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The Corrosion Control Of Aluminium Using Lawsonia Inermis Seed Extract In Acid Medium

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Abstract : The corrosion inhibition effect of alcoholic extract of Lawsonia inermis leaves on Aluminium in 0.5N Hydrochloric acid medium has been studied by mass loss measurement with various period of contact and temperature. The present study revealed that the percentage of inhibition efficiency is enhanced with increase of inhibitor concentration and decreased with raise in immersion time. The temperature studies reflect that the adsorption of inhibitor on metal surface takes place via chemisorption followed by physisorption. The calculated values of Q_{ads} , ΔG_{ads} suggests that the adsorption may be exothermic and endothermic and spontaneous process. Adsorption of LIS inhibitior was found to follow Temkin adsorption isotherm. The protective film formed on the metal surface may also confirmed by spectral studies.
Keywords: Aluminum, Corrosion, Inhibition, Lawsoina inermis seed, Mass loss, Temkin.

INTRODUCTION

Next to iron and copper, aluminum & its alloy are very attractive materials for engineering applications due to their low cost, easy availability, light weight, high thermal and electrical conductivity, and mechanical strength (1). It is used in electronics, for the production of wires, sheets, tubes etc. However, aluminium and its alloy are severely affected when exposed to the action of acid in industrial process where acids play an important role in oil well acidizing, acid pickling, acid cleaning and acid descaling (2-3). The use of inhibitors is one of the most important practical methods to solve this problem. Most of the investigators have normally organic and inorganic compounds which are used in acid solution as corrosion inhibitors, but most of these inhibitors are toxic, non-biodegradable and more expensive. In order to overcome these difficulties, we attempt to find the corrosion inhibitors which are environmentally safe by the use of natural products such as leaves, stem, fruits, flowers of plants extract as corrosion inhibitors for metals in acid cleaning process. This is because plants serve as incredibly rich sources of naturally occurring chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable source of materials. Curently most of the investigators have used the various part of the plants extract such as *Euphorbia hirta* (4) , *Aloe* Plant (5) , *garlic extract* (6) , *Anthocleista vogelii* (7), Ginseng Root (8), *Ananas sativum*(9), Lawsonia inermis leaves (10-14) , *Punica Granatum* peel, *Emblica Officinalis* leaves, *Andrographis paniculata*, *Jatropha curcas*, *Citrullus Vulgaris* peel (15-19) as a corrosion inhibitor. In continuity of these work, our present investigation is the inhibitive and adsorption properties of *Lawsonia inermis* seed extract on the corrosion of Aluminium in 0.5N Hydrochloric acid have been observed at various concentration of inhibitor using mass loss measurements at different time duration and temperature. The formation of film on the metal surface may also confirmed by the spectral studies.

EXPERIMENTAL

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 present study.

Preparation of *Lawsonia inermis* seed (LIS) extract

Freshly available *Lawsonia inermis* seed (LIS) 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 100,250,500,750,1000ppm stock solution was prepared and used throughout the present investigation. All reagents used for this present study were Analar grade and double distilled water for their preparation.

Mass Loss measurement

In mass loss measurements, specimen of Aluminium 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

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6\times W}{DAT} \qquad (1)$$

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

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

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

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

RESULTS AND DISCUSSION

The Corrosion parameters of Aluminium in 0.5N Hydrochloric acid containing various concentration of LIS extract with different exposure time is given in Table 1. It reveals that the loss of mass moderately increased from 76mg to 232mg with increase of exposure time (24 hrs to 168 hrs) in the absence of inhibitor concentration. But in the presence of Lawsonia inermis seed (LIS) extract, the corrosion rate is significantly reduced from 5.1370 to 0.8111 (mmpy) for 24hrs and 2.2402 to 0.7435 (mmpy) for 168 hrs respectively. The maximum of 84.52% inhibition efficiency is achieved at 1000 ppm of inhibitor concentration even after 72hrs exposure time. This is mainly due to the presence of π- bonds and hetero atoms such as nitrogen, oxygen present in the phyto chemical constituent of LIS extract. It is clearly indicate that the surface coverage (θ) is almost greater than 84% is mainly due to the binding between the ion in the metal surface and the hetero atom present in the LIS extract.

