IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN: 2278-5736.Volume 8, Issue 2 Ver. II. (Feb. 2015), PP 10-16
www.iosrjournals.org

Acid Extract of Polyalthia Longifolia as a Green Corrosion Inhibitor for Mild Steel in H_2SO_4 Solution

K. Shanmuga Priya[1], V.G. Vasudha[2]
[1]*(Department of Chemistry, BNMIT, Bangalore, VTU, Belgaum, Karnataka, India).*
[2]*(Department of Chemistry, Nirmala College for women, Coimbatore, Tamilnadu, India).*

Abstract: *The corrosion inhibition behavior of Polyalthia longifolia (PL) leaves on mild steel in 1N H_2SO_4 medium was investigated by gravimetric, polarization, electrochemical impedance measurements and temperature studies. Effect of temperature (35-75^{0}C) on the corrosion behavior of mild steel in the presence of plant extract was studied. The inhibition efficiency of PL showed an improvement with increasing concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir, Temkin, Freundlich adsorption isotherms. The results obtained prove that the leaves of Polyalthia Longifolia act as a good corrosion inhibitor having efficiency of 92% at 1.5% inhibitor concentration. The surface adsorbed film was analyzed by scanning electron microscope technology with energy dispersive X-ray spectroscopy (SEM-EDX).*
Keywords: *Mild steel, acid corrosion, Polyalthia Longifolia, H_2SO_4 medium.*

I. Introduction

Due to various industrial application and economic importance of mild steel, its protection against corrosion has attracted much attention. One of the most practical methods for protection against excessive dissolution of metal by corrosion is use of proper inhibitors [1]. The use of organic compounds containing oxygen, sulphur and nitrogen to reduce the corrosion of mild steel has been studied in detail [2-7]. Extracts of naturally occurring products contain mixtures of compounds having oxygen, sulphur and nitrogen elements and are eco friendly in nature. Ricimus communis leaves were studied for corrosion inhibition of mild steel in acid media in addition to the herbs such as coriander, hibiscus, anis, black cumin, and garden cress as new type of green inhibitors for acidic corrosion of steel [8-13]. In the present study, the inhibitive performance of PL on mild steel in 1N H_2SO_4 at different temperatures has been studied by gravimetric, thermodynamic, potentiodynamic polarization and electrochemical impedance studies.

II. Experimental

A. Samples and test solution

Mild steel coupons were mechanically polished with emery sheet of fine quality, washed with double distilled water, degreased with alcohol and finally dried at room temperature before being immersed in the acid solution. Weight loss experiments were performed using an electronic balance. For polarization studies mild steel coupons with 1 cm^2 exposed area were used as the working electrode.

A 5% stock solution of Polyalthia Longifolia inhibitor was prepared by refluxing 12.5g of dry PL leaves powder with 250 mL of 1N H_2SO_4 for 3 hours. The refluxed solution was allowed to stand overnight and filtered through ordinary filter paper. The residue was washed repeatedly washed with 1N H_2SO_4 and the filtrate was made up to 250 mL. This was taken as the stock solution and from this different concentration of inhibitor solutions ranging from 0.1% to 1.5% were diluted.

B. Gravimetric measurements

Gravimetric experiments were carried out using a solution volume of 100 cm^3 in glass beakers. The mild steel specimens used were rectangular with a dimension of 5x1 cm^2 and 2mm thickness. The initial weight of the specimen was recorded using an analytical balance. After the corrosion test in 1N H2SO4 with and without the inhibitor in different concentration (0.1% to 1.5%), the specimens were carefully washed in double distilled water, dried and then weighed. The weight loss was determined after different immersion periods (1 hr, 3 hr, 5 hr, 7 hr, 12 hr and 24 hr) at 303 K. The weight loss experiments were conducted at different temperatures (308, 318, 328, 338 and 348 K). Triplicate experiments were performed in each case, and the mean value was taken from which the % Inhibition Efficiency was calculated using the formula

$$IE\ \% = \frac{w_0 - w_i}{w_i} \times 100;$$

(Where w_0 and w_i are weight loss without and with plant extract respectively).
Acid concentration was changed and the % inhibition efficiency was studied at different time of immersion.

