



## Anti-corrosive effect of *Cassia alata* leaves extract on Mild steel in 1.0N Hydrochloric acid

A. Petchiammal, P.Deepa Rani, S.Seetha lakshmi and S.Selvaraj.

Post graduate and Research Department of chemistry,  
Sri Paramakalyani College, Alwarkurichi-627412, Tamil Nadu, India.

Mail id: [ap\\_mscchem@yahoo.in](mailto:ap_mscchem@yahoo.in)

Phone No. 9442064252

Fax no: 04634-283530.

### ABSTRACT

The inhibition effect of *Cassia alata* leaves extract on corrosion of mild steel in 1N HCl was investigated through mass loss measurements with various time and temperature. The observed result indicated that the corrosion inhibition efficiency and degree of surface coverage were increased with increase of inhibitor concentration and temperature. The thermodynamic parameters ( $E_a$ ,  $\Delta H_{ads}$ ,  $\Delta G_{ads}$ ,  $\Delta S_{ads}$ ) were evaluated for corrosion inhibition process which suggests that the adsorption is endothermic, spontaneous and chemisorptions and also the inhibitor follows Langmuir adsorption isotherm. The protective film formed on metal surface was analyzed using spectroscopic studies viz, UV, FT-IR and EDX techniques.

**KEYWORDS:** Mild steel, Corrosion, *Cassia alata* leaves, Mass loss, Adsorption isotherm



# Council for Innovative Research

Peer Review Research Publishing System

**Journal:** Journal of Advances in Chemistry

Vol 2, No. 2

[editor@cirworld.com](mailto:editor@cirworld.com)

[www.cirworld.com](http://www.cirworld.com), [member.cirworld.com](http://member.cirworld.com)



## INTRODUCTION

Mild steel is the material of choice almost all the field in Worldwide due to its low cost and easy availability. It has been extensively used under different condition in chemical and allied industries in handling alkaline, acid and salt solution. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate the corrosion. One of the best way of protecting mild steel from corrosion is the use of inhibitors [1]. But the use of chemical inhibitor has been found to be more expensive, toxic, non bio-degradable and harmful to living things. Hence there is a big problem for researchers to search the non-toxic, eco-friendly corrosion inhibitors. Recent years, several green inhibitors have been used for the prevention of corrosion by most of the investigators. Few examples are *Allium Cepa* [2], *Eucalyptus globulus* [3], *Phyllanthus amarus* [4], bitter leaf powder [5], Carob seed oil [6], *Bacopa monnieri* [7], *Citrullus Vulgaris* peel [8], *Albizia lebbek seed* [9], *Hibiscus Esculenta* leaves [10], *Jatropha curcas* [11], *Eugenia Jambolana* [12]. In continuous of our research work, our present investigation is an anti-corrosive effect of *Cassia alata* leaves on mild steel in 1N Hydrochloric acid have been investigated with various period of contact and temperature using the mass loss measurements and the corrosion product on metal surface is analysed by UV, FT-IR, EDX spectral studies.

## EXPERIMENTAL

### Specimen preparation

Mild steel specimen were mechanically pressed to cut different coupons, each of dimension exactly 20cm<sup>2</sup> (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 and used throughout our present study.

### Preparation of *Cassia alata* leaves (CAL) extract

Freshly available *Cassia alata* leaves were dried well, grinded and soaked in required alcohol for about 48hrs, and then filtered, followed by evaporation in order to remove the excess of alcohol completely and the pure plant alcoholic extract was collected. From this extract the different concentration (0-1000ppm) of stock solution was prepared and used throughout the present investigation.

### Mass loss measurement

In mass loss measurement, the specimen of mild steel is immersed exactly in 100ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after 24 to 360hrs at room temperature and one hour at the temperature range of 303K to 323K. From this observed data, the corrosion rate (mmpy), percentage of inhibition efficiency (%I.E) and surface coverage ( $\theta$ ) was calculated using the following formulae (1-3).

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

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

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

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

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 stretching frequency of functional groups in the corrosion product was analysed by FT-IR spectrum using the model Jasco/Japan. The absorption maximum of the corrosion product was analysed by UV spectra using the Model Jasco V670.

