**Dennettia tripetala** extract as green corrosion inhibitor of mild steel in Hydrochloric acid.

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The inhibiting action of **Dennettia tripetala** extract on corrosion of mild steel in 1M HCl solution was examined using gravimetric technique. The results showed that **Dennettia tripetala** extracts (leave, stem and root) reduced the rate of corrosion in 1M HCl and inhibition efficiency increased with increase in concentration of the extract. Adsorption characteristics of the extract are approximated by Langmuir isotherm. The inhibition mechanism estimated from temperature dependence of inhibition efficiency as well as activation parameters show that the extracts inhibits corrosion via physical adsorption of the extract on the surface of the mild steel.

**Keywords:** Mild steel, Corrosion Inhibition, **Dennettia tripetala**, Adsorption mechanism

**INTRODUCTION**

Metallic materials are extensively used in industries, where they are exposed to aggressive environments. Excessive corrosion is known to occur on metals deployed in service in these aggressive environments. To protect such metals from corrosion, corrosion inhibitors such as inorganic substances like phosphates, chromates dichromates, silicates, borates, tungstates, molybdates and arsenates were introduced to reduce the corrosion rate. These inorganic inhibitors have been found effective as inhibitors of metal corrosion Oguzie (2008). Regrettably the inhibitors face severe criticism because of their toxicity. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, oxygen and sulphur, in the conjugated system have been reported to exhibit good inhibiting properties. Quvaishi and Sharma (2005). Following these findings, natural products of plant origin containing these polar functions have been recently employed in the inhibition of metallic corrosion. Buchweishaia (2009) Besides being environmentally friendly and ecologically acceptable these natural products are inexpensive, readily available and renewable sources of materials.

In this study investigation is carried on the inhibitory effect of **Dennettia tripetala** leave, root and stem extract on corrosion mild steel in acidic media using gravimetric technique. **Dennettia tripetala** is a well-known forest spicy fruit, commonly known in English as pepper fruit. It is widely found and used for numerous purposes in southern Nigeria, within West Africa it is a common ethno medicinal plant and can be used to treat cough and enhance appetite. Aside medicinal value it also possess insecticidal properties. Ejechi et al (1999), Okogun (1969) and Okwu (2004) stated that D. Tripetela Contains essential oils and phenolic acid, ethanol, ethyl acetate, flavanoid, tannin and glycoside. Further isolations on D. Tripetela showed that it contain vanillin, 2,6-dimethoxy chromone argentine and uvariopsin Janvier (2002). Elemental analysis showed that it contains mainly Ca, Fe and other elements like Mg, Zn, Mn and Co. Generally the fruits contain minerals, vitamins, flavouring oils, crude proteins, fibre ach, carbon and sulphur. Udoessien (1984) Equipped with this information about **Dennettia tripetala**, we reasoned it will be interesting employing the extract of this plant in corrosion studies.

To the best of our knowledge nothing has been reported on the use of **Dennettia tripetala** root, leave and stem extracts respectively on corrosion inhibition. The present study investigates the inhibitory effect of **Dennettia tripetala**, leave, stem and root extracts on corrosion of mild steel in acidic medium, using gravimetric technique.
**Table 1: Dennettia tripetala leave extract**

<table>
<thead>
<tr>
<th>System (mg/l)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mdd)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0140</td>
<td>3.2385</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
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<td>0.0090</td>
<td>2.0819</td>
<td>0.3571</td>
<td>35.71</td>
</tr>
<tr>
<td>600</td>
<td>0.0085</td>
<td>1.9662</td>
<td>0.3929</td>
<td>39.29</td>
</tr>
<tr>
<td>800</td>
<td>0.0065</td>
<td>1.5036</td>
<td>0.5357</td>
<td>53.57</td>
</tr>
<tr>
<td>1000</td>
<td>0.0050</td>
<td>1.5660</td>
<td>0.6429</td>
<td>64.29</td>
</tr>
</tbody>
</table>

