ISSN (Online): 2455-3662
EPRA International Journal of Multidisciplinary Research (IJMR) - Peer Reviewed Journal
Volume: 8| Issue: 6| June 2022|| Journal DOI: 10.36713/epra2013 || SJIF Impact Factor 2022: 8.205 || ISI Value: 1.188

PHYLLANTHUS MELLERIANUS STEM INHIBITION PROPERTIES FOR MILD STEEL CORROSION IN 1.0 M HCL MEDIUM: ADSORPTION, KINETICS AND THERMODYNAMIC INVESTIGATION

Okechukwu Paul Nsude[1], Kingsley John Orie[2],* Okoro Ogbobe[1]
[1]*Department of Industrial Chemistry, Enugu State University of Science and Technology Enugu State, Nigeria*
[2]*Department of Pure and Industrial Chemistry, University of Port Harcourt, Rivers State Nigeria*

Corresponding author: Kingsley John Orie

Article DOI: https://doi.org/10.36713/epra10473
DOI No: 10.36713/epra10473

ABSTRACT

***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 minimize the damage caused by the corrosion process. The research reports the corrosion inhibition properties of* Phyllanthus mellerianus *stem on mild steel in 1.0 M HCl solution using weight loss and hydrogen evolution techniques. The powdered sample was extracted with ethanol and concentrated with a rotary evaporator. The functional group of the extract, elemental analysis, and morphology of the mild steel were studied with FTIR and SEM. The FTIR analysis confirms the presence of functional groups with nitrogen, oxygen, sulphur, and aromatic rings, whereas the SEM reveals the elements and the morphological structure of the mild steel in the presence and absence of inhibitors in an acid corrodant. Some models were used to extrapolate the inhibition efficiency, enthalpy, enthropy, activation energy, Gibbs free energy, adsorption isotherms, and kinetics investigation. The inhibition efficiency increased with an increase in the concentration of the extract. The values of change in Gibbs free energy obtained at 303K, 313K, and 323K were negative, indicating that the stem extract of* Phyllanthus mellerianus *was strongly adsorbed on mild steel surfaces and stable at high temperatures. The change in Gibb's free energy, enthalpy, and activation energy were less than and within the value of 21 kJ/mol. The extrapolation from the thermodynamic and kinetic models shows the effectiveness of the stem extract of PM and confirms the physical (physisorption) adsorption mechanism for the corrosion of mild steel surfaces. The R^2 values obtained from the linear regression are strongly fitted to the Langmuir, Temkin, Freundlich, and El-Wadys thermodynic/kinetic isotherms. The inhibitory effectiveness of extracts has been attributed to the presence of the hetero atoms N, O, and S present in the stem extract of* Phyllanthus mellerianus.**

KEYWORDS: ***Adsorption, Corrosion Inhibition, Kinetics, Mild Steel, Phyllanthus mellerianus stem, Thermodynamic Parameters***

1.0 INTRODUCTION

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 [1-3]. Chemical processes such as acid cleaning, pickling, and descaling expose mild steel to acid solutions. This causes mild steel to easily corrode, necessitating the use of an inhibitor. Metal corrosion can be controlled in many ways, but one of the best ways to protect metals from corrosion is to use inhibitors [4, 5]. In acidic environments, many organic compounds are used to prevent mild steel from corroding. The molecules of these compounds are absorbed by the metal surface and act as a barrier to corrosive attack [2, 5, 6]. They are typically composed of nitrogen, oxygen, or sulphur in a conjugated system. Natural plant-based corrosion inhibitors are becoming more popular as a result of their low toxicity, low cost, and increasing awareness and strict environmental regulations [1,3, 7]. Plant extract-derived corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [7, 8].

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 [8, 9]. Antibacterial activity in high concentrations was also found in the extracts of the leaf and the bark. Staphylococcus aureus, Streptococcus faecalis, and Neisseria gonorrhoea are all sensitive to its ethanol extract and phytochemicals [9]. The ethanol leaf extract of PM has been used for corrosion inhibition of mild steel in 0.5M HCl corrosant [3].

Scientists have been concerned in recent years about the use of certain organic compounds as corrosion inhibitors. Some examples of biorenewable green chemicals used as corrosion inhibitors include Carica papaya [10], water hyacinth [7], bread food peel (Orie and Christian, 2016), Tinosporacrispa [6], Citrus aurantium leaves [6], Folic Acid [11].

The use of plant extracts as corrosion inhibitors for metals in various aggressive media has been studied in various ways. However, little is known about the use of the stem ethanol extract of *Phyllanthus mellerianus* plant as an inhibitor against mild steel corrosion in HCl (1.0M). The paper is aimed at investigating the Phyllanthus mellerianus stem inhibition properties for mild steel corrosion in 1.0 M HCl solution. The considered the adsorption, kinetics, and thermodynamic properties of ethanol extract from PM stem on mild steel metal. The choice of mild steel is based on its vest industrial applications, whereas the choice of PM stem is based on its availability, chip, and eco-friendly. In most regions, it is seen as a weed and served as biomass waste.

2.0 METHODOLOGY

2.1. 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 sand paper to produce a smooth finish shape then cleaned and washed with absolute alcohol (ethanol) and dry with acetone before each of the coupons were weighted.

2.2. Corrosive Medium

The corrodent used was a concentrated hydrochloric acid of 1.0M, and different concentrations of stem extract of *Phyllanthus mellerianus* were tested for their potential to inhibit the activity of the acid.

2.3. Inhibitor Preparation (Phyllanthus mellerianus)

The stems of *Phyllanthus mellerianus*, (nvo nkwu) was collected from Agbani in Nkanu LGA and Aku in Igbo Etiti LGA area of Enugu state and was identified in Department of Microbiology, Enugu State University of Science and Technology (ESUT). It was properly dried in a shade for 2–4 weeks, then it was ground to powder using wood land electric grinding machine and stored in air tight bottles. The ethanol extraction was achieved a conventional Soxhlet extraction system and the solvent was removed with a rotary evaporator. The inhibitor, *phyllanthus mellerianus* was prepared following masses: 0.1g, 0.2g, 0.3g, 0.4g and 0.5g, and were each dissolved in 100ml of distilled water.

