Seed Extract of *Dypsis lutescens* as Ecofriendly Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Medium

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Abstract : The seed extract of *Dypsis lutescens*, had been analyzed for mild steel corrosion inhibition in acid medium with weight loss, thermodynamic, adsorption and electrochemical parameters. The results reflected that the extract is a potential corrosion inhibitor. IR spectra and SEM photographs recorded for functional group and surface modification analysis of mild steel, were agreeing with other parameters. Entire study revealed that the inhibitor works through adsorption of its molecules over the mild steel. From this study it is inferred that the seed extract of *D. lutescens* is an efficient, eco-friendly and alternate corrosion inhibitor for mild steel in acid medium.

Key words : *D. Lutescens,* mildsteel, corrosion, polarization, impedance, eco-friendly.

Introduction

Mild steel is widely used as a constructional material for various industrial applications due to its high mechanical properties and low cost. Several corrosion problems aggravate by the excessive use of hydrochloric acid in pickling, rescaling and cleaning functions on mild steel surface [1]. Corrosion is an electrochemical process that leads to the flow of electric current in acidic media which results in metal loss. Mild steel corrosion in acidic media is significant because of the increased industrial applications of acid solutions. Use of inhibitors is one of the most practical methods for protection of metal against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [2-5]. The effectiveness of inhibitor depends upon the interaction, adsorption of molecules and ions on metal surface [6]. Not long, the researches on plant extracts are in progress for corrosion inhibition and the most of them are proved to be successful. *Phyllanthus amarus*[7], *vegetal tannins*[8], *Parthenium Hystophrous* [9], *Ficus Exasperata* [10], *Citrus aurantiifolia* [11], *Eclipta Alba*[12],

Solanum Tuberosum[13], *Azadirachta indica*[14], *Andrographis paniculata*[15], *Withania somnifera*[16], *Beet root*[17]and*Musa acuminate* [18] are evaluated for anticorrosion properties. The corrosion inhibition effect of acid extract of the seed of *D. lutescens* on mild steel in hydrochloric acid medium is examined in this study.

D. lutescens , is a commonly grown fancy palm belongs to the family Arecaceae. The drupaceous fruits of this plant resemble Areca catechu, but are smaller in size and attractive. The fruits are not of any food value; hence do not have any commercial significance. The fruits and seed are bio-waste materials only.

Experimental

Mild steel specimen

Weight loss and SEM studies were carried out using mild steel specimen of size 4.0 x 2.0 x 0.19 cm. For IR spectral studies MS powder was used and specimens with an exposed area of 1 cm^2 were used for electrochemical studies. For the entire study mild steel of composition Fe = 99.51%, P = 0.08%, Mn = 0.034%, Si = 0.6% and C = 0.16% is used. The specimens were polished mechanically with different grades of emery paper and then degreased with trichloroethylene.

Preparation of the extract and corrosive environment

100 ml of 5% HCl and 50g of dried powder of *D. lutescens* seed were mixed and refluxed for one hour. The extract is cooled, filtered off and made up to 100 ml using double distilled water.

The corrosive environment was prepared using 5% (v/v) HCl solution and double distilled water. This is the stock solution. From this 100 ml each of standard solutions were prepared with and without different concentrations of *D. lutescens* seed extract.

Pure HCl (Merck-61752605031730) and doubly distilled water were used for the entire study.

Weight loss study and thermodynamic studies

Previously degreased, polished and weighed mild steel specimens were immersed in 100 ml test solutions with and without different concentrations of inhibitor, separately at four different temperatures viz., 303, 308, 313, and 318K. After one hour the above specimens were washed with doubly distilled water, dried well and weighed using Schimadzu AUX220 balance.

Infra Red Spectroscope studies

FTIR spectra were recorded for *D. lutescens* liquid extract and the dried adsorption product formed between finely powdered MS specimen and concentrated solution of the extract using Bruker FTIR model-Tensor27.

