Adsorption and Corrosion Inhibition of *Gnetum Africana* Leaves Extract on Carbon Steel

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**Abstract** Adsorption of *Gnetum africana* leaves extract and corrosion inhibition of carbon steel in hydrochloric acid solutions have been investigated using gravimetric technique. Inhibition efficiency increased with extract concentration and time of exposure. The effect of temperature on the corrosion behavior of mild steel in 1.0 M HCl with addition of plant extracts was studied at the temperature range of 303–333±1K. Inhibition efficiency of 92.42% was obtained. An adsorption mechanism involving physisorption and chemisorptions of extract constituents at low and high temperatures, respectively, has been proposed from the trend of adsorption free energies. The experimental data complied to the Langmuir and Temkin adsorption isotherms and the negative values of the Gibb’s free energy of adsorption obtained suggested that inhibitor molecules have been spontaneously adsorbed onto the C-steel.

**Keywords** Adsorption Isotherm, Corrosion Inhibition, *Gnetum Africana*, Free Energy of Adsorption

1. Introduction

The use of inhibitors is one of the most practical methods for protecting metals against corrosion, especially in acidic media[1]. Acid solutions are widely used in industry: some of the important fields of application are acid pickling of steel, chemical cleaning and processing, ore production and oil well acidizing. As ordinary acids, HCl and H<sub>2</sub>SO<sub>4</sub> are usually used as industrial acids, cleaning and pickling acids. Due to the general aggression of acid solutions, inhibitors are commonly used to retard the corrosive attack on metallic materials. During past decades, some commercial inhibitors have been synthesized and used successfully to inhibit corrosion of steel in acidic media. However, the major problem associated with most of these inhibitors is that they are not eco-friendly but toxic and expensive. Therefore, the study of new non-toxic corrosion inhibitors is essential to overcome this problem. The research in the field of eco-friendly corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or “zero” environmental impact.

Plant extracts are low-cost and biodegradable, and so the study of plant extracts as corrosion inhibitors is an important scientific research field due to both economic and environmental benefits. It has been found that certain organic substances containing polar functions with nitrogen, sulphur and/or oxygen atoms in the conjugated system have been reported to exhibit good inhibiting properties of steel in acidic and alkaline environments[2-7]. The results of parallel studies of the inhibiting effects of organic compounds suggest that the inhibitory behavior of the organic compounds subsists in some chemical species or molecules in the inhibiting substances forming a protective layer between the metal surface and the corroders. The adsorbate layer formed isolates the metal surface from the corroders thereby reducing the corrosion rate of the metal surface. It has been recognized that the use of organic inhibitors, particularly the naturally occurring organic inhibitors of plant origin, are viable and highly beneficial since they are essentially non-toxic, environmentally benign, readily available, renewable and inexpensive[3-5],[8-20]. Through these studies, it is agreed that the inhibition performance of plant extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centres. In the present work, *Gnetum africana* leaf extract is chosen to be the corrosion inhibitor.

2. Materials and Methods

2.1. Materials Preparation

The sheets of mild steel used for this study were obtained...
from Federal University of Petroleum Resources, Effurun-Warri, Nigeria. Each sheet was 1.32 mm in thickness and were mechanically pressed cut into 2 cm × 2 cm coupons. These coupons were polished mechanically with Sic papers of grade 200, 400 and 600. They were degreased in ethanol, dried in acetone and stored in moisture free desiccators before their use in corrosion studies. The weight percentage composition of the mild steel is: Si-0.051%, Cu-0.185%, Mn-1.102%, P-0.919%, Pb-0.074%, S-0.783%, Mo-0.027%, V-0.014% and the remainder being Fe was used.

2.2. Preparation of the leaf extracts of Gnetum africana

The procedure for the preparation of the leaf extracts is similar to that reported recently by [21]. Gentum africana leaves were collected from Abiriba, Abia State, Nigeria. They were dried in an N53C-Genlab Laboratory oven at 50°C, and ground to powder form. 10 g of the powder was digested in 1 L of 1 M HCl solution. The resultant solution was kept for 24 h, filtered and stored. From the stock solution, test solutions of the leaf extracts were prepared at concentration range of 0.1 – 0.5 g/L using excess acid as solvent at room temperature and 60°C using water baths.

