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Elaeis Guiniensis Exudates (Palm Wine) as a Corrosion Inhibitor for Mild Steel in Acidic Solution.

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Abstract

This work has explored the possibility of using a typical plant extract other than the use of conventional materials as corrosion inhibitor. Elaeis guinensis exudates (Palm wine), which contains carbonyl groups, double bonds and triple bonds as shown by the FTIR, Gas chromatography mass spectrometry and phytochemical tests is a one of good natural materials as corrosion inhibitor. This paper was focus on the behaviour of palm wine as corrosion inhibitor for mild steel in 0.1M and 0.5m H_2SO_4 solution at 303K and 333K temperatures and inhibitor concentrations using weight loss measurement. Results showed that rate of corrosion increases with increase in concentration of solution. Temperature decreases with increase in concentration of inhibitor. The kinetics showed that activation energy increases with increase in temperature and concentration of corrosion inhibitors. Palm wine inhibitor adsorbed on the surface of mild steel through physical adsorption.

Keywords: Mild steel, H_2SO_4 solution, palm wine, corrosion inhibitor, weight loss.

Introduction

Mild Steel is the most commonly used engineering material [1]. It is cheap, is readily available in a wide range of standard forms and sizes, and can easily be worked upon and welded. It has a good tensile strength and is ductile in nature. However, mild steel is not resistant to corrosion, except in certain specific environments such as concentrated tetraoxosulphate (vi) acid and sodium hydroxide solutions. Acids are widely used in the industries, the most important areas of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [2].

Organic compounds are found to be effective corrosion inhibitors due to the adsorption of molecules and ions on the metal surface [3]. The presence of large molecules with functional groups containing of hetero-atoms (such as oxygen, nitrogen, sulphur, and phosphorus), triple bonds or aromatic rings in the inhibitor's chemical structure enhance the adsorption process [4]. Considerable efforts are made to find suitable compounds to be used as corrosion inhibitors in various corrosive media.

Some works were conducted to examine extracts from natural substances [5, 6]. The extracts contain mixtures of compounds having oxygen, sulphur, and nitrogen elements, which help in the corrosion inhibition process [3]. These naturally occurring compounds are environmentally friendly, safe, cheap and an anti oxidants. The inhibitive mechanism of a corrosion inhibitor affects the formation of passivating layer that blocks the access of corrosive agent to the steel, inhibiting either the oxidation or reduction part of the redox reaction or by scavaging and dissolved oxygen. Investigation of the use of palm olein from crude palm oil as corrosion inhibitor for mild steel in acidic solution was done by [6]. The Elaeis guiniensis exudates (Palm wine) contain equal amounts of saturated and unsaturated fatty acids. The unsaturated fatty acid portion consists of oleic, octadecanoic, and hexadecanoic (stearic) acids. The acids contain carbonyl groups and double bonds [7]. Consequently, the large molecular structure, double bonds, reactive centres or

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groups are among the attributes that give the compound the ability to cover a large area of a metal surface [5]. Hence, palm wine has a good characteristic as a corrosion inhibitor owning to the fact that it contains inhibitive components such as tannins, alkaloids, phenolic compounds, saponins, oligosaccharides, and flavonoids [8].

The inhibitive action of palm wine is as a result of the adsorption of its phytochemical components on the steel surface which protects the metal surface from corrosion process. There are virtually little or no reports on the use of palm wine as corrosion inhibitor on mild steel which necessitated this work. This work will also cover the operating conditions and characteristics of the corrosion environment as the Elaeis guiniensis exudates (palm wine) acts as corrosion inhibitor for mild steel exposed in varying concentration of H_2SO_4 solution.

Materials and Experimental Procedure

The material studied was mild steel. The palm wine (Elaeis guiniensis exudates) was obtained from Awka South, Anambra State, Nigeria. Two different concentrations of 5g and 15g/100ml of inhibitor were used. H_2SO_4 of analytical grade was procured from an accredited chemical dealer at Onitsha, Anambra State, Nigeria. Concentrations of 0.1M and 0.5M of H2SO4 were used for the experiment.

