



## Study of The Inhibitive Effect of Dennattia Tripattalla on Aluminum in Tetraoxosulphate (XI) Acid Medium

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*Abstract: Inhibitive effect of Dennattia tripetala (DT) (pepper fruit) extract on corrosion of aluminum in 0.5 M H<sub>2</sub>SO<sub>4</sub> medium was investigated. The pepper fruits were obtained from Egbudu market, Warri and was processed to powder. Phytochemical analysis was carried out using quantitative and qualitative methods respectively. Fourier Transform Infra-Red (FTIR) spectroscopy was carried out to determine the functional groups of the phytochemicals. Gravimetric (weight loss) and electrochemical techniques was used for the corrosion study within a temperature range of 303 to 323K. The results from the phytochemicals analysis revealed the presence of alkaloids, flavonoids, phenols, saponins, tannins, steroids, phytates and glycoside. The gravimetric studies revealed that inhibition efficiency increased from 62.3% to 95.5% with increasing concentration of extracts from 200mg/l to 1000mg/l. Activation energy increased from 36.019 KJ/Mol to 59.628KJ/Mol as inhibitor concentration increased from 0.45 to 1.20g/L indicating the difficulty of corrosion to take place and also free energy reduced from -18.689 KJ/Mol to -26.592KJ/Mol for the same concentration of the inhibitor. The electrochemical impedence study gave a convincing proof, that corrosion inhibition of aluminum in acid medium takes place through adsorption process that occurs on the surface. Polarization curve measurements really indicate that the studied extract showed to be a mixed type inhibitor. The increasing value of constant phase element exponent, that is, the phase shift (n) with increasing inhibitor concentration indicated that surface roughness decreased with increasing inhibitor concentration which is also seen in the scanning electron microscopy. The adsorption of DT extracts in acid environment on aluminum obey Langmuir adsorption isotherm since it is the isotherm that gave the best fit for the experimental data. SEM confirms the existence of film coating layer on the metal solution interface. It was observed that bio-sourced plant extract, Dennattia Tripattalla (DT) is very effective as green corrosion inhibitor for aluminum in acidic medium*

*Key terms: Dennattia Trapettallia, inhibitive effect, pepper fruit, egbudu market, aluminum corrosion*

### 1. INTRODUCTION

Corrosion is the destructive attack of metallic materials by their environments. These metallic materials are the drivers of industrial revolution (Briggs, 1980; Kolozsvary, 2019). Their usefulness is due to their wide mechanical and electrical properties (Miralrio & Vazquez, 2020). One of the most widely used metal is aluminum (El-Katori & Al-Mhyawi, 2019). They are of great economic importance in the transportation and engineering industries. They are used as reaction vessels, pipes, machineries and chemical batteries due to

their advantages, which include; low cost, lightness and good corrosion resistance at moderate temperature (Kotz & Treichel, 1996). Oxide film quickly form when it gets contact with these environments. This oxide film, alumina ( $\text{Al}_2\text{O}_3$ ) is inert at lower temperature and mild environments.

Its seemingly corrosion resistance vanishes when the surface film break down in higher acid concentrated environment. Pickling of aluminum, descaling, industrial acid cleaning, oil well acidizing operations etc., make use of acid medium

Corrosion inhibitors are substances that are added in small doses chemical solutions to inhibit corrosion on metal surfaces. The unfriendliness of inorganic inhibitors to the eco-system have led to the use of organic inhibitors.

Discovery and development of new inhibitors are still necessary because known and used inhibitors are costly, dangerous to the environment and human health (Ameh, Ikpeseni & Lawal, 2014). Plant extracts are cheap and eco-friendly corrosion inhibitors. They are widely used due to increasing environmental awareness and vigilance of the importance of protecting and preserving the natural environment (Okafor, Osabor & Ebenso, 2011; Sastri, 2011). Several leaves, peels and fruits extracts have been used on the corrosion inhibition effectiveness on aluminum and steel in both acidic and alkaline solutions respectively (Akalezi, Ogukwe, Ejele, & Oguzie, 2016; Akoma, S. & Osarolube, 2017; Bouyanzer, Hammouti, & Majidi, 2006; Aisha & Khadijah, 2015 etc.). To the best of my knowledge nothing has been reported on the use of *Dennettia tripetala* seed extracts on corrosion of aluminum in 0.5M acidic ( $\text{H}_2\text{SO}_4$ ) medium, using gravimetric technique. The aim of this study is to investigate corrosion inhibition of Aluminum in 0.5 M  $\text{H}_2\text{SO}_4$  medium using *Denettia tripetala* extract as inhibitor using gravimetric technique.

## 2. METHODOLOGY

### Materials

The materials include: *Dennettia tripetala* (pepper fruit), Aluminum coupon sheet of dimension 3cm × 3cm × 1cm, Sodium Hydroxide solution, Tetraoxosulphate (VI) acid solution, Ethanol, Acetone

### Equipments

The equipments include: Beakers, Electronic balance of series J.A 1003A, Water bath, Glass jars, Glass rod, Bristle brush, Emery paper, Filter paper, FTIR Spectrophotometer (Shimadzu, Model IR affinity GCMS-QP2010 plus Shimadzu, Japan), Scanning Electron Microscope (SEM) (Model: Rhenom Prox, Phenom World Eindhoven, Netherlands), Potentio-stat/galvano-stat (263 electrochemical work station).

