



CORROSION STUDIES WITH *ANTIGONON LEPTOPUS* IN 1 M HCl

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ABSTRACT

The inhibition efficiency of an acid extract of *Antigonon leptopus* (AL) used as corrosion inhibitor for mild steel in 1 M HCl medium is inspected by weight loss, temperature and electrochemical studies in the presence and absence of extract. The polarization studies reveal that this AL extract as a good mixed type inhibitor. Thermodynamic parameter such as free energy value was negative, that indicates spontaneous adsorption of inhibitor on mild steel (MS). The *Antigonon leptopus* extract obeys Langmuir and Temkin adsorption isotherm. FTIR spectra revealed that the protective film formed between the active principle of the AL extract and Fe²⁺. All the reported *Antigonon leptopus* extract was found to inhibit the corrosion of mild steel in HCl acid media.

Key words: *Antigonon leptopus*, Mild steel, Langmuir, Temkin and polarization studies.

INTRODUCTION

Corrosion is the destruction of the metal by the chemical reaction with its environment. Corrosion is a serious problem in all fields where metals are used. The loss of metal resources whose abundance is limited, is cumulative and poses a danger to conservation and serious economic problem. There are several methods to effectively control and minimize corrosion. The industries give more preference to use the mild steel because of easy availability and fabrication of machineries. When it comes in contact with acid, it would be corroded. HCl acid has been widely used in pickling and descaling operations in industries. The prevention of corrosion is better than elimination. Corrosion can be play down by using various method such as coating, making alloy, adding inhibitor etc. The organic compounds having π electrons rich in hetero atoms N, O and S, which help

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to reduce the corrosion¹. The natural corrosion inhibitors are widely used to control the corrosion process². Hydrochloric acid extract of *AL* was subjected to preliminary phytochemical analysis for the detection of constituent such as alkaloid, glucoside falavanoid, carbohydrate and sponin³. Hence, the acid extract of *AL* are done with the aim of finding out cost effective bio products, which could be used as corrosion inhibitor for mild steel.

EXPERIMENTAL

Methods and materials

Preparation of plant extract

The *AL* leaves were collected, washed by water and then the leaves were shade dried and ground to fine powder. It is stored in clean closed container. The mixture of 5 g *AL* powder and 100 mL 1 M HCl was taken in RB flask and refluxed for 3 hrs and parting it overnight. Next day, it was filtered and the filtrate stored in clean standard flask.

Specimen preparation

The rectangular mild steel strips of size 2 cm × 5 cm × 0.2 cm is cut from a large MS sheet and holes are drilled on the top of MS coupons, numbered by punching. During the study, the specimens were mechanically polished to mirror finish and degreased by acetone, washed with distilled water, finally air dried with filter paper and stored in desiccators for further use.

Weight loss measurements

The MS specimens were pre-weighed and suspended with the help of glass hook in 100 mL of each of 1 M HCl solution with and without different concentration of inhibitor at different time intervals and temperature. After the exposure period, the specimen were removed, dried and weighed. From the before and after immersion weight of the mild steel, the weight loss, inhibition efficiency (IE), surface coverage (θ) and corrosion rate were determined.

The various constraints :

Concentration of the inhibitors: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 (% v/v)

Immersion time intervals: 0.5, 2, 4, 6, 8 and 24 hrs

Temperature: 303 K, 313 K, 323 K, 333 K and 343 K

The inhibition efficiency was calculated using the following formula.

$$IE (\%) = \frac{W_U - W_I}{W_U} \times 100 \quad \dots(1)$$

W_U – weight loss in the absence of inhibitor

W_I – weight loss in the presence of inhibitor

Determination of corrosion rate

In this present study, the rate of dissolution of metal (CR) is expressed in American units, mpy (mils per year). The corrosion rate was calculated using the following expression (Eq. 2).

$$\text{Corrosion rate (CR)} = \frac{534 \times W}{DAT} \text{ mpy} \quad \dots(2)$$

Where, mpy - mils per year, W - Weight loss in mg, D - Density in g/cm² (7.9 g/cm² for mild steel), A - Area in square inch and T - immersion time in hours.

