

Thermodynamic and Adsorption Analysis of Corrosion Inhibition of Mild Steel in 0.5M HCl Medium via Ethanol Extracts of *Phyllanthus mellerianus*

Okechukwu Paul Nsude¹, Kingsley John Orie^{2, *}

¹Department of Industrial Chemistry, Enugu State University of Science and Technology, Enugu, Nigeria

²Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

Email address:

Oriekingsley81@gmail.com (K. J. Orie)

*Corresponding author

To cite this article:

Okechukwu Paul Nsude, Kingsley John Orie. 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*. Vol. 10, No. 3, 2022, pp. 67-75.

doi: 10.11648/j.ajac.20221003.12

Received: May 6, 2022; Accepted: May 23, 2022; Published: May 31, 2022

Abstract: The corrosion of mild steel is a problem in industrial processes based on its deterioration on exposure to acids, alkalis, and salt solutions. This issue has prompted an increase in research interest in order to mitigate the harmful effects of corrosion on metals and their alloys. The thermodynamic and adsorption analysis of mild steel in 0.5M hydrochloric acid solutions via ethanol leaf extract of *Phyllanthus mellerianus* was investigated using weight loss and hydrogen evolution techniques. The powdered sample was extracted with ethanol and concentrated with a rotary evaporator. The phytochemical analysis reveals the presence of tannins, flavonoids, phenols, and terpenoids at reasonable percentages. 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. The values of change in Gibbs free energy obtained at 303K, 313K, and 323K were negative, indicating that the leaf extract of *Phyllanthus mellerianus* was strongly adsorbed on mild steel surfaces and stable at high temperatures. The enthalpy of activation ranges from 43.08kJ/mol to 80.64kJ/mol. An increase in activation energy with inhibitor concentration confirmed the physical (physisorption) adsorption mechanism for the corrosion of mild steel surfaces. The R² values obtained from the linear regression are strongly fitted to the Langmuir and freundlich isotherms. The inhibitory effectiveness of extracts has been attributed to the presence of the hetero atoms N, O, and S present in their phytochemical composition.

Keywords: Adsorption, Corrosion Inhibition, Mild Steel, *Phyllanthus mellerianus*, Thermodynamic Parameters

1. Introduction

Corrosion is a natural phenomenon that degrades the metallic properties of metals and alloys, making them unsuitable for specific roles. Metal corrosion is a major industrial concern that has attracted much research. Metals are susceptible to corrosion when exposed to aggressive media (acid, base, or salt). Several steps have been taken to reduce the threat of corrosion to industrial facilities [1, 2]. Corrosion Scientists and engineers have long been concerned about the persistence of corrosion on metal structures. This is attributed to its recurring issue that is difficult to eliminate from metals [3]. Mild steel is one of the most desirable metal

alloys in the industry. It contains carbon, silicon, phosphorous, sulphur, manganese, and iron (98.9%) [2].

Corrosion reactions change the composition and properties of both the metal surface and the local environment, such as oxide formation, metal cation diffusion into the coating matrix, local pH, and electrochemical potential [4].

Recent studies on corrosion inhibition have focused on natural, non-toxic, plant-based inhibitors. These compounds, whether aromatic or aliphatic, have been shown to have an inhibitory effect via gain, loss, and structural arrangement [5, 6].

Phyllanthus mellerianus is a small, frequently stunted tropical plant found throughout West Africa. It occurs in savannahs and drier secondary forests as a glabrous shrub or woody climber

that is occasionally arborescent, as well as coastal thickets and scrub, and is found throughout tropical Africa [7, 8]. The leaf and the back extract were also found to have good antibacterial activity at high concentrations. Its ethanol extract and phytochemicals are sensitive to *Staphylococcus aureus*, *Streptococcus faecalis*, and *Neisseria gonorrhoea* [8].

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* [9], water hyacinth [10], bread food peel [11], *Tinosporacrispa* [12], *Citrus aurantium* leaves [13], Folic Acid [5].

Because acids (HCl, H₂SO₄, H₃PO₄, etc.) are commonly used for pickling, industrial cleaning, descaling, and other purposes, acid media are always used in the study of mild steel corrosion [11]. Corrosion damage caused by metal exposure to these media results in a decrease in the functional properties of materials. Various methods have been used to protect mild steel from corrosion, including material upgrades, production fluid blending, process control, and chemical inhibition [2, 3, 14].

