Concentration, Temperature and Kinetic Studies of *Kola nitida* Leave Extracts in Corrosion Prevention

Lawrence Adebayo Oluwafemi¹*, Grace Ajayi Morenike¹ and Ayorinde Daodu Kayode ²

¹Department of Chemistry, College of Education, Ikere. Ekiti State, Nigeria.
²Department of Biology, College of Education, Ikere. Ekiti State, Nigeria.

*E-mail address: femtay41@yahoo.co.uk

**Keywords:** Inhibition; *Kola nitida*; corrosion; isotherm; kinetics; Adsorption.

**Abstract.** The inhibition efficiency and adsorption mechanism of kola nitida leaves extracts on mild steel protection in 2M HCl at various concentration, exposure time and working temperature was studied using Weight loss measurement. The results showed that ethanol extract of *Kola nitida* leaves is a good inhibitor for the corrosion of mild steel in acidic medium. The corrosion rate of mild steel decreases with increase in the concentration of the extract. The inhibition efficiency increases progressively as the concentration of the extract increases but decreases with rise in temperature and exposure time. The highest inhibition efficiency observed in the presence of the extract was 88.51%. The kinetics of the reaction in the presence of the extracts revealed that it follows a first-order reaction and the half-life increases as the concentration of the extract increases. Adsorption studies revealed that Langmuir adsorption isotherm is the best adsorption model applicable to the adsorption of the extract on mild steel surface.

1. Introduction

Corrosion can be explained as the influence of the surrounding environments on metals causing a change in its physical and chemical properties. This phenomenon causes a serious economic loss due to the replacement of equipment, structure and plant repairing shutdown [1].

The usefulness of Mild steel in industries cannot be overemphasized; this has made researchers to search for various types of inhibitors to protect the mild steel from corrosion when exposed to various environmental conditions. In acidic condition, the use of inhibitors is the best way of preventing mild steel from corrosion [2–4]. The inhibitive reactivity of an inhibitor is fundamentally affected by the molecular structure of the inhibiting molecules [5]. Majority of the well-known corrosion inhibitors are organic compounds that have nitrogen, sulphur, oxygen, and phosphorus in their functional groups [6–9]. The system of these compounds has been suggested by some researcher to be by adsorption of a lone pairs of electron, of the organic functional groups on the metal surfaces [10]. Moreover, most of these functional groups are present in most of the inhibitors which has prompted researchers to identify cheap drugs, which are environmentally safe as corrosion inhibitors [11, 12].

*Kola nitida* plant is native to Sierra Leone, Liberia, Ivory Coast, Ghana and Nigeria. It is an evergreen tree growing to a height of 12 to 20 meters. The leaves have stalks and are alternate, oblong, glabrous, leathery and tough, with untoothed wavy margins and up to 33 cm (13 in). The leaves, twigs, bark, flowers and nuts serve many important purposes. The nuts are used industries for the production of drugs, soft drinks, wines, candies, and beverages such as Coca-Cola and Pepsi-Cola [13]. It has many pharmacological properties and contains some active principles: it prevents sleep, thirst, and hunger and acts as an antidepressant [14]. The cola nuts are source of antioxidants and contain a wide array of complex secondary plant metabolites such as theobromine, d-catechin, L-epicatechin, and kolatin [15]. The leaves, twigs, bark and flowers are also used in traditional medicine for maintenance of health as well as in the prevention, diagnosis, improvement or treatment of physical and mental illness [16].
2. Materials and Methods

2.1 Materials

The mild steel used in this study was obtained from the Metallurgy department of the Federal University of Technology Akure, Ondo State, Nigeria and were mechanically press-cut into 4.00 x 8.00 x 5.00cm samples. The mild steel was polished with different grade of emery paper and washed, decreased in absolute ethanol, rinsed in acetone and air dried and stored in a moisture free desiccators prior to use [17-19]. The 2M HCl was prepared by dilution of an appropriate volume of concentrated HCl with distilled water and all experiments were carried out in unstirred solutions and all weighing was carried out using analytical weighing balance (Metler Toledo PB153).

