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Litsea Deccanensis Leaves Extract as Corrosion Inhibitor for Mild Steel in 1N HCL Medium

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Abstract: *The Litsea deccanensis leaves (LDL) extract acted as a corrosion inhibitor for mild steel (MS) in 1N HCl medium. The various techniques handled were weight loss measurement, electrochemical studies, FTIR and surface analysis etc. The inhibition efficiency was increased as increasing the concentration of Litsea deccanensis extract. The electrochemical technique proved that the plant extract actedas a mixed type of inhibitor. The temperature studies stated that as the temperature increases the corrosion rate decreases and also obeyed the Langmuir adsorption isotherm. The surface analysis proved that the protective film of adsorbed layer was formed on the metal surface and the composition of the surface was evaluated using EDX. Organic moieties present in the extract was examined by FTIR analysis.*

Keywords: *Litsea deccanensis leaves, Mild steel, Corrosion inhibitor, SEM-EDS, FTIR*

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I. Introduction

The construction industries mainly focused on constructional safety as well as the low cost. In constructional and metallurgical works the priority is given to the metals like mild steel and aluminium [1]. Mild steel is called as plain – carbon steel and its cost is very low while it′s given physical properties that are respectable for abundant application [2]. Acid solutions are generally used in acid pickling, industrial cleaning, oil well cleaning etc. Hydrochloric acid is a strong inorganic acid that is used in many industrial processes [3].Metal corrosion is prevented by the addition of corrosion inhibitor to the corrosion medium. Small quantity of inhibitor which is added will, increase the life time of the metal [4]. "Green inhibitors" is defined as that the plant extracts are high sources of molecule with high inhibition efficiency [5]. These inhibitors are ecological and do not contain heavy metals [6]. The various ways used for preventing corrosion, are by using lubricants, painting, cathodic and anodic protection, electro-painting, material selection, and the use of inhibitors [7]. The present study investigated the inhibition effect of *Litsea deccanensis* leaves (LDL) for mild steel corrosion in 1N HCl acid solution by using various methods.

II. Materials And Method

2.1 Preparation of the specimens:

The composition of MS specimens containing C-0.025, Si-0.018, Mn-0.176, P-0.014, S-0.0076, Cr-0.020, Mo- 0.0024, Ni-0.0093, Al-0.064, Co-0.0005, Nb-0.0005, Ti-0.005, V-0.0005, Pb-0.005, Sn- 0.0003, Mg-0.0031, Bi-0.0010, Sb-0.0005, Z-0.019, Fe-99.62. The area of the specimen is found to be (5*2*.1) cm. The impurities are removed using emery sheet, washed with doubly distilled water and finally degreased with acetone.

2.2 Preparation of plant extracts:

The fresh leaves of *Litsea deccanensis* werewashed, dried in room temperature. The dried leaves were ground well. 25 g of powdered leaves were mixed with 500 mL of doubly distilled water and boiled for 3 hours. After that the solution was refluxed overnight and then filtered. The filtrate is made up to 500 mL and used for further corrosion studies [8].

2.3 Weight loss method:

Weight loss measurement proved that the MS specimens in 1N HCl solution were inhibited by using various concentration of leaves extract. Each sample is weighed by an electronic balance and then immersed in the acid solution. The duration of the immersion is 24 hours and the experiment is carried out at various immersion period (1, 3, 5, 7, 24 hours) at room temperature. After immersion, the surface of the metals were washed by doubly distilled water rinsed with acetone, the samples are weighed repeatedly to calculate Inhibition

efficiency (%) and Corrosion rate (CR). The experiments were done in triplicate and the average value of the weight loss was noted. For all experiments, a recently prepared solution was used [9].

