

Comparative Study of *Elaeis Guiniensis* Exudates (Palm Wine) as a Corrosion Inhibitor for Mild Steel in Acidic and Basic Solutions

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Abstract: This study has explored the possibility of using a typical plant extract other than the use of conventional materials as corrosion inhibitor. *Elaeis guiniensis* 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 focused on the behaviour of palm wine as corrosion inhibitor for mild steel in (0.1 and 0.5 M) H₂SO₄ and NaOH solutions at 303 and 333 K temperatures and inhibitor concentrations using weight loss measurement. Results showed that weight loss decreases as concentration of both solutions studied increase. The inhibitor performs better under the basic solution compared to the acidic solution. The kinetics results showed that activation energy increases as temperature and inhibitors concentration increase. Palm wine inhibitor adsorbed on the surface of mild steel through physical adsorption.

Key words: H₂SO₄, NaOH solutions, weight loss

INTRODUCTION

Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid, and salt solutions.

One of the various ways of protecting mild steel from corrosion attack is the use of corrosion inhibitors. The hazardous nature of the synthetic corrosion inhibitors prompted the use of some non-conventional materials as corrosion inhibitors. The non-toxic, biodegradable, availability, anti-oxidants and cheapness of these natural materials make them suitable for use as environmentally friendly corrosion inhibitors. Mild Steel is the most commonly used engineering material (Sinnott and Towler, 2009). 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 (Yordanov and Petkov, 2008b). Organic compounds are found to be effective corrosion inhibitors due to the adsorption of molecules and ions on the metal surface (Jai *et al.*, 2009). 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 (El-Etre, 2007). 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 (El-Etre, 2003; Yaakob, 2007). The extracts contain mixtures of compounds having oxygen, sulphur, and nitrogen elements, which help in the corrosion inhibition process (Yordanov and Petkov, 2008b).

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 (Yaakob, 2007).

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 (Ababio, 2001). Consequently, the large molecular structure, double bonds, reactive centres or groups are among the attributes that give the compound the ability to cover a large area of a metal surface (El-Etre, 2003). Hence, palm wine has a good characteristic as a corrosion inhibitor owing to the fact that it contains inhibitive components such as tannins, alkaloids, phenolic compounds, saponins, oligosaccharides, and flavonoids (Akachukwu, 2001). The

Table 1: 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

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 study.

Materials and experimental procedure: The material studied was mild steel. The constituents of the materials are as shown in Table 1. With these values of the constituents, one can easily classify the low carbon steel. Peculiar properties may also be compared in any standard handbook. The palm wine (*Elaeis guineensis* exudates) was obtained from Awka South, Anambra State, Nigeria. Two different concentrations of 5 g and 15 g/100 mL of inhibitor were used. H₂SO₄ and NaOH solutions of analytical grade were procured from an accredited chemical dealer at Onitsha, Anambra State, Nigeria. Concentrations of (0.1 and 0.5 M) of H₂SO₄ and NaOH 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 300 mL beaker with 100 mL of the acid (0.1 and 0.5 M H₂SO₄ and NaOH) without and with different concentrations of the inhibitor. To prevent evaporation of solution and contamination, the corrosion vessel was covered with Parafin. 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 sodium hydroxide, and then washed with washing liquor thoroughly, rinsed with distilled water, dried in acetone before reweighed. The corrosion test was performed at two different temperatures of 303 and 333 K.

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.

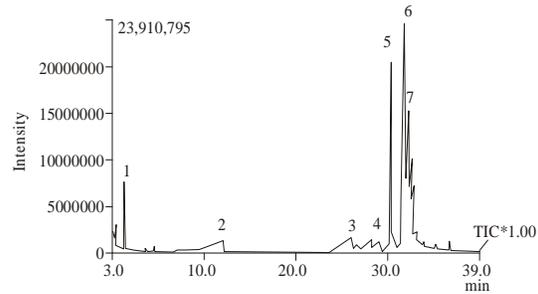


Fig. 1: GCMS of the Palm wine

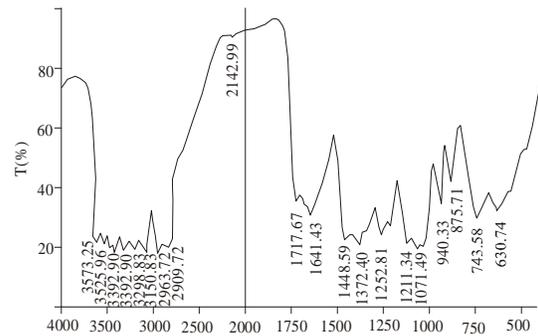


Fig. 2: FTIR spectrometry of the palm wine

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 DISCUSSION

Figure 1 gives the GCMS result of the palm wine. The oleic acid, hexadecanoic acid (palmitic acid) and octadecanoic acid (stearic acid) are the main active 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 corrosion of mild steel. 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.

