Chemical Science International Journal

31(2): 21-34, 2022; Article no.CSIJ.89311
ISSN: 2456-706X
(Past name: American Chemical Science Journal, Past ISSN: 2249-0205)

Phytochemical Constituent and Anti-corrosion Properties of the Root Extract of *Phyllanthus mellerianus* (Nvo-nkwu) Plant on Mild Steel in 1.5M HCl Medium

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2022/v31i230278

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/89311

Original Research Article

Received 28 April 2022
Accepted 05 July 2022
Published 06 July 2022

ABSTRACT

The research reports on the phytochemical constituents and anti-corrosion properties of the root extract of *Phyllanthus mellerianus* on mild steel in 1.5M HCl. The powdered root was extracted with ethanol and concentrated with a rotary evaporator. The phytochemical constituents' were achieved through GC-MS, FTIR and wet analysis. The anticorrosion properties were investigated *via* weight loss, hydrogen evolution techniques, and SEM analysis. The phytochemical investigation reveals the presence of tannins, flavonoids, phenols, and terpenoids at reasonable percentages. At different temperatures of 303K, 313K, and 323K, the inhibition efficiency, enthalpy, entropy, activation energy, Gibbs free energy, and adsorption isotherms were extrapolated with some models. The inhibition efficiency increased with an increase in the concentration of the extract, an indication of the inhibitive property of the root extract. This was supported through the extrapolation of Gibbs free energy, activation energy, enthalpy, and entropy change. The thermodynamic variable shows that the mechanism of inhibition was physisorption, whereas the kinetics study confirmed a first-order kinetic on the corrosion of mild steel in hydrochloric acid. The values of the linear regression R^2 confirm the inhibitive impact of

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the root extract on mild steel in an acid medium. The presence of the heteroatoms N, O, and S in the root extracts of Phyllanthus mellerianus has been attributed to their inhibitory effectiveness.

Keywords: Anticorrosion; mild steel; Phyllanthus mellerianus; phytochemical constituent.

1. INTRODUCTION

Plants are of great importance to the health of individuals and communities. The essential value of plants lies in some chemical substances that produce a definite physiological action on the human body. The most important of these are the bioactive constituents like alkaloids, tannins, flavonoids, and phenolic compounds they contain. The majority of these plants are weeds that are not useful to humans; however, some are indigenous medicinal plants that are used as spices or food for humans or animals [1,2]. In the view of Larayetan et al. [3], and Orie and Christian [4]], plants serve as a reservoir for potentially valuable chemical compounds which can be used to produce drugs, resulting in phyto-molecules used for current design and synthesis. Plant extracts, together with their phytochemicals, possess antimicrobial properties which are of great importance for pharmaceutical industries [1]. Phytochemicals are important compounds found in medicinal plants that are not essential for the normal functioning of the human body, but are active and exert beneficial effects on health or in the amelioration of diseases. Although many phytochemicals are already known, many are yet to be identified [5,6].

Phyllanthus mellerianus is a small, frequently stunted tropical plant that can be found in West Africa and the surrounding region. It can be found in savannahs, secondary forests, and coastal thickets and scrub throughout tropical Africa as a glabrous shrub or woody climber that is occasionally arborescent [7,8]. Antibacterial activity in high concentrations was also found in the extracts of the leaves and the bark. Staphylococcus aureus, Streptococcus faecalis, and Neisseria gonorrhoea are all sensitive to its ethanol extract and phytochemicals [9]. The ethanol leaf and stem extract of Phyllanthus mellerianus has been used as an anticorrodant in the acid medium [2,10].

Corrosion is the destructive attack of a metal by a chemical or electrochemical reaction within its environment. It is often associated with the rusting and tarnishing of metals. However, corrosion damage can also occur in other ways as well, failing by cracking or loss of strength or ductility [11,12]. The corrosion of mild steel is a problem for most industries and the environment at large. It is a natural phenomenon that degrades the metallic properties of metals and alloys, making them unsuitable for specific roles [2,3]. Chemical processes such as acid cleaning, pickling, and descaling expose mild steel to acid solutions.

The application of green plants as anti-corrosion agents has become one of the emerging key approaches to controlling corrosion in modern society, based on its availability, low cost, and low environmental impacts. Some of the plants recently used as corrosion inhibitors are Carica papaya [13], water hyacinth [14], breadfruit peel [4], Tinosporacrispa [15], Citrus aurantium leaves [16] and Folic Acid [17].

The deterioration of mild steel when exposed to acids, alkalis, and salt solutions is a problem in industrial processes. The corrosion of metals and their alloys has sparked a surge in research efforts to minimise the damage caused by the corrosion process. Thus, the study investigates the phytochemical constituents and anticorrosion properties of the root extract of *Phyllanthus mellerianus (*Nvo-nkwu) plant on mild steel in an acid medium

2. METHODOLOGY

2.1 Inhibitor Preparation of the Root Extract of *Phyllanthus Mellerianus*

The root extract of *Phyllanthus mellerianus*, (nvo nkwu) was collected from Agbani in Nkanu LGA and Aku in the Igbo Etiti LGA area of Enugu State and was identified in the Department of Microbiology, Enugu State University of Science and Technology (ESUT). It was properly dried in the shade for 5–8 weeks, then it was ground to powder using a wood-land electric grinding machine and stored in airtight bottles. The ethanol extraction was achieved with a conventional Soxhlet extraction system and the solvent was removed with a rotary evaporator. The root extract used as an inhibitor was prepared into masses of 0.1g, 0.2g, 0.3g, 0.4g and 0.5g, and were each dissolved in 100ml of distilled water.