**Table 2: Dennettia tripetila Root extract**

<table>
<thead>
<tr>
<th>System (mg/l)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mdd)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.014</td>
<td>3.2385</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.0085</td>
<td>1.9662</td>
<td>0.3929</td>
<td>39.29</td>
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<tr>
<td>400</td>
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<td>1.6193</td>
<td>0.5000</td>
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<tr>
<td>600</td>
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<td>1.5036</td>
<td>0.5357</td>
<td>53.57</td>
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<tr>
<td>8000</td>
<td>0.0055</td>
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<td>60.71</td>
</tr>
<tr>
<td>1000</td>
<td>0.0045</td>
<td>1.0409</td>
<td>0.6786</td>
<td>67.86</td>
</tr>
</tbody>
</table>

**Table 3: Dennettia tripetila stem extract**

<table>
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<tr>
<th>System (mg/l)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mdd)</th>
<th>Surface coverage (θ)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0140</td>
<td>3.2385</td>
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<td></td>
</tr>
<tr>
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<td>2.4289</td>
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</tr>
<tr>
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<td>0.0085</td>
<td>1.9662</td>
<td>0.3929</td>
<td>39.29</td>
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<tr>
<td>600</td>
<td>0.0075</td>
<td>1.7349</td>
<td>0.4643</td>
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<td>8000</td>
<td>0.0060</td>
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<td>57.14</td>
</tr>
<tr>
<td>1000</td>
<td>0.0045</td>
<td>1.0409</td>
<td>0.6786</td>
<td>67.86</td>
</tr>
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</table>

**MATERIALS AND METHODS**

Mild steel sheets used for the study were of weight composition, C: 0.05% Mn; 0.60%, P:0.36, Si: 0.03% and the rest Fe. The sheets were mechanically press-cut into test panels of dimension 3 x 3cm and a hole drilled at the centre of the coupons with radius 2.5mm. Its thickness is 1mm. Each coupon was degreased in absolute ethanol, dried in acetone, weighed and stored in moisture free desiccators prior to use. Oguzie and Ebenso (2006).

All chemicals and reagents used were analar grade. The blank corroder was 1M HCl solution. Stock solutions of the plant extract were prepared by refluxing weighed amount of the dried and grounded samples of *Dennettia tripetala* leaves, stem and root separately for 3 hours in 1M HCl solution. The resulting solution were cooled then filtered and stored. From the respective stock solutions inhibitor test solutions were prepared in concentrations range of 200-1000 (mg/l) Oguzie (2008).

**Gravimetric experiments**

The weight loss experiments were conducted under total immersion conditions in 250ml of test solution maintained at room temperature and 323k for 3 hours. The mild steel coupons were retrieved after the 3hrs scrubbed with bristle brush under running water until clean. The cleaned test coupons were dried in acetone and reweighed. The weight loss was taken as the difference between the weight of the test coupons before and after immersion, according to equation below

\[ \Delta W_t = W_{t_i} - W_{t_f} \]  

Where \( \Delta W_t \) is weight loss, \( W_{t_i} \) is initial weight before immersion and \( W_{t_f} \) is weight of the coupon after immersion.

**RESULTS AND DISCUSSION**

**Weight loss and corrosion rate (\( \rho \))**

The corrosion rate of the mild steel in the absence and the presence of *Dennettia tripetala* root, leave and stem extracts were assessed from the weight loss measurements. The weight loss data for inhibited and uninhibited samples were shown in tables 1, 2 and 3. Table 1 shows the inhibited data sample in various concentrations of the D. Tripetala leaves extract with the uninhibited indicated as blank. Table 2 shows the sample data in various concentrations of root extract and table 3 has the sample data in stem extract.
Table 4: At 50°C

<table>
<thead>
<tr>
<th>System</th>
<th>Weight Dw (g)</th>
<th>CR (Mdd)</th>
<th>θ</th>
<th>I(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.032</td>
<td>7.4023</td>
<td>0.2108</td>
<td>21.88</td>
</tr>
<tr>
<td>Stem</td>
<td>0.0250</td>
<td>5.7830</td>
<td>0.2031</td>
<td>20.31</td>
</tr>
<tr>
<td>Root</td>
<td>0.033</td>
<td>5.8987</td>
<td>0.0150</td>
<td>1.56</td>
</tr>
<tr>
<td>Leave</td>
<td>0.0315</td>
<td>7.2866</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1: Corrosion rate of mild steel with concentrations of D. Tripetela extract.