Determination of activation energy (E_a)

The Arrhenius plot obtained for the plot of log CR Vs 1/T with slope equal to $E_a/2.303 R$. Thus the E_a values can be calculated from the slope of the Arrhenius plot by using the equation⁴,

$$E_a = -2.303 R \times \text{slope} \quad \dots(3)$$

Where, E_a is the activation energy, T is the absolute temperature and R is the universal gas constant.

Electrochemical method

The Electrochemical measurements were carried out in a conventional three electrode cell consisting platinum electrode as auxiliary electrode, saturated calomel electrode (SCE) as reference electrode and mild steel as working electrode. The three-electrode set up was immersed in 1M HCl acid solution in the absence and presence of inhibitor at room temperature.

Tafel method

$$IE\% = \frac{I_{\text{corr}}(b) - I_{\text{corr}}(I)}{I_{\text{corr}}(b)} \times 100 \quad \dots(4)$$

Where, $I_{\text{corr}}(I)$ and $I_{\text{corr}}(b)$ are Corrosion current with and without inhibitor.

LPR method

$$IE\% = \frac{[R_p(b) - R_p(I)]}{R_p(b)} \times 100 \quad \dots(5)$$

Where, $R_p(I)$ and $R_p(b)$ – Resistant polarization with and without inhibitor.

Surface analysis

Surface characterization by SEM, energy dispersive X-ray study and FTIR

Scanning electron microscopy was used to study the morphology of corroded mild steel surface in 1 M HCl in the presence and absence of inhibitor. The mild steel specimens, immersed in acid solutions in the presence and absence of inhibitor for 4 hr at room temperature were taken out washed carefully with doubly distilled water and dried. Then the surfaces were analyzed by using Shimadzu FTIR, energy dispersive X-ray fluorescence spectrometer and photographed at appropriate magnification.

RESULTS AND DISCUSSION

Preliminary phytochemical screening of 1 M HCl extract of *Antigonon leptopus*

The results of the preliminary phytochemical screening are given in Table 1. The extract was found to contain alkaloids, terpenoids, flavanoids, glycosides, steroids and saponins⁵.

Table 1: Preliminary phytochemical screening of HCl extract of AL

Plant	AL
Tannins	-
Alkaloids	+
Triterpenoids	+
Glycosides	+
Flavanoids	+

Cont...

Plant	AL
Saponins	+
Anthraquinones	-
Steroids	+
Lignin	-

Note: (+) - presence and (-) - absence

Weight loss measurements

Effect of concentration of inhibitor and time of immersion

Table 2 represents the corrosion rate of mild steel specimen in 1 M HCl in the presence of different concentrations of AL extract, for different immersion periods at room temperature. The maximum inhibition efficiency of 96.0% was noticed at a concentration 0.7% of the inhibitor at 4 hrs in 1 M HCl medium. Since more adsorption takes place on the metal surface, the inhibitor efficiency increases with an increase in immersion time and after reached 4 hrs did not cause any appreciable change in the performance of the inhibitor⁶ (Fig. 1).

Table 2: Influence of concentration of AL extract on the corrosion of MS in 1 M HCl

Inhibitor conc. (%v/v)	1/2 hr		2 hrs		4 hrs		6 hrs		8 hrs		24 hrs	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	111.45		172.75		278.6		293.49		300.92		303.38	
0.1	64.86	41.8	58.51	66.1	52.9	81.0	86.00	70.7	130.54	56.6	138.85	54.2
0.2	60.18	46.0	50.71	70.6	47.9	82.8	68.73	76.6	119.81	60.2	129.42	57.3
0.3	53.50	52.0	47.37	72.6	41.8	85.0	59.25	79.8	103.09	65.7	119.62	60.6
0.4	49.04	56.0	40.68	76.5	33.7	87.9	52.57	82.1	97.05	67.8	111.45	63.3
0.5	42.35	62.0	30.09	82.6	25.1	91.0	45.51	84.5	79.45	73.6	101.23	66.6
0.6	33.01	70.4	19.50	88.7	18.9	93.2	32.51	88.9	61.58	79.5	85.45	71.8
0.7	27.86	75.0	11.15	93.5	11.1	96.0	21.92	92.5	52.98	82.4	72.02	76.3
0.8	31.21	72.0	16.72	90.3	14.8	94.7	25.45	91.3	54.61	81.9	84.52	72.1
0.9	31.65	71.6	17.83	89.7	15.88	94.3	25.82	91.2	55.52	81.6	89.16	70.6