### Method

#### Preparation of Corrosion Medium 0.5M $\text{H}_2\text{SO}_4$ Solutions

Electronic weighing balance, volumetric flasks and beakers were use. 0.5M  $\text{H}_2\text{SO}_4$  was prepared from 27.2ml of concentrated acid and 1000ml of distilled water for the corrosion study.

#### Metal Specimen preparation

The aluminum metal sheets of 3cm x 3cm x 1cm with a hole drilled on its side for easy suspension into the corroding solution was cut from sheet aluminum. They were degreased in absolute ethanol, rinsed with water and dipped into acetone, air dried and initial weight taken before being immersed in acidic medium.

#### Preparation of extracts

Seeds of *Dennettia tripetala* (DT) were collected, washed, sun dried to a constant weight, ground to a fine powder, and pen stored in labeled glass jars before use. The stock solution of the fruit is prepared by dissolving 40g in ethanol solution. The resultant solutions are boiled under reflux for 3 hours, allowed to cool to room temperature, then filtered and stored in air tight containers and kept under room. From the respective stock solutions, inhibitor test solutions are prepared in the concentration range of 200mg/L – 1200mg/L for gravimetric analysis.

#### Qualitative analysis of the extracts

The solvent free extract obtained was subjected to qualitative test for the identification of various plant constituent from the sample. The materials from which these phytochemicals determination are performed are shadow-dried and converted to dust using a laboratory mill. The processed materials are exposed to hexane for fat

removal. The materials are kept under hexane for 24 hours, filtered, and left for 5 to 7 days to allow the residual hexane to evaporate. The processed materials were covered with ethanol and maintained for 24 hours. Series of several filtering were performed until the liquid material turned into hyaline aspect. Assays (tests) are conducted with this liquid to determine the presence or absence of each one of the above-mentioned metabolites.

### Gravimetric Method

$$\Delta W = W_o - W_1 \quad (2.1)$$

$$\text{Corrosion rate CR, (mm/year)} = 8.76 \times 10^3 \frac{W_o - W_1}{A \rho t} \quad (2.2)$$

$$\text{Corrosion efficiency, IE\%} = \frac{W_o - W_1}{W_o} \times 100 \quad (2.3)$$

$$\text{Surface coverage, } \theta = \frac{W_o - W_1}{W_o} \quad (2.4)$$

Where  $W_o$  and  $W_1$  are the initial and final weight of aluminum samples, respectively,  $A$  is the total area of the aluminum samples,  $\rho$  = The Density ( $\text{g/cm}^3$ ) of the coupon and  $t$  is the time of immersion.  $\Delta W$  is the weight loss, CR is the corrosion rate, IE% is the corrosion efficiency and  $\theta$  is the degree of surface coverage

### Effect of Temperature on the Corrosion Rate

Effect of temperature on the corrosion rate was described using Arrhenius equation;

$$\text{CR} = A A e^{-\frac{E_a}{RT}} \quad (2.5)$$

Where CR is the corrosion rate of the mild steel, A is the pre-exponential factor,  $E_a$  is the activation energy, R is the gas constant.

Equation (2.5) can be linearized to form Equation (2.6) as shown below.

$$\ln(\text{CR}) = \ln A - \left[ \frac{E_a}{R} \right] \left[ \frac{1}{T} \right] \quad (2.6)$$

Considering the corrosion rates of the metal at  $T_1$  and  $T_2$  as  $\text{CR}_1$  and  $\text{CR}_2$ , Equation (2.6) can be expressed by Equation (2.7)

$$\ln \left( \frac{\text{CR}_2}{\text{CR}_1} \right) = \left( \frac{E_a}{2.303R} \right) \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2.7)$$

### Thermodynamic parameter for the adsorption process

The heat of adsorption  $Q_{\text{ads}}$  ( $\text{kJmol}^{-1}$ ) was calculated using Equation(2.8).

$$Q_{\text{ads}} = 2.303 R \left[ \log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_2 \cdot T_1}{T_2 - T_1} \quad (2.8)$$

Where R is the gas constant,  $\theta_1$  and  $\theta_2$  are the degree of surface coverages at temperatures  $T_1$  and  $T_2$ , respectively.

### Consideration of the adsorption isotherms

The data obtained from the degree of surface coverage were used to test see whether they into the different adsorption isotherms: Langmuir, Frumkin, Temkin and Flory-Huggins isotherms.

#### Langmuir isotherm

Langmuir isotherm can be expressed by Equation (2.9)

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2.9)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and  $\theta$  is the degree of surface coverage. When it is expressed in logarithmic form, Equation (2.9) can be expressed in Equation (2.10).

$$\log \frac{C}{\theta} = \log C - \log K \quad (2.10)$$

#### Frumkin isotherm

Frumkin adsorption isotherm can be expressed according to Equation (2.10).

$$\log \left[ (C) X \left( \frac{\theta}{1-\theta} \right) \right] = 2.303 \log K + 2\alpha\theta \quad (2.11)$$

Where K is the adsorption-desorption constant and  $\alpha$  is the lateral interaction term describing the interaction in adsorbed layer.

### Temkin isotherm

Temkin isotherm can be expressed by Equation (2.12).

$$\theta = \frac{2.303 \log K}{2\alpha} - \frac{2.303 \log C}{2\alpha} \quad (2.12)$$

Where K is the adsorption equilibrium constant,  $\alpha$  is the attractive parameter,  $\theta$  is the degree of surface coverage, C is the concentration of the inhibitor.