## RESULTS AND DISCUSSION

Table 1 reflects that the variation of corrosion parameters with concentration of CAL extract on mild steel at different period of contact in 1N Hydrochloric acid. It revealed that the corrosion rate was decreased gradually with the addition of inhibitor. The maximum of 73.62% inhibition efficiency was achieved at 1000 ppm of inhibitor concentration after 360 hrs exposure time. The almost greater than 73% of surface coverage ( $\theta$ ) was achieved due to the co-ordination between the mild steel metal and the hetero atom (oxygen, nitrogen) present in the inhibitor.



**Table 1: Variation of corrosion parameters with Concentration of CAL extract on mild steel 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	5.3635	----	3.1113	---	2.3405	----	2.2987	----	2.1615	---	2.0123	----
10	4.1097	23.3	2.3451	24.6	1.5185	35.1	1.2804	44.2	0.9668	55.2	0.6780	66.3
50	3.7615	34.9	2.2445	27.8	1.4674	37.3	1.2074	47.4	0.8422	61.0	0.5960	70.3
100	3.5989	32.9	1.8575	40.3	1.4489	38.0	1.1278	50.9	0.7809	63.8	0.5789	71.2
500	3.4828	35.0	1.6718	46.2	1.4135	39.6	1.1046	51.9	0.7493	65.3	0.5665	71.8
1000	3.3203	38.0	1.1919	61.6	1.3560	42.0	1.0348	54.9	0.7367	65.9	0.5309	73.6

Variation of corrosion parameters with various concentration of CAL extract on mild steel at different temperature in 1N Hydrochloric acid is shown in Table-2. As can be seen from Table-2 that the corrosion rate was decreased and the percentage of inhibition efficiency increased with increase of inhibitor concentration with rise in temperature from 303 to 323K. It suggested that the adsorbed layer retards the corrosion rate when rise in temperature from 303 to 323K. The maximum of 75.00% inhibition efficiency was achieved at 323K. The value of inhibition efficiency was increased with rise in temperature. Thus, the inhibitor efficiencies were temperature dependent and it being chemically adsorbed at all temperatures. This was 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 mild steel at different temperature in 1N Hydrochloric acid**

Temperature (K)	Concentration of inhibitor (ppm)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
303	0	372	207.29	--
	10	211	117.58	43.27
	50	200	111.45	46.23
	100	183	101.97	50.80
	500	147	081.92	60.48
	1000	135	075.23	63.70
313	0	502	279.74	---
	10	289	161.04	42.43
	50	200	111.45	60.15
	100	187	104.20	62.74
	500	175	097.52	65.13
	1000	152	084.70	69.72
323	0	572	318.74	----
	10	298	166.06	47.90
	50	208	115.90	63.63
	100	198	110.33	65.38
	500	147	094.73	70.27
	1000	135	079.68	75.00



### Adsorption isotherm

The adsorption process was 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 ( $\theta$ ) were tested graphically for fitting a suitable adsorption isotherm. In those cases, the plot of  $\log C/\theta$  versus  $\log C$  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 (7).

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

Where  $\theta$  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 ( $\Delta G_{ads}$ ) is calculated by the following Equation (8) and the corresponding values are shown in Table-2. The negative values of  $\Delta G_{ads}$  suggested that the adsorption of CAL extract onto the metal surface is a spontaneous process and the adsorbed layer is more stable.

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

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

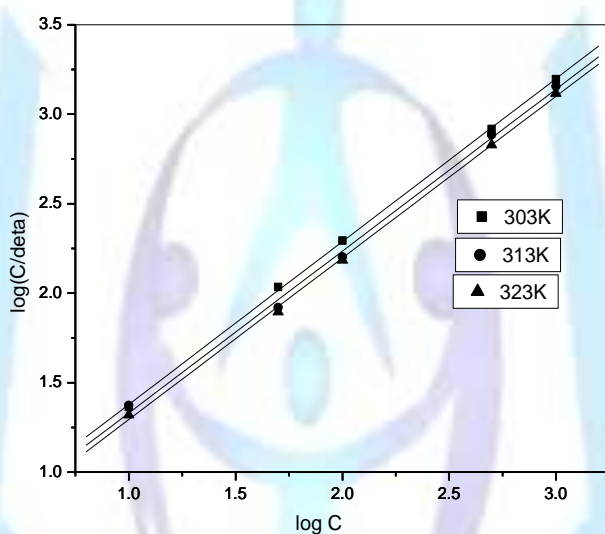


Figure 1 Langmuir isotherm for the adsorption of CAL inhibitor on mild steel in 1N Hydrochloric acid.