For the weight loss test, the mild steel (specimens) were mechanically polished with silicon carbide abrasive paper, degreased with ethanol, washed in distilled water and dried. The plate dimensions and weight were measured accurately. Each metal coupon was of the size 4cm × 3cm × 0.3cm. Before polishing, a hole of about 0.1cm was drilled on each coupon. The coupon was suspended with the aid of nylon thread and glass rod in a 300ml beaker with 100ml of the acid (0.1M and 0.5M H_2SO_4)

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without and with different concentrations of the inhibitors. To prevent evaporation of solution and contamination, the corrosion vessel was covered with parafilm. At various time intervals the sample was retrieved dipped in distilled water and immersed in saturated sodium carbonate solution scrubbed with bristle brush, to remove residual acids and then washed with washing liquor (NaOH + Zn dust) thouroughly, rinsed with distilled water, dried in acetone before reweighed. The corrosion test was performed at two different temperatures of 303K and 333K.

Table 1.0 Composition of Mild Steel

Chemical Constituents	Percentage Composition (wt. %)
Carbon	0.14
Silicon	0.03
Manganese	0.32
Sulphur	0.05
Phosphorus	0.20
Copper	0.01
Chromium	0.01
Iron	Balance

Phytochemical Test Analysis

Preliminary phytochemical screening

1gm of the Palm wine was dissolved in 100ml of its own mother solvents to obtain a stock of concentration 1% (v/v). The extracts obtained were subjected to preliminary phytochemical screening using the recommended standard screening procedure.

Determination of Alkaloids

5ml of the palm wine was added to 2ml of HCl followed by addition of 1ml of Dragendroff's reagent. An orange or red precipitate produced immediately indicates the presence of alkaloids.

Determination of Saponins

5ml of palm wine was diluted with 20ml of distilled water, agitated in a graduated cylinder for 15minutes. The formation of 1cm layer of foam showed the presence of saponins.

Determination of Flavonoids

1ml of the palm wine, few drops of dilute NaOH was added. An intense yellow colour was produced in the plant extract, which becomes colourless on addition of a few drops of dilute acid (HCl) indicates the presence of Flavonoids.

Determination of Anthraquinones

5ml of the palm wine solution was hydrolysed with diluted conc. H_2SO_4 extracted with benzene. 1ml of dilute ammonia was added to it.

Table 2.0 Chemical Constituent of the Palm wine.

Chemical Constituents	Percentage Compositions (%)
Tannins	6.5
Saponins	3.1
Alkaloids	10.6
Anthraquinones	Nil
Flavonoids	1.6

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Determination of the functional group in the palm wine.

The Fourier transforms infrared spectrophotometer (FTIR 8400S) SHIMADZU was used for the identification of the palm wine functional group.

Determination of Compounds in the Palm wine

Gas chromatography mass spectrometry (GC MS QP2010) plus SHIMADZU was used to identify the different compounds present in the palm wine.

Results and Discussions

Fig. 1.0 2.0 shows the weight loss of mild steel in 0.1M and 0.5M H_2SO_4 solution with and without the presence of inhibitor at 303K. The weight loss of mild steel in the absence of palm wine was very much higher as compared to the weight loss in other solutions in the presence of inhibitor. The corrosion was due to the presence of the OH^-, air, H_2^+, and SO_4^{2-} which accelerate the corrosion process of the mild steel.

Increased in concentration of palm wine inhibitor reduced the weight loss of mild steel which indicated the positive effect of the inhibitor on corrosion of mild steel.

