Research Article

Corrosion Inhibition of Mild Steel in H_2SO_4 Media using *Polyalthia Longifolia* Leaves

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Abstract

Inhibition efficiency of dry *Polyalthia longifolia* (Asoka tree) leaves on corrosion of mild steel in 1N H_2SO_4 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. Surface analysis was studied by SEM analysis. The results obtained prove that the leaves of *Polyalthia Longifolia* act as a good corrosion inhibitor having efficiency of 92% at 1.5% inhibitor concentration.

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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 heteroatom like nitrogen, sulphur and oxygen have been investigated as corrosion inhibitors [1-6]. Extracts of naturally occurring products contain mixtures of compounds having oxygen, sulphur and nitrogen elements and are eco friendly in nature. Corrosion inhibition of mild steel by herbs such as coriander, hibiscus, anis, black cumin, and garden cress has been studied [7-12]. Inhibitive efficiency of acid extract of *Polyalthia Longifolia* leaves in 1N H_2SO_4 is studied in the present work using weight loss and thermodynamic studies.

Experimental

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 H_2SO_4. 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 H_2SO_4. 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 H_2SO_4 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

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

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

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

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

where D is density and a is area

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 up to a certain temperature (338 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.

Table 1 % IE of PL in H_2SO_4 at different concentrations and different temperatures

Temperature in K	%IE							
	0.1	**0.3**	**0.5**	**0.7**	**0.9**	**1.1**	**1.3**	**1.5**
308	32.1	36.8	44.7	51.3	68.4	71.1	72.9	74.0
318	33.7	37.6	58.3	59.4	70.5	73.3	74.0	75.0
328	35.2	45.5	62.3	65.0	73.3	76.5	85.5	88.5
338	30.4	38.7	67.0	75.0	76.2	79.8	88.2	90.5
348	36.0	41.0	54.8	71.3	74.0	75.6	78.0	82.0

Different Immersion Time

Weight loss measurement was performed in 1N H_2SO_4 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 slightly 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 H_2SO_4 solution.

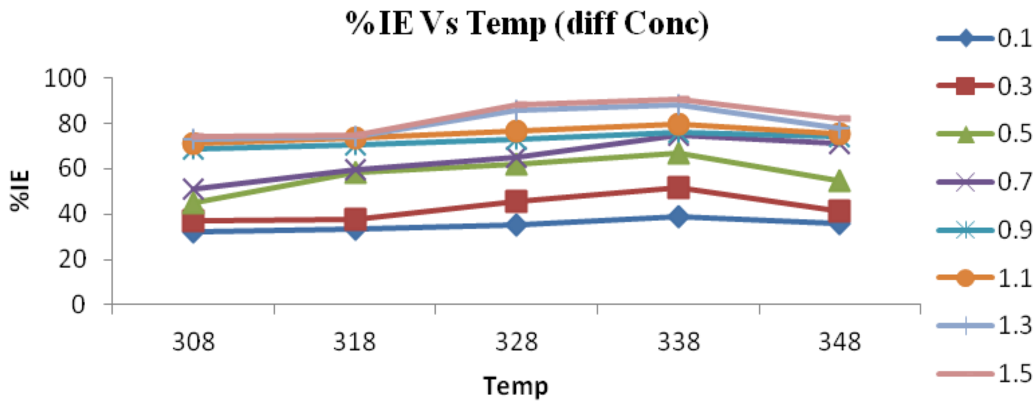

Figure 1 Plot of % IE Vs Temp at different concentrations

Table 2 % IE of PL in H_2SO_4 at different concentrations and different immersion periods

Time in hrs	% IE							
	0.1	**0.3**	**0.5**	**0.7**	**0.9**	**1.1**	**1.3**	**1.5**
1	52.8	59.9	70.3	73.6	76.7	80.5	84.3	85.3
2	59.6	70.7	73.7	77.5	81.7	82.3	85.0	86.7
5	33.0	66.1	72.1	75.0	78.9	79.6	81.3	90.5
7	62.8	79.8	82.8	84.6	86.9	88.2	88.7	92.1
12	82.6	88.7	88.8	89.1	89.9	91.5	92.6	92.9
24	68.6	78.2	82.3	84.5	86.4	87.8	89.9	92.4