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

Adsorption Isotherms	Temperature (Kelvin)	$\Delta G_{ads}$ kJ/mol
Langmuir	303	-1.914
	313	-2.222
	323	-2.522

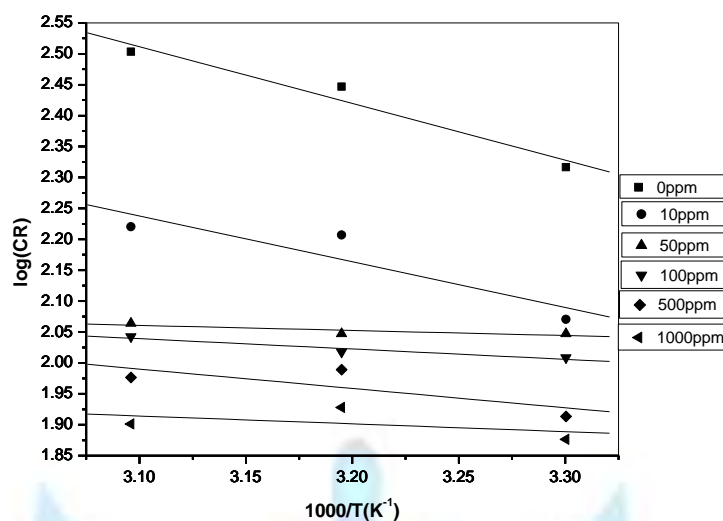
### Thermodynamics parameters

A plot of  $\log CR$  vs.  $1000/T$  gave straight lines as shown in Fig.2. The apparent activation energy ( $E_a$ ) was calculated by using following relationship.

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

$$\log CR = \log A - E_a/RT$$

Where  $E_a$  is the apparent activation energy for the corrosion of mild steel in 1N HCl solution, R the gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The values of  $E_a$  obtained from the slope of the lines are given in Table-4



**Figure 2 Arrhenius plots of mild steel in acid with and without different concentrations of CAL**

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

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT)$$

where h is the Planck's constant, N the Avogadro's number,  $\Delta S$  the entropy of activation, and  $\Delta H$  the enthalpy of activation. A plot of  $\log(CR/T)$  vs.  $1000/T$  should give a straight line (Fig.3) with a slope of  $(-\Delta H/R)$  and an intercept of  $[\log(R/Nh) + (\Delta S/R)]$ , from which the values of  $\Delta S$  and  $\Delta H$  were calculated and listed in Table-4. The data shows that the thermodynamic parameters ( $E_a$  and  $\Delta H$ ) of the corrosion of mild steel in 1N HCl solution in the presence of the inhibitors are lower than those in the free acid solution indicating less energy barrier for the reaction in the presence of the inhibitor is attained. The positive value of enthalpy of activation reflects the endothermic nature of metal dissolution process meaning that dissolution of metal is difficult. The increase of  $\Delta S$  is generally interpreted by increase in disorder taking place on going from reactants to the activated complex [13]

**Table 4: Thermodynamic parameters for mild steel in 1N HCl solution obtained from weight loss measurements.**

S.No	Concentration of CAL (ppm)	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J K <sup>-1</sup> mol <sup>-1</sup> )
1	0	7.63142	6.5022	8.5795
2	10	6.15111	5.0219	9.4771
3	50	0.68416	0.4450	11.8856
4	100	1.38511	0.2559	11.6249
5	500	2.60444	1.4752	11.1840
6	1000	1.04889	0.8230	11.8972

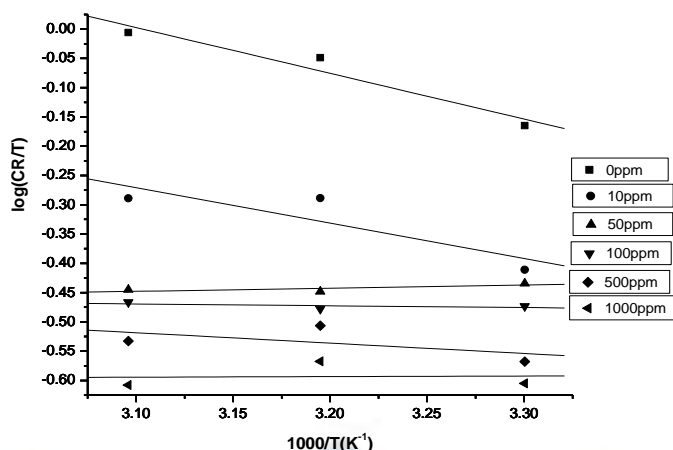


Figure 3 The relation between  $\log(CR/T)$  and  $1/T$  for different concentrations of CAL extract