2.3. Gravimetric experiment

The cleaned and dried specimens were weighed before immersion into the respective test solutions of 1 M HCl using JA 1003A electronic weighing balance with the accuracy of ±0.005. Tests were conducted with different concentrations of inhibitor. At the end of the tests, the specimens were carefully washed in absolute ethanol having used nitric acid to quench further corrosion from taking place, and then reweighed. Triplicate experiments were performed in each case and the mean values reported.

3. Results and Discussion

3.1. FTIR of Gnetum africana

Fourier transform in frared (FTIR) is a powerful technique that is always used to determine the type of bonding for organic inhibitors adsorbed on the metal surface [22-24]. Figure 3 shows the FTIR spectrum of the G. africana powder. The strong 3520 cm⁻¹ is attributed to N-H or O-H stretching vibration and that at 2880 cm⁻¹ is related to C-H stretching vibration. The strong band at 1643 cm⁻¹ is assigned to C=C and C=O stretching vibration. Owing to the conjugation effect of flavonoids of G. africana, the C=C peak shifts from about 1700 cm⁻¹ to lower wave number (approximately 1644 cm⁻¹), C=C and C=O stretching vibration bands are superposition [25]. The adsorption bands at 1452 and 1122 cm⁻¹ could be assigned to the framework vibration of aromatic ring. These results indicate that G. africana contains O and N atoms in functional groups (O-H, N-H, C=C, C=O) and aromatic ring, which meets the general structural consideration of the corrosion inhibitor.

3.2. Gravimetric technique and corrosion rates

The corrosion rates of the mild steel in 1 M HCl solutions in the absence and presence of Gnetum africana leaf extract were determined at room temperature (303K). Figure 1 illustrates the variation of the corrosion rates of the mild steel in 1 M HCl with inhibitor concentration for an exposure time of 9 hours. Figure 1 shows clearly that the leaf extract retards the corrosion rate of the mild steel in the test solutions. The equation for corrosion rate is given by

\[ C = \frac{K\Delta W}{\rho At} \]  

where C is the corrosion rate, ΔW is the weight loss in mg; ρ is the density of the steel (g cm⁻³); A is the exposed area of the coupon (m²; 1 m² = 6.5146 cm²); t is the immersion time (h); K is the rate constant (534 mpy; mils per year; 1 mil = 10⁻³ in). Moreover, it can be seen from Figure 2 that the corrosion rate decreases with increase in the concentration of the inhibitor. The inhibition efficiency of the Gnetum africana leaf extract on the corrosion of the mild steel in 1 M HCl containing different concentrations of the leaf extract was computed by using the relation [3],[26-27].

\[ I\% = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \]  

where I% represents the inhibition efficiency expressed in percentage, ρ_{inh} is the corrosion rate in the presence of the inhibitor while ρ_{blank} is the corrosion rate in the absence of inhibitor. Optimum value of 92.42% at 0.5g/L 1 M HCl for concentration of Gnetum africana extract was obtained as shown in Figure 2 below. The results show Gnetum africana leaf extract is a good inhibitor.

![Figure 1. Corrosion rate of 1.0 M HCl on mild steel in the presence of Gnetum africana against concentration of Gnetum africana after 9 hours of exposure at 30°C](image1.png)

