Studies on Corrosion Inhibitory Effect of *Phyllanthus Amarus* Leaf Extract on Aluminum in Acidic Medium

O.M. Olutayo[1], S.O. Olayiwola[1], P.G. Oni[2], O. Awolesi[1]*, B.S. Olubusoye[1], O.M. Alabi[1], E.A. Omakagu[3]
[1]Department of Chemical Sciences, Faculty of Science, Olabisi Onabanjo University, Ago-Iwoye, Nigeria
[2]Department of Pure and Applied Chemistry, Faculty of Science, Osun State University, Osogbo, Nigeria
[3]Department of Zoology and Environmental Biology, University of Nigeria, Nsukka, Enugu, Nigeria

Abstract. This paper is aimed at inspecting the corrosion inhibition efficiency (IE) of *Phyllanthus amarus* leaf extract on aluminum in acidic medium and the protective film formed on the aluminum by surface examination using Fourier Transmission Infra-Red (FTIR) spectra. *Phyllanthus amarus* was extracted with ethanol using rotary evaporator. The weight-loss method was used to establish its inhibition efficiency while the FTIR analysis was used to ascertain the formation of the protective film. The weight-loss result indicates that the inhibition efficiency increases as the concentration of the plant extract increases. The FTIR analysis showed that the lone pair of electrons present in the heteroatoms of *Phyllanthus amarus* is responsible for the adsorption inhibition on the metal surface. In regard to the inhibition efficiency that ranged from 11.16% - 85.71% even at low concentrations of 10-50ml/L, *Phyllanthus amarus* leaf extract is considered effective, eco-friendly, affordable, biodegradable, renewable, non-toxic and can serve as an alternative corrosion inhibitor for aluminum, thereby displacing toxic chemical corrosion inhibitors.

Keywords: Corrosion; Inhibition Efficiency; Aluminum; *Phyllanthus amarus*; FTIR

Introduction

Protection of metals against corrosion has attracted much attention globally, due to the loss of natural resources and finances that are sustained annually all over the world due to corrosion (Ating *et al.*, 2010). Aluminum with its alloys, which has an important feature for corrosion resistance, is commonly used in industries such as reaction vessels, pipes, machinery, and chemical batteries (Amin *et al.*, 2009). However, the failure of aluminum equipment due to acid corrosion in industries is widely reported, and the use of chemical inhibitors is regarded as the most practical and best way of controlling corrosion of metals in acid solutions (Abiola *et al.*, 2007). A number of heterocyclic compound have been reported to be a corrosion inhibitor and the screening of synthetic heterocyclic compound is still in progress. Different inorganic inhibitors including but not limited to Chromate, Phosphate, and Nitrite were used as corrosion inhibitors coupled with metal ion, Zn^{2+} in particular, for synergistic function. Although many of the synthesized compounds have shown good anti-corrosive behaviour, but they pose great threat to human beings and the environment, due to their toxicity (Sangeetha *et al.*, 2011).

Currently, due to environmental laws on toxic chemicals, the use of heavy metal-based and/or toxic inhibitors is being restricted. This has precipitated in the use of eco-friendly and affordable, non-toxic, biodegradable and renewable source, such as extract of naturally occurring plant materials as corrosion inhibitors (Sangeetha *et al.*, 2011).

Natural products of plant origin containing different organic compounds, namely, alkaloids, steroids, amino acids, tannins, and flavanoids are known to have inhibitive action