## MORPHOLOGY EXAMINATION OF MILD STEEL

### UV spectrum:

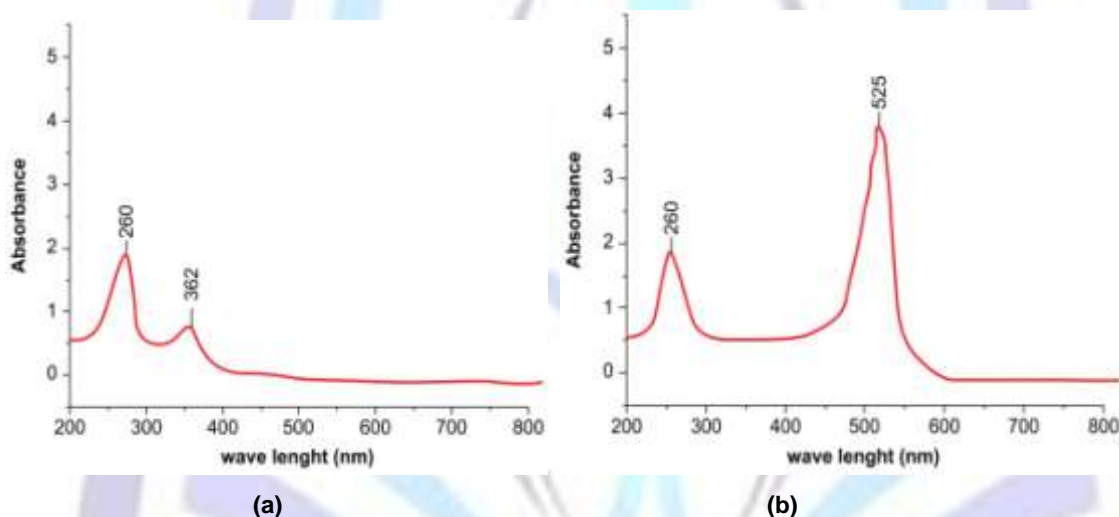


Figure 4 UV spectrum of ethanolic extract of CAL (a), the corrosion product on mild steel in 1N HCl in the presence of CAL extract (b).

Fig.4(a) and (b) shows that the UV visible spectrum of ethanolic extract of CAL and the corrosion product on the surface of Mild steel in the presence of CAL extract in 1N Hydrochloric acid respectively. In the UV spectrum, the two absorption bands around 260 and 362nm and bands around 260 and 525nm were noticed in Fig.4(a) and (b) respectively. In the presence of inhibitor one band (260nm) remains unchanged and another band (362nm) shifted to higher wavelength region. The change of absorption band from the above may confirmed the strong co-ordination between the active group present in the inhibitor molecules and the metal surface.

### FT-IR analysis

The Fig.5 and 6 reflects that the FT-IR spectrum of the ethanolic extract of CAL inhibitor and the corrosion product on mild steel in the presence of inhibitor in 1N Hydrochloric acid. On comparing these spectra, the prominent peak is shifted from  $3317.34$  to  $3355.88\text{cm}^{-1}$  for  $-\text{OH}$  group, the frequency at  $1119.93\text{cm}^{-1}$  is attributed to  $-\text{C}-\text{N}$  stretching in amine is shifted to  $1149.38\text{cm}^{-1}$  indicates that the binding between metal and inhibitor takes place through amino group. Thus the FT-IR spectra support the fact that the corrosion inhibition of CAL inhibitor on mild steel in 1N Hydrochloric acid may be the adsorption of active molecule in the inhibitor and surface of the metal.