2.2 Plant extraction with ethanol

The kola nitida leaves were collected from the local bush in Nigeria and ascertained in the Biology department, College of Education, Ikere, Ekiti State. The leaves were air dried for thirty days in order not to lose major organic components, after which they were grinded into powdered form to attain smaller particle size. The powdered sample was extracted continually with absolute ethanol using maceration method for 72 hours. It was then filtered and the filtrate was placed in a water bath maintained at 60°C until most of the ethanol evaporated [20-22].

2.3 Corrosion inhibition studies

The corrosion inhibition studies of the plants extracts on mild steel were carried out by weight loss measurement. In the procedure, a previously weighed mild steel coupon was completely immersed in 50 ml of 2M HCl in the absence and presence of different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0g/L) of the inhibitor with the aid of glass hooks at different temperatures (303, 313, 323 and 333 K) using thermostated water bath and monitored daily (after 24 hours) for seven days. The initial weight of the specimens was noted before immersion, and after 24 hours of immersion, the mild steel was withdrawn from the test solution and the corrosion product was removed by washing each coupon in distilled water, rinsed in acetone and dried in the air completely before reweighing. From the initial and final weights of the mild steel, the weight loss, corrosion rate (g hr⁻¹cm⁻²) in the absence and presence of inhibitors and the inhibition efficiency (I.E %) of the inhibitors were calculated using equation 1 and 2 respectively [23,24].

\[
\text{CR} = \frac{W_i - W_f}{A t}
\]

Inhibition Efficiency = \(1 - \left(\frac{WL_2}{WL_1}\right) \times 100\)

where \(W_i\) and \(W_f\) are the initial and final weight of the mild steel in grams, \(A\) is the surface area of the mild steel(cm²), \(t\) is the immersion time in hours while \(WL_1\) and \(WL_2\) are the weight loss of the mild steel in the uninhibited and inhibited acidic solution respectively.

3. Results and Discussion

3.1 Effect of extract concentrations on corrosion rates

The consequences of the extract concentrations on the corrosion rate of mild steel in 2 M HCl is shown in Fig. 1. The corrosion rate was investigated by varying the temperature of the reaction medium from 303K to 333 K. The result revealed that the corrosion rate of mild steel in 2M HCl decreases with an increase in the concentrations of the extract at all temperature studied due to an increase in the rate at which the phytochemical constituents are adsorbed on the surface of the mild steel which creates a barrier for charge and mass transfer that results into a decrease in the interaction between the metal and the corrosive medium and hence, reduces the corrosion [25].
3.2 Effect of extract concentration on inhibition efficiency

As observed in Fig. 2, the inhibition efficiency of the plant extract increases as its concentration increases from 0.2 g/L – 1.0g/L due to the increase in the fraction of the surface of the mild steel been covered by the phytochemical constituents of the extracts at higher concentration. The inhibition efficiency increases from 78.77% to 88.51 % within the concentration if the extracts studied.

3.3 Effect of temperature on the corrosion rate

As shown in Fig. 3, the rate of corrosion of the mild steel in the blank and the inhibited acid solution increased with increase in temperature. This is expected due to an increase in oxidation reaction that takes place [26]. However, the corrosion rate of the mild steel is much more delayed in the solution containing the extracts than the uninhibited acid solution as a result of the alleviating effects of the phytochemical constituents of the extracts on the corrosion rate of mild steel. This finding is in agreement with the reports of earlier researcher [25].
3.4 Effect of temperature on inhibition efficiency.

The effect of temperature on the inhibition efficiency of Kola nitida leaves extract on mild steel is shown in Fig. 4. From the figure, it was revealed that as the reaction temperature increases from 303-333K, the inhibition efficiency decreases due to many changes such as rapid etching, rapture, desorption of the inhibitor, decomposition or rearrangement of the inhibitor on the metal surface [25]. This occurrence is consistent with the mechanism of physical adsorption [27, 28].