The surface coverage (θ), Inhibition efficiency (%) were determined by using this formula,

$$\theta = \frac{W_0 - W_i}{W_0} \qquad (1)$$

$$\text{IE (\%)} = \frac{W_0 - W_i}{W_0} \text{ X } 100 \qquad (2)$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor
Corrosion rate of mild steel is calculated by using the formula,

$$\text{CR (mmpy)} = \frac{K \; X \; Weight \; loss}{D \; X \; A \; X \; t \; (in \; hours)} \qquad (3)$$

Where, K = 8.76×10^4 (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.

2.4 Temperature studies:

The shiny and pre- weighed sample was immersed in 100 mL of the test solution, inhibited and uninhibited using different concentrations of leaves extract for 1 hour in the temperature range of 313-353K using water thermostats. The sample was removed from the test solution, washed with doubly distilled water, dried and weighed. Inhibition efficiency and corrosion rate were calculated using the equation (2) [10].

2.5 FTIR measurements:

FTIR spectra were recorded in a Bruker ALPHA 8400 S spectrophotometer. The film was sensibly removed, mixed thoroughly with KBr, made into pellets and FTIR spectra were recorded.

2.6 Electrochemical studies:

The electrochemical technique was carried out using PAR 2273 advance electrochemical system. In this technique three electrode cell was used and MS acted as the working electrode. The working electrode was fabricated from MS rod of 5 mm dia and 15 mm length, which was secured in a Teflon tube and shined using various grades of sand paper. Silver and platinum electrodes were used as reference and platinum electrode. A stabilization period of 1 hour was allowed for potentiodynamic polarization and electrochemical impedance technique. Tafel runs were conducted in the potential range from -250 mV to 500 mV relative to the corrosion potential. A scan rate of 1 mVs^{-1} was used for the Tafel run. Corrosion current and other Tafel fit parameters were calculated from Tafel extrapolation method. The EIS run was conducted from 1 KHz to 0.01 KHz. The impedance measurement was conducted at OCP. This technique was conducted at room temperature using 1N HCl and different con. of LDL extract [11].

2.7 Surface analysis study:

The surface morphology was tested for mild steel coupon. The mild steel coupon was immersed in 100 ml of inhibited and uninhibited solution for 24 hours. After, it was removed, rinsed with doubly distilled water, dried and tested for their surface morphology and energy dispersive x-ray spectrum [EDS] using Scanning electron microscopy [12].

2.8 Phytochemical Screening:

Phytochemical screening was carried out on the freshly prepared aqueous LDLextract according to the common phytochemical method. The different chemical constituents tested includes Alkaloids, Phenolic compounds, Saponins, Tannins etc.

III. Result And Discussion

3.1 Weight loss measurement:

The MS samples were immersed in test solution at different concentrations of the extract for 24 hours. The weight loss attained from the weight loss method were tabulated in Table-1. The tabulated values precisely proved that with the rise in concentration of the inhibitor, weight loss was controlled distinctly.The utmost inhibition efficiency (97.68 %) was reached at 25 mLwhich was the optimum concentration [13].

Table.1 Weight loss determination of mild steel in 1N HCl solution containing different concentration of LDL extract

Conc. of LDL (mL)	CR (mmpy)	IE%
Blank	1175.10	*
5	108.43	90.77
10	64.82	94.48
15	40.81	96.52
20	29.48	97.49
25	27.16	**97.68**

3.2 Immersion time:

Datas of corrosion rate and inhibition efficiency were given in table-2. It was proved from the table that thecorrosion rate decreases with the rise in concentration of LDL extract. Table-2 disclosed that the inhibition efficiency wasincreased with increasing in concentration of LDL extract. This was signifying that thelarger amount of inhibitor molecules were absorbed on MS surface. It was achieved that higher the surface coverage, the inhibition efficiency was also high [14].

