# Investigation on the Corrosion Inhibition of *Eucalyptus Camaldulensis* Bark Extract on Mild Steel in Nitric Acid Medium

[1]Muhammad Yahaya Abdullahi, [2]Salim Aliyu Yusuf, [3]Abubakar Suraja Ibrahim, [4]Sadiq Fahad Ahmad

Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria.

*Abstract:* **The inhibitory effects of Eucalyptus camaldulensis bark extract on the corrosion of mild steel in a nitric acid medium were investigated through weight loss measurement. Eucalyptus camaldulensis, commonly referred to as the river red gum, is a flowering plant species of the Myrtaceae family. The research found that the bark extract had the highest efficiency at a concentration of 0.8g/l and a temperature of 303K, with a 59.34% inhibition rate. The study also showed that the inhibition rate increased with higher concentrations of the inhibitor but decreased with higher temperatures, suggesting that physical adsorption mechanisms were involved.**

*Keywords:* **Corrosion inhibitor, Eucalyptus camaldulensis, Inhibition efficiency, Mild steel, Nitric acid medium and Weight loss measurement.**

## 1. INTRODUCTION

By using chemical or electrochemical processes, corrosion is the degradation or annihilation of metals and alloys in the presence of an environment. Corrosive or aggressive medium refers to the environment in which a metal experiences corrosion. Corrosion has a significant negative influence on the environment and the economy on practically all metallic objects used in daily life as well as on the surfaces of the nation's infrastructure, including roads, bridges, buildings, chemical processing facilities, and waste water treatment (Geethamani, 2019).

Mild steel is used extensively across a wide range of sectors due to its superior mechanical strength and comparatively affordable price. It degrades when subjected to acidic environments including pickling, acid cleaning, descaling, and oil well acidification (Ikeuba and okafo, 2018). Corrosion inhibitors are typically employed to restrict the dissolving of the metal in corrosive acidic environments, which are frequently used for industrial purposes. Compounds with nitrogen, sulfur, and oxygen atoms are common in recognized acidic organic corrosion inhibitors. Many N-heterocyclic compounds have been shown to be efficient corrosion inhibitors of metals and alloys in aqueous settings (Amini et al., 2017).

## 2. METHODOLOGY

### 2.1 SAMPLE COLLECTION/PREPARATION OF MILD STEEL

**Sample collection and Preparation:** The mild steel utilized in this investigation was purchased from Kofar Ruwa Metal Works in Kano, Kano State, Nigeria. The 2 cm 2 cm coupons were mechanically squeezed out of each metal sheet. 600, 800, and 1000 grade emery paper were used to polish the coupons. The samples were polished, then cleaned with ethanol, dried in acetone, and kept in a desiccator to remove any remaining oil (Musa et al., 2020).

## PREPARATION OF THE EXTRACT *EUCALYPTUSCAMALDULENSIS*

On the Bayero University's Kano old campus, Eucalyptus camaldulensis bark extract was gathered. The bark was thoroughly cleaned with distilled water to get rid of any foreign objects, let to air dry for 10 days, and then was crushed into a fine powder and sieved. For maceration extraction, 200g of the fine powder was weighed and dissolved in 2.5 liters of ethanol. After being left for 3 days, the mixture was filtered and allowed to air dry for 8 days. The acquired dry extract was utilized throughout the entire experiment (Musa et al., 2020)

## PREPARATION OF ACIDIC MEDIUM

Using varying concentrations of nitric acid solution, distilled water was used to prepare the solution.

$$V_C = \frac{V_D MZ}{10 PS} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots...3.1$$

Where:

VC = the volume of the concentrated acid to be diluted and M is the acid's molarity

VD = the amount of distilled water to be utilized, and Z is the acid's molar mass.

P = assay purity

S = the acid's specific gravity (Ugwuoke and Amula, 2017).

Several inhibitor concentrations were created (0.2, 0.4, 0.6, and 0.8g/l) in different concentrations of nitric acid solution, and they were left for 24 hours (Musa et al., 2020).

