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Polyalthia Longifolia as a Corrosion Inhibitor for Mild Steel in HCl Solution

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Abstract

Corrosion inhibition efficiency of dry Polyalthia longifolia (Asoka tree) leaves in 1N HCl medium was investigated by weight loss and temperature studies. Effect of temperature (35-75^{0}C) on the corrosion behavior of mild steel in the presence of plant extract was studied. Inhibition was found to increase with increase in concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir, Temkin, Freundlich adsorption isotherms. The results obtained prove that the leaves of Polyalthia Longifolia act as a good corrosion inhibitor having efficiency of 87% at 1.5% inhibitor concentration.

Keywords: *Polyalthia Longifolia*, plant extract, corrosion inhibitor, mild steel, HCl medium.

Introduction

Mild steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths etc. It gets rusted when it comes in contact with any acid. Acid solution, mostly HCl is used to remove any undesirable scale or rust. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. Use of hazardous chemical inhibitors is totally reduced because of environmental regulations. Chromates, phosphates, molybdates etc. and a variety of organic compounds containing heteroatoms like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors[1-6]. Plant extracts are mostly preferred because they are cheap, easily available, non-toxic and renewable. They are also eco friendly. Several leaf extracts have been studied as corrosion inhibitors. Extracts of natural products like *Murraya koenigii*[7], *Nypa fruticans wurmb*[8], *Emblica officinalis*[9], *Phyllanthus amarus*[10], *Michelia champaca*[11], *khillah seeds*[12], *Ficus carica*[13], *piper guinensis*[14], *fenugreek seeds and leaves*[15], *Nyctanthes arbortristis*[16], *Caffeic acid*[17], etc. have been reported to act as good corrosion inhibitors for mild steel in acid medium. Inhibitive efficiency of acid extract of *Polyalthia Longifolia* leaves is studied in the present work using weight loss and thermodynamic studies.

Material and Methods

Fresh green leaves of *Polyalthia Longifolia* (PL) were collected washed and shade dried and powdered. 25g of this powder was weighed and added to 500ml of 1N HCl. This mixture was refluxed for three hours and kept overnight. The following day it was filtered and the filtrate was made upto 500ml using 1N HCl. This was taken as the stock solution. The required concentrations were prepared by diluting the stock solution.

Mild steel sheets cut into rectangular coupons of size 5 X 1cm^2 provided with holes to enable suspension in test solutions were used for the study. These steel pieces were mechanically polished to remove any rust on it. The metal pieces were then degreased with acetone washed with distilled water and polished with emery paper, cleaned, dried and stored in desiccators.

Metal samples were weighed using electronic balance. Weighed rectangular coupons of the metal samples were immersed in triplicate in 100mL of 1N HCl with different concentrations of plant extract (0.1%, 0.3%, 0.5%, 0.7%, 0.9%, 1.1%, 1.3% and 1.5% v/v) and without plant extract (Blank). After 1 hour immersion in the test solution the coupons were removed washed, dried and weighed.

The experiment was carried out at different immersion periods (1 Hr, 2 Hr, 5 Hr, 7 Hr, 12 Hr and 24 Hr). Weight loss was measured for all the above mentioned timings at 303K. Corrosion inhibition studies were also carried out at different temperatures (308, 318, 328, 338 and 348K). After measuring the weight loss, surface coverage (θ), percentage inhibition efficiency (IE %) and corrosion rate (C_R) were calculated using the following formula

$$\theta = (IE\ \% / 100); \quad (1)$$

$$IE\ \% = \frac{w_0 - w_i}{w_i} \times 100; \quad (2)$$

(Where w_0 and w_i are weight loss without and with plant extract respectively.)

$$C_R\ (m/y) = \frac{534 \times 6.4516 \times 1000 \times \text{weight loss};\ (\text{where D is density and a is area})}{D \times a \times \text{Time in hours}} \quad (3)$$

Results and Discussion

Gravimetric studies: Different Temperature: Weight loss measurement was carried out at different temperatures (308 – 348K) in presence and absence of the inhibitor to evaluate the stability of the adsorbed film on the mild steel piece. This was done for a period of 1 Hour each. The results obtained are shown in figure 1. The graph depicts that as the temperature increases the inhibition efficiency increases upto a certain temperature (328 K) and then decreases. At elevated temperature as time lag between adsorption and desorption of inhibitor over metal surface becomes shorter the IE decreases. Metal surface remaining exposed to acid environment for a longer period increases the rate of corrosion and thus decreases the inhibition efficiency.