### Flory-Huggins isotherm

The Flory-Huggins isotherm can be expressed by Equation(2.12)

$$\log \left[ \frac{\theta}{C} \right] = \log K + x \log (1 - \theta) \quad (2.12)$$

where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

The free energy of adsorption ( $\Delta G_{ads}$ ) was calculated according to Equation (2.13).

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \quad (2.13)$$

Where R is the gas constant, T is temperature, K values obtain from the isotherms(Langmuir, Frumkin, Temkin and Flory-Huggins isotherms) were used to obtain the values of  $\Delta G_{ads}$  according to Equation (2.13).

### Potentiodynamic Polarization Measurements

Electrochemical measurements were conducted in a three electrode corrosion cell using a VERSASTAT 400 complete DC voltammetry and corrosion system with V3 studio software for electrochemical impedance spectroscopy and potentiodynamic/galvanostat corrosion system with E-chem software for potentiodynamic polarization experiments. A platinum sheet was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode. Aluminum for electrochemical experiment was machined into cylindrical specimen and fixed in polytetrafluoroethylene (PTFE) rod by epoxy resin in such a way that only one surface area  $1\text{cm}^2$  was left uncovered. The electrode (cylindrical specimen sample of metals) used were polished with emery paper from (800 to 1200), rinsed with distilled water, degreased with ethanol and dried with acetone.

The saturated calomel electrode was connected via a lugging capillary. Impedance measurement were performed in aerated and unstirred solutions at the end of 1800s at  $30 \pm 1^\circ\text{C}$  and corrosion potentials ( $E_{corr}$ ) over a frequency range of 100 KHz – 0.1Hz with a signal amplitude perturbation of 10mV.

Potentiodynamic polarization studies were carried out in the potential range  $\pm 250$  mV versus corrosion potential at a scan rate of  $0.5\text{mVs}^{-1}$ . Each test was run three (3) times verify the reproducibility of the data. All experiments were carried out in freshly prepared solution at constant temperature of  $30 \pm 1^\circ\text{C}$  using a thermostat.

### Scanning Electron Microscopy Analysis of Surface Metals.

The test specimens were immersed in 100ml of 0.5M  $\text{H}_2\text{SO}_4$  Solutions with the extract concentration of 300mg/L and 1500mg/L for 15h. After the duration of the experiment, the specimens were washed with distilled water, dried and examined for their surface electron microscope (SEM), Phenom Prox, MVE 016477830, manufacture, Phenom world Eindhoven Nether Land

## 3. RESULTS AND DISCUSSIONS

### Phytochemical analysis of plant extracts

Phytochemical studies had been performed on the plant extracts, the end result revealed the presence of alkaloids, flavonoids, phenol, saponins, tannins, steroids, phytates and glycoside. The extract established their inhibitive action via adsorption of phytochemical components molecules on the metal surface. The result of the qualitative evaluation is shown in table 3.1.

**Table 3.1:** Qualitative and quantitative analysis of DT

PARAMETERS	Qualitative	Quantitative (mg/100g)
Alkaloids	+++	616
Cardiac Glycosides	+	58

+++ =	Flavonoids	++	232	highly
	Phenolics	+	148	
	Phytates	+	166	
	Saponins	-	52	
	Terpenoids	+++	930	
	Steroids	+	132	
	Tannins	+++	984	

concentrated, ++ = concentrated, + = in trace; - absent or too little to identified qualitatively.

### FTIR Graphical Analysis

#### The analysis of DT extract and corrosion product of Aluminum in H<sub>2</sub>SO<sub>4</sub>.

The FTIR spectrum analysis of *Dennetia tripetala* pure extract and corroded product is presented in tables 3.2 by comparing the values with the standard infra-red (IR) data spectrum. Wave bands 3975.56cm<sup>-1</sup> to 3388.84cm<sup>-1</sup> represent strong and sharp stretch of free bonds of alcohol and phenol. 3261.4cm<sup>-1</sup> to 3045.30cm<sup>-1</sup> represents broad stretch of acids and carboxylic group. Wave band 2987.40cm<sup>-1</sup> to 2836.85cm<sup>-1</sup> are variable stretch bond of alkyl Sps C-H group. Band of 2771.2cm<sup>-1</sup> to 2705.62cm<sup>-1</sup> are medium representative stretch of aldehydes. Sharp and variable wave band of 2122.76cm<sup>-1</sup> to 2024.6cm<sup>-1</sup> are for stretch bond of alkynes and nitrite. Wave band 1844.84cm<sup>-1</sup> is very strong and represent anhydrides bond. Wave band 1596.92cm<sup>-1</sup> is for medium and strong stretch bond of amines and amides. Wave band 1416.38cm<sup>-1</sup> are for medium and strong stretch bond of akenes while wave band of 1285.14cm<sup>-1</sup> and 1030.38cm<sup>-1</sup> are strong and represent stretch of acids, esters and ethers respectively.

