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Corrosion Protection of Mild Steel in Hydrochloric acid Medium by *Dalgerbia latifolia* Leaves Extract

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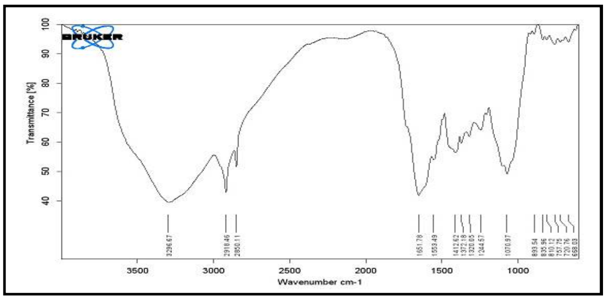
ABSTRACT

The present work is devoted to the study of Dalgerbia Latifolia (DL) leaves as green corrosion inhibitor to afford the protection of mild steel in 1N HCl medium at room temperature. The weight loss measurements, Potentiodynamic polarization, and electrochemical impedance spectrocopy revealed that inhibiting action increasedwith increasing concentration of the inhibitor. The highest inhibiton efficiency 86.67% was obtained at 10 ppm DL solution. Polarization measurements also showed that DL acts as good mixed type inhibitor. The SEM morphology of the absorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract.

Graphical Abstract



FTIR Spectra of *Dalgerbia Latifolia* leaves Extracts.

Keywords: Corrosion inhibition; EIS; Metals; SEM.

INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion can be controlled by suitable modification of the environment which in turn stifle retards or completely stop the anodic and cathodic reactions or both [1-5]. This is achieved by the use of inhibitor. The corrosion inhibition of mild steel in acidic media in the presence of various organic and inorganic compounds has been reported. Attention has been focused on the corrosion inhibiting properties of plant extracts because plant extracts serve as incredibly rich source of natural chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable sources of materials and can be extracted by simple procedures [6-9].

Many plant extracts such as *Madhuga longifolia* (Sivakumar P R 2015), have been studied for the corrosion inhibition of mild steel in acidic media. The gum extract of *Raphia hookeri* (Umoren, 2009) have also been analysed for corrosion inhibition properties [10-12]. The role of an inhibitor is to form a barrier of one or several molecular layer against acid attack. This protective action is often associated with chemical and/or physical adsorption involving in the change of the adsorbed substance and transfer of change from one phase to the other. Sulphur and/or nitrogen containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitor [13-30]. The present research work aims at establishing the effectiveness of aqueous extract of DL leaves extract of corrosion inhibitor in 1N HCl media using weight loss measurement at various time and temperature, electrochemical techniques. The influence of temperature on adsorption and inhibition efficiency has been studied.

MATERIALS AND METHODS

Preparation of leaves extract: The leaves of medicinal plants *Dalgerbia latifolia* (DL)were dried and ground nice into powder. From this, 25 g of sample was refluxed in 200ml distilled water for 3 h and kept overnight. The aqueous solution was filtered and volume was made up to in 500mL.The extract was used a corrosion inhibitor in the present study.

Preparation of mild steel specimen: Mild steel strips containing the different composition of the following materials C-0.030%, Mn-0.169%, Si-0.015%, P-0.031%, S-0.029%, Cr-0.029%, Ni-0.030%, Mb-0.016%, Cu-0.017%, and the reminder Fe, were mechanically cut into 4cm x 2 cm x 0.1 cm and were used for weight loss studies.

Weight loss methods: The polished mild steel specimens with uniform size tied and threads and immersed in 200 mL test solution absence and presence of inhibitor mild steel for 24 h. The mild steel of the specimens was washed, dried and the weight loss was calculated.

$$CR\ (mmpy) = \frac{K \times Weight\ loss}{D \times A \times t\ (in\ hours)} \quad (1)$$

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

The inhibition efficiency (%) was calculated using equation (2) respectively,

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

Where, W_0 and $W_i$are the weight loss in the absence and presence of the inhibitor.