2.4. Gravimetric Measurement and Hydrogen Evolution

The rectangular mild steel specimens of dimension: thickness =0.026cm, width =0.17cm, height =0.17cm were immersed (complete immersion) in 100 mL of deaerated electrolyte in the absence and presence of different concentrations of *Phyllanthus mellerianus* at different temperature of 303 K, 303K and 323K. The weight loss of mild steel specimens was determined after 1 hours of immersion for the duration of 5 hours [3].

2.5. 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 [12].

The gasometric assembly measures the volume of hydrogen gas evolution from the reaction system, about five coupon 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 temperature of 30 – 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 extrapolated the parameters by changing the wight to volume [13].

2.6. Determination of Inhibition effect of the Phyllanthus mellerianus Extract

In order to investigate the corrosion inhibition effect of *Phyllanthus mellerianus* extract on mild steel in 0.5 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.[11] and James et al. [12], 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: $I\% = 1 - (W_I/W_2) \times 100$ and $1 - (V_I/V_2) \times 100$ respectively (2)
$Cr = \Delta W/At$, and $Cr = \Delta V/t$ (3)

ΔW and ΔV is 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,

2.7. Adsorption Isotherm and Adsorption Constant

Studies of adsorption isotherms provide a descriptive mechanism for how organic inhibitors adsorb on metal surfaces [6, 14, 15]. A linear fit of the corrosion rate (CR), the degree of surface coverage (θ), and inhibition efficiency to the Langmuir-Frendlich adsorption isotherm models yielded the best description of the effects of *Phyllanthus mellerianus* extract adsorption on mild steel in 0.5 M HCL medium:

Longmuir adsorption isotherm: $C/\theta = 1/K_{ads} + C_{inh}$ (4)
Freundlich adsorption isotherm, $\theta = Kads.\ C^{-n}$ (5)

Temkin adsorption isotherm, θ=InC +Kads (6)
El-awady's adsorption isotherm, log θ/1- θ=ylogC+logK (7)

2.8. Determination of Adsorption Thermodynamics Parameters

To investigate the feasibility and nature of the adsorption, the expression for Gibb's free energy change of adsorption, ΔG, presented in Equation (6) was used [6, 7].

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

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

2.9. Determination of Activation Energy (Ea)

The slope of the plot of ln CR against 1/T in Equation (9) was used to estimate the activation energy, Ea. The relationship between corrosion rate (CR) and temperature (T) is described by the Arrhenius equation as [3, 6].

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

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

2.10. Determination of Enthalpy and Entropy Change

The changes in enthalpy and entropy were calculated using Equation (8), an alternate form of the Arrhenius equation for the transition state [11, 19].

$$\text{Cr} = \frac{RT}{Nh}\exp(\Delta S/R)\exp(-\Delta H/RT) \quad (8)$$

$$\text{In}\ (Cr/T) = \{\text{In}\ (R/Nh) + \Delta S/R\} - \Delta H/RT \quad (9)$$

Where h is the Planck's constant (6.6261 x 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}

2.11. Determination of kinetics parameters (Rate constant and half – life)

The corrosion reaction is a heterogeneous reaction which is composed of anodic reactions at the same or different rates [6, 16]. The first order kinetics were employed and evaluated using the integral method of analysis. This is given by equation 10:

$$\text{Log}\ (\Delta W) = k_1\ t/2.303 \quad (10)$$

$$T_{1/2} = 0.693/k_1 \quad (11)$$

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), [17]

3. RESULTS AND DISCUSSIONS

3.1. FTIR Analysis of the Stem Extract of Phyllanthus Mellerianus

The FT-IR analysis was used to identify the functional groups of the active components present in the extract based on the peaks of IR active moieties. Table 1 shows the FTIR analysis of the ethanol extraction of Phyllanthus Mellerianus stem.

Table 1: FTIR Analysis of the Stem Extract of Phyllanthus Mellerianus

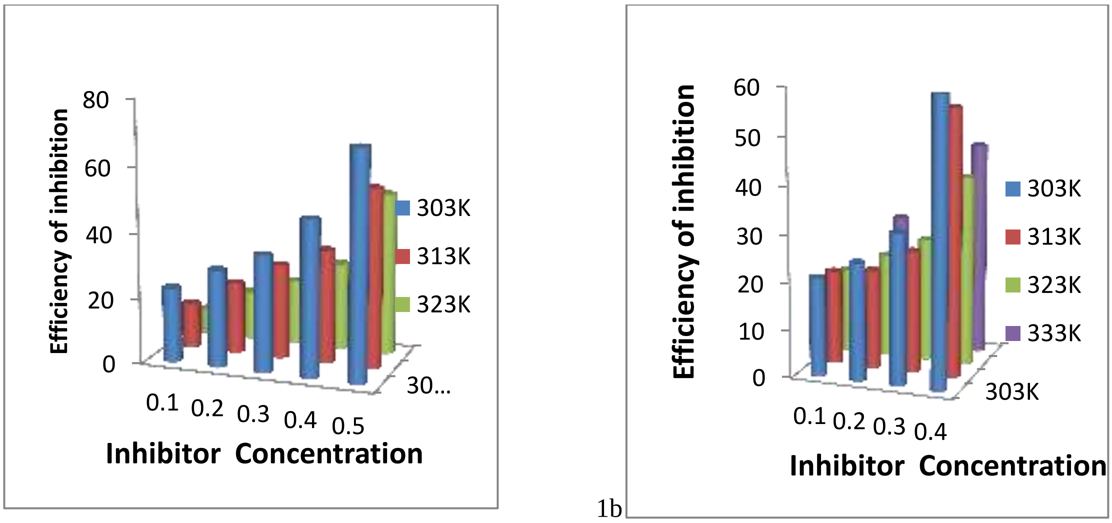
No	Vibration frequency (cm^{-1}) Stem extract	Vibration frequency (cm^{-1}) (literature)	Functional group assignment	Phyto compounds Identified
1	3543.56	3500-3700	O-H stretch,	Alcohols & Phenol
	2991.05	2850- 3000;	N-H stretching	Amine compound
2	2873.42	2970-2950	C-H stretch, Aliphatic	Alkanes,
3	2836.87 2850	2850-3000	C-H stretch, Ether group	Methoxy methyl ether
4	1716.34	1706-1720	C=O stretching	Carboxylic acid or Ketone,
5	1646.91	1640-1690	C=N stretching vibration	Imine/ Oxime in the compound
	1530.24	1500-1550	N-O stretching	Nitro-compound
6	1454.06	1400-1500	C=C-C, Aromatic	Aromatic compound

			ring stretch	
7	1246.75	1020-1250	C-N stretching	Amino compound
8	590.111	550- 850	-C-Cl bend vibration	alkyl halides
9	412-510	390-550	M-C, metal linked to carbon	Metal complexes

