Investigation of Anti-Corrosive Effects of Lebbeck Seed Extract On Aluminum in Acid Environment.

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ABSTRACT

The inhibition and adsorption properties of alcoholic extract of *Albizia lebbeck* seed on Aluminum in 1N Hydrochloric acid was investigated by mass loss measurement with various periods of contact and temperature ranging from 303 to 333K. The observed results revealed that the percentage of inhibition efficiency enhanced with increase of inhibitor concentration and decreased with rise in period of contact. However, in temperature variation, the inhibition efficiency decreased with increase of temperature. It clearly indicates that the inhibitor adsorbs on the metal surface by physisorption process. The thermodynamic parameters viz heat of adsorption (Q_{ads}), energy of activation (E_a) and Gibbs Free Energy (ΔG_{ads}) values have been evaluated and suggests that the adsorption process is exothermic and spontaneous. The inhibitor obeys Langmuir adsorption isotherm. The protective film formed on the metal surface may also be confirmed by spectral studies namely UV, FT-IR, EDX.

(Keywords: aluminum, aluminium, Al, corrosion, inhibition, *Albizia lebbeck* seed, mass loss, adsorption, isotherm)

INTRODUCTION

Aluminum is an important metal in many industries owing to its many excellent characteristics especially its good electrical and thermal conductivities, low density, high ductility, low cost and availability for the fabrication and construction industries. It is widely used as a material for automobiles, aviation, household appliances, containers, electronic devices, pipes, machinery, and chemical batteries [1].

The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Most of the effective and efficient chemical inhibitors are those compounds containing hetero-atoms such as oxygen, nitrogen, sulphur, and olefins which allowed adsorption on the metal surface. However, using these inhibitors for corrosion control, factors such as cost, toxicity, availability, and environmental friendliness are very important.

In recent years, most researchers are focusing on natural products as corrosion inhibitors *viz*, G*ossipium hirsutum L* [2], *Cola Acuminata* and *Camellia Sinensis [3]*, *Citrullus Vulgaris* Peel [4], *Andrographis paniculata, Jatropha curcas* [5-6], *Stevia rebaudiana [7]*, *Hibiscus sabdariffa* calyx [8], Rosemary Extract [9], Eggplant Peel [10], *Psidium guajava* [11]*, Euphorbia hirta* and *Dialum guineense* [12]*, Azadirachta Indica* [13]. In this present investigation, we study the inhibition and adsorption capability of various concentration of *Albizia lebbeck* seed (ALS) extract on the corrosion of Aluminum in 1N HCl. The effect of temperature is also observed. The formation of thin film on the metal surface may confirmed by spectral studies viz, EDX, FT-IR, UV.

MATERIALS AND METHODS

Specimen Preparation

Aluminum specimens were mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm), polished with emery wheel of 80 and 120, degreased with trichloroethylene, washed with distilled water cleaned, dried, and then stored in desiccator for the present study.

Preparation of *Albizia lebbeck* seed (ALS) Extract

Freshly available *Albizia lebbeck* seed (ALS) were dried, grinded and soaked in a solution of alcohol for about 48hrs, and then filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant seed extract was collected.

From this extract the different concentration of 100, 250, 500, 750, 1000 ppm stock solution was prepared and used throughout the present investigation. All reagents used for this present study were Analytical grade and double distilled water for their preparation.

Mass Loss Method

In mass loss measurements, specimen of Aluminum is immersed exactly in 50ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after an hour at the temperature range of 303K to 333K and after 24 to 168hrs at room temperature. From this mass loss, the corrosion rate (mmpy), percentage inhibition efficiency was calculated using the formulae:

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6 \times W}{DAT} \quad \textbf{(1)}$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3), A = Area of specimen (cm^2), T = time in hours.

$$\% IE = \frac{W_1 - W_2}{W_1} \times 100 \quad \textbf{(2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \quad \textbf{(3)}$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor, respectively.