C. Electrochemical and impedance measurements

A conventional three electrode glass cell consisting of a working electrode (mild steel sample), a pure platinum counter electrode and a saturated calomel reference electrode was used for the measurements. The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. All tests were performed in unstirred conditions at 303 K using CH1660D electrochemical workstation. The working electrode was maintained at open circuit conditions for 1 Hr and thereafter anodic and cathodic polarization curves were recorded in the potential range from -800 to +500 mV with a scan rate of 0.4 mV s^{-1}. The AC impedance measurements were performed in the frequency range of 0.1 to 10,000 Hz with signal amplitude of 10mV.

D. Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The surface morphology of the mild steel specimen was evaluated by SEM-EDX analysis with. Mild steel samples immersed in 1 N H_2SO_4, lowest inhibitor concentration and highest inhibitor concentrations were examined for the above study.

III. Results And Discussion

Based on weight loss measurements, the values of % IE for various concentrations of PL at different temperatures are given in Table I.

Table I: % Ie Of Pl In H_2so_4 At Different Concentrations And Different Temperatures

T in K	%IE							
	0.1	**0.3**	**0.5**	**0.7**	**0.9**	**1.1**	**1.3**	**1.5**
308	32.1	36.8	44.7	51.3	68.4	71.0	72.8	73.9
318	33.7	37.5	58.2	59.4	70.5	73.3	73.9	74.7
328	35.1	45.4	62.2	64.9	73.2	76.4	85.5	88.4
338	30.4	38.7	66.9	74.9	76.2	79.7	88.2	90.4
348	36.0	41.0	54.7	71.3	74.0	75.5	77.9	82.0

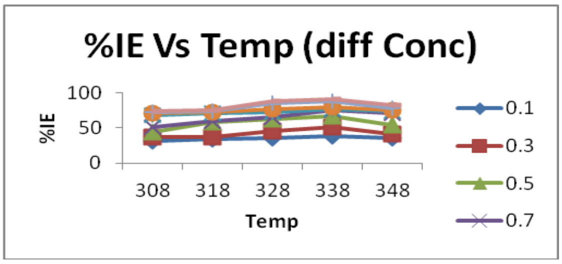

Fig. 1: Plot of % IE Vs Temp at different concentrations.

From the values in Table 1 it is clear that the % IE increases with the increase of concentration reaching a maximum value of 90% at an inhibitor concentration of 1.5% at 338 K. The graph in Fig.1 depicts that as the temperature increases the inhibition efficiency increases up to a certain temperature (338 K) and then decreases. At elevated temperature as time lag between adsorption and desorption of inhibitor over metal surface becomes shorter the IE decreases. Metal surface remaining exposed to acid environment for a longer period increases the rate of corrosion and thus decreases the inhibition efficiency. This clearly shows that increase in the inhibitor concentration increases the number of molecules adsorbed over the mild steel surface, blocking the active sites of acid attack and hence protecting the metal from corrosion.

Corrosion rate (CR) of mild steel in the absence and presence of PL extract was calculated and the data obtained for different immersion timings is shown in Table II. Plot of corrosion rates against different time are shown in Fig.2.

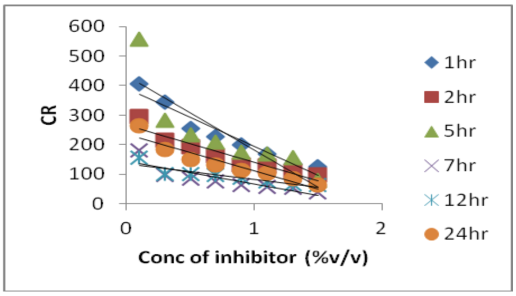

Fig .2: Plot of CR Vs Conc. at different immersion periods.

Table II: Cr Of Pl In H_2so_4 At Different Concentrations And Different Immersion Periods.