## WEIGHT LOSS MEASUREMENT

In order to conduct the weight loss experiment, a weighted mild steel coupon was submerged entirely in 100 cm3 of a 0.2M nitric acid solution, both with and without inhibitors at various concentrations (0.2, 0.4, 0.6, and 0.8g/l). To keep particles out and prevent the corrosive medium from evaporating at high temperatures, the beaker was wrapped with aluminum foil before being placed in a water bath that was kept at the appropriate temperature. The coupons were taken out of the test solution after a predetermined amount of time (1 hour), rinsed in distilled water, ethanol, and then acetone, and finally dried in the air. At different temperatures (303, 313 and 323K), the procedure was done in duplicate, and the weight difference was interpreted as weight loss. Weight loss (g), corrosion rate (gcm$^{-2}$h$^{-1}$), surface coverage (%), and inhibitor inhibition efficiency (%I.E) were calculated using equations 1, 2, 3, and 4.

A is the area of the coupon, W1 is the weight loss in the absence of an inhibitor, W2 is the weight loss in the presence of an inhibitor, and t is the period in hours. Once weight loss occurs, the surface coverage and inhibitor's effectiveness at preventing e. (Musa et al., 2020)

$$\Delta W = W1 - W2 \dots\dots\dots\dots\dots\dots\dots\dots...\dots\dots\dots\dots\dots.\textbf{3.1}$$

$$\theta = \frac{W1-W2}{W1} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots...\dots\dots...\textbf{3.2}$$

$$I.E = \frac{W1-W2}{W1} X100 \dots\dots\dots\dots\dots\dots\dots\dots\dots.\dots\dots...\textbf{3.3}$$

$$CR = \frac{W1-W2}{At} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots...\dots......\textbf{3.4}$$

Where: W1 is the weight loss of a coupon in the absence of inhibitor and W2 is the weight loss in the presence of an inhibitor, A is the area of the coupon and t is the time in hour. $\theta$ I the surface coverage and %I.E inhibition efficiency of the inhibitor while $\Delta W$ is the weight loss (Musa *et al*., 2020).

## 3. RESULTS

The results of the weight loss measurement are reported below, with information on weight loss, inhibitory effectiveness, corrosion rate, and surface coverage at room temperature as well as at 303K, 313K, and 323K, respectively.

**Table: I; variation of weight loss with concentration of HNO₃**

| S/N | Concentration (M) | Initial weight $(W_1)$/g | Final weight $(W_2)$/g | Weight loss (WL)/g | Corrosion rate $CR(gcm^{-2}hr^{-1})$ |
|-----|-----|-----|-----|-----|-----|
| 1 | 0.25 | 0.8589 | 0.7780 | 0.080 | 0.0200 |
| 2 | 0.50 | 0.8160 | 0.6190 | 0.197 | 0.0493 |
| 3 | 0.75 | 0.8560 | 0.5750 | 0.497 | 0.0688 |
| 4 | 1.00 | 0.9300 | 0.3650 | 0.365 | 0.1243 |

**Table: II; variation of inhibition efficiency of 0.2gl⁻¹ inhibitor with concentration of HNO₃ acid at room temperature**

| S/N | Concentration (M) | $W_1$ (g) | $W_2$ (g) | $W_3$ (g) | $W_4$ (g) | WL Blank (g) | WL Inhibitor (g) | θ | %I.E | CR Blank $(gcm^{-1}h^{-1})$ | CR inhibitor $(gcm^{-1}h^{-1})$ |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1 | 0.25 | 0.897 | 0.920 | 0.824 | 0.8645 | 0.073 | 0.0555 | 0.2397 | 23.97 | 0.0183 | 0.0139 |
| 2 | 0.50 | 0.909 | 0.865 | 0.752 | 0.7435 | 0.150 | 0.1215 | 0.1920 | 19.20 | 0.0375 | 0.0304 |
| 3 | 0.75 | 0.902 | 0.890 | 0.640 | 0.6587 | 0.269 | 0.2313 | 0.1401 | 14.01 | 0.0673 | 0.0578 |
| 4 | 1.00 | 0.870 | 0.901 | 0.365 | 0.4970 | 0.505 | 0.4672 | 0.060 | 6.000 | 0.1263 | 0.1168 |

$W_1$ = Initial weight of blank coupon.

