Corrosion Inhibition Effect of *Lannea nigritana* Leaves and Stem Bark Extract on Mild Steel in Acidic Medium

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Abstract

Lannea nigritana leaves and stem bark extracts respectively were studied as corrosion inhibitor for mild steel in 1M HCl at temperatures 30°C, 50°C and 60°C using gravimetric technique. The extracts were found to inhibit corrosion of mild steel in acidic medium. The inhibition efficiency increased with increase in concentration of the extracts, with the leaves extract showing its maximum inhibition efficiency of 87.05% in 400mg/l concentration, while the stem bark extract showed its maximum inhibition efficiency of 88.39% in 600mg/l of the extracts. The inhibitory effect was as a result of the extract molecules ability to be adsorbed to the mild steel surface. The adsorption mechanism involved was discovered to be physisorptive between the temperature of 30°C and 50°C, but chemisorptive between 50°C and 60°C. Adsorption of extract molecules on mild steel surface was found to fit into Langmuir adsorption isotherm.

Keywords: Adsorption, Corrosion inhibition, *Lannea nigritana*, gravimetric technique, mild steel

1. Introduction

Most metals occur naturally in combined state or form, and are therefore proceed by man into their pure states where they can be more useful as metals and alloys. Manufacturing industries depend so much on use of metallic materials for their operations, but these metals tend to return to their natural form (ore-like compound). This is due to the high energy content of the elements in metallic form. As the energy content of the metals and alloys is greater than that of their ores, chemical combination of the metals to form ore-like compounds becomes a natural process. Huge amount of money is spent annually by industries in corrosion control and this scourge has really affected the world's best economy, and many researches have been carried out to get a lasting solution to problem of corrosion.(1) Results from some of these researches proved that organic inhibitors of plant source can be used to retard corrosion of metals in corrosive environment. These organic corrosion inhibitors which are eco-friendly and sustainable, are usually composed of hetero-atoms such as N, S, and O in conjugate systems, with which they get absorbed to the metal surface.(2 – 6) More so, It is stated by Abiola, (31) that the corrosion inhibition properties in many plants extracts is due to their heterocyclic constituents like alkaloids, tannins, flavonoids, phenols, saponins steroids etc. Owing to these facts we suggest that *Lannea nigritana* extract will possess good corrosion inhibition properties because phenolic compound lanneanol was reported to be isolated from the plant. (8)

Lannea nigritana is small tree of 3-6m of height, found in the tropical rain forest. It is used in the traditional medicine for the treatment of various infectious diseases.(9) The present study investigates the corrosion inhibition and adsorption of *Lannea nigritana* leaves and stem bark extract on mild steel in 1M HCl solution using gravimetric technique.

2.0 MATERIALS AND METHODS

2.1 Materials preparation: Material used for the study were mild steel sheet of composition (wt%) Mn (0.6), P (0.36), C (0.15), and Si (0.03). The rest of the composition is Fe. The sheet was mechanically pressed cut to form different coupons, each of dimensions 3cm X 3cm X 0.1cm. Each coupon was degreased by washing with ethanol dried in acetone and preserved in a desiccator prior to use. All the reagents used are of analytical grade and double distilled water was used for their preparation.

2.2 Preparation of Plant Extract: *Lannea nigritana* leaves, and bark were collected from plants around Michael Okpara University of Agriculture Umudike, Abia state, Nigeria. The samples were cut into small pieces, and were then dried in a laboratory oven at 50^oC and grinded to powdered form. 10g of the powdered *Lannea nigritana* leaves and stem bark separately, were dissolved in 1M HCl and refluxed for 3hrs. The resultant solutions were filtered and the filtrate stored. The amount of dissolved samples in the extracts was calculated, and from the stock solution in mgl^{-1} the various test solution of the extracts in $200mgl^{-1}$, $400mgl^{-1}$, $600mgl^{-1}$, $800mgl^{-1}$ and $1000mgl^{-1}$ studied were prepared.