The results of FT-IR analysis confirmed the presence of nitrogen, oxygen, aromatic rings, halogen, and carbon-metal bonds. 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 Nsude and Orie [3], who worked on the phytochemical, qualitative and quantitative analysis of the ethanol leaf extract of *Phyllanthus mellerianus*. It also corroborates the phytochemical constituents estimated by Orubite and Ngobiri [14], Orie and Christian [17], and James & Akarenta [19].

3.2 Inhibition efficiency and Concentration of *Phyllanthus mellerianus* Stem

The data shown in Figure 1 explains the relationship between inhibition efficiency, concentration of inhibitor and temperature. The solution with a concentration of 0.5g of the inhibitor has the highest inhibition efficiency of 70% at 30 ^{o}C temperature for gravimetric analysis, whereas the hydrogen evolution method has the highest inhibition efficiency of 65% at 30 oC. There was a decrease in inhibition efficiency, as the temperature of the system increased from 30 ^{o}C to 50 ^{o}C for both gravimetric techniques and hydrogen evolution techniques. This trend of an increase in the efficiency of inhibition as a result of increased concentrations, and decreased temperatures is consistent with Orubite and Ngobiri [14], Don-Lawson et al. [20], and Nsude and Orie [3].



1a 1b

Figure 1: Efficiency of corrosion Inhibition *via* (a) Gravimetric techniques (b) Hydrogen evolution techniques

3.3 Corrosion Inhibition and Adsorption Isotherms of Mild Steel in Phyllanthus mellerianus Stem Ethanol Extract

The adsorption isotherm describes the reaction between the metal surface and the concentrations of the inhibitor, whereas the surface coverage (θ) indicates the extent to which inhibitor molecules cover the metal surface [3, 21]. The corrosion rate is delayed when there is an interaction between the metal surface and inhibitor molecules, leading to the adsorption of the inhibitor on the metal surface. The data in Table 2 were extrapolated from Figures 2 to 5, and it shows the Temkin adsorption isotherm, Freundlich adsorption isotherm, Langmuir adsorption isotherm and El-Awadys thermodynamic /kinetic adsorption isotherm of mild steel in *Phyllanthus mellerianus* stem ethanol extract of the data obtained from gravimetric techniques and hydrogen evolution techniques.

Table 2. Adsorption Isotherm of Phyllanthus mellerianus Stem Ethanol Extract

Gravimetric techniques				**Hydrogen evolution techniques**		
Langmuir adsorption isotherms				Langmuir adsorption isotherms		
Temp.	K_{ads}	ΔG^{O}_{ads} (KJ/mol)	R^2	K_{ads}	ΔG^{O}_{ads} (KJ/mol)	R^2
303	1.2459	-10.671	0.8497	1.263	-10.71	0.7636
313	1.1660	-10.851	0.9195	1.305	-11.44	0.9942
323	1.0624	-10.948	0.8788	1.571	-12.00	0.9775
				1.601	-12.423	0.9120

Freundlich adsorption isotherm			R^2	n	Freundlich adsorption isotherm			n
303	5.654	-13.157	0.952	0.11	9.383	-15.763	0.988	0.15
313	8.972	-16.162	0.980	0.13	7.762	-15.782	0.890	0.33
323	17.023	-18.397	0.978	0.75	7.789	-16.298	0.947	0.12
333					9.386	-17.320	0.973	0.16
El-awadys adsorption isotherms			y		El-awadys adsorption isotherms			y
303	1.5929	-10.290	0.9527	0.202	1.6565	-11.389	0.9942	0.219
313	1.5520	-11.596	0.9864	0.191	1.1.453	-11.481	0.7943	0.172
323	1.3388	-11.569	0.9786	0.228	1.4568	-11.796	0.9270	0.163
					1.3427	-11.935	0.9177	0.122
Temkin adsorption isotherms					Temkin adsorption isotherms			
303	1.2809	-10.741	0.9903		1.3311	-10.838	0.9205	
313	1.2251	-10.980	0.9882		1.1819	-10.887	0.4412	
323	1.2190	-11.317	0.9790		1.1860	-11.243	0.8864	
333					1.2485	-11.734	0.9215	

Based on Table 2 and Figures 2 to 5, the R^2 values obtained from the linear regression of the experimental data showed they are close to unity, which suggests that the molecules in the stem ethanol extract of *Phyllanthus mellerianus are* adsorbed on the surface of mild steel and are strongly fitted to Temkin, Langmuir, El-Awadys, and Freundlich isotherms, considering the two techniques in the research. This is consistent with Umoren et al. [13], Oloruntoba et al. [22], and Orie et al. [11], who worked on different adsorption isotherms via organic corrosion inhibitor.

The graphs at elevated temperatures have a straight line relationship that indicates that the extract from the stem of PM followed all the adsorption isotherms in the two methods considered, except for the Temkin isotherm of hydrogen evolution technique, with an R^2 value of less than 0.5 at the temperature of 313K. The R^2 value of less than 0.5 implies less interaction of the inhibitor molecules with the metal surface. This is in conformity with James and Akarenta [19], who worked on an extract of red onion skin, and Okewale and Adesina [23], who researched cocoa leaf, and Nsude and Orie [3], who worked on the leaf extract of *Phyllanthus mellerianus*. Their adsorption isotherm investigation followed the same pattern.