Ext Conc. (%v/v)	CR					
	1 hr	**2 hr**	**5 hr**	**7 hr**	**12 hr**	**24 hr**
Blank	859.1	728.2	831.1	487.8	890.7	843.4
0.1	405.5	294.3	557.3	181.2	155.1	265.0
0.3	344.5	213.6	281.7	98.7	100.3	183.8
0.5	255.1	191.8	232.0	84.1	99.5	149.2
0.7	226.7	163.5	207.5	75.3	97.0	130.5
0.9	200.6	133.0	175.3	64.1	89.7	114.6
1.1	167.8	128.6	169.2	57.6	75.5	102.6
1.3	135.1	109.02	155.6	54.8	66.3	85.5
1.5	126.4	97.0	78.9	38.6	63.2	64.1

The result obtained shows that the rate of corrosion of mild steel decreases with increase in the concentration of PL extract but increases with increase in temperature. This confirms the inhibitive action of the extract in H2SO4 medium. The concentration of the acid was increased from 1 N to 5N and 7 N. The inhibitor concentration was also increased accordingly varying from 1% to 2.5% (v/v) and the % IE was found out gravimetrically for different immersion periods (15 mins, 30 mins and 45 mins). The results obtained are shown in Table III. In most of the industries corrosion inhibition of mild steel is done within a short span of time and these industries use higher concentration of acids. From the values obtained in Table III, it is clear that PL acts as a good corrosion inhibitor for short time duration. Fig.3 shows a maximum inhibition efficiency of 98.78% for an inhibitor concentration of 2.5% during an immersion period of 45 minutes for 7N H_2SO4 acid concentration. For the same conditions it shows 93.18 % IE for 5N H_2SO_4 acid concentration.

Table III: %Ie For Increased Acid Concentration.

	% IE					
	5 N acid			**7 N Acid**		
Inh Conc (%)	15 mins	30 mins	45 mins	15 mins	30 mins	45 mins
1	69.54	74.22	77.99	84.76	87.03	90.55
1.5	74.64	79.08	83.11	90.46	91.20	94.67
2	78.07	87.15	90.64	92.22	93.45	96.10
2.5	86.35	90.27	93.18	95.92	97.38	98.78

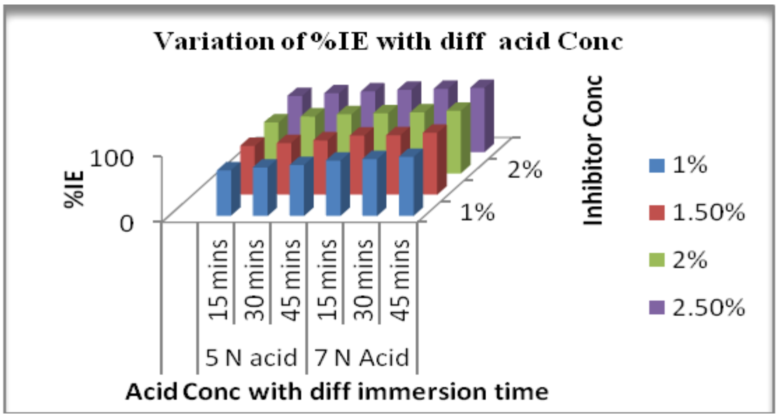

Fig. 3: Plot showing %IE with higher acid concentration.

The interaction between inhibitor and mild steel surface can be understood from the adsorption isotherms. The values of surface coverage (θ) were evaluated using CR values obtained from the weight loss method. The values of surface coverage at different concentrations of Polyalthia longifolia leaves extract in H_2SO_4 media in temperature range of 308 K to 348 K is used to explain the adsorption process. The θ values for different concentration of inhibitors from the acid were tested graphically by fitting to various isotherms. It was observed that the data fitted the Langmuir adsorption isotherms with correlation coefficients >0.9.

Table IV gives the parameters of Langmuir isotherm. The plots of log(**θ** /1- **θ**) vs log C yielded a straight line as shown in Fig.4, where C is the inhibitor concentration, proving that the inhibition is due to the adsorption of the active compounds onto the metal surface and obeys the Langmuir isotherm.