The Corrosion parameters of Aluminium in 0.5N Hydrochloric acid containing various concentration of LIS extract with different temperature is given in Table 2. It is clear that LIS extract is a suitable inhibitor on corrosion of Aluminium in 0.5N Hydrochloric acid. The observed results reveal that the corrosion rate decreased and the percentage of inhibition efficiency increased with increase of inhibitor concentration with rise in temperature from 303 to 313K. It is also suggested that the adsorbed layer is shielded when rise in temperature from 303 to 313K. The maximum of 75.61% inhibition efficiency is achieved at 313K. Beyond that, the inhibition efficiency is decreased upto 323K and it is once again increased at 333K. It indicates that the adsorbed layer is breakdown upto 323K and then reform the film once again on the metal surface at 333K leads to prevent the further dissolution of the metal. This change of observed results suggested that the inhibitor adsorption on the metal surface by physical as well as chemical process.

Table 1 Corrosion parameters of Aluminium in 0.5N Hydrochloric acid containing various concentration of LIS extract with different exposure time.

S.No	Time (hrs)	Electrolyte (HCl+LIS) (ppm)	Mass loss (mg)	C.R (mmpy)	I.E (%)
1	24	Blank	76	5.1370	---
		100	35	2.3657	53.94
		250	26	1.7574	65.79
		500	33	2.2306	56.58
		750	19	1.2843	75.00
		1000	12	0.8111	84.21
2	48	Blank	122	4.1231	----
		100	49	1.6560	59.82
		250	46	1.5546	62.30
		500	40	1.3519	67.21
		750	33	1.1153	72.95
		1000	20	0.6759	83.61
3	72	Blank	168	3.7852	----
		100	89	2.0052	47.02
		250	78	1.7574	53.57
		500	64	1.4420	61.90
		750	59	1.3293	64.88
		1000	26	0.5858	84.52
4	96	Blank	179	3.0248	---
		100	102	1.7326	43.02
		250	85	1.4363	52.52
		500	69	1.1660	61.45
		750	58	0.9801	67.60
		1000	47	0.7942	73.74
5	120	Blank	205	2.7713	----
		100	135	1.825	34.15
		250	113	1.5276	44.88
		500	87	1.1761	57.56
		750	73	0.9869	64.39
		1000	57	0.7706	72.19
6	168	Blank	232	2.2402	----
		100	188	1.8153	18.35
		250	139	1.3422	40.0
		500	124	1.1974	46.55
		750	82	0.7918	64.65
		1000	77	0.7435	66.81

Table 2 Corrosion parameters of Aluminium in 0.5N Hydrochloric acid containing various concentration of LIS extract with different temperature

S.No	Temp (K)	Electrolyte (HCl+LIS) (ppm)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
1	303	Blank	24	38.9333	-----
		100	22	34.4143	11.61
		250	20	32.4444	16.67
		500	17	27.5778	29.17
		750	10	16.2222	58.33

		1000	8	12.9778	66.67
2	313	Blank	41	66.511	----
		100	38	59.4429	10.63
		250	34	55.1556	17.07
		500	26	42.1778	36.59
		750	14	22.7111	65.85
		1000	10	16.2222	75.61
3	323	Blank	54	87.6000	-----
		100	47	76.2000	12.92
		250	45	73.0000	16.67
		500	37	60.0222	31.48
		750	21	34.0667	61.11
		1000	16	25.9556	70.37
4	333	Blank	61	98.9556	----
		100	55	89.2200	9.83
		250	53	89.2222	9.84
		500	42	68.1333	31.15
		750	24	45.4222	54.10
		1000	17	27.5778	72.13

Effect of temperature

The value of activation energy (E_a) for the corrosion of Aluminium in the presence and absence of LIS extract is calculated using the following Arrhenius equation (4) and its derived form (5)

$$CR= A exp(-E_a/RT) \qquad (4)$$

$$log (CR_2/CR_1) = E_a/2.303 R (1/T_1-1/T_2) \qquad (5)$$

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 for blank (26.088 kJ/mol) is lower than in the presence of inhibitors upto 250ppm (**Table 3).** But this value is higher than the presence of inhibitor upto 1000ppm which clearly indicates that the adsorption process is physisorption followed by chemisorptions.