3.5 Kinetics study

To explain the inhibitive action of the crude extract on a time scale from the result obtained from the plot of weight loss against time (Fig. 5), the results show that weight loss increases as the immersion time increases. Meanwhile, the weight loss is much more pronounced in the absence of the kola nitida leaves extract than the inhibited acidic solution. The decrease in the weight loss in the presence of inhibitor may be as a result of the adsorption of the phytochemical constituents in the extract on the surface of the mild steel.
Figure 5: Effect of immersion time on the weight loss of mild steel

Moreover, to obtain information about the order of the reaction, the chemical kinetic treatment of the data was necessary. In this study, $W_i$ represents the initial weight of the mild steel at time $t$ while $W_L$ represents the weight loss at time $t$. Therefore, the weight change at time $t$ is the difference between the initial and final weight of the mild steel ($W_i-W_L$), while $k$ is the first order rate constant [29].

$$\ln (W_i - W_L) = -k1t + \ln W_L$$  \hspace{1cm} (3)

A plot of $\log (W_i - W_L)$ against time $t$ gives a straight line graph, and the first order reaction rate constants ($K$) calculated from the slope of the graph were presented in Table 1.

Figure 6: Variation of $\log (W_i - W_L)$ with time (days) for mild steel coupons in 2M HCl Solution Containing Kola nitida leaves extract at 303K

The half-life ($t_{1/2}$) which is the time required for the mild steel to disintegrate to half of its original value was calculated from the relationship in equation 4 and the values obtained were presented in Table 1.

$$t_{1/2} = 0.693 / K$$  \hspace{1cm} (4)
From the result, it was shown that the half-lives (t1/2) of the mild steel in the presence of the extract are higher than that in the blank acidic solution and the half-life increases as the concentration of the extract increases which resulted into a decrease in the corrosion rate.

**Table 1: Rate constant and half-life parameters at various concentrations**

| Extracts concentration (g) | Rate constant (K) | Half life (days) |
|---------------------------|-------------------|-----------------|
| Blank                     | 0.200             | 3.5             |
| 0.2                       | 0.143             | 4.9             |
| 0.4                       | 0.101             | 6.9             |
| 0.6                       | 0.046             | 15.1            |
| 0.8                       | 0.014             | 49.5            |
| 1.0                       | 0.011             | 63.0            |

### 3.6 Adsorption isotherm

Adsorption isotherm studies is very important in the designing of sorption system as it gives the capacity of the sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent [30]. In an adsorption study, it’s a good practice to find out the possible mode by testing the experimental data with several adsorption isotherms since the action of corrosion inhibitors are in most cases believed to be by adsorption on the metal surface by the inhibitor molecules using their adsorption centers. The degree of surface coverage values for different concentrations of kola nitida leaves extract obtained at different temperatures from the weight loss measurement was calculated using Equation 5 [31, 32]

\[
\text{Surface coverage (θ)} = 1 - \frac{C_{R2}}{C_{R1}}
\]  

(5)

where: CR₁ and CR₂ are the corrosion rate of the mild steel in the absence and presence of the inhibitor respectively.

Based on this, the experimental data were fitted into three different isotherm equations: the Langmuir, Temkin and Freundlich adsorption isotherms. The Langmuir adsorption models can be represented as shown in equation 6 [33].

\[
\frac{C_{inh}}{θ} = \frac{1}{K_{ads}} + C_{inh}
\]

(6)

where C is the concentration of the inhibitor in the electrolyte, θ is the degree of surface coverage of the inhibitor and k is the equilibrium constant of adsorption. The plot of C/ θ versus C (Fig. 7) gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of ethanol extract of kola nitida leaves extract on the surface of the mild steel.
The Tempkin adsorption isotherm was also found to occur according to this equation 7 below

$$\Phi = \frac{RT}{b_T} \ln A_T + \frac{RT}{b} \ln C$$  \hspace{1cm} (7)

where: $\Phi$ is the degree of surface coverage of the inhibitor, $b_T$ is the adsorption constant [J/mol K], $A_T$ is the equilibrium binding constant [L/g], $R$ is the universal gas constant (8.314 J/mol K), $T$ is the absolute temperature value [303, 313, 323 and 333 K] and $B$ is a constant related to the heat of sorption [J/mol].