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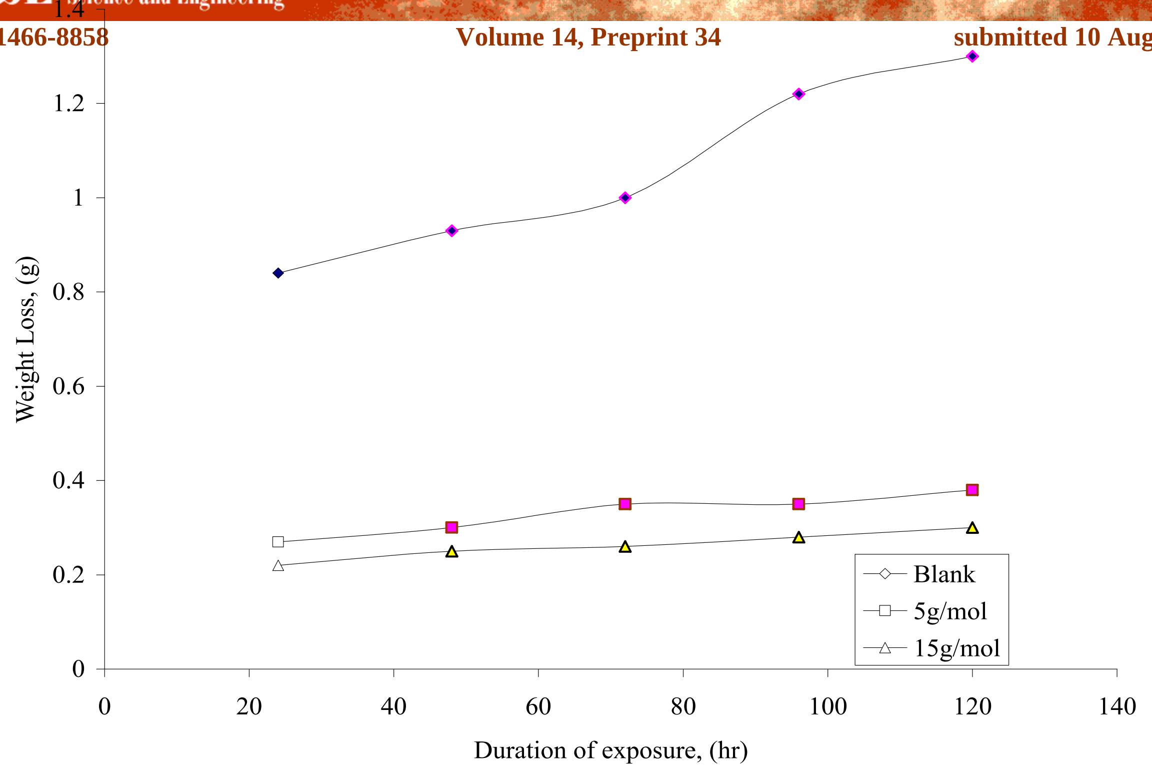