Table IV: Parameters Of Langmuir Isotherm Of Pl In H_2so_4.

log C	**log θ/1-θ**				
	308	**318**	**328**	**338**	**348**
-1	-0.32	-0.29	-0.26	-0.35	-0.24
-0.52288	-0.23	-0.22	-0.07	-0.19	-0.15
-0.30103	-0.09	0.14	0.21	0.30	0.08
-0.1549	0.02	0.16	0.26	0.47	0.39
-0.04576	0.33	0.37	0.43	0.50	0.45
0.041393	0.38	0.43	0.51	0.59	0.49
0.113943	0.42	0.45	0.77	0.87	0.54
0.176091	0.45	0.47	0.88	0.97	0.65

From the results obtained, it is significant to note that these plots are linear with the slopes equal to unity, which indicates a strong adherence of the adsorption data to the assumptions confirming Langmuir adsorption isotherm.

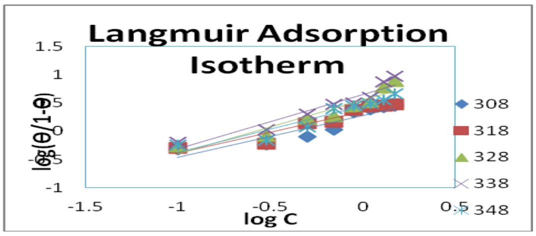

Fig.4: Langmuir isotherm of PL in H_2SO_4.

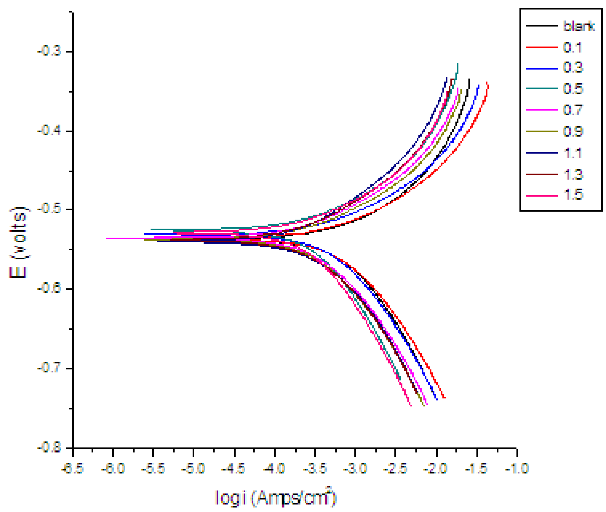

Fig. 5: Potentiodynamic polarization of mild steel in 1N H_2SO_4 with and without PL extract.

The potentiodynamic polarization data are shown as the Tafel plots for mild steel in 1N H_2SO_4 with the addition of various concentrations of the inhibitor in Fig.5. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) were derived from these curves and are given in Table 5. The % IE was calculated using the formula

$$\%IE = \frac{I_{corr\ (blank)} - I_{corr\ (inh)}}{I_{corr\ (blank)}} * 100$$

Where $I_{corr\ (blank)}$ and $I_{corr\ (inh)}$ are the values of corrosion current densities of mild steel without and with the inhibitor respectively, which was determined by extrapolation of the cathodic and anodic Tafel lines to the corrosion potential E_{corr}. The values given in the Table V shows that corrosion current (I_{corr}) decreases markedly in the presence of extract, which confirms the inhibitive action of PL extract in H_2SO_4 medium. The anodic and cathodic Tafel slopes b_a and b_c are changed markedly in the presence of the extract, which confirms that the extract contained the active molecules which behaved as mixed-type of acid corrosion inhibitors.

Table V: Potentiodynamic Polarization Parameters For Mild Steel In 1n H2so4 In Presence Of Pl Extract.