2.2 Phytochemical Srceening of the Inhibitor *Phyllanthus Mellerianus* (Nvo-nkwu)

The phytochemical screening of the root extract of *Phyllanthus mellerianus* (nvo nkwu) was investigated using the same adopted by Edeoga et al. [1], Larayetan et al. [3], Don-Lawson et al. [6]**,** Nsude and Orie [10] and Ogbuanu et al. [18]

2.3 Preparation of Mild Steel Coupon

Mild Steel coupon was mechanically press cut to the thickness =0.026cm, Width =0.17cm, Height =0.17cm. The coupons were polished with sandpaper to produce a smooth finish shape then cleaned and washed with absolute alcohol (ethanol) and dry with acetone before each of the coupons was weighted.

2.4 Corrosive Medium

The corrodent was concentrated hydrochloric acid at 1.5M, and different concentrations of the root extract of *Phyllanthus mellerianus* were tested for inhibition potential.

2.5 Gravimetric Measurement and Hydrogen Evolution

The rectangular mild steel specimens of dimension: thickness =0.026cm, width =0.17cm, and height =0.17cm were immersed (complete immersion) in 100 mL of deaerated electrolyte in the absence and presence of different concentrations of root extract of *Phyllanthus mellerianus* at different temperature of 303 K, 313K and 323K. The differences in weight loss both in the presence and absence of inhibitor were recorded at interval of 1day for 5 days of the experimental period [2,10]. The formulas in equation (1)-(11) were used to calculate some essential parameters to aid decision on the level of inhibitions.

2.6 Hydrogen Evolution Determination, *via* the Gasometric Assembly

The gasometric assembly used for the measurement of hydrogen gas evolution from the corrosion reaction was designed following the method described (James et al., 2007). The gasometric assembly measures the volume of hydrogen gas evolution from the reaction system, about five coupons of mild steel were used in the experiments for test solutions containing (1.5M HCl with the five different concentrations of investigated inhibitors from 0.1 – 0.5 g and at a temperature of 30^o, 40^o, 50^o and 60°C. A 50 cm^3 of each test solution was introduced into the reaction vessel connected to a burette through a delivery tube. The initial volume of air in the burette was recorded, thereafter, one mild steel coupon was dropped into the corroded solution and the reaction vessel quickly closed. Variation in the volume of hydrogen gas evolved with time was recorded every 20 min, for 80 min. each experiment was conducted on a fresh specimen. The equations (1) to (6) are used to extrapolate the parameters by changing the weight to volume [14,19].

2.7 Determination of Inhibition Effect of the Root Extract of *Phyllanthus Mellerianus*

To investigate the corrosion inhibition effect of the root extract on mild steel in a 1.5 M HCl medium, the inhibition efficiency and corrosion rate were measured. The gravimetric method and the hydrogen evolution method were used to determine the inhibition efficiency and the corrosion rate, respectively. These methods were described by Orie et al. [17] and James et al. [19], who used Equations (1) to (3) to substantiate their claims.

Weight loss/ volume loss: $\Delta W = W_I - W_F$ and $\Delta V = Vi - Vf$ (1)

Inhibition efficiency: $I\% = 1 - (W_1/W_2) \times 100$ and $1 - (V_1/V_2) \times 100$ respectively (2)

$Cr = \Delta W/At$, and $Cr = \Delta V/t$ (3)

ΔW and ΔV are the weight and volume loss of the uninhibited mild steel, W_I and W_F is the initial and final weight of the inhibited mild steel, CR is corrosion rate, I% is inhibition efficiency in %, A is the area of the mild steel, t is immersion time,

2.8 Adsorption Thermodynamic Isotherm

Studies of adsorption isotherms provide a descriptive mechanism for how organic inhibitors adsorb on metal surfaces [20]. A linear fit of the corrosion rate (CR), the degree of surface coverage (θ), and inhibition efficiency was explained with different adsorption isotherms in (4)-(7)

Longmuir adsorption isotherm: $C/\theta=1/K_{ads} + C_{inh}$ (4)

Freundlich adsorption isotherm, θ= Kads. C^{-n} (5)

Temkin adsorption isotherm, θ=InC +Kads (6)

El-awady's adsorption isotherm, log θ/1-θ=ylogC+logK (7)

2.9 Determination of Adsorption Thermodynamics Parameters

To investigate the nature of the adsorption, the expression for Gibb's free energy change of adsorption, ΔG, presented in Equation (8) was used [20,21].

$$\Delta G_{ads} = -RT \text{ In } (55.5\ K_{ads}) \quad (8)$$

K_{ads} is the adsorption equilibrium constant obtained from the isotherm

2.10 Determination of Activation Energy (Ea)

The slope of the plot of ln CR against 1/T in Equation (7) was used to estimate the activation energy, Ea. The relationship between corrosion rate (CR) and temperature (T) is described by the Arrhenius equation by Olasehinde et al. [20] and Nsude & Orie [10].

$$\text{In Cr= In A- Ea/RT} \quad (9)$$

Ea is the activation energy, R is the gas constant, T is the temperature in Kelvin and A is the exponential factor.

In a plot of In Cr against 1/T, the slope=Ea/ RT

2.11 Determination of Enthalpy and Entropy Change

The changes in enthalpy and entropy were calculated using Equation (10), an alternate form of the Arrhenius equation for the transition state [15,19].

$$\mathrm{Cr} = \frac{RT}{Nh}\exp\,(\Delta S/\mathrm{R})\exp(-\Delta\mathrm{H}/\mathrm{RT}) \quad (10)$$

$$\text{In (Cr/T) = \{In (R/Nh) + }\Delta S/R\}-\Delta H/RT \quad (11)$$

Where h is the Planck's constant (6.6261 $\times 10^{-34}$ Js), N is Avogadro's number (6.0225 x 10^{23} mol^{-1}), and R is the Universal constant (8.314 J/mol K).