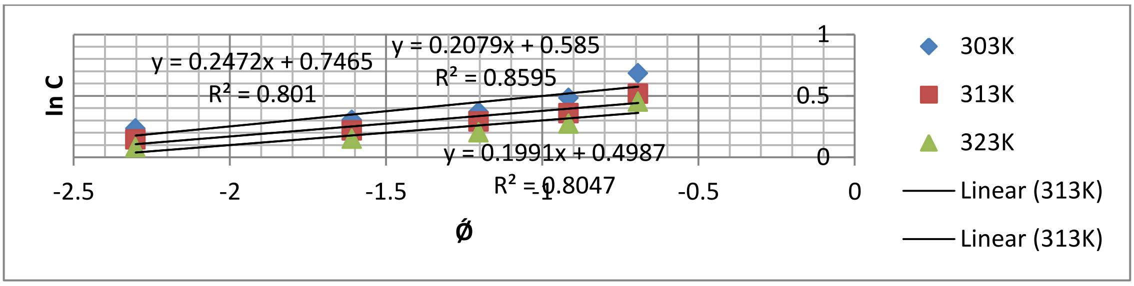


Figure 2: T***emkin Adsorption Isotherm Study of Phyllanthus Mellerianus Stem Extract for Inhibitor On Mild Steel Surface***

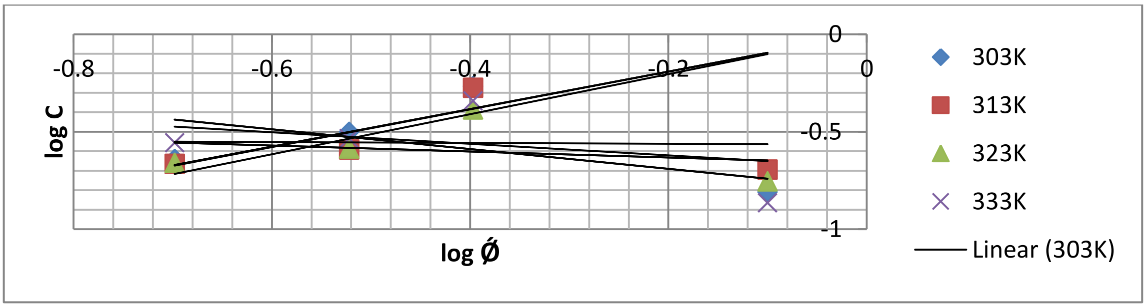


Figure 3*: Freundlich Adsorption Isotherm Analysis of Phyllanthus Mellerianus Stem*

Extract for Inhibitor on Mild Steel Surface

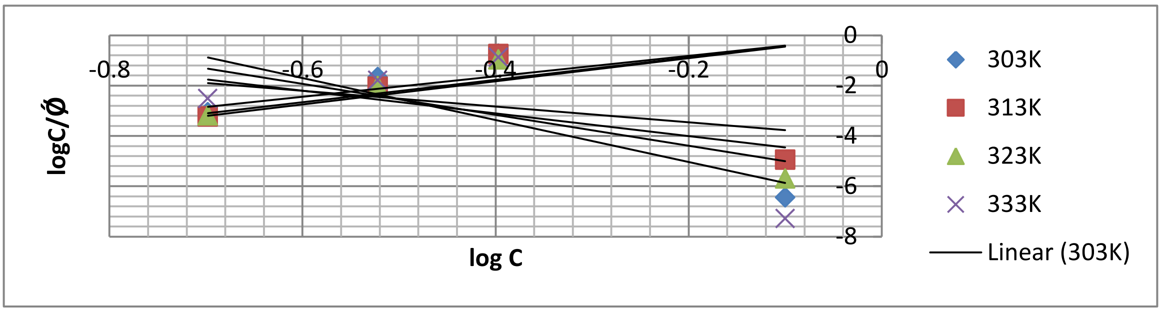


Figure4: Langumuir Adsorption Isotherm ***Analysis of Phyllanthus Mellerianus Stem Extract For Inhibitor On Mild Steel Surface***

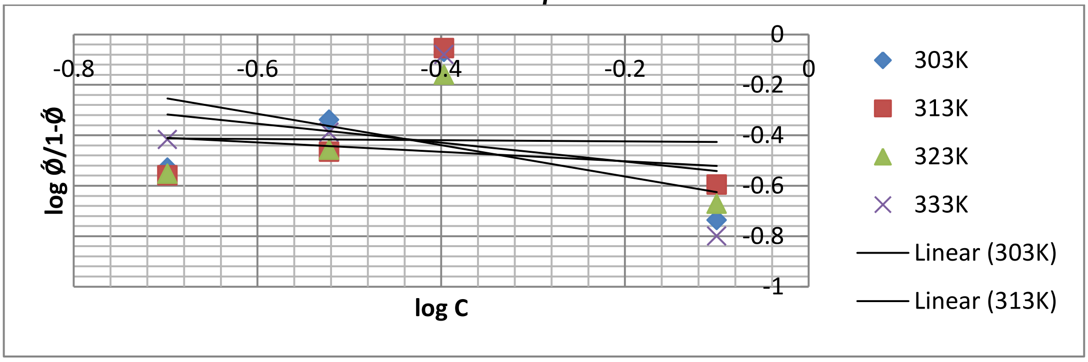


Figure 5: ***El-Awadys Thermodynamic /Kinetic Isotherm Adsorption Analysis of Phyllanthus Mellerianus Stem Extract for Inhibitor on Mild Steel Surface***

3.4 Corrosion inhibition and Kinetics investigation of Mild Steel in *Phyllanthus mellerianus* Stem Ethanol Extract

The rate constant (k) indicates how fast or slow a given chemical reaction occurs, i.e., high and low rate constant values signify faster and slower rates, respectively. Table 3 shows that the k values are high in the blank solution and are lower at increased concentrations of inhibitor. This signifies that the inhibitor retarded the mild steel corrosion rate in 1.0 M HCl. The t1/2 value was calculated and is presented in Table 4. It was observed that the $t_{1/2}$ values increased with higher inhibitor concentrations. This shows that PM raised the $t_{1/2}$ values, thereby reducing the rate at which mild steel corroded in the acidic medium. The findings were in conformity with Okewale and Adesina [23], Orie & Christian [18], and Nwosu & Muzakir [21], who researched the adsorption and kinetic studies of plants on different metals.

