A Study on Corrosion Resistivity Property of *Alangium salviflorum* on Carbon Steel in Acidic Medium

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Abstract

The ethanolic extract of *Alangium salviflorum* was used as corrosion inhibitor on carbon steel in acidic medium. The corrosion resistive power of *Alangium salviflorum* was determined by weight loss method, for various concentrations of the extract with Zn^{2+} ion and fructose and sucrose as additives in 0.5 M HCl medium. The resistive film that protects the surface of the metal was confirmed by the electrochemical studies such as FT-IR, UV and fluorescence spectra. It also shows the formation of complex between the metal cation, additive and the compounds present in the extract of *Alangium salviflorum*.

Keywords: *Alangium salviflorum, Carbon Steel, Corrosion, Fructose, Sucrose*

1. INTRODUCTION

Now-a-days metal are used almost in all fields of technology, industries and home appliances. Metallic corrosion is the process of destructive attack on the metal surface through the interaction with the environment. Corrosion is a natural deterioration process which can be controlled but cannot be completely prevented. In past years, chemical inhibitors were used to control corrosion. Later it was found that the chemical inhibitors were hazardous and toxic. So eco-friendly, non–toxic chemical inhibitors were used. In recent days, green inhibitors from natural products have been used as inhibitors which are eco-friendly and completely non-toxic[1-3]. *Alangium salviflorum* is a plant which belongs to the family 'Alangiaceae'. It is widely distributed in Western Africa, Southern and Eastern Asia, Australia, Goa, Gujarat, Kerala and Tamil Nadu. It is medicinally used to cure many diseases.[4]

The present determination is done,

- to evaluate the corrosion resistivity property of *Alangium salviflorum* (ALA) by the inhibition efficiencies of ALA-Zn^{2+}-fructose/sucrose systems in resisting the corrosion on carbon steel in acidic medium.
- to analyse the protective film formed on the metal surface by FT-IR, UV and fluorescence spectra.

2. MATERIALS AND METHODS

2.1 Metal Specimens

The metal specimens taken for this study is carbon steel with the composition (wt%) ofS-0.026 , P -0.06, Mn- 0.4, C- 0.1 and balance iron. The dimensions of the metal active surface are 1.2 X 4.1 X 0.2 cm which was used for weight loss measurements. The carbon steel specimens were mechanically polished, washed in double distilled water and degreased with acetone and used for the weight loss method and surface examination studies.

2.2 Extraction

The leaves of *Alangium salviflorum* were collected from Pachaimalai hills. The leaves were washed thoroughly for about 7 times in the running tap water and it was taken and dried under shade. About 100g of the powder was soaked in 500ml of ethanol under cold percolation method. At regular intervals of time the extract was filtered and distillation was carried out to collect the crude extract. The extract was stored in an amper bottle and refrigerated [5].

2.3 Weight-Loss Method

2.3.1 Determination of Corrosion Rate

Weight loss measurements were carried out using an Acculab Electronic top loading balance, with readability/sensitivity of 0.1 mg in 210 g range. The specimens were immersed in beaker containing 100ml acid solutions without and with different concentration of *Alangium salviflorum* leaves extract using hooks. Before it was immersed, the specimens were cleaned and the weight is recorded. After 72 hours, the test specimens were removed and then washed with double distilled water, dried and reweighed. The average mass loss of two parallel carbon steel specimens were obtained.[6] From the change in weight of specimens the corrosion rate was calculated using the following relationship,

$$\text{Corrosion Rate} = \frac{87.6 \times W}{A \times T \times D} \text{ (mpy)} \qquad \text{...(1)}$$

where

W = Loss in weight in mg
A = Surface area of the specimen (cm^2)
T = Time in hours
D = Density ($7.2 g/cm^3$)

Corrosion Inhibition Efficiency (IE) was then calculated using the equation

$$IE = 100[1-(W_2/W_1)] \% \qquad \text{...(2)}$$

$$IE = \frac{1}{(W_2/W_1)} \times 100 \qquad \text{...2}$$

where,

W_1 = Corrosion rate in the absence of inhibitor and
W_2 = Corrosion rate in the presence of inhibitor

2.4 Infra Red (IR) Spectroscopy

Infrared spectroscopy is a well-developed technique to identify chemical compounds. The specimens were suspended by means of hooks in solution having with and without inhibitor for 72 hours. After 72 hours the specimen were taken out. Then the film formed on the metal surface was scratched off and taken for FT-IR spectral study.