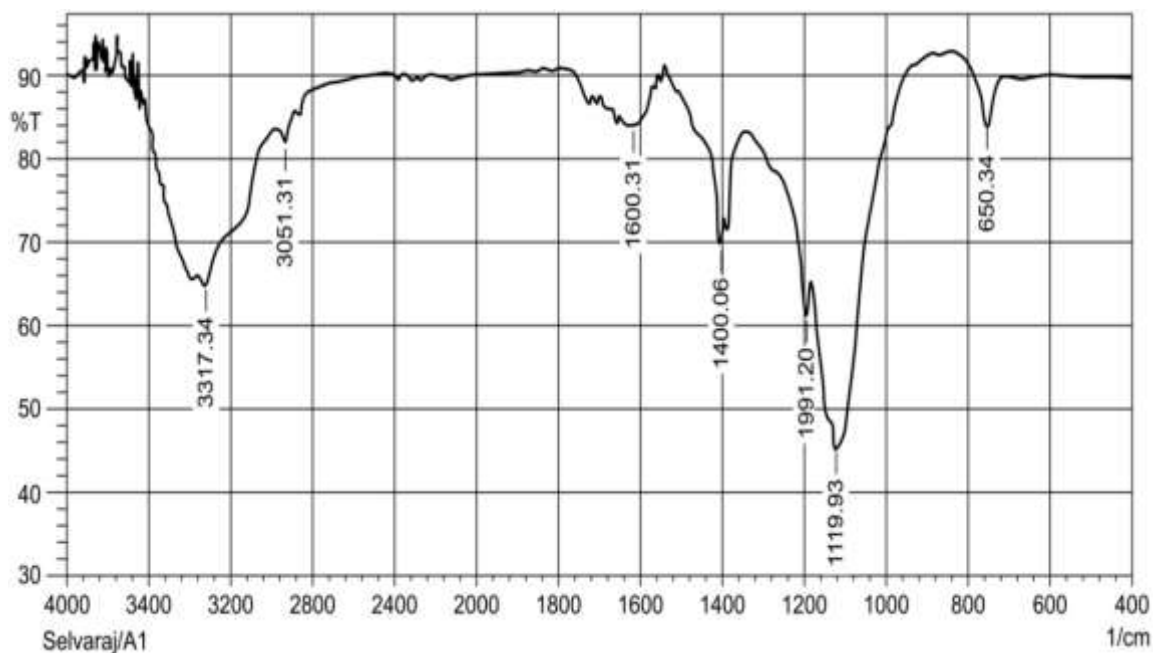


Figure 5 FT-IR spectrum of ethanolic extract of *Cassia Alata* leaves (CAL)

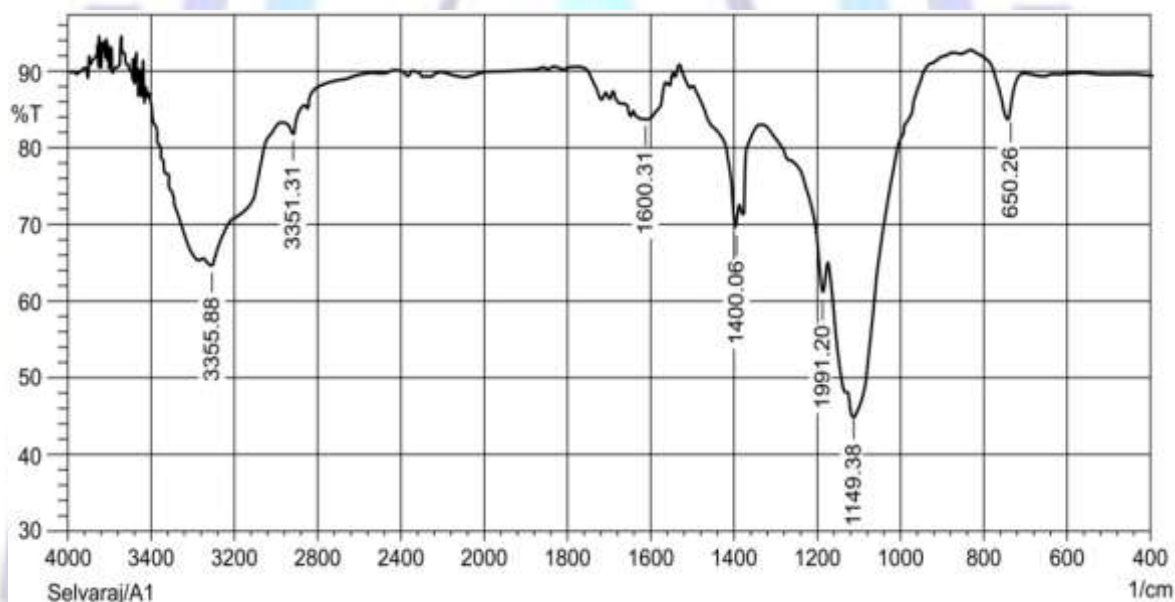


Figure 6 FT-IR spectrum for the corrosion product on mild steel in the presence of CAL extract with 1N Hydrochloric acid