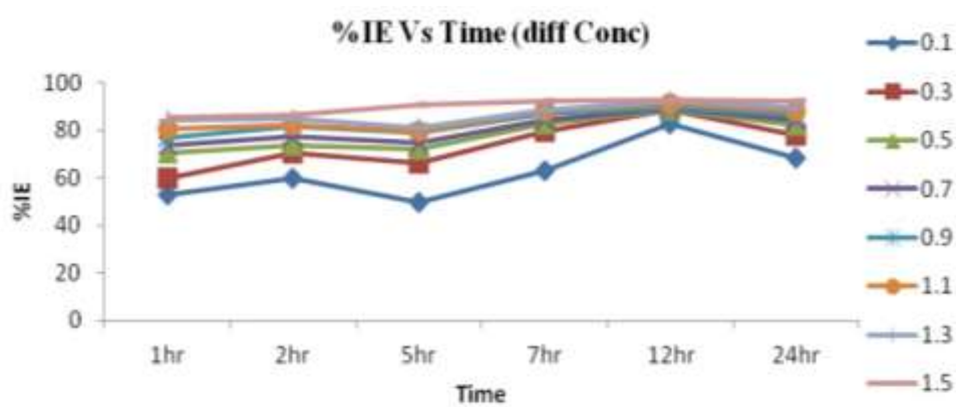

Figure 2 Plot of % IE Vs Time different concentrations

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. The values of E_a (activation energies) obtained from the slope of the straight line of Arrhenius Plot (**Figure 5**) are also listed in **Table 3.**

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 H_2SO_4 medium. The activation energies in the presence of inhibitors may be higher, equal to or lower than those in the absence of the inhibitor [13]. 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.

Table 3 CR of PL in H_2SO_4 at different concentrations and different temperatures

Extract Conc.(%v/v)	CR					**E_a** KJ/mol
	308 K	**318 K**	**328 K**	**338 K**	**348 K**	
Blank	1657.161	2664.54	7435.42	12618.41	18499.15	57.003
0.1	1125.125	1766.185	4818.85	8778.592	11831.26	55.212
0.3	1046.628	1663.702	4055.684	7731.964	10906.74	53.406
0.5	915.7995	1112.042	2804.091	4169.068	8364.302	52.184
0.7	806.7758	1081.516	2603.487	3157.328	5302.915	51.746
0.9	523.314	784.971	1988.593	3002.514	4805.767	51.546
1.1	479.7045	710.8349	1748.741	2551.156	4517.944	51.369
1.3	449.1779	693.3911	1077.155	1487.084	4079.669	45.822
1.5	431.7341	671.5863	859.1072	1199.261	3327.405	41.210

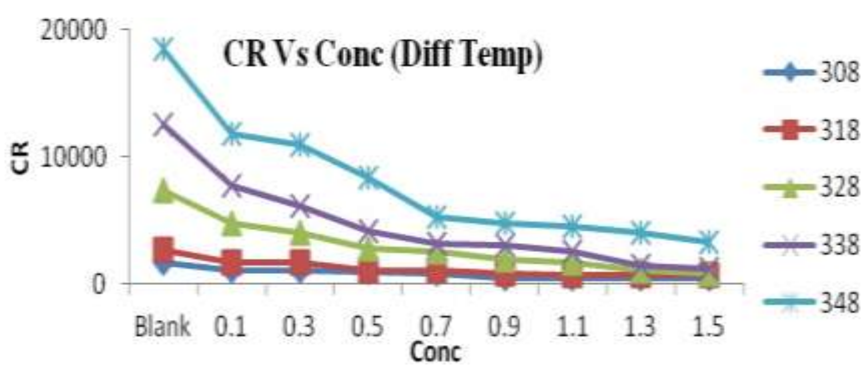

Figure 3 Plot of CR Vs concentration at different temperatures.

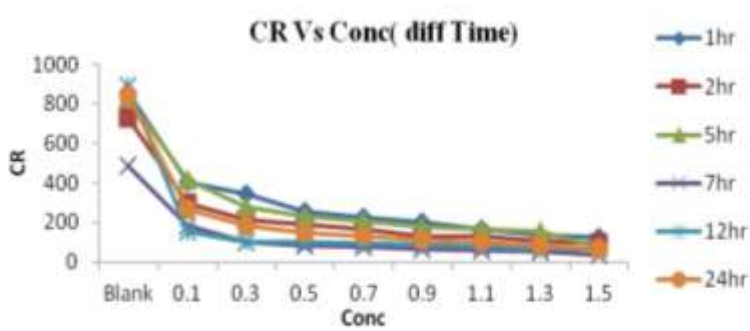

Figure 4 Plot of CR Vs Conc. at different immersion periods

Table 4 CR of PL in H_2SO_4 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	859.1072	728.277	831.1971	487.8012	890.7179	843.407
0.1	405.5684	294.3635	557.3294	181.2901	155.1761	265.024
0.3	344.5151	213.6861	281.7174	98.74392	100.3012	183.8905
0.5	255.1156	191.8814	232.0025	84.10365	99.57434	149.2748
0.7	226.7694	163.5353	207.5812	75.38179	97.03047	130.5586
0.9	200.6037	133.0087	175.3102	64.16797	89.76227	114.659
1.1	167.8966	128.6477	169.2049	57.62658	75.58928	102.6662
1.3	135.1895	109.0235	155.6859	54.82312	66.32233	85.58541
1.5	126.4676	97.03092	78.9332	38.62538	63.23334	64.14363