2.5 UV-Visible Spectroscopy

The possibility of the formation of film on the metal surface was examined by mixing the respective solution and recording their UV-visible absorption spectra using Lambda 35 UV-visible spectrophotometer which is a PC controlled single beam scanning spectrophotometer. It covers wavelength range from 200 nm to 1000 nm with a setting accuracy of ± 1 nm.

2.6 Fluorescence Spectroscopy

Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F-6300 spectrofluorometer.

3. RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

3.1.1 Effect of Inhibitor Concentration

The Weight loss method of monitoring corrosion rate is useful because of its simple application and reliability[6].Inhibition efficiency of carbon steel with different concentration of *Alangium salviflorum* extract in 0.5M HCl at room temperature are presented in Table 1.From the table, it is clear that the corrosion rate decreases with an increase in inhibitor concentration ,i.e. the corrosion inhibition enhances with the inhibitor concentration. This behavior is due to the fact that the adsorption and coverage of the inhibitor on the carbon steel surface increase with the inhibitor concentration. The maximum inhibition efficiency of 63% was obtained at 50 ppm of *Alangium salviflorum* and 25 ppm of $ZnSO_4$ in 0.5M HCl at 72 hours of immersion period. The high inhibitive performance of *Alangium salviflorum* suggests a higher bonding ability of inhibitor on carbon steel surface.

Further, it is observed that the inhibition efficiency increases due to the addition of sucrose as additive, it is found that, at 40ppmof concentration shows an IE of 65%. Similarly, it is observed in addition of fructose as additive it is found that, at 40ppmshows an IE of 85%. The variation in IE of the additives are graphically represented in Figure 1.

Table 1

Inhibition efficiency and corrosion rate of carbon steel in 0.5 M HCl (Immersion Period = 72 hours)

Con. of ALA (ppm)	Con. of Zn^{2+} ion (ppm)				Con. of ALA-Zn^{2+} ion (ppm)	Con. of additives (ppm)	Sucrose		Fructose	
	0		25							
	IE %	CR (mpy)	IE %	CR (mpy)			IE %	CR (mpy)	IE %	CR (mpy)
10	53	1.53	58	1.88	50:25	10	62.00	1.72	79.9	0.90
20	49	1.88	44	2.51		20	55.00	2.01	80.9	0.86
30	43	1.76	56	1.96		30	61.70	1.73	79.7	0.91
40	62	2.29	36	2.88		40	65.00	1.56	85.0	0.66
50	59	1.86	63	1.74		50	38.60	2.77	78.0	0.98
60	61	2.25	61	1.66		60	37.90	2.80	81.5	0.83
Blank		8.50		8.50		Blank		9.90		9.90

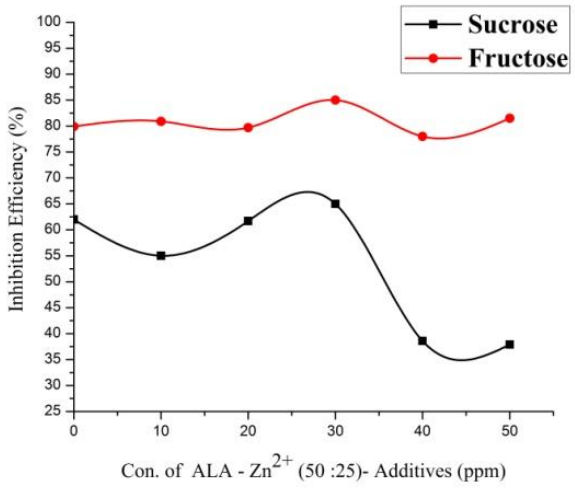


Fig. 1: Inhibition Efficiencies of ALA-Zn^{2+}-Additives

3. 2 Analysis of FTIR

FTIR is a powerful tool for identifying the functional groups associated with the adsorption of an inhibitor. The FTIR spectrum of the extract and the film formed on the surface of the metal immersed in 0.5 M HCl in the presence of the inhibitor were taken and shown in Figures 2-5 respectively.

