Assessment of Performance of Velvet Tamarind-furfural resin as Corrosion Inhibitor for Mild Steel in Acidic Solution

N. B. Iroha¹ and A. O. James²*

¹Department of Chemistry, Federal University, Otuoke, Bayelsa State, Nigeria
²Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

*Correspondence Author: abosede.james@uniport.edu.ng
Received 12 January 2018; accepted 04 May 2018, published online 17 July 2018

Abstract
Furfural obtained from peanut husk by acid hydrolysis was utilized to form a resin with the pulp of Velvet Tamarind. The resultant resin was investigated as corrosion inhibitor for mild steel in 1 M HCl solutions by using weight loss, electrochemical impedance spectroscopy and potentiodynamic polarization measurements. The studies reveal that at constant acid concentration, Velvet Tamarind-furfural (VT-F) resin acts as an effective inhibitor for mild steel corrosion in 1M HCl media. Weight loss measurement showed that inhibition efficiency increased with extract concentration and exposure time but decreased with increase in temperature. Potentiodynamic polarization results showed VT-F resin to be a mixed type inhibitor in 1M HCl environment, whereas the impedance results revealed adsorption of the inhibitor species on the steel surface. The adsorption was in accordance with Langmuir adsorption isotherm and negative adsorption energy, ΔG° ads obtained inferred that the adsorption rate was spontaneous.

Keynotes: Velvet Tamarind-furfural resin, Corrosion Inhibitor, Mild Steel, Weight Loss, Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization

1. Introduction
Mild steel is widely employed in most industries due to its low cost and availability for the fabrication of various vessels and piping systems [1]. The protection of metals from corrosion have been one of the most challenging and difficult tasks for industries. The study of the corrosion of mild steel using acid media has become important because of the industrial applications of acids, such as acid pickling, industrial cleaning, acid descaling and petrochemical processes [2, 3]. Since acid solutions are widely used for industrial purposes, inhibitors are commonly used to reduce the corrosive attack of these aggressive solutions on metallic materials.

Most synthesized inhibitors are organic compounds containing heteroatoms, such as N, O, S and multiple bonds. In recent times, the use of most of these compounds as corrosion inhibitors has been limited. This is due to the fact that, they are not ecologically friendly as they are toxic to both human beings and the environment. Several authors have reported the use of natural products of plant origin as effective corrosion inhibitors for various metals under different environments [4-7]. Souza and co-workers [4] assessed the inhibitory action of *Ilex paraguariensis* extracts on the corrosion of carbon steel in HCl solution. Soltani and Khayatkashani [6] studied the inhibitive effect of *Gundelia tournefortii* as a green corrosion inhibitor for mild steel in HCl and H₂SO₄ solutions. Fouda et al [7] investigated the effectiveness of *Melilotus officinalis* extract as save corrosion inhibitor for aluminium in 1 M hydrochloric acid solutions. These plant extracts have been reported to be a rich source of
environmentally friendly and ecologically acceptable corrosion inhibitors.

In search of more eco-friendly inhibitor, this work examines resin formed with the pulp of Velvet Tamarind and furfural as a potential corrosion inhibitor of mild steel in acidic media. The pulp of Velvet Tamarind contains high content of vitamin C (Ascorbic acid), moisture, dry matter and ash, organic matter, crude fat, crude fibre, carbohydrate, protein and minerals which include magnesium, sodium, iron, calcium and potassium [8]. In our present study, furfural obtained from peanut husk by acid hydrolysis was utilized to form a resin with the pulp of Velvet Tamarind.

This work is a continuation of the earlier work [2] and an attempt to evaluate the inhibitive action of the resin form with the pulp of velvet tamarind and furfural on the corrosion of mild steel in 1 M HCl using gravimetric and electrochemical techniques.

2. Materials and Methods
2.1. Metal Preparation
The mild steel sheets used in this work were obtained from Mechanical Engineering Department, Uniport with percent composition as follows: C (0.18), Si (0.19), Mn (0.51), P (0.044), S (0.057), Cr (0.14), Ni (0.09), Mo (0.02), Cu (0.06), and the remainder Fe. The Mild steel coupons of dimension 2 x 4 x 0.15 cm were prepared and cleaned as described elsewhere [2]. The blank corroden was a solution of 1.0 M HCl.