Figure 2 shows the FTIR result of the palm wine with the peak of the double bond carbon functional group also confirms the palm wine as good corrosion inhibitors on the mild steel. The presence of the tannins and alkaloids with functional groups containing (nitrogen, oxygen, and carbon), aromatic rings in the palm wine chemical structure as depicted by the phytochemical test in Table 2 also enhance the process of adsorption on the mild steel.

Figure 3, 4 shows the weight loss of mild steel in (0.1 and 0.5 M) H₂SO₄ and NaOH solutions with and without the presence of inhibitor at 303 K. The weight loss

Table 2: Characterisation of the palm wine

Chemical constituents	Percentage composition (%)
Tannins	6.50
Saponins	3.10
Alkaloids	10.6
Anthraquinones	Nil
Flavonoids	1.60

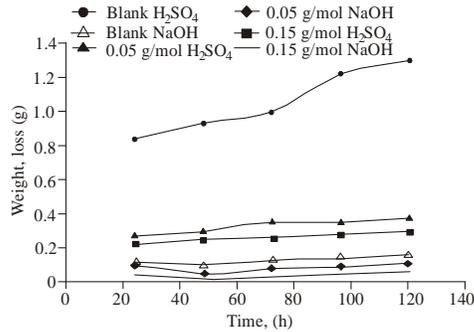


Fig 3: 3.0 wight loss (g) against duration of exposure (Hr.) at 30°C for 0.1 M H₂ SO₄ and Na OH solutions

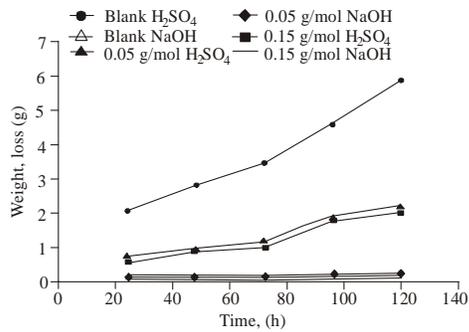


Fig 4: 4.0 wight loss (g) against duration of exposure (Hr.) at 30°C for 0.5 M H₂SO₄ Na and OH solutions

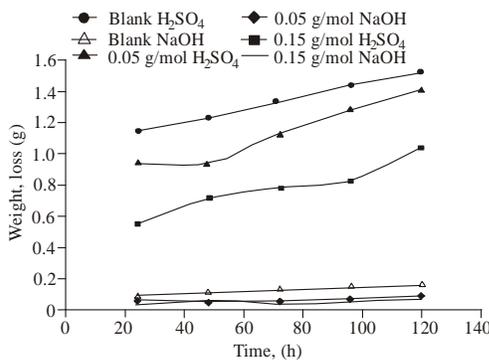


Fig 5: 5.0 wight loss (g) against duration of exposure (Hr.) at 60°C for 0.1 M H₂ SO₄ and Na OH solutions

of mild steel in the absence of the inhibitor was much higher compared to the weight loss of mild steel in other solutions in the presence of an inhibitor.

The corrosion process in the acidic solution can be attributed to the presence of the OH⁻, air, H₂⁺ and SO₄²⁻ which accelerate the corrosion process of the mild steel.

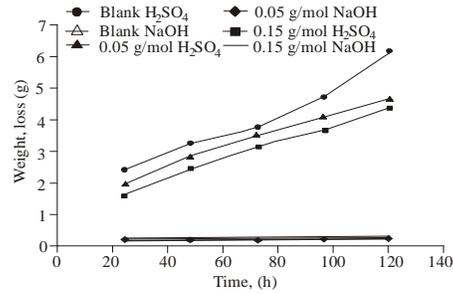


Fig. 6: 6.0 wight loss (g) against duration of exposure (Hr.) at 60°C for 0.5 M H S O4 and Na OH solutions

Increased in inhibitor concentration reduced the weight loss of mild steel in both acidic and alkaline solutions studied but corrosion decrease more in NaOH compared to acidic solution which shows the positive effect of the inhibitor on the corrosion of mild steel.

Figure 5 and 6 indicates that as concentration of acid and bases increases with temperature the weight loss of the mild steel decrease which shows that increase in temperature decrease the corrosion rate. For each concentration at both temperatures, an increase in duration of exposure from 24 h showed decrease in the corrosion of mild steel in both solutions studied.