**Table 3.2: FTIR Analysis on the shifting mechanism of *Dennetia tripetala* extracts functional group in H<sub>2</sub>SO<sub>4</sub>**

<i>Dennetia tripetala</i> pure extract			<i>Dennetia tripetala</i> corrosion product		
Peak (cm <sup>-1</sup> )	Intensity	Assignment	Peak (cm <sup>-1</sup> )	Intensity	Assignment
3975.56 to 3388.84	Strong and sharp	O-H, free bonds of alcohols and phenol	3940.92 to 35415.86	sharp and Strong	O-H, free bonds of alcohols and phenol
3261.4 to 3045.30	Broad	O-H stretch of acids, carboxylic	3288.48	Medium	N-H stretch bond of amines
2987.40 to 2836.85	Variable	Alkyl sp <sup>2</sup> C-H	3147.80 to 3076.18	Variable	aryl or vinyl sp <sup>2</sup> C-H
2771.2 to 2795.62	Medium	C-H stretch of aldehydes	2925.64 to 2802.12	Variable	Alkyl sp <sup>3</sup> C-H
2122.76 to 20226.26	Sharp variable	C≡ or C≡N stretch of alkynes, nitrites	2740.36	Medium	C-H stretch of aldehydes
1844.84	Very strong	C=O bonds for anhydrides	273.30 to 2122.76	Sharp	C≡N stretch of nitrites
1596.92	Medium, strong	N-H bond of amines, amides	1972.22 to 1875.72	Very strong	C=O bonds of anhydrides
1416.38	Variable	C=C stretch of arenes	1563.06	Medium strong	N-H bond of amines
1285.14	Strong	C-O stretch of acids, esters	1454.98 to 1350.76	Variable	C=C stretch bond of arenes
1030.38	Strong	C- stretch of ethers	1258.12	Strong	C-O stretch of acids, ethers
			1130.74 to 1072.84	Strong	C- stretch of ethers

The analysis of *Dennetia tripetala* extract and corrosion product of Aluminum in H<sub>2</sub>SO<sub>4</sub> wave bands 3975.56cm<sup>-1</sup> to 3388.84cm<sup>-1</sup> represent strong and sharp stretch of free bonds of alcohol and phenol. 3261.4cm<sup>-1</sup> to 3045.30cm<sup>-1</sup> represents broad stretch of acids and carboxylic group. Wave band 2987.40cm<sup>-1</sup> to 2836.85cm<sup>-1</sup> are variable stretch bond of alkyl Sps C-H Group Band of 2771.2cm<sup>-1</sup> to 2705.62cm<sup>-1</sup> are medium representative stretch of aldehydes. Sharp and variable wave band of 2122.76cm<sup>-1</sup> to 2024.6cm<sup>-1</sup> are for stretch bond of alkynes and nitrite. Wave band 1844.84cm<sup>-1</sup> is very strong and represent anhydrides bond. Wave band 1596.92cm<sup>-1</sup> is for medium and strong stretch bond of amines and amides. Wave band 1416.38cm<sup>-1</sup> are for medium and strong stretch bond of akenes while wave band of 1285.14cm<sup>-1</sup> and 1030.38cm<sup>-1</sup> are strong and represent stretch of acids, esters and ethers respectively.

### Results of the Gravimetric Method, One Factor at a Time

From the appendix 1, it was discovered that weight losses and corrosion rates reduces in acidic solutions when inhibitor concentration was increased compared with the blank solution where no inhibitor solution was added. When inhibitor concentration was increased from 0.2g/l to 1.2g/l, weight loss and corrosion rate reduces from 0.251g and 2.324mg/cm<sup>2</sup>/hr to 0.091g and 0.843mg/cm<sup>2</sup>/hr respectively in the H<sub>2</sub>SO<sub>4</sub> solution. In the same way, corrosion efficiency which is a percentage reduction increased from 56.12 to 84.09% at 303K temperature. But when the temperature was increased to 323K weight loss and corrosion rate increased slightly and efficiency too reduced slightly. However, the temperature effect was analyzed subsequently.

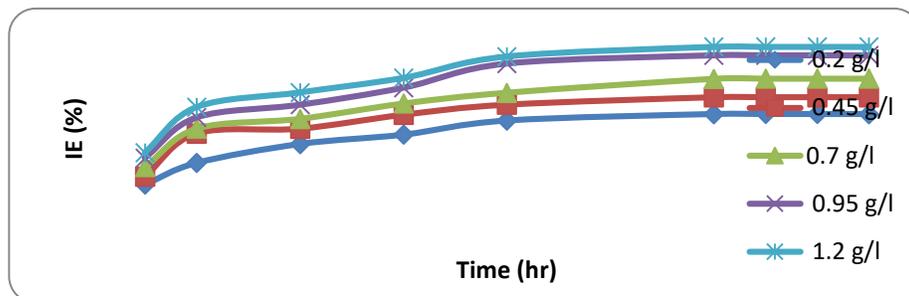


Figure 3.1: Plot of inhibition efficiency of Al in H<sub>2</sub>SO<sub>4</sub> versus time at various concentration of DT extract.

The graph in figure 3.1 shows the efficiency of DT in acidic solution. As inhibitor concentration increases, efficiency also increases with time.