Different Immersion Time: Weight loss measurement was performed in 1N HCl in presence and absence of extract at 303K for different immersion periods from 1 Hr to 24 Hr. Figure 2 shows a plot of IE% with different timings. Inhibition efficiency increases from 1 hour to 12 hours and at 24 hours it decreases. Increase in IE from 1- 12 hours shows the strong adsorption of constituents present in the plant extract on the surface of mild steel giving it a protective layer. Immersion for a longer period leads to desorption of plant constituents. From this it is clearly shown that leaves of *Polyalthia Longifolia* acts as a very good corrosion inhibitor for mild steel in 1N HCl solution.

Table-1
% IE of PL in HCl at different concentrations and different temperatures

Temp in K	% IE							
	0.1	**0.3**	**0.5**	**0.7**	**0.9**	**1.1**	**1.3**	**1.5**
308	19.61	21.56	37.25	39.21	40.19	45.09	52.94	64.7
318	48.88	60.74	64.07	71.11	80	80.74	81.85	83.71
328	62.44	65.89	67.36	71.13	71.65	77.4	87.23	87.45
338	38.11	45.88	52.7	54.82	58.82	61.17	64.94	69.64
348	64.93	65.26	66.54	67.63	67.91	68	75.99	78.54

Table-2
% IE of PL in HCl at different concentrations and different immersion periods

Time in Hr.	% IE							
	0.1	**0.3**	**0.5**	**0.7**	**0.9**	**1.1**	**1.3**	**1.5**
1	20	36	44	48	50	56	58	62
2	66.66	67.54	70.17	71.05	71.93	75.43	78.07	78.94
5	75	75.85	77.54	77.97	79.23	81.35	82.2	83.05
7	66.93	67.12	67.57	73.98	75.67	76.69	77.7	84.46
12	68.25	71.74	73.12	77.02	80	81.55	82.02	87.79
24	41.33	57.03	63.93	69.79	72.83	75.29	80.21	81.38