This paper reports the inhibition effects of *Phyllanthus mellerianus* on mild steel through 0.5 M HCl hydrochloric acid as a corrodent. This is in furtherance of the search for efficient eco-friendly corrosion inhibitors for mild steel in hydrochloric acid.

2. Methodology

2.1. Preparation of Mild Steel Coupon

Mild Steel coupon (with % compositions listed as follows Fe = 86.500%, Ni = 0.005%, Cu = 0.130%, Ca = 0.048, Mg = 0.006%, Mn = 0.125%, Cd = 0.011%, Cr = 0.004%) was mechanically press cut to, 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 0.5M, and different concentrations of *Phyllanthus mellerianus* were tested for their potential to inhibit the activity of the acid.

2.3. Inhibitor Preparation (*Phyllanthus mellerianus*)

The leaves 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 1 – 2 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.

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 [3].

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 (0.5M HCl with the five different concentrations of investigated inhibitors from 0.1 – 0.5 g and at temperature of 30 – 60°C. A 50 cm³ 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 [15].

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 Orié et al. [5] and James et al. [2], who used Equations (1) to (3) to substantiate their claims.

$$\text{Weight loss/ volume loss: } \Delta W = W_1 - W_f \text{ and } \Delta V = V_i - V_f \quad (1)$$

$$\text{Inhibition efficiency: } I\% = 1 - (W_f/W_2) \times 100 \text{ and } 1 - (V_f/V_2) \times 100 \text{ respectively} \quad (2)$$

$$Cr = \Delta W/At, \text{ and } Cr = \Delta V/t \quad (3)$$

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 [3, 13]. 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:

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

$$\text{Freundlich adsorption isotherm, } \theta = K_{\text{ads}} \cdot C^{-n} \quad (5)$$

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 [13, 14].

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K_{\text{ads}}) \quad (6)$$

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 (7) was used to estimate the activation energy, E_a . The relationship between corrosion rate (CR) and temperature (T) is described by the Arrhenius equation as [15, 16].

$$\ln Cr = \ln A - E_a/RT \quad (7)$$

E_a 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 $\ln Cr$ against $1/T$, the slope= E_a/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 [12, 14].

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

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

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

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

3. Results and Discussions

3.1. Phytochemical Screening of *Phyllanthus Mellerianus* Leaf Extract

Table 1 shows the presence of tannin, flavonoids, terpenoids and glycosides in the *phyllanthus mellerianus* leaf extract.

Table 1. Phytochemical Qualitative and Quantitative Analysis of *phyllanthus mellerianus*.

	Phytochemicals	Inference	Compositions in (mg/100g)
1	Tannins	++++	3250.4095
2	Flavonoids	+++	550.617
3	Alkaloids	+	1113.821
4	Saponins	+	0.4725
5	Phenols	++++	735.484
6	Steroids	++	0.287
7	Terpenoids	+++	670.433
8	Glycosides	+++	
9	Carbohydrates	++	

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

The table also shows the composition of the phytochemicals, with tannin and phenol abundantly present and high in concentration. Tannins are phenolic-based natural products that contain hydroxyl and aromatic rings. These phytochemicals have the capacity to 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 [15]. This also corroborates the work of Okofo and Ebenso [9], who research the inhibitory capacity of Carica papaya.

3.2. Effect of Temperature and Inhibitor Concentration on the Corrosion Rate of Mild Steel

Figures 1 and 2 show the relationship between corrosion rates, inhibitor's concentrations and temperature. The corrosion rate of mild steel increases as the temperature increases from 30°C-50°C. This could be attributed to metal dissolution, which is facilitated by high temperatures, and also consistent with the general rule that reaction rates increase with a 10°C rise in temperature. The molecule in reaction gains energy rapidly and effectively doubles the number of activated molecules at high temperatures [6, 11]. High Temperature increases the solubility of protective films on metals and their susceptibility to corrosion. The effects of inhibitor concentration on the corrosion rate of mild stills are depicted in Figures 1 and 2.