Surface characterization studies

Tafel polarization plots were recorded potentio-dynamically using platinum electrode, calomel electrode and MS specimen as auxiliary, standard and working electrodes respectively. A sweep rate of 1mV/sec is maintained for the potential potentio-dynamic polarization studies. Impedance measurements are carried out in the frequency Range of 10 KHz to 10 MHz .The electrochemical parameters were studied in HCl medium and also with different concentrations of natural inhibitors. Solartron model SI1280B electrochemical measurement unit is used for these studies.

SEM images were recorded for polished mild steel, specimen exposed to 5% HCl corrosive environment and specimen immersed in 10% inhibitor concentration in 5% HCl, using Hitachi S-3000H model Scanning Electron Microscope.

Results and discussion

Weight loss studies

Weight loss studies were carried out at four different temperatures. From the experimental weight loss data, percentage inhibition efficiencies were calculated in the classical way as follows, $\%IE = \left(\frac{W_0 - W}{W_0}\right) \times 100$, where W_0 and W are the weight loss observed for MS specimens in the absence, and presence of the inhibitor in acid medium, respectively [19]. The results are given in (Table 1).From the table, it is clear that the extent of weight loss was found to be dependent on the inhibitor concentrations. The IE increases with increase in concentration of the inhibitor as shown in Fig 1. Further it is also noted that at higher concentrations, the inhibition efficiency is found to decrease with rise in temperature Fig 2. This reveals that the adsorption of the inhibitor molecules is physical because desorption is possible at elevated temperatures in the case of physisorption.
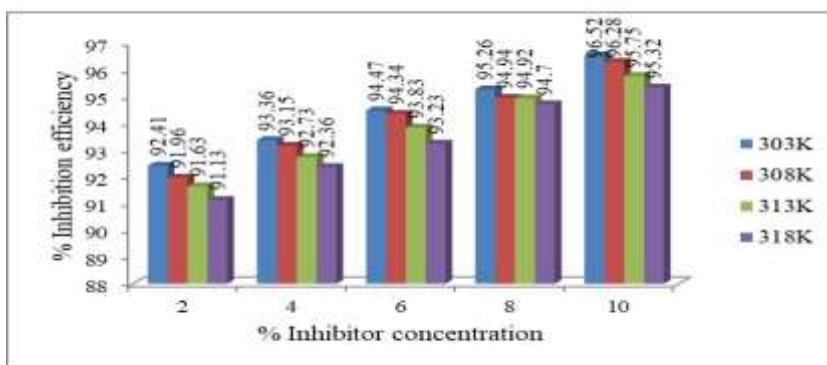

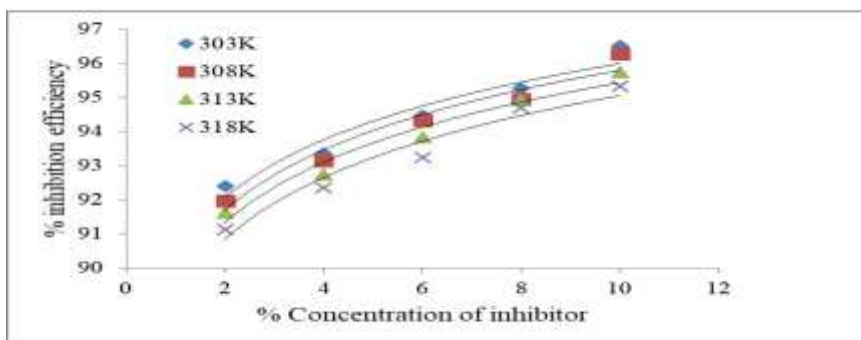**Figure 1: Effect of temperature on inhibition efficiency of *D. lutescens* extract**

Figure 2: Plot between % IE against % concentration of *D. lutescens* extract.