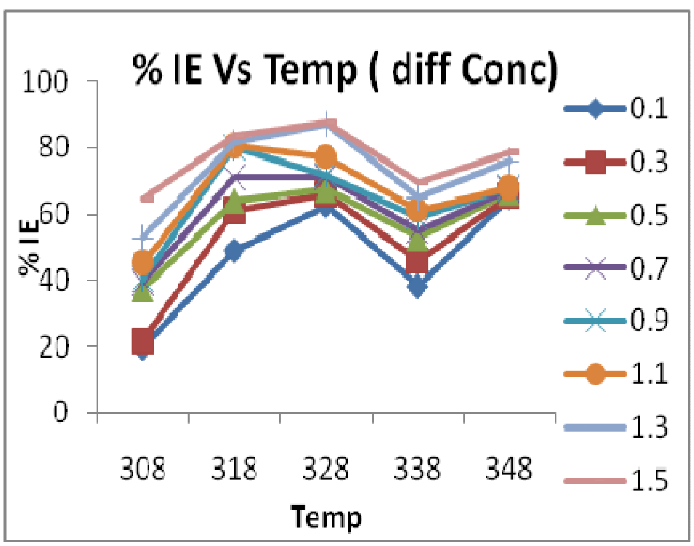

Figure-1
Plot of % IE Vs Temp at different concentrations

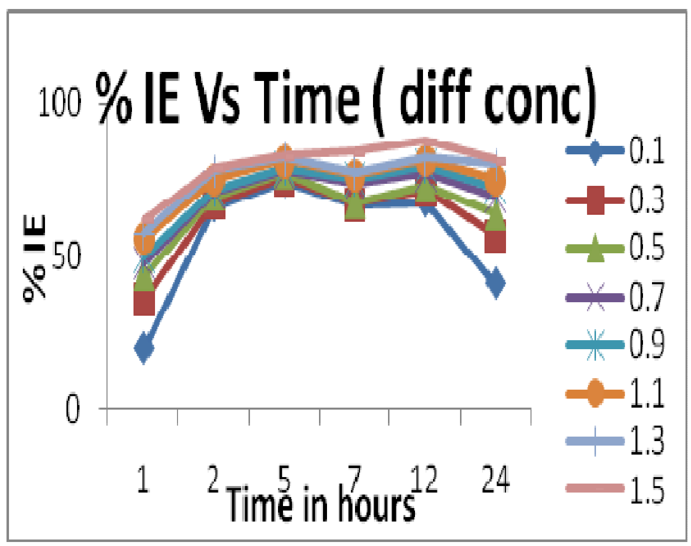

Figure-2
Plot of % IE Vs Time different concentrations

Kinetic studies: Effect of inhibitor concentration: Corrosion rate (CR) of mild steel in the absence and presence of PL extract was calculated using the equation (3) and the data obtained for different temperatures and different immersion timings are shown in tables 3 and 4 respectively. Plots of corrosion rates against different temperatures and different time are shown in figure 3 and 4 respectively.

Table-3
CR of PL in HCl at different concentrations and different temperatures

Extract Conc.(%v/v)	CR				
	308 K	**318 K**	**328 K**	**338 K**	**348 K**
Blank	222.41	588.73	2084.53	1853.40	4613.89
0.1	178.8	300.9	782.8	1146.9	1617.9
0.3	174.4	231.1	710.8	1003	1602.6
0.5	139.6	211.5	680.3	876.5	1543.8
0.7	135.2	170.1	601.8	837.3	1493.6
0.9	133	117.7	590.9	763.1	1480.5
1.1	122.1	113.4	470.9	719.6	1476.18
1.3	104.7	106.8	268.2	649.8	1107.68
1.5	78.5	95.9	261.7	562.6	989.9

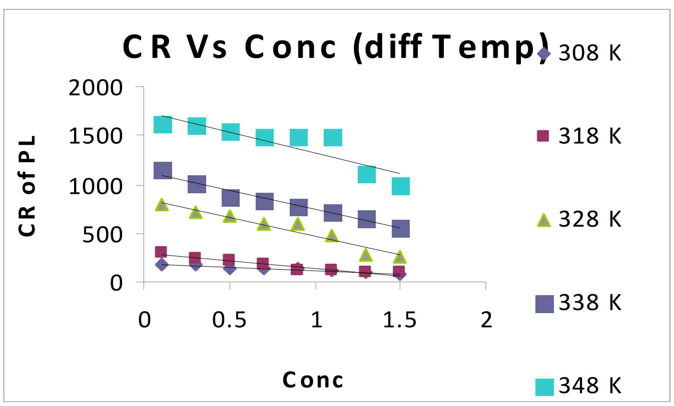

Figure-3
Plot of CR Vs concentration at different temperatures

The result obtained shows that the rate of corrosion of mild steel decreases with increase in the concentration of PL extract but increases with increase in temperature. This confirms the inhibitive action of the extract in HCl medium.

Table-4
CR of PL in HCl at different concentrations and different immersion periods

Extract Conc. (%v/v)	CR					
	1 hr	**2 hr**	**5 hr**	**7 hr**	**12 hr**	**24 hr**
Blank	109.02	124.28	102.92	62.3	198.06	77.59
0.1	87.22	41.43	25.73	50.77	62.87	45.52
0.3	69.77	40.34	24.86	48.28	55.96	33.34
0.5	61.05	37.07	23.11	29.90	53.24	27.98
0.7	56.69	35.98	22.67	23.99	45.43	23.44
0.9	54.51	34.89	21.37	22.42	39.61	21.08
1.1	47.97	30.53	19.19	21.49	38.52	19.17
1.3	45.79	27.26	18.32	20.56	35.61	15.35
1.5	41.43	26.17	17.44	14.32	24.17	14.44