In a plot of In (Cr/T) against 1/T, the change in enthalpy was calculated from the slope ΔH/RT. The entropy change, ΔS was evaluated from the intercept, = {In(R/Nh) + ΔS/R}

2.12 Determination of Kinetics Parameters (Rate Constant and Half-life)

The corrosion reaction is a heterogeneous reaction that is composed of anodic reactions at the same or different rates [21]. The first-order kinetics was employed and evaluated using integral method of analysis. This is given by equation 5:

$$\text{Log } (\Delta W)=k_1\, t/2.303 \quad (12)$$

$$T_{1/2} = 0.693/k_1 \quad (13)$$

Where ΔW is the weight loss in (g), k_1 is the first-order rate constant in (hr^{-1}), and t is the immersion time in (hr). The half-life of this corrosion study was gotten from equation (6), [10, 21].

3. RESULTS AND DISCUSSIONS

3.1 Phytochemical Screening of the Root Extract *Phyllanthus Mellerianus*

Table 1 shows the presence phytochemical constituents of the root extract of *phyllanthus mellerianus*.

The table reveals the presence of tannins, flavonoids and phenols as abundantly present. Tannins are phenolic-based natural products that contain hydroxyl and aromatic rings. These phytochemicals can enhance the process of corrosion inhibition of mild steel in an acidic medium. The presence of these compounds has been reported to promote the corrosion inhibition of mild steel in aggressive acid media [14]. This also corroborates the work of Okoafor and Ebenso [13], who research the inhibitory capacity plant extracts

Table 1. Phytochemical constituents the root extract of *phyllanthus mellerianus*

	Phytochemicals	Inference
1	Tannins	**++++**
2	Flavonoids	**++++**
3	Alkaloids	**+**
4	Saponins	**+**
5	Phenols	**++++**
6	Steroids	**+++**
7	Terpenoids	**+++**
8	Glycosides	**+++**
9	Carbohydrates	**++**

Key: Absent+ Present++ Moderatly Present+++ Abundantly Present++++

3.2 GC-MS Analysis of the Root Extract *Phyllanthus Mellerianus*

Table 2 shows the GC-MS investigation of the root extract of *Phyllanthus Mellerianus* with retention time, molecular formula, weights and peak area.

The phytochemical constituents of the root extract of *Phyllanthus Mellerianus* contain twelve different compounds, and have been confirmed bioactive by researchers. Some of the compounds have been used in the field of medicinal chemistry as an analgesic, tranquilizing, and antifungal agent and worm-expeller (ascaridole) [22]; promote weight loss, prevent cancer, and treat bronchitis (Limonene) [23]: fight fungal infections and ant-food spoilage (2,6-octadien-1-ol, 3,7-dimethyl-,(z)-(Nerol) [24], anti-inflammatory, anti-tumor, and chemotherapy supplement(pinene) [25].

3.3 FTIR Analysis of the Root Extract of *Phyllanthus Mellerianus*

The FT-IR analysis identified the functional groups of the active components present in root extract based on the IR active moieties. Table 3 shows the FTIR analysis of the root extract of *Phyllanthus Mellerianus*.

The results of FT-IR analysis confirmed the presence of nitrogen, oxygen, aromatic rings, halogen and carbon-metal bond. These IR active compounds contain lone pair electrons that are viable for the role of corrosion inhibition. These findings on phyto-constituents were consistent with Nsede and Orie [10], who worked on the phytochemical qualitative and quantitative analysis of the ethanol leaf extract of *phyllanthus mellerianus*. The findings reveal the presents of tannin, flavonoids, terpenoids and glycosides in the *phyllanthus mellerianus* leaf extract. It also corroborates the phytochemical constituents estimated by, Orie and Christian [4], James and Akarenta [26] and Nsude et al. [2].

3.4 Inhibition Efficiency and Concentration of the Root Extract *Phyllanthus mellerianus*

The relationship between inhibition efficiency, inhibitor concentration, and temperature is illustrated in Fig. 1. For gravimetric analysis, the solution containing 0.5g of the inhibitor has the highest inhibition efficiency of 80% at 30 ^{o}C, while the hydrogen evolution method has the highest inhibition efficiency of 70% at 30 ^{o}C. As the temperature rose from 30 ^{o}C to 50 ^{o}C, both gravimetric and hydrogen evolution techniques demonstrated a reduction in inhibition efficiency. Consistent with Don-Lawson et al. [27] and Nsude and Orie [10], thay had the same trend of increase in the inhibition efficiency, as a result of increased concentrations and decreasing temperatures.

3.5 Corrosion Inhibition and Adsorption Isotherms of Mild Steel in the Root Extract *Phyllanthus mellerianus*

Table 4 depicts the adsorption isotherms of the root extract of Phyllanthus mellerianus mild steel surface.

As seen in Table 4 and Figs. 2-5, the R^2 values from the linear regression of the experimental data were close to unity, which indicates that the molecules in the root extract of *Phyllanthus mellerianus* are adsorbed on the surface of mild steel and are strongly fitted to Temkin, Langmuir, El-Awadys, and Freundlich isotherms. This is in line with the findings of Umoren et al. [14], Olasehinde et al. [20] and Orie et al. [17], who investigated various adsorption isotherms using an organic corrosion inhibitor.