Conc	E_{corr}	I_{corr}	b_a	b_c	R_p	% IE	
	V	µAmp/cm²	1/v	1/v	Ohm/cm²	Tafel	Linear
Blank	-0.53	870.4	8.357	6.734	33	-	-
0.1	0.538	599.6	11.426	6.967	39	**31.11**	**15.38**
0.3	-0.54	562.9	10.329	7.233	44	**35.32**	**25**
0.5	-0.51	368	9.538	6.462	52	**57.72**	**36.53**
0.7	-0.53	357.1	12.962	7.688	59	**58.97**	**44.06**
0.9	-0.54	351.1	10.362	7.642	69	**59.66**	**52.17**
1.1	-0.54	342.3	10.616	7.32	71	**60.67**	**53.52**
1.3	-0.54	299.1	12.209	7.69	73	**65.63**	**54.79**
1.5	-0.55	230.9	11.981	6.247	103	**73.47**	**67.96**

The inhibitive properties of the extract have also been evaluated by the determination of the polarization resistance R_p. The linear polarization values R_p in the absence and presence of different concentrations of inhibitor are given in the Table V. The % IE was calculated as follows

$$\%IE = \frac{R_{p\,(inh)} - R_{p\,(blank)}}{R_{p\,(inh)}} * 100$$

Where $R_{p\,(inh)}$ and $R_{p\,(blank)}$ are linear polarization values in presence and absence of inhibitor. From the results, R_p values gradually increased with increase in the concentration of inhibitor confirming that the extracts of PL acted as a good corrosion inhibitor.

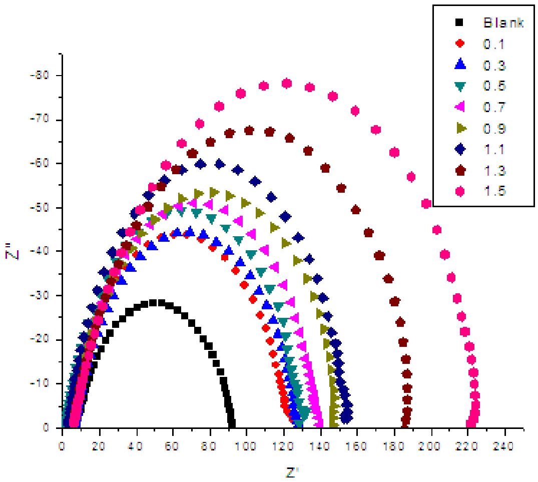

Fig.6: Nyquist plots showing inhibitive effect of PL extract on corrosion of mild steel in 1N H_2SO_4.

The corrosion behavior of mild steel in 1N H_2SO_4 in the absence and presence of different concentrations of PL extract were also investigated by Electrochemical Impedance Spectroscopy (EIS) technique. The resultant Nyquist plots are shown in Fig.6. The existence of single semicircle in each plot shows that there was only single charge transfer process during the anodic dissolution of MS. There was a gradual increase in the diameter of each semicircle of the Nyquist plot due to increase in the number of inhibitive molecules in the extract when the concentration was raised from 0.1 to 1.5 % v/v.

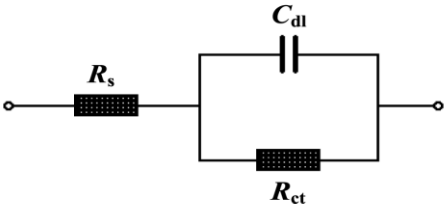

Fig. 7: Randle's Equivalent circuit diagram.

A simple equivalent Randle circuit shown in Fig. 7 is used to get the values of the solution resistance (R_s), charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}). The inhibition efficiency was calculated using the charge transfer resistance as follows.

$$\%IE = \frac{R_{ct\,(inh)} - R_{ct\,(blank)}}{R_{ct\,(inh)}} * 100$$

Where $R_{ct\,(inh)}$ and $R_{ct\,(blank)}$ are linear polarization values in the presence and absence of inhibitor.

Table VI: Impedance Parameters For Mild Steel In 1n H_2so_4 In The Presence Of Pl Extract.

Conc % v/v	**C_{dl} µ farads**	**R_{ct} ohms**	**Inhibitor Efficiency Linear**
Blank	122.8	90	-
0.1	107.1	123	26.83
0.3	100.5	127	29.13
0.5	95.89	130	30.76
0.7	81.67	140	35.71
0.9	78.77	149	39.59
1.1	73.7	158	43.03
1.3	54.78	183	50.82
1.5	48.76	220	59.09

From the values obtained in Table VI the R_{ct} values increased with the increasing concentration of the inhibitor indicating that more inhibitor molecule adsorb on the metal surface at higher concentration and form a protective film on the metal-solution interface [14-15]. The values of C_{dl} decreased with increasing inhibitor concentration. Decrease of C_{dl} indicates a reduction in local dielectric constant by increase in thickness of the electrical double layer. Thus the results obtained indicate that the extract of PL function by adsorption on the metal surface causing a decrease in the C_{dl} values and an increase in the R_{ct} values.