At the different temperatures considered, the charts show that the corrosion rate slows down as the inhibitor concentration rises. The observed inhibitive action of the extract of *phyllanthus mellerianus* could be attributed to the adsorption of its components on mild steel. The adsorbing

molecules form a layer that separates the metal surface from the aggressive medium. This layer blocks the corrosion sites, which stops the coupon from dissolving. Thus, the corrosion rate decreases with increased efficiency as well as the inhibitor's concentrations. The observation was consistent with Okoafor and Ebenso [9] that worked on *Carica papaya*, and Oloruntoba *et al.* [12] that worked on water hyacinth.

It was also observed in Figure 2 that *phyllanthus*

mellerianus ethanol extract has the highest inhibitive action at the concentration of 0.5g. This is associated with the multiple layers formed as a result of more leaf extract of the inhibitor. A comparison of the time considered during the reaction (Figure 2), the corrosion rate at 0.5g concentration indicates that the ethanol extract of *phyllanthus mellerianus* was stable and offered inhibition to mild steel throughout the period of the reaction [11].

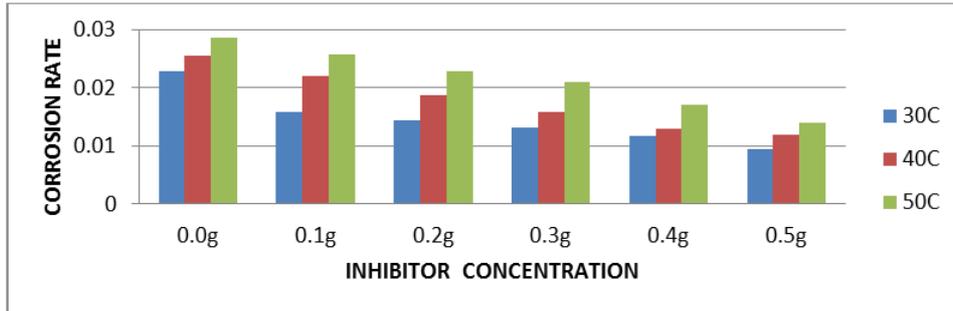


Figure 1. Variation in of inhibitors concentration and corrosion rate over temperature in 0.5M HCl.

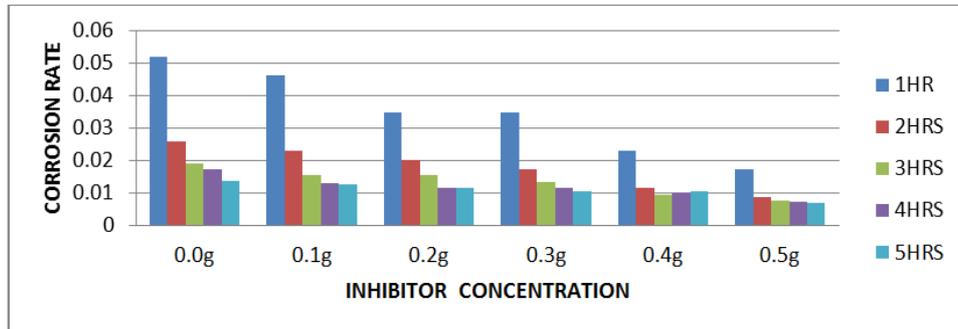


Figure 2. Variation in of inhibitors concentration and corrosion rate over time in 0.5M HCl.

3.3. Effect of Temperature and Inhibitor Concentration on Hydrogen Evolution Rate of Mild Steel

Figures 3 and 4 show the hydrogen evolution rate and inhibitor concentration at a temperature of 30–60°C. In a basic reaction, metals liberate hydrogen gas from acidic solutions. It must be mentioned that the hydrogen evolution technique enables us to assess the inhibitory effect of the inhibitor at very high corrosive concentrations. From the graph, the blank at each of the different temperatures considered has a high hydrogen gas evolution rate. The

increase in the concentration of inhibitors leads to a reduction in the hydrogen evolution rate. The increase in temperature illustrated in the chart corresponds to an increase in the gas evolved. This finding corroborates with Fouda *et al.* [16] that reported the dissolution of inhibitors' protective films at increasing temperatures. The charts (Figures 3 and 4) show that the concentration of 0.4 g has the highest inhibition with the lowest hydrogen gas evolution. The maximum effectiveness of that inhibitor was 0.4g at 80 minutes, which means that more of it slows down corrosion.