Adsorption Studies

The heat of adsorption (Q_{ads}) on Aluminium specimen in the presence of inhibitor is arrived by the following equation (6)

$$Q_{ads} =2.303 R [\log (\theta_2/1- \theta_2)-\log (\theta_1 /1- \theta_1)] x (T_2T_1/T_2-T_1) \qquad (6)$$

Where R is the gas constant, $\theta_1$and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

The Q_{ads} values are ranged from -16.95 to 07.214kJ/mol (Table 4). This value clearly indicates that the adsorption of LIS extract on the surface of Aluminium metal is exothermic followed by endothermic. The inhibitor obeys Temkin adsorption isotherm. It can be expressed by the equation (7) given below (20)

$$\exp(2a\theta)= K_{ads} C_{inh} \qquad (7)$$

where, b designates the adsorption coefficient in equation (7), *a* the molecular interaction parameter, *K*ads is the equilibrium constant of the adsorption process in equation. By plotting values of logC Vs θ , the observed linear plots suggested that the experimental data fitted with the Temkin adsorption isotherm. It assumes that the uniform distribution of adsorption energy which decreases linearly with increase of surface coverage (*θ*) values (21).

The equilibrium constant of adsorption of LIS extract on the surface of Aluminium metal is related to the free energy of adsorption (ΔG_{ads}) which is represented by the following equation (8)

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

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 Temkin adsorption isotherm is substituted in equation (8) and the calculated values of ΔG_{ads} are placed in Table 4. The negative values of ΔG_{ads} suggested that the adsorption of LIS extract on to Aluminium metal surface is a spontaneous process and the adsorbed layer is more stable one.

Table 3 Thermodynamic parameters such as Activation energy (E_a) and heat of adsorption (Q_{ads}) of LIS extract on Aluminium in 0.5N Hydrochloric acid.

S.No	Electrolyte (HCl+LIS) (ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		303K	333K		
1.	Blank	---	---	26.088	-----
2.	100	11.61	09.83	26.642	-05.21
2.	250	16.67	09.84	28.291	-16.95
3.	500	29.17	31.15	25.295	02.63
4.	750	58.33	54.10	28.795	-03.18
5.	1000	66.67	72.13	21.081	07.21

Table 4 Temkin adsorption parameters for the adsorption of LIS extract on Aluminium in 0.5N Hydrochloric acid.

Isotherm	Temp. (K)	Slope	logK	R^2	ΔG_{ads} KJ/mol
Temkin	303	0.5633	0.0420	0.8342	-10.363
	313	0.6677	0.1226	0.8748	-11.188
	323	0.5955	0.0663	0.8296	-11.197
	333	0.6270	0.1060	0.8188	-11.797

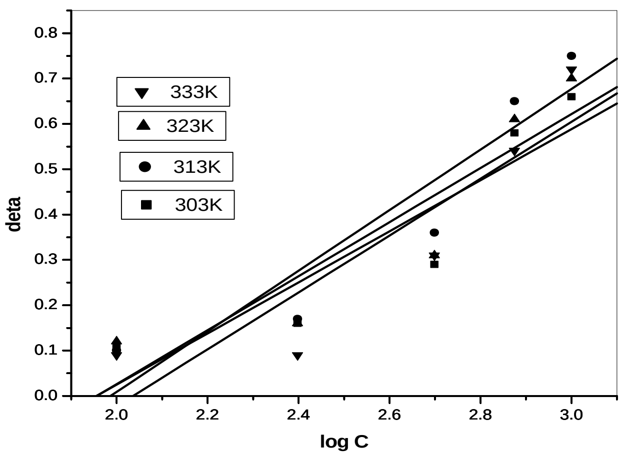

Fig. 1 Temkin adsorption isotherm for LIS extract on Aluminium in 0.5N Hydrochloric acid.