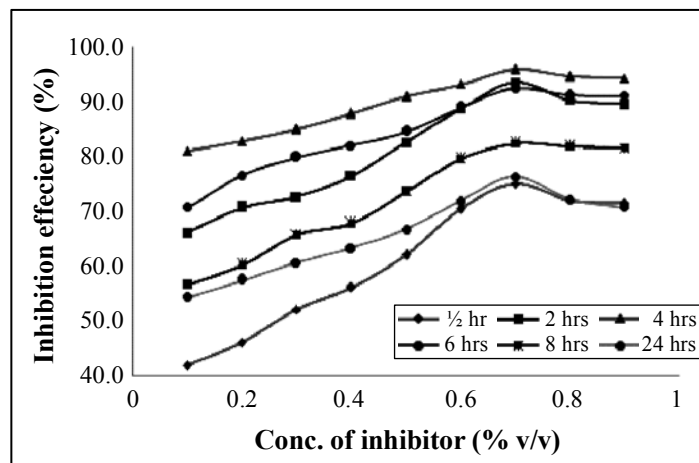


Fig. 1: Inhibition efficiency of AL extract on mild steel in 1 M HCl for different immersion periods, at room temperature

Effect of temperature

The influence of temperature on acid extracts of AL in 1 M HCl was investigated in the temperature range, 303 K - 343 K, for 1/2 an hour of immersion and the results are presented in Table 3. Analysis of the data indicates that, it can be inferred that the protective layer formed on MS surface, due to adsorption of plant extract, was stable up to 323 K and after that there may be desorption of plant extract^{7,8} at 333 K.

Table 3: Effect of temperature on the corrosion of MS in the presence of various concentration of AL extract in 1 M HCl

Inhibitor conc. (%v/v)	303 K		313 K		323 K		333 K		343 K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	111.45		267.48		780.15		1136.79		1225.95	
0.1	64.86	41.8	122.60	54.2	267.48	65.7	423.51	62.7	512.67	58.2
0.2	60.18	46.0	104.54	60.9	200.61	74.3	402.78	64.6	468.09	61.8
0.3	53.50	52.0	85.15	68.2	176.09	77.4	289.77	74.5	423.51	65.5

Cont...

Inhibitor conc. (%v/v)	303 K		313 K		323 K		333 K		343 K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
0.4	49.04	56.0	57.73	78.4	144.89	81.4	227.36	80.0	378.93	69.1
0.5	42.35	62.0	45.69	82.9	113.68	85.4	176.09	84.5	312.06	74.5
0.6	33.01	70.4	40.12	85.0	60.18	92.3	131.51	88.4	222.90	81.8
0.7	27.86	75.0	21.40	92.0	22.29	97.1	66.87	94.1	156.03	87.3
0.8	31.21	72.0	22.29	91.7	40.12	94.9	102.09	91.0	182.78	85.1
0.9	31.65	71.6	26.75	90.0	44.58	94.3	122.60	89.2	200.61	83.6