FTIR spectroscopy has been used to analyze the protective film formed on the metal surface.[7,8,9] The FTIR spectrum of the pure extract ALA is shown in Figure 2. The >C=O stretching frequency of the carboxyl group appears at 1592.98 cm^{-1}. The -OH stretching frequency isobserved at 3198.71 cm^{-1}. The C-H stretching frequency peakat 1424.07 cm^{-1}. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing 50 ppm of ALA and 25 ppm of Zn^{2+} ion is shown in Figure 3. It is observed that the >C=O stretching frequency has shifted from 1592.98 to 1570.41 cm^{-1}. The -OH stretching frequency is shifted from 3198.71 cm^{-1} to 3430.37 cm^{-1}. The C-H stretching frequency varies from 1424.07 cm^{-1} to 1420.88 cm^{-1} This indicates that the oxygen atoms of the carboxyl group and -OH have coordinate with Fe^{2+} resulting in the formation of Fe^{2+}-ALA complex formed on the anodic sites of the metal surface. The peaks at 1350.02 cm^{-1} and 637.93cm^{-1} are due to Zn-O bond. The –OH stretching frequency appears at 3430 cm^{-1}. These observationS suggest that $Zn(OH)_2$ is formed on the cathodic sites of the metal surface. [10-13]

The FTIR spectrum of 50 ppm ALA-25 ppm Zn^{2+} & 40 ppm Fructose is shown in Figure 4. The>C=O stretching frequency has shifted from 1570.41 to 1569.80 cm^{-1}. The -OH stretching frequency has shifted from 3430.37 cm^{-1} to 3431.41 cm^{-1}. The C-H stretching frequency varies from 1420.88 cm^{-1} to 1420.47 cm^{-1}. The peaks at 1299.07 cm^{-1} and 621.84 cm^{-1} are due to Zn-O bond. The –OH stretching frequency appears at 3431 cm^{-1}.

The FTIR spectrum of 50 ppm ALA-25 ppm Zn^{2+} & 40 ppm Sucrose is shown in Figure 5. The >C=O stretching frequency has shifted from 1570.41 cm-1 to 1568.51 cm^{-1}. The -OH stretching frequency has shifted from 3430.37 cm^{-1} to 3436.26 cm^{-1}. The C-H stretching frequency varies from 1420.88 cm^{-1} to 1418.26 cm^{-1}. The peaks at 1346.28 cm^{-1} and 650.89 m^{-1} are due to Zn-O bond. The –OH stretching frequency appears at 3436.26 cm^{-1}.

This indicates that the oxygen atoms of the carboxyl group and -OH have coordinate with Fe^{2+} resulting in the formation of Fe^{2+}-ALA-Fructose/Sucrose complex formed on the anodic sites of the metal surface. These observations suggest that $Zn(OH)_2$ is formed on the cathodic sites of the metal surface.

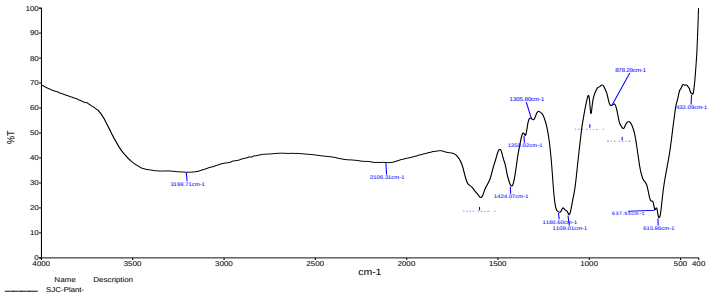


Fig. 2: FTIR Spectrum of pure extract of *Alangiumsalvifolium* (ALA)

