

Performance Evaluation of the Mechanism, Kinetics and Thermodynamic Studies of Paw-Paw and Guava Leaves Extracts for Corrosion Inhibition Process on Mild Steel in Acidic Environment

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Abstract: The research work, the use of plant leaves extracts (Guava and Pawpaw leaves) to prevent corrosion effect on mild steel metal in an acidic environment (such as creek region in the Niger Delta as our case study) was investigated. Studies have shown that plant leaves extracts are green, environmentally friendly, and good corrosion inhibitors to corrosion attacks on metal surfaces. In this experiment, prepared Guava and Pawpaw leave extracts were characterized, and morphology of the surface analyzed before and after corrosion inhibition experiment on the metal coupon. The corrosion attack on the mild steel in acidic medium was investigated with and without the presence of extracts at different conditions of time, temperature, concentration, and performance of the inhibition efficiency. Physiochemical analysis on the extracts was conducted and corrosion inhibition mechanism studied based on the kinetics, isotherm constants, and Gibb's free energy values obtained from the kinetic corrosion rate, isotherm and thermodynamic models applied. The results of the analysis showed that the physiochemical analysis gave peroxide and acid values of the Guava and Pawpaw extracts as 29.63Mea/g and 38.25Mea/g, and 7.86mg KOH and 4.63mg KOH respectively, indication of the presence of oxygen containing compounds and Alkaloid as a protective layer on the metal surface, preventing the metal from corrosive environment. Corrosion inhibition efficiency of the extracts increased with increasing extracts concentrations, decreased with time, temperature, and corrosion rate. Pawpaw extract was seen to be a better corrosion inhibitor compared to Guava extract as 99.7% was obtained as against 98% inhibition efficiency for pawpaw and guava extract respectively. Based on the corrosion inhibition mechanism, Pawpaw extract gave higher values of Arrhenius constants and activation energies ranging from 0.602m/day to 2.272m/day and 1.421kJ/mol to 9.491kJ/mol compared with Guava extract of values 0.189m/day to 0.606m/day and 1.029 kJ/mol to 1.48 kJ/mol respectively. The result of the surface morphology analysis showed that corrosion rate on the metal steel surface was highest for uninhibited process and least for Pawpaw extract with highest concentration compared to guava extract with the same concentration. The result also indicated that the adsorption of extracts onto the metal surface was suitable with monolayer Langmuir isotherm and a physical adsorption principle since the adsorption kinetic constants and Gibbs free energies for guava and Pawpaw extracts for the Langmuir isotherm gave values ranges from 0.129 to 12.626, 0.081 to 769.321, and -164.505kJ/mol to -47.862 kJ/mol, -267.687 kJ/mol to -34.202 kJ/mol respectively. The negative values of the free energy and the more negative values from Pawpaw extracts showed that the adsorption process was spontaneous and more stable compared to the Guava extract. Finally, the higher values of the activation energies from the Pawpaw leaves extract proved that it's inhibition efficiency was better compared to Guava leaves extract.

Keywords: Mechanism, Kinetics, thermodynamics, inhibition process, mild steel, acidic environment

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I. Introduction

Mild steel is an engineering metallic material that gradually breaks down due to chemical or electrochemical reactions with its surroundings, this natural phenomenon which transforms the refined metal into a more stable oxide is known as corrosion (Uwah *et al.*, 2013; Khalid & Arshad, 2020).

According to the International Union of Pure and Applied Chemistry, corrosion is defined as an irreversible reaction between a material like metal, polymer or ceramic and its environment which results to the deterioration or dissolution of the material (Oguzie *et al.*, 2013; Aguma *et al.*, 2025).

Corrosion poses significant environmental and economic risks to various industries, including construction, energy, manufacturing, transportation and electronics. It occurs when materials, such as metals reacts with their environment, leading to degradation and loss of properties over time (Loto & Loto, 2021; Wosu, 2024; Wosu *et al.*, 2024; Ojong *et al.*, 2023). Mild steel is particularly susceptible to corrosion. To mitigate this, corrosion inhibitors are used to slow down the corrosion process (Olubambi & Fayomi, 2015; Izionworu *et al.*, 2021; Izionworu *et al.*, 2020a). These inhibitors can be classified into different types, including cathodic, anodic or mixed depending on how they interfere with the corrosion reaction. When used at optimal concentrations, they can effectively protect metallic surfaces without altering the corrosive environment.