*Corresponding Author

due to the presence of heteroatoms, such as O, N, P, S, which coordinate with the corroding metal ions; hence, protective films are formed on the metal surface, thereby preventing corrosion (El-Etre *et al.*, 2005). Lamaka *et al.* (2007) discussed the inhibition effects of different types of organic compounds for 2024 aluminum alloy in a neutral chloride solution. A comparison between organic complexing agents and salt of rare earth elements inhibition effects were carried out and were studied using electrochemical impedance spectroscopy (EIS) test method. The results showed salicylaldoxime, 8-hydroxyquinoline and quinaldic acid to be the most effective organic inhibitors. Further investigations carried out in the study showed that salicylaldoxime, 8-hydroxyquinoline and quinaldic acid exhibit anti-corrosion property due to the thin adsorptive protective layer formed on the surface of the alloy. A study on the leave extract of Ananas sativum as green corrosion inhibitor for aluminum in 2 M of HCl solution was carried out by Ating *et al*. (2010). The result showed that using weight loss and hydrogen evolution method, the corrosion rate increased with increase in time and temperature due to over-potential of hydrogen evolution. It was reported that the weight loss was found to be lower in the presence of A. sativum than it was in the absence of A. sativum, due to the inhibitive effect of the plant extract on aluminum. The inhibitive efficiency was also studied and it was shown that inhibition efficiency increased with increase in the concentration of the plant extract and temperature. The adsorption study reported shows that adsorption of A. sativum extract on aluminum surface follows Langmuir isotherm, indicating that adsorption increase with increase in temperature, hence increasing the inhibition efficiency (Refaey *et al.*, 2004). Sangeetha *et al.* (2011) studied the inhibition efficiency of *Phyllanthus amarus* extract (PAE)-Zn^{2+} system in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl^-. Using weight loss method and the result showed that the highest inhibition efficiency occurred when 2 ml of PAE was added to 25 ppm of Zn^{2+} in controlled solution of carbon steel immersed in an aqeous solution containing 60 ppm of Cl^-, 98% inhibition efficiency was observed. Synergism parameter was used to confirm that synergistic effect exist between PAE and Zn^{2+} (Rajendran *et al.*, 2012). Polarization study was used to detect the formation of protective film on the metal surface; result obtained showed that the system functioned as mixed type of inhibitor, controlling the cathodic reaction and anodic reaction to an equal extent (Yesu *et al.*, 2009). In addition, the FTIR spectra revealed that the protective film consisted of Fe^{2+}-Phyllanthus complex.

Phyllanthus amarus plant is bitter, febrifuge and antiseptic; useful in dropsy, jaundice, diarrhea, dysentery, intermittent fevers, and diseases of urino-genital system, scabies ulcers and wounds.

Figure 1. ***Phyllanthus amarus***

Several other reviews and researches exist on the use of *Phyllanthus amarus* as corrosion inhibitors for several metals. However, scarce work has been done on its application with respect to aluminum. This paper aims at examining the corrosion inhibition efficiency (IE) of *Phyllanthus amarus* leaves extract on aluminum in acidic medium and the protective film formed on the aluminum by surface examination using FTIR spectra.

Experimental Section

Preparation of *Phyllanthus Amarus* Extract

Phyllanthus amarus was obtained from Aiyegbami, Ago-Iwoye, Southwestern, Nigeria. The plant was air dried for three weeks at room temperature. The leaves of the plant were grinded using a grinder and the pulverized stock was weighed using a manual balance. The weighed pulverized stock was then poured into a round bottom flask. Enough quantity of ethanol was added to the stock for extraction. After 24 hours, the extract was then filtered and was concentrated for four hours using a rotary evaporator. The extract was then diluted with appropriate quantity of 0.5 M HCl in the given mls per 250ml. The procedure was repeated for 10 ml, 20 ml, 30 ml, 40 ml and 50 ml, to give (10 ml/L, 20 ml/L, 30 ml/L, 40 ml/L, 50 ml/L) respectively.

Preparation of the Specimens

Aluminum specimens (0.2106% Zn, 0.0001% C, 0.6970% Fe, 0.0001% Sn, 0.3683% Cu and rest Al) cut into an average rectangular shape of 1.4cm × 3.75cm were polished to a mirror-like surface, and washed with distilled water and then degreased with acetone, and used for weight- loss method and surface examination study.

Weight-Loss Method

The coupon was wrapped with a filter paper and then desiccated over night. The coupon was later removed and weighed to get the initial weight before immersing it into 0.5 M HCl solution, and then removed after the designated time. The coupon was then washed with distilled water and scrubbed with hard brush to remove the oxide formed on the surface of the metal as a result of corrosion. It was then wrapped with filter paper and then desiccated over night. It was later retrieved and weighed to get the final weight. The coupon was repolished for the next experiment. This process was repeated for 2, 4, 6, 8 and 10 hours respectively.