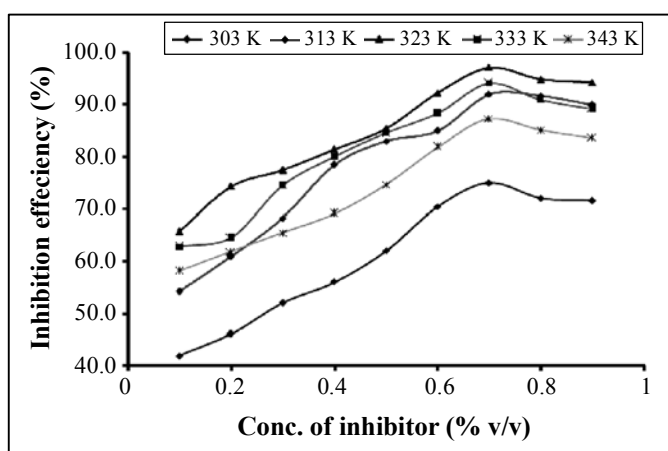


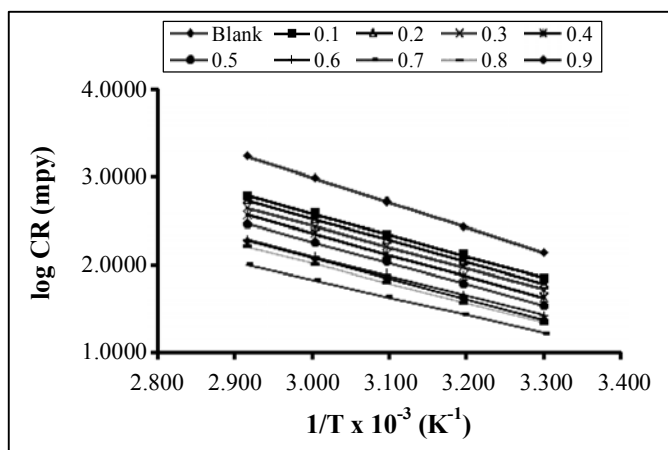
Fig. 2: Variation of inhibition efficiency of *AL* extract, at different concentrations, on mild steel in 1 M HCl at different temperatures

Thermodynamic consideration

Figure 3 shows Arrhenius plot of the corrosion rate of mild steel in 1 M HCl in the presence and absence of *AL* extract at different temperatures. From the Table 4, it is evident that the E_a value decrease with an increase in inhibitor concentration indicates that the inhibitory action of on mild steel in 1 M HCl occurs via chemical adsorption^{9,10}. The negative value of free energy of adsorption (ΔG_{ads}) indicates the spontaneous adsorption of the inhibitor on MS^{11,12}. The positive values of enthalpy indicate the endothermic reaction suggesting that a high temperature favours the complexation process and the same is in good agreement with the increasing stability with temperature¹³.

Table 4: Thermodynamic data for mild steel in 1 M HCl in the presence and absence of acid extract of AL at 303 K to 343 K

Conc. (%)	E_a KJ/mol	- (ΔG) (KJ/mol)					(ΔH) KJ/mol	- (ΔS) KJ/mol
		303 K	313 K	323 K	333 K	343 K		
Blank	54.52	-	-	-	-	-		
0.1	46.73	15.06	16.86	18.69	18.91	18.38	10.53	0.0870
0.2	47.27	13.75	15.77	17.93	17.21	16.89	8.62	0.0772
0.3	46.41	13.33	15.54	17.31	17.40	16.20	8.56	0.0759
0.4	47.08	13.01	16.17	17.19	17.47	15.86	6.65	0.0700
0.5	46.00	13.07	16.34	17.37	17.71	15.99	7.15	0.0720
0.6	42.95	13.56	16.83	18.80	18.14	16.67	9.44	0.0809
0.7	38.71	13.76	17.71	21.19	19.76	17.41	12.23	0.0935
0.8	43.35	13.04	17.25	19.19	18.13	16.54	8.60	0.0787
0.9	44.82	12.69	16.42	18.57	17.24	15.90	7.23	0.0724

**Fig. 3: Arrhenius plot for the dissolution of mild steel in 1 M HCl with and without inhibitor**

Adsorption consideration

Since corrosion inhibition is related to the adsorption of the inhibitor molecules on

the metal surface, the surface coverage θ of the adsorption process was calculated using the equation:

$$\theta = IE/100 \quad \dots(6)$$

In order to find out the adsorption isotherm for the current study, attempts were made to fit the data with various isotherms viz, Langmuir, Temkin and Freundlich isotherms give the best fit with the correlation co-efficient almost near to unity.

Thus a plot of C/θ and C should be a straight line. Indeed, a straight line was obtained and shown in Figs. 4 & 5 with almost unity slope. This is indicative the adsorption follows Langmuir adsorption isotherm. Langmuir adsorption isotherm could be represented as –

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \dots(7)$$

A plot of $\log C$ vs. θ also furnishes a straight line indicating that it obeys Temkin adsorption isotherm and the behaviour of adsorption is affected by the heterogeneity of the electrode surface.