3.3. Corrosion Inhibition and Adsorption Mechanism

The mechanism of action of a corrosion inhibitor depends on the electron density and polarizability of the functional groups present in the molecule. Such determination of inhibition mechanisms for G. africana is complicated by the fact that most of the constituents such as alkaloids, saponins, flavonoids, phenols, tannins, sterols, terpenoids, vitamins as well as their acid hydrolysis products inhibit the corrosion reaction in different ways, which makes it rather difficult to
attempts to assign the observed corrosion inhibiting effect to any particular constituent. For instance, in the acid extract of *G. africana* used in this study, some of the constituents may be adsorbed as protonated species and some as (non-protonated) molecular species, with the predominant adsorption mode depending on the prevailing test conditions at any time. It is noteworthy that chloride ions present in the test solutions have the tendency to be specifically adsorbed on metal surfaces, where they facilitate adsorption of protonated inhibitor species by forming intermediate bridges between the metal surfaces and the inhibitor[31]. Such protonated species are often adsorbed at cathodic sites on the metal surface and hence retard the hydrogen evolution reaction[32], which is probably responsible for the pronounced cathodic inhibiting effect of *G. africana* at ambient temperature (30 °C).

It is obvious from Figure 4 that corrosion rates are higher at 60°C. This is because rise in temperature exponentially accelerates the rates of corrosion processes in media where hydrogen gas evolution accompanies corrosion, resulting in higher dissolution rates of metals. Higher rates of hydrogen gas generation increasingly agitate the metal/corrodents interface and could hinder inhibitor adsorption or perturb already adsorbed inhibitor, especially when the interaction between the metal and the inhibitor is relatively weak. As a result, the efficiency of a considerable number of organic inhibitors is significantly reduced when the temperature of the system is increased, a trend often attributed to physical rather than chemical adsorption of the inhibiting species on the corroding metal surface. Interestingly, Figure 4 clearly shows that the efficiency of *G. africana* at all studied concentrations improved with rise in temperature, which means that interaction between *G. africana* and the C-steel surface scale up significantly as temperature is increased. This is again evidence that *G. africana* is an effective corrosion inhibitor for C-steel in hydrochloric acid. Improvement in inhibition efficiency with increasing temperature has also been attributed to a change in the nature of adsorption, wherein the inhibitor is physically adsorbed at lower temperature whilst chemisorptions is favoured at higher temperature[2].

![Figure 2. Inhibition efficiency of *Gnetum africana* in 1.0M HCl on mild steel against concentration of *Gnetum africana* after 9 hours of exposure at 30°C.](image)

![Figure 3. Fourier transform infrared of *Gnetum africana*.](image)
The relationship between corrosion rate (C) and temperature (T) is often expressed by the Arrhenius equation $C = A \exp(-E_a/RT)$. $E_a$ is the activation energy, $A$ the Arrhenius pre-exponential factor and $R$ is the gas constant. The apparent activation energies ($E_a$) for C-steel corrosion in the absence and presence of *G. africana* were evaluated from Arrhenius equation as follows:

$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  \hspace{1cm} (3)

where $\rho_1$ and $\rho_2$ are the corrosion rates at temperature $T_1$ and $T_2$, respectively, and other parameters retain their previous meanings. $E_a$ is observed from Table 1 to decrease in inhibited systems containing *G. africana*.

Figure 4. Corrosion rate of 1.0M HCl on mild steel in the presence of *Gnetum africana* against concentration of *Gnetum africana* after 9 hours of exposure at 60°C

Table 1. Apparent activation energies, and heat of adsorption, for the corrosion of C-steel in 0.1M HCl solutions containing *Gnetum africana* leaf extract in different concentrations in the temperature range of 303-333K

<table>
<thead>
<tr>
<th>G. africana Conc (g/L)</th>
<th>Activation Energy (kJmol⁻¹)</th>
<th>Heat of Adsorption (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>12.95</td>
<td>-</td>
</tr>
<tr>
<td>0.10</td>
<td>-25.83</td>
<td>-1.32</td>
</tr>
<tr>
<td>0.20</td>
<td>-104.59</td>
<td>1.07</td>
</tr>
<tr>
<td>0.30</td>
<td>-117.85</td>
<td>1.29</td>
</tr>
<tr>
<td>0.40</td>
<td>-199.90</td>
<td>2.79</td>
</tr>
<tr>
<td>0.50</td>
<td>-199.65</td>
<td>2.63</td>
</tr>
</tbody>
</table>

Such behaviour, coupled with the trend of increased inhibition efficiency is evidence of chemisorptive interactions between some extract species and the C-steel surface[28-29]. This reasoning is corroborated by[30], where it is suggested that the corrosion process in the presence of powerful inhibitors is characterized by lower activation energies compared to that in the absence of the inhibitor.