Table.2 Inhibition efficiency of LDL extract in different immersion time

Conc. of LDL(mL)	Inhibition efficiency (%)				
	1h	3h	5h	7h	24h
5	24.88	79.77	72.13	97.00	82.93
10	25.33	80.97	74.91	97.88	87.32
15	28.50	82.54	78.19	98.30	88.99
20	42.98	86.51	81.80	98.75	90.94
25	57.01	89.49	84.09	99.58	91.96

3.3 Temperature study:

Table.3 displayed the datas of percentage of inhibition efficiency which was obtained from mass loss calculation for various concentrations of the LDL extract in 1N HCl at 313K to 353K temperature. The increase in inhibition efficiency values were due to the rising of temperature. The chemisorption occurred withincrease in temperature on account of build-up of chemical bonds and there by the inhibition efficiency wasincreased with temperature till 333K and thereafter the decay of the inhibitor cropped up. This was expressing that the chemical adsorption of the inhibitor on the metal had taken place [15].

Table.3 Inhibition efficiency of LDL extracts at different temperatures

Conc. of LDL(mL)	313K		323K		333K		343K		353K	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
Blank	328.77	*	775.97	*	2545.2	*	2995.22	*	6404.21	*
5	222.90	32.20	154.63	80.07	178.32	92.99	392.86	86.88	367.78	94.25
10	156.03	52.74	143.49	81.50	162.99	93.59	351.06	88.27	261.90	95.91
15	136.52	58.47	128.16	83.48	147.67	94.19	332.95	88.88	193.64	96.97
20	135.13	58.89	115.62	85.09	114.23	95.51	221.50	92.60	192.25	96.99
25	132.34	59.74	112.84	85.45	96.12	96.22	210.36	92.97	168.56	97.36

3.4 FTIR Spectrum:

The FT-IR spectrum was used to analyze various functional groups present in the plant species. Some of the functional groups present in the LDL extract was shown in the Figure1. The peak at 3529.73 cm^{-1} and 3714.90 $cm^{-1}$was due to the presence of O-H stretching frequency. The peak in the frequency range 2850.79 cm^{-1} and 2154.49 cm^{-1}could be assigned to the presence of C-C and C-H stretching frequency. The absorption band which was observed in the region 1724.36 cm^{-1} was due to aldehyde or ketonic C=O stretching vibration. The frequency at 1625.99 cm^{-1} was due to C=C bending bond. Some peaks in the range of 1448.54 cm^{-1} weredue to C-H bending bonds. Some of the peaks below 1000 cm^{-1} were due to aliphatic C-H groups. The presence of all these groups showed that the plant extract acted as a good inhibitor by means of the adsorbed or protective layer formed on the metal surface [16].

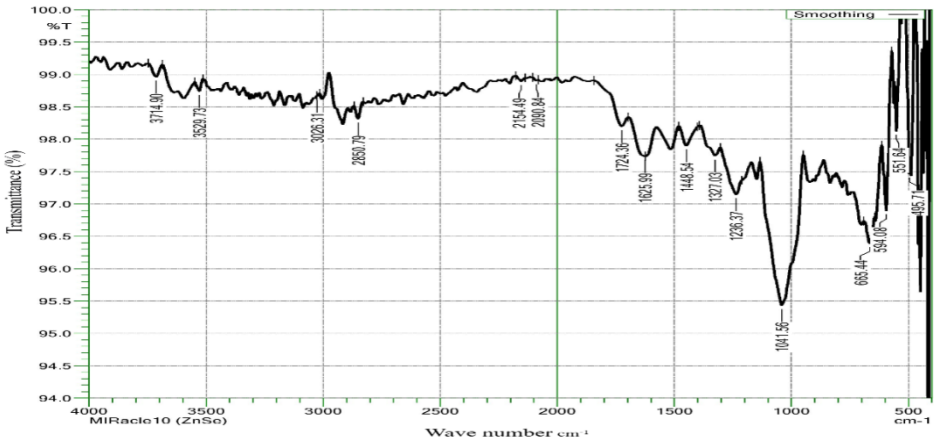


Figure 1. FTIR spectrum of *Litsea deccanensis* leaves extract

3.5 Potentiodynamic polarization measurement:

The polarization technique were accomplished for MS in 1N HCl solution in the absence and presence of different concentrations of LDL extract wasas shown in Figure 2. Electrochemical parameters such as Tafel constant (β_a& β_c), corrosion potential (E_{corr}), corrosion current density (I_{corr}) and inhibition efficiency were attained by the Tafel extrapolation technique. The IE (%) were calculated using the formula,

$$IE\ (\%) = \frac{I_{corr\ (blank\ )} - I_{corr\ (inhibitor\ )}}{I_{corr\ (blank\ )}}\ X\ 100 \qquad (4)$$