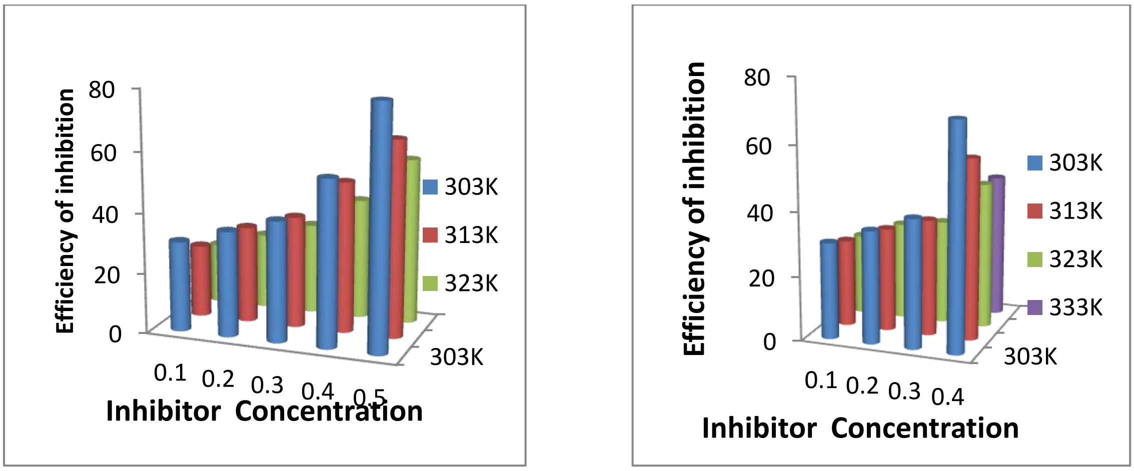
The inhibitors' Langmuir isotherm values were discovered to be large (> 1), indicating a physical adsorption process between the inhibitors and the mild steel surface. The inhibitor has a strong interaction with the surface, and the adsorption process is based on the Langmuir isotherm values for both inhibitors (k > 1) [27-29].

Table 2. GC-MS analysis of the root extract *Phyllanthus Mellerianus*

RT	Name of compounds	Formula	Weight	Peak area
7.463	Cycloheptasiloxane, tetradecamethyl	$C_{14}H_{42}O_7Si_7$	518	3.26
8.486	Limonene	$C_{10}H_{16}$	136	4.69
9.445	D-Fructose,diethylmercaptal, pentaacetate	$C_{20}H_{32}O_{10}S_2$	496	9.88
10.139	Copaene	$C_{15}H_{24}$	204	3.67
10.833	∝ - Pinene	$C_{10}H_{16}$	136	9.77
11.457	2,6-Octadien-1-ol, 3,7-Dimethyl,(Z)-	$C_{10}H_{18}O$	154	7.50
12.027	Bicyclo [3.1.0] hex-2-ene, 2-methyl-5-(1-methylethyl) -	$C_{10}H_{18}$	136	5.05
12.516	5-cyclopropylcarbonyl oxypentadecane	$C_{19}H_{36}O_2$	296	6.06
12.616	Linalool	$C_{10}H_{18}O$	154	2.89
21.239	Ascaridole	$C_{10}H_{16}O_2$	168	6.78
22.750	Benzene,1.2.3-trimeth oxy-5-(2-propenyl)-	$C_{12}H_{16}O_3$	208	3.80
22.915	Androstonane-11,17-dione,3-[(trimethylsily)oxy]-,17-[O -(phenylmethyl) oxime], (3∝, 5∝)-	$C_{29}H_{43}NO_3Si$	481	2.89

Table 3. FTIR analysis of the stem extract of *Phyllanthus Mellerianus*

No	Vibration frequency (cm^{-1})	Vibration frequency (cm^{-1}) (literature)	Phyto compounds Identified
1	3565.56	3500-3700	Alcohols & Phenol
2	2987.05	2850- 3000;	Amine compound
3	2803.42	2970-2950	Alkanes,
4	2836.87	2850-3000	Methoxy methyl ether
5	1776.34	1706-1720	Carboxylic acid or Ketone,
6	1646.91	1640-1690	Imine/ Oxime in the compound
7	1530.24	1500-1550	Nitro-compound
8	1454.06	1400-1500	Aromatic compound
9	1246.75	1020-1250	Amino compound
10	412-510	390-550	Metal complexes



1a **1b**

Fig. 1. Efficiency of corrosion Inhibition *via* (a) Gravimetric techniques and (b) Hydrogen evolution techniques

Table 4. Adsorption parameters for the Root extract of *Phyllanthus mellerianus* on the mild steel surface

isotherms	temperature	R^2	K_{ads}	ΔG^O_{ads} (KJ/mol)	1/nor 1/y
Langmuir adsorption isotherms	303	0.9132	7.612	-15.23	-
	313	0.9932	6.183	-15.19	-
	323	0.9513	6.810	-15.94	-
Freundlich adsorption isotherm	303	0.884	0.942	-15.292	0.150
	313	0.9726	0.885	-15.425	0.131
	323	0.9607	0.692	-16.302	0.117
Temkin adsorption isotherms	303	0.9024	1.2094	-10.597	-
	313	0.9682	1.2892	-11.113	-
	323	0.9643	1.2990	-11.488	-
El-awadys adsorption isotherms	303	0.9949	0.890	-15292	0.184
	313	0.8716	0.838	-15.425	0.163
	323	0.9014	0.893	-16.302	0.181

Table 5. Kinetics investigation of Mild Steel in the Root Extract *Phyllanthus mellerianus*

Concentration g/l	Rate const. k (hr^{-1})	Half life (hr)	R^2
0.0	1.2379	3.2474	0.9871
0.1	1.1241	5.9230	0.9333
0.2	1.1152	6.3577	0.9924
0.3	1.1140	6.4167	0.9895
0.4	1.0887	8.1529	0.8824
0.5	1.0844	8.5556	0.9481

El-Awady isotherms characterise the adsorption sites on the mild steel surface. Table 4 shows that the 1/y values are less than one, indicating that the inhibitors occupied more than one active site and functioned well in 1.5 M HCl. The inhibitors' y values decreased as temperature increased, implying that weak Van der Waal forces were holding the inhibitors to the mild steel surface [25-29]. This was also confirmed by the physical adsorption properties of the inhibitors.