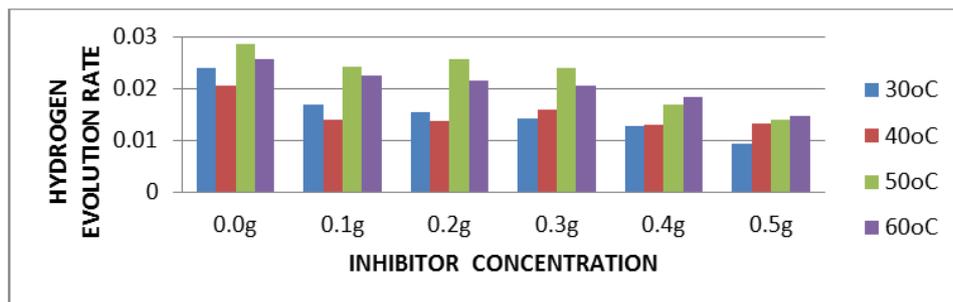


Figure 3. Variation in of inhibitors concentration and hydrogen evolution rate over temperature in 0.5M HCl.

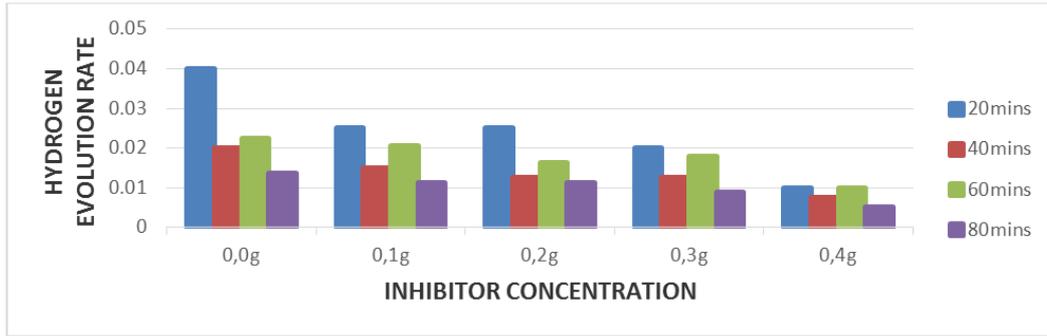


Figure 4. Variation in of inhibitors concentration and hydrogen evolution rate over time in 0.5M HCl.

3.4. Corrosion Inhibition and Adsorption Isotherms of Mild Steel in *Phyllanthus mellerianus* Ethanol Extract

The adsorption isotherm describes the reaction between the metal surface and the inhibitor, whereas the surface coverage (θ) indicates the extent to which inhibitor molecules cover the metal surface [1, 2, 17]. By establishing an interaction with the metal surface,

inhibitor molecules delay the corrosion process. Thus, the molecules are said to be inhibited when they are adsorbed on the metal surface. The data in table 2 are extrapolated from figures 5 to 8, and it shows the Langmuir adsorption isotherm and Freundlich adsorption isotherm of *Phyllanthus mellerianus* ethanol extract. The data were obtained from gravimetric and hydrogen evolution techniques.

Table 2. Adsorption Isotherm of *Phyllanthus mellerianus*.

Langmuir adsorption isotherms				Freundlich adsorption isotherm			
Gravimetric techniques				Gravimetric techniques			
Temp.	K_{ads}	$\Delta G^{\circ}_{ads}(\text{KJ/mol})$	R^2	K_{ads}	$\Delta G^{\circ}_{ads}(\text{KJ/mol})$	R^2	n
303	1.802	-11.60	0.8034	1.367	-10.91	0.9075	0.5688
313	2.880	-13.20	0.8576	1.348	-11.23	0.9191	0.6077
323	1.955	-12.59	0.7798	1.289	-11.46	0.891	0.5817
Hydrogen evolution techniques				Hydrogen evolution techniques			
303	1.263	-10.71	0.7636	1.094	-10.34	0.8942	0.6919
313	1.305	-11.44	0.9942	1.257	-11.04	0.9595	0.7406
323	1.571	-12.00	0.9775	1.728	-12.25	0.9618	0.9597
333	1.369	-11.99	0.9463	1.194	-11.61	0.9101	0.8836