Fig. 8 shows a plot of $\Phi$ versus $\ln C$ and the constants involved ($B$ and $b$) were determined using the slope and intercept of linear equation for Temkin model.

The Freundlich’s adsorption isotherm of the extract of kola nitida leaves extracts on the surface of the mild steel is given by equation 8 and 9 [34].
\[
\frac{x}{m} = KC_n \quad (8)
\]
\[
\log \frac{x}{m} = \log K + \frac{1}{n} \log C \quad (9)
\]

From equation 9, \( \log \frac{x}{m} \) is taking as the inhibition efficiency of the inhibitor at different concentration, while \( \frac{1}{n} \) and \( \log k \) are taking as the slope and intercept respectively. A plot of log of inhibition efficiency (I.E. %) versus log C (Fig. 9) produces a straight line graph with correlation coefficient that ranges between 0.815 - 0.937.

**Figure 9:** Freundlich adsorption isotherm plot for mild steel corrosion in 2M HCl for kola nitida leaves extract at different temperatures.

The constant parameters and the correlation coefficients (r²) for the different isotherm equations considered are presented in Table 2. As revealed on the table, Langmuir adsorption isotherm best described the adsorption of Kola nitida leaves extracts on the mild steel with high correlation coefficients for the different concentrations of the extract studied. Langmuir adsorption isotherm is the ideal adsorption isotherm for physical and chemical adsorption on a smooth surface [35]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

**Table 2:** Langmuir, Freundlich and Temkin Isotherm parameters

| Temp (K) | Langmuir adsorption parameters | Freundlich adsorption parameters | Temkin adsorption parameters |
|----------|--------------------------------|----------------------------------|-----------------------------|
|          | Slope | K_ads | \( r^2 \) | Kf | 1/n | \( r^2 \) | B1 | K_T | r² |
| 303      | 1.137 | 18.18 | 0.996 | 1.921 | 0.068 | 0.854 | 45802.6 | 1.00002 | 0.837 |
| 313      | 1.125 | 13.16 | 0.993 | 1.916 | 0.089 | 0.815 | 37175.5 | 1.00002 | 0.800 |
| 323      | 1.191 | 17.24 | 0.998 | 1.901 | 0.073 | 0.886 | 48825.9 | 1.00002 | 0.879 |
| 333      | 1.233 | 13.89 | 0.998 | 1.884 | 0.096 | 0.937 | 40124.1 | 1.00002 | 0.933 |

**Conclusion**

From the present studies, it can be deduced that kola nitida leave extract is found to be a future inhibitor for the corrosion control of mild steel in 2M HCl solution. Its inhibition efficiency increases as the concentration of the extract increases but decreases with increase in temperature. From the Kinetic studies, it was also found that as the immersion time increases the weight loss increases but
the weight loss is much more pronounced in the blank solution than the inhibited acidic solution due to the adsorption of the phytochemical constituents in the extract on the surface of the mild steel. Moreover, the adsorption of kola nitida leaves extract on the surface of the mild steel followed Langmuir adsorption isotherm.