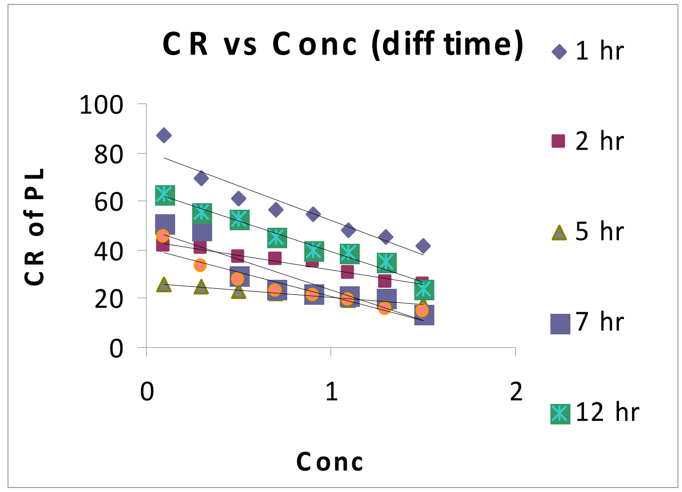

Figure-4
Plot of CR Vs Conc. at different immersion periods

Effect of Temperature: The Arrhenius equation was employed to study the effect of temperature on the rate of corrosion of mild steel in HCl containing various concentrations of PL extract as expressed by

$$CR = A\, e^{-Ea/RT} \quad (4)$$

Where CR is the corrosion rate of mild steel, A is Arrhenius or pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature.

A plot of log of corrosion rate obtained by gravimetric measures against 1/T gave a straight line as shown in figure 5 with a slope of $-E_a / 2.303R$, where E_a is the activation energy.

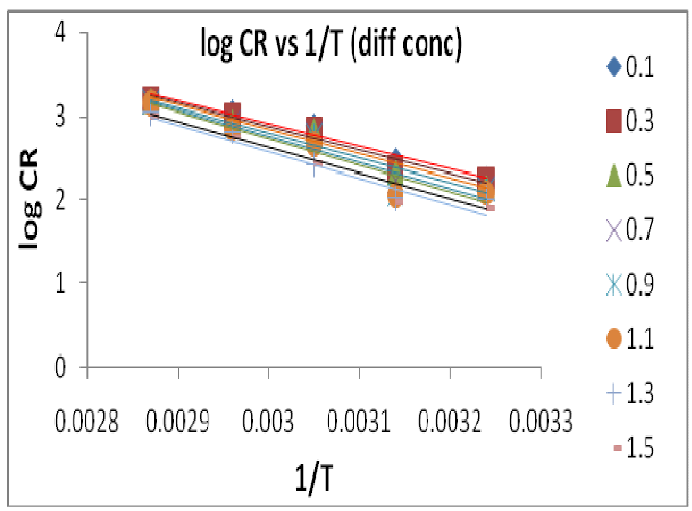

Figure-5
Arrhenius plot (log CR vs 1/T) for PL extract in HCl

The values of E_a (activation energies) obtained from the slope of the straight line are listed in table 5.

Table-5
Activation energy values for different concentrations of PL in HCl

Conc. Of plant Extract (%v/v)	E_a KJ/mol
Blank	65.5
0.1	52.15
0.3	53.52
0.5	56.48
0.7	57.96
0.9	60.55
1.1	61.75
1.3	61.78
1.5	61.8

The activation energies in the presence of inhibitors may be higher, equal to or lower that those in the absence of the inhibitor[18]. In the present study, it could be seen that E_a is more in the absence of inhibitor. Decrease in E_a in presence of inhibitor is attributed to an appreciable increase in the adsorption process of the inhibitor on the steel surface with increase in temperature. This also indicates corresponding decrease in reaction rate as the surface is less exposed to acid in presence of inhibitor.

Adsorption and thermodynamic studies: The interaction between inhibitor and mild steel surface can be understood from the adsorption isotherms. The values of surface coverage (θ) were evaluated using CR values obtained from the weight loss method. The values of surface coverage at different concentrations of *Polyalthia longifolia* leaves extract in HCl media in temperature range of 308 K to 348 K is used to explain the adsorption process. The θ values for different concentration of inhibitors from the acid were tested graphically by fitting to various isotherms. It was observed that the data fitted the Langmuir, Temkin and Freundlich adsorption isotherms with correlation coefficients >0.9.