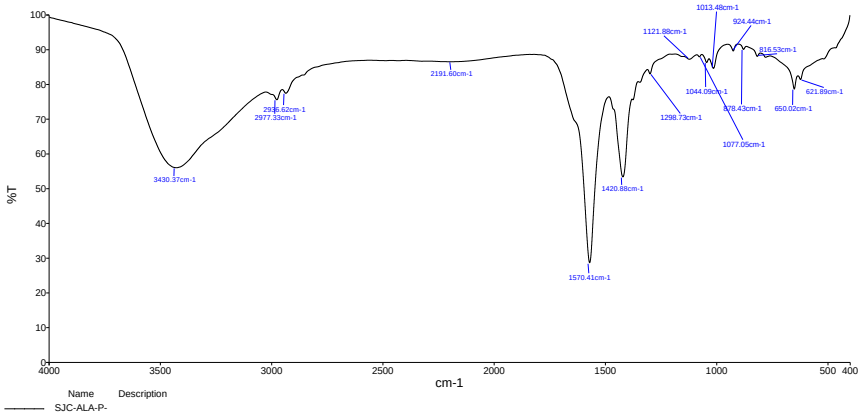


Fig. 3: FTIR Spectrum of 50ppm ALA + 25ppm Zn^{2+}

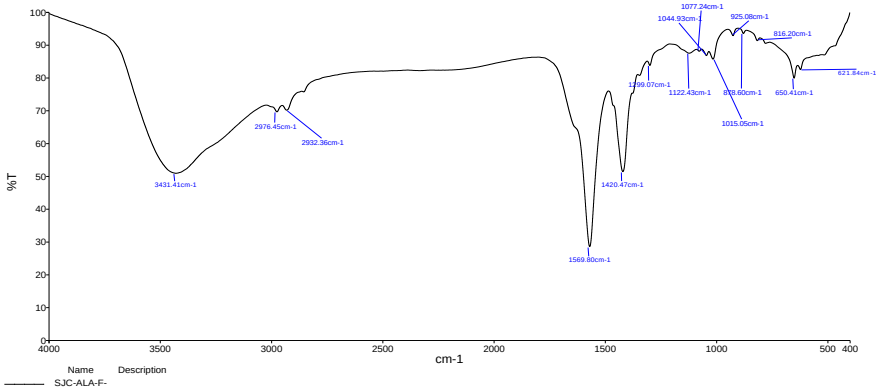


Fig. 4: FTIR Spectrum of 50ppm ALA + 25ppm Zn^{2+} + 40ppm Fructose

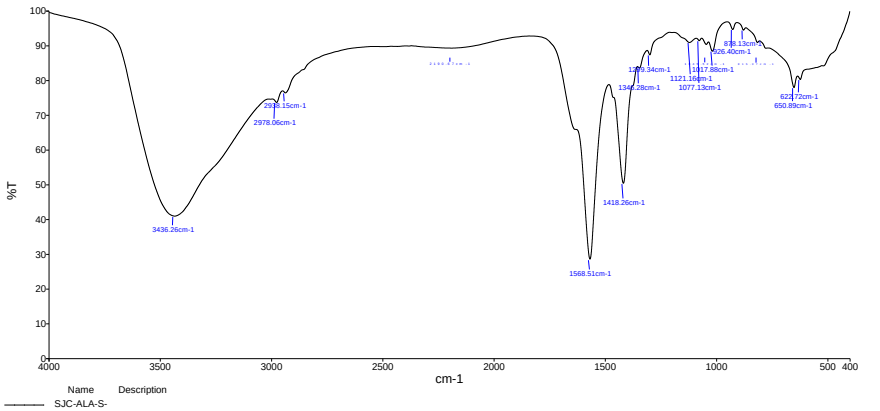


Fig. 5: FTIR Spectrum of 50 ppm ALA + 25 ppm Zn^{2+} + 40 ppm Sucrose

3.3 Analysis of UV-Visible Absorption Spectra

The UV-Visible absorption spectra of the solution containing ALA, 50 ppm ALA – 25 ppm Zn^{2+}, 50 ppm ALA –25 ppm Zn^{2+}-40 ppm Fructose and ALA - Zn^{2+} - 40 ppm Sucrose are shown in Figures 6-9 respectively. A peak appears at 830.20 nm, when Zn^{2+}ion is added a peak appears at 202.0 nm, the intensitydecreases. This indicates that a complex formation occurs between ALA and Zn^{2+}ion. It is observed that, when fructose is added to ALA- Zn^{2+} systemthe peak appears at 199.6 nm, the intensitydecreases. This indicates the complexationof ALA - Zn^{2+} & Fructose. Similarly, it is observed that, when sucrose is added to ALA- Zn^{2+} system a peak appears at 203.9 nm. There is a negligible change in intensity. This indicates that a complex is formed between ALA and Zn^{2+} & Sucrose.