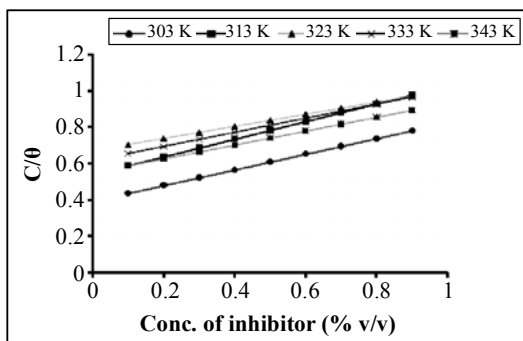


Fig. 4: Langmuir adsorption isotherm plot for the different concentrations of AL extract on the mild steel in 1 M HCl

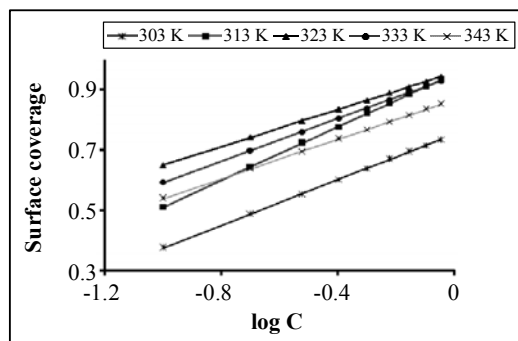


Fig. 5: Temkin adsorption isotherm plot for the different concentrations of AL extract on the mild steel in 1 M HCl

Electrochemical method

Tafel polarization studies

Polarization parameters are presented in Table 5. From the table, it can be seen that as the concentration of the AL extract increases, the value of I_{corr} decreases. This indicates

the *AL* extract is mixed type inhibitor¹². The values of Tafel slopes “ b_a ” and “ b_c ” vary with increase in concentration of the *AL* extract. Increase in R_p values with increase in concentration of extract revealed that the inhibition process takes place by adsorption of the extract on the MS surface. From Fig. 6, it is observed that *AL* extract behaved as a mixed type of inhibitor.

Table 5: Electrochemical polarization (Tafel) parameters for the corrosion of mild steel in 1 M HCl containing with and without *AL* extract

Con. (%)	$-E_{\text{corr}}$ (mV)	I_{corr}		b_a (mV/dec)	b_c (mV/dec)	R_p	
		(mA/cm ²)	IE (%)			(Ωcm^2)	IE(%)
Blank	502.9	0.412	-	83	125	67.03	-
0.2	480	0.220	46.71	68	146	117	42.71
0.4	475.9	0.150	63.72	65	141	165	59.38
0.7	471.8	0.111	73.13	64	138	219.6	69.48

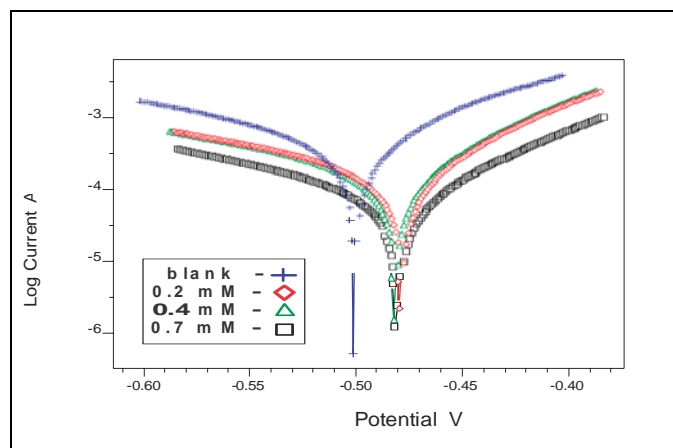


Fig. 6: Potentiodynamic polarization curves for mild steel in 1M HCl in the absence and presence of different concentrations of *AL* extract

Electrochemical impedance measurement

The impedance parameters for mild steel in 1 M HCl with and without *AL* extract is given in Table 6. It is observed that the charge transfer resistance (R_{ct}) values are increased and double layer capacitance (C_{dl}) the values are decreased with the increase in *AL* extract

concentrations. The decrease in C_{dl} values indicates that the adsorption of phytochemical constituents in the acid extracts of *AL* on the mild steel surface. Decrease in C_{dl} , which can result from a decrease in local dielectric constant and an increase in the thickness of the electrical double layer, suggests that the inhibitor functions by adsorption at the metal-solution interface.