Potentiodynamic Polarization method: Potentiodynamic polarization measurements were carried out using CHI660 electrochemical work station analyzer. The experiments were carried out in conventional three electrode cell assembly with mild steel specimen 1 cm^2 as working electrode platinum electrode was used as counter electrode and calomel electrode was used as reference electrode. The polarization was carried out from cathodic potential to anodic potential at a sweep rate of 1 mV per second.

$$IE\% = \frac{I_{Corr} - I^{*}_{Corr}}{I_{Corr}} X100 \qquad (3)$$

WhereI_{corr} and I^{*}_{corr} are corrosion current in the absence and presence of inhibitors.

Electrochemical impedance method: Experiments were carried out in three cells assembly as that used for potentiodynamic polarization studies. A plot of z' versus z'' was made.

$$C_{dl} = 1/2\pi f_{max} Rct \qquad (4)$$

Where R_{ct} is charge transfer resistance and C_{dl} is double layer capacitance.

$$IE\% = \frac{R_{ct} - R^{0}_{ct}}{R_{ct}} X100 \qquad (5)$$

Where R_{ct} and R^{0}_{ct} are the charge resistance values in the inhibited and uninhibited solution respectively.

RESULTS AND DISCUSSION

Weight loss method: The weight loss method was done with concentrations of DL extract ranging from 5 to 25 mg L^{-1} for mild steel in 1N HCl with various concentrations and the corresponding values of inhibition efficiency and corrosion rate are given in table 1.It was observed from the table that the corrosion rate decreased and thus the inhibition efficiency increases with increasing concentration of DL extract. This result indicated that DL extract could act as an excellent corrosion inhibitor.

Table 1. Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Conc. of DL Extract (mg L^{-1})	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	0.0174	-
5	0.0052	70.00
10	0.0063	63.33
15	0.0046	73.33
20	0.0034	80.00
25	0.0040	76.66

Fourier Transform Infrared (FTIR) Spectrum: FT-IR spectrum was recorded for DL leaves extract in order to confirm the presence of various compounds which contributed in effective working of the inhibitor is shown in fig.1. The free N-H stretching was observed at 3100-3500 cm^{-1}. The broad

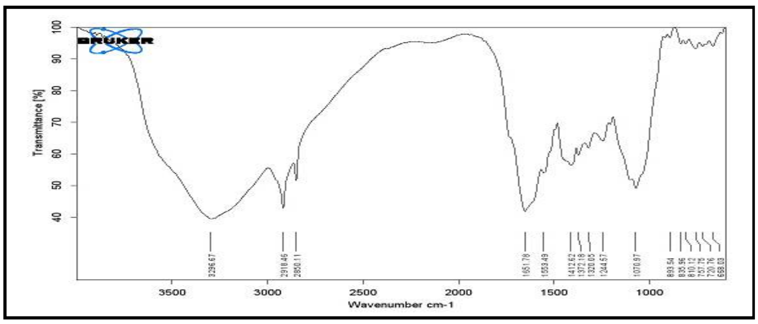


Figure 1. FTIR Spectra of *Dalgerbia latifolia* leaves Extracts.

peak obtained at 3296 cm^{-1} can be assigned to C-H stretching. Another strong peak obtained at 2918 cm^{-1} may be strong O-H stretching. Adsorption peak obtained at 2850 cm^{-1} may be due to stretching of =C-H. The strong peaks observed at 1651 cm^{-1} is attributed to C=O stretching vibration. The free N-O stretching was observed at 1515 to 1560 cm^{-1}.

Potentiodynamic polarization Studies: Current-Potential characteristics resulting from cathodic and anodic polarization curves for mild steel in 1N HCl with and without inhibitor are shown in figure 2 and data are given in table 2. It is evident from the figure that the anodic and cathodic curves for mild steel inhibited with extract were shifted towards positive potential region compared to the blank metal immersed in 1N HCl. From the table 2, it is observed that the I_{corr} values are found to decrease with increase in the inhibitor concentrations. This observation clearly showed that the inhibition of mild steel in the presence of the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors.