Another thermodynamic parameter which further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption, $Q_{ads}$. It is connected to the degree of surface coverage, $\theta$ ($\eta% = 100 \times \theta$), through the relation:

$$Q_{ads} = 2.303R \left[ \log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right]$$  \hspace{1cm} (4)

where $\theta_1$ and $\theta_2$ are values of the degree of surface coverage at temperatures $T_1$ and $T_2$, respectively. The calculated values of $Q_{ads}$ shown also in Table 1 are mostly positive and in the range of 0.57 and 2.79 kJ/mol. The positive $Q_{ads}$ values indicate that the adsorption of *G. africana* onto the C-steel and hence the inhibition efficiency increases with rise in temperature.

### 3.4 Adsorption Isotherms

Assuming a direct relationship between inhibition efficiency and the degree of surface coverage ($\theta$) for different inhibitor concentrations, data obtained from gravimetric measurements were adapted to determine the fit to some well-known adsorption isotherms including the Langmuir, Temkin, Freundlich and the Flory-Huggins isotherms as well as the kinetic-thermodynamic model of El-Awady et al. The generalised expression for the common adsorption isotherms is of the form[33-34]:

$$f(\theta, x) \exp(-\alpha \theta) = kC$$  \hspace{1cm} (5)

where $f(\theta, x)$ is the configuration factor, which depends on the physical model adopted and the assumptions made in deriving the isotherms. The parameter x is the size ratio which represents the relative size of the adsorbed molecule to the solvent molecule. Specifically, in the case of corrosion inhibitors in aqueous solutions, x represents the number of water molecules replaced by adsorbed inhibitor ($\text{Inh}_{ads} + x\text{H}_2\text{O}_{sol} \rightarrow \text{Inh}_{ads} + x\text{H}_2\text{O}_{ads}$); $\alpha$ is the molecular interaction parameter which accounts for the lateral interaction between adsorbed species[35], whilst the quantity C is the inhibitor concentration and $k$ is the adsorption equilibrium constant. Sometimes, it may be sufficient to just confirm inhibitor adsorption from the data fit to the isotherms. At times also it is desirable to extend the scope to include deduction of the thermodynamic parameters associated with the adsorption process using the relationship between the adsorption constant ($k$) and the standard free energy of adsorption, $\Delta G_{ads}^o$:

$$k = \frac{1}{55.5} \exp \left( -\frac{\Delta G_{ads}^o}{RT} \right)$$  \hspace{1cm} (6)

Negative $\Delta G_{ads}^o$ values indicate spontaneity of the adsorption process. Generally, $\Delta G_{ads}^o$ values with magnitude much less than 40 kJ/mol have typically been correlated with the electrostatic interactions between organic molecules and charged metal surface (physiosorption), whilst those of magnitude in the order of 40 kJ/mol and above are associated with charge sharing or transfer from the organic molecules to the metal surface (chemisorptions)[2]. There is, however, some controversy regarding the correctness of $\Delta G_{ads}^o$ values obtained in this way for plant extracts since their molar concentrations cannot be determined with much accuracy.
and precision[36-37]. However, if one takes into consideration that the extracts comprise definite molecular entities whose specific concentrations, though unknown, change in mol/L units as the extract concentration is varied, it may actually be possible to determine free energy values that acceptably describe the experimental data. We thus tried to evaluate $\Delta G_{ads}$ values from different isotherms at 30 and 60 ºC. The corresponding results are presented in Table 2. All the $\Delta G_{ads}$ values are negative, implying that the adsorption of *G. africana* on the C-steel in hydrochloric acid is a spontaneous process.