Table 3: Kinetics investigation of Mild Steel in PM Stem Ethanol Extract

Concentration g/l	Rate const. k (hr^{-1})	Half life (hr)	R^2
0.0	1.2422	3.1950	0.9721
0.1	1.0935	7.7516	0.8890
0.2	1.0851	8.4822	0.7872
0.3	1.0851	8.5344	1.0846
0.4	1.0718	10.8450	0.9318
0.5	0.0456	15.197	0.9587

Figure 6 depicts the plot of In(ΔW) against exposure time in (hours) in the presence and absence of inhibitor extracted from the stem of *Phyllanthus mellerianus*. The plot showed a linear relationship between the slope and the rate constant, thus confirming a first order kinetics on the corrosion of mild steel in hydrochloric acid using PM stem extract as an inhibitor. The high value of the correlation coefficient obtained showed that the experimental value fitted well to the first order kinetics. This result is in conformity with reports of Olasehinde *et al*. [7] and Orie & Christian [18], who worked on different plant extracts.

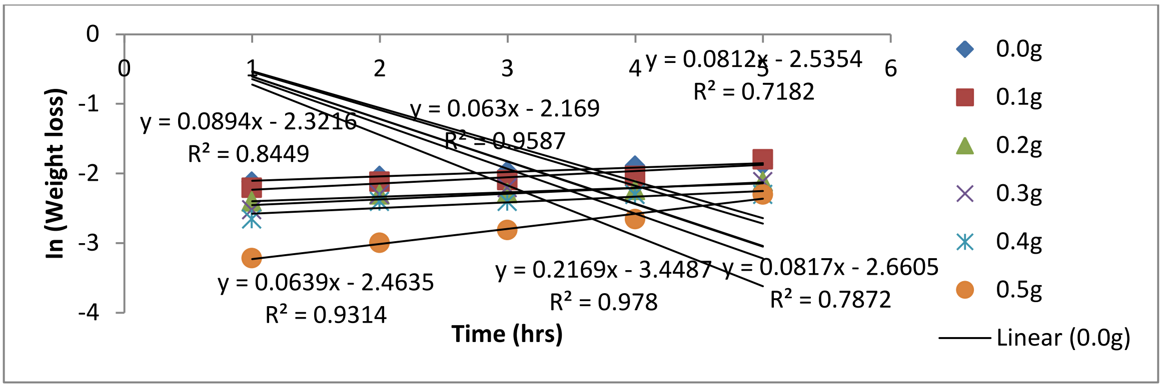


Figure 6. *Kinetics analysis of Phyllanthus Mellerianus Stem Extract for Inhibitor of Mild Steel Surface*

3.5 Gibb's Free Energy Change in the Adsorption of Mild Steel in Phyllanthus mellerianus Stem Ethanol Extract

In general, values of change in Gibb's free energy of adsorption around -20 kJ mol-1 or lower are coherent with electrostatic interaction between charged molecules and charged metals (physical adsorption); those around -40 kJ mol-1 or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [3, 13, 22]. As seen in Table 5, 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 ethanol extract of PM stem 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 343 K suggests that the adsorption was more spontaneous and stable as the temperature rose. An additional finding from the experiment's data in Table 2 was the high degree of consistency between the two experimental methods (gravimetric and hydrogen evolution techniques). This is consistent with Iroha & James, [24] and Okaforet al. []10] who worked on the leaf extract.

*3.6*Activation Energy (Ea) of Stem Ethanol Extract of *Phyllanthus mellerianus* for Mild Steel Corrosion Inhibition

The minimum amount of energy that is required to activate molecules to a condition in which they can undergo chemical transformation or physical transport [25]. In transition-state theory, the 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. Table 4 contains the activation energy and Arrhenius factor of stem ethanol extract of PM for corrosion inhibition of mild steel.

Table 4: Thermodynamic parameters for mild steel in the presence and absence of inhibitor

Concentration of inhibitor	A	Ea (kJ mol^{-1})	-ΔH° (kJ mol^{-1})	ΔS° (Jmol^{-1}K^{-1})
blank	I.018	8.74	-8.70	-196.89
0.1g/l	1.056	9.16	-9.10	-196.59
0.2g/l	5.33	13.65	-13.56	-183.12
0.3g/l	3.85	12.97	-13.05	-185.91
0.4g/l	36.30	14.89	-14.81	-180.32
0.5g/l	36.30	20.45	-21.28	-167.18

With an increasing concentration of PM stem extract, corrosion activation values increase. The blank solution has less activation energy than the solution with corrosion inhibitor, and the activation energy increases as the concentration of the inhibitor increases. This is because of the molecular barrier that mild steel creates by adsorbing molecules of PM stem ethanol extract. It is based on the fact that more corrosion reactions on a better protected surface will require more energy to occur. There has been a trend of increasing Ea values as well as inhibitor concentrations reported by other researchers in studies on various plant extracts, such as jujube leaves, black pepper [26], breadfruit peel [18], leaf extract of *Phyllanthus* mellerianus [3], sunflower leaves [27] and piper nigrum extract [28]. The corrosion mechanism can be attributed to physical adsorption (physisorption) because the Ea increased in the presence of the inhibitor compared to the blank. An increase in Ea values clearly indicated that mild steel surfaces had been physically adsorbed with inhibitor molecules. This is associated with the electrostatic force between the negatively charged metal surface and the positively charged organic species [29]. Physiosorption has an activation energy below 40 KJmol^{-1} and chemisorption has an activation energy above 80 KJmol^{-1} [28]. These findings are consistent with previous research by Abeng, *et al.* [30] and Zakir Hossain et al. [31]. The fluctuation in the activation energy could be based on the biological degradation of organic inhibitors, thereby losing their inhibition potential over time.

Figure 8 depicts log CR versus 1/T plots for different concentrations of *Phyllanthus mellerianus* stem extract. The slopes obtained from the plots are thus appropriate for estimating the activation energy of the process for different concentrations.