Surface Characterization

The predominant elements present in the corrosion products was recorded by an EDX detector using a model Oxford Instrument Model - INCA Penta xFET. The change of frequency of the functional groups in the corrosion product was analyzed by FT-IR spectrum using the model Jasco/Japan**.** The UV spectrum was analyzed by the instrument Model Jasco V670**.**

RESULTS AND DISCUSSION

Effect of Immersion Time

Table 1 shows the corrosion parameters of Aluminum in 1N Hydrochloric acid containing various concentration of ALS extract with different exposure time. It reveals that the loss of mass significantly enhanced (from 150mg to 546mg) with increase of exposure time (24 hrs to 168 hrs) in inhibitor free solution. But in the presence of *Albizia lebbeck* seed (ALS) extract, the value of corrosion rate is significantly reduced from 10.1388 to 1.0138 (mmpy) for 24hrs, and 5.2722 to 1.1104 (mmpy) for 168 hrs, respectively.

The maximum of 90% inhibition efficiency is attained at 1000 ppm of inhibitor concentration at 24hrs exposure time. However it was slowly declined with rise in immersion time. This is mainly due to the presence of main phytochemical compounds namely dichlorophenolindophenol, tannins, Phenyl alanine, tyrosine which consists of π bonds, and hetero atoms such as nitrogen, oxygen in the phyto-chemical constituent in the ALS extract. 90% of surface coverage (θ) is observed due to the coordination between the Aluminum metal and the hetero atoms present in the ALS extract inhibitor

Effect on Temperature

The Table 2 reflects the corrosion parameters of Aluminum in 1N Hydrochloric acid containing various concentration of ALS extract with different temperature ranges from 303K to 333K. It is clearly indicates that the maximum of 88.39% and 79.28% is achieved at 303K and 333K, respectively. This is mainly due to the desorption of the active molecules present in the inhibitor molecules on the metal surface is more preferential than adsorption process at high temperature.

Table 1: Variation of Corrosion Parameters of Aluminum at different Concentration of Inhibitor (ALS) in 1N Hydrochloric Acid.

Time Immersion (hrs)	Concentration of Inhibitor (ppm)	Mass Loss (mg)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
24	0	150	10.1388	---
	100	32	2.1629	78.66
	250	24	1.6222	84.00
	500	19	1.2843	87.33
	750	17	1.1490	88.66
	1000	15	1.0138	90.00
48	0	222	7.2662	---
	100	54	1.8250	74.88
	250	37	1.2504	82.79
	500	33	1.1152	84.65
	750	29	0.8787	87.90
	1000	24	0.8111	88.83
72	0	286	6.4438	----
	100	74	1.6673	74.13
	250	67	1.5096	76.57
	500	62	1.3969	78.32
	750	53	1.1941	81.47
	1000	48	1.0815	83.22
96	0	326	5.5088	---
	100	99	1.6729	69.63
	250	87	1.4701	73.31
	500	71	1.1997	78.22
	750	63	1.0645	80.68
	1000	59	0.9969	81.90
120	0	368	4.9748	-----
	100	149	2.0142	59.51
	250	108	1.4600	70.65
	500	96	1.2977	73.91
	750	81	1.0950	77.98
	1000	72	0.9733	80.44
144	0	456	5.1370	---
	100	186	2.0953	59.21
	250	129	1.4532	71.71
	500	113	1.2729	75.22
	750	104	1.1716	77.19
	1000	99	1.1153	78.29
168	0	546	5.2722	----
	100	194	1.8733	64.47
	250	167	1.6126	69.41
	500	133	1.2843	75.64
	750	129	1.2456	76.37
	1000	115	1.1104	78.93

Table 2: Variation of Corrosion Parameters with Concentration of LIS Extract on Aluminum at Different Temperatures in 0.5N Hydrochloric Acid.

