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INFLUENCE OF *CASSIA ALATA* LEAVES ON ALUMINIUM IN 1.0N HYDROCHLORIC ACID

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ABSTRACT

The inhibitive nature of alcoholic extract of *Cassia alata* leaves toward the corrosion of aluminum in 1N HCl was investigated by using mass loss measurement with various contact period and temperature. The observed results suggest that the percentage of inhibition efficiency is enhanced with increase of inhibitor concentration and temperature. In temperature studies, the adsorption of inhibitor on the metal surface takes place through chemisorptions process. The calculalated values of ΔH_{ads}, ΔG_{ads} suggests that the adsorption may be endothermic and spontaneous process. It was found out that the adsorption of CAL inhibitor follows Langmuir adsorption isotherm. Also the protective film formed on the metal surface may confirmed by UV, FT-IR and EDX spectral studies.

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Key Words:

Aluminium, Corrosion, *Cassia alata* leaves, Mass loss, Adsorption isotherm.

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1. INTRODUCTION

Aluminum and its alloys have low density, very attractive appearance, relatively good corrosion resistance, excellent thermal and electrical conductivity. Combination of these properties makes it a preferred choice for many industrial applications such as automobiles, food handling, containers, electronic devices, buildings, aviations, etc. So many attempts have been made to evaluate the corrosion inhibition by organic inhibitors in acid solutions [1]. However the use of chemical inhibitor has been found to be more expensive, highly toxic, non bio-degradable and very harmful to the living things. Hence there is a search to be need of non-toxic, eco-friendly, plenty and less expensive corrosion inhibitors. In recent years, several green inhibitors have been used and to evaluate for the prevention of corrosion by many investigators. Few of them are G*ossipium hirsutum* [2], *Cola Acuminata* and *Camellia Sinensis* [3], *Citrullus Vulgaris* Peel, *Albizia lebbeck* seed, *Hibiscus Esculenta* leaves [4-6], *Andrographis paniculata, Jatropha curcas* [7-8], *Stevia rebaudiana* [9], *Hibiscus sabdariffa* calyx [10], Rosemary Extract [11], Eggplant Peel [12]. In our contiuous research work, the influence of *Cassia alata* leaves on the corrosion of aluminium in various concentration of Hydrochloric acid have been investigated at different period of contact and temperature by using mass loss measurements and the corrosion product formed on the metal surface is analyzed and characterized by UV, FT-IR and EDX spectral studies.

2. EXPERIMENTAL DETAILS

2.1 Specimen preparation

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

2.2 Preparation of Cassia alata leaves (CAL) extract

Freshly available CAL extract were collected from the source, dried well, grinded and soaked in alcohol solvent for about 48hrs, and then filtered followed by evaporation in order to remove the alcohol completely and the pure plant alcoholic extract was collected. From this extract the different concentration (10, 50, 100, 500 and1000ppm) of stock solution was prepared and used throughout our present investigation.

2.3 Mass loss measurement

In mass loss measurement, aluminium specimen 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 323K and after 24 to 360hrs at room temperature. From this observed data, the corrosion rate (mmpy), percentage inhibition efficiency (%I.E) and surface coverage (θ) was calculated using the following formulae

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

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

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

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

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

2.4 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 analysed by FT-IR spectrum using the model Jasco/Japan**.** The UV spectrum was analysed by the instrument Model Jasco V670

3. RESULTS AND DISCUSSION

The variations of corrosion parameters with concentration of CAL extract on aluminium with different period of contact in 1N Hydrochloric acid are placed in Table-1. It reveals that the corrosion rate is decreased gradually with the adsorption of inhibitor. The maximum of 77.06% inhibition efficiency is achieved at 100ppm of inhibitor concentration even after 120hrs exposure time. However, beyond that contact period, the corrosion inhibition almost maintain even after 360hrs exposure in acid media. This is due to the co-ordination between the metal ion and lone-pair of electron in the hetero atom (oxygen and nitrogen) present in the active inhibitor molecules.