2.2. Hydrolysis of Peanut Husk
Furfural was obtained from peanut husk by acid hydrolysis. 50 g of peanut husk powder sieved using a 60 mesh screen and 1.5 L of 4.5 M hydrochloric acid were used for the hydrolysis. The mixture was allowed to reflux for 1 h. Thereafter, it was cooled, filtered and the filtrate containing the furfural stored in an amber coloured bottle at room temperature and used up within 24 h [9].

2.3 Preparation of Velvet Tamarind
The African black velvet tamarind was obtained from steel market in Port Harcourt, Nigeria. The pulp of the velvet tamarind was dried and ground into powdered form. The powder obtained was sieved to remove the chaff and then used with furfural to prepare the resin.

2.3 VT-F resin Preparation
The VT-F resin was prepared according to the method reported in literature [13]. A mixture of weighed amounts of the dried and ground pulp of Velvet Tamarind and 90 mL of furfural were refluxed for 3 h. The resin that developed was filtered off, washed free of acid and stored. Stock solution of the resin was prepared by refluxing weighed amounts of the resin for 3 h in 500 mL of 1 M HCl. The solution was cooled, filtered and stored. From the stock solution, inhibitor test solutions were prepared in concentrations of 10, 20, 30, 40 and 50 % v/v in 1 M HCl.

2.2. Weight Loss Measurements
Weight loss experiments were conducted under total immersion conditions maintained at 30, 40 and 50 °C. The pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using a glass rod and hook. All tests were made in aerated solutions. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 24 h interval, appropriately cleaned, dried, and reweighed. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. All tests were run in triplicate and the data showed good reproducibility. From the weight loss data, the surface coverage (θ) as a result of adsorption of inhibitor molecules, and inhibition efficiencies of the molecules (η%) were determined using equations (1) and (2), respectively.

\[
\theta = \frac{\Delta W_{\text{blank}} - \Delta W_{\text{inh}}}{\Delta W_{\text{blank}}} 
\]

\[
\eta\% = \frac{\Delta W_{\text{blank}} - \Delta W_{\text{inh}}}{\Delta W_{\text{blank}}} \times \frac{100}{1} 
\]

where \(\Delta W_{\text{blank}}\) and \(\Delta W_{\text{inh}}\) are the weight loss in the absence and presence of the inhibitor respectively.

2.3. Electrochemical measurements
Electrochemical tests were conducted using a PAR-2273 Advanced Electrochemical System
workstation, with a conventional three-electrode corrosion cell. A platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. A metal specimen fixed in epoxy resin with a surface area of 1 cm² served as the working electrode. Electrochemical measurements were carried out in aerated and unstirred solutions at the end of 3600 s of immersion, which allowed the OCP values to attain steady state. Temperature was fixed at 30±1 °C. Impedance measurements were performed at corrosion potentials (E_corr) over a frequency range of 100 kHz - 0.1 Hz, with a signal amplitude perturbation of 5 mV. Potentiodynamic polarization studies were conducted in the potential range +250 to –800 mV versus corrosion potential at a scan rate of 0.333 mV/s. Each test was run in triplicate to verify the reproducibility of the systems.

3. RESULTS AND DISCUSSION
3.1. Weight Loss Measurements
Figures 1 presents the effects of VT-F resin on the corrosion behaviour of mild steel in 1 M HCl solution at 30, 40 and 50 °C. The results show that weight loss reduced in the presence of VT-F resin compared to the blank acid solution. It was also observed that weight loss of mild steel in the presence of the inhibitor decreased with increase in concentration, indicating that the protection ability of the inhibitor is concentration dependent. From Figure 2, the inhibition efficiency increases with increase in the concentration of VT-F resin. This behaviour could be attributed to the increase of the surface coverage (θ) by the adsorption of the inhibitors on the corroding steel surface [10]. The adsorption of these organic compounds on the metal surface probably creates a barrier for mass and charge transfers thus protecting the metal surface from corrosion. The degree of protection increases with the increasing surface coverage occupied by the adsorbed molecules.