A case study investigated the effectiveness of plant extracts in preventing corrosion of mild steel in acidic environments. The results showed that the extracts were effective to corrosion inhibitors, as confirmed by weight loss and electrochemical measurements. According to various studies, plant extracts have been successfully used to prevent mild steel corrosion in acidic media (Umoren *et al.*, 2015; Okafor *et al.*, 2019; Izionworu *et al.*, 2020b; Umoren, 2021). Natural materials including plant extracts and biopolymers have been explored as eco-friendly corrosion inhibitors. Specifically, extracts from papaya and psidium guajava have garnered interest as potential green inhibitors for mild steel corrosion.

Ismail *et al* in 2021 showed that certain natural substances such as chitosan can effectively inhibit corrosion on mild steel surfaces in acidic environments with its effectiveness increasing with concentration with maximum inhibition efficiency of 93.3%. Also, Gupta and his co researchers in 2020 discovered that punica granatum peel extract exhibited high inhibition efficiency capable of preventing mild steel from corrosion attacks. Shukla *et al* (2021) in their research showed that certain natural extracts and cellulose derivatives can effectively inhibit mild steel corrosion. In 2020, Zucchi *et al* investigated the potential of pseudomonas aeruginosa to inhibit biocorrosion of mild steel in artificial seawater. The results showed that pseudomonas aeruginosa effectively reduced corrosion on mild steel surfaces after 30days of exposure.

Ajibade *et al.*, 2021 in their research found that papaya leaf extract is an effective green corrosion inhibitor for mild steel in acidic environments. The extract achieved a maximum inhibition efficiency of 86.2% at a concentration of 0.4g/L in 1M HCl. It acted as a mixed type inhibitor, reducing both anodic and cathodic reactions. The extract's corrosion-inhibiting properties are attributed to the presence of organic compounds like tannins, flavonoids and phenolic compounds which forms a protective layer on the mild steel surface.

Ashraf *et al* in 2020 investigated guava leaf extract as a green corrosion inhibitor for mild steel in acidic media and found it effective with a maximum inhibition efficiency of 93.3% at 1.0g/L concentration. The extract acted as a mixed-type inhibitor, reducing both anodic and cathodic reactions. The inhibition was attributed to the adsorption of compounds onto the mild steel surface, forming a protective layer. Previous studies have shown that plant extracts can be utilized as green corrosion inhibitors (Dulta *et al.*, 2020; Ikeuba *et al.*, 2022).

This research aims to study the performance evaluation of the mechanism, kinetics and thermodynamic studies of pawpaw and guava leaves extracts for corrosion inhibition process on mild steel in acidic environment.

II. Materials and Methods

The study used guava and pawpaw leaves, mild steel coupons and equipment like soxhlet apparatus, pH meter and digital scale. The chemical reagents used are ethanol, hydrochloric acid and water. The research combined both experimental and theoretical approaches, involving steps like preparation of the leaf extracts, characterization of the leaf extracts and performance of corrosion experiments in an acidic environment for data generation. The study also examined the morphology of the metal surface after corrosion as well as performance evaluation of the mechanism, kinetics and thermodynamic studies of the leaves extracts for corrosion inhibition of the mild steel.

2.1 Preparation of Mild Steel Coupon

Mild steel coupons (6cm x 10cm x 0.8cm) were prepared by drilling a 0.1cm diameter hole. The coupons were then polished with silicon carbide abrasive paper, cleaned with distilled water, dried and stored in a desiccators.