Where, $I_{corr\ (blank)}$ the Corrosion current without inhibitor, $I_{corr\ (Inhibitor)}$the Corrosion current with inhibitor.

From table - 4, it was achieved that corrosion current density, decreased with increased concentration of inhibitor. Inhibition efficiency have increasedand the rate of electrochemical reaction was diminished due to the development of adsorbed layer on the MS surface. The dissolution of E_{corr} value showed that the values were less than 85 mV when compared to blank proved that the extract acted as a mixed type of inhibitor [17].

Table.4 The different parameters of potentiodynamic polarization for mild steel in differentconcentrations of LDL extract with 1N HCl

Conc. of LDL (ml)	E_{corr} (mV) vs (SCE)	I_{corr} (mA/cm^2)	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
Blank	-483	2.975	1.359	215	140	*
5	-476	0.4173	0.1905	169	92	85.97
10	-477	0.3056	0.1395	168	84	85.97
15	-479	0.2520	0.1151	162	86	91.52
20	-485	0.2540	0.1160	161	94	91.46
25	-484	0.2086	0.09528	152	98	**92.98**

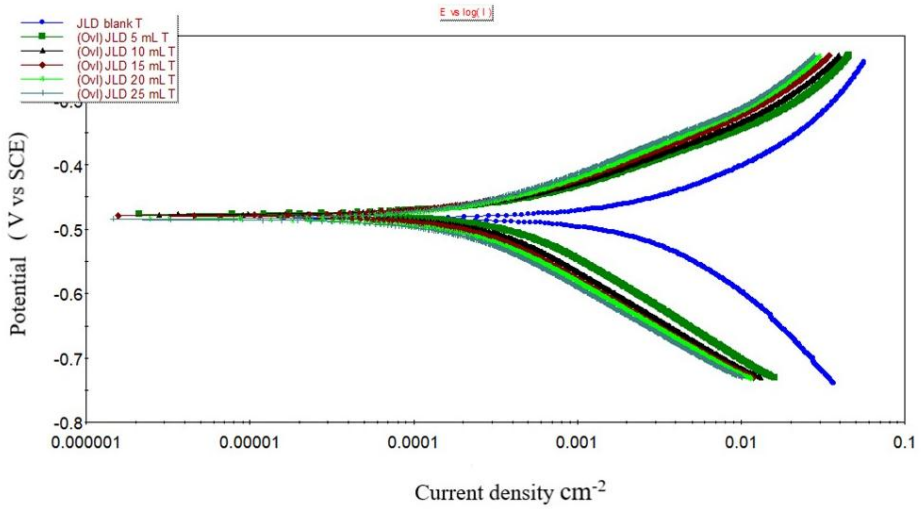


Figure 2. Tafel slope of mild steel in the blank and LDL extract of different concentration

3.6 Electrochemical impedance method:

Impedance spectroscopy is a best and simple technique which gives the characterization of surface behaviour in 1N HCl solution with and without plant extracts. Figure 3 showed the Nyquist plot at various concentrations of leaves extract. The various corrosion parameters were derived from EIS measurement which were presented in table - 5. The impedance spectrum showed, that theconcentration of inhibitor increased with increase in semicircle angle because of the charge transfer process which controls the corrosion of MS surface and formed astrong protective layer. It could be observed from the table-5 it was shown that the increase in the R_{ct} values and decrease in the C_{dl} values with increasing the concentration of the inhibitor. So inhibition efficiency of the inhibitor was also increased [18].