Effect of Temperature

The Arrhenius equation was employed to study the effect of temperature on the rate of corrosion of mild steel in H_2SO_4 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.

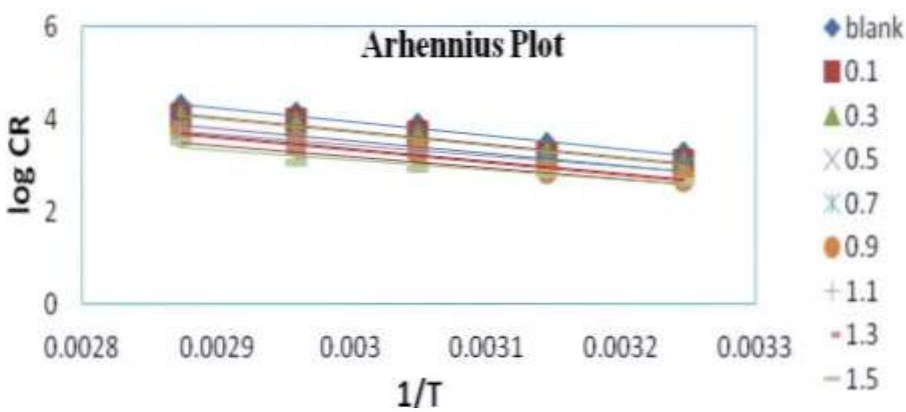

Figure 5 Arrhenius plot (log CR vs 1/T) for PL extract in H_2SO_4

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 H_2SO_4 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.

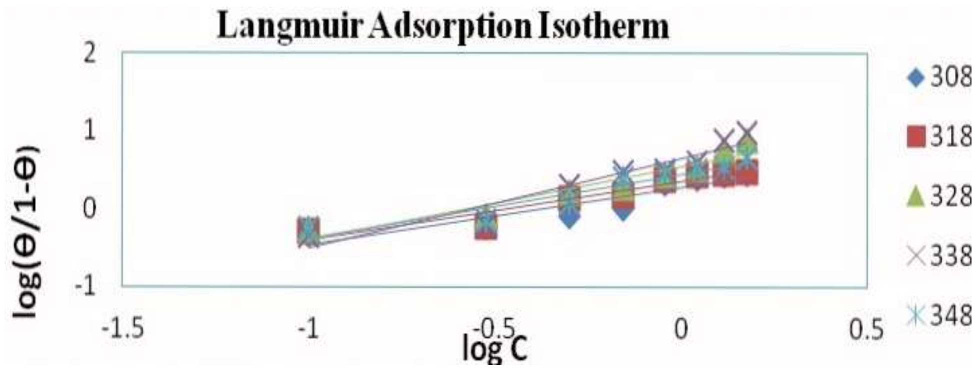

Figure 6 Langmuir isotherm of PL in H_2SO_4

Figure 6 shows the 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.