Table-6
Parameters of Langmuir isotherm of PL in HCl

log C	log θ/1-θ				
	308	318	328	338	348
-1	-0.6127	-0.01945	0.2207	-0.2106	0.2675
-0.5228	-0.5609	0.1895	0.2859	-0.07175	0.2738
-0.301	-0.2629	0.25117	0.3146	0.0469	0.2985
-0.1549	-0.1904	0.39118	0.3916	0.08398	0.31998
-0.0457	-0.1726	0.60205	0.4026	0.15483	0.3255
-0.04139	-0.0856	0.6224	0.5346	0.19736	0.3273
0.1139	0.0511	0.65413	0.8344	0.26768	0.50035

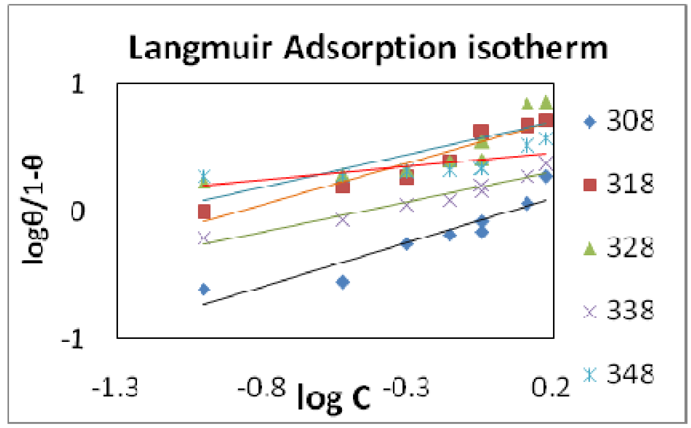

Figure-6
Langmuir isotherm of PL in HCl

Table 6 gives the parameters of Langmuir isotherm. The plots of log(**θ** /1- **θ**) vs log C yielded a straight line, where C is the inhibitor concentration, proving that the inhibition is due to the adsorption of the active compounds onto the metal surface and obeys the Langmuir isotherm. From the results obtained, it is significant to note that these plots are linear with the slopes equal to unity, which indicates a strong adherence of the adsorption data to the assumptions confirming Langmuir adsorption isotherm.

Table-7
Data for Temkin adsorption of PL in HCl

log C	θ				
	308	318	328	338	348
-1	0.1961	0.4888	0.6244	0.3811	0.6493
-0.5228	0.2156	0.6074	0.6589	0.4588	0.6526
-0.301	0.3725	0.6407	0.6736	0.527	0.6654
-0.1549	0.3921	0.7111	0.7113	0.5482	0.6763
-0.0457	0.4019	0.8	0.7165	0.5882	0.6791
-0.0413	0.4509	0.8074	0.774	0.6117	0.68
0.1139	0.5294	0.8185	0.8723	0.6494	0.7599
0.17609	0.647	0.8371	0.8745	0.6964	0.7854

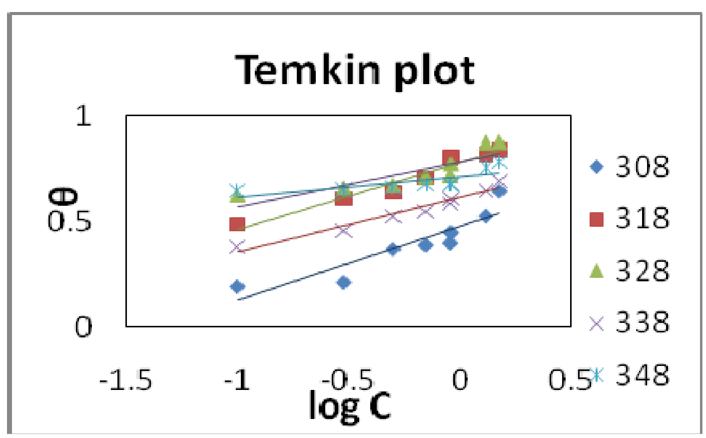

Figure-7
Temkin isotherm of PL in HCl

Table 7 gives the parameters of Temkin isotherm. Plots of θ against log C as shown in figure 7 gave a linear relationship indicating that the adsorption of the compounds on the mild steel surface from the acid followed Temkin adsorption isotherm, supporting the hypothesis that corrosion inhibition by these compounds results from adsorption on the metal surface. The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on an uniform, homogeneous metal surface with an interaction in the adsorption layer[19].

The values of ΔG ads calculated from the adsorption isotherm were found to be in the range of -9 to -20 KJ/mol indicating that the plant constituents are adsorbed on the metal surface by a strong physical adsorption process. The values of ΔG were found to be negative which indicates that the adsorption of extracts of PL on the surface of mild steel is a spontaneous process. In the action mechanism of inhibitor in acid media the first step is adsorption on the metal surface20. The formation of donor-acceptor surface complexes between pi-electrons of inhibitor and the vacant d-orbital of metal was postulated in most of the inhibition studies[21].