The SEM micrographs of different slides of mild steel after immersion in the aqueous solution with the absence and presence of the inhibitor are shown in Fig.8 and Fig.9.

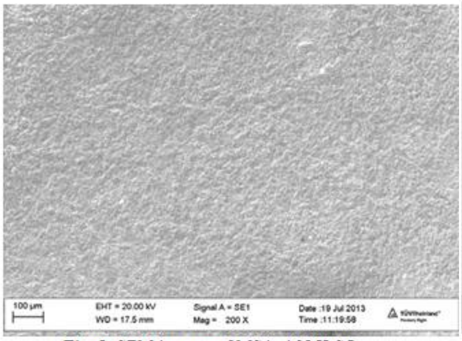

Fig. 8: SEM images of MS in 1 N H_2SO_4

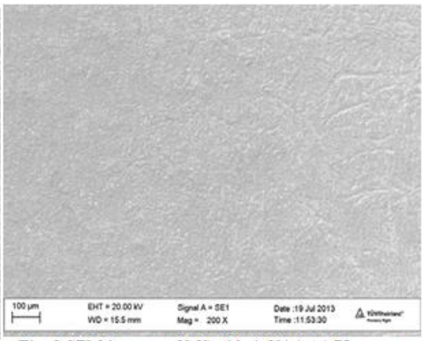

Fig. 9 SEM images of MS with 1.5% (v/v) PL extract.

The SEM images in Fig.8 shows that the surface of mild steel was extremely damaged in the absence of the extract while Fig.9 shows the formation of a film by the constituents present in leaf extract of Polyalthia Longifolia (PL) on the mild steel surface which was responsible for corrosion inhibition.

The Energy Dispersive X-Ray Spectroscopy (EDX) is shown in Fig. 10, Fig. 11 and Fig. 12. On evaluation of the spectra it is clear that the value of C is increasing as the inhibitor concentration is increased, which shows that it might be due to the presence of C in the plant constituents that gets adsorbed on the steel surface. The values of other constituents are also shown in Table VII.