The linearity of adsorption is represented by the 1/n value in the Freundlich equation, which ranges from 0.7 to 10. In this study, the n values were less than 0.7, indicating increased relative adsorption [10, 18, 30].

As seen in Table 4, the adsorption Gibb's free energy changes (ΔG_{ads}) for different isotherms models at various temperatures were negative and less than 20 kJ/mol. The adsorption of the root extract of *Phyllanthus Mellerianus* on a mild steel surface was found to be spontaneous, feasible, and occurred according to the physical adsorption mechanism. The increase in ΔG_{ads} at 323 K suggests that the adsorption was more spontaneous and stable as the temperature rose. This is consistent with Marques et al. [26] who worked on the leaf extract. The ΔG_{ads} investigation is also in conformity with James and Akarenta [27], who worked on an extract of red onion skin, and Dakhil et al. [23], who researched Citrus aurantium leaves, and Nsude and Orie [3], who worked on the leaf extract of *Phyllanthus mellerianus.*

3.6 Corrosion Inhibition and Kinetics Investigation of Mild Steel in Root Extract of *Phyllanthus mellerianus*

Table 5 depicts the chemical kinetics extrapolation from the root extract of *Phyllanthus Mellerianus* on mild steel in 1.5M HCl. The rate constant (k) represents how quickly or slowly a given chemical reaction occurs, with higher and lower rate constant values indicating faster and slower rates, respectively [10].

The k values in the blank solution are high and decrease as the inhibitor concentration increases. This indicates that the inhibitor slowed the corrosion rate of mild steel in 1.5 M

HCl. The estimated half-life value increased as the inhibitor concentration increased. The root extract of the inhibitor of *Phyllanthus Mellerianus* reduced the corrosion of mild steel in the acidic medium. The findings were consistent with Okafor [12], and Okafor and Ebenso [13], who investigated plant adsorption and kinetic studies on various metals via plant extract.

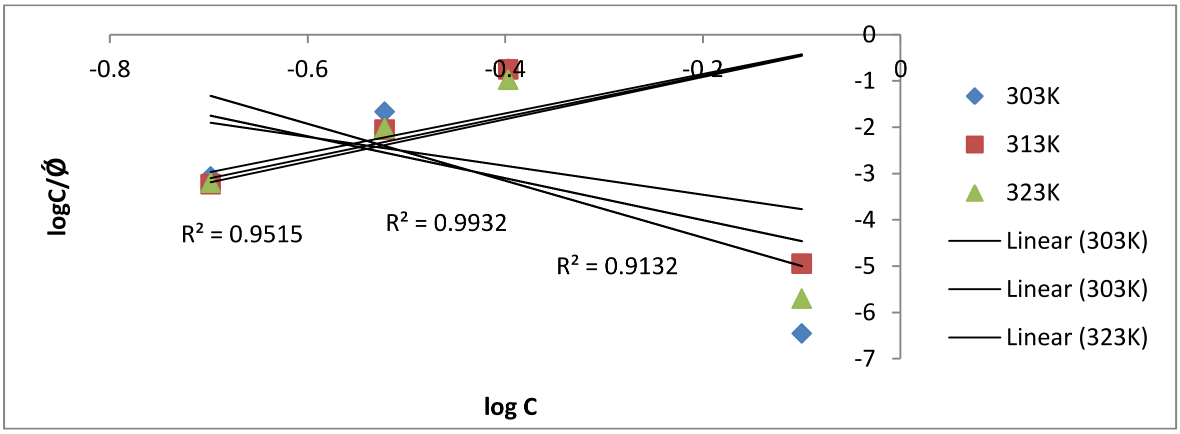


Fig. 2. Langmuir adsorption isotherm *of* the root extract *Phyllanthus Mellerianus* for mild steel surface

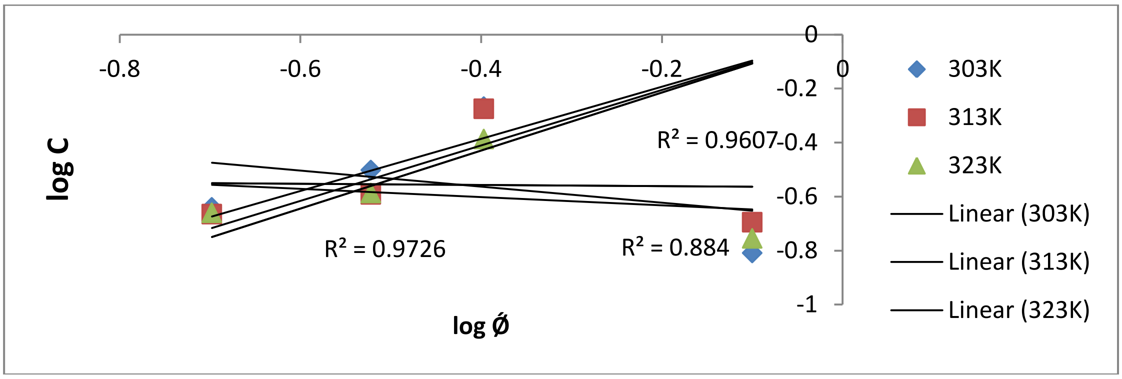


Fig. 3. Freundlich adsorption isotherm of the root extract of *Phyllanthus Mellerianus* for mild steel surface