Fig. 1.0 Weight loss (g) against duration of exposure (hr) at 303K, 0.1M H_2SO_4

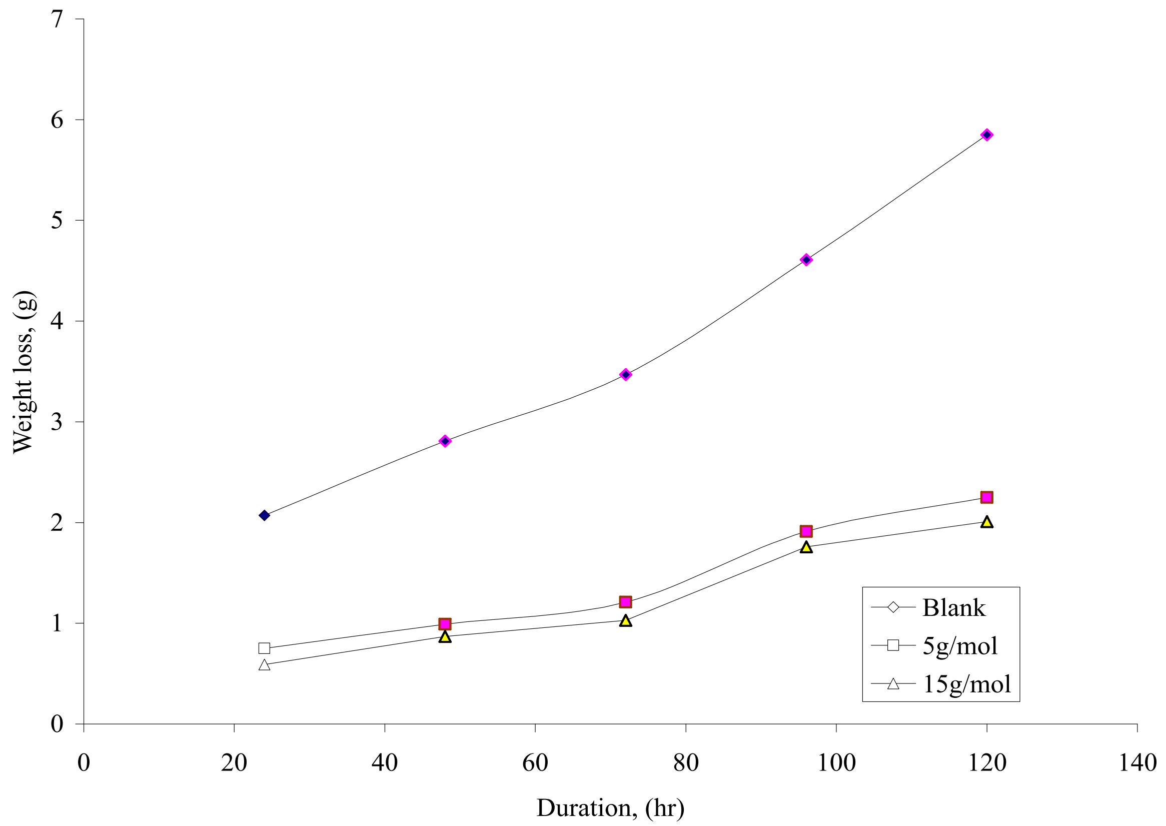

Fig. 2.0 Weight loss (g) against duration of exposure (hr), at 303K, 0.5M H_2SO_4

Fig. 3.0 4.0 indicates that as concentration of acid increases with temperature the

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weight loss of the mild steel decrease. For each concentration at both temperatures, an increase in duration of exposure from 24hours showed decrease in the corrosion of mild steel.