Morphology examination of aluminium:

FT-IR Analysis

The Fig. 2(a) & (b) reflects that the FT-IR spectrum of the ethanolic extact of inhibitor and the corrosion product on aluminium in the presence of LIS extract in 0.5N Hydrochloric acid. On comparing both of these spectra, the change of frequency ie. the C-O stretching of carbonyl group is shifted from 1446.35 to 1457.92cm^{-1} . It has also been seen that some peaks are disappeared in Fig. 2(b) which is present in Fig. 2(a). The band at 1336.32 corresponds to the C-O stretching frequency in ketone, the band at 1028.8cm^{-1} and 1105.01cm^{-1} is attributed to the C-N stretching frequency of amine, the peak at 768.49cm^{-1} is attributed to the –OH bending in alcohol are vanished in Fig.2(b). It is clearly indicates the fact that the co-ordination between the adsorption of active molecules present in the inhibitor and surface of the metal ion through nitrogen atom, may also confirm the film formation on the metal surface.

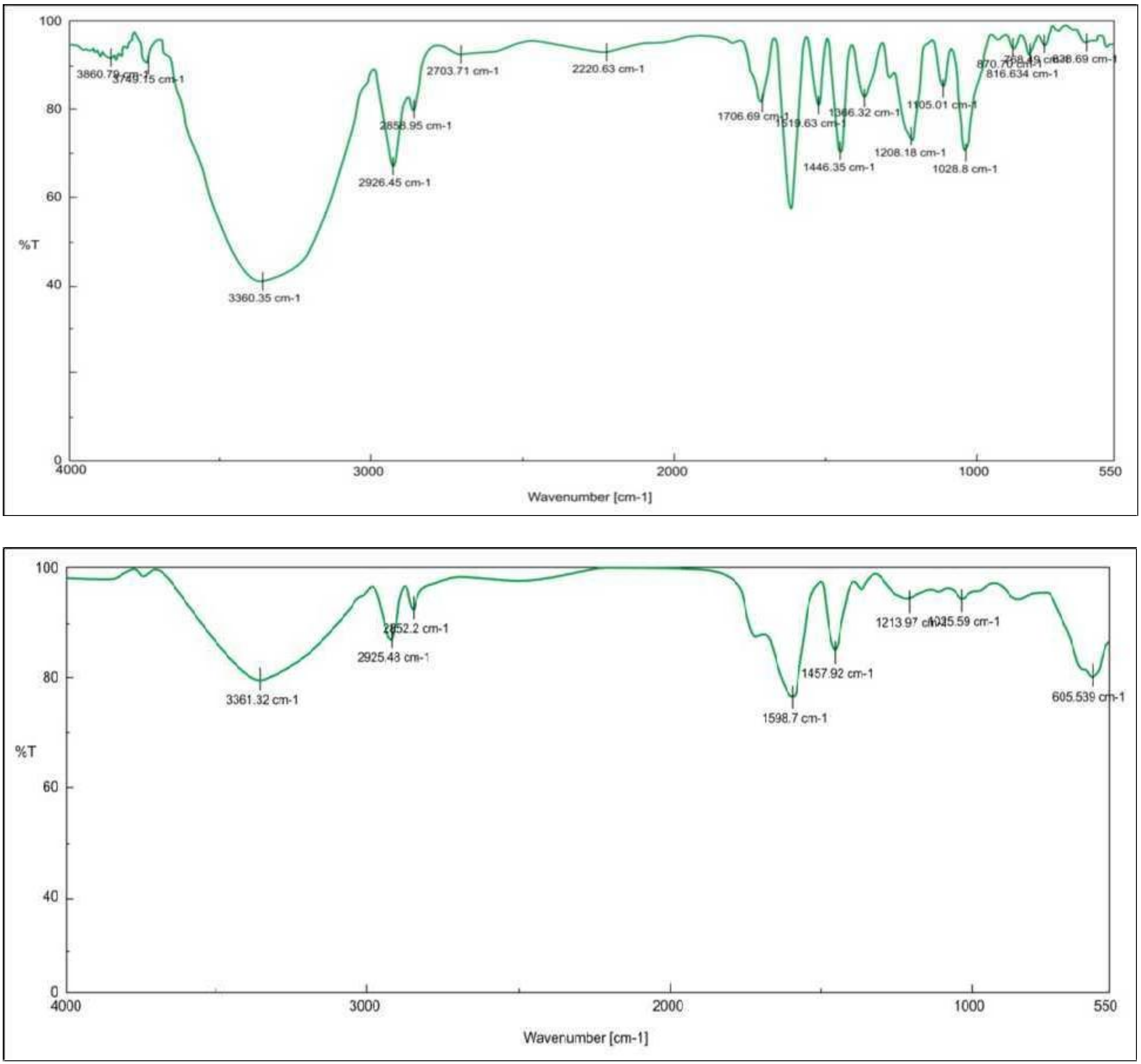

Fig. 2 FT-IR spectrum of (a) the alcoholic extract of *Lawsonia inermis* seed and(b) the corrosion product on aluminium in the presence of LIS extract with 0.5N Hydrochloric acid environment.