Table 6: Electrochemical impedance parameters for mild steel in 1 M HCl containing different concentrations of extract

Conc. (%)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} $\mu\text{F}/\text{cm}^2$	IE (%)
Blank	25.66	53.14	-
0.2	59.05	61.16	56.55
0.4	75.68	62.93	66.10
0.7	109.74	60.99	76.62

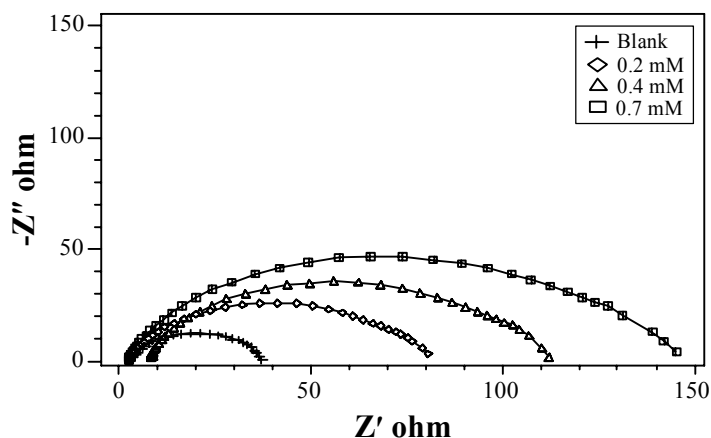


Fig. 7: Impedance diagram for mild steel in 1 M HCl in the presence and absence of different concentrations of *AL* extract

Characterisation of *AL* extract by FTIR spectrum

The FTIR spectrum of powder of *AL* (Fig. 8) shows a strong absorption band at 3599 and 3516 cm^{-1} indicating the presence of $-\text{OH}$ group. The bands at 2929 and 2924 cm^{-1} indicate the presence of Ar-H stretching. The peak at 1657 and 1264 cm^{-1} indicates the presence of hydrogen bonded $\text{C}=\text{O}$ group. The peak at 1346 cm^{-1} indicates the presence of N-O group. An absorption band in the region 1600-1430 cm^{-1} indicates the presence of a

C=C (in ring). The FTIR spectrum of *AL* residue dissolved in 1 M HCl medium (Fig. 9) shows the absorption band at 3349, 2363, 2310, 1986, 1638, 1515, 1365, 1276, 1218, 1144, 1068, and 540-651 cm^{-1} indicating the presence of NH, OH group of polyhydric phenol, C=O, CN, tri-substituted benzene and C-OH, respectively.