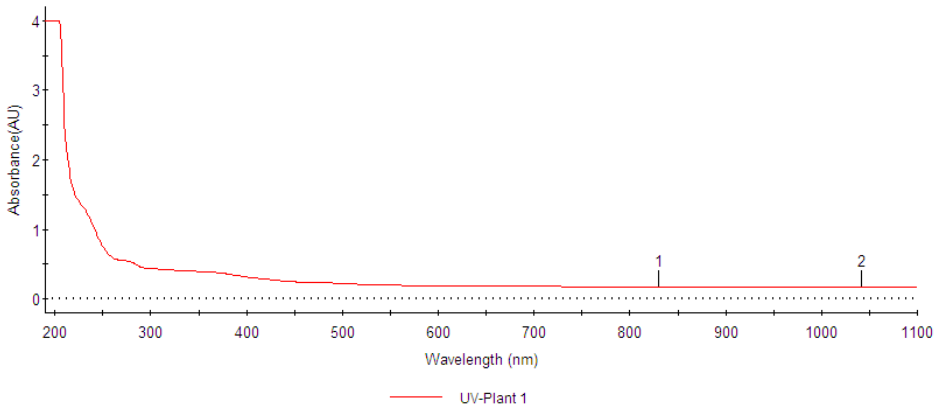


Fig. 6: UV-Visible spectrum of pure extract of *Alangium salviflorum* (ALA)