Temperature (K)	Concentration of Inhibitor (ppm)	Mass Loss (mg)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
303	0	13	7.2442	---
	100	5	2.7863	61.54
	200	4	2.2290	69.24
	300	4	2.2209	69.23
	400	2	1.1145	84.62
	500	1	0.5573	92.31
313	0	36	20.0610	----
	100	30	16.7170	16.66
	200	29	16.1600	19.45
	300	28	15.5300	22.59
	400	25	13.9300	30.56
	500	10	5.57250	72.22
323	0	37	20.618	-----
	100	32	17.832	13.51
	200	28	15.603	24.32
	300	25	13.931	32.43
	400	23	12.817	37.84
	500	18	10.031	51.35
333	0	43	23.9600	----
	100	25	13.9310	41.86
	200	23	12.8170	46.51
	300	18	10.0310	58.13
	400	13	07.2440	69.77
	500	9	05.0150	79.07

The value of activation energy (E_a) for the corrosion of Aluminum in the presence and absence of ALS extract is calculated using the following Arrhenius Equation (4) and its derived form (5):

$$CR = A\exp(-E_a/RT) \quad \textbf{(4)}$$

$$\log(CR_2/CR_1) = E_a/2.303R(1/T_1 - 1/T_2) \quad \textbf{(5)}$$

Where CR_1 and CR_2 are the corrosion rates of Aluminum at temperatures, T_1 and T_2, respectively. E_a is the activation energy and R is the universal gas constant.

The value of activation energy for blank (6.240kJ/mol) is lower than in the presence of ALS extract inhibitor (22.439kJ/mol). This increase of apparent activation energy for Aluminum dissolution with inhibitor may be interpreted as physical adsorption mechanism [14].

Adsorption Studies

The heat of adsorption (Q_{ads}) on Aluminum metal in the presence of inhibitor is arrived by the following Equation (6):

$$Q_{ads} = 2.303\,R\,[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad \textbf{(6)}$$

Where R is the gas constant, θ_1 and θ_2 is the degree of surface coverage at temperatures T_1 and T_2 respectively.

The observed Q_{ads} values are ranged from -07.287 to -19.241kJ/mol (Table 3). This negative value clearly indicates that the adsorption of ALS extract on the surface of Aluminum metal is exothermic. This inhibitor obeys Langmuir adsorption isotherm (Figure 1) which follows Equation 7.

Table 3: Thermodynamic Parameters for Aluminum in 1N HCl containing ALS Extract.

S. No	Conc. of Inhibitor (ppm)	% of I.E		Activation Energy (E_a) (KJ/mol)	Heat of Adsorption (Q_{ads}) (KJ/mol)
		303K	333K		
1.	0	181.69	227.11	06.240	---
2.	100	74.6222	113.55	11.740	-07.287
3.	250	71.3777	100.57	09.589	-05.742
4.	500	63.2666	90.844	10.118	-06.206
5.	750	40.5555	76.244	17.655	-15.790
6.	1000	21.0888	47.044	22.439	-19.241

Table 4: Langmuir Adsorption Parameters for the Adsorption of ALS Extract on Aluminum in 1N Hydrochloric Acid.

Adsorption Isotherms	Temperature (K)	Slope	K	R^2	ΔG_{ads} kJ/mol
Langmuir	303	0.8293	0.6056	0.9948	-08.855
	313	0.8395	0.6274	0.9955	-09.240
	323	0.7262	0.7927	0.9974	-10.163
	333	0.8218	0.6605	0.9955	-09.973

This isotherm assumed that the adsorbed molecules occupied only on one site and there was no interaction with other molecules adsorbed [15].

$$\log C/\theta = \log C - \log K \quad \textbf{(7)}$$

Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface. It reveals that there is no interaction between the adsorbate and adsorbent. The equilibrium constant of adsorption of ALS extract on the surface of Aluminum metal is related to the free energy of adsorption (ΔG_{ads}) by the following Equation (8):

$$\Delta G_{ads} = -2.303RT\log(55.5\,K) \quad \textbf{(8)}$$

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption.

The values of intercept (K) obtained from Langmuir adsorption isotherm is substituted in Equation (7) and the calculated values of ΔG_{ads} are placed in Table 4.

The negative values of ΔG_{ads} suggested that the adsorption of ALS extract on to Aluminum metal surface is a spontaneous process and the adsorbed layer is more stable one.