Table-1: Variation of corrosion parameters with Concentration of CAL extract on aluminium at different period of contact in 1N Hydrochloric acid

Conc.of inhibitor (ppm)	24hrs		72hrs		120hrs		168hrs		216hrs		360hrs	
	C.R	%I.E	C.R	%I.E	C.R	%I.E	C.R	%I.E	C.R	%I.E	C.R	%I.E
0	20.1426	----	7.7281	---	7.7731	----	6.0351	----	4.8851	---	4.0285	----
10	8.8546	56.0	3.3346	56.8	2.5144	67.6	1.9795	67.2	1.7267	64.6	2.5279	37.2
50	7.5703	62.4	2.9515	61.8	2.3522	69.7	1.9022	68.4	1.6652	65.9	1.2437	69.1
100	5.8806	70.8	2.7938	63.6	2.0954	73.0	1.7570	70.8	1.5669	67.9	1.2257	69.5
500	5.6102	72.1	2.2756	70.5	1.9467	74.9	1.6802	72.1	1.5362	68.5	1.2077	70.0
1000	5.1370	74.5	2.2080	71.4	1.7844	77.0	1.3905	76.9	1.4625	70.1	1.1175	72.2

Table-2 represents that the variation of corrosion parameters with various concentration of CAL extract on aluminium at temperature ranges from 303 to 323K in 1N Hydrochloric acid and the e corrosion rate decreased with increase of inhibitor concentration. The maximum of 87.67% inhibition efficiency is achieved at 323K. The value of inhibition efficiency is increased with rise in temperature. Thus, the inhibitor efficiencies is temperature dependent and it is being chemically adsorbed at higher temperatures. This is mainly due to the adsorption of active molecules on the metal surface is higher than the desorption process.

Table-2: Variation of corrosion parameters with Concentration of CAL extract on aluminium at different temperature in 1N Hydrochloric acid

Temperature (K)	**Concentration of inhibitor (ppm)**	**Mass loss (mg)**	**Corrosion rate (mmpy)**	**Inhibition efficiency (%)**
303	0	92	149.244	---
	10	46	074.622	49.99
	50	38	061.644	58.69
	100	30	048.666	67.39
	500	23	037.311	74.99
	1000	19	030.822	79.34
313	0	221	358.51	---
	10	98	158.97	55.71
	50	74	120.04	66.59
	100	67	108.68	69.76
	500	48	077.86	78.36
	1000	34	055.15	84.70
323	0	357	579.13	---
	10	135	219.00	62.18
	50	112	181.68	68.62
	100	87	141.13	75.63
	500	72	116.80	79.83
	1000	45	071.37	87.67

3.1 Adsorption isotherm

The adsorption process is influenced by the chemical structures of molecule present in CAL, the distribution of charge in molecule, the nature and surface charge of metal and the type of aggressive media. The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. In those cases, the plots of log C versus log C/ θ yield a straight line, clearly proving that the adsorption of the used inhibitors from 1N HCl solutions on the metal surface obeys the Langmuir adsorption isotherm (Fig.1) which is represented by equation (4).

$$\log C/\theta = \log C - \log K \qquad \text{--------(4)}$$

Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant from which the free energy of adsorption (ΔG_{ads}) is calculated by the following Equation (5) and the corresponding values are shown in Table-3. The negative values of ΔG_{ads} suggested that the adsorption of CAL extract onto the metal surface is a spontaneous process and the adsorbed layer is more stable.

$$\Delta G_{ads} = -2.303\ RT \log (55.5\ K) \qquad \text{-------- (5)}$$

Where R is the gas constant, T is the temperature. The above adsorption isotherm reveals that there is no interaction between the adsorbate and adsorbent

Table-3: Langmuir adsorption parameters for the adsorption of CAL extract on Aluminium in 1N Hydrochloric acid

Adsorption Isotherms	Temperature (Kelvin)	ΔG_{ads} kJ/mol
Langmuir	303	-2.337
	313	-2.852
	323	-3.444

3.2 Thermodynamics parameter

The activation energy of the corrosion reaction in the various range of temperature (303-323K) was calculated using Arrhenius equations (6) and its derived form (7)

$$CR= A\exp (-E_a/RT) \qquad \text{-------(6)}$$

$$\log (CR_2/CR_1) = E_a /2.303\ R\ (1/T_1-1/T_2) \qquad \text{------- (7)}$$

Where CR_1 and CR_2 are the corrosion rates of aluminium 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 is shown in Table-4. As can be seen from the table-3 that the E_a in the presence of inhibitor is lower than that in the absence of inhibitor. Such low activation energy indicates that there is a strong chemical adsorption between the CAL inhibitor molecules and the aluminium surfaces [13].