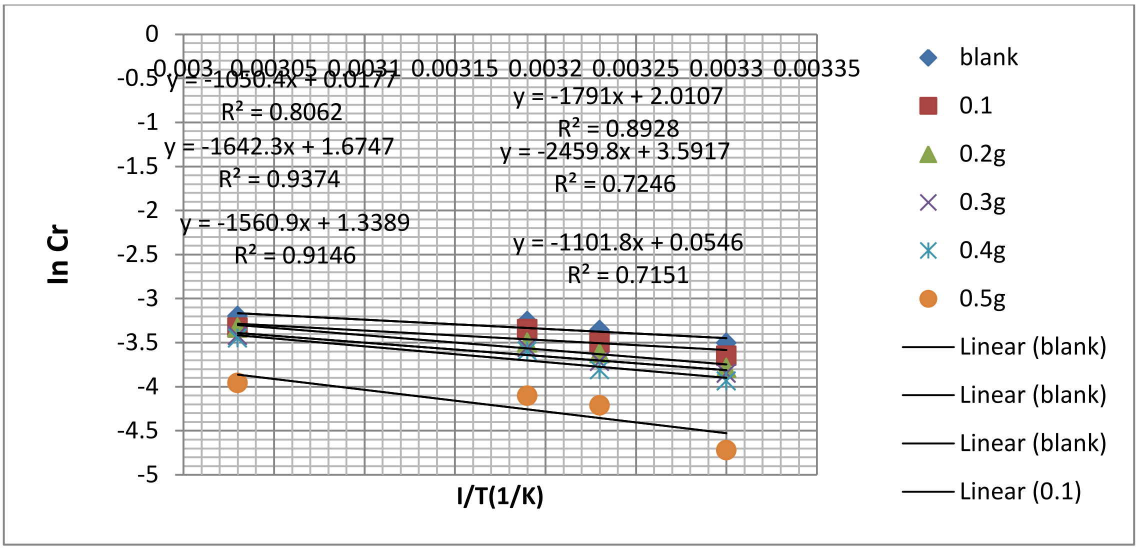


Figure 8 Activation Energy *Analysis of Phyllanthus Mellerianus Stem Extract for Inhibitor on Mild Steel Surface*

3.7 Enthalpy and entropy change investigation of mild steel in Phyllanthus mellerianus ethanol extract

The values of enthalpy change, ΔH and entropy change, ΔS obtained at different concentrations of *Phyllanthus mellerianus* stem extract are shown in Table 4, and a chart showing the relationship of InCr/T and inverse of temperature is shown in Figure 8. The values of ΔH at different concentrations of inhibitor were negative and increased as the inhibitor's concentration increased. The negative sign of ΔH indicates that the extracted molecular adsorption is an exothermic process. In general, an exothermic process denotes physisorption [31].

The activation entropy (ΔS^{o}) was negative in the absence and presence of *Phyllanthus mellerianu* stem extract. 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. This result agrees with the work of Abeng, *et al.* [30]. Further observation shows that the Ea values are more significant than the values of ΔH. This result indicates that the corrosion process must have involved a gaseous reaction [27].

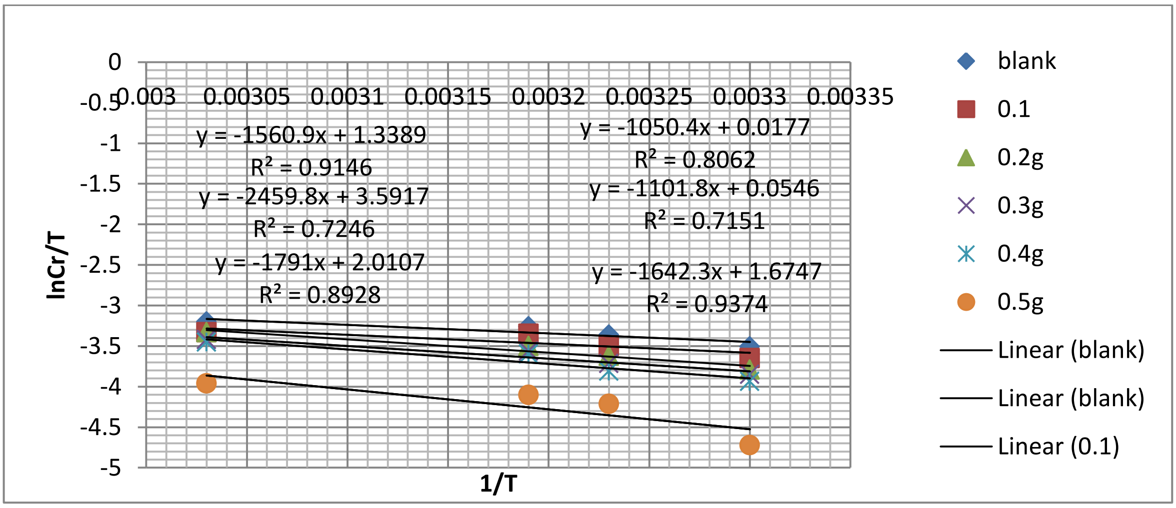


Figure 7: *Enthalpy and Entropy Study for Phyllanthus Mellerianus Stem Extract Inhibitor On Mild Steel Surface*

3.8 SEM analysis of the Corrosion Rate of Mild Steel in 1.0M HCl Acid Corrodent and Inhibitor

The SEM analysis reveals the elemental composition and the morphology of the mild steel surface. It also reveals the components of mild steel coupons that are affected by the corrodent and the efficiency of the ethanol extract of *Phyllanthus Mellerianus* stem. Table 5 shows the SEM analysis of mild steel coupons in the presence and absence of inhibitor for a period of 5 days.

Table 5: SEM Analysis of Mild Steel in Presence and Absence of Inhibitor

No.	Elements	Raw coupon (%)	Acid Coupon	Inhibited coupon
1	Iron	68.15	50.0	65.0
2	Copper	0.132	-	0.15
3	Calcium	2.00	0.79	1.60
4	Magnesium	2.00	1.45	1.89
5	Manganese	0.25	-	0.125
6	Zinc	8.50	7.12	8.22
7	Chromium	-	-	-
8	Sodium	2.22	1.42	2.10
9	Carbon	3.54	3.00	3.30
10	Oxygen	10.00	10.35	20.10

The SEM analysis of the raw, acid, and inhibited mild steel coupons reveals that the percentage values of the elements in the acid mild steel coupon were reduced when compared with the raw and inhibited mild steel coupon. All the metallic elements showed a lower percentage value, which implies that the HCl (1.0M) affected the metals, thus contributing to the deterioration of the mild steel coupon [24, 25]. In the presence of ethanol extract of *Phyllanthus Mellerianus* stem, the percentage composition of each metal was reduced but was better than in the element acid medium (see Table 5). Among the metals in the mild steel, metallic iron was highly corroded with a percentage value of 50.00% in HCl (1.0 M) and 65.0% in the presence of inhibitor.