Table 1: Weight loss data

% Conc. of the inhibitor	Weight loss, g				Inhibition efficiency, %			
	303 k	308 k	313 k	318k	303 k	308 k	313 k	318k
0	0.0633	0.0672	0.0729	0.0812	--	--	--	--
2	0.0048	0.0054	0.0061	0.0072	92.41	91.96	91.63	91.13
4	0.0042	0.0046	0.0053	0.0062	93.36	93.15	92.73	92.36
6	0.0035	0.0038	0.0045	0.0055	94.47	94.34	93.83	93.23
8	0.0030	0.0034	0.0037	0.0043	95.26	94.94	94.92	94.70
10	0.0022	0.0025	0.0031	0.0038	96.52	96.28	95.75	95.32

Table 2: Heat of corrosion reaction and change in free energy data

% Conc. of the inhibitor	Q in KJ/mol	ΔS in J/mol	ΔG in KJ/mol			
			303K	308K	313K	318K
2	-8.92	-250.02	-14.67	-14.75	-14.87	-14.95
4	-8.37	-248.97	-13.29	-13.42	-13.47	-13.55
6	-11.22	-250.33	-12.76	-12.90	-12.87	-12.82
8	-5.71	-258.52	-12.44	-12.47	-12.66	-12.81
10	-17.31	-260.97	-12.69	-12.72	-12.57	-12.75

Thermodynamic parameters of *D. lutescens* extract

A graph was plotted between $log\, \theta/1 - \theta$ and $1/T$, where θ is the fraction of the metal surface covered by the inhibitor at temperature T respectively. A negative slope was obtained that was equivalent to $- Q/2.303R$ from which Q, the heat of adsorption was calculated [20] and tabulated in (Table 2). The Q values were found to be very low ranging from 2.77 KJ/mol for 2% to 4.07 KJ/mol for 10% inhibitor concentration. This indicates that the increase in inhibitor concentration retards the corrosion reaction. This is due to the formation of a protective layer over the MS surface.

The free energy change, ΔG for the adsorption is calculated using the following formula

$$\Delta G = -2.303RT \log 55.5K, \text{ where } "K = (\theta/1 - \theta)/ C" \qquad (1)$$

The negative free energy change values substantiate the spontaneity of adsorption and stability of the adsorbed inhibitor layer on the mild steel surface. The mean value of change in free energy (Table 2) for this adsorption process is -12 KJ/mol. It has been reported that Gibbs free energy values between -49 KJ/mol and -58 KJ/mol are indicative of chemisorption [21]. The very low free energy change values in the present study confirm that the adsorption is physical in nature. This is in agreement with weight loss study.

The corrosion rate in mmpy is calculated using the formula

$$\text{Corrosion rate} = \frac{87.6xW}{DAT} \qquad (2)$$

where 'W' is the weight loss in mg, 'D' is the density of mild steel, 'A' is the area of exposure in $(cm)^2$ and 'T' is the time in hours [9].

The corrosion rate is found to decrease suddenly and tremendously even for the addition of a small quantity of *D. lutescens* extract i.e. 2% (Table 3). The maximum concentration of 10% inhibitor is found to decrease the corrosion rate massively from the blank value. This is further confirmed from Fig 3. This decrease in corrosion rate is also due to the formation of a passive layer over the MS surface by the inhibitor constituents.

Table 3: Corrosion rate and energy of activation data

% Conc. of the inhibitor	Corrosion rate, mmpy				E in KJ/mol for the range (K)		
	303K	308K	313K	318K	303-308	308-313	313-318
0	38.64	41.02	44.50	49.57	9.27	13.05	17.87
2	2.93	3.29	3.72	4.39	17.98	19.68	27.43
4	2.56	2.81	3.24	3.78	14.46	22.81	25.53
6	2.14	2.32	2.75	3.36	12.53	27.24	33.19
8	1.83	2.08	2.26	2.62	19.87	13.29	24.48
10	1.34	1.53	1.89	2.32	20.57	33.86	33.96

E, energy of activation is obtained using the formula

$$\frac{\log CR_2}{CR_1} = \frac{E}{2.303R} x \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{3}$$