$W$ = Initial weight of coupon with inhibitor.

$W_3$ = final weight of blank coupon.

$W_4$ = final weight of coupon with inhibitor.

**θ** = surface coverage.

%I.E = percentage inhibition efficiency

CR = Corrosion rate.

**Table: III; variation of inhibition efficiency 0f 0.2gl⁻¹ inhibitor in 0.25M HNO₃ with time**

| S/N | Time (min) | $W_1$ Blank (g) | $W_2$ Inhibitor (g) | $W_3$ Blank (g) | $W_4$ Inhibitor (g) | WL Blank (g) | WL. Inhibitor (g) | θ | %I.E | CR Blank $(gcm^{-1}h^{-1})$ | CR Inhibitor $(gcm^{-1}h^{-1})$ |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 1 | 20 | 0.8750 | 0.8770 | 0.8344 | 0.8426 | 0.0406 | 0.0344 | 0.153 | 15.3 | 0.0102 | 0.0086 |
| 2 | 40 | 0.8344 | 0.8426 | 0.7749 | 0.7936 | 0.0595 | 0.0490 | 0.177 | 17.7 | 0.0149 | 0.0123 |
| 3 | 60 | 0.7749 | 0.7936 | 0.7141 | 0.7465 | 0.0608 | 0.0471 | 0.226 | 22.6 | 0.0152 | 0.0118 |
| 4 | 80 | 0.7141 | 0.7465 | 0.6442 | 0.6944 | 0.0699 | 0.0521 | 0.2546 | 25.46 | 0.0175 | 0.0131 |

Where:

$W_1$ = Initial weight of blank coupon.

W = Initial weight of coupon with inhibitor.

$W_3$ = final weight of blank coupon.

$W_4$ = final weight of coupon with inhibitor.

WL = weight loss.

$\theta$ = surface coverage.

%I.E = percentage inhibition efficiency.

CR = Corrosion rate.

**Table: IV; Weight loss data at 303K**

| S/N | Concentration(g/l) | Initial weight (W1) | Final weight (W2) | Weight loss (WL) | Surface coverage ($\theta$) | Inhibition efficiency | Corrosion Rate CR) |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0.8589 | 0.7888 | 0.0701 | - | - | 0.01753 |
| 2 | 0.2 | 0.8560 | 0.8029 | 0.0531 | 0.2425 | 24.25 | 0.01328 |
| 3 | 0.4 | 0.8460 | 0.8018 | 0.0442 | 0.3639 | 36.39 | 0.01105 |
| 4 | 0.6 | 0.8740 | 0.8372 | 0.0368 | 0.4750 | 47.50 | 0.00920 |
| 5 | 0.8 | 0.8588 | 0.8303 | 0.0285 | 0.5934 | 59.34 | 0.00713 |

**Table: V; variation of inhibition efficiency with concentration of inhibitor at 312K for 0.2M HNO₃ solution.**

| S/N | Concentration(g/l) | Initial weight (W1) | Final weight (W2) | Weight loss (WL) | Surface coverage ($\theta$) | Inhibition efficiency (%I.E) | Corrosion Rate CR) |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0.8734 | 0.7908 | 0.0826 | - | - | 0.02065 |
| 2 | 0.2 | 0.8832 | 0.8154 | 0.0678 | 0.1792 | 17.92 | 0.01695 |
| 3 | 0.4 | 0.8692 | 0.8103 | 0.0589 | 0.2829 | 28.29 | 0.01473 |
| 4 | 0.6 | 0.8677 | 0.8180 | 0.0497 | 0.3983 | 39.83 | 0.01243 |
| 5 | 0.8 | 0.8498 | 0.8191 | 0.0407 | 0.5073 | 50.73 | 0.01018 |