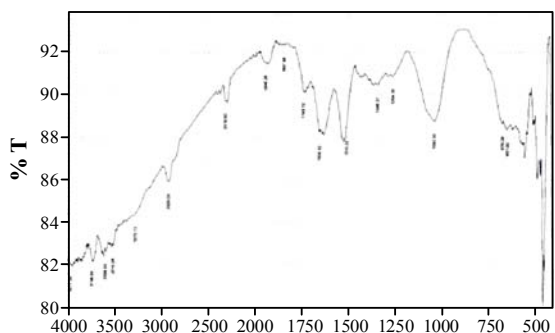


Fig. 8: FTIR spectrum of *AL* plant

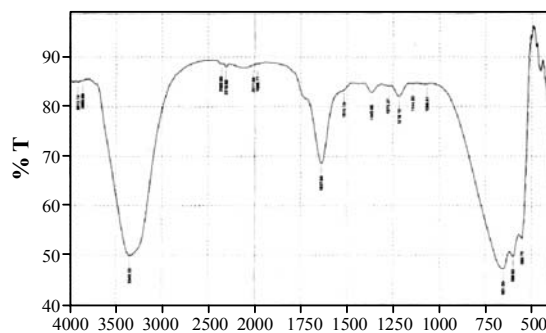


Fig. 9: FTIR spectrum of HCl extract of *AL* plant

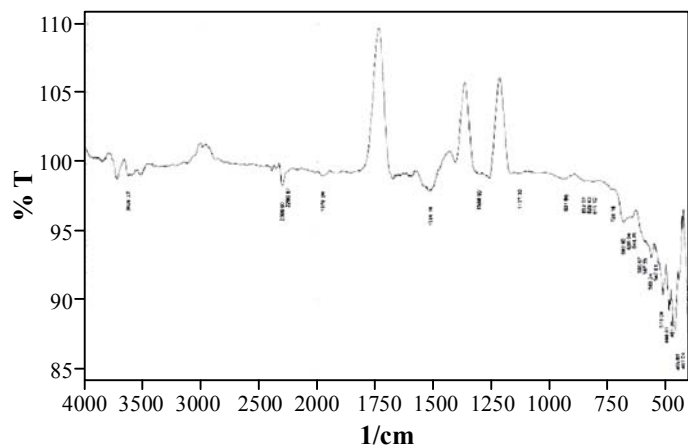


Fig. 10: FTIR spectrum of mild steel immersed in 1 M HCl containing 0.7% of *AL* extract

Morphology examination of mild steel with extract

The SEM photographs for polished mild steel, MS in blank 1 M HCl and acid containing 0.7% *AL* extract after 6 hrs immersion is given in Figs. 11 & 12. It is seen from the photographs that the attacks in presence of *AL* extract in 1 M HCl is less in comparison with the blank acid.

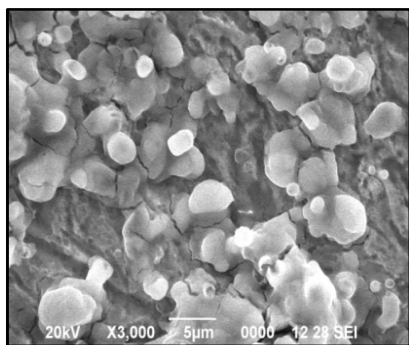


Fig. 11: SEM photograph of MS immersed in 1 M HCl

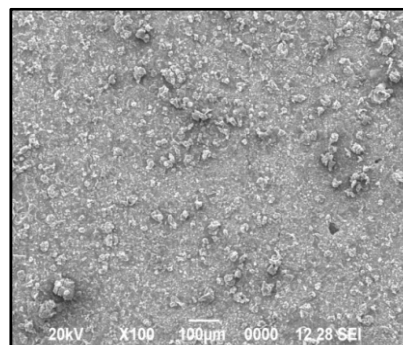


Fig. 12: SEM photograph of MS immersed in 1 M HCl containing 0.7% of AL extract

Energy-dispersive X-ray spectroscopy

The EDX spectrum in Fig. 13 shows the characteristics peaks of some of the elements constituting the polished mild steel surface. Fig. 14 & 15 presents the EDX spectra for the samples in the absence and presence of optimum concentration of AL. In Fig. 14 & 15, the decreasing of the Fe band indicates the strongly adherent protective film of inhibitor formed on the polished mild steel surface, which leading to a high degree of inhibition efficiency. The oxygen signal is due to the mild steel surface exposed to the formation water in absence of inhibitor. This indicates that the inhibitor molecules are adsorbed on the mild steel surface and hence protect the mild steel surface against corrosion¹⁴.