From the data shown the tables 1, 2 and 3, the weight loss values in the inhibited system are smaller than that in uninhibited system. That implies the extracts retard corrosion of mild steel in acidic media by reducing the corrosion rate. The corrosion rate (ρ) was calculated from equation 2 below:

\[ \rho = \frac{\Delta W}{AT} \]

Where \( \Delta W \) is equal to weight loss, A is area of the coupon and T is equal to period of immersion. From the data represented in Figure (1) the corrosion rate decreases as the concentrations of the D. Tripetela extract increases, showing that the degree of inhibition depends on the concentration of the extract present in the system.

### Inhibition efficiency

The inhibition efficiency was calculated from the equation

\[ IE(\%) = (1 - \frac{\rho_{in}}{\rho_{blank}}) \times 100 \]

Where IE is inhibition efficiency, \( \rho_{in} \) and \( \rho_{blank} \) corresponds to corrosion rates in inhibited and uninhibited systems respectively.

In Figure 2 the plot of inhibition efficiency against concentrations of the D. Tripetela leaves, root and stem extract are shown. From the graph the inhibition efficiency was found to increase as the concentration of the extracts increases. From the data it is observed that inhibition was more efficient in root and stem extract than that of leave which has inhibition efficiency of 64.29% at 1000(mg/l) with both stem and root extract having inhibition efficiencies of 67.36 respectively. The observed inhibition can be attributed to the adsorption of the extract on the metal surface. As the inhibitor gets adsorbed to the metal surface corrosion rates then depends on the number of corroding sites remaining. Assuming corrosion occurs only on the free sites such that the covered sites has zero corrosion rate, the degree of surface coverage (θ) is calculated with equation 4 below

\[ \theta = (1 - \frac{\rho_{in}}{\rho_{blank}}) \]

Absorption of the extract on the metal surface can be attributed to alkaloids contained in D. Tripetela Isolations carried on D. Tripetela by Jauier et al. (2002) Rossana et al (2004) shown that D. Tripetela contains alkaloids like Uvariopsine, stephenanthrine, argentinine, vanilline and chromone. These compounds except chromone are
amines and can therefore form complexes with the metal (Fe) by the ability of the amines to bond with iron with the lone pairs from nitrogen to which they donate to the orbitals of the metal. Chromone being a ketone gets absorbed to the metal surface by forming Fe II chromone complex. According to Riggs (1973), Buchweishaika (1997); Raja and Sethuraman (2008) as reviewed in Buchweishaja (2009) organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous and oxygen show significant inhibition efficiency. This explains the inhibitory ability of D. Tripetela extracts on corrosion of mild steel in acidic media. But since D. Tripetela contain more than one alkaloid of which all of them have inhibiting abilities, it is difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of the organic matter on the corroding steel surface creates a barrier that isolates the metal from the corrodent. Oguzie (2008)

Figure 3 represent relationship between the concentration of D. Tripetela extract Conc and C/θ for mild steel in D. Tripetela leave, stem and leaf extracts respectively. It is observed from the Figure that every relation give a straight line with almost unit slope. These results indicate that the adsorption of D. Tripetela leave, stem and root extracts molecules on the tested metal in different concentration follow Langmuir adsorption isotherm El-Etre and El-Tantawy (2006) Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent Eddy and Ebenso (2008). Adsorption of Langmuir relates the concentration(C) of the adsorbate in the bulk of the electrolyte to the degree of surface coverage (θ) according to equation 5. 

\[
\frac{c}{\theta} = \frac{1}{K} + \frac{C}{R_T} 
\]

Where K is the equilibrium constant of adsorption.

When values of C/θ is plotted against Conc a straight line graph is obtained as in Figure 3. On applying langmuir adsorption isotherm to the adsorption of D. Tripetela on mild steel the formation of multimolecular layer of adsorption is confirmed, where there is no interaction between the adsorbate and the adsorbent. Eddy (2008)

As reported by El-Etre (2006) Langmuir isotherm postulates that the interacting force between the adsorbed molecules and the free energy of adsorption (\(\Delta G_{ad}\)) does not depend on the surface coverage (θ). The standard free energy of adsorption were calculated using equation 6

\[
\ln K = \ln \frac{1}{55.5} - \frac{\Delta G_{ad}}{R_T} 
\]