**Table: VI; variation of inhibition efficiency with concentration of inhibitor at 312K for 0.2M HNO₃ solution.**

| S/N | Concentration(g/l) | Initial weight (W1) | Final weight (W2) | Weight loss (WL) | Surface coverage ($\theta$) | Inhibition efficiency (%I.E) | Corrosion Rate CR) |
|---|---|---|---|---|---|---|---|
| 1 | Blank | 0.8950 | 0.7928 | 0.1028 | - | - | 0.02570 |
| 2 | 0.2 | 0.8756 | 0.8154 | 0.0909 | 0.114 | 11.4 | 0.02273 |
| 3 | 0.4 | 0.8601 | 0.7785 | 0.0816 | 0.2047 | 20.47 | 0.02040 |
| 4 | 0.6 | 0.8831 | 0.8134 | 0.0697 | 0.3207 | 32.07 | 0.01743 |
| 5 | 0.8 | 0.8641 | 0.8089 | 0.0552 | 0.4620 | 46.20 | 0.01380 |

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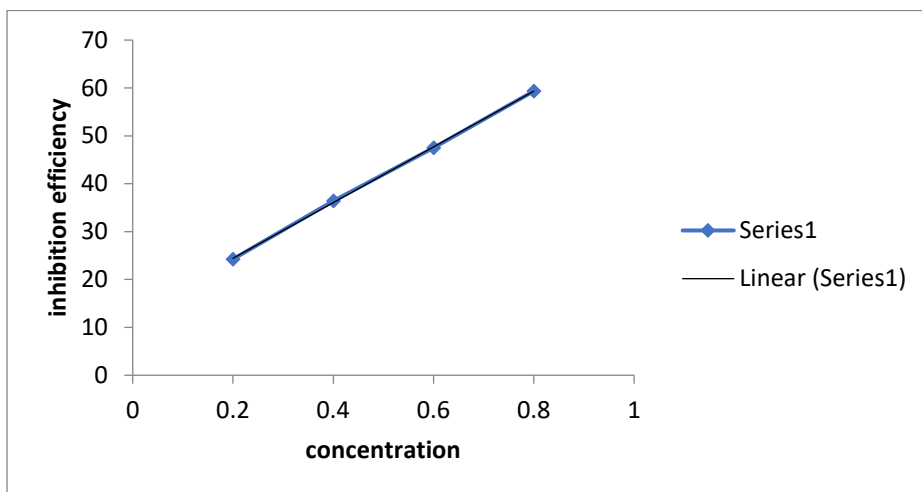
**Fig. I: Variation of Inhibition efficiency with the concentration of *Eucalyptus camaldulensis* bark extracts for mild steel coupons in 0.2M HNO₃ Solution at 303K.**
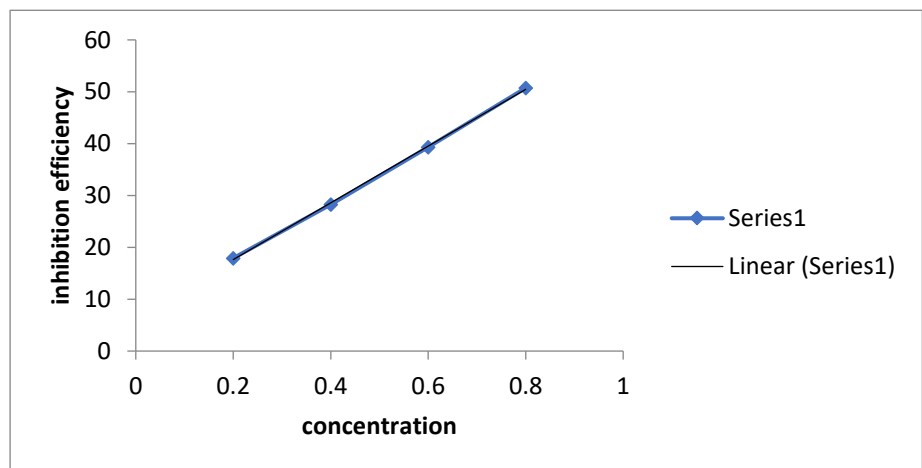