Where CR_1 and CR_2 are the corrosion rates at temperatures T_1 and T_2 respectively [22, 23]. The values of corrosion rate and E are given in (Table 3).
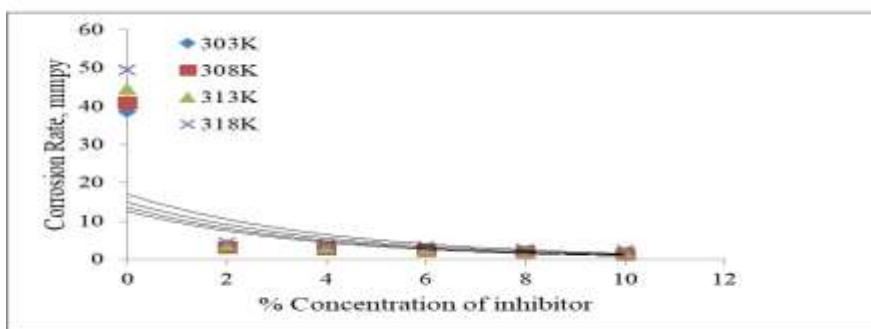
Figure 3: Correlation between corrosion rate and % concentration of *D. lutescen*extract

There was no vast variation in the 'E' values for a particular range of temperature (303-318 K) irrespective of change in concentrations of the inhibitor.The energy of activation, E was very high for 10% inhibitor concentration than the blank value. This indicates the requirement of more energy for corrosion reaction to occur at higher concentrations of inhibitor [24].

An adsorption isotherm was obtained by plotting log C versusθ, where 'C' is the concentration of the inhibitor Fig 4. The graph revealed the increase in adsorption of the inhibitor constituents on the metal surface as the inhibitor concentration was raised [11].
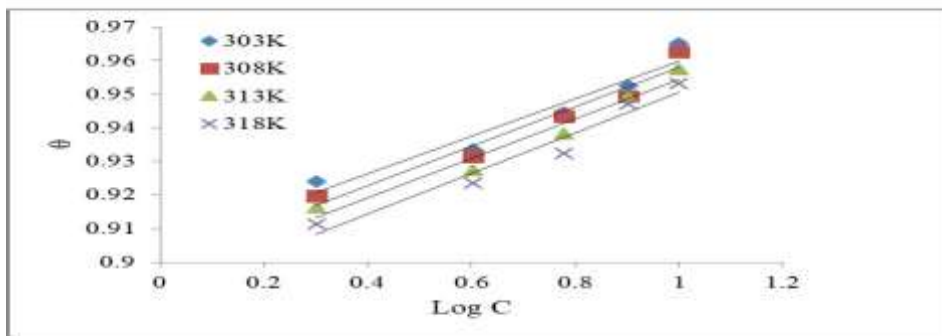
Figure 4: Temkin adsorption isotherm of *D. lutescens* extract.

Infra-Red Spectroscopic Studies

　　　Fig 5 and 6, depict the IR spectra of *D. lutescens* extract and the adsorption product formed between the extract and MS powder respectively. From the spectra, it was observed that the OH stretching frequency had been shifted from 3370.3 to 3434.3 cm^{-1}. The amine salt frequency was up-shifted from 2357.7 to 2359.0 cm^{-1}. A downshift was observed from 1637.6 to 1629.0 cm^{-1} for C-O stretching frequency of amide. C-N stretching of amide was also changed from 1408.6 to 1368.8 cm^{-1}. There was also a downshift from 1066.6 to 1057.5 cm^{-1}. The comparison of the IR spectra of *D. lutescens* extract and the adsorption product revealed the changes in group frequency for the functional groups of the organic compounds. This is attributed to the adsorption of organic compounds of the extract on the metal surface, which prevents corrosion.
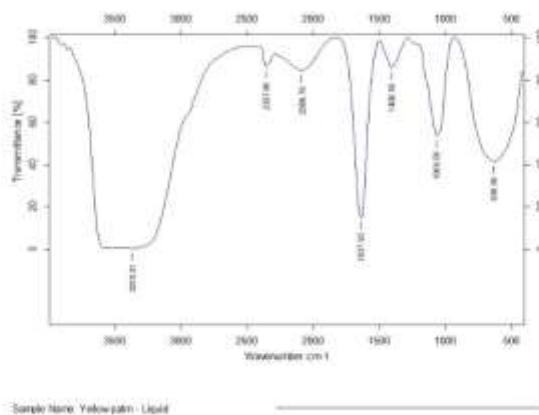