Figure 5. Langmuir isotherm for *Gnetum africana* adsorption on carbon steel in 1M HCl at 30ºC

Figure 6. Langmuir isotherm for *Gnetum africana* adsorption on carbon steel in 1M HCl at 60ºC

Figure 7. Temkin isotherm for *Gnetum africana* adsorption on carbon steel in 1M HCl at 30ºC

Figure 8. Temkin isotherm for *Gnetum africana* adsorption on carbon steel in 1M HCl at 60ºC

As far as corrosion inhibitor studies are concerned, a large number of experimental adsorption data fit the Langmuir isotherm$[C/\theta = 1/k + C]$, at least qualitatively (i.e. good linear fit). Similar linear fit is illustrated for *G. africana* extract on C-steel at 30 and 60 ºC in Figures 5 and 6 above. Oftentimes, however, however, the linear fits intercept the y-axis ($C/\theta$) or the x-axis (C) and the slopes is about unity, which corroborates to the isotherm prediction. A number of modifications to the Langmuir equation have been suggested, with the molecular interaction term included[38]. Nevertheless, the possibility of adapting the Langmuir isotherm to describe chemical adsorptions and physisorption processes (at least qualitatively) may account for its widespread applicability.

Table 2. Adsorption isotherm parameters obtained from the corrosion data for C-steel in 1.0M HCl containing *G. africana* extract

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Intercept</th>
<th>Slope</th>
<th>k</th>
<th>$R^2$</th>
<th>$\Delta G_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>303K</td>
<td>0.033</td>
<td>1.046</td>
<td>1.035</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>333K</td>
<td>0.040</td>
<td>0.999</td>
<td>1.041</td>
<td>0.996</td>
</tr>
<tr>
<td>Temkin</td>
<td>303K</td>
<td>0.943</td>
<td>0.0739</td>
<td>1.072</td>
<td>0.823</td>
</tr>
<tr>
<td></td>
<td>333K</td>
<td>1.002</td>
<td>0.108</td>
<td>1.114</td>
<td>0.964</td>
</tr>
</tbody>
</table>

The adsorption of uncharged molecules on a heterogeneous surface is appropriately described by the Temkin isotherm$[\theta = (1/f) \ln k_{ads} C]$, where $\theta$ is a linear function of $\ln C$[39]. This isotherm contains a factor ($f$) that clearly takes in account adsorbent-adsorbates interactions and considers the fact that the adsorption heat of all molecules in the layer decreases with coverage due to the adsorbate-adsorbent interaction. This makes the isotherm quite suitable for systems where chemical interaction of inhibiting species with the metal surface is more pronounced as observed for *G. africana* extract on C-steel at 60 ºC in this study. The linear of $\theta$ versus $\ln C$ shown in Figures 7 and 8 agree well with the Temkin equation. More importantly, the trend of $\Delta G_{ads}$ values obtained from the Temkin isotherm with temperature (-10.881 kJ/mol at 30 ºC and -12.427
kJ/mol at 60 °C) is evidence that the observed improvement in inhibition efficiency with increasing temperature actually results from a change in the nature of adsorption from physisorption at lower temperature to chemisorptions at higher temperature. This corresponds to an improvement in the rate of chemisorptions of non-protonated species with increasing temperature suggested earlier.

4. Conclusions

(1) *Gnetum africana* acts as a good inhibitor for the corrosion of carbon steel in 1.0 M HCl solution. Inhibition efficiency increases with the inhibitor concentration, and the maximum of 92.42% was obtained at 0.5 mg/l concentration.

(2) The adsorption of *G. africana* on C-steel surface obeys the Langmuir adsorption isotherm and is a spontaneous, exothermic process accompanied by an increase in entropy.

(3) The corrosion rate of steel in HCl solution without and with *G. africana* acts as a function of immersion time from 1 to 10 h, with optimum result at the 9th hour of exposure.

(4) The FTIR result indicates the presence of a uniform and dense adsorptive film over the steel surface, which efficiently inhibits the corrosion of C-steel.

REFERENCES


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