**Fig. II; Variation of Inhibition efficiency with concentration of *Eucalyptus camaldulensis* bark extract in 0.2M HNO₃ Solution at 313K**
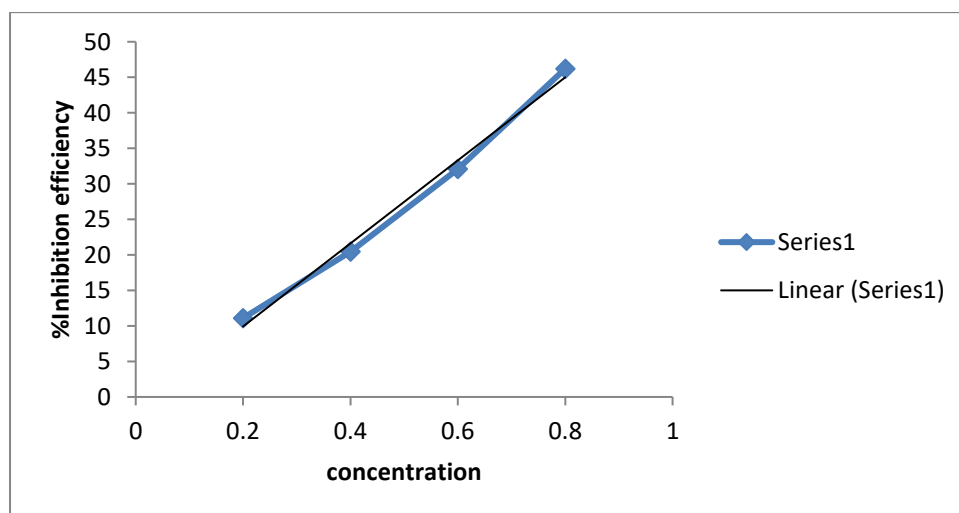


**Fig. III: Variation of Inhibition efficiency with the concentration of *Eucalyptus camaldulensis* bark extracts in 0.2M HNO₃ Solution at 323K**

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**Table: VII; variation of activation energy with concentration of *Eucalyptus camaldulensis* bark extract**

| Concentration g/l | Log(A) | $R^2$ | $E_a$(kJmol$^{-1}$) | $Q_{ads}$(kJmol$^{-1}$) |
|---|---|---|---|---|
| Blank | 0.9174 | 0.9898 | 15.54 | - |
| 0.2 | 1.8830 | 0.9898 | 21.84 | -209.77 |
| 0.4 | 2.3352 | 0.9971 | 24.92 | -117.42 |
| 0.6 | 2.4372 | 0.9973 | 25.98 | -68.20 |
| 0.8 | 2.4872 | 0.9993 | 26.89 | -27.53 |

## 4. DISCUSSION

### EFFECT OF INHIBITOR CONCENTRATIONS ON CORROSION RATE

The findings in Tables IV, V and VI demonstrate how mild steel corrosion rates in 0.2M HNO$_{3(aq)}$ are affected by inhibitor concentrations. When compared to the blank solution, the values of the inhibited system's corrosion rate were determined to be lower. By changing the reaction medium's temperature from 303K to 323K, the corrosion rate was examined. The outcome demonstrates that, at all specified temperatures, mild steel corrosion rates in 0.2M HNO$_{3(aq)}$ decrease with increasing inhibitor concentrations. The rate at which inhibitor molecules adsorb on the surface of mild steel increases in response to an increase in inhibitor concentration, creating a barrier for charge and mass transfer that lessens the contact between the metal surface and corrosive fluids and slows the rate of corrosion (Musa et al., 2020).