To test the inhibition efficiency, different concentrations of the plant extract was measured (10ml/L 20ml/L, 30ml/L, 40ml/L, 50ml/L) respectively and then diluted with 0.5 M HCl. The coupon was then immersed in the solution for various hours (2hrs, 4hrs, 6hrs, 8hrs and 10hrs) respectively. The coupon was subsequently removed and desiccated overnight; removed and weighed again to get the final weight. From the experiment, weight loss data was calculated as:

$$\Delta W = W_1 - W_2 \tag{1}$$

W_1 = Initial weight

W_2 = Final weight

From weight loss, inhibition efficiency was calculated as:

$$IE\ [\%] = (W_a - W_b)/W_a \times 100 \tag{2}$$

Where IE [%] = Inhibition efficiency

W_a = Weight loss in the absence of inhibitor

W_b = Weight loss in the presence of inhibitor

Observed corrosion rate was also calculated from the weight loss data with formula:

$$\text{Corrosion rate} = K\Delta W/\rho AT \tag{3}$$

Where ΔW = Change in weight (before and after immersion)

K= corrosion constant (87.6)
ρ= density ($2.7 g/cm^3$)
A = Area of the coupon in cm^2
T = Time in hours

Observed surface coverage was calculated from inhibition efficiency with the formula:

$$\text{Surface coverage} = IE \times 10^{-2} \quad (4)$$

Log C was also calculated from surface coverage with the formula:

$$\text{Log } C = \text{Log } \theta/1-\theta \quad (5)$$

Where C = concentration of extract
θ = surface coverage

Adsorption Consideration

Adsorption isotherm has been found to be an important technique in determining the mechanism of heterogenous organo-electrochemical reaction (Bockris *et al.*, 1993) in solid surfaces. The inhibition corrosion of aluminum in 0.5M HCl medium with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extract on the metal surface. In this study, Langmuir and Temkin adsorption isotherms were found to be suitable for the experimental findings. The isotherm is described by the equation below as given in Adeyemi and Olubomehin (2010) and Ismail, *et al*. (2011).

$$C/\theta = 1/ K_{ads} + C \quad (6)$$

Where C is the Inhibitor concentration, K_{ads} is the Adsorption equilibrium constant and Θ is the Surface coverage. Taking logarithm of equation (6) above yields equation (7)

$$\log (C/\theta) = \log C - \log k_{ads} \quad (7)$$

Surface Examination Study

The nature of the film formed on the surface of the metal specimen was analyzed by a single surface analysis technique: FTIR spectroscopy.

FTIR Spectra

These spectra were recorded with a Perkin-Elmer 1600 spectrophotometer. The FTIR spectrum of the protective film was recorded and subsequently elucidated.

Results and Discussion

Table 1. Corrosion parameters of aluminum in 0.5 M HCl and in the presence of inhibitor

Time (hrs)	Concentration	Weight loss (g)	Corrosion penetration rate (mmy^{-1})	Inhibition efficiency (%)	Surface coverage (θ)	Log θ/1-θ
2 hrs	0.5 M HCl	0.0007	0.0022			
	10 ml	0.0006	0.0019	14.28	0.1428	-0.7784
	20 ml	0.0005	0.0016	28.57	0.2857	-0.398
	30 ml	0.0004	0.0013	42.86	0.4286	-0.125
	40 ml	0.0002	0.0006	71.43	0.7143	0.398
	50 ml	0.0001	0.0003	85.71	0.8571	0.778
4 hrs	0.5 M HCl	0.0054	0.0084			
	10 ml	0.004	0.0063	25.92	0.2592	-0.456
	20 ml	0.0025	0.0039	53.7	0.5370	0.0644
	30 ml	0.002	0.0031	62.91	0.6291	0.2303
	40 ml	0.0017	0.0026	68.52	0.6852	0.3378

	50 ml	0.0010	0.0016	81.48	0.8148	0.6434
6 hrs	0.5 M HCl	0.015	0.0157			
	10 ml	0.0112	0.0117	25.33	0.2533	-0.4695
	20 ml	0.007	0.0073	53.33	0.5333	0.0579
	30 ml	0.006	0.0063	60	0.6	0.1761
	40 ml	0.0057	0.006	62	0.62	0.2126
	50 ml	0.0053	0.0055	64.67	0.6467	0.2626
8 hrs	0.5 M HCl	0.0215	0.0168			
	10 ml	0.0191	0.0149	11.16	0.1116	-0.9009
	20 ml	0.0164	0.0128	23.72	0.2372	-0.5073
	30 ml	0.0126	0.0099	41.39	0.4139	-0.1511
	40 ml	0.0088	0.0069	59.07	0.5907	0.1593
	50 ml	0.0078	0.0061	63.72	0.6372	0.2446
10 hrs	0.5 M HCl	0.0502	0.0314			
	10 ml	0.0288	0.0180	42.63	0.4263	-0.1289
	20 ml	0.0252	0.0158	49.80	0.4980	-0.0035
	30 ml	0.0173	0.0108	65.54	0.6554	0.2791
	40 ml	0.0094	0.0059	81.27	0.8127	0.6374
	50 ml	0.0082	0.0051	83.67	0.8367	0.7096

The weight loss of aluminum at various time intervals in the absence and presence of *Phyllanthus amarus* at different concentrations in 0.5M HCl was investigated (Table 1 and Figure 2). The value of weight-loss, inhibition efficiency (%), surface coverage (θ), and corrosion rate (C.R) are given in Table 1.