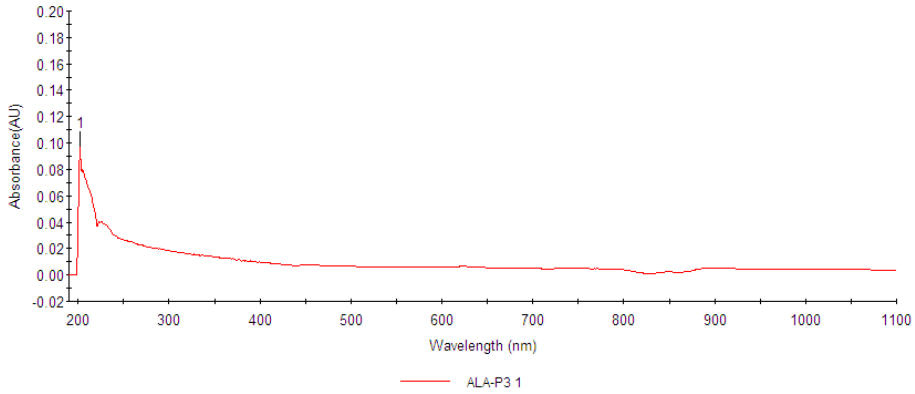


Fig. 7: UV-Visible spectrum of 50 ppm ALA + 25 ppm Zn^{2+}

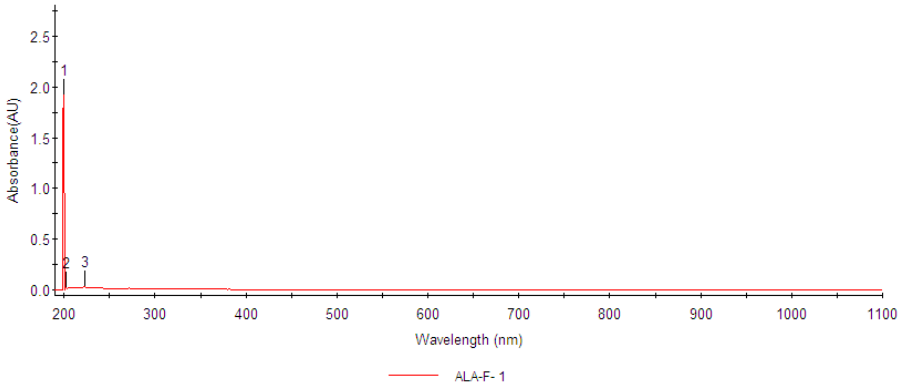


Fig. 8: UV-Visible spectrum of 50 ppm ALA + 25 ppm Zn^{2+} & 40 ppm of Fructose

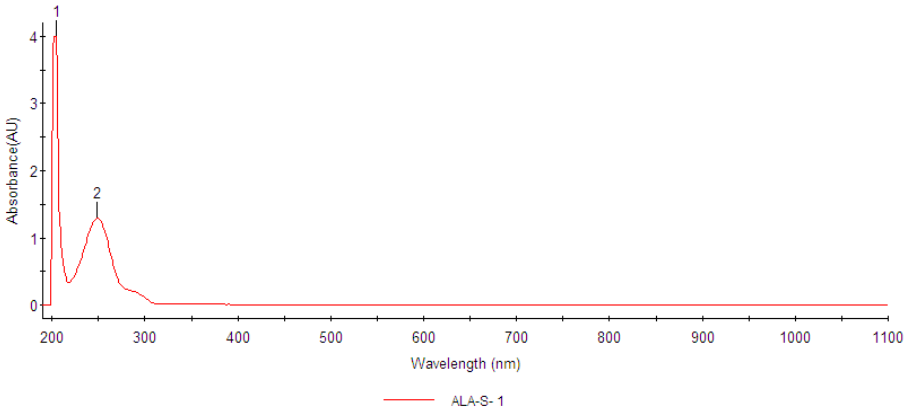
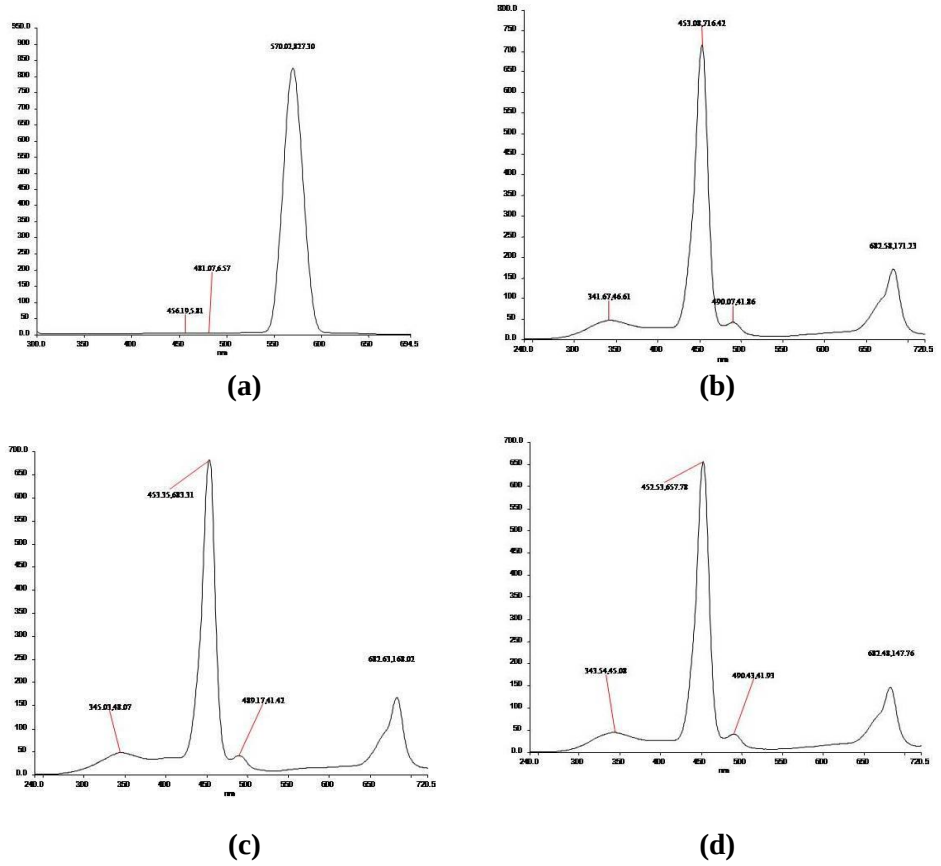