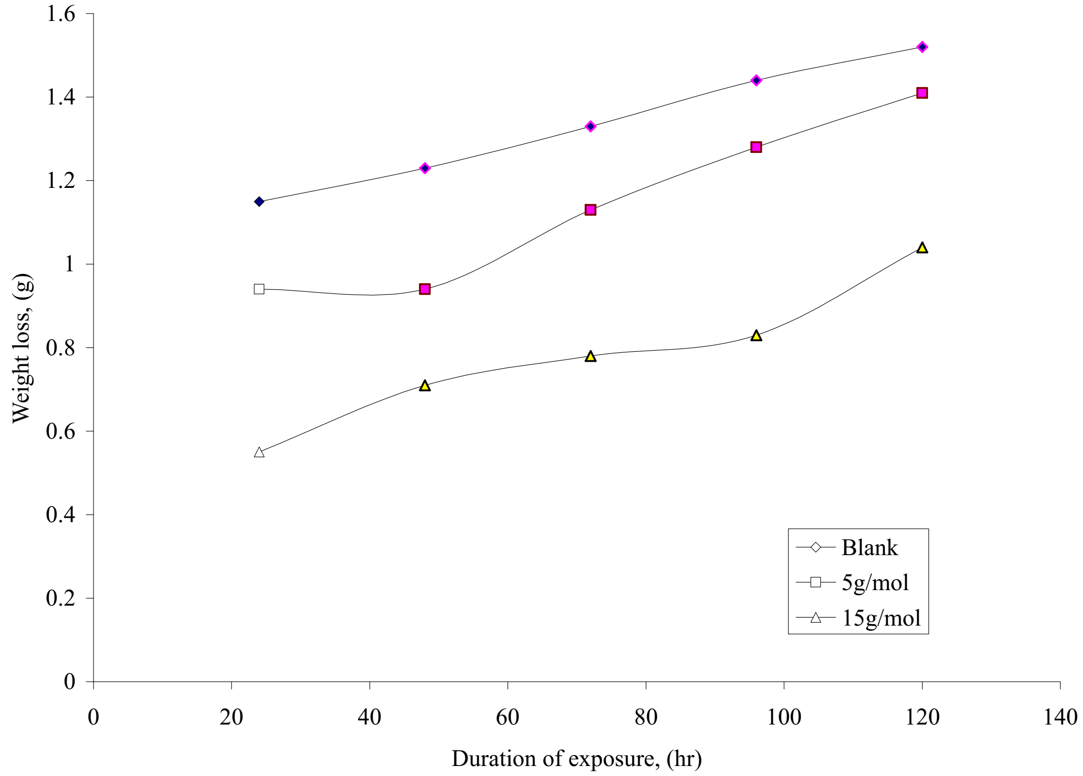

Fig.3.0 Weight loss (g) against duration of exposure (hr) at 333K, 0.1M H_2SO_4

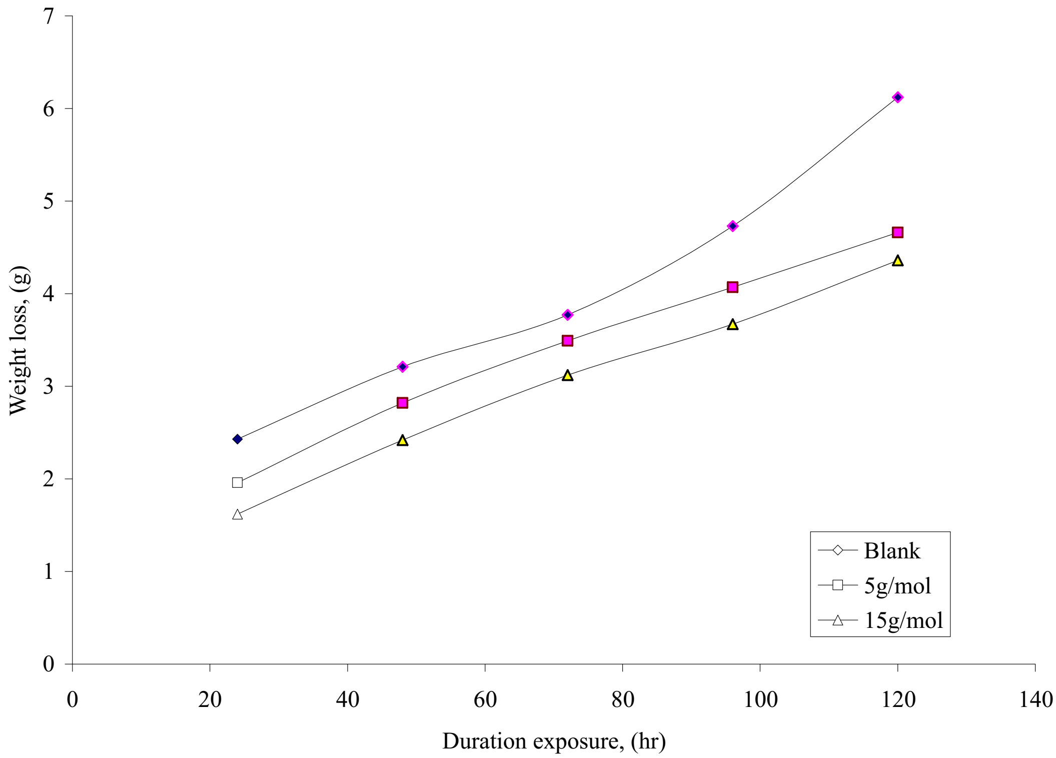

Fig. 4.0 Weight loss (g) against duration of exposure (hr) at 333K, 0.5M H_2SO_4

Fig. 5.0 gives the GCMS result of the palm wine. The oleic acid, hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid) are the main compounds present in the palm wine but oleic acid which is a monosaturated omega- 9 fatty acid has the highest peak value.

The carbonyl group and double bonds carbon present in oleic acid compound suggest that the palm wine inhibited the mild steel corrosion. The presence of the stearic acid that results from the hydrogenation of the double bond of oleic acid also suggests the palm wine as a good corrosion inhibitor.