Where K is adsorption constant, R is gas constant and T stands for temperature of the system. The value 1/55.5 represents molarity of water, where one molecule of water is replaced by one molecule of inhibitor. The values of \(\Delta G_{ad}\) for the studied systems are listed in the table 5

Observations on the Figures in the table reveals that the values of \(\Delta G_{ad}\) at 323K of D. Tripelte extracts (leave, stem and root) studied are negative, suggesting spontaneous adsorption. El-Etre and El-Tantawy (2006). On the contrary \(\Delta G_{ad}\) at 298K in all the samples is positive which suggests that adsorption is not spontaneous.
Adsorption isotherms for leaf, stem and root extracts of *D. Tripetela*

![Adsorption isotherms graph](image)

**Figure 3.** Adsorption isotherms for leave, stem and root extracts of *D. Tripetela*

**Table 5:** The values of $\Delta G^0_{ad}$ for the studied systems

<table>
<thead>
<tr>
<th></th>
<th>Stem</th>
<th>Leave</th>
<th>Root</th>
</tr>
</thead>
<tbody>
<tr>
<td>$DG^0_{ad}$ (KJmol$^{-1}$K$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298K</td>
<td>323K</td>
<td>298K</td>
</tr>
<tr>
<td></td>
<td>5.90</td>
<td>-10.79</td>
<td>6.26</td>
</tr>
</tbody>
</table>

**Adsorption and Temperature Relations**

It was observed that the inhibitor, *D. Tripetela* (root, leaf and stem) extract adsorbed to the mild steel at both temperatures studied (298 K and 323K) studied. From the results obtained in this study increase in temperature from 298k to 323K increased the corrosion rate of mild steel both in the absence and presence of the inhibitor. This is because increase in temperature accelerates corrosive process, giving rise to higher dissolution rates of the metal.

Figure 4 Shows a plot of inhibition efficiency of *D. Tripetela* leave stem and root extract against temperature from the Figure. It is observed that inhibition efficiency decreases as temperature increases indicating that the inhibitor was physically adsorbed to metal surface Ferrend (2004). As stated by Hackerman (1954) and Popova et al., (2003) reviewed in Oguzie and Ebenso (2006) inhibitor molecules are either physically or chemically adsorbed on a corroding metal surface, where the physically adsorbed molecules essentially retard metal dissolution by inhibiting the cathodic reaction while chemisorbed molecules inhibit the anodic reaction by reducing the inherent reactivity of the metal at the adsorption site.

**Thermodynamic and adsorption consideration**

Values of activation energy for corrosion of mild steel in and absence of *D. Tripetela* (leave, stem and root) extract have been calculated using equation 7.
ρ = A exp (- Ea /RT) ........................................... 7

Taking logarithm of both side of equation 7 equation 8 is obtained.

\[ \log \rho = \log A - \frac{E_a}{2.303RT} \]

Where ρ is corrosion rate of the coupon. A, represents Arrhenius constant or pre exponential factors, Ea stands for activation energy of the reaction, R is gas constant and T, temperature. Considering temperature change from 298K (T1) and 323K (T2) the values of corrosion rates at these temperatures are ρ1 and ρ2 respectively. Inserting these Figures (ρ1 & ρ2) into equation 8 we have equation 9

\[ \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \] ........................................... 9

The value of the activation energy of the blank system studied is 26.47KJmol⁻¹ whereas that of inhibited system of the leave extract is 50.53KJmol⁻¹, the stem extract has activation energy of 45.68KJmol⁻¹ and Root extract with activation energy of 49.11KJmol⁻¹. The activation energy of the inhibited system being greater than that of the blank indicates physiadsorption while the reverse signifies chemisorbtion. The extracts of leave, stem and root of Dennetia tripetala proved to be physically adsorbed to the mild steel surface, having activation energies greater that of the blank, and being less than 80KJmol⁻¹ Ebenso (2003a, b 2004) Sheatty et al., (2006), Eddy and Ebenso (2008).

CONCLUSION

Extracts from leaves, stem, and root of Dennetia tripetala separately subdued mild steel corrosion in 1M HCl at the temperatures studied. Inhibition efficiency increased with an increase in extract concentration. Analyses of experimental result suggest that the extract inhibits corrosion by being physically adsorbed on the metal, surface.

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