Fig. 9: UV-Visible spectrum of 50 ppm ALA + 25 ppm Zn^{2+} & 40 ppm of Sucrose

3.4 Analysis of Fluorescence

Fluorescence spectrumis used to detect the presence of ALA-Zn^{2+} inhibition complex formed on the metal surface. The λ_{ex} for the emission spectrum of the pure ALA is found to be 570.02 nm and for ALA-Zn^{2+} the peak is obtained at 452.53 nm are shown in Figure 10 (a, b) respectively. The peaks appeared at 343.54 nm, 40.43 nm & 682.48 nm, indicates the formation of protective film on the surface of the metal. Figure 10(c), shows the λ_{ex} for the emission spectrum of the 50 ppm ALA-25 ppm Zn^{2+}-40 ppm Fructose, the peak is obtained at 453.08 nm. The peaks also appear at 341.67 nm, 40.07 nm & 682.58 nm. There is a decrease in the intensity ,which indicates the formation of protective film on the surface of the metal. Figure 10 (d), shows that the λex for the emission spectrum of the 50 ppm ALA-25 ppm Zn^{2+}-40 ppm Sucrose, the peak is obtained at 453.35

nm. The peaks also appear at 345.03 nm, 489.17 nm & 682.63 nm. There is a decrease in the intensity value indicates the formation of protective film on the surface of the metal.



(a) **(b)**

(c) **(d)**

Figure 10: Fluorescence Spectra

a) pure extract of *Alangium salviflorum*(ALA)
b) 50 ppm ALA + 25 ppm Zn^{2+} ion
c) 50 ppm ALA + 25 ppm Zn^{2+} & 40 ppm of Fructose
d) 50 ppm ALA – 25 ppm Zn^{2+} & 40 ppm of Sucrose

4. CONCLUSION

From the above study it is concluded that:

1. *Alangiumsalviflorum* is a good corrosion inhibitor for corrosion of carbon steel in 0.5 M HCl solution. The maximum efficiency was found to be 63%

at 50 ppm ALA + 25ppm Zn^{2+}. And the inhibitive efficiency was found to be near to the maximum efficiency with the additive sucrose of 65 % IE & fructose of 85% IE.

2. The FT-IR, UV-Visible spectra prove the formation of the film on the surface of the metal.
3. The Fluorescence study results clearly confirm the formation of the film on the surface of the metal.

REFERENCE

1. Kilbourn, B. T., *Cer. Eng. Sci. Proc.*, 6 (1985) 1331.
2. Bethencourt, M., Botana, F. J., Calvino, J. J., Marcos, M., *Corros. Sci.*, 40 (1998), 1803.
3. Arenas, M. A., Conde, A., de Damborenea, J., *Corros. Sci.* 44 (2002), 511.
4. Arinathan, V., Mohan, V. R., Debritto, A. J., Murugan, C. "*Wild edibles used by Palliyars of the Western Ghats, Tamil Nadu, Indian. J. Tradit. Know*" 6 (2007), 163-168.
5. Bharath Kumar, R., Suryanarayana, B. Promising antidote plant species from the Tribals of Sriharikota Island, Andhra Pradesh. *Life Sciences Leaflets*, 19 (2011), 769-779.
6. Deves Plecher and Frank Walsh C, "*Industrial Electrochemistry Chapman and hall London*" (1990).
7. Amar, H., Braisaz, T., Villemin, D., Moreau, B., *Materials Chemistry and Physics*. 1101 (2008) 1-6.
8. Kalaivani, R., Narayanasamy, B., Selvi, J. A., Amalraj, A., Jayasundari, J. and Rajendran, S., *Portugaliae Electrochimica Acta*. 27(2009), 177.
9. Rajendran, S., Apparao, B. V. and Palanisamy, N., *Proc. 8th Europ. Symp. Corros. Inhibitors*, Ferrara, Italy, 1(1995), 465.
10. Vera, R., Schrebler, R., Cury, P., Del Reo, R. and Romero, H., *J. Appl. Electrochem*., 37(2007), 519-525.
11. Domas, Ph., Bouffakhreddine, B., Am, C., Vatel, O., Ands, E., Galindo, R. and Selvan, F., *Quantitative microroughness analysis down to the nanometer scale, Europhys. Lett*., 22(1993), 717-722.
12. Bennett, J. M., Jahannir, J., Podlesny, J. C., Baiter, T. L. and Hobbs, D. T., *Appl. Opt*., 43(1995), 213-230.
13. Duparre, A., Kaiser, N., Truckenbrodi, H., Berger, M. and Kohler, A., "*Microtopography Investigations of Optical Surfaces and Thin Film by light scattering, Optical Profilometry and Atomic Force Microscopy, Int. Symp. On Optics*", Imaging and Instrumentation, 11-16 Jul. (1993), San Diego CA. Proc. SPIE, 1995 (1993), 181-192.