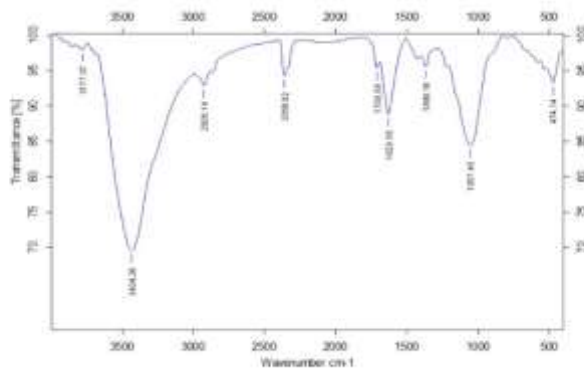**Figure5: IR spectra of the *D. Lutescens* extract**

Figure 6:IR spectra of the adsorption product between *D. Lutescens* extract and MS powder
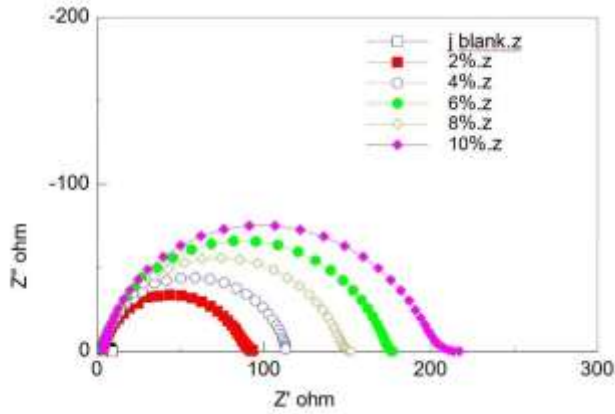
Figure 7: Impedance spectra of mild steel in HCl in the absence and presence of different concentrations of *D. Lutescens* extract
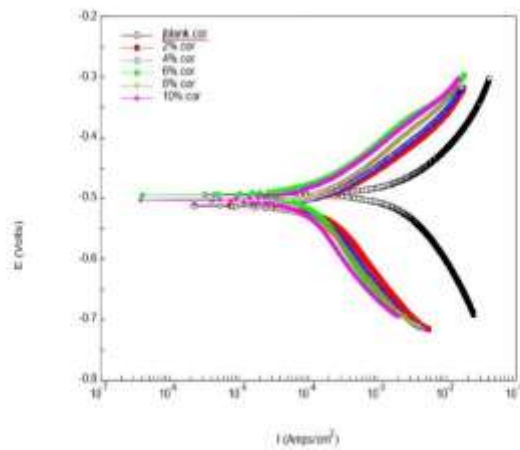

Figure 8: Tafel curves of mild steel in HCl in the absence and presence of various concentrations of *D. Lutescens* extract

Electrochemical Studies

The impedance and polarization curves of the inhibition process are given in Fig 7 and 8. The values of open circuit potential (OCP), corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c), charge transfer resistance (C_{dl}), corrosion rate (CR) and IE obtained from electrochemical measurements are shown in (Table 4). There is no remarkable shift in the values of E_{corr}, indicating that the inhibitor works through mixed mode of inhibition [25]. The mixed mode of inhibition is also evident from the b_a and b_c values as they do not vary in a regular manner with increase in inhibitor concentration. The I_{corr} values descend sharply from the blank value reflecting the decreased rate of corrosion. This is because corrosion current is proportional to the magnitude of corrosion reaction.
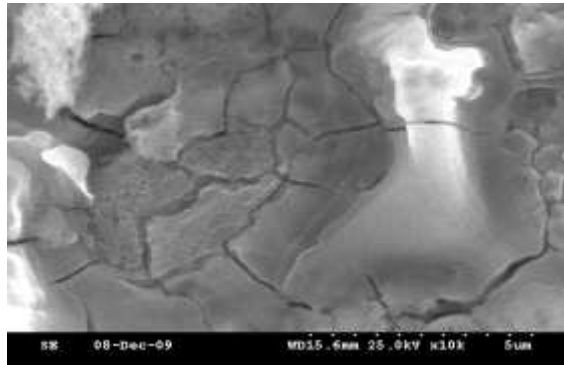
Table 4: Electrochemical parameters of corrosion inhibition by *D. lutescens* extract