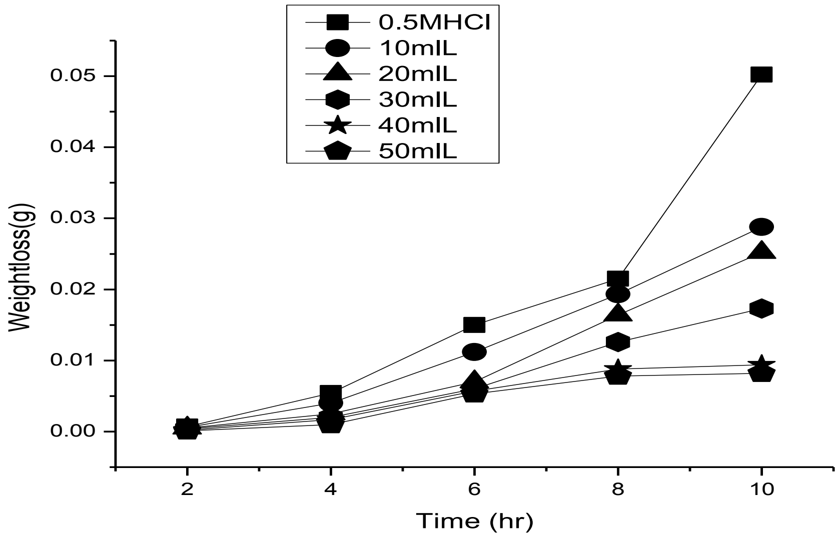

Figure 2. Variation of weight loss (g) with time (hrs) in the absence and presence of Leave Extract of *Phyllanthus amarus* at different concentrations

Effect of Concentration on Corrosion Penetration Rate

The variation of corrosion rate of aluminum in 0.5 M HCl in the absence and presence of different concentration of acid extract of *Phyllanthus amarus* is shown in Figure 3 where the corrosion rate of aluminum in 0.5 M of HCl increases with increasing time but decreases with increasing concentration of the inhibitor at room temperature. This result leads to the suggestion that as the concentration of the extract increases, there is increase in the number of adsorption constituents on the surface of aluminum which create a mass transfer barrier and prevent further corrosion (Wabene & Okafor, 2001).

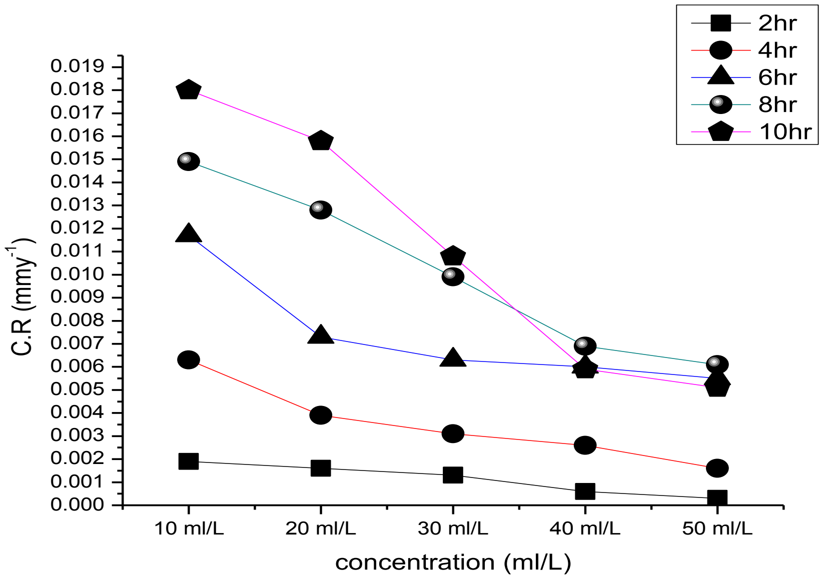

Figure 3. Variation of corrosion penetration rate (mmy^{-1}) with concentration of Leave Extract of *Phyllanthus amarus* varying time intervals