2.3 Gravimetric Analysis

Weight loss experiments were conducted under total immersion conditions in 250ml of test solution, maintained at 30^oC, 50^oC, and 60^oC for 3hrs. The test coupons which were weighed before immersion were retrieved at the end of 3hrs, scrubbed with bristle brush under running water until clean. The clean test coupons were dried in acetone and reweighed. The weight loss was taken as the difference between the weight of coupon before and after immersion. [11 & 12]

From the weight loss data corrosion rate was calculated using equation 1

$$CR = \frac{\Delta Wt}{AT} \quad \text{--} \; 1$$

Where CR is the corrosion rate, A, is the surface area of the coupon, T, is time in days and ΔWt represents weight loss. From the corrosion rate of inhibited system and uninhibited system relation the inhibition efficiency and degree of surface coverage were calculated using equation 2 and 3 respectively.

$$IE = \left(1 - \frac{CR_{in}}{CR_{bl}}\right) \times 100 \qquad \text{............. ....2}$$

$$\theta = \left(1 - \frac{CR_{in}}{CR_{bl}}\right) \qquad \text{...............................3}$$

Where IE is inhibition efficiency, θ is degree of surface coverage, CR_{in} and CR_{bl} are corrosion rates in inhibited and uninhibited systems respectively.

3. Results and discussion

3.1 Gravimetric studies: The gravimetric analysis of mild steel in 1M HCl solution, in the absence of inhibitor and in solutions containing different concentrations of *Lannea nigritana* leaves and bark extracts studied are represented graphically in figure 1, 2, and 3T. he graph in figure 1 shows weight loss of mild steel coupons in the test solutions studied against various concentrations of plant extract

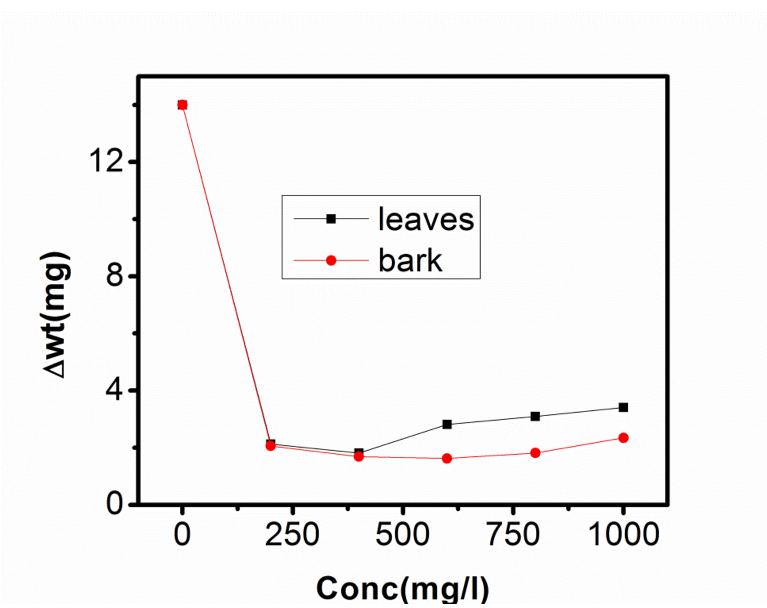

Figure 1: Graphical results of weight loss against concentration *Lannea nigritana* leaves and bark extract in 1M HCl solution.

From the graphical results it can be observed that there is a marked decrease in weight loss shown by the mild steel coupons immersed in the 1M HCl solutions containing the *Lannea nigritana* extract, when compared with the observed value shown by mild steel that was immersed in same acid solution without the plant extracts. These observations indicate a reduction in corrosion rate of mild steel in 1M HCl solution in the presences of *Lannea nigritana* extract. Results of the corrosion rate behavior of the metal in the acid solution containing the plant extract is represented in figure 2.