2.2 Preparation of Carica Papaya and Psidium Guajava Leaves and Extraction Process

Fresh guava and pawpaw leaves were collected, cleaned and ground into fine paste approximately 123.26g. The leaves were then subjected to soxhlet extraction using 500ml of ethanol for 3hours. The extract was obtained

after recovering the ethanol in a rotary evaporator at 80°C under vacuum. The soxhlet apparatus, which included a distillation tank, heating mantle, reflux condenser and thimble was used for the extraction process. The setup allowed the solvent (ethanol) to evaporate, condense and continuously reflux through the shredded leaves, ultimately yielding the extract. The experiment setup is shown in Figure 1.



Figure 1: Pictures of Paw-Paw and Guava leave Extracts

2.3 Corrosion Inhibition Experiment

The corrosion inhibition experiment involved immersing cleaned and weighed mild steel coupons in 100ml test solutions with a pH of 1.0 and varying concentrations of the extract (0.5g/100 ml, 1.0g/100 ml, 1.5g/100 ml and 2.0g/100 ml) at variable time intervals (i.e., 5, 10, 15, 20, 25, and 30 days) and temperatures of 30°C, 40°C and 50°C with variable time of 24, 48, and 72 hours. The experiment was conducted with and without inhibitor to compare the corrosion rates. The setup is illustrated in Figure 2 and 3, which shows the beakers used for the corrosion experiments and the effect of temperature on corrosion rate using water bath.



Figure 2: Pictures of Beakers to carryout Corrosion Experiments (Starting with Paw-Paw Extracts as Inhibitor, without Inhibitor, and finally Guava Extracts as Inhibitor)



Figure 3: Effect of temperature using water bath on the Corrosion Rate

2.4 Weight Loss Method of Corrosion Experiment

The weight loss method involved suspending mild steel coupons in 100ml test solutions using a polyethylene hook. The coupons were retrieved at set intervals, cleaned, dried and reweighed to determine the weight loss in grams due to corrosion. The weight loss was calculated as the difference between the initial and final weights of the coupons.



Figure 4: Digital Scale Machine to Measure Weight Loss of Coupons

From the weight loss values, corrosion rates were computed accordingly using the expression:

$$C_R = \frac{kw}{At\rho} \quad (1)$$

where; k = Weight loss constant, w = corrosion weight loss of mild steel (mg), A = Area of the coupon 6.0cm by 12cm, t = Exposure time and ρ = Density of mild steel (7.85g/cm³).

2.5 Surface Morphology Analysis

The surface morphology of the corroded mild steel coupons was analyzed using Scanning Electron Microscopy (SEM) to study the surface structure and Energy-Dispersive X-ray spectroscopy (EDX) to determine the elemental composition of the corroded surface.

2.6 Corrosion Inhibition Factors

Corrosion inhibition factors such as surface coverage, inhibition coefficient, temperature, concentration and time were all studied and related models developed for the process through the experiment.

The inhibition efficiency η (%) and surface coverage θ was determined by the following equations.

$$\theta = \frac{w_0 - w_i}{w_i} \quad (2)$$

$$\eta_w = \frac{w_0 - w_i}{w_i} * 100 \quad (3)$$

where, w_i and w_0 are the weight loss value in presence and absence of inhibitor, respectively.

The rate constant for corrosion rate is determined based on the rate law given as,

$$(-r) = -\frac{dC}{dt} = kC^n \quad (4)$$

where, $(-r)$ is the rate expression for corrosion, k is the corrosion rate constant, n is order of the reaction and C is the concentration of corrosion defined mathematically as,

$$C = \frac{\text{Weight Loss}}{\text{Volume}} \quad (5)$$

2.7 Determination of Acid Value or Acid Number, ASTM D664

The acid value was determined using ASTM D664. A 0.05M KOH solution was prepared, and a by dissolving 2.805g KOH (pellet) with 1000ml distilled water. Furthermore, a 1:1 mixture of ethanol and benzene was used to dissolve about 1g of oil. The solution was then titrated with 0.1N KOH using phenolphthalein as an indicator until a pale pink endpoint appeared. The acid number in mgKOH/g was calculated using the titre volume of KOH.