Effect of Concentration on Inhibition Efficiency and Surface Coverage

The inhibitive efficiency and surface coverage of aluminum in various concentration of plant *Phyllanthus amarus* in 0.5 M HCl was studied. The result in Figure 4 shows that the inhibition efficiency and surface coverage increase with increase in concentration of the extract in acidic medium as a result of increase in the fraction of the aluminum surface covered by adsorbed constituents of the plant extract, as there is an increase in the concentration of the extract (Olasehinde *et al.*, 2013). The inhibition efficiency increases progressively as the concentration of the extracts increases up to 50 ml. At this concentration of the plant extract, it indicates that the reaction of the inhibitors on the surface of aluminum has gotten to its peak at 85.71 % at a concentration of 50 ml/L at 2hours. While the lowest inhibition efficiency was observed to be 11.16 % at a concentration of 10ml/L in 8hours, the surface coverage was found to increase with increase in inhibition efficiency.

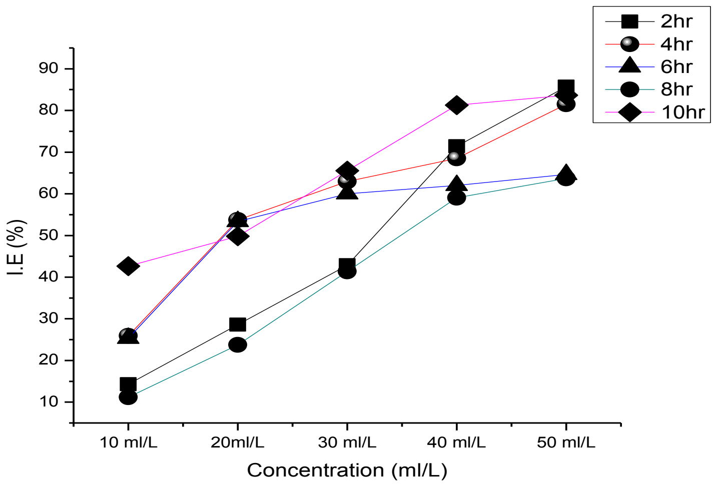

Figure 4. Variation of Inhibition efficiency (%) with concentration of Leave Extract of *Phyllanthus amarus* varying time interval

Adsorption Isotherm

A plot of log θ/1-θ against log C at a fixed temperature is a linear graph over a wide range of concentration (Adeyemi & Olubomehin, 2010). This is confirmed in Figure 5. The plot supports the assertion that the mechanism of corrosion inhibition is due to the formation and maintenance of a protective film on the metal surface and that through uniform adsorption the additive acts as a covering to both the anodic and cathodic sites (Adeyemi & Olubomehin, 2010).