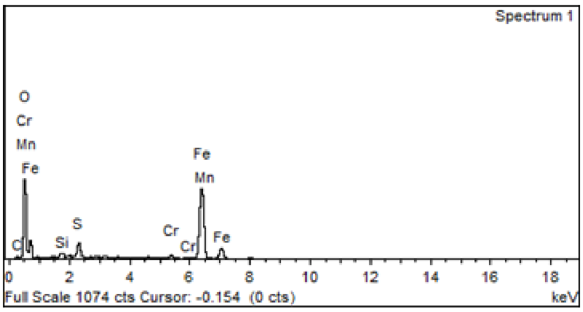

Fig.10: EDX spectra of mild steel in without inhibitor

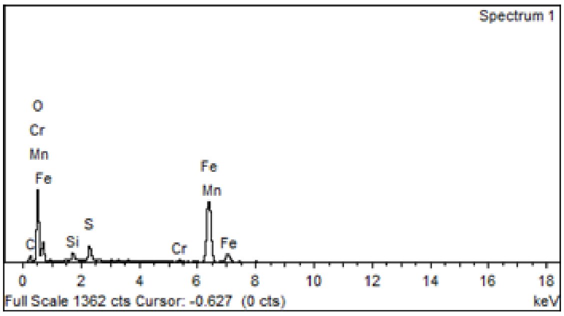

Fig.11: EDX spectra of mild steel with 0.1% (v/v) inhibitor

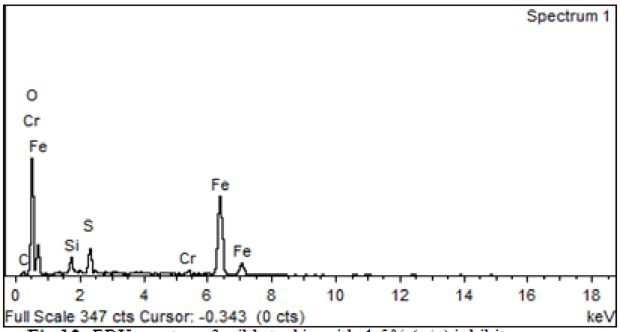

Fig.12: EDX spectra of mild steel in with 1.5% (v/v) inhibitor

Table VII: Composition Of The Samples With Respect To Edx Analysis.

ELEMENT	MS without Inhibitor (%)	MS with 0.1% Inhibitor conc (%)	MS with 1.5% Inhibitor conc (%)
C	2.83	4.82	10.25
S	1.15	3.56	2.84
O	35.95	41.43	36.88
Fe	55.65	46.71	47.71

IV. Conclusion

The molecules present in the extract of Polyalthia Longifolia leaves effectively inhibited the corrosion of mild steel in 1N H_2SO_4 at various concentrations by forming a protective barrier layer. The inhibition efficiency increased gradually with increase in the concentration. Potentiodynamic polarization measurements have shown that the extract of PL leaves acted as a mixed type inhibitor inhibiting both anodic and cathodic reactions. The results of the weight loss, electrochemical polarization and AC impedance were all in good agreement as a support to the above conclusions. Thus acid extract of PL leaves is considered to be a cheap, eco-friendly and effective corrosion inhibitor.

References

[1]. J.M. Sykes, Br. Corros. J. 25 (1990) 175.

[2]. M. Elachauri, M.S. Hajji, S. Kertit, E.M. Salem, R. Coudert, Corros. Sci. 37 (1995) 381.

[3]. B. Mernari, H. Elattari, M. Traisnel, F. Bentiss, M. Lagrenee, Corrosion 40 (1998) 391.

[4]. L. Wang, Corros. Sci. 43 (2001) 2281.

[5]. M. E. Azhar, M. Mernari, M. Traisnel, F. Bentiss, M. Lagrenee, Corros. Sci. 43 (2001) 2229.

[6]. M. A. Quraishi, M.A.W. Khan, M. Ajmal. S. Muralidharan, S.V. Iyer, J. Appl. Electrochem. 26 (1996) 443.

[7]. F. Bentiss, M. Traisnel, M. Lagrenee, Corros. Sci. 42 (2000) 127.

[8]. E.A. Noor, " Comparitive study on the corrosion inhibition of mild steel by aqueous extract of Fenugreek seeds and leaves in acidic solution," Journal of Engineering and Applied Sciences, vol.3, no. 1, pp. 23-30, 2008.

[9]. J. Buchweishaija and G.S. Mhinzi, "Natural products as a source of environmentally friendly corrosion inhibitors: the case of gum exudates from Acacia seyal var. seyal," Portugaliae electrochimica Acta, vol. 26, no. 3, pp. 257-265, 2008.

[10]. E.E. Oguzie, "Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel," Corrosion Science, vol. 50, no. 11, pp. 2993-2998, 2008.

[11]. P.C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umoren, " Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media," Corrosion Science, vol. 50, no. 8, pp. 2310-2317, 2008.

[12]. M. a. Quarishi, A. Singh, V.K. Singh, D.K. Yadav, and A.K. Singh, "Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves," Materials Chemistry and Physics, vol. 122, no. 1, pp. 114-122, 2010.

[13]. E. A. Noor, "Potential of aqueous extract of Hibiscus sabdariffa leaves for inhibiting the corrosion of aluminium in alkaline solutions, "Journal of Applied Electrochemistry, vol. 39, no. 9, pp. 1465-1475, 2009.

[14]. F. Bentiss, M. Traisnel and M. Lagrenee: Corros. Sci., 2000, 42, 127.

[15]. S. Muralidharan, K.L.N. Phani, S. Pitchumani and S. Ravichandran: J. Electrochem. Soc., 1995, 142, 1478.