$$AV = \frac{MW * N * V}{W} \quad (6)$$

where, AV is acid number, MW = Molecular weight of potassium hydroxide (56.1g), N = Normality of potassium hydroxide solution (0.1 N), V = Volume of potassium hydroxide solution used in titration, and W = Weight of oil sample.

$$\%FFA = \frac{AV}{2} \quad (7)$$

where, FFA is free fatty acid

2.8 Peroxide Value

The peroxide value (PV) was determined by weighing 5g of sample into a conical flask, adding a mixture of acetic acid and chloroform, and then potassium iodide (KI) solution. The mixture was titrated with sodium thiosulphate until the yellow iodine color disappeared, and starch indicator was added to detect the endpoint. A blank titration was also performed. The peroxide value was thus estimated from the formula in Meq/Kg

$$PV = \frac{(S-B) * N * 1000}{\text{Weight of oil}} \quad (8)$$

where, PV is peroxide value, S = Sample titre value, B = Blank titre value, N = mol of thiosulphate

III. Results and Discussion

The results of the mechanism, kinetics and thermodynamics study on the extracts performance in corrosion inhibition on mild steel pipes is shown in Tables and Figures.

3.1 Relationship of the factors affecting corrosion rates and the plant extracts

Concentration of extracts, time and temperature are majorly affecting corrosion rates of mild steel pipes and discussed with table 1 and figures 1 to 5. These profiles are used to determine the kinetic constants and the coefficient of determination as shown.

Table 1 shows the results of the kinetic corrosion rate constants generated for the green corrosion of mild steel coupon in acidic environment using guava and pawpaw leaves extracts. Also, the kinetic constant from pawpaw leaf extract was better than those obtained from guava leaf extract. This is because the R^2 values from pawpaw are greater than R^2 values for guava leaf extracts. As the R^2 values tend towards unity, the better the performance of the inhibitor. The higher the k-values, the lower the corrosion effect on the mild steel coupon.

Table 1: Results obtained from Rate Constant Values from Inhibition of Corrosion using Guava and Paw-Paw Extracts

Time (hr.)	Temperature (°C)	Inhibition Parameters			
		Guava Extract		Paw-Paw	
		K	R^2	K	R^2
24	30	0.4278	0.166	0.41098	0.624
48		0.21294	0.089	0.2059	0.667
72		0.14259	0.167	0.13730	0.668
24	40	0.4391	0.772	0.41156	0.660
48		0.21895	0.731	0.21634	0.625
72		0.14589	0.734	0.13985	0.753
24	50	0.43687	0.728	0.42101	0.665
48		0.21821	0.725	0.2261	0.794
72		0.14503	0.722	0.16122	0.734

3.1.1 Effects of Time on Corrosion Rate with Increasing Extract Concentrations

Table 1 was used to generate Figures 1a to 1b to see the effects of time in corrosion rate due to extracts concentration application/

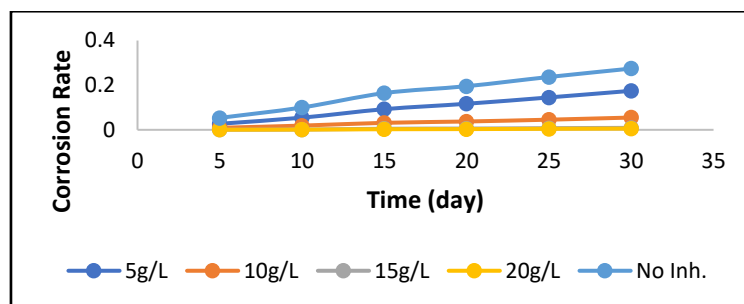


Figure 5: Effects of Time on Corrosion Rate with Concentration of Guava Extract

Corrosion rate is proportional to time at different concentration of the Guava extract, as shown in Figure 5. The corrosion rate is highest for the mild steel coupon without extract and lowest for mild steel coupon with highest concentration. The reason is due to the fact that Guava extract is more concentrated on the metal coupon which play a major role in inhibiting corrosion of mild steel coupon in acid environment since the active site of the metal coupon attack is repelled as agreed with literatures (Okafor *et al.*, 2018). It is observed that as the time spent during the experiments, the corrosion rate is highest for the mild steel coupon without inhibitor. It is also observed that as the concentration of extracts increases, the corrosion rate decreases.