Based on Table 2 and Figures 5 to 8, the R^2 values obtained from the linear regression of the experimental data showed they are close to unity, which suggests that the adsorption of *Phyllanthus mellerianus* extract molecules onto the surface of mild steel is strongly fitted to Langmuir, and freundlich isotherms. However, the Freundlich adsorption isotherm is better with good linear correlation coefficient values [18, 19]. This implies that there are species of adsorbed inhibitor molecules. The value of intensity adsorption shown in Table 2 is less than unity,

which indicates moderate adsorption. The graphs also show that, even at elevated temperatures, the straight line relationship indicates that *Phyllanthus mellerianus* leaf extract adsorption on the metal follows more of the Freundlich adsorption isotherm than the Langmuir adsorption isotherm.

This is in conformity with James and Akarenta [20], who worked on an extract of red onion skin, and Okewale and Adesina [17], who researched on cocoa leaf. Their adsorption investigation followed the same pattern.

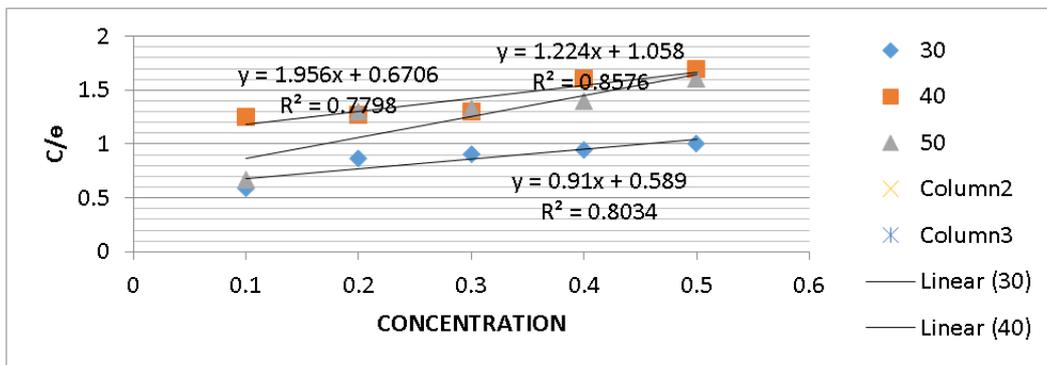


Figure 5. Langmuir isotherm Adsorption for *Phyllanthus ellermanus* leaf extract (Gravimetric data Analysis) inhibitor on mild steel surface.

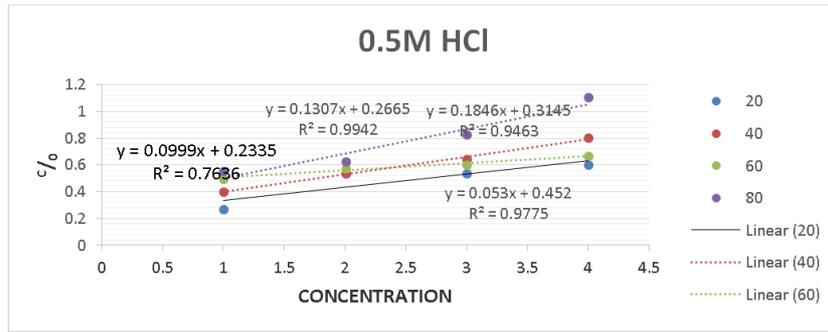


Figure 6. Langmuir Isotherm Adsorption for *Phyllanthus mellerianus* leaf extract (hydrogen evolution data Analysis) inhibitor on mild steel surface.

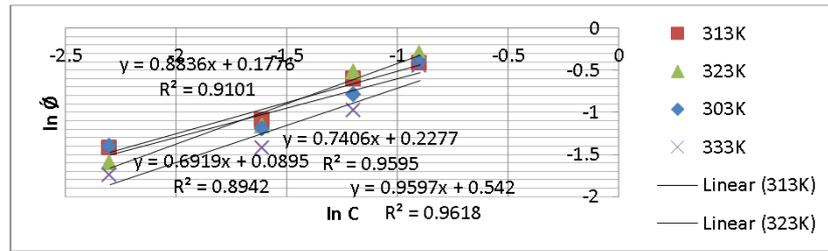


Figure 7. Freundlich Isotherm Adsorption for *Phyllanthus mellerianus* leaf extract (hydrogen evolution data Analysis) inhibitor on mild steel surface.