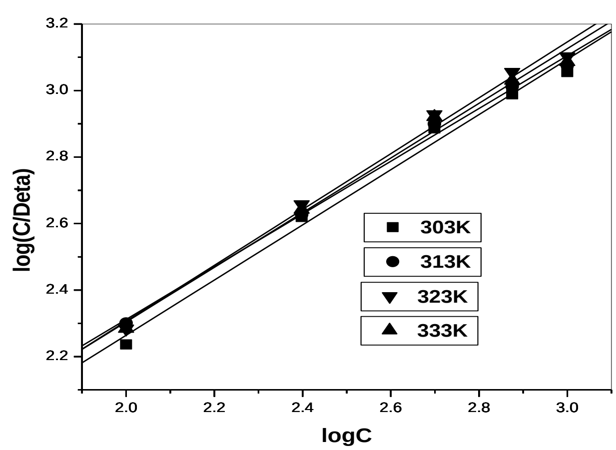

Figure 1: Langmuir Isotherm for the Adsorption of ALS Inhibitor on Aluminum in 1N Hydrochloric Acid.

MORPHOLOGY EXAMINATION OF ALUMINIUM

EDX Analysis

The protective film formed on Aluminum surface is analyzed by using EDX spectra. Figures 2 and 3 represent the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of ALS extract with 0.5N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum shows the existence of chlorine and oxygen due to the formation of chlorides and oxides of aluminum complexes.

In addition the spectrum consists of aluminum, iron, silicon which is the part of composition of aluminum metal. However, in the presence of the optimum concentrations of the inhibitors, appearance of nitrogen band is observed due to the formation of a strong protective film of the inhibitor molecules on the surface of aluminum metal. This may clearly indicates that the nitrogen atom present in the inhibitor molecules is involved in the adsorption process with metal atom and hence protects the metal surface against corrosion.

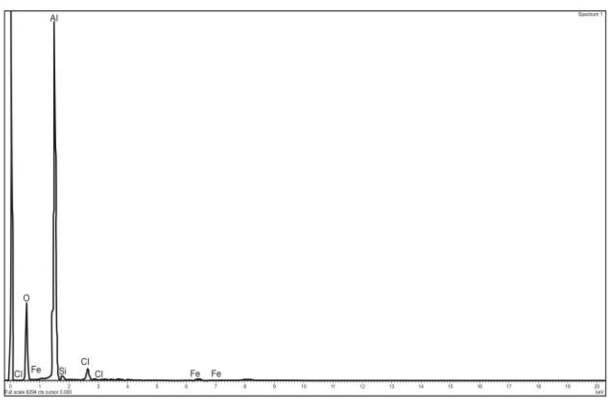

Figure 2: EDAX Spectrum of the Corrosion Product on Aluminum Surface in 1N HCl.

FT-IR Analysis

The Figure 4(a) and (b) reflects the IR spectrum of ethanolic extract of ALS and the corrosion product on Aluminum, respectively. The observed stretching frequency and the corresponding band assignment are given in Table 5.

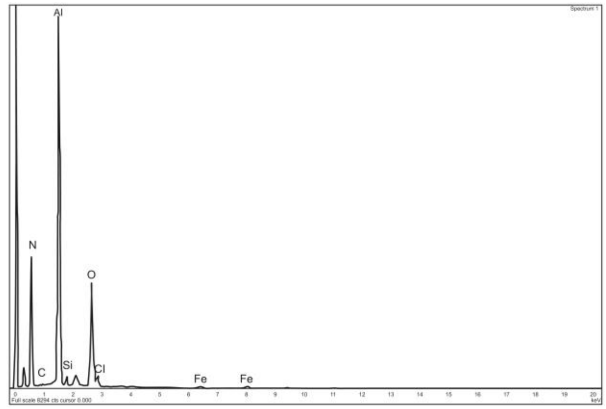

Figure 3: EDAX Spectrum of the Corrosion Product on Aluminum Surface with the Presence of ALS Extract in 1N HCl.