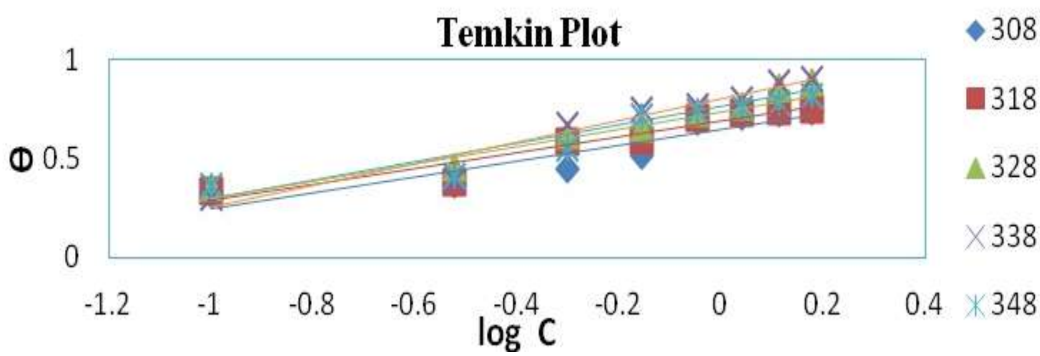

Figure 7 Temkin isotherm of PL in H_2SO_4

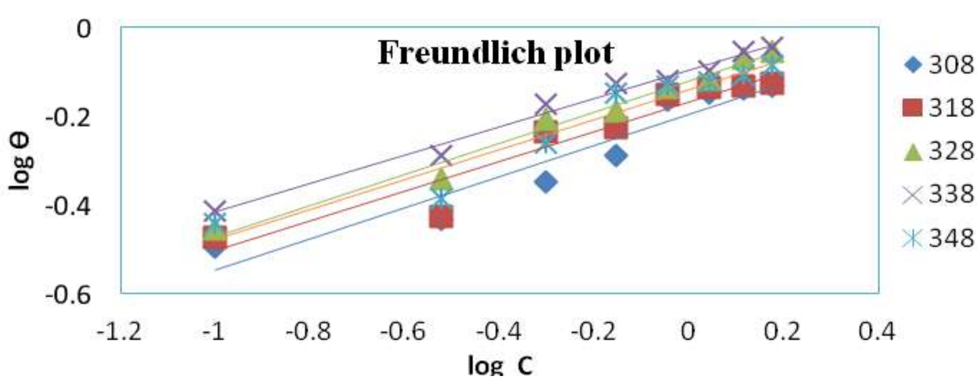

Figure 8 Freundlich isotherm of PL in H_2SO_4

Figure 7 shows the 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 a uniform, homogeneous metal surface with an interaction in the adsorption layer [14].

Figure 8 shows a plot of log θ vs log C (Freundlich isotherm). Linear lines confirm that the adsorption obeys Freundlich isotherm. The values of ΔG ads calculated from the adsorption isotherm were found to be in the range of -11 to -16 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 surface [15]. 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 [16].
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 5 Thermodynamic parameters of adsorption of PL in H_2SO_4 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	14.24	14.896	15.542	16.443	16.598	0.0626	4.994
0.3	11.964	12.434	13.714	14.819	14.03	0.0651	7.977
0.5	11.495	13.31	14.187	15.194	14.155	0.072	9.963
0.7	11.31	12.545	13.587	15.348	15.264	0.1071	21.524
0.9	12.511	13.182	13.963	14.828	14.929	0.0648	7.3761
1.1	12.317	13.016	13.884	14.851	14.587	0.0637	7.1805
1.3	12.123	12.663	15.054	16.181	14.488	0.0824	12.951
1.5	11.895	12.399	15.373	16.455	14.811	0.0988	18.250

Surface analysis was done by taking SEM. The SEM micrographs of different slides of mild steel after immersion in the aqueous solution with the absence and presence of the inhibitor are shown in **Figure 9** and **Figure 10**.

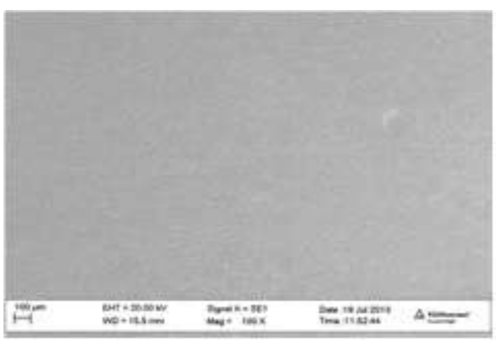

Figure 9 SEM images in 1 N H_2SO_4

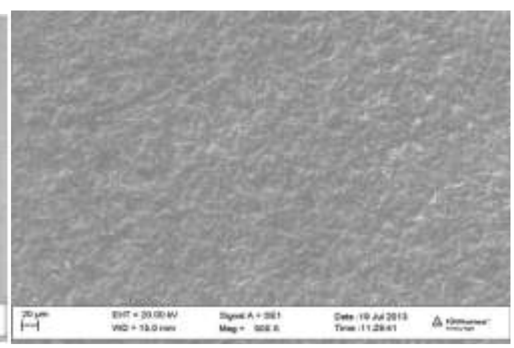

Figure 10 SEM images with 1.5% (v/v) PL extract.

The SEM images in **Figure 9** shows that the surface of mild steel was extremely damaged in the absence of the extract while **Figure 10** shows the formation of a film by the constituents present in leaf extract of *Polyalthia Longifolia (PL)* on the mild steel surface which was responsible for corrosion inhibition.

Conclusion

The present study shows that acid extract of *Polyalthia longifolia* is a good inhibitor for the corrosion of mild steel in H_2SO_4. 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 92% 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 Freundlich.

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