_{ct} and reduces the C_{dl} may be due to the adsorption of the inhibitor to form an adherent film on the metal surface and suggest that the coverge of the metal surface with this film decreases the double layer thickness.

Table 4 Impendance Parameters for the corrosion of for mild in 1 M HCl containing different concentrations of the extract at room temperature.

Conc (%)(v/v)	Rct (Ω cm^2)	Cdl (μF cm^{-2})	I.E (%)
Blank	54.89	172.90	-
0.005	74.29	128.22	26.11
0.05	436.79	92.36	87.43
0.15	530.97	80.46	89.66
0.50	646.77	74.19	91.51
2.5	657.44	51.87	91.65

Mechanism of Corrosion Inhibition

The acid extract investigated in the study are oganic in nature and found to contain the following compounds.
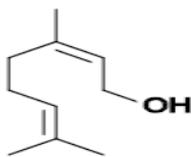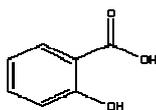
Nerol   **Salicylic-acid**   **Anthraquinone**
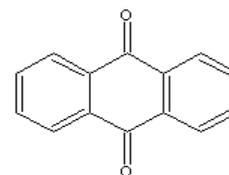
The probable mechanism can be explained on the basis of adsorption process and structure of the constituents present in the extract.most of th phytochemical constituents present are oxygen containing compounds. The compounds may be adsorbed on the mild steel surface through their oxygen atom of the hydroxyl group, oxygen atom on the ring and the Π electrons in the ring which inhibits the corrosion of mils steel. Th aromatic compounds with large cross sectional area are able to pack close enough to make an impervious covering on the metal. Hence the corrosion inhibition may be due the formation of a complex, which can cause blocking of micro anodes and micro cathodes that are generated on the metal surface when the metal comes in contact with the corrodent and hence can retard the dissolution of the metal.

Surface Analysis

The polished specimen and the test specimens which are immersed in the blank (1 M HCl) and in certain concentrations of the inhibitor TG for 24h were observed under a metallurgical microscope and photomicrographs are shown in the Fig 7-10.

Fig 7. Photomicrographs of Mild Steel Samples
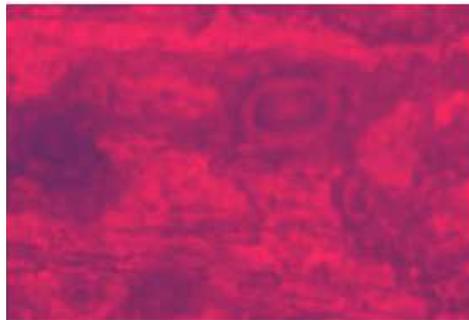
Fig 8. Sample Immersed in 1M HCl

Fig 9. Sample Immersed in 0.2% inhibitor solution
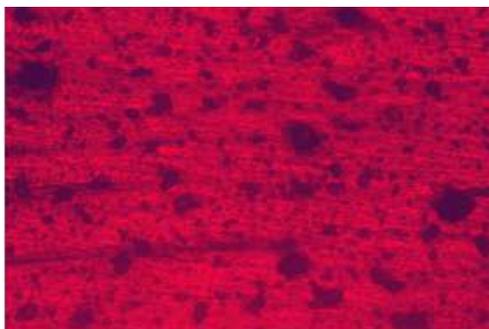
Fig 10. Sample immersed in 2.5% inhibitor solution

Fig 7 shows the polished mild steel surface before exposure to the acid medium, which is associated with polishing scratches. It is clear from the Fig 8, that the surface of the mild steel was heavily corroded in 1 M HCl medium, whereas in the presence of inhibitor, the surface condition was comparatively better(Fig 9 and 10). This depends on the concentration of the inhibitor solution suggesting that thereby the presence of a protective adsorbed layer of the inhibitor on ild steel surface which impedes corrosion rate of metal appreciably.

CONCLUSION

From the results of the present study it can be concluded that *Tectona Grandis* acts as a good inhibitor for mils steel in 1 M HCl medium. *Tectona Grandis* inhibited the corrosion of mild steel by physical adsorption on the surface. Based on the variations in the inhibition efficiencies with temperature, values of activation energy and free erergy changes, the reaction is found to be spontaneous physical adsorption. The inhibition is found to be of mixed type.

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