Table.5 Measurement of impedance with different concentrations of LDL extract with 1N HCl

Conc. of LDL (mL)	C_{dl} (μFcm^{-2})	R_{ct} Ωcm^2	IE (%)
Blank	$5.09x10^{-5}$	6.534	*
5	$3.081x10^{-5}$	27.5	76.24
10	$2.784x10^{-5}$	37.35	82.50
15	$2.549x10^{-5}$	41.16	84.12
20	$2.827x10^{-5}$	44.52	85.32
25	$2.58x10^{-5}$	49.56	**86.81**

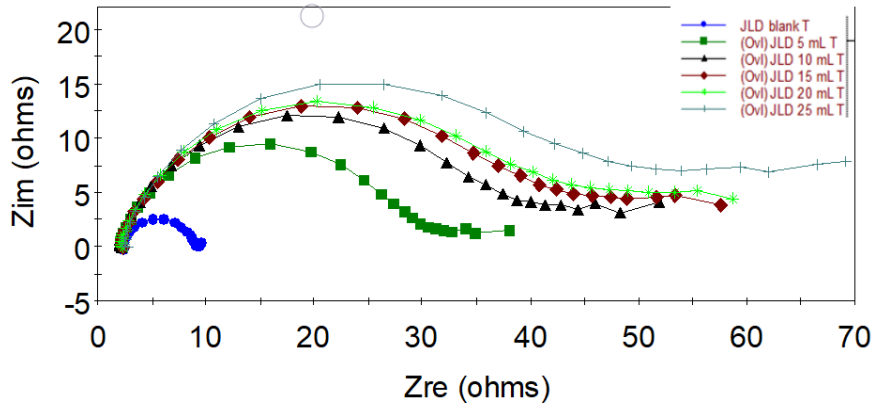


Figure.3 Nyquist plot of electrochemical impedance spectroscopy in the presence and absence of LDL inhibitor

Bode plots of mild steel with and without inhibitor containing different concentration of LDL extract were presented in Figure 4. It was obvious that the MS specimens with LDL extract showed increase in maximum phase angel value, which signified that the inhibition property on the MS surface [19].

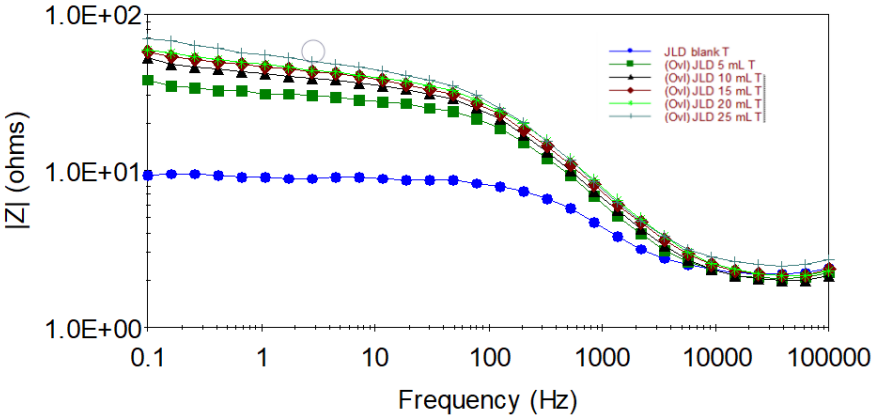


Figure 4. Bode plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of LDL leaves extract

3.7 Surface analysis study:

3.7.1 SEM analysis:

SEM appearance of MS sample dipped in 1N HCl along with occupancy of 25 mL of LDL extract were shown in Figure 5. The morphology of MS sample dipped in 1N HCl solution in the absenteeism of inhibitor was irregular and surface was highly injured because of metal dissolution. But, the occupancy of 25 mL of LDL extract restrained the rate of corrosion and the surface injured had been decreased as correlated to the blank solution, and there coat the resolution of establishment of inhibitor layer on the MS surface [20].