EDX Analysis:

EDX spectroscopy was used to determine the elements present on the aluminium surface before and after exposure to the inhibitor solution. Fig. 3 and 4 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of LIS extract with 0.5N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum confirms the existence of chlorine and oxygen due to the formation of oxides and chlorides of aluminium complexes. In addition to this the spectrum consists of aluminium, iron, silicon which is the part of composistion in aluminium metal. However, in the presence of the optimum concentrations of the inhibitors, nitrogen and carbon atoms are found to be present on the aluminium surface. This indicates that the nitrogen atom present in the inhibitor molecules may also confirm the adsorption process with metal atom and hence it may protects the metal surface against corrosion.

UV SPECTRAL Analysis

Fig. 5 and 6 shows that the UV visible spectrum of the corrosion product on the surface of aluminium in the absence and presence of LIS extract in 0.5N Hydrochloric acid. On comparing both these spectra, a band at 240 and 308 nm is shifted to shorter wavelength region (210 and 300nm) ie, Hypsochromic shift or Blue shift in the presence of inhibitor. However the band at 350.5nm is shifted to higher wavelength region (Bathochromic shift or red shift) viz 360nm. The observed results concluded that the co-ordination between the hetero atoms (oxygen and nitrogen) present in the inhibitor and surface of the metal ion.

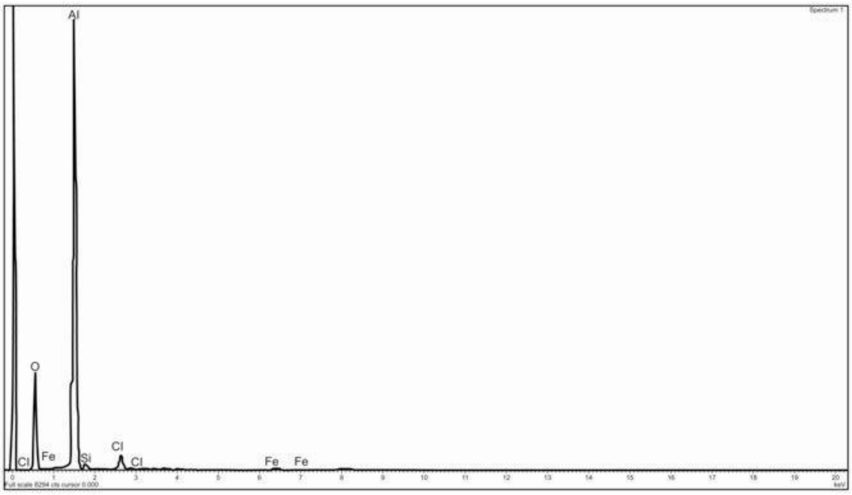

Fig. 3 EDAX spectrum of the corrosion product on aluminium surface in 0.5NHCl

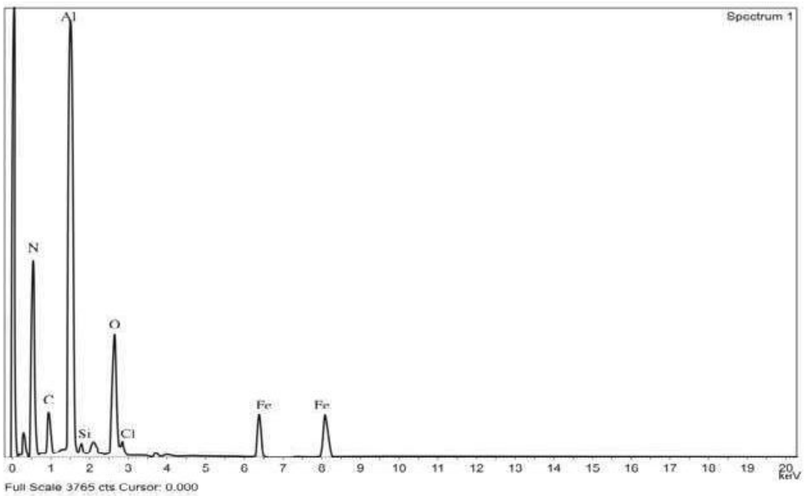

Fig. 4 EDAX spectrum of the corrosion product on aluminium surface with the presence of LIS extract in0.5NHCl