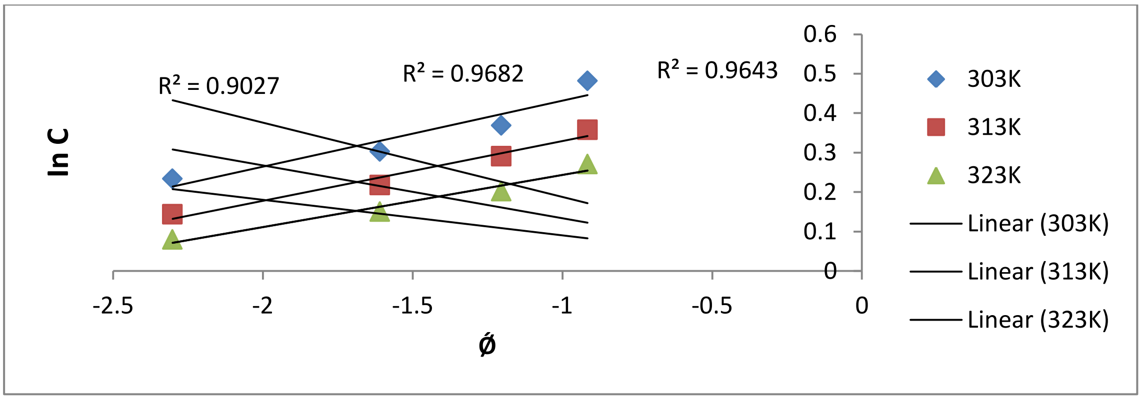


Fig. 4. Temkin adsorption isotherm of the root extract of *Phyllanthus Mellerianus* for mild steel surface

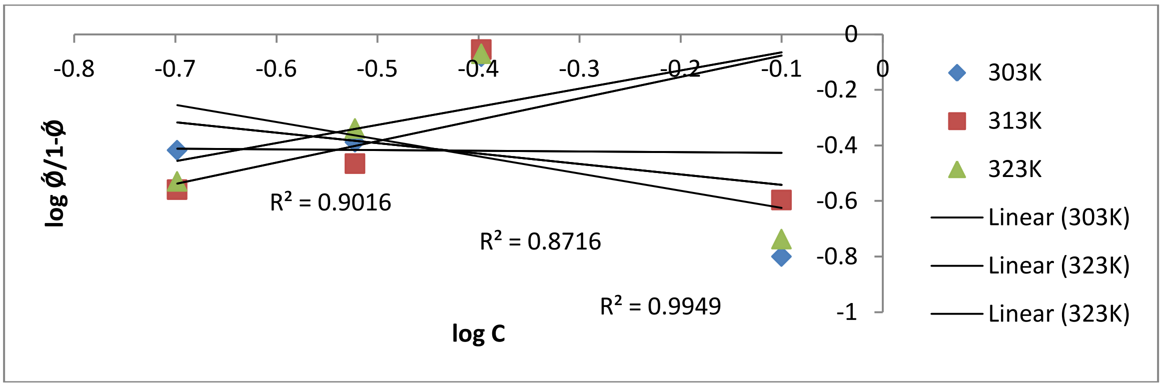


Fig. 5. El-Awadys thermodynamic /kinetic isotherm adsorption of the root extract of *Phyllanthus Mellerianus* for mild steel surface

Fig. 6 depicts the plot of In(ΔW) against exposure time in (hours) in the presence and absence of inhibitor root extract of *Phyllanthus mellerianus*. The plot showed a linear relationship between the slope and the rate constant, thus confirming the first-order kinetics of the corrosion of mild steel in hydrochloric acid. The high value of the correlation coefficient obtained showed that the experimental value fitted first-order kinetics. This result conforms with reports of Omran et al. [14] and Hussin,[15], who worked on different plant extracts.

3.7 Activation Energy (Ea) of Root Extract of *Phyllanthus mellerianus* for Mild Steel Corrosion Inhibition

In transition-state theory, activation energy is the difference in energy content between molecules in an activated or transition-state configuration and the corresponding molecules in their initial configuration [28]. Table 6 contains the activation energy and Arrhenius factor of root extract of *Phyllanthus Mellerianus* for corrosion inhibition of mild steel.

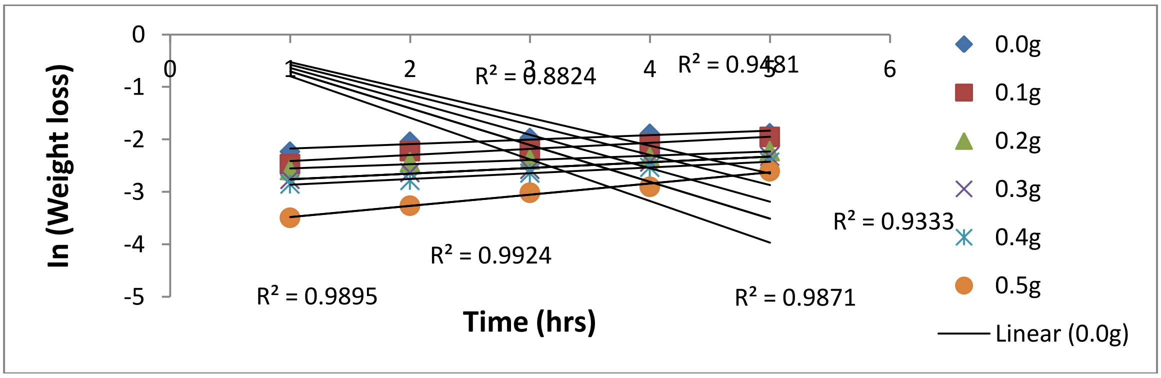


Fig. 6. Kinetics analysis of the root extract of *Phyllanthus Mellerianus* for Inhibitor of Mild Steel Surface

Table 6. Thermodynamic parameters for mild steel in the presence and absence of inhibitor

Concentration of inhibitor	**A**	**Ea (kJ mol^{-1})**	**-ΔH^{o} (kJ mol^{-1})**	**ΔS^{o} (Jmol^{-1}K^{-1})**
blank	I.885	9.214	-6.075	-195.76
0.1g/l	1.051	10.508	-6.400	-189.77
0.2g/l	1.352	10.314	-7.012	-188.11
0.3g/l	3.367	12.987	-11.298	-185.98
0.4g/l	2.592	13.285	-23.931	-158.38
0.5g/l	6.240	20.817	-32.023	-135.22