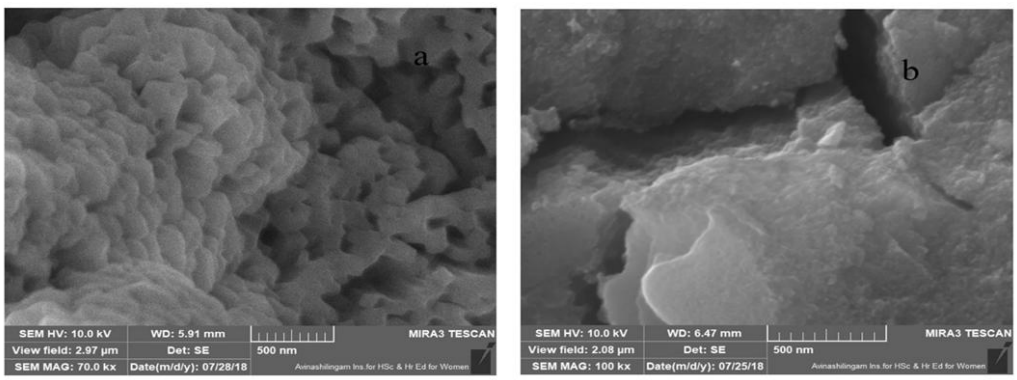
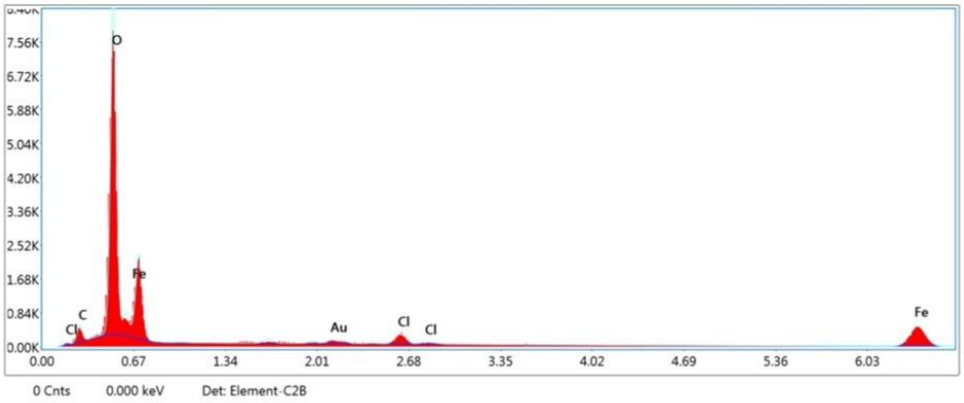


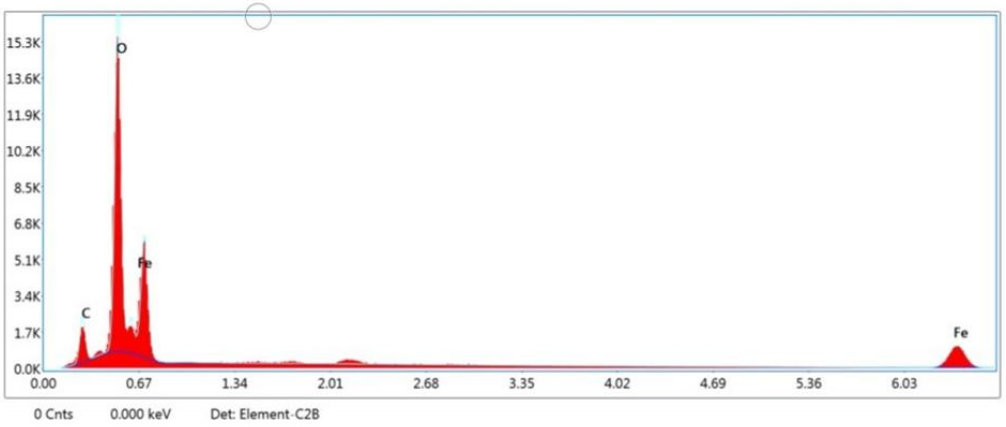
Figure.5 SEM morphology of mild steel in the absence of inhibitor (5a) presence of inhibitor (5b)