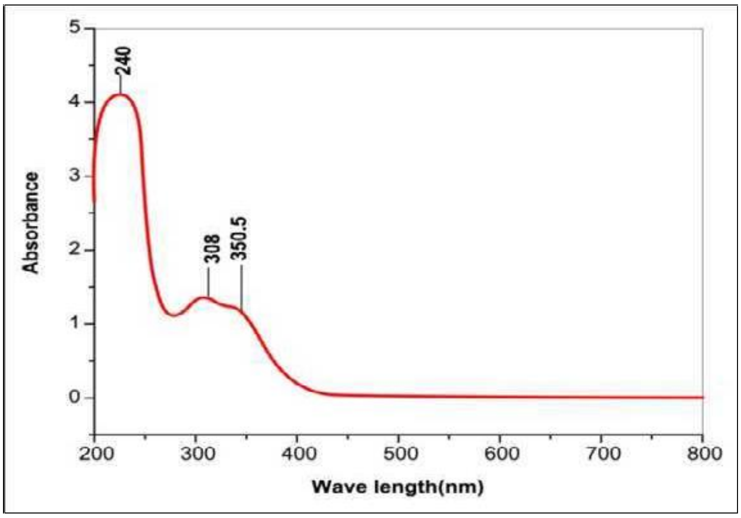

Fig. 5 UV spectrum for corrosion product on aluminium with 0.5N Hydrochloric acid

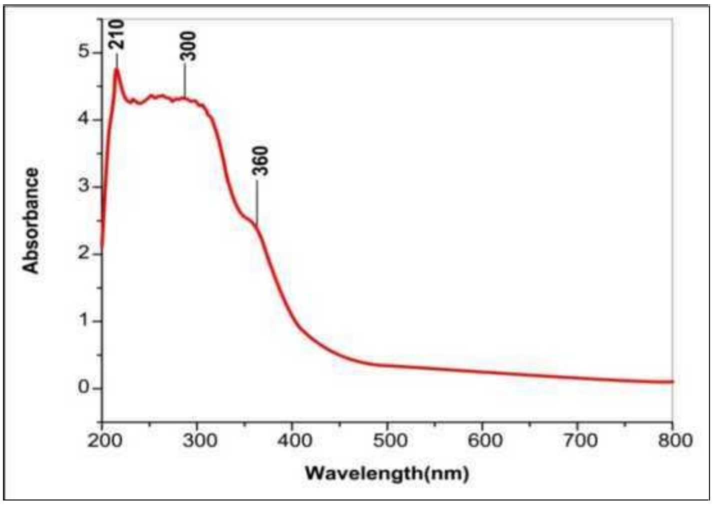

Fig. 6 UV spectrum for corrosion product on aluminium in the presence of LIS extract with 0.5N Hydrochloric acid

CONCLUSION

The alcoholic extract of Lawsonia inermis seed (LIS) is act as a good corrosion inhibitor on Aluminium metal in 0.5N Hydro chloric acid . The corrosion rate is increased with increase of exposure time in inhibitor free solution. However in the presence of inhibitor the value corrosion rate is moderately reduced and the maximum of 84.52% Inhibition efficiency is attained even after 72hrs immersion time. In temperature studies, initially the inhibitive effect is significantly increased with rise in temperature is suggestive of chemisorptions process. However beyond 313K, the inhibitive efficacy is slowly decreased with increase in temperature may be concluded that the adsorption process is chemisorptions followed by physisorption. The inhibitor obeys Temkin adsorption isotherm. The formation of protective layer over metal surface may also confirmed by FT-IR, EDAX, UV spectral studies.

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