3.2. Effect of Temperature
The effect of rising temperature on the corrosion rate and inhibition efficiency of VT-F resin on mild steel corrosion in 1 M HCl was studied by weight loss measurements over a temperature
range from 30 – 50 °C. Corrosion rate is seen to increase with increase in temperature both in the absence and in the presence of the resin. From Figures 2, it is observed that inhibition efficiency increases with increase in the concentration of VT-F resin but decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption of VT-F resin onto the mild steel surface [11].

The apparent activation energies (Eₐ) were determined from the Arrhenius-type relationship between the corrosion rate (ρ) of mild steel in acidic media and temperature (T) often expressed by the Arrhenius equation:

\[ \rho = A \exp(-E_a/RT) \]  

A is the pre-exponential factor and R the universal gas constant. The variation of logarithm of corrosion rate with reciprocal of absolute temperature is shown in Figure 3 for 1 M HCl without and with different concentrations of VT-F resin. The calculated values of Eₐ are given in Table 1.

An estimate of heat of adsorption (Q₂₀) was obtained from the trend of surface coverage with temperature as follows [12]:

\[ Q_{ads} = 2.303R[\log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right)] \times \frac{T_1T_2}{T_2 - T_1} \]  

θ₁ and θ₂ are the degrees of surface coverage at temperatures T₁ and T₂. The calculated values for both parameters are given in Table 1.

Increased Eₐ in the presence of inhibitor compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower Eₐ in the presence of inhibitor suggest chemisorptions [13]. In the present study, it could be seen that with increasing concentration of VT-F resin the apparent activation energy increased, supporting the earlier proposed physisorption mechanism for VT-F resin. The increase of the activation energies in the presence of inhibitors is attributed to an appreciable decrease in the adsorption process of the inhibitor on the mild steel surface with increase of temperature and corresponding increase in the reaction rate because of the greater area of the metal that is exposed to acid [14]. The negative Q₂₀ values indicate that the degree of surface coverage decreased with rise in temperature. This further supports the proposed physical adsorption mechanism for VT-F resin [15].

![Figure 3: Arrhenius plots for carbon steel corrosion in 1 M HCl without and with different concentrations of VT-F resin](image)

### 3.3 Potentiodynamics Polarization Consideration

The potentiodynamic polarization curves of mild steel in the absence and presence of VT-F resin are shown in Figure 4, for the sample in 1 M HCl solution. The values of the polarization parameters are provided in Table 2 where E₉₀₀₀₃ and i₉₀₀₀₃ are, respectively the corrosion potential and current density. Both were obtained from the extrapolation of the anodic and cathodic Tafel slopes with respect to the E₉₀₀₀₃ values. The inhibition efficiency was calculated using the formula presented elsewhere [16]. The values in Table 2 reveal that in the presence of VT-F resin and at higher concentration of 50 (v/v %) mild steel displayed lower i₉₀₀₀₃ and slightly more positive E₉₀₀₀₃ values in studied environment. Therefore, one may conclude that VT-F resin plays a major role in slowing down the evolution rate of hydrogen at the identified concentrations by forming a stable or insoluble film, which impedes further dissolution, and the degree of inhibition depends on the concentration of the inhibitor. Corrosion decreases and η% values increases by increasing the concentration of VT-F resin. Therefore, it can be affirmed that inhibitors’ addition causes delay to mild steel’s cathodic and anodic reactions in the tested solution. The transformation of the interface of the solution from active to passive dissolution state is due to the adsorption of VT-F resin.
species on a corroding metal surface; thereby, developing a protective film.

In this environment the corrosion potential, \(E_{\text{corr}}\), and the corresponding \(i_{\text{corr}}\) of mild steel in the absence and presence of VT-F resin are presented in Table 2. The result shows that the introduction of VT-F resin reduces both the cathodic and the anodic corrosion current densities, thus implying that the corrosion rate of mild steel sample in the presence of the inhibitor was reduced when compared to the uninhibited mild steel. Also, the \(E_{\text{corr}}\) of the inhibited mild steel is more positive (anodic) than the uninhibited mild steel. This shows that in the absence of VT-F resin mild steel have a higher susceptibility to corrosion in this environment than the inhibited mild steel sample.