3.7.2 EDX spectrum:

Energy dispersive X-ray analysis (EDX) method explained the composition of the surface of the MS specimen in absence and presence of inhibitor in 1N HCl medium. The outcome of EDX spectrum was shown in Figure 6. The atomic percentage of inhibited and uninhibited elemental values were summarized in table - 6. The Fe atomic percentage of MS immersed in 1N HCl was about 15.60%. But for MS sample immersed in presence of 25 Ml of LDL extract was 19.38%. The restrained Fe atomic percentage proved that the MS sample was inhibited, which was confirmed by the formation on MS surface [20].



6(a)



e

6(b)

Figure.6 (6a) mild steel in the absence, (6b) mild steel in the presence inhibitor

Table.6 Element composition (Atomic %) of mild steel sample in the presence and absence of inhibitor in 1N HCl solution after 24 h of immersion

Inhibitors/elements	C	O	Fe	Cl
Mild steel in 1N HCl	9.25	71.55	15.60	3.60
Mild Steel in LDL extract	16.68	63..95	19.38	-

3.8 Adsorption isotherm:

The corrosion inhibition could also be explained in terms of adsorption. The interaction between C/θ and C (concentration) of inhibitor can be symbolized by the Langmuir adsorption isotherm.

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Where, K is constant of adsorption. The connection between C/θ and C at 313K -353K for MS in 1N HCl with different concentration of plant extract was shown in Figure 7. The straight line graph proved that it obeyed Langmuir adsorption [21].

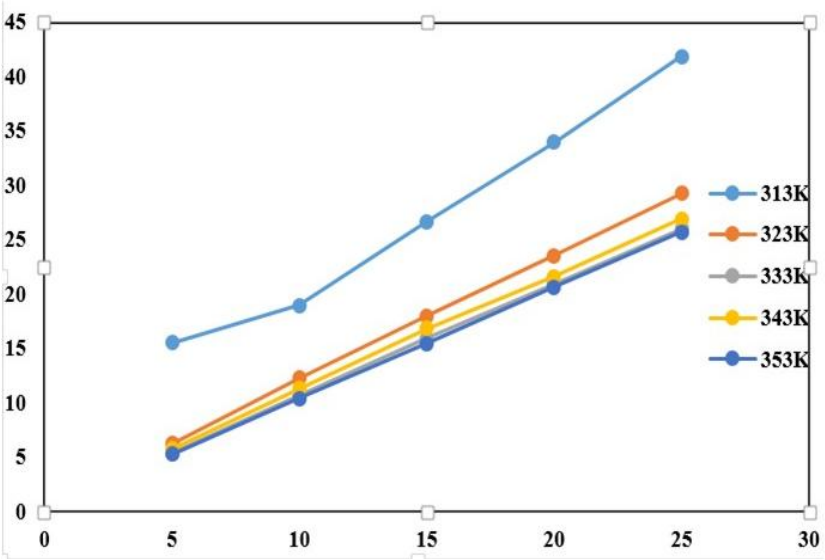


Figure.7 Langmuir adsorption isotherm of different temperatures of LDL extract

3.9 Phytochemical analysis:

Phytochemical screening was tested using the aqueous extract to the ordinary phytochemical method derived by Harborne [22]. The LDL extract acted as a good corrosion inhibitor because of the presence of some chemical constituent such as Alkaloids, Carbohydrate, Triterpenoid, Phenolic compounds, Flavonoids, Proteins, Steriods.