## EDX spectrum

EDX spectroscopy was used to determine the elements present on the mild steel surface in the absence and presence of inhibitor. Fig.7 and 8 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CAL extract in 1N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum may concluded that the existence of chlorine due to the formation of metal chloride and in addition to this, spectrum consists of iron, silicon, carbon which is the part of composition of mild steel. However, in the presence of the optimum concentrations of the inhibitors, nitrogen and oxygen atoms are found to be present in the corrosion product on the metal surface. It clearly indicates that these hetero atoms present in the inhibitor molecules may involve the complex formation with metal atom during the adsorption process and prevent the further dissolution of metal against corrosion.

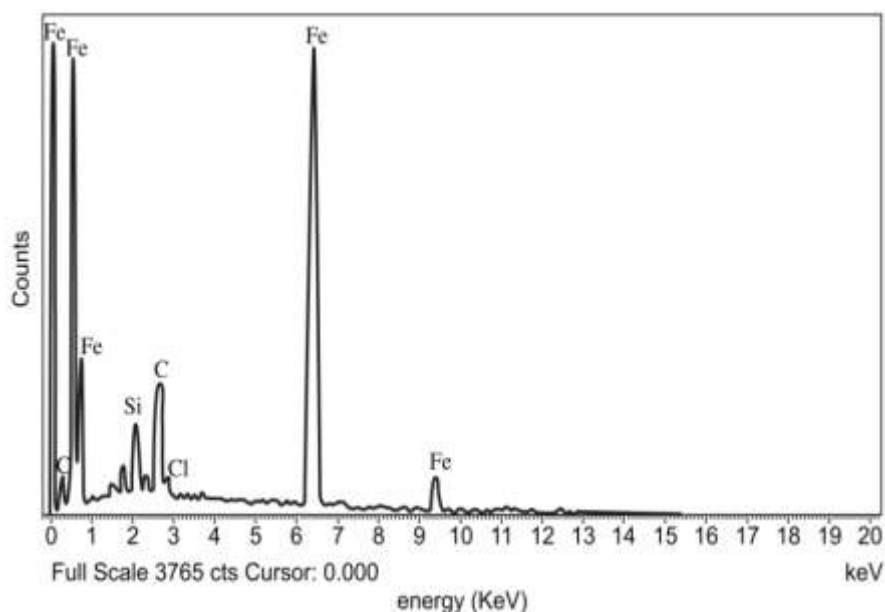


Figure 7 EDX spectrum of the corrosion product on mild steel surface in 1N HCl

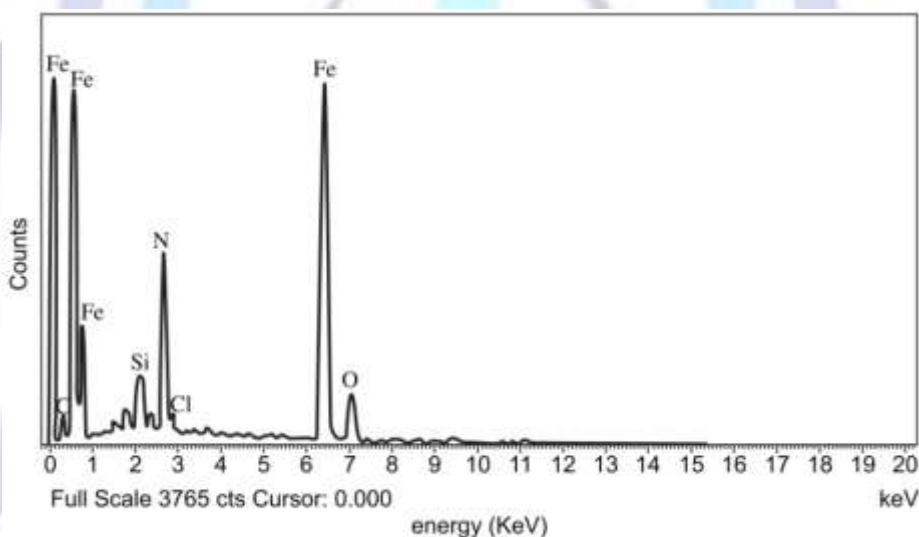


Figure 8 EDX spectrum of the corrosion product on mild steel in the presence of CAL extract in 1N HCl