On the other hand, it is observed that as time increases, the corrosion rate of the mild steel coupon increases for the mild steel coupon without inhibitor which agrees with the works of (Umoren, 2021) and literature (Uwah *et al.*, 2018).

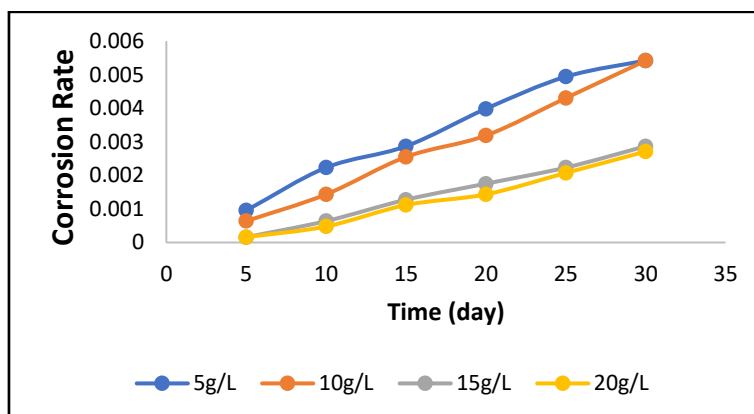


Figure 6: Effects of Time on Corrosion Rate with Concentration of Paw-Paw Extract

The corrosion rate varies with time at different concentrations of Paw-Paw extract, as shown in Figure 6. The corrosion rate is highest on the mild steel coupon when the concentration of extract is the least and lowest when the concentration is highest. The reason for this process is that when the concentration of the Paw-Paw extract is highest, then it will create more active site to inhibit the corrosion of mild steel coupon. However, the lesser the concentration of extract, then lesser active site will be created on the metal surface for the corrosion process to take place as agreed with literatures (Uwah *et al.*, 2018). On the other hand, it is observed that for varying concentrations of the Paw-Paw extract that corrosion rate increases with time on the metal surface as agreed with literature (Okafor *et al.*, 2018).

The assessment of environmental impact of using the paw-paw and guava extracts as green corrosion inhibitor gave the reduction of corrosion rate and a protective barrier on the mild steel coupon surfaces formed and increased as time changes from 0hrs, 24hrs, 48hrs and 72hrs. These results show that corrosion inhibition of paw-paw and guava leaf extract performances are higher as time changes from 0hrs, 24hrs, 48hrs and 72hrs according to literatures (Uwah *et al.*, 2018; Shashi, 2019).

3.1.2 Effects of Temperature on Corrosion of Mild Steel Metal in Acidic Medium

The effect of kinetics on corrosion of mild steel in pipes transport of fluids is studied using temperature effect on the extract concentration and composition in acidic environment. See Figures 7 and 10 for better explanation.

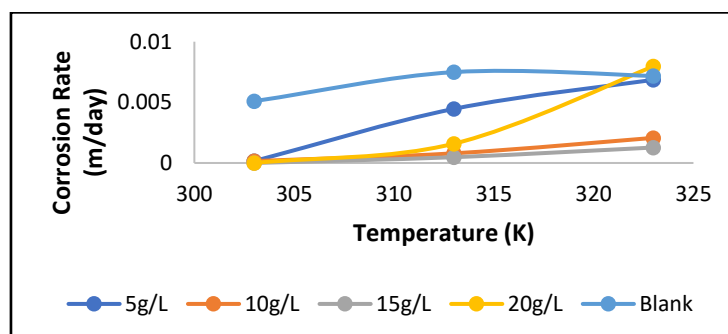


Figure 7: Variation of Corrosion Rate with Temperature at varying Guava Extract Concentration after 24hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