### EFFECT OF INHIBITOR CONCENTRATIONS ON INHIBITION EFFICIENCY

Tables IV, V and VI display the results for the impact of inhibitor concentration on inhibition effectiveness. It is evident from all the tables that, at all temperatures, the inhibition efficiency rises as the inhibitor concentration does. (303,313 and 323K). This is caused by the larger concentration of the inhibitor's adsorbed molecules covering a greater percentage of the surface area of mild steel. At a concentration of 0.8g/l inhibitor and 0.2M medium at a temperature of 303K, the inhibition efficiency improves gradually as the inhibitor concentration increases, reaching a maximum value of 59.34%. (Musa et al., 2020).

### EFFECTS OF TEMPERATURE ON CORROSION RATE AND EFFICIENCY

With rising temperatures, both the rate of corrosion and the effectiveness of the inhibition were negatively impacted. This could be explained by the fact that at high temperatures, Eucalyptus camaldulensis bark extract desorbs, exposing mild steel to the corrosive elements. (Nwakwasi et al., 2017). The extract was more effective as an inhibitor at a low temperature (303K) compared to temperatures of 313 and 323K, according to a comparison of the inhibition efficiencies obtained at various temperatures (303, 313 and 323K). The fact that the inhibitor coating on the metal surface weakens as temperature rises may account for the extract's excellent inhibitory performance at low temperature (303K). Consequently, at high temperatures, a larger portion of the metal surface is available for corrosion reaction. (Nwakwasi et al., 2017).

### 4.1 KINETICS PARAMETERS

The Arrhenius equation was employed to determine the activation parameters for the corrosion process.

$$C_R = A\,exp^{-Ea/RT} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 4.1$$

Where the corrosion rate (CR), the gas constant (R), the absolute temperature (T), and the pre-exponential factor (A) are all present. By using a linear regression between logCR and 1/T, the apparent activation energies (Ea) at the optimal inhibitor dose were calculated. The results are shown in table VII. The linear regression coefficient was very close to 1, showing that the kinetic model may explain mild steel corrosion in nitric acid. The value of Ea measured in 0.2M nitric acid including Eucalyptus camaldulensis was higher (26.89kJ mol-1) than that for an uncontrolled solution, according to Table VII. (15.54kJmol-1). It is possible to interpret the rise in apparent activation energy as first-stage physical adsorption. The greater surface area of mild steel comes into touch with a hostile environment because more inhibitor molecules are desorbing at higher temperatures, increasing corrosion rates as temperature rises. (Rekkab et al., 2012).

The pattern of surface coverage with temperature was used to estimate the heat of adsorption (Q$_{(ads)}$) using the equation:

$Q_{(ads)}=2.303R[\log(\theta2/1-\theta1)-\log(\theta1/1-\theta2)]$ xT1T2/T2-T1….4.3

Where: The $Q_{(ads)}$ that were calculated are shown in Table VII. The degree of surface covering reduced with increasing temperature, according to the negative values of the heats of adsorption (Q(ads)), further indicating that the inhibitor's effectiveness rises as temperature decreases. (Akalezi et al., 2016).

## 5. CONCLUSION

Natural processes such as corrosion cause materials' useful characteristics to deteriorate and lower the binding energy of metals. Corrosion leads to an oxidized state in which a metal atom loses one or more electrons.

The bark extract of Eucalyptus camaldulensis is an excellent and powerful mild steel corrosion inhibitor. This study examines the rate of mild steel corrosion, effectiveness of the inhibitors, surface coverage, and the impact of temperature on mild steel corrosion in an acidic medium. The highest corrosion rate of 0. 0.1243cm-2hr-1 in 1.0M of the medium was discovered to decrease with an increase in Eucalyptus camaldulensis concentration, while Eucalyptus camaldulensis concentration increased surface coverage and inhibition efficiency, which decreased with an increase in the concentration of the corrosive medium and temperature but increased with Eucalyptus camaldulensis concentration. At 303K and the lowest acid content of 0.2M for an hour of immersion, the highest inhibition efficiency of 59.34% was attained.

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