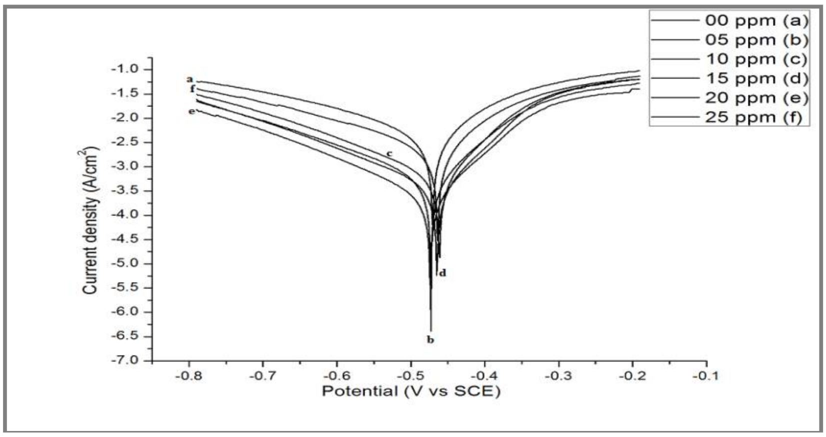


Figure 2. Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of *Dalgerbia latifolia* extracts of leaves.

Table 2. Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Conc. of DL Extract(mg L^{-1})	E_{corr} (mV) vs. SCE	I_{corr} (mA cm^{-2})	CR (mmpy)	b_c mV/dec)	b_a (mV/dec)	IE (%)
Blank	-471	5.220	0.0139	199	140	-
5	-473	0.598	0.0041	174	85	88.54
10	-461	0.723	0.0051	165	82	86.14
15	-465	0.402	0.0031	167	68	92.29
20	-474	0.256	0.0027	152	73	95.09
25	-0.464	0.281	0.0032	198	126	94.61

Electrochemical impedance spectroscopy (EIS) studies: Nyquist plots of mild steel in uninhibited and inhibited acid solution containing various concentrations of DL extract are presented in figure 3 and EIS measurements parameters derived are given in table 3. It was followed from fig.3 that the impedance of the inhibited mild steel increases with increase in the inhibitor concentration and consequently the inhibition efficiency increased. The presence of a single semicircle in the blank and for different concentrations of the inhibitor systems corresponds to the single charge transfer mechanism during dissolution of mild steel, which is unaltered by the presence of inhibitor components. All the electrochemical parameters clearly proposed that the corrosion control depends on the concentration of the inhibitor. The decreased in the C_{dl} values results from a decrease in local dielectric constant and/or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the mild steel corrosion by adsorption at the metal/acid interface.

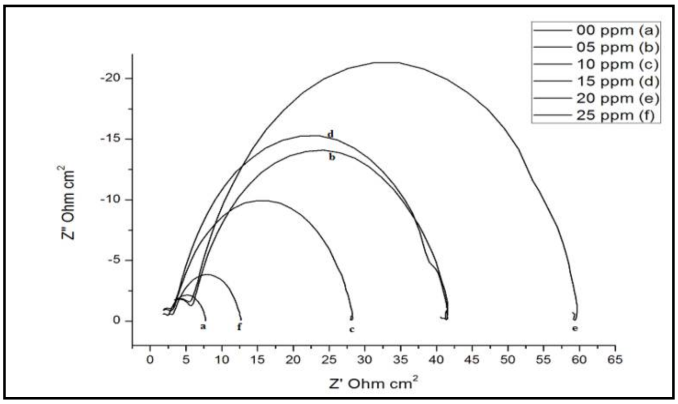


Figure 3. Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of *Dalgerbia latifolia* extract of leaves.

Table 3. Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of inhibitor.