References

[1] V.S. Sastri, Corrosion Inhibitors Principles and Applications. John Wiley & Sons: New York; 1998.
[2] P. S. Desai, S. M. Kapopara, Indian J. Chemical Tech. 16(6) 486–491, (2009).
[3] S. Fouda, G. Y. Elewady, M. N. El-Haddad, Can. Scientific Ind. Reser. 2(1) 1–18 (2011)
[4] M. Ramananda Singh, K. Bhara, G. Singh, Port. Elect. Acta. 26 479–492, (2008).
[5] Akpan, Nnanake-Abasi O. Offiong, Inter. J. Corro. Vol. 2013 , Article ID 301689, 5 pages (2013).
[6] H. P. Sachin, M. H. M. Khan, N. S. Bhujangaiah. Int. J. of Elect. Sci. 4(1) 134–143,(2009).
[7] S. A. Umoren, U. M. Eduok, E, E. Oguzie. Port. Elect. Acta. 26 533–546 (2008).
[8] A. Kumar, E J of Chem, vol. 5, no. 2, pp. 275–280 (2008).
[9] A. K. Maayta, M. M. Fares, A. F. Al-Shawabkeh, Inert. J. of Corro., vol. 2010, Article ID 156194, 9 pages, (2010).
[10]P. M. Niamien, A. Trokourey, D. Sissouma, Int. J. Res. Chem. Env., vol. 2, no. 4, pp. 204–214 (2012).
[11]S.U. Ofoegbu, P. U. Ofoegbu, ARPN J. Eng. Applied Sci. 7(3) 272–276, (2012).
[12]S. H. Kumar, S. Karthikeyan, J. Mat. Env. Sci. vol. 3, no. 5, pp. 925–934, (2012).
[13]C. O.Jayeola Preliminary studies on the use of kolanuts (Cola nitida) for soft drink production. Journal of Food Technology in Africa. 2001;6(1):25–26. doi: 10.4314/jfta.v6i1.19280.
[14]F. C. Mokwunye, Functional characterisation of kola nut powder for beverage production [M.S. thesis] Abeokuta, Nigeria: University of Agriculture; 2009.
[15]S. T. Lowor, P. C. Aculey, M. K. Assuah, Analysis of some quality indicators in cured Cola nitida (Vent) Agriculture and Biology Journal of North America. 2010;1(6):1206–1214. doi: 10.5251/abjna.2010.1.6.1206.1214.
[16]E. K. Ayebe et al., In vivo, in vitro antioxidant activity assessment & acute toxicity of aqueous extract of Cola nitida (Sterculiaceae) Asian Journal of Biochemical and Pharmaceutical Research. 2012;2(4):144–155.
[17]B.S. Davi, S. Rajandran, Inter. J. Chem. Sci. Tech. 1 79 – 87(2011).
[18]P.C. Okafor, V. I. Osabor, E.E. Ebenso, Pig. Resin Tech. 35(5) 299–305 (2007).
[19]E.E. Oguzie, Mat. Chem. Phy. 87(1) 212–217 (2005).
[20]P.C. Okafor et al., Cor. Sci., 50:2310 (2008).
[21]I.E. Uwah et al., Int. J. of Applied Chem. 9(1) 73–88 (2013).
[22]E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi, Afr. J. Pure App. Chem.(2)11 107–115(2008).
[23]J. I. Bhat, V. Alva, Indian J. of Chem. Tech. 16(3) 228–233 (2009).
[24]M. Abdallah et al., J. Am. Sci. 8(11) 49–55 (2012).
[25]E.F. Olasehinde et al., J. of Am. Sci.11(1s) (2015).
[26] Y. Y. Emriadi, N. J, Gunawarman, Inter. Conf. Bio, Chem. Env. Sci. (BCES- 2014) June 14-15, ( 2014).
[27] E.E. Ebenso, N.O. Eddy, A.O. Odiongenyi, Port. Electr. Acta. 27(1) 13-22 (2009).
[28] E. E. Ebenso, Electrochem.; 19: 209 – 216 (2003).
[29] A. I. Akpan, N. A. Offiong, Inter. J. Corr. 2013, Article ID 301689, 5 pages (2013).
[30] Y.S.Ho et al., Hydrometallurgy, 7 (8) .(2003).
[31] I. A. Akpan, N. O. Offiong, Chem. and Mat. Res. 2(7) 40–47 (2012).
[32] I. A. Akpan, Bulletin of Pure and Applied Sci., vol. 31, no. 2, pp. 49–58 (2012).
[33] Y.K. Agrawal et al., Corro. Sci. 46: 633- 651 (2003).
[34] K. K. Sharma, L. K. Sharma, A textbook of Physical Chemistry, 4th edition, New Delhi Indian: Vikas publishing house Ltd, 1999, p 608.
[35] S.Bilgic, N.Caliskan, J.Appl. Electrochem., 31 79-83 (2001).