## CONCLUSION

On the basis of the above results, it can be seen that *Cassia alata* leaves is a good inhibitor for mild steel in 1N HCl. The inhibition efficiency of CAL attains a maximum value of 73.62%. This inhibition effect increases with the increase of inhibitor concentration. The inhibition efficiency of CAL is dependent on temperature. CAL shows an adsorption on the metal surface according to the Langmuir adsorption isotherm model. The value of activation energy ( $E_a$ ), enthalpy of adsorption ( $\Delta H_{ads}$ ) and free energy changes ( $\Delta G_{ads}$ ) indicates that the adsorption of inhibitor on metal surface follows chemical, endothermic and spontaneous process respectively. The corrosion product over the surface of mild steel is characterized by UV, FT-IR and EDX studies also confirm protective film completely shielded the entire metal surface and reduce the further dissolution of metal against corrosion.

## REFERENCE

- [1]. Anand B, Balasubramanian, V. 2011. Corrosion Behaviour of Mild Steel in Acidic Medium in Presence of Aqueous Extract of *Allamanda Blanchetii*, E-J.of Chem. 8, 226-230.
- [2]. Sulaiman S, Nor-Anuar A, Abd-Razak A.S, Chelliapan S. 2012. A study of using *Allium Cepa* (onion) as natural corrosion inhibitor in industrial chill wastewater system, Res.j.chem.sci, 2, 10-16
- [3]. Rekkab S. et.al, 2012. Green corrosion inhibitor from essential oil of *Eucalyptus globulus* (myrtaceae) for C38 steel in sulfuric acid solution, j. Mater. Environ. Sci, 3, 613-627.





- [4].Sribharathya V, Susai Rajendran and Sathiyabama, J. (2013). Inhibitory action of Phyllanthus amarus extracts on the corrosion 2-thiophene carboxaldehyde as corrosion inhibitor for zinc in phosphoric acid solution of mild steel in seawater, Chem. Sci Trans, 2, 315-321.
- [5]. Ayeni F.A, et.al, (2012). Effect of aqueous extracts of bitter leaf powder on the corrosion inhibition of Al-Si alloy in 0.5 M caustic soda solution, Advanced Mater. Res, 367: 319-325.
- [6]. Dris Ben Hmamou et.al, (2012). Carob seed oil: an efficient inhibitor of C38 steel corrosion in Hydrochloric acid, Inter. J. of Industrial Chem, 3:25
- [7]. Ambrish Singh et.al, (2012). Stem extract of brahmi (Bacopa Monnieri) as green corrosion inhibitor for aluminum in NaOH solution, Int. J. Electrochem. Sci, 7: 3409 – 3419.
- [8]. Petchiammal A, Deepa Rani P, Selvaraj S, and Kalirajan K 2012. Corrosion Protection of Zinc in Natural Sea Water using *Citrullus Vulgaris* peel as an Inhibitor, Res. J. of Chem. Sci, 2, 24-34.
- [9]. Petchiammal A, Selvaraj S, and Kalirajan K. 2013. *Albizia lebbbeck* seed extract as effective corrosion inhibitor for Mild steel in acid medium. Bio interface res. in App. Chem, 3, 498-506
- [10]. Petchiammal A, Selvaraj S, and Kalirajan K. 2013. Influence of *Hibiscus Esculenta* leaves on the corrosion of stainless steel in acid medium, Inter. J. of Univ. Pharm. and Bio Sci, 2, 242-252
- [11]. Deepa Rani P and Selvaraj S. 2011. Comparitive account of *Jatropha curcas* on Brass(Cu- 40Zn) in acid and Natural sea water environment, Pacific J. of Sci. and Technol, 12, 38- 49.
- [12]. Deepa Rani P et al. 2013. *Eugenia Jambolana* Used as Corrosion Inhibitor on Mild Steel in 1N Hydrochloric Acid Medium, 2, 215-225
- [13]. Ayatia N.S et al. 2011. Inhibitive effect of synthesized 2-(3-pyridyl)-3,4-dihydro-4- quinazolinone as a corrosion inhibitor for mild steel in hydrochloric acid, Mater. Chem. and Phy, 126, 873–879