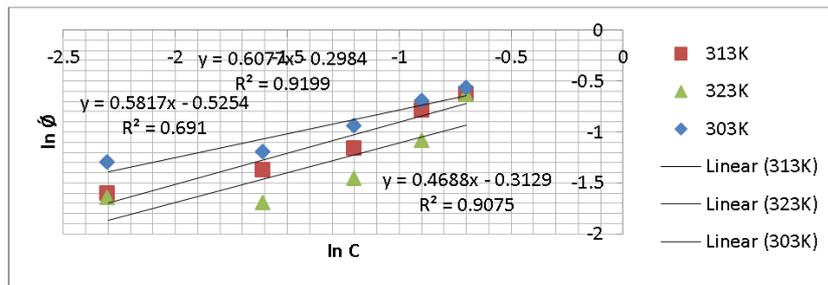


Figure 8. Freundlich Isotherm Adsorption for *Phyllanthus mellerianus* leaf extract (hydrogen evolution data Analysis) inhibitor on mild steel surface.

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

Table 2 obviously shows that Gibb's free energy of adsorption has a good relationship with temperature, which demonstrates that thermodynamic parameters are related. The negative values of change in Gibb's free energy of adsorption reflect that the adsorption process of studied inhibitors on mild steel surfaces is spontaneous and stably adsorbed on the mild steel surface. 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) [18, 21]. The values of ΔG_{ads} are negative and less than 20 kJ/mol. This finding indicates that *Phyllanthus mellerianus* extract adsorption on a mild steel surface is spontaneous, feasible, and occurred *via* the physical adsorption mechanism. The decrease in ΔG_{ads} at 333 K implies a decrease in the spontaneity and stability of adsorption at higher temperatures. Based on the values ΔG_{ads}, the data in table 2

also showed high level of consistent in the two methods (*Gravimetric and hydrogen evolution techniques*) used in the experiment.

Table 3. Thermodynamic parameters for mild steel in the presence and absence of inhibitor.

Concentration of inhibitor	E _a (kJ mol ⁻¹)	-ΔH° (kJ mol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)
blank	12.45	59.35	32.56
0.1g/l	16.28	80.69	54.33
0.2g/l	15.51	53.99	15.65
0.3g/l	16.08	58.59	12.44
0.4g/l	17.04	43.08	65.09
0.5g/l	20.16	44.61	55.40

3.6. Activation Energy (E_a) of the Adsorption of Mild Steel in *Phyllanthus mellerianus* Ethanol Extract

Figure 9 depicts log CR versus 1/T plots for different concentrations of *Phyllanthus mellerianus* leaf extract. The slopes obtained from the plots are thus appropriate for estimating the activation energy of the process for different concentrations. Table 3 shows the activation energy, E_a, at various extract concentrations. The activation energy of the inhibited process is higher than that of the uninhibited process,

as shown in the tables. This observation demonstrates that the adsorption process is physisorption [22].

The increased energy barrier was responsible for the higher value of E_a in the presence of an inhibitor. This finding also supports the formation of a complex compound between the inhibitor and mild steel [15]. This result suggests that corrosion inhibition by *Phyllanthus mellerianus* is possible due to an increase in the energy barrier for metal dissolution. A thin film formed on the metal surface acts as a barrier to both energy and mass transfer, increasing the activation energy. As a result, the results show that *Phyllanthus mellerianus* physically adsorbs on mild steel. The adsorbed molecules on the surface of mild steel create a

physical barrier that reduces the energy required for corrosion reactions. Adding inhibitors strengthens the film barrier on mild steel. Other researchers have reported the same trend with jujube leaves [21], black pepper and piper nigrum extract [22]. Since the activation energy increased in the presence of the inhibitor compared to the blank, the corrosion mechanism is physical adsorption. Physisorption has activation energy below 40 KJmol^{-1} and chemisorption has activation energy above 80 KJmol^{-1} [23]. These findings are consistent with previous research [14, 16]. The fluctuation in the activation energy could be based on the biological degradation of organic inhibitors, thereby losing their inhibition potential over time.