The polarization curves for the mild steel samples in this environment exhibit passivation behavior and do not differ in nature of transition from active to passive states. The similarity of the polarization curves of both the uninhibited and inhibited mild steel samples indicates that the mechanism of the corrosion of mild steel in the absence of the inhibitor did not change even when VT-F resin was introduced into the aggressive solutions.

![Figure 4: Potentiodynamic polarization curves of mild steel in 1 M HCl in the absence and presence of VT-F resin.](image)

### Table 2: Polarization parameters for mild steel in 1 M HCl solution in the absence and presence of VT-F resin

<table>
<thead>
<tr>
<th>System</th>
<th>(E_{\text{corr}}) (mV vs SCE)</th>
<th>(i_{\text{corr}}) (µA/cm²)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl (Blank)</td>
<td>-495</td>
<td>179.9</td>
<td></td>
</tr>
<tr>
<td>10 (v/v%)</td>
<td>-489</td>
<td>64.2</td>
<td>64.3</td>
</tr>
<tr>
<td>50 (v/v%)</td>
<td>-482</td>
<td>21.6</td>
<td>88.0</td>
</tr>
</tbody>
</table>

### 3.4 Electrochemical impedance spectroscopy considerations

The Nyquist plots showed a capacitive loop followed by an inductive loop for the mild steel samples in 1 M HCl solution as shown in Figure 5. The diameter of the semi circles are related to charge transfer resistance. The size of the capacitive loops was greater in the presence of VT-F resin, compared to that in the absence of the inhibitor; an indication of a higher corrosion resistance for mild steel in the presence of VT-F resin. The occurrence of an inductive loop in both aggressive solutions may indicate certain non–faradaic processes, such as adsorption and desorption of corrosion products, occurring at the sample/electrolyte interface. The equivalent circuit model shown in Figure 6 was used to model the impedance results obtained for mild steel in both solutions, after fitting with Zsimpwin software. The obtained results are presented in Table 3.

The \(R_s\) is the solution resistance, \(Q_{\text{dl}}\) and \(R_{\text{ct}}\), respectively, show the values of capacitance of charge and the resistance of the charge layer to penetration of the electrolyte solution. On the other hand, the inductance, \(L\), and charge transfer resistance, \(R_{\text{ct}}\), characterize the processes beneath the store of charges. Similarly, the value of inductance was greater for the inhibited mild steel sample than for the uninhibited. It may indicate that introduction of VT-F resin can modify the electrochemistry of the mild steel sample by reducing the penetrations of the electrolyte into the substrate–electrolyte interface, thus, decreasing the rate of the corrosion in the acid solutions. This observation increased with an increase in concentration of the inhibitor. This can also be evidenced by the higher value of \(R_{\text{ct}}\), for mild steel in the presence of the inhibitor than the value obtained in the absence of VT-F resin.
In the presence of VT-F resin, its species adsorbs on the surface of mild steel, this creates a strong barrier between the mild steel surface and the electrolyte solutions. In this way, the corrosion potential of the mild steel sample shifts to more positive regions (noble values) implying a decreased surface area available for the electrochemical processes. Furthermore, addition of the inhibitor also reduces the rate of penetration of the electrolyte, hence, the rate of the electrochemical processes in the Fe/electrolyte interface. From the present result, the introduction of VT-F resin in both solutions seems to reduce the susceptibility of the mild steel substrate to dissolution and to the electrochemical processes occurring at the substrate/electrolyte interface. This was made evident by the shift of $E_{\text{corr}}$ 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 deduce that the adsorption of VT-F resin species serve as a barrier blocking the contact between the mild steel substrate and the electrolyte solutions [17].

![Figure 5: Nyquist plots of the electrochemical impedance spectra on mild steel in 1 M HCl in the presence and absence of VT-F resin](image)

**Figure 5:** Nyquist plots of the electrochemical impedance spectra on mild steel in 1 M HCl in the presence and absence of VT-F resin.