The corrosion rate varies with temperatures of mild steel coupon at various concentrations of Guava extract in acidic medium with pH of 1.0 as shown in Figure 7. The corrosion rate on mild steel coupon is highest for blank and lowest for concentration of extract at 15g/l. The reason is due to the fact that for the blank (without extract), the corrosion rate is very high since there is no inhibitor to prevent corrosion attack on the metal surface but the corrosion rate is lowest on the mild steel coupon in the acid medium due to the fact that as temperature affects the corrosion rate at very high concentration of the extract. This is because the active site which is being inhibited will be affected due to temperature increase. Hence the inhibition properties of the extract is affected at high temperature. The activation energy (E) of the corrosion/corrosion inhibition process is determined using the Arrhenius equation. The rate of corrosion is inversely proportional to temperatures. This means that even though the Guava extract concentration is more, the temperature increase should not be very high for the corrosion attack on mild steel coupon to be repelled properly as agreed with literature (Uwah *et al.*, 2018).

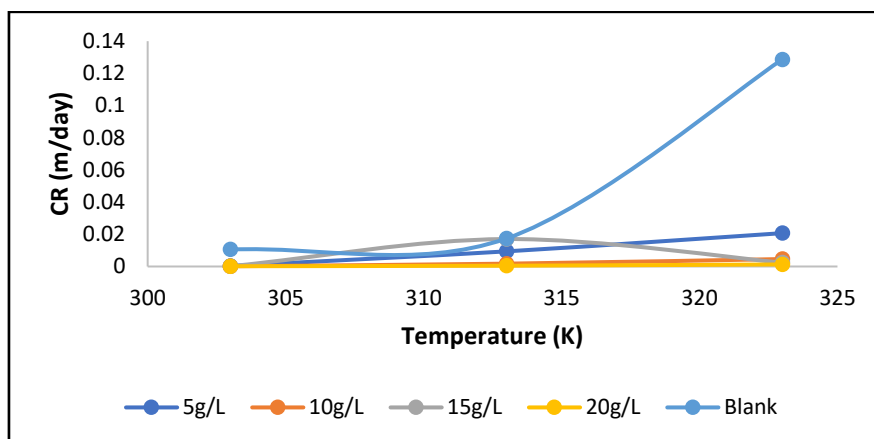


Figure 8: Variation of Corrosion Rate with Temperature at varying Guava Extract Concentration after 48hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

Corrosion rate variation with temperature at different concentrations of the Guava extract at 48hours on the mild steel coupon in acidic medium of pH of 1.0 is shown in Figure 8. The corrosion rate on the mild steel coupon is highest on the blank while it is lowest on the mild steel coupon with highest concentration. This is due to the fact that temperature affect the corrosion rate according to Arrhenius equation principle. When the concentration of the Guava extract is more on the mild steel coupon, the active site on the metal surface is inhibited by the action of the Guava extract and as such reduce the corrosion rate on the mild steel coupon but the temperature should not be high enough as high temperature affects the active sites of the inhibition properties of the Guava extract as agreed with literature (Uwah *et al.*, 2018). Higher temperature affects corrosion inhibition properties, hence weakens the efficiency of the extract and likelihood of corrosion takes place. Corrosion attack on the metal surface with the inhibitor is more compared to Figure 7.

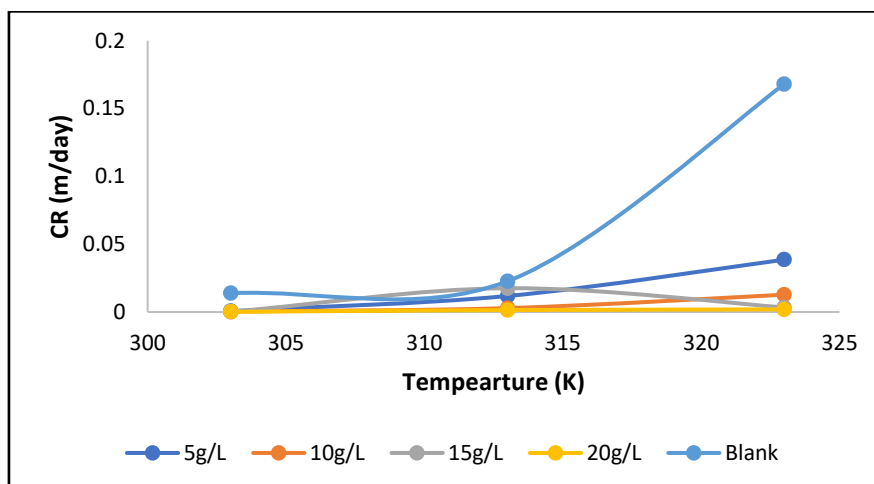


Figure 9: Variation of Corrosion Rate with Temperature at varying Guava Extract Concentration after 72hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