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:

$$\text{Langmuir relationship: } \frac{c}{\theta} = \frac{1}{k} + c \quad (1)$$

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:

$$\text{Taking logarithm of both sides of Eq. (1): } \frac{c}{\theta} = \log c - \log k \quad (2)$$

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 (Umoren *et al.*, 2008). 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:

$$\ln K = \frac{\ln 1}{555} - \frac{G^o_{ads}}{RT} \quad (3)$$

Table 3: Values of K and G°_{ads} for 0.1M H₂SO₄ solution

Inhibitor conc.	Temperature(K)	K (M ⁻¹)	G°_{ads} (kJ/mol)
5 g/100 mL	303	0.041	-10.58
15 g/100 mL	303	0.012	-20.89
5 g/100 mL	333	0.013	-23.03
15 g/mol	333	0.014	-33.67

Table 4: Values of K and G°_{ads} for 0.1M NaOH solution

Inhibitor conc.	Temperature (K)	K (M ⁻¹)	G°_{ads} (kJ/mol)
5 g/100 mL	303	0.043	-3.63
15 g/100 mL	303	0.016	-19.40
5 g/100 mL	333	0.049	-22.47
15 g/mol	333	0.016	-31.58

Table 5: Values of K and G°_{ads} at 0.5M H₂SO₄ solution

Inhibitor conc.	Temperature (K)	K (M ⁻¹)	G°_{ads} (kJ/mol)
5 g/100 mL	303	0.047	-19.39
15 g/100 mL	303	0.015	-24.31
5 g/100 mL	333	0.036	-26.40
15 g/100 mL	333	0.014	-5.87

Table 6: Values of K and G°_{ads} for 0.5M NaOH solution

Inhibitor conc.	Temperature (K)	K (M ⁻¹)	G°_{ads} (kJ/mol)
5 g/100 mL	303	0.041	-18.46
15 g/100 mL	303	0.012	-23.75
5 g/100 mL	333	0.013	-25.03
15 g/100 mol	333	0.014	-34.48

Table 7: Correlation co-efficient of Langmuir's plot for 0.1M (H₂SO₄ and NaOH) solutions

Inhibitor conc.	Temperature (K)	R ² (H ₂ SO ₄)	R ² (NaOH)
5 g/100 mL	303	0.8795	0.8697
15 g/100 mL		0.9061	0.9618

Table 8: Correlation co-efficient of Langmuir's plot for 0.5M (H₂SO₄ and NaOH) solutions

Inhibitor conc.	Temperature (K)	R ² (H ₂ SO ₄)	R ² (NaOH)
5 g/100 mL	333	0.9890	0.9870
15 g/100 mL		0.9980	0.9998

Table 9: Activation energies of reaction at 303 and 33 K, respectively 0.1M H₂SO₄ solution

	Activation energy (kJ)
Blank	4.461
5 g/100 mL	24.50
15 g/100 mL	34.52

Table 10: Activation energies of reaction at 303 and 33 K, respectively 0.1M NaOH solution

	Activation energy (kJ)
Blank	3.38
5g/100mL	11.04
15g/100mL	30.37

Table 11: Activation energies of reaction at 303 and 33 K, respectively 0.5M H₂SO₄ solution

	Activation energy (kJ)
Blank	8.679
5 g/100 mL	24.67
15 g/100 mL	91.83

Table 12: Activation energies of reaction at 303 and 33 K, respectively 0.5M NaOH solution

	Activation energy (kJ)
Blank	5.296
5 g/100 mL	17.92
15 g/100 mL	30.41

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

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 (Cheng *et al.*, 2007).

Table 3 and 6 shows the value of K and G°_{ads} at 303K and 333K temperatures at 0.1 and 0.5 M (H₂SO₄ and NaOH) solutions. The negative sign of the free energy of adsorption indicates that the adsorption of the inhibitor at the surface of mild steel is a spontaneous process. The G°_{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 (Yaakob, 2007). The values on Table 7 and 8 shows the correlation coefficient of the Langmuir plot for 0.5 and 0.1 M each of H₂SO₄ and NAOH, respectively. Table 8 shows a better correlation than Table 7 for both concentrations studied. Table 8 depicts a better behaviour of corrosion inhibition studied.

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

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

where CR₁ and CR₂ are the corrosion rates at temperatures T₁ and T₂, respectively.

The activation energy as evaluated from Eq. (5) gives:

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

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

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

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 9, 12, it was shown that an increase in temperature from 303 to 333 K had an increase in the value of activation energy value for both acidic and basic solutions studied. However, increases in concentrations of the inhibitor for both (0.1M and 0.5M H₂SO₄ and NaOH) increase the activation energy which indicated the resistance of mild steel towards corrosion in acidic solution compared to the basic solution. The increase in activation energy indicated that physical adsorption of palm wine occurred on the surface of mild steel (Solmaz *et al.*, 2008).

CONCLUSION

Increase in temperature favours a decrease in corrosion of mild steel. The Langmuir adsorption isotherm fitted well for the experimental data of both solutions for both temperatures studied. Increase in concentration of both acid and basic solutions decrease rate of mild steel corrosion. Activation energy increase with inhibitors concentrations and solutions concentrations. The inhibitor performs better under basic solution compared to the acidic solution studied. FTIR result of the palm wine with the peak of the double bond carbon functional group also confirms the palm wine as good corrosion inhibitors on the mild steel while the presence of tannins in the phytochemical analysis also suggest palm wine as a good corrosion inhibitor. However, the palm wine has shown to be a good corrosion inhibitor on mild steel.

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