![Figure 6: Equivalent Circuit Model for mild steel sample](image)

**Figure 6:** Equivalent Circuit Model for mild steel sample.

**Table 3: Electrochemical Impedance Parameters for mild steel in 1 M HCl in the Absence and Presence of VT-F resin**

<table>
<thead>
<tr>
<th>System</th>
<th>$R_e$ (Ωcm$^2$)</th>
<th>$R_{tt}$ (Ωcm$^2$)</th>
<th>$R_{el}$ (Ωcm$^2$)</th>
<th>$Q_{ad}$ (Ω$^{1/2}$ cm$^2$)</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>3.44</td>
<td>6.4</td>
<td>395</td>
<td>3.17</td>
<td>5.15</td>
</tr>
<tr>
<td>10 (v/v %)</td>
<td>4.18</td>
<td>1662</td>
<td>1754</td>
<td>4.03</td>
<td>1756</td>
</tr>
<tr>
<td>50 (v/v %)</td>
<td>5.12</td>
<td>3081</td>
<td>3219</td>
<td>3.71</td>
<td>3249</td>
</tr>
</tbody>
</table>

**3.5 Adsorption Considerations**

The fundamental concept in adsorption science is adsorption isotherm. Adsorption isotherm values are important to explain the mechanism of corrosion inhibition. The frequently used adsorption isotherm include: Langmuir, Frumkin, Hill de Boer, Parsons, Temkin, Flory-Huggins, among others. Data obtained from weight loss measurements were adapted to determine the adsorption characteristics of VT-F resin on mild steel in 1 M HCl. The data were tested graphically with different adsorption isotherms and was found to be best fitted to Langmuir isotherm, which can be expressed by Equation 5:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C$$  \hspace{1cm} (5)

Where $\theta$ is the degree of surface coverage, $C$ is the inhibitor concentration, $K_{\text{ads}}$ is the equilibrium constant of adsorption process. The plots of $C/\theta$ against $C$ are shown in Fig. 5. Linear plots were obtained with good correlation coefficient ($R^2$) which suggests that adsorption of the inhibitor follow Langmuir adsorption isotherm. Since it obeys Langmuir adsorption isotherm, it implies monolayer adsorption of inhibitor. The adsorption of the inhibitor on the metal surface leads to high degree of surface coverage and hence shows better inhibitive
The equilibrium constant of adsorption $K_{ads}$ decreases with increase in temperature (Table 4), indicating that the interactions between the adsorbed molecules and the metal surface are weakened and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature [19].

The equilibrium constant of adsorption of VT-F resin on the surface of carbon steel is related to the free energy of adsorption $\Delta G_{ads}$ by Equation 6.

$$\Delta G_{ads} = -2.303 \text{ RT log (55.5K}_{ads} \text{)}$$ (6)

Where $R$ is the molar gas constant, $T$ is the absolute temperature and 55.5 is the concentration of water in solution. The result is presented in Table 4. The negative values of $\Delta G_{ads}$ suggest that the adsorption of VT-F resin onto mild steel surface is spontaneous. The values of $\Delta G_{ads}$ obtained indicate that adsorption of VT-F resin occurs via physical adsorption mechanism. Generally, values of $\Delta G_{ads}$ less negative or equal to -20 kJmol$^{-1}$ (as obtained in this study) are consistent with electrostatic interaction between the charged metals and charged molecules which signifies physical adsorption while values more negative than -40 kJmol$^{-1}$ signify chemical adsorption [20, 21].

### Table 4. Calculated thermodynamic parameters from Langmuir adsorption isotherm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$K_{ads}$</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>48.87</td>
<td>-19.92</td>
<td>0.941</td>
</tr>
<tr>
<td>40</td>
<td>22.11</td>
<td>-18.51</td>
<td>0.993</td>
</tr>
<tr>
<td>50</td>
<td>9.68</td>
<td>-16.88</td>
<td>0.985</td>
</tr>
</tbody>
</table>

### 4. CONCLUSION

VT-F resin was found to be an efficient inhibitor for mild steel in 1 M HCl solution. The rate of corrosion of the mild steel in 1 M HCl is a function of the concentration of the inhibitor. This rate decreased as the concentration of the inhibitor is increased. The percentage inhibition efficiency of this inhibitor decreased as the temperature increases which indicate that physical adsorption was the predominant inhibition mechanism. VT-F resin is an eco-friendly corrosion inhibitor for mild steel in 1 M HCl solution, so it can be used to replace toxic and expensive corrosion inhibitors.

### References

5. N. B. Iroha, O. Akaranta and A. O. James (2012), Red onion skin extract-furfural resin as corrosion inhibitor for