**Table 3.3: Activation energy and heat of adsorption for the corrosion inhibition of Al in H<sub>2</sub>SO<sub>4</sub> medium**

Inhibition concentration (g/L)	DT	
	E <sub>a</sub> (KJ/Mol)	G <sub>ads</sub> (KJ/Mol)
0.2	41.524	-27.564
0.45	36.019	-18.689
0.70	30.324	-12.025
0.95	42.613	-17.723
1.20	59.628	-26.592

The table3.3 shows how inhibitor concentration increase affected the activation energy and Gibbs free energy of adsorption. It indicated that when inhibitor concentration increased from 0.2g to 1.20g respectively, activation energy from 41.524KJ/Mol to 59.628KJ/Mol (not regular). The Gibbs free energy showed some negative signs for Al in H<sub>2</sub>SO<sub>4</sub> medium

### Analysis of Adsorption Isotherm

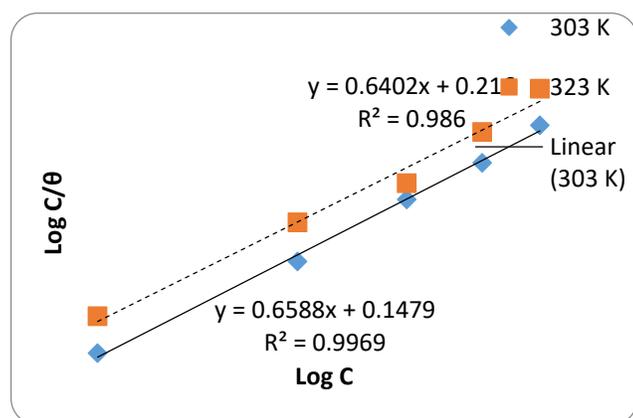


Figure 3.2: Plot of Langmuir isotherm for Aluminum in H<sub>2</sub>SO<sub>4</sub> with DT extract.

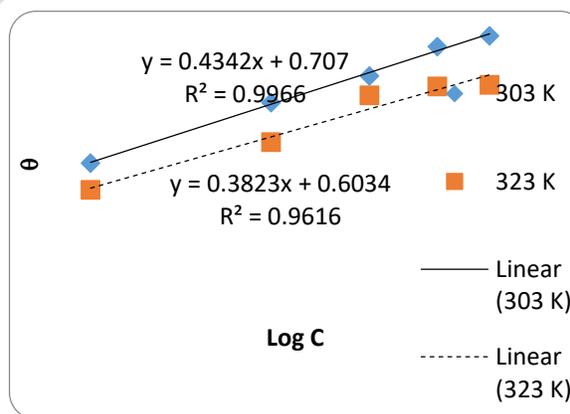


Figure 3.3: Plot of Temkin isotherm for Aluminum in H<sub>2</sub>SO<sub>4</sub> with DT extract.

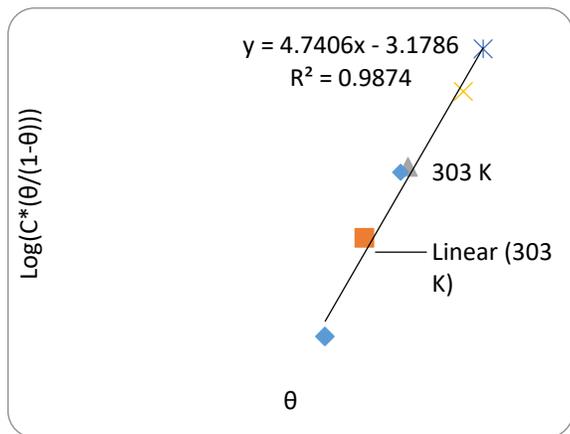


Figure 3.4: Plot of Frumkin isotherm for Aluminium in H<sub>2</sub>SO<sub>4</sub> with DT extract.

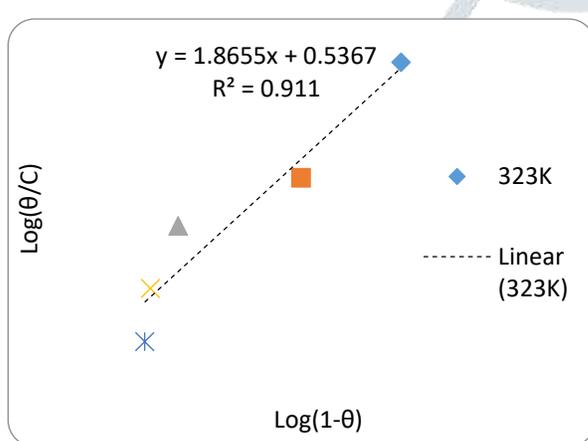


Figure 3.5: Plot of flory-huggins isotherm for Aluminium in H<sub>2</sub>SO<sub>4</sub> with DT extract.

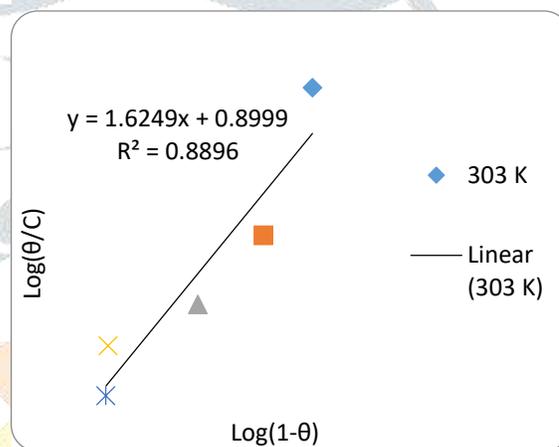


Figure 3.6: Plot of flory-huggins isotherm for Aluminium in H<sub>2</sub>SO<sub>4</sub> with DT extract.