Figure 8 depicts the morphology of mild steel used with and without inhibitor. Figure 8b shows a rough surface, characterised by a uniform pits showing corrosion of mild steel in acid, whereas figures 8a and 8c show unused and inhibited coupons. The mild steel coupon in figure 8c has some deposition on the surface of the metal, indicating the adsorbed layer of PM stem ethanol extract.

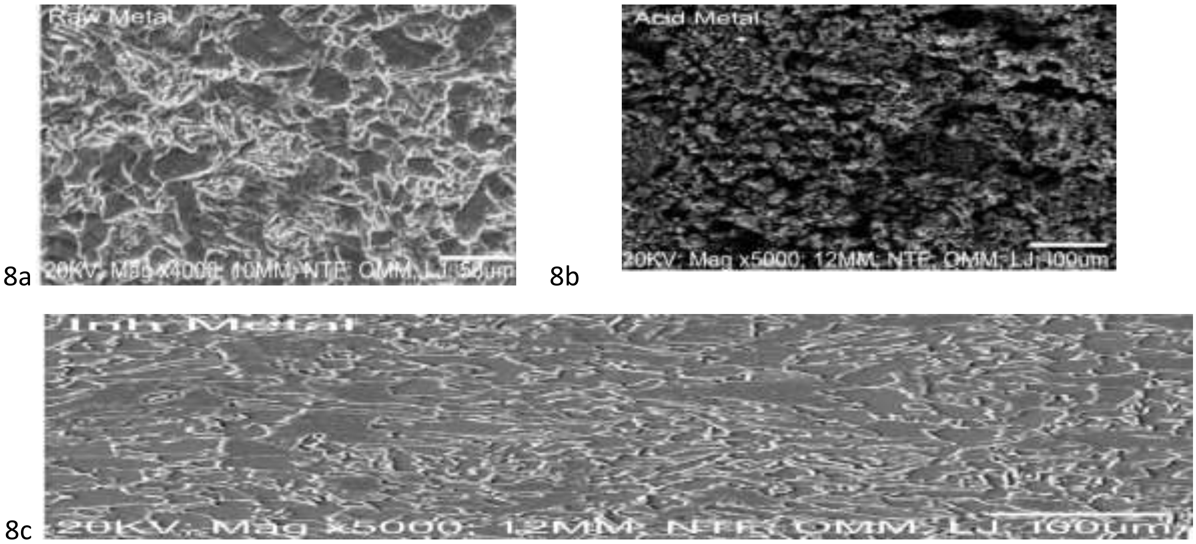


Figure 8; Morphology Structure of Mild Steel (8a) Raw Coupon (8b) Acid Coupon (8c) Inhibited Coupon

4.0 CONCLUSION

*T*he research reports the adsorption, thermodynamic, and kinetic investigation of corrosion inhibition of mild steel in an acid medium *via an* ethanolic extract of *Phyllanthus mellerianus* stem. The powdered sample was extracted with ethanol and concentrated with a rotary evaporator. The samples were prepared in different concentrations, along with the corrodent. The functional groups were investigated via FTIR analysis, with affirmation of the presence of the functional groups that contain nitrogen, oxygen, sulphur, carbohydrate aromatic rings, and metallic complexes. The two methods adopted in the research were gravimetric and hydrogen evolution techniques. The inhibition efficiency, enthalpy, enthropy, activation energy, Gibbs free energy, and different adsorption isothems were extrapolated with some models. The inhibition efficiency increased with an increase in the concentration of the extract. The values of ΔGads, obtained between 303K, 313K, and 323K, were all negative, indicating that the inhibitors are strongly adsorbed on mild steel surfaces and that the adsorption process is spontaneous and stable. The inhibition effectiveness of extracts has been attributed to the presence of the hetero atoms N, O, and S present in their phytochemical composition.