An alternative formula of the Arrhenius equation is the transition state equation

$$CR=RT/Nh \exp (\Delta S/R) \exp (-\Delta H/RT) \qquad \text{----- (8)}$$

where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) vs. 1000/T should give a straight line (Fig. 2) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-4. The positive value of enthalpy of activation reflects the endothermic nature of metal dissolution process meaning that dissolution of metal is difficult. The positive value of enthalpy of activation reflects the endothermic nature of aluminium dissolution process meaning that dissolution of metal is difficult. The increase of ΔS is generally interpreted by increase in disorder taking place on going from reactants to the activated complex. The positive sign of **ΔS** also interpreted with increase of disorders due to the more water molecules which can be desorbed from the metal surface by one inhibitor molecule [14].

Table-4: Thermodynamic parameters for aluminium in 1N HCl solution obtained from weight loss measurements.

S.No	Concentration of CAL (ppm)	Ea (kJ mol−1)	ΔH (kJ mol−1)	ΔS (J K−1 mol−1)
1	0	55.17	22.8953	1.64481
2	10	43.80	17.9693	4.0943
3	50	43.98	18.0095	4.1812
4	100	43.32	17.7784	4.3704
5	500	46.43	19.0893	3.9464
6	1000	34.17	13.7624	6.3353

3.3 MORPHOLOGY EXAMINATION OF ALUMINIUM

3.3.1 UV spectrum

The UV visible spectrum of ethanolic extract of CAL and the corrosion product on the surface of aluminium in the presence of CAL extract in 1N Hydrochloric acid as shown in

Figures- 3(a) and (b) respectively. In this spectrum, the two absorption bands around 260 and 362nm (Fig- 3 (a)) and two bands around 255 and 450nm (Fig-3(b)) were noticed respectively. In the presence of inhibitor one band (260nm) was shifted to lower wavelength region and another band (362nm) shifted to higher wavelength region (Bathochromic or Red shift). The change of adsorption band from the above spectrum concluded that the formation of strong co-ordination bond between the active group present in the inhibitor molecules and the metal surface.

3.3.2 FT-IR analysis

The Figure-4 and 5 reflects that the FT-IR spectrum of the ethanolic extact of inhibitor and the corrosion product on aluminium in the presence of CAL extract in 1N Hydrochloric acid. On comparing both of these spectra the prominent peak is shifted from 3317.34 to 3339.06cm^{-1} for –OH group, the frequency at 1119.93cm^{-1} is attributed to –C-O stretching in ether is shifted to 1191.90cm^{-1}, the C-N stretching frequency of amine band is shifted from 1120.56 to 1116.70cm^{-1} indicates the binding between metal atom and inhibitor takes place through nitrogen atom. The peak corresponds to 651.89cm^{-1} (Fig-5) is attributed to the C-Cl stretching frequency of alkyl halide which is due to the presence of electrolyte in the corrosion product which is disappeared in Fig-4. This observation may also confirm the formation of protective layer on the metal surface.

3.3.3 EDX spectrum

The protective film formed on Aluminium surface is analyzed by using EDX spectra. Fig.6 and 7 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CAL extract with 1N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum shows the existence of chlorine due to the formation of metal chlorides. In addition the spectrum consists of aluminium, iron, silicon which is the part of composition of aluminium metal. However, in the presence of the optimum concentrations of the inhibitor, appearance of nitrogen and oxygen elements are observed due to the formation of the strong protective film of the inhibitor molecules on the surface of metal. This clearly indicates that the nitrogen atom present in the inhibitor molecules is involved in the adsorption process with metal atom and hence it protects the metal surface against corrosion**.**

4.CONCLUSION

(1).*Cassia alata* leaves has shown excellent inhibition performance for aluminium in 0.5 M HCl
solution. The inhibition efficiency increases with the increase of concentration of inhibitor and temperature.
(2).The adsorption of the CAL inhibitor on the aluminium surface in 1N HCl obeys the Langmuir adsorption isotherm and exhibits strong chemisorptions. The adsorption process is a spontaneous and endothermic process accompanied by an increase in entropy.
(3).The thin film formation on the metal surface may also be confirmed by EDX, FT-IR and UV spectral studies.

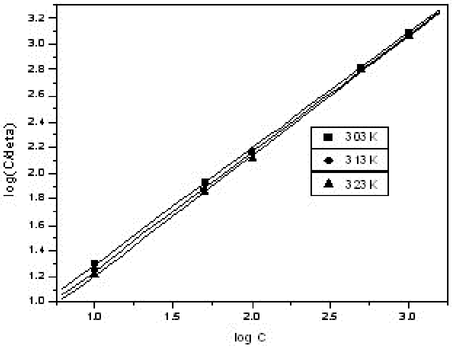


Fig.1 Langmuir isotherm for the adsorption of CAL inhibitor on aluminium in 1N Hydrochloric acid.