The adsorption isotherm as shown figures 3.2. The negative values of  $\Delta G^0_{ads}$  indicate the spontaneous adsorption of the plant extract as the value of the free energy of adsorption is not only negative but is less than the threshold value of  $-40 \text{ kJ mol}^{-1}$  required for chemical adsorption, tables 3.4. This is in compliance to the previous studies of Gopal and Ebenso (2013). From the Frumkin adsorption parameter, the lateral interaction term ( $\alpha$ ) gave positive values suggesting attractive behavior of the inhibitor on the aluminum surface (tables 3.4). From Temkin adsorption parameter, the attractive value ( $a$ ) is negative, showing that repulsion exists in the adsorption layer. The value of the size parameter ( $x$ ) is positive; the positivity of the value indicates that the adsorbed species of the extract is bulky. The values of  $k_{ads}$  are relatively small indicating that the interaction between the adsorbed extract of DT molecules and aluminum surface is physically adsorbed. This is also supported by lower negative ( $\Delta G^0_{ads}$ ) values for extract (Moretti et al,2004). Generally, close examination of isotherm studies of corrosion inhibition of Aluminum in extract suggest that the process of film formation supersedes that of destruction of the metal surface and occurred according to the mechanism of physical adsorption

Table 3.4: Adsorption parameters for the corrosion inhibition of Al in H<sub>2</sub>SO<sub>4</sub> by DT extract

Adsorption isotherm	Temperature (k)	R <sup>2</sup>	Log K	K	$\Delta G^0_{ads}$ (KJ/mol)	Isotherm property	
Langmuir isotherm	303	0.994	-0.145	0.7161	-9.278	$\alpha$	2.37
	323	0.996	-0.100	0.7943	-10.169		
Frumkin isotherm	303	0.987	-1.3799	0.0417	-2.114	1.9635	
	323	0.993	-1.0443	0.0903	-4.329		

Temkin isotherm	303	0.937	-2.1549	0.0070	2.382	a	-3.1291
	323	0.976	-1.5160	0.0305	-1.413		-2.4552
Flory-Huggins isotherm	303	0.832	0.734	5.4200	-14.378	x	1.163
	323	0.929	0.508	3.211	-13.929		1.200

### Electrochemical Measurements

Corrosion reaction is an electrochemical process and therefore, electrochemical techniques are most suitable for obtaining detailed insights into the corrosion process. Tests to ascertain the influence of plant extracts on the electrochemical corrosion behavior of aluminum in 0.5M H<sub>2</sub>SO<sub>4</sub> were performed using different concentrations of DT.

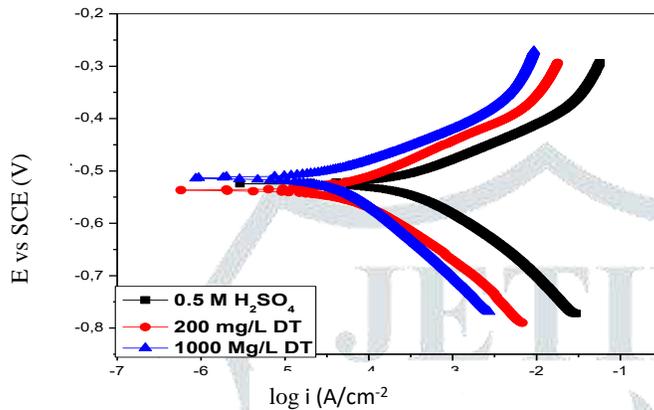


Figure 3.7: Potentiodynamic polarization curves for Al in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of different concentrations of DT extracts.

### Potentiodynamic Polarization Measurements

Polarization measurements were performed to distinguish the effect of DT on the anodic and cathodic reactions. Typical potentiodynamic polarization curves for aluminum in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of DT at 30°C are shown in Figure 3.7. The aluminum specimen is seen to exhibit active dissolution with no distinctive transition to passivation within the studied potential range. Careful scrutiny of the polarization curves in 0.5 M H<sub>2</sub>SO<sub>4</sub> environment indicates that the presence of DT shifted the cathodic and anodic parts towards lower current densities in each case. The addition of DT into the aggressive solutions has no significant effect on the corrosion potential ( $E_{corr}$ ). If the displacement in  $E_{corr}$  is greater than 85 mV we could classify the inhibitor as anodic or cathodic and if the displacement is less than 85 mV the inhibitor may be seen as a mixed type. Figure 3.7 indicates that the maximum displacement in  $E_{corr}$  value in the studied environments was not up to 85 mV, therefore, DT is regarded as a mixed-type inhibitor. The figure showed that the corrosion current density decreased.

Considerably in the presence of the inhibitor compared to the uninhibited solution and also decreased with an increase in the concentration of the extract. In 0.5 M H<sub>2</sub>SO<sub>4</sub> it was 95.5% at a concentration of 1000 mg/L at  $30 \pm 1^\circ$

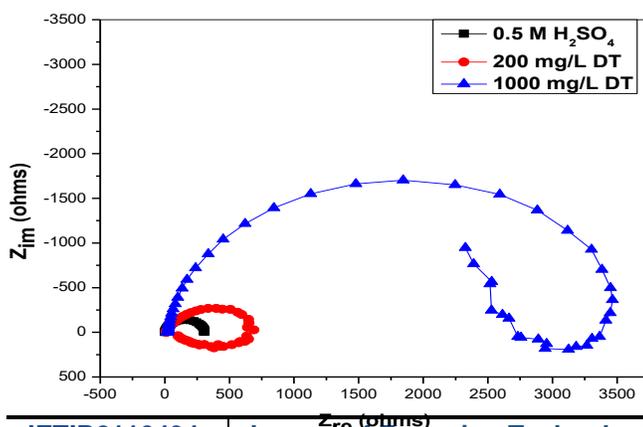


Figure 3.8: Impedance spectra of curves of Aluminum in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence DT.