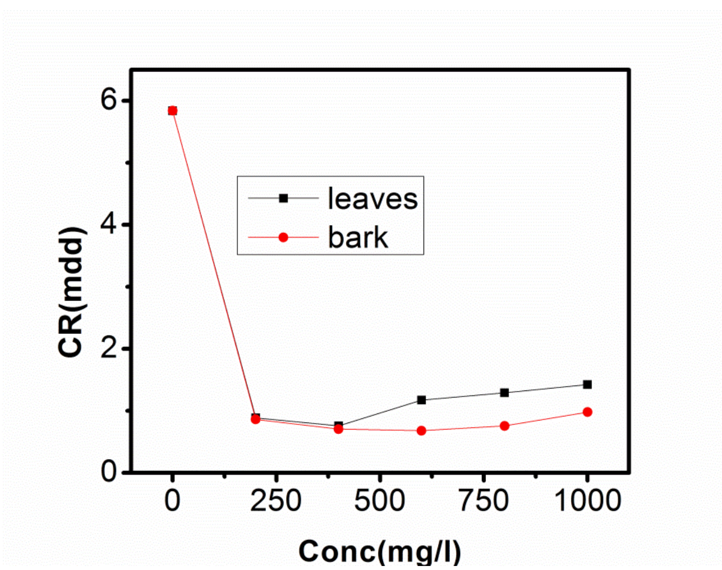

Figure 2: Corrosion rates of mild steel in 1M HCl against concentration of the plant extract.

Results from the graph show reduction in corrosion rate when *Lannea nigritana* leaves and bark extracts, each and respectively were added in 1M HCl solution. The reduction in corrosion rate by *Lannea nigritana* leaves became more pronounced as the extract concentration increases from 200mg/l to 400mg/l, but as the concentration increases to 600mg/l through 1000mg/l the reduction in concentration was observed to be less susceptible. In *Lannea nigritana* bark extract the reduction in corrosion rate was more pronounced as the extract concentration increases to 600mg/l, but it became less susceptible between the extract concentration of 800mg/l and 1000mg/l. The reduction in corrosion rate indicates inhibitory effect of the plant extract molecules.

3.2 Corrosion Inhibition

Inhibitory behavior of *Lannea nigritana* leaves and bark extracts is shown in figure 3 below, and a study of the figure reveilles graphical results of inhibition efficiency against concentration of the plant extract.

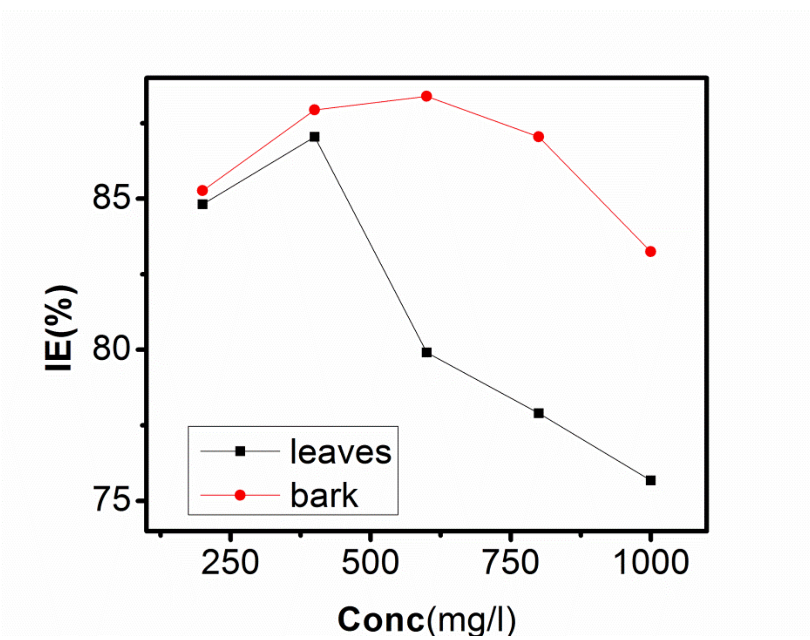

Figure 3: Inhibition efficiency against concentration of the plant extract.