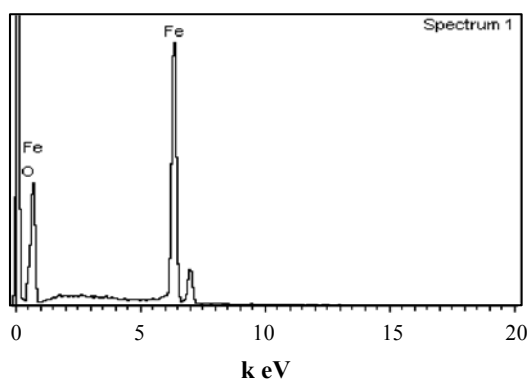


Fig. 13: EDX spectrum of polished mild steel

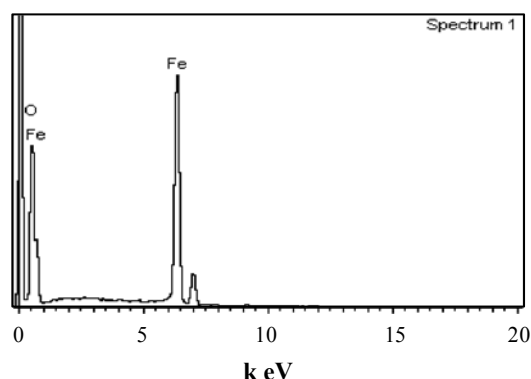


Fig. 14: EDX spectrum of mild steel immersed in 1 M HCl

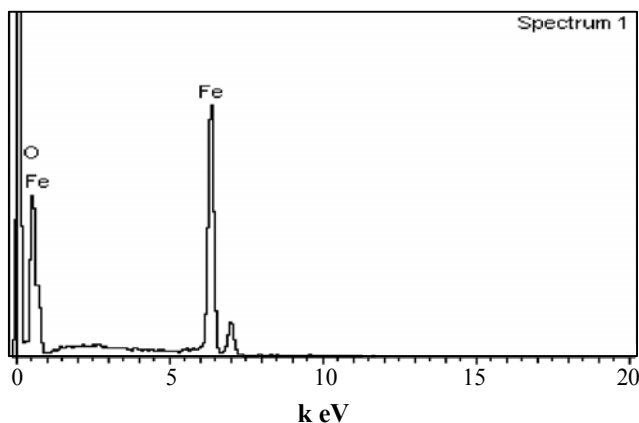


Fig. 15: EDX spectrum of mild steel immersed in 1 M HCl containing 0.7% of AL extract

CONCLUSION

The inhibition efficiency increased and corrosion rate decreased with the increasing concentration of inhibitor. The maximum inhibitor efficiency of 96% was observed at an optimum concentration of 0.7% v/v at 6 hours of immersion.

Inhibition efficiency increases upto 323 K in most cases and thereafter there was no uniformity with increasing temperature indicating adsorption-desorption process.

The adsorption of AL plant extracts onto the metal surface followed Langmuir and Temkin adsorption isotherms in 1 M HCl acid media with a correlation coefficient greater than 0.9.

The results of potentiodynamic polarization measurements revealed that the extracts of AL act as a mixed type of inhibitor.

Surface studies involving SEM and EDX confirmed the efficiency of the plant extract as corrosion inhibitor for mild steel.

Data obtained from the weight loss method and electrochemical measurements have shown that the AL extract has excellent inhibiting properties for mild steel in acid.

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REFERENCES

1. M. R. Singh and G. Singh, J. Mater. Environ. Sci, **3(4)**, 698-70 (2012).
2. K. Olusegun and A. O. Abiola James, Corros. Sci., **52**, 661-664 (2010).
3. Naga Deepthi Bolla and P. K. Bhogavalli, Arch. Appl. Sci. Res., **1(4)**, 229-233 (2010).
4. S. K. Therese and V. G. Vasudha, Chem. Sci. Rev. Lett., **2(6)**, 498-506 (2014).
5. J. M. Antonisamy, J. S. Aparna, S. Jeeva, S. Sukumaran and B. Anantham, Asian Pacific J. Tropical Biomedicine, S79-S82 (2012).
6. J. Rosaline Vimala, A. Leema Rose and S. Raja, Int. J. Chem. Tech. Res., **4**, 1791-1801 (2011).
7. V. G. Vasudha and P. K. Shanmuga, Res. J. Chem. Sci., **3**, 21-26 (2013).
8. M. Znini, L. Majidi, A. Bouyanzer, J. Paolini, J.-M. Desjobert, J. Costa and B. Hammouti, Arabian J. Chem., **5**, 467-474 (2012).
9. T. H. Ibrahim and M. A. Zour, **6**, 6442-6455 (2011).
10. K. Anbarasi and V. G. Vasudha, J. Environ. Nanotechnol, **3**, 16-22 (2014).
11. S. A. Aghaward, J. Basrah Researches (Sciences), **38**, 4-A (2012).
12. R. Salghi, A. Anejjar, O. Benali, S. S. Al-Deyab, A. Zarrouk, C. Jama and B. Hammouti, Int. J. Electrochem. Sci., **9**, 5315-5327 (2014).
13. J. Rosaline Vimala, A. Leema Rose and S. Raja, Int. J. Chem. Tech. Res., **3(3)**, 602-612 (2012).
14. M. H. Hussin and M. J. Kassim, J. Phys. Sci., **21(1)**, 1-13 (2010).
15. S. Aejitha and P. K. Kasthuri, Int. J. Sci. Res., **3(9)**, 607-611 (2014).

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