Positive values for enthalpy of adsorption indicate that the adsorption process is endothermic. The values of ΔG do not show a gradual increase or decrease with change in inhibitor concentration. This might be due to the fact that the adsorption of the phytoconstituents is dependent not only on concentration but also on other factors like presence of other constituents, electronic and steric interaction of the inhibitor constituents among themselves as well as with the other constituents present in the corrosive media, etc.

Table-8
Data for Freundlich adsorption of PL in HCl

log C	**log θ**				
	308	**318**	**328**	**338**	**348**
-1	-0.70752	-0.31087	-0.20454	-0.41896	-0.18755
-0.5228	-0.66635	-0.21653	-0.18118	-0.33838	-0.18535
-0.301	-0.42887	-0.19335	-0.1716	-0.27819	-0.17692
-0.1549	-0.4066	-0.14807	-0.14795	-0.26106	-0.16986
-0.0457	-0.39588	-0.09691	-0.14478	-0.23047	-0.16807
-0.04139	-0.34592	-0.09291	-0.11126	-0.21346	-0.16749
0.1139	-0.27622	-0.08698	-0.05933	-0.18749	-0.11924
0.17609	-0.1891	-0.07722	-0.05824	-0.15714	-0.10491

Table-9
Thermodynamic parameters of adsorption of PL in HCl on mild steel

Extract Conc. (%v/v)	**-ΔG KJ/mol**					**-ΔS KJ/mol**	**ΔH KJ/mol**
	308 K	**318 K**	**328 K**	**338 K**	**348 K**		
0.1	12.55	16.56	18.59	16.37	20.04	0.15	31.7
0.3	10.04	14.93	16.01	14.18	16.9	0.13	28.16
0.5	10.7	13.95	14.79	13.51	15.59	0.093	16.89
0.7	10.05	13.92	14.36	12.81	14.76	0.08	14.05
0.9	9.51	14.54	13.74	12.56	14.07	0.07	10.5
1.1	9.512	14.13	14.03	12.27	13.49	0.06	7.36
1.3	9.89	13.88	15.45	12.25	14.17	0.07	9.59
1.5	10.77	13.85	15.12	12.45	14.17	0.05	4.45

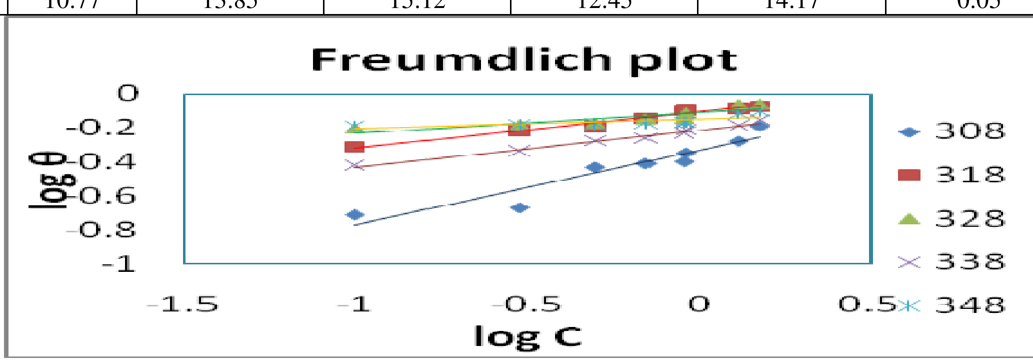

Figure-8
Freundlich isotherm of PL in HCl

Conclusion

The present study shows that acid extract of *Polyalthia longifolia* is a good inhibitor for the corrosion of mild steel in HCl. The inhibition efficiency increases with the increase in inhibitor concentration and thus increases the protective action of the inhibitor on mild steel. The compound seems to function as inhibitor by being adsorbed on the metal surface. The inhibitor showed maximum inhibition efficiency of 87.79% at 1.5% v/v inhibitor concentration for an immersion period of 12 hours at 303K. The % IE increases with increase in temperature, which confirms that PL acts as an effective inhibitor at high temperature also. The adsorption of acid extract of *Polyalthia Longifolia* on the surface of mild steel is spontaneous, endothermic and is consistent with the isotherm models of Langmuir, Temkin and Freumdlich.

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