Conc. of DL Extract (ppm)	Cdl (μF cm^{-2})	b_c (mV dec^{-1})	b_a (mV dec^{-1})	Rct (Ω cm^2)	IE (%)
Blank	1.3052x10-^{2}	199	140	5.690	-
5	2.9084x10^{-4}	174	85	38.981	85.40
10	5.8353x10^{-4}	165	82	27.603	79.38
15	2.5560x10^{-4}	167	68	40.843	86.06
20	1.2783x10^{-4}	152	73	58.037	90.19
25	4.0238 x10^{-3}	198	126	10.215	79.52

Scanning electron microscopy (SEM): SEM images for the mild steel specimens exposed to 1N HCl in the absence and presence of DL leaves extract are shown in figure 4a and b. Examination of figure 4a revealed that the specimen immersed in 1N HCl was rough and highly damaged due to the attack of aggressive acids. Figure 4b clearly showed that the mild steel surface was remarkably decreased. Therefore, smooth and much less corroded morphology of mild steel in the presence of inhibitor. The results indicate that the mild steel covered with the strong protective layer formed by inhibitor which prevents the metal from further attack of acid medium thus inhibiting corrosion [31-34].

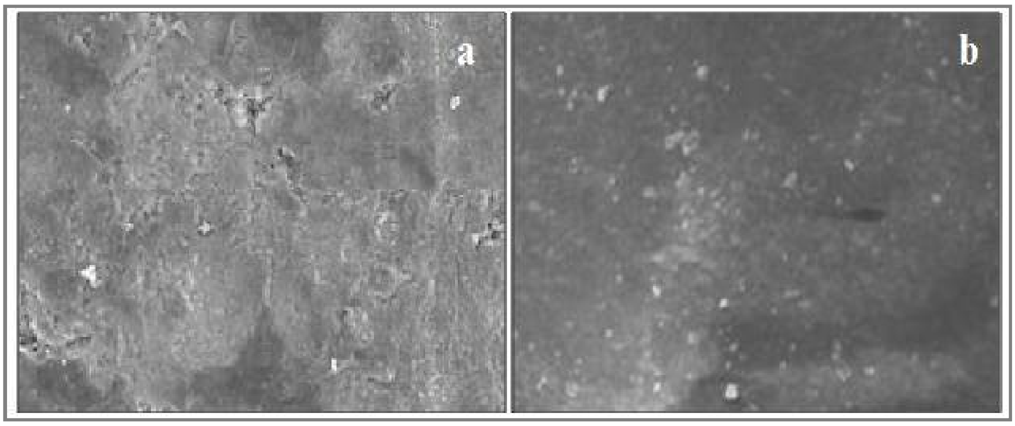


Figure 4. SEM image of the surface of mild steel after immersion for 24 h in 1N HCl solution absence (4a) and in the presence (4b) of optimum concentration of the *Dalgerbia latifolia* plan Leaves extracts.

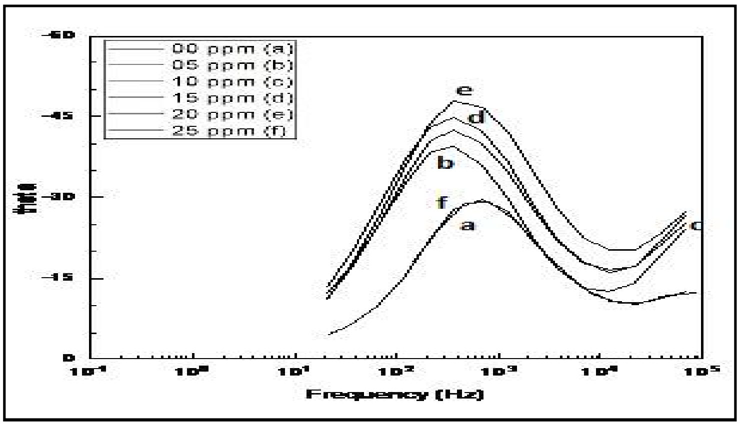


Figure 5. Bode plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of *Dalgerbia latifolia* leaves extract.

Bode plots of mild steel in uninhibited and inhibited acid solution containing various concentrations of DL leaves extract are presented in figure 4. It is apparent that the mild steel specimens with DL leaves extract showed increase in maximal phase angle value, which indicated that inhibition property on the surface mild steel.

Phytochemical screening method: Phytochemical screening of the aerial parts of plant's powder (aqueous) extract was tested in order to find the presence of various chemical constituent included Alkaloids, Carbohydrates, Proteins, Glycoside, Flavonoids, Tannins, Phenolic compounds and the results are listed in table 4.