% Conc. of the inhibitor	OCP (V)	E_{corr} (V)	I_{corr} (A)	b_a (V/dec)	b_c (V/dec)	R_{ct} (Ohm/ cm^2)	C_{dl} (A/cm^2)	%IE
Blank	-0.5151	-0.4939	26.78×10^{-4}	150.91	226.11	5.80	6.08×10^{-5}	--
2	-0.5275	-0.5121	2.09×10^{-4}	88.571	151.25	88.067	3.05×10^{-5}	92.18
4	-0.5185	-0.5133	1.67×10^{-4}	88.059	152.48	110.67	2.74×10^{-5}	93.76
6	-0.5148	-0.5118	1.34×10^{-4}	92.552	145.77	143.79	3.46×10^{-5}	94.98
8	-0.5155	-0.4940	1.13×10^{-4}	87.518	170.70	170.25	3.21×10^{-5}	95.77
10	-0.5127	-0.5024	9.45×10^{-5}	87.969	154.16	198.79	2.88×10^{-5}	96.46

The decrease in C_{dl} values from the blank with increase in inhibitor concentration is attributed to an increase in thickness of the electronic double layer on the metal surface. This further confirms the physisorption of the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface, which leads to an increase in inhibition efficiency. The diameters of the semicircles increase with increasing concentration of inhibitor indicating its inhibition effect. The increase in resistance towards electrochemical corrosion reaction with increase in inhibitor concentration from the blank value is reflected from R_{ct} data. All the electrochemical parameters show that the corrosion control depends on the concentration of the inhibitor.

SEM Studies

To validate the above results, the surface morphology of mild steel surface was recorded for polished MS surface Fig 9,and polished specimens with and without inhibitor in hydrochloric acid medium using Scanning Electron Microscopy (SEM). The SEM photographs show that, in the presence of inhibitor Fig 11, the MS surface does not undergo any noticeable change, when compared with the specimen exposed to acid medium alone Fig 10. However the relatively small change in the surface morphology is attributed to the formation of an inert layer by the inhibitor on the metal surface [26].
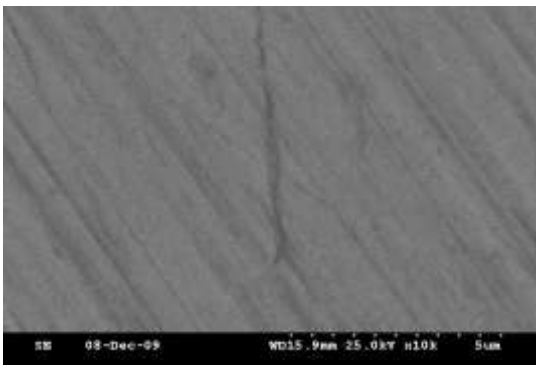
Figure 9:Polished mild steel surface   **Figure10: SEM image of mild Steel Sample exposed to 5% HCl**
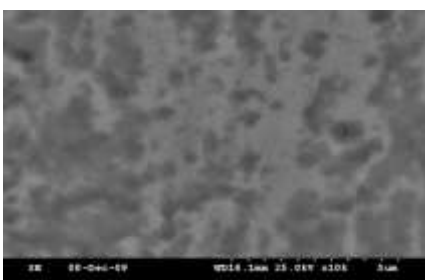
Figure11. SEM image of mild steel sample exposed to 5% HCl having 10% of *D. Lutescens* extract

Conclusion

The corrosion inhibition efficiency of *D. lutescens* extract increases along with the increase in inhibitor concentration and decreases as the temperature is raised. The inhibition efficiency is due to the adsorption of the lone pair of electrons present in the hetero atoms of the inhibitor. The inhibitor works through mixed mode of inhibition. Weight loss studies, thermodynamic analysis, adsorption studies, electrochemical measurements, IR spectral studies and SEM photographs confirm the adsorption reaction of the inhibitor on the metal surface and hence the increase in inhibition efficiency. From the above results it is concluded that *D. lutescens* extract can be used as an effective, green and alternate corrosion inhibitor for mild steel in HCl medium.

Acknowledgement

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