Observations from the graphical results show increase in the inhibition efficiency as concentration of *Lannea nigritana* leaves extract increases from 200mg/l to 400mg/l. when the concentration was increased beyond 400mg/l inhibition efficiency starts decreasing and this became more pronounced as the concentration increases to 1000mg/l. In the bark extract inhibition efficiency increased with increase in concentration from 200mg/l to 600mg/l where it exhibited maximum inhibition efficiency, showing reduction in inhibition efficiency as the concentration exceeds 600mg/l. when the inhibition efficiencies of the leaves extract and the bark extract are compared, it can be deduced that inhibition efficiency was more susceptible in *Lannea nigritana* bark extract which showed maximum inhibition efficiency of 88.4% at concentration of 600mg/l than its leaves extract which showed maximum inhibition efficiency of 87.1% at concentration of 400mg/l. It is suggested that the corrosion inhibition ability of *Lannea nigritana* leaves and bark extracts is as a result of the extract molecules' ability to be absorbed to the metal surface creating a barrier between the metal surface and the acid.

3.4 Adsorption Consideration

Isolation carried on *Lannea nigritana* extract by Kapche *et al* [8] reveals that *Lannea nigritana* contains a phenolic compound lanneanol, with molecular formula $C_{23}H_{42}O_3$, and chemical structure as shown in figure 4. The compound lanneanol contains hydroxyl functionality which can serve as Lewis base. So there is the possibility of the compound to donate lone pair of electrons to the vacant d-orbitals of the metal to form iron (ii) complexes, which results to the chemisorptions of the extract molecules to the mild steel surface. [10]

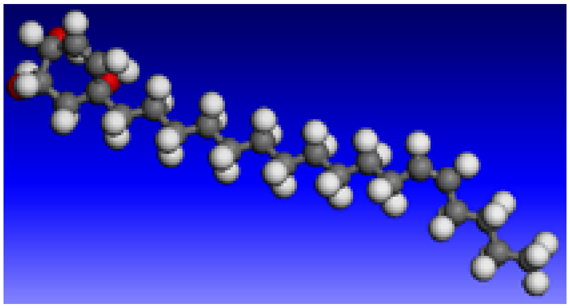

Figure 1: Optimized structure of lanneanol, the red balls represent oxygen, the white balls represent hydrogen while the gray is for carbon atoms

The adsorption of the extract molecule on the metal surface can be examined following adsorption isotherms like Langmuir adsorption isotherm, Temkim adsorption isotherm etc. The relationship between the degree of surface coverage (θ) and *Lannea nigritana* extract molecules can be represented by the Langmuir adsorption isotherm.

$$\frac{C}{\theta} = C + \frac{1}{K_{ad}} ------4$$

Where K is the constant for adsorption which is related to the free energy of adsorption (ΔG^0_{ad}) by equation 5

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G^0_{ad}}{RT}\right) ------------------------ 5$$