REFERENCES

1. *Oguzie, E. E. (2005). Inhibition of acid corrosion of mild steel by Telfaria occidentalis extract. Pigment & Resin Technology.*
2. *Singh, A. K., Chugh, B., Saha, S. K., Banerjee, P., Ebenso, E. E., Thakur, S., & Pani, B. (2019). Evaluation of anti-corrosion performance of an expired semi synthetic antibiotic cefdinir for mild steel in 1 M HCl medium: An experimental and theoretical study. Results in Physics, 14, 102383.*
3. *Nsude O. P. & Orie K. J. (2022). Thermodynamic and adsorption Analysis of corrosion inhibition of mild steel in 0.5M HCl medium via ethanol extracts of Phyllanthus mellerianus. American Journal of Applied Chemistry, 10(3) 67-75*
4. *Chauhan, L. R., & Gunasekaran, G. (2007). Corrosion inhibition of mild steel by plant extract in dilute HCl medium. Corrosion science, 49(3), 1143-1161.*
5. *Alaneme, K. K., Olusegun, S. J., & Adelowo, O. T. (2016). Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions. Alexandria Engineering Journal, 55(1), 673-681.*
6. *Hussin, M. H., Kassim, M. J., Razali, N. N., Dahon, N. H., & Nasshorudin, D. (2016). The effect of Tinospora crispa extracts as a natural mild steel corrosion inhibitor in 1 M HCl solution. Arabian Journal of Chemistry, 9, S616-S624.*
7. *Olasehinde, E. F., Ogunjobi, J. K., Akinlosotu, O. M., & Omogbehin, S. A. (2015). Investigation of the Inhibitive Properties of Alchornea laxiflora leaves on the Corrosion of Mild Steel in HCl: Thermodynamics and Kinetic Study.*
8. *Harborne, I. B (1973) Phytochemical methods: A guide to modern techniques of plant analysis. 2nd Edition, Chapman and Hall, New York, 88-185.*
9. *Ogbuanu, C. C., Amujiogu, S. N., Ehiri, R. C., Omaka, O. N., Lloh, M., Chime, C. C. & aneke. I. B. (2013) Phytochemical and Antibiotic Screening of phyllanthus mellerianus plant. World journal of biotechnology. 14 (2); 2148-2153.*
10. *Okafor, P. C., Ebenso, E. E., & Ekpe, U. J. (2010). Azadirachta indica extracts as corrosion inhibitor for mild steel in acid medium. Int. J. Electrochem. Sci, 5 (7), 978-993.*
11. *Orie, K. J., James, A. O., & Akaranta, O. (2015). The Corrosion Inhibition of Mild Steel in 0.5 m Phosphoric Acid and Crown Cork in Water By Folic Acid. International Journal of Science and Research (IJSR), 4, 1380-1385.*
12. *James, A. O., Oforka, N. C., Abiola, O. K., & Ita, B. I. (2007). A study on the inhibition of mild steel corrosion in hydrochloric acid by pyridoxol hydrochloride. Eclética Química, 32 (3), 31-37.*
13. *Umoren, S. A., Ogbobe, O., Igwe, I. O., & Ebenso, E. E. (2008). Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives. Corrosion science, 50 (7), 1998-2006.*
14. *Ngobiri, N., & Okorosaye-Orubite, K. (2017). Adsorption and corrosion inhibition characteristics of two medicinal molecules. Chem. Int, 3, 185.*
15. *Arukalam, I. O., Madufor, I. C., Ogbobe, O., & Oguzie, E. E. (2016). Understanding the Influence of Molecular Weight on the Corrosion Inhibition Performance of Two Cellulosic Polymers. environment, 10, 12.*
16. *Nwabanne, J. T., & Okafor, V. N. (2012). Adsorption and thermodynamics study of the inhibition of corrosion of mild steel in H 2 SO 4 medium using Vernonia amygdalina. Journal of Minerals and Materials Characterization and engineering, 11(09), 885.*
17. *Njoku, V. O. (2014). Biosorption potential of cocoa pod husk for the removal of Zn (II) from aqueous phase. Journal of Environmental Chemical Engineering, 2(2), 881-887.*
18. *Orie, K. J., & Christian, M. (2015). The Corrosion Inhibition of Aluminium Metal in 0.5 M Sulphuric Acid Using Extract Of Breadfruit Peels. International Research Journal of Engineering and Technology (IRJET), 2 (8), 2395-0072.*
19. *James, A. O. & Akarenta, O. (2002). Corrision Inhibition of Aluminum in Hydrochloric Acid Solution by the Action Extract of Red Onion Skin, African Journal of Fine & Applied Chemistry, 12, 262 – 268*
20. *Don-Lawson, C., Okah, R., & Orie, K. J. (2020)Synthesis and corrosion inhibition study of mild steel in 0.5 M hydrochloric acid by 1-((2-arbamoylguanidino) (furan-2-ylmethyl) urea. Direct Research Journal of Chemistry and Material Science.7 (1), 1-6.*
21. *Nwosu, F. O., & Muzakir, M. M. (2016). Thermodynamic and adsorption studies of corrosion inhibition of mild steel using lignin from siam weed (Chromolaena odorata) in acid medium. J. Mater. Environ. Sci, 7 (5), 1663-1673.*
22. *Oloruntoba, D. T., Abbas, J. A., & Olusegun, S. J. (2012). Water hyacinth (eichhornia crassipes) leaves extract as corrosion Inhibitor for AISI 1030 steel in sea water. Proceedings of 4th West Africa Built Environment Research (WABER), 1131-1140.*
23. *Okewale, A. O., & Adesina, O. A. (2020). Kinetics and thermodynamic study of corrosion inhibition of mild steel in 1.5 M HCl medium using cocoa leaf extract as inhibitor. Journal of Applied Sciences and Environmental Management, 24 (1), 37-47*
24. *Iroha, N. B., & James, A. O. (2018). Assessment of performance of velvet tamarind-furfural resin as corrosion inhibitor for mild steel in acidic solution. Journal of Chemical Society of Nigeria, 43(3).*
25. *Mathew, C., & Orie, K. J. (2015). Roadside Sand Deposits as Toxic Metals' Receptacles along three Major Roads in Port Harcourt Metropolis, Nigeria.*
26. *Quraishi, M. A., & Shukla, S. K. (2009). Poly (aniline-formaldehyde): a new and effective corrosion inhibitor for mild steel in hydrochloric acid. Materials Chemistry and Physics, 113 (2-3), 685-689.*
27. *Cang, H., Shi, W., Shao, J., & Xu, Q. (2012). Study of Stevia rebaudiana leaves as green corrosion inhibitor for mild steel in sulphuric acid by electrochemical techniques. Int. J. Electrochem. Sci, 7(4), 3726-3736.*
28. *Shivakumar, S. S., & Mohana, K. N. S. (2012). Ziziphus mauritiana leaves extracts as corrosion inhibitor for mild steel in H2SO4 and HCl solutions. European Journal of Chemistry, 3(4), 426-432.*
29. *Akinbulumo, O. A., Odejobi, O. J., & Odekanle, E. L. (2020). Thermodynamics and adsorption study of the corrosion inhibition of mild steel by Euphorbia heterophylla L. extract in 1.5 M HCl. Results in Materials, 5, 100074.*
30. *Abeng, F. E., Idim, V. D., & Nna, P. J. (2017). Kinetics and thermodynamic studies of corrosion inhibition of mild steel using Methanolic extract of erigeron floribundus (Kunth) in 2 M HCl solution. World news of natural sciences, 10.*
31. *Zakir Hossain, S. M., Kareem, S. A., Alshater, A. F., Alzubair, H., Razzak, S. A., & Hossain, M. M. (2020). Effects of cinnamaldehyde as an eco-friendly corrosion inhibitor on mild steel in aerated NaCl solutions. Arabian Journal for Science and Engineering, 45 (1), 229-239*