The corrosion rate varies with temperatures of the mild steel coupon at different concentrations of Guava extract after 72hours in acidic medium with pH 1.0 as shown in Figure 9. The corrosion rate on the mild steel coupon is highest for the blank while lowest for the highest concentration. This is due to the fact that the more concentration of the Guava extract is in the active site of the mild steel coupon preventing or inhibiting the corrosion process but the temperature should not be high enough as increase in temperature affects the activeness of the inhibitor to repel the corrosion on metal surface as agreed with literature (Uwah *et al.*, 2018; Umoren, 2021). There is a clearer corrosion effect here because even though the inhibitor efficiency is high the corrosion rate is feasible as the time of the inhibitor stay in the acidic medium.

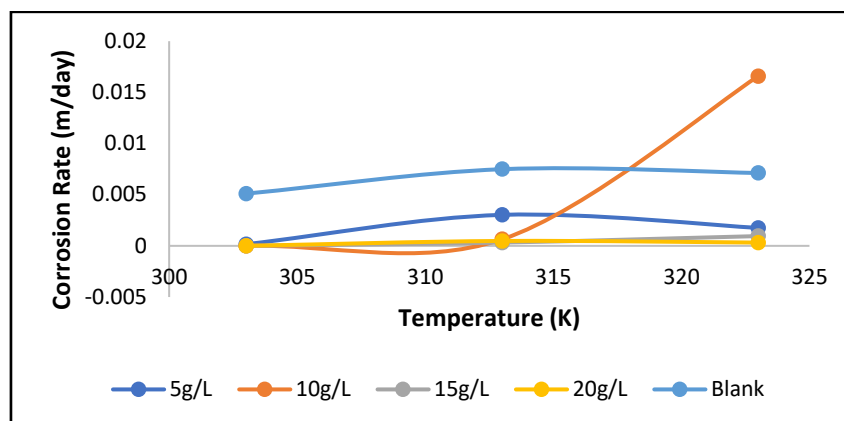


Figure 10: Variation of Corrosion Rate with Temperature at varying Paw-Paw Extract Concentration after 24hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

The corrosion rate varies with temperatures of the mild steel coupon at different concentrations of the Paw-Paw extract in acidic medium for 24hours with pH of 1.0 as shown in Figure 10. The corrosion rate is highest for blank and lowest for 10g/L concentration. This is due to the fact that at very high temperature of about 315K, the activeness of the Paw-Paw extract inhibition properties have been affected so the more concentration of the Paw-Paw extract on the metal surface will not be effectively inhibiting the metal surface from corroding. It then means that for the corrosion process to be inhibited properly by the Paw-Paw extract (inhibitor), the temperatures have to be regulated or controlled to optimum value of 310K, as temperature increases the rate of corrosion. This agrees with Arrhenius principle and other literatures (Uwah *et al.*, 2013).