From the table, the concentration of the inhibitor leads to a general increase in activation energy. The blank solution has less activation energy than the solution with a corrosion inhibitor, and the activation energy increases as the concentration of the inhibitor increases. This is because of the molecular barrier created by adsorption of the molecules the root extract on that mild steel surface. The same trend of activation energy and inhibitor concentrations has been reported on the extracts of jujube leaves, black pepper [24], breadfruit peel [4], leaf and stem extract of *Phyllanthus* mellerianus [2, 10], jatropha leaf [29] and piper nigrum extract [30]. The corrosion mechanism can be attributed to physical adsorption (physisorption) on the rationale that the activation energy was higher in the presence of the inhibitor. Physiosorption has activation energy below 40 KJmol^{-1} and chemisorption has an activation energy above 80 KJmol^{-1} [27]. These findings are consistent with previous research by Salehi et al. [25] and Fadare et al. [21].

Fig. 7 depicts log CR versus 1/T plots for different concentrations of the root extract of *Phyllanthus mellerianus*t. The slopes obtained from the plots are thus appropriate for estimating the activation energy of the process for different concentrations.

3.8 Enthalpy and Entropy Change Investigation of Mild Steel in Root Extract of *Phyllanthus mellerianus*

The values of enthalpy change, ΔH and entropy change, ΔS obtained at different concentrations of the root extract of *Phyllanthus mellerianus* are shown in Table 6, and a plot in Fig. 7. The values of ΔH at different concentrations of the inhibitor were negative and increased as the inhibitor's concentration increased. The negative sign of ΔH indicates an exothermic process of adsorption and, thus, physisorption [27, 30]. The change in entropy (ΔS^0) was negative in the absence and presence of the root extract of *Phyllanthus mellerianu*. This implies that the activated complex in the rate-determining step represents association rather than dissociation, implying that there was a decrease in the degree of orderliness during the adsorption process when moving from the reactants to the activated complex [17-19].

3.9 SEM analysis of the Corrosion Rate of Mild Steel in 1.5M HCl Acid and Inhibitor

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Table 7 shows the SEM analysis of mild steel coupons in the presence and absence of an inhibitor for 5 days.

The SEM analysis reveals that the mild steel in 1.5M HCl has lower percentage values in the constituents elements when compared to the raw and inhibited coupons. The lower percentage composition is associated with the corrosion rate of the mild steel coupon, whereas, the values of the element in the inhibited coupon are attributed to the effect of the root extract of *Phyllanthus mellerianu* (see Table 7). Among the metals in the mild steel, metallic iron was highly corroded with a percentage value of 45.00% in HCl (1.5 M) and 63.0% in the presence of inhibitor.

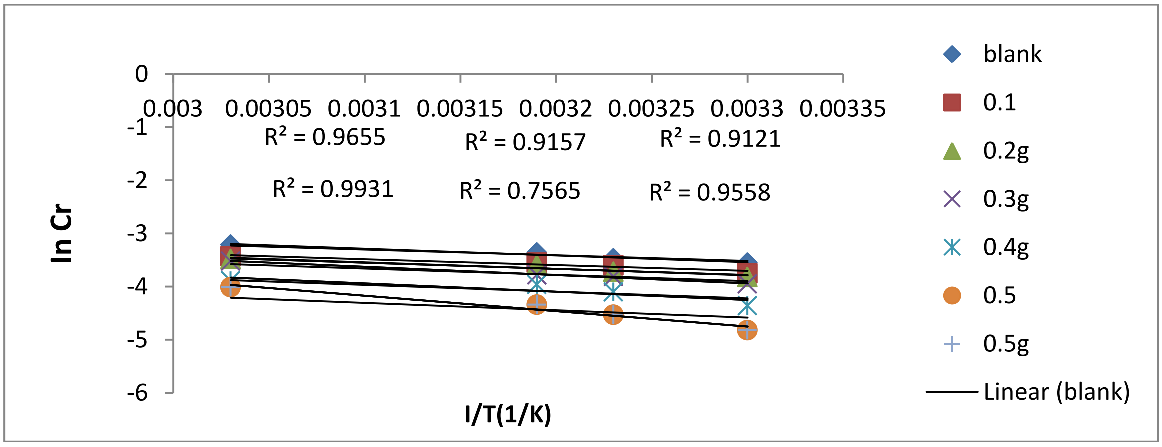


Fig. 7. Activation energy analysis of *Phyllanthus Mellerianus* stem extract for inhibitor on mild steel surface

Table 7. SEM analysis of mild steel in presence and absence of inhibitor

No.	Elements	Raw coupon (%)	Acid Coupon	Inhibited coupon
1	Iron	68.15	45.0	63.0
2	Copper	0.132	-	0.15
3	Calcium	2.00	0.59	1.60
4	Magnesium	2.00	1.25	1.89
5	Manganese	0.25	-	0.16
6	Zinc	8.50	7.01	8.31
7	Chromium	-	-	-
8	Sodium	2.22	1.31	2.22
9	Carbon	3.54	2.90	3.29
10	Oxygen	10.00	10.26	20.11