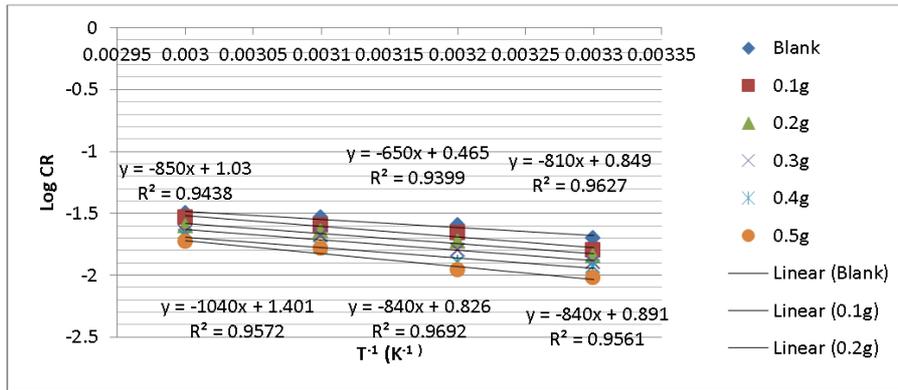


Figure 9. Arrhenius plot for the mild steel in different concentration of through ethanolic extract of *Phyllanthus mellerianus*.

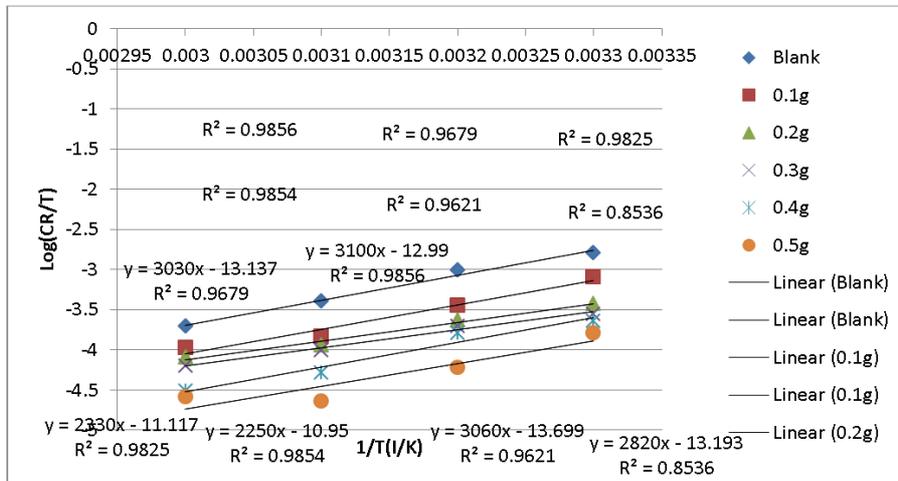


Figure 10. Variation of $\log (CR/T)$ with $1/T$ for the inhibition of mild steel in different concentration of through ethanolic extract of *Phyllanthus mellerianus*.

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* extract are shown in Table 3 and a chart showing the relationship of $\ln Cr/T$ and inverse of temperature shown in Figure 9. From the report of Fouda et al. [16] which is consistent with Umoren et al. [15], the thermodynamic standard for adsorption process is endothermic and chemisorptions when heat content of

adsorption is greater than zero ($\Delta H_{ads} > 0$), and exothermic adsorption process for either physisorption or chemisorption or mixture of both processes when the heat content is less than zero ($\Delta H_{ads} < 0$). The values of ΔH at different concentrations of inhibitor were negative. The negative sign of ΔH indicates that the extracted molecular adsorption is an exothermic process. In general, an exothermic process denotes physisorption.

The activation entropy (ΔS^\ddagger) was positive in the absence and presence of *Phyllanthus mellerianus* leaf extract [24]. This implies that the activated complex in the rate-

determining step represents dissociation rather than association, implying that an increase in the degree of orderliness occurs during the adsorption process when moving from the reactants to the activated complex. The more complex the order of the activated complex becomes entangled in the rate-determining step of the corrosion reaction, the higher the inhibitor concentration. As a result, as reactants are transformed into activated complexes, orderliness increases [25].