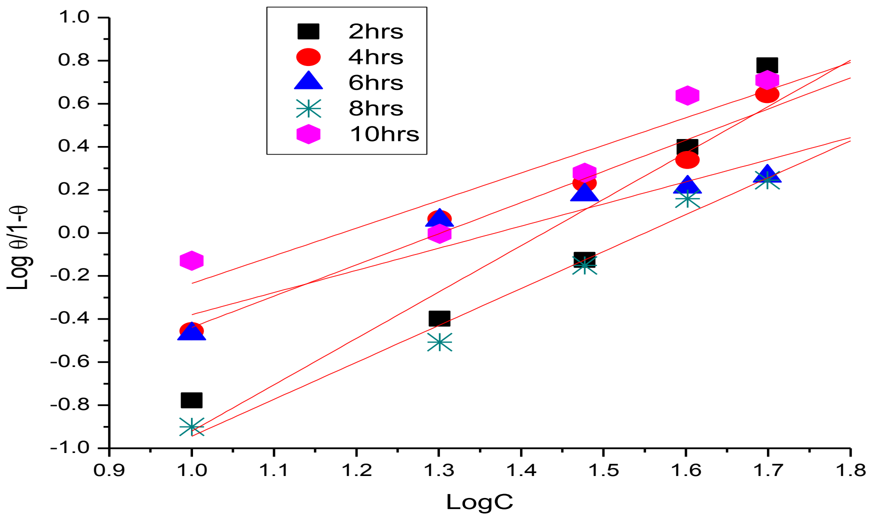

Figure 5. Variation of Log Ɵ/1-Ɵ with Log of concentration varying time interval

FTIR Analysis

FTIR analysis was carried out on *Phyllanthus amarus* in its aqueous form. In Figure 6, the spectrum shows a C=O stretching at 1630.08 cm^{-1} and OH stretching at 3356 cm^{-1}. The peak at 1081.2 cm^{-1} is due to the conjugated oxygen ring atom. Thus the structure of 5-hydroxymethyl-2-furaldehyde is confirmed by the FTIR spectrum. The stretching in 3356 cm^{-1} may also signify the presence of N-H of amine and C-N of amine stretching at 1206.18 cm^{-1} to give D-panthenol. The FTIR spectrum of protective film formed on the surface of the metal after immersion in the solution containing 0.5 M acid and 20 ml extract of *Phyllanthus amarus* is shown in Figure 7. Comparing the two spectra, it is found that the OH stretching is shifted from 3356 cm^{-1} to 3366.63 cm^{-1}. The oxygen ring atom is shifted from 1081.2 cm^{-1} to 1089.27 cm^{-1}. The C=O stretching frequency is shifted from 1630.08 cm^{-1} to 1652.17 cm^{-1}. There is also a shift in the C- N stretching of amine from 1206.18 cm^{-1} to 1274.47 cm^{-1}. This confirms the presence of Al^{3+}- *Phyllanthus* extract complex on the metal surface. Al^{3+} has coordinated with the O of OH group, C=O group and oxygen atom and N of the N-H group. These shifts confirm the formation of Al^{3+}-*Phyllanthus amarus* complex on the metal active site.