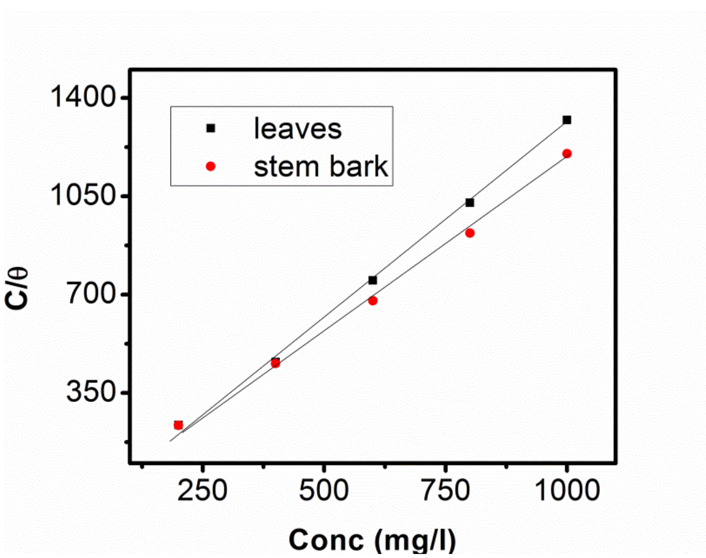

Figure 4: Langmuir adsorption isotherm

Figure 4 shows the plot of C/θ versus concentration of *Lannea nigritana* leaves and bark extracts in 1M HCl solution. The graph is observed to be linear, with a unique slop and intercept of $\frac{1}{K}$ which suggests that the experiment fits into Langmuir adsorption isotherm. The calculated values of ΔG^0_{ad} are presented in table 1. The negative signs on the values indicate spontaneous adsorption of *Lannea nigritana* extract molecules to the surface of the mild steel in corrosive medium. [12-16].

Table 1: Results of free energy of adsorption of *Lannea nigritana* leaves and stem bark extracts

System (mg/l)	ΔG^o_{ad} (KJ) leaves	ΔG^o_{ad} (KJ) stem bark
200	-36.20	-35.84
400	-41.34	-40.52
600	-50.75	-44.19
800	-54.89	-48.19
1000	-91.89	-53.67

3.5 Effect of Temperature

Temperature has a significant influence on metal corrosion rates and inhibition efficiencies of corrosion inhibitors, when the corrosion reaction involves a cathodic process of hydrogen evolution, the corrosion rate increases exponentially with rise in temperature according to Arrhenius type dependence [13].

The inhibition efficiency relation gives insight to mechanism of adsorption of the inhibitor molecules to the surface of the metal, when the inhibition efficiency increases with rise in temperature the inhibitor molecules are said to be chemically adsorbed to the metal surface, but when it reduces with rise in temperature inhibitor molecules are said to be physically adsorbed to the metal surface. [21], [13][14,15,17].

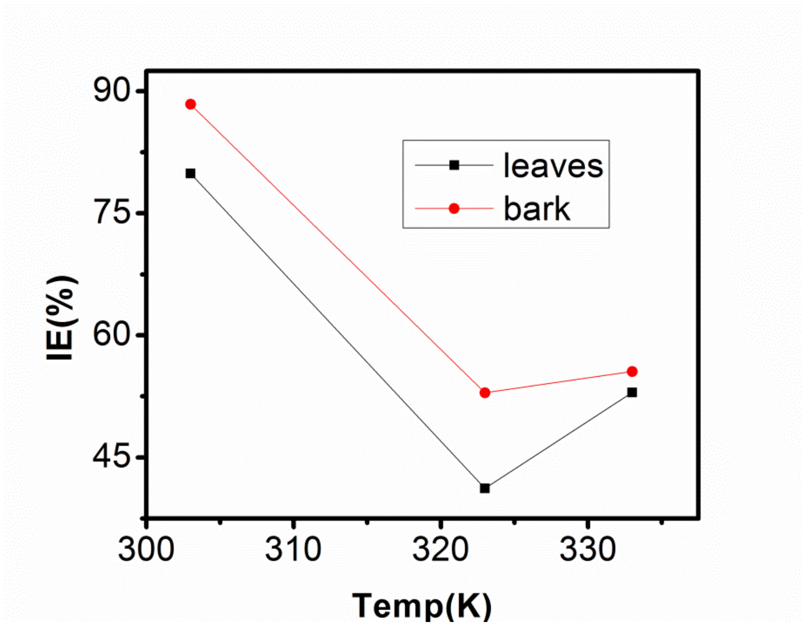

Figure 5: plot of inhibition efficiency against temperature

Observations from the results of inhibition efficiency versus temperature graph show reduction in inhibition efficiency as temperature rises from 303K to 323K by both leaves and bark extracts of *Lannea nigritana*, but as the temperature increases further to 333K the bark extract is observed to increased slightly with rise in temperature from 323K to 333K, while the leaves extract shows a marked increase in inhibition efficiency as temperature rises from 323K to 333K. This behavior indicates that *Lannea nigritana* leaves and bark extracts were physically adsorbed to the metal surface at low temperature (303K t0 323K) but as temperature of the system rises beyond 323K the adsorption mechanism changes to chemisorptions.