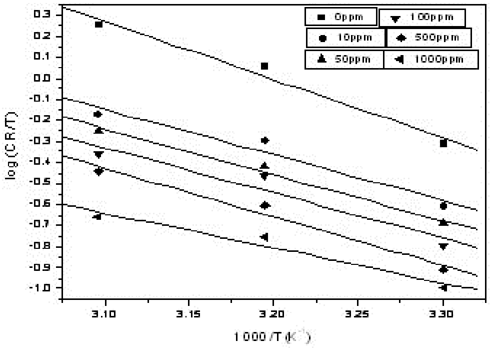
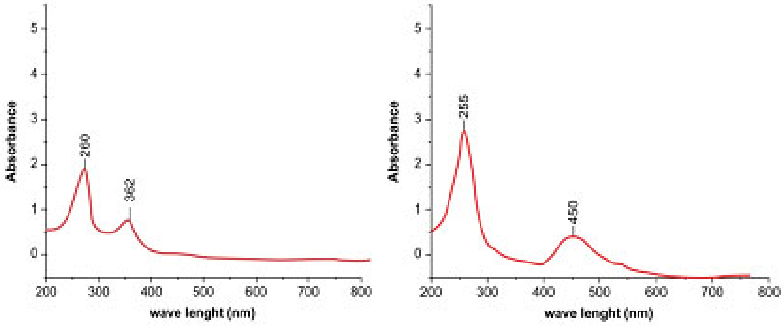


Fig.2 The relation between log(CR/T) and 1/T for different concentrations of CAL extract



(a) (b)

Fig.3 UV spectrum of ethanolic extract of CAL (a), the corrosion product on aluminium in 1N HCl in the presence of CAL extract (b).

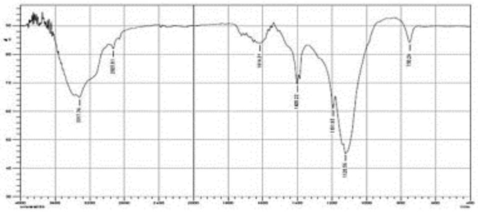


Fig.4 FT-IR spectrum of ethanolic extact of *Cassia Alata* leaves (CAL)

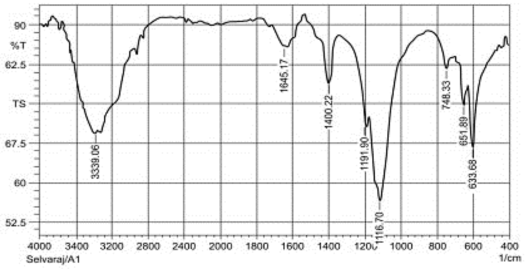


Fig.5 FT-IR spectrum for the corrosion product on aluminium in the presence of CAL extract with 1N Hydrochloric acid

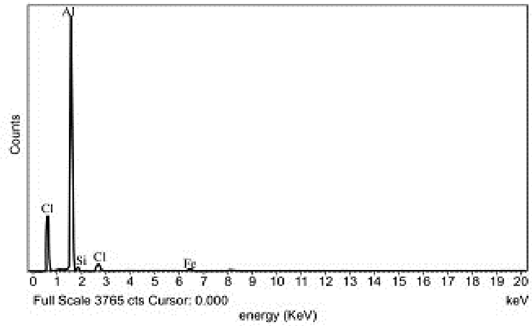


Fig.6 EDX spectrum of the corrosion product on aluminium surface in 1N HCl

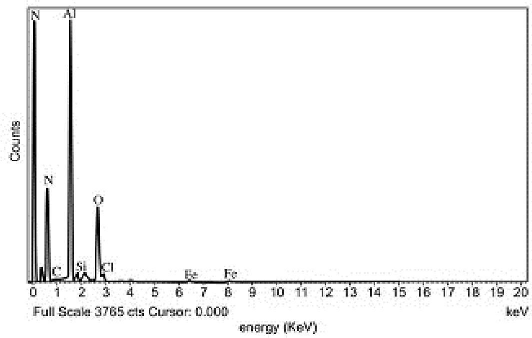


Fig.7 EDX spectrum of the corrosion product on aluminium in the presence of CAL extract in 1N HCl

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