The Nyquist plots showed a capacitive loop followed by an inductive loop for the Al samples in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution as shown in Figure 3.8. The diameter of the semi circles is related to charge transfer resistance. The size of the capacitive loops was greater in the presence of DT, compared to that in the absence of the inhibitor; an indication of a higher corrosion resistance for aluminum in the presence of DT. The occurrence of an inductive loop for in both aggressive solutions may indicate certain non – faradaic processes, such as adsorption and desorption of corrosion products, occurring at the sample / electrolyte interface.

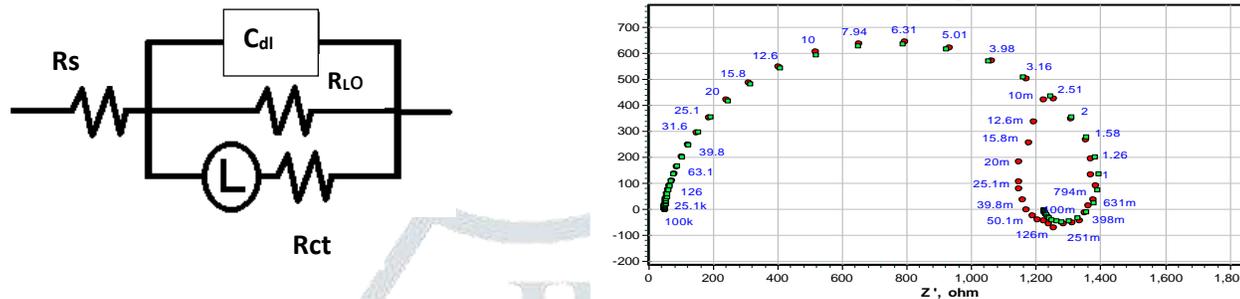


Figure 3.9: Equivalent Circuit Model for Aluminum sample.

### 3.5 Impedance Parameters for Aluminum in H<sub>2</sub>SO<sub>4</sub> in the Absence and Presence of DT Extract

Extract	System	R <sub>s</sub>	R <sub>ct</sub>	N	C <sub>dL</sub>	IE(%)
DT	0.5M H <sub>2</sub> SO <sub>4</sub>		8.4	0.89	258.8	-
	200mg/l	3.29	142.5	0.84	83.7	94.1
	1000mg/l	3.41	195.3	495.3	60.6	98.1

The equivalent circuit model shown in Figure 3.9 was used to model the impedance results obtained for Al in solution, after fitting with Zsimpwin software. The R<sub>s</sub>, C<sub>dl</sub>, R<sub>Lo</sub>, L & R<sub>ct</sub> are solution resistance, capacitance of charge, resistance of the charge layer, inductance and charge transfer resistance respectively. Higher value of R<sub>ct</sub>, as shown in table 3.5 means greater inductance which is occurred in the presence of the inhibitor than the value obtained in the absence of DT.

It is well known that Al surfaces can form a protective layer of Al<sub>2</sub>O<sub>3</sub> when in contact with aqueous solutions which is consonance with Meyer (1992) and Sastri *et al* (2007) which will lower the rate of corrosion. Adsorption of DT species into the aluminum layer however increased the resistance.

This has shifted the corrosion potential to the positive region which denoted decreased surface area availability for corrosion to occur. Electrolyte penetration was also reduced due to blockage caused by DT adsorption. This was made evident by the shift of E<sub>corr</sub> to more positive potentials, the reduction of current densities in the inhibited environment and the increased size of the diameter of the Nyquist plots. It can be deduced that the adsorption of DT species serves as a barrier blocking the contact between the Al substrate and the electrolyte solutions.

### Scanning Electron Microscopy

Table 3.5: Specimen Specifications and properties

S/NO	Materials.	Dimensions	Composition (%)
1	Aluminum AA3003	2.6cm x 2.6cm x 0.04 cm. weight loss. 1.0 cm <sup>2</sup> exposed surface area for electrochemical analysis.	0.017cu, 1.22mn, 0.55fe, 0.36si, 0.064Pb, 0.026Ti, 0.009V, 0.19 others, 97.672Al

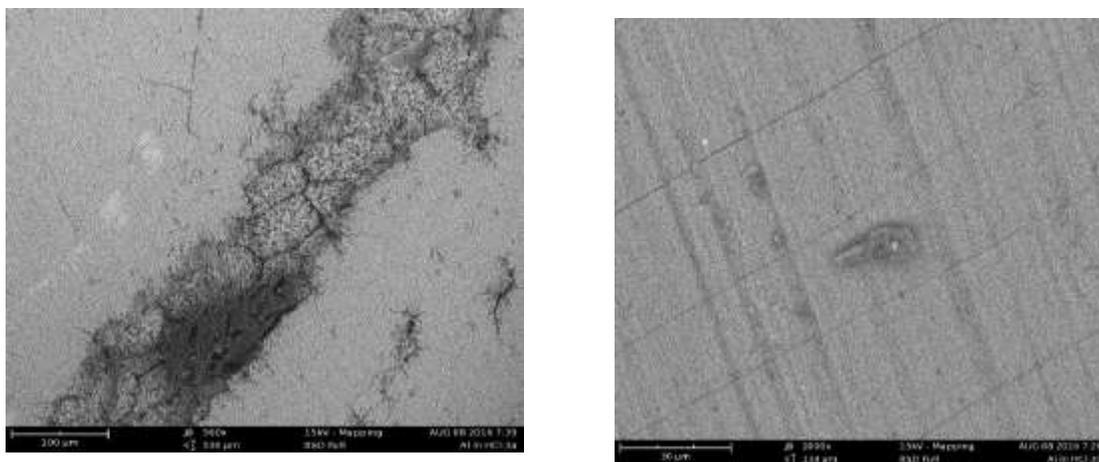


Figure 3.10: (a) Al in  $H_2SO_4$  in absence of inhibitor (b) Al in  $H_2SO_4$  in Presence of inhibitors