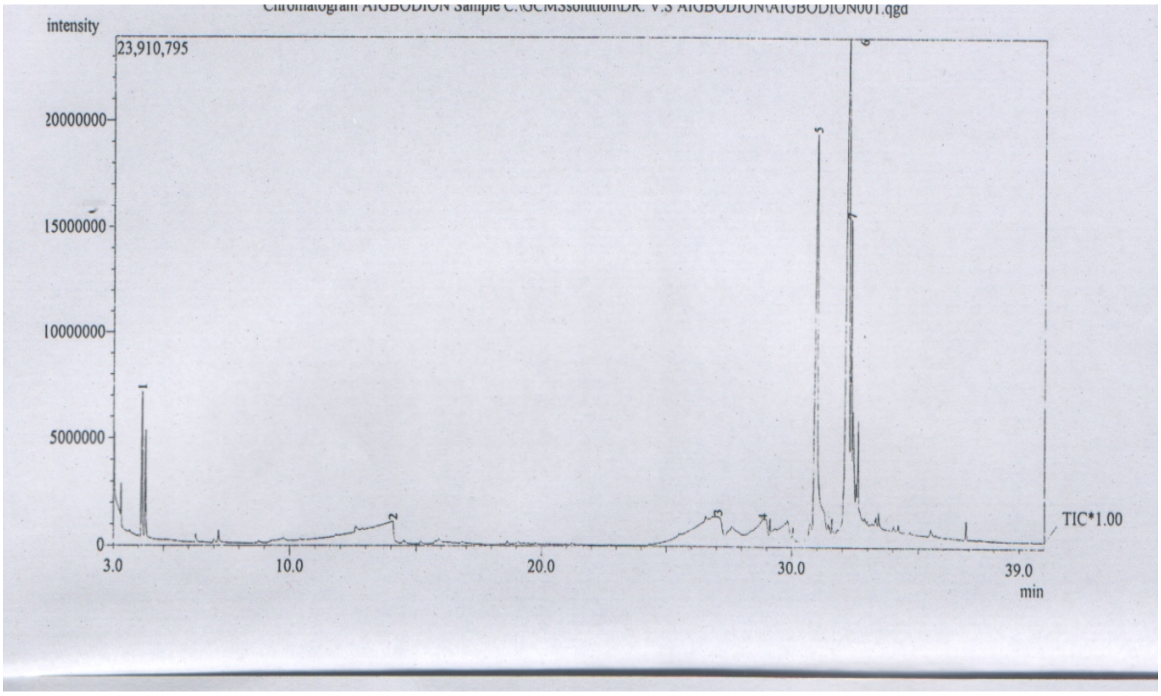

Fig. 5.0 GCMS of the Palm wine

Fig. 6.0 shows the FTIR result of the palm wine with the peak of the double bond carbon functional also confirms the palm wine as good corrosion inhibitors on the mild steel. The presence of the tannins and alkaloids in the phytochemical test also aided corrosion inhibition of the mild steel.

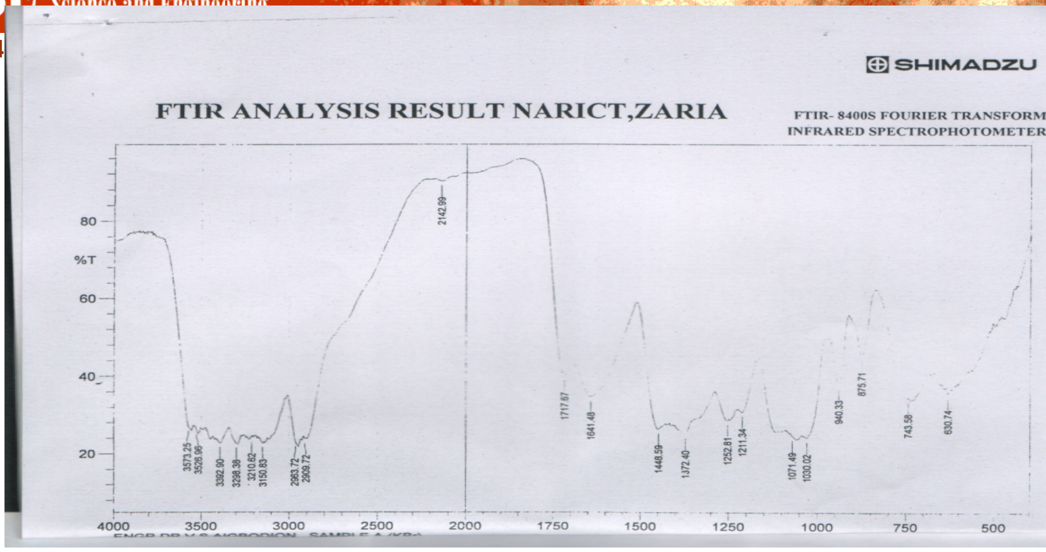

Fig. 6.0 FTIR spectrometry of the palm wine

Fig. 6.0 shows the FTIR result of the palm wine with the peak of the double bond carbon functional also confirms the palm wine as good corrosion inhibitors on the mild steel. The presence of the tannins and alkaloids in the phytochemical test also aided corrosion inhibition of the mild steel.