3.5 Thermodynamic Parameters and Adsorption Relations

The relation between corrosion rate and temperature is often expressed by the Arrhenius equation.

$$K = A \exp(-\frac{E_a}{RT}) \quad \text{--} \; 6$$

Where E_a is the activation energy, A is the Arrhenius pre-exponential factor and R is the gas constant while T is the temperature. The above equation can be evaluated to

$$\text{Log} \frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{--} \; 7$$

Where CR_1 and CR_2 are the corrosion rates at temperatures T_1 and T_2 respectively, other parameters retain their previous meanings. The apparent activation energies for mild seel in the absence and presence of *Lannea nigritaana* leaves and bark extracts were calculated using equation 7 above.

The trend in activation energy gives insight to the mechanism of adsorption involved in corrosion inhibition. When the value of activation energy of the blank system is less than apparent activation of the inhibited system the adsorption mechanism involved in the reaction is physisorption , but when the apparent activation energy of the blank system is greater than that of the inhibited system chemisorption mechanism is involved. [13-15, 18-20]

Table 2: Results of apparent activation energies of blank and inhibited system

System	Ea (KJ) 303K-323K	Ea (KJ) 323K-333K
Blank 1M HCl	25.08	103.38
Leaves extract	68.79	83.37
Stem bark extract	81.99	98.26

The results of apparent activation energies of mild steel in the systems studied are presented in table 2. Observations from the results show that apparent activation energy of blank 1M HCl solution is less than that of the inhibited systems, both in *Lannea nigritana* leaves extract and bark extract between 303K and 323K, but between 323K and 333K the apparent activation energy of the blank is greater than that of the inhibited systems. These observations suggest that *Lannea nigritana* leaves and bark extracts were physically adsorbed to the mild steel surface between the temperatures of 303K to 323K, but chemically adsorbed between 323K and 333K.

Besides activation energy another thermodynamic parameter which further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption (Q_{ad}). It is related to the surface coverage through the relation in equation 9

$$Q_{ad} = 2.303\,R\left(\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right) X \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots\ldots\ldots\ldots\ldots 9$$

Where Q_{ad} is heat of adsorption, θ_1 and θ_2 are degrees of surface coverage at temperatures T_1 and T_2 respectively. A positive value of heat of adsorption suggests chemisortion while negative values suggest physisorption. [10, 14, 16 & 18].

Table 3: Results of heat of adsorption of the plant extract studied

System	Q_{ad} (KJ/mol) 303K-323K	Q_{ad} (KJ/mol) 323K-333K
Leaves extract	-2.95×10^{-6}	0.36×10^{-6}
Stem bark extract	-3.25×10^{-6}	0.08×10^{-6}

The calculated values of heat of adsorption of *Lannea nigritana* leaves and bark extract are recorded in table 3. From the results in the table it can be observed that the heat of adsorption of both leaves and bark extracts of *Lannea nigritana* show negative values between the temperature of 303K and 323K, which is an evidence of physisorption mechanism, while they (*Lannea nigritana* leaves and bark extracts) show positive values of heat of adsorption between the temperature of 323K and 333K, suggesting chemisorptions mechanism.

Conclusion

From the results of our finding we therefore conclude that:

1. *Lannea nigritana* leaves and bark extracts each and respectively inhibits corrosion of mild steel in 1M HCl solution.

2. The inhibitory effect resulted from the extract molecules adsorption on the mild steel surface, and the adsorption fits into Langmuir adsorption isotherm.

3. The inhibitor molecules were physically adsorbed to mild steel surface between the temperature of 303K to 323K, but chemically adsorbed between 323K to 333K.

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