Table 4. Phytochemical screening test of extract of *Dalgerbia latifolia*

S.No	Phytochemical Test	Aqueous extract of *Dalgerbia latifolia*
1	Alkaloids	-
2	Carbohydrates	+
3	Proteins	-
4	Glycoside	+
5	Flavonoids	+
6	Tannins	-
7	Phenolic compounds	+

+ is Present, - is absent

Effect of immersion time: The variation of inhibition efficiency for different concentration of plant extract of DL was listed in the table 5. Maximum inhibition efficiency for 1N HCl was found to be96.12 % at 24 h with 25 mg L^{-1} concentration of the inhibitor respectively.

Table 5. Inhibition efficiency as a various immersion time

Concentration of *Dalgerbia latifolia* Extract (ppm)	IE (%)				
	1h	3h	5h	7h	24h
5	60.37	56.15	65.14	78.00	83.30
10	78.89	62.39	76.22	83.36	83.72
15	88.92	72.97	82.14	89.75	92.73
20	89.56	80.16	87.15	91.00	94.82
25	90.02	83.56	89.17	93.16	96.12

Effect of temperature: To assess the effect of temperature on corrosion and corrosion inhibition process, gravimetric experiments were performed at different temperature (303-323K) in the absence and presence of various concentration of the inhibitor during 3 h of immersion. The results are given in table 6.

Table 6. The Percentage inhibition efficiency of *Dalgerbia latifolia* Plants at various temperatures

Concentration of *Dalgerbia latifolia* Extract (ppm)	IE (%)		
	303K	313K	323K
5	49.40	44.90	42.00
10	62.50	57.57	47.09
15	72.90	70.62	69.86
20	75.18	77.89	75.66
25	76.65	81.16	76.89

Adsorption isotherm: The adsorption isotherm is processes which are used to investigate the mode of adsorption and its characteristic of inhibitor on the metal surface. In our present study the Temkin adsorption isotherm is investigated. The straight line in fig.6 clearly indicated that the inhibitor obey Temkin adsorption isotherm (figure 6).

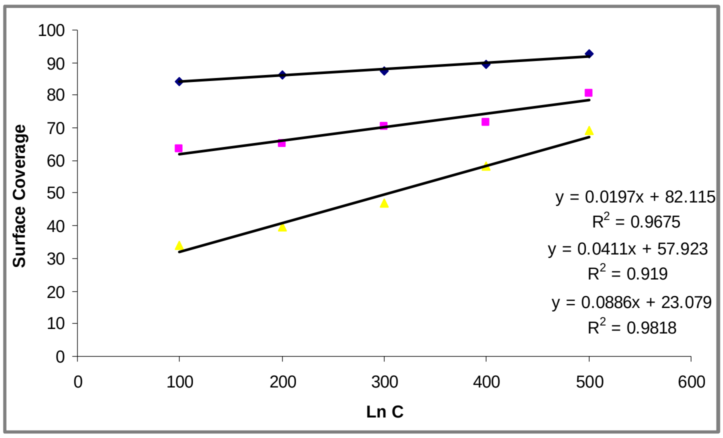


Figure 6. Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration of the extract.

APPLICATION

The ZJ leaves extract exhibit excellent corrosion resistance to the mild steel in HCl medium. The ZJ inhibitor that has little or no impact on the environment i.e. the inhibitor is Ecofriendly, safe and some extent good corrosion resistance with temperature. Therefore this inhibitor can be used for the corrosion protection of mild steel in acid medium for various industries.

CONCLUSION

The inhibition efficiency is increase with increasing inhibitor concentration. Potentiodynamic polarization studies reveal that *Dalgerbia latifolia* Leaves extract act as a mixed type inhibitor. Electrochemical impedance measurements indicate the formation of a protective film on the mild steel surface in hydrochloric acid solution. SEM results clearly indicates that the presence of a protective surface layer on the mild steel surface. The adsorption fits well to the Temkin adsorption isotherm model. The results suggest that *Dalgerbia latifolia* leaves are a corrosion inhibitor for mild steel in HCl and they can be used to replace toxic and non-biodegradable inhibitors.

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