Table.7 Phytochemical screening of LDLextract

Phytochemical Test	LDLextract
Alkaloids	+
Carbohydrates	+
Triterpenoids	-
Phenolic compounds	+
Flavanoids	+
Proteins	+
Steriods	+

(+) Presence (-) Absence

IV. Conclusion

It was concluded that the LDL acted as a good corrosion inhibitor in the corrosive medium. The inhibition efficiency increased with increase in the concentration of the inhibitor and was observed that the highest value was found to be 97.68% at 25mL which was the optimum concentration. PDP studies proved that the LDL extract acted as a mixed type of inhibitor. The impedance values examinedthat the protective layer was formed on MS surface in acid solution. SEM & EDS results clearly proved that the protective layer was formed on the metal surface. The adsorption fits well to the Langmuir adsorption isothermmodel.

References

[1]. E. N. Dim, P.O. Ukoha and N. L. Obasi, Asian J Chem, 24, 5 (2012).
[2]. D. K. Singh, S. Kumar, G. Udayabhanu, and R.P.John, J Mol Liq, 216, (2016).
[3]. W. A. W. Elyn Amira, A.A. Rahim, H. Osman, K. Awang, P. Bothi Raja, Int. J. Electrochem. Sci., 6, (2011).
[4]. R. Godec, Colloids Surf A Physicochem Eng Asp, 280, (2006).
[5]. P. Bothi Raja, M. G. Sethuraman, Mater. Lett, 62, 113, (2008).
[6]. S. K. Sharma, Ackmez Mudhoo, Gargi Jain, Jyothi sharma, Rasayan, J. Chem, 2, (2009).
[7]. C. G. Dariva, A.F. Galio, (2014) Corrosion inhibitors–principles, mechanisms and applications. Developments in Corrosion Protection, pp: 365-379.
[8]. A. Mesbah, C. Juers, F. Locouture, S. Mathieu, E. Rocca, M. Francois and J. Steinmetz, J.Solid state sci, 9, **(**2007).
[9]. Ambrish Singh, V. K. Singh, M. A. Quraishi, Rasayan J. Chem, 3, 4, (2010).
[10]. P. R. Sivakumar, K. Vishalakshi and A. P. Srikanth, J.Applicable. Chem, 5, 5, (2016).
[11]. S. Noyel Victoria, Rohith Prasad and R. Manivannan, Int. J. Electrochem. Sci, 10 (2015).
[12]. O. Sunday, Ajeigbe, Norazah Basar, A. Muhammad, Hassan and Madzlan Aziz. ARPN. J. Eng. Appl. Sci, 12, 9, (2017).
[13]. R. Sivakumar, and A. P. Srikanth, Asian J Chem, 29, 2, (2017). http://dx.doi.org/10.14233/ajchem.2017.20160.
[14]. A. Mathina and R. Rajalakshmi, RASAYAN. J. Chem, 9, 1, (2016).
[15]. Subbaian Aejitha, Periyaiah Kannaiah Kasthuri and Palanisamy Geethamani, Che Sci Rev Lett, 2, 7, (2014).
[16]. M. J. Judithaa, R. Jeevitha, P. R. Sivakumar and A.P. Srikanth, J. Applicable. Chem, 8, 1, (2019).

[17]. L. P. Chaudhari, S. N. Patel, Journal of Bio- and Tribo-Corrosion 5, 20, (2019). https://doi.org/10.1007/s40735-018-0212-6
[18]. P.R. Sivakumar and A.P. Srikanth, Asian J Chem, 30, 3, (2018), https://doi.org/10.14233/ajchem.2018.20939
[19]. P. R. Sivakumar, M. Karuppusamy, R. Jeevitha, M. J. Judithaa and A. P. Srikanth, J. Applicable. Chem, 8, 1, (2019).
[20]. M. Yadav, R. R. Sinha, Sumit Kumar, T. K. Sarkar, RSC Adv, 5, (2015). DOI: 10.1039/C5RA14406J
[21]. L.R. Chauhan, G. Gunasekaran, Corros. Sci, 49, (2007)
[22]. J.B. Harborne, Phytochemical Methods, (A guide to modern techniques of plant analysis, Chapman and Hall, London, 1998).

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