Adsorption Isotherms

Adsorption isotherms are very important in understanding the mechanism of corrosion inhibition reaction of mild steel. From the weight loss measurement data, Langmuir adsorption isotherm was performed in the analysis.

Langmuir relationship: $$\frac{C}{\theta} = \frac{1}{K} + C \qquad (1)$$

where K is the equilibrium constant of adsorption (M^{-1}), C (M) is the concentration of the adsorbate in the bulk of the electrolyte (inhibitor), θ is the degree of surface coverage.

Taking logarithm of both sides of equation (1) above $$\log \frac{C}{\theta} = \log C - \log K. \qquad (2)$$

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A plot of log C/ θ against log C gives a slope of K. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and the adsorbent. The applicability of Elaeis guinensis exudates on mild steel confirms the formation of multi-molecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent [9]. Using the K value determined from the Langmuir isotherm relationship, the standard free energy of adsorption $?G^o_{ads}$ (kJ/mol) value at different temperature can be determined according to the following equation;

$$\ln K = \ln \frac{1}{55.5} - \frac{?G^o_{ads}}{RT} \quad (3)$$

$$?G^o_{ads} = -2.303RT \log (55.5K) \quad (4)$$

Where (1/55.5) is the standard molar of water in the solution, R is the gas constant (8.314 J/mol K) and T (K) is the temperature [10].

Table 3.0 and 4.0 shows the value of K and $?G^o_{ads}$ at 303K and 333K temperatures and 0.1M and 0.5M H_2SO4 solution. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitor at the metal surface is a spontaneous process. The $?G^o_{ads}$ values which were below 40 KJ/mol indicate physical adsorption on the transfer of unit mole of the inhibitor from solution on to the metal surface [10].

Table 3.0. The values of K and $?G^o_{ads}$ at 0.1M H_2SO_4 solution

Inhibitor Conc.	Temperature (K)	K (M^{-1})	$?G^o_{ads}$ (kJ/mol)
5g/100ml	303	0.041	-10.58
15g/100ml	303	0.012	-20.89
5g/100ml	333	0.013	-23.03
15g/mol	333	0.014	-33.67

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Table 4.0 The values of K and ? G^{o}_{ads} at 0.5M H_2SO_4 solution

Inhibitor Conc.	Temperature (K)	K (M^{-1})	? G^{o}_{ads} (kJ/mol)
5g/100ml	303	0.047	-19.39
15g/100ml	303	0.015	-24.31
5g/100ml	333	0.036	-26.40
15g/100ml	333	0.014	-35.87

Kinetics

Activation energies (Ea) of the corrosion process were evaluated from the Arrhenius equation;

$$\log \frac{CR_2}{CR_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (5)$$

Where CR_1 and CR_2 are the corrosion rates at temperatures T_1 and T_2, respectively.

The activation energy as evaluated from equation (5) above gives;

$$Ea = \frac{[2.303R \log (CR_2/CR_1)]}{(1/T_1) - (1/T_2)} \quad (6)$$

Corrosion rate of the mild steel by the inhibitors is as follows;

$$R = \frac{534\, w}{l\, AT} \quad (7)$$

where T is the operational time, w is the weight loss of mild steel, l is the density of mild steel, and A is the exposed area of corrosion.

From Table 5.0, it was shown that an increase in temperature from 303K to 333K had an increase in the value of activation energy value. However, increases in concentrations of the inhibitor increase the activation energy which indicated the resistance of mild steel towards corrosion. The increase in activation energy indicated that physical adsorption of palm wine occurred on the mild steel surface [11].

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Table 5.0 Activation Energies of Reaction at 303K and 33K respectively.

0.1M H_2SO_4 solution	Activation Energy (kJ)
Blank	8.679
5g/100ml	24.5
15g/100ml	34.52
0.5M H_2SO_4 solution	**Activation Energy (kJ)**
Blank	4.461
5g/100ml	24.67
15g/100ml	91.83

Conclusion

Increase in temperature favours a decrease in corrosion of mild steel. The Langmuir adsorption isotherm fitted well for the experimental data for both temperatures studied. Increase in concentration of acid solutions increase rate of mild steel corrosion. Activation energy increase with inhibitors concentrations. FTIR result of the palm wine with the peak of the double bond carbon functional also confirms the palm wine as good corrosion inhibitors on the mild steel.

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