Table 5: IR Spectrum of the Corrosion Product on Aluminum in the presence of Ethanolic Extract of ALS as an Inhibitor in Acid Environment.

Frequency(cm^{1}) Pure extract of ALS	Frequency(cm^{-1}) Extract adsorbed on Aluminum	Band assignment
3317.64	3425.5	-OH in alcohol
1654.81	1600.25	C=C in alkene
1400.22	1492.75	C=C in aromatic ring
1122.49	1116.71	C-N in amine
----	651.75	C-Cl in chloroalkane

These shifting frequencies may suggest that the formation of barrier film on the metal surface which may confirm the co-ordination between inhibitor molecule and metal surface.

SV Spectral Analysis

Figure 5 and 6 shows that the UV visible spectrum of the corrosion product on the surface of Aluminum in the absence and presence of ALS extract in 1NHydrochloric acid environment. In the absence of inhibitor (Figure 5) three maximum absorption band around 350.5nm, 308nm and 240nm and in the presence of inhibitor three band around 340nm, 280 and 235nm are noticed. It is clearly indicates that all the adsorption bands are shifted to shorter wavelength region (i.e., Hypsochromic shift (or) Blue shift). These results reveals that the binding between the active group present in the inhibitor and the surface of the metal ion.

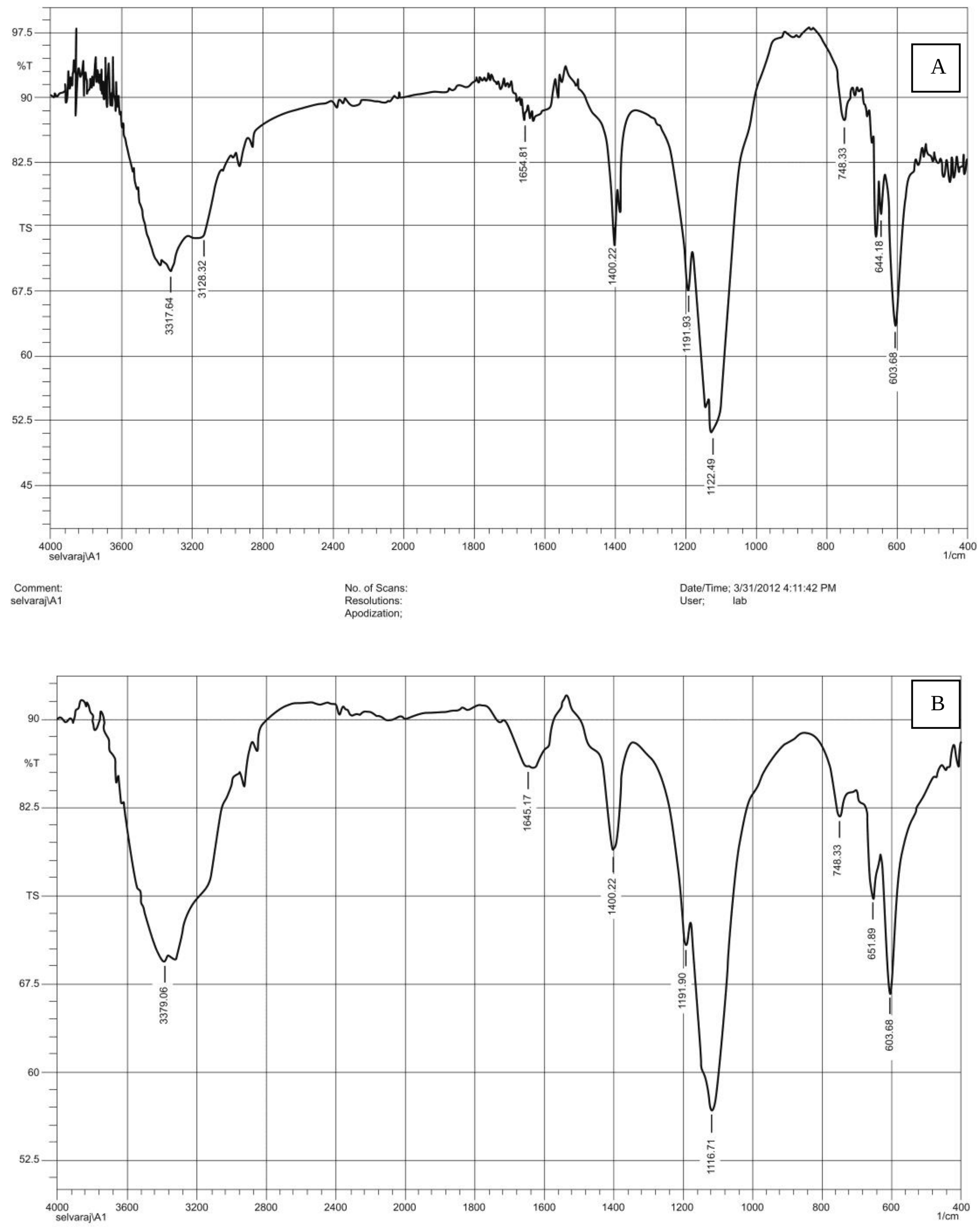

Figure 4: FT-IR Spectrum of (a) the alcoholic extract of *Albizia lebbeck* seed and (b)the corrosion product on aluminum in the presence of ALS extract with 1N Hydrochloric acid environment.

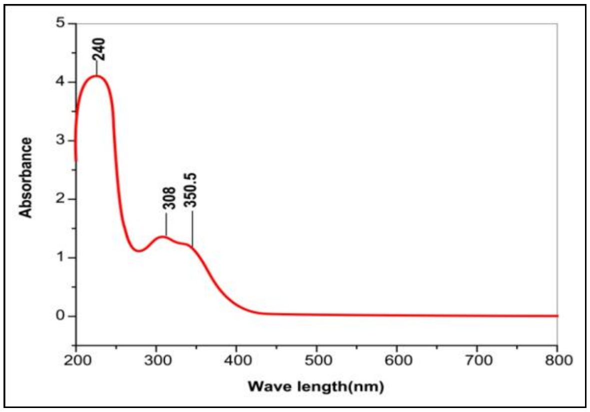

Figure 5: UV Spectrum for Corrosion Product on Aluminum with 1N Hydrochloric Acid.

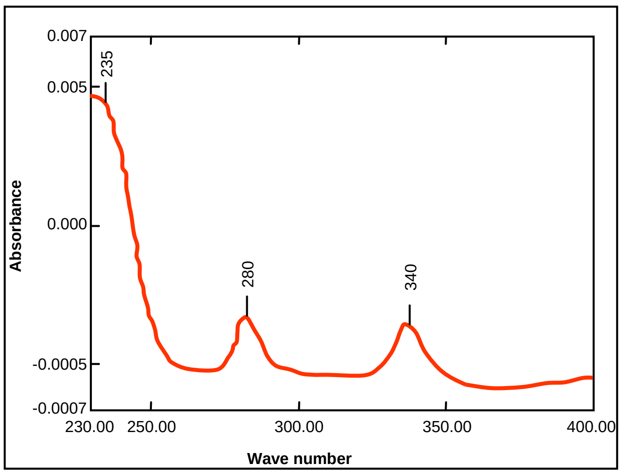

Figure 6: UV Spectrum for Corrosion Product on Aluminum in the Presence of ALS Extract with 1N Hydrochloric Acid.

CONCLUSION

Albizia lebbeck seed has been found to be a best inhibitor for Aluminum in 1N Hydrochloric acid.

The maximum inhibition efficiency attained was 90% and the corrosion resistance of the Aluminum increased with increase in inhibitor concentration.

The inhibition efficiency decreased with raise in temperature ie, 88.39% to 79.28% for 303K and 333K. This is due to the dissolution of protective film on metal surface.

The ALS inhibitor is found to obey Langmuir adsorption isotherm. It follows physical adsorption mechanism.

The adsorption process is spontaneous and exothermic.

The thin film formation on the metal surface may also be confirmed by EDX, FT-IR and UV spectral studies.

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