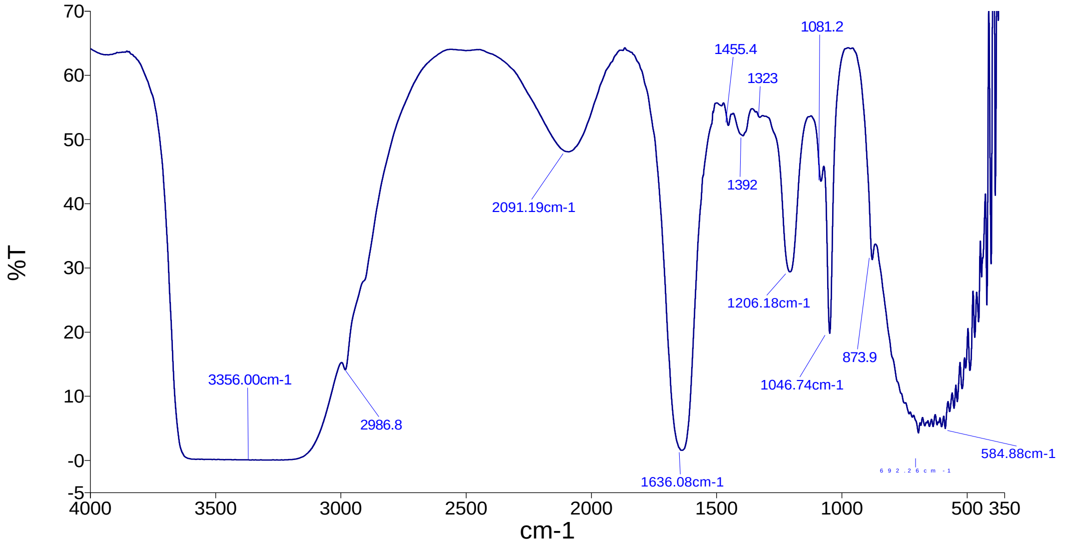

Figure 6. FTIR spectrum of pure PAE

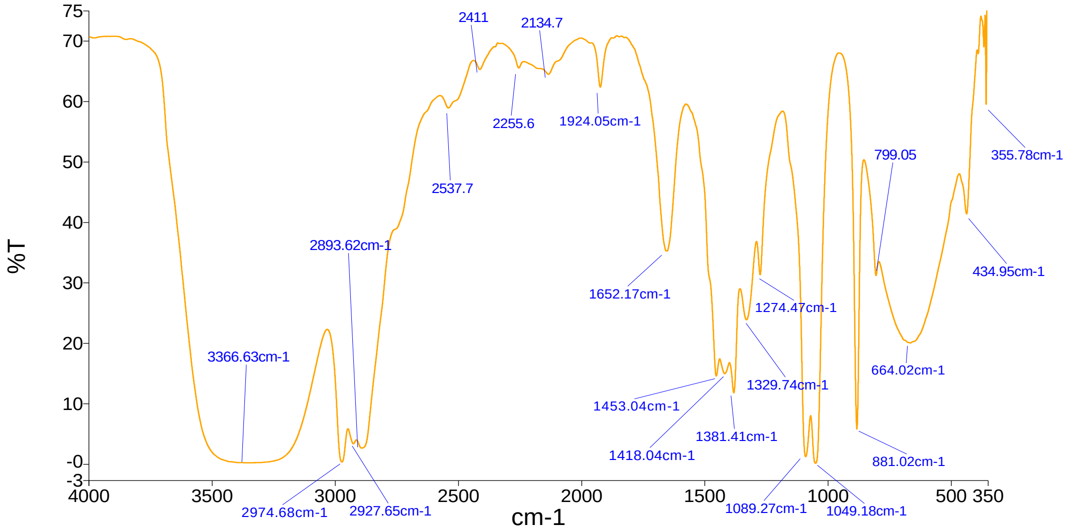

Figure 7. FTIR spectrum of the film formed on aluminum surface after immersion in a solution containing acid + PAE (20ml)

The FTIR result shows that the extract contains alkaloids such as 1-Formylpyrrolidine, 2-Chloro-4-methylaniline, L-prolinol and D-panthenol. These alkaloids contain some hetero atoms such as oxygen and nitrogen. These atoms coordinate with the corroding metal atoms (their ions), through their electrons. Hence protective films are formed on the metal surface and hence corrosion is prevented. Adeyemi and Olubomehin (2010) revealed that corrosion inhibition by plant extracts is attributed to the presence of bio-active ingredients or phytochemical compounds, some of which contains hetero atoms. They also observed that the inhibition is concentration and time dependent. The same trend is observed in this present studies. Studies have shown that organic compounds containing hetero atoms have been reported as corrosion inhibitors in acid and neutral media (Mairia & Chakraverty, 1974; Singh & Adeyemi, 1989; Adeyemi, 2006). These reports have shown that corrosion inhibition of these compounds is done principally in the presence of charge density on hetero atoms of the organic molecule and these compounds donate electrons to the vacant d-orbitals of the metal atoms, leading to the formation of adsorption complex on metal surface. Riggi and Murd (1967) reported that in the presence of adsorbed inhibitor, the dissolution of the metal proceeds with two distinct processes corresponding to the covered area and bare metal surface. They concluded that at high degree of coverage, the dissolution process is not only determined by the reaction of metal from the bare surface but involves the adsorbed inhibitor. Thus E_{act} can assume values greater or smaller than those calculated in the absence of the inhibitor.

In this study, the inspection of the chemical structures of the bio-active substance in the extract shows the presence of bondable double bonds and hetero atoms. The hetero atoms form co-ordinate bond with metal in leading to arrest of metal dissolution. The organic molecules get adsorbed on the metal surfaces forming (metal-inhibitor)$_{ads}$.complex. In the adsorption process, the phytochemicals are assumed to have completely blocked the active sites of the metal surface. This blockage hinders the activity of the metal in the process of metal dissolution. This is further confirmed by the FTIR studies as shown in Figure 6 and Figure 7.

Conclusion

The results obtained from this study depict that leaves extract of *Phyllanthus amarus* inhibits corrosion of aluminum in an acidic medium to an appreciable extent. As the concentration of the plant extract increased, the inhibition efficiency of the plant extract also increased. The weight-loss study clearly showed that corrosion inhibition efficiency of *Phyllanthus amarus* increased with increase in the plant extract concentration due to the significant reduction in the weight-loss value. The FTIR analysis showed that the lone pair of electrons present in the hetero atoms of *Phyllanthus amarus* is responsible for the adsorption inhibition on the metal surface and it showed the presence of Al^{3+} as the protective film formed on the metal active site. The inhibition efficiency ranged from 11.16% - 85.71% even at low concentrations from 10-50ml/L. The authors therefore conclude that *Phyllanthus amarus* leave extract is effective, eco-friendly, affordable, biodegradable, renewable, non-toxic and is an alternative corrosion inhibitor for aluminum which can supplant toxic chemical corrosion inhibitors.

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