Optical microscope test of the aluminum revealed that when a smooth surface of Al is immersed in an acidic and alkaline media for hours, in absence and presence of DT extract, corrosion pits were created on the surface due to aggressive attack of acid. A rough surface with flakes of dark color is observed (figure 3.10a) which indicate deposition of corrosion products and/or chloride ions on the surface. But in the presence of inhibitor as shown in figure 3.10b. Smooth layers were recognized due to adsorption of organic species present in the extract at most active sites, brightness of the image indicates good interaction of inhibitor with the metal. On the basis of the information provided by the optical microscope, it can be concluded that plants extract protects metals in acid environments, forming good protective film on the surface of the metals, which proceeds to a considerable reduction of the corrosion process

## 4. CONCLUSION AND RECOMMENDATION

### 4.1 Conclusion.

- a. From the discussion so far, it is quite glaring that bio-sourced plant extract, *Dennattia Tripatalla (DT)* is very effective as green corrosion inhibitor for aluminum in acidic medium.
- b. The extract is quite a good inhibitor for aluminum corroding effect in acid environment studied. Inhibition efficiency certainly increases from 62.3% to 95.5% for 0.5 M  $H_2SO_4$  with increasing concentration of extracts from 200mg/l for 1000mg/l for 0.5M  $H_2SO_4$  and the values employed are closely in agreement with Akalezi, et al (2016), 91.01%; Bammou, et al (2014), 94.01%
- c. Activation energy increased from 36.019 to 59.628KJ/Mol as inhibitor concentration increased from 0.45 to 1.20g/L indicating the difficulty of corrosion to take place and also free energy reduced from -18.689 to -26.592KJ/Mol for the acidic medium for the same concentration of the inhibitor indicating the difficulty of corrosion to take place and also free energy reduced from -11.961 to -45.545KJ/Mol for the same concentration of the inhibitor is indicating a better efficiency.
- d. The electrochemical impedance study gave a convincing proof, that corrosion inhibition of aluminum in acid medium takes place through adsorption process that occurs on the surface.
- e. Polarization curve measurements really indicate that the studied extract showed to be a mixed type inhibitor.
- f. The increasing value of CPE exponent, that is, the phase shift (n) with increasing inhibitor concentration indicated that surface roughness decreased with increasing inhibitor concentration which is also seen in the scanning electron microscopy.
- g. The adsorption of DT extracts in both acid alkaline environments on aluminum obey Langmuir adsorption isotherm since it is the isotherm that gave the best fit for the experimental data.
- h. SEM confirms the existence of film coating layer on the metal solution interface.

## 4.2 Recommendations.

1. Massive planting of pepper fruit is encouraged.
2. Computational modeling of the major extract components on aluminum is yet to be done. When this done, it will help in establishing detailed mechanism of corrosion inhibition.
3. There is need for further work on the exploration of the plant materials in other corrosive environments such as carbon dioxide, sulfur dioxide and hydrogen sulfide.
4. Weight loss or gravimetric method should be employed to evaluate corrosion because as plant base inhibitors are water soluble, it is easy to obtain accelerated corrosion condition and small amount of inhibitors for testing.
5. Fourier transform infrared is the best method for monitoring the shift mechanism of the functional groups in the corrosion products and scanning electron microscopy is the best method to monitor corrosion morphology.

## 4.3 Contributions to Knowledge.

The use of dennattia tripettala extract as an inhibitor on aluminum in acid and alkaline media is a new area of study that has been tested to be effective. The extract is biodegradable, cheap, do not contain heavy metals and are readily available.

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#### APPENDIX 1: CORROSION INHIBITION OF AL IN H<sub>2</sub>SO<sub>4</sub> WITH DT EXTRACT.

Factors	Inhibitor Conc. (g/l)	Weight Loss (g)	Corrosion Rate (mg/cm <sup>2</sup> hr)	Inhibition Efficiency (%)	Degree of Surface Coverage
12 hr 0.5M 303 K	0	0.572	5.296		
	0.2	0.251	2.324	56.12	0.5612
	0.45	0.211	1.954	63.11	0.6311
	0.7	0.167	1.546	70.8	0.708
	0.95	0.111	1.028	80.59	0.8059
	1.2	0.091	0.843	84.09	0.8409
12 hr 0.5M 313 K	0	0.6	5.556		
	0.2	0.351	3.25	41.5	0.415
	0.45	0.271	2.509	54.83	0.5483
	0.7	0.194	1.796	67.67	0.6767
	0.95	0.145	1.343	75.83	0.7583
	1.2	0.131	1.213	78.17	0.7817
12 hr 0.5M 323 K	0	0.645	5.972		
	0.2	0.391	3.62	39.38	0.3938
	0.45	0.31	2.87	51.94	0.5194
	0.7	0.23	2.13	64.34	0.6434
	0.95	0.175	1.62	72.87	0.7287
	1.2	0.172	1.593	73.33	0.7333