This result is consistent with the findings of Abeng et al. [14]. Further examination reveals that the E_a values are more significant than the ΔH values. This means that there must have been a gaseous reaction during the corrosion process [16].

4. Conclusion

Corrosion is a natural process that causes metals and alloys to lose their metallic properties, rendering them unsuitable for specific applications. Metal corrosion is a major industrial concern that has received a lot of attention. *Phyllanthus mellerianus* is a biomass waste with essential phytochemical constituents like tannins, flavonoids, phenols, and terpenoids at reasonable percentages. The reports on the thermodynamic and adsorption analysis of corrosion inhibition of mild steel in acid medium via ethanolic extract of *Phyllanthus mellerianus* was analysed via gravimetric and hydrogen evolution techniques, and the findings depict ΔG and a consistent Langmuir adsorption and Freundlich adsorption isotherm extrapolated with some models via the methods used in the research.

The inhibition efficiency increased with an increase in the concentration of the extract and decreased with temperature. The values of ΔG_{ads} , 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 values of ΔH at different concentrations of inhibitor were negative. The negative sign of ΔH indicates that the extracted molecular adsorption is an exothermic process. In general, an exothermic process denotes physisorption. The inhibitory effectiveness of extracts has been attributed to the presence of the hetero atoms N, O, and S present in their phytochemical composition.

Competing Interests

All the authors do not have any possible conflicts of interest.

References

- [1] 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.
- [2] Don-Lawson, C., Okah, R., & Orié, 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.
- [3] James, A. O., Oforika, 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.
- [4] 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).
- [5] Orié, 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.
- [6] Ahmed, S. K., Ali, W. B., & Khadom, A. A. (2019). Synthesis and investigations of heterocyclic compounds as corrosion inhibitors for mild steel in hydrochloric acid. *International Journal of Industrial Chemistry*, 10 (2), 159-173.
- [7] Harborne, I. B (1973) *Phytochemical methods: A guide to modern techniques of plant analysis*. 2nd Edition, Chapman and Hall, New York, 88-185.
- [8] 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.
- [9] 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.
- [10] 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.
- [11] Orié, 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.
- [12] 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.
- [13] Hassan, K. H., Khadom, A. A., & Kurshed, N. H. (2016). Citrus aurantium leaves extracts as a sustainable corrosion inhibitor of mild steel in sulfuric acid. *south african journal of chemical engineering*, 22, 1-5.
- [14] 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.
- [15] 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.

- [16] Fouda, A. S., Fouda, A. E. A. S., Abo-shohba, R., Husien, W. M., & Ahmed, E. S. (2016). Chemical and electrochemical study on the effectiveness of *Melilotus officinalis* extract as a corrosion inhibitor for aluminium in 1 M hydrochloric acid solutions. *Global Journal of Research In Engineering*.
- [17] 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.
- [18] Nwanonenyi, S. C., Madufor, I. C., Uzoma, P. C., & Chukwujike, I. C. (2016). Corrosion inhibition of mild steel in sulphuric acid environment using millet starch and potassium iodide. *International research journal of pure and applied chemistry*, 12 (2), 1-15.
- [19] Alhaffar, M. T., Umoren, S. A., Obot, I. B., & Ali, S. A. (2018). Isoxazolidine derivatives as corrosion inhibitors for low carbon steel in HCl solution: experimental, theoretical and effect of KI studies. *Rsc Advances*, 8 (4), 1764-1777.
- [20] James, A. O. & Akarenta, O. (2002). Corrosion Inhibition of Aluminum in Hydrochloric Acid Solution by the Action Extract of Red Onion Skin. *African Journal of Fine & Applied Chemistry*, 12, 262 – 268.
- [21] 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.
- [22] 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.
- [23] 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.
- [24] Shabani-Nooshabadi, M., & Ghandchi, M. S. (2015). Introducing the *Santolina chamaecyparissus* extract as a suitable green inhibitor for 304 stainless steel corrosion in strong acidic medium. *Metallurgical and Materials Transactions A*, 46 (11), 5139-5148.
- [25] Sivakumar, K., Mohan, N. K., & Sivaraman, B. (2012). Performance Analysis on Briquetting Bio Mass with Different Size in 10 kW Down Draft Gasifier. *Procedia engineering*, 38, 3824-3832.