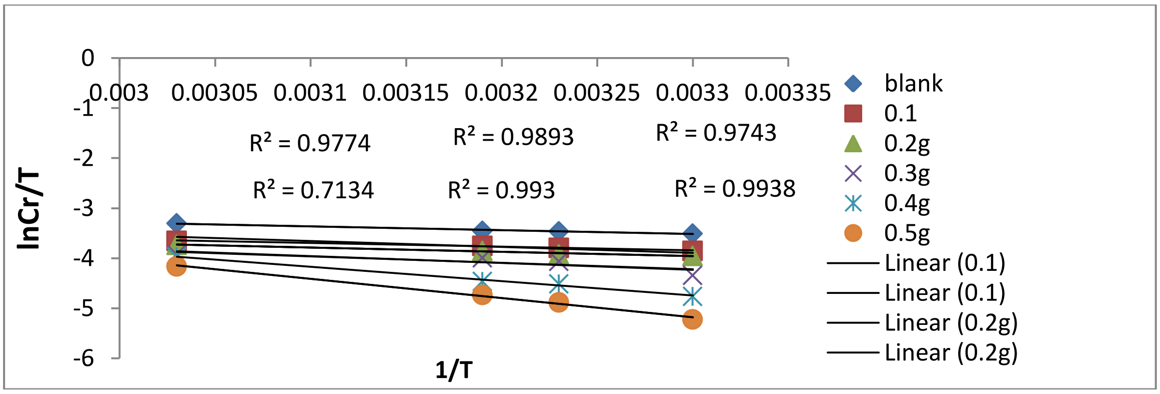
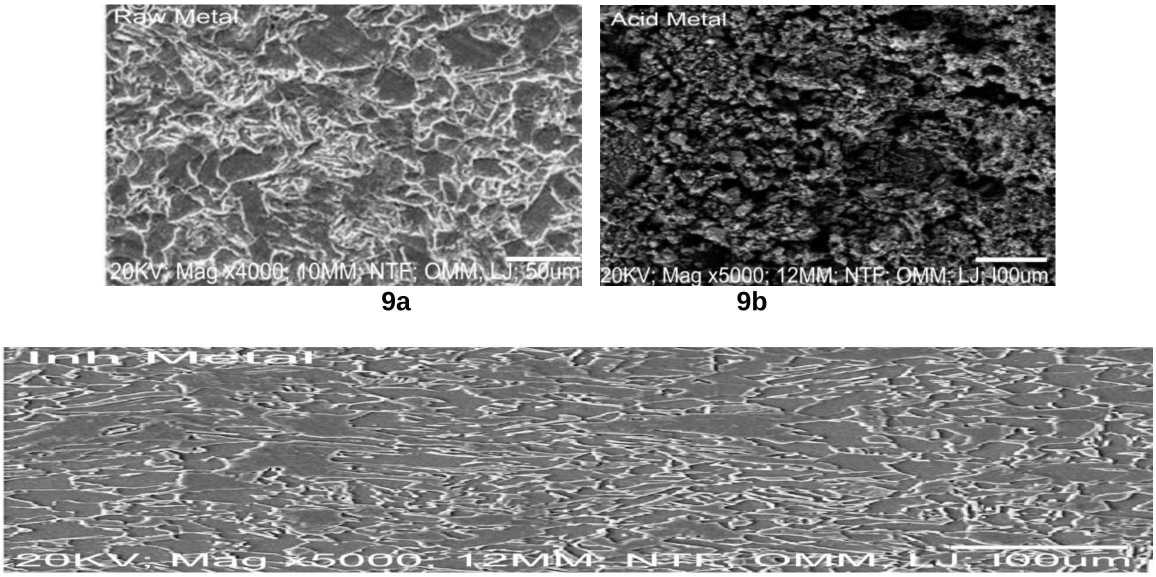


Fig. 8. Enthalpy and entropy study for root extract of *Phyllanthus Mellerianus* on mild steel surface



9a

9b

9c

Fig. 9. Morphology Structure of Mild Steel (8a) Raw Coupon (8b) Acid Coupon (8c) Inhibited Coupon

Fig. 9 illustrates the morphology of mild steel in the presence and absence of an inhibitor. Fig. 9b depicts a rough surface with uniform pits indicative of mild steel corrosion in acid, while Figs. 9a and 9c depict unused and inhibited coupons, respectively. The deposition on the surface of the mild steel sample in Fig. 9c indicates that the root extract of *Phyllanthus mellerianu* adsorbed on the metal surface.

The metal surface was completely destroyed in the acid solutions, indicating that it could not withstand the free acid solutions [31,32]. The situation changed when an inhibitor was added. The effectiveness of the inhibitor was shown by the fact that it was able to protect the surface from damage caused by the root extract molecules binding to the active sites of the metal surface and causing some deposition on the metal surface [33,34].

4. CONCLUSION

The study discovered that the root extract of *Phyllanthus mellerianu* contains flavonoids, tannins, phenols, amines, nitro-compounds, aromatic rings, metal complexes, and other bioactive functional moieties. Researchers have confirmed that these phytochemical constituents and elements are bioactive and essential in the field of medicinal chemistry.

Based on the weight loss method and hydrogen evolution technique used in this study, the root extract of *Phyllanthus mellerianu* has an inhibition efficiency of 80% and 70%, respectively. Adsorption of inhibitors was found to be strong at low temperatures, but inhibition increased with inhibitor concentration when tested at different temperatures. The isotherms revealed that the inhibitors occupied multiple active sites, resulting in a monolayer. The kinetic data indicates a first order reaction, while the thermodynamic data shows that the inhibitors were stable, spontaneous, physically adsorbed, and decreased in disorderliness. The morphological analysis reveals that the mild steel surface was completely destroyed in the acid solutions, as well as the inhibitor's effectiveness in 1.5M HCl acid medium. The constituents of phytochemicals have been linked to their ability to inhibit mild steel corrosion in the presence of heteroatoms such as N, O, and S in their composition. Because of the presence of bioactive moieties, the root extract of *Phyllanthus mellerianu* will be essential to pharmaceutical industries as well as corrosion industries due to its availability, low cost, and environmental friendliness.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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Peer-review history:
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