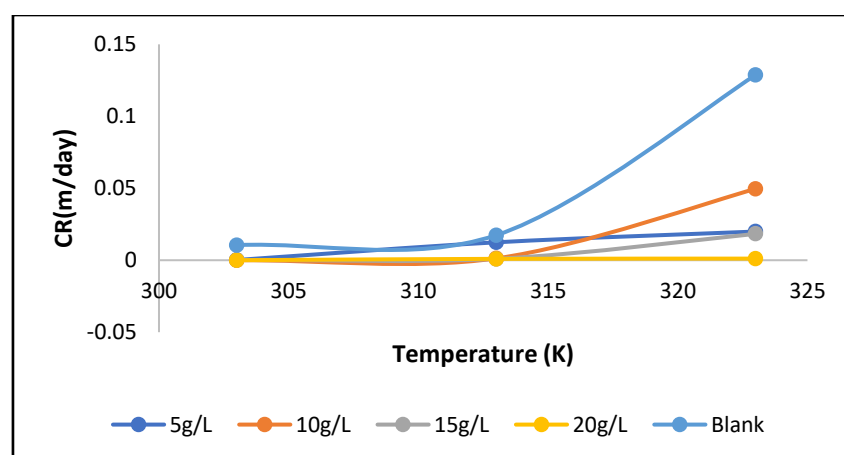


Figure 11: Variation of Corrosion Rate with Temperature at varying Paw-Paw Extract Concentration after 48hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

The corrosion rate varies with temperature of the mild steel at different concentrations of the Paw-Paw extract at 48hours for acidic medium with pH of 1.0 as shown in Figure 11. The corrosion rate of the metal coupon is highest for the blank and lowest for 10g/L concentration of extract. This is due to the fact that the mild steel coupon with more concentration of the extract will cause more inhibition on the metal surface attacking the active site on which corrosion is taken place but temperature affects the corrosion rate and the inhibiting properties of the Paw-Paw extract will be affected according to Arrhenius principle. It then means that the Paw-Paw extract which shows a better inhibition property occupies more the active site of the metal surface thereby inhibiting the corrosion process and hence reduces the rate of corrosion of the metal surface even though the temperatures and time of the process are at higher values as agreed with literatures (Uwah *et al.*, 2013; Uwah *et al.*, 2018). Hence corrosion rate values obtained from the inhibition of mild steel metal with Paw-Paw extract are generally low compared to those with Guava extract since the latter extract is a better inhibitor of the metal surface, to prevent the corrosion attack on the active site as agreed with literature (Uwah *et al.*, 2013; Solmaz *et al.*, 2018).

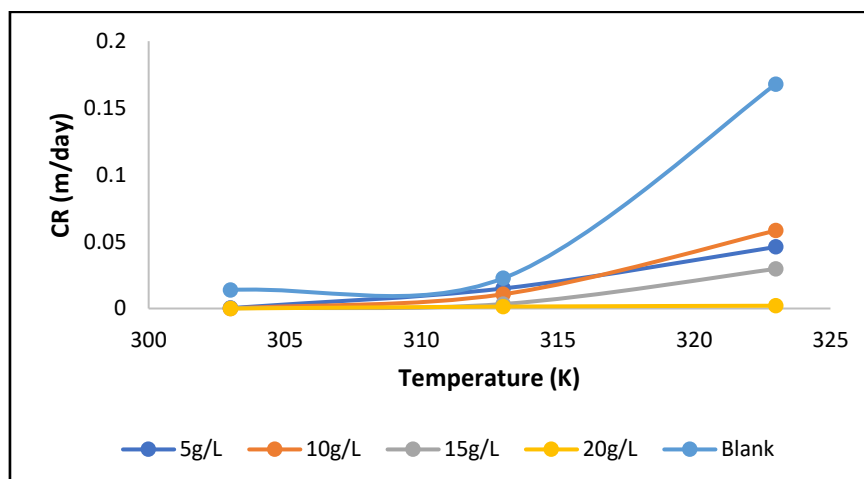


Figure 12: Variation of Corrosion Rate with Temperature at varying Paw-Paw Extract Concentration after 72hrs Corrosion of Mild Steel Metal in Acidic pH 1.0

The corrosion rate variation with temperature of the mild steel coupon at different concentrations of Paw-Paw extract at 72 hours in acidic medium for pH of 1.0 is shown in Figure 12. The corrosion rate of the mild steel coupon is highest for the blank at 72 hours while lowest for 20g/L. This is due to the fact at 72 hours, the Paw-Paw extract acting as inhibitor weakens and reduces the performance of the extract and the adsorptive property of the extract on to the surface of the metal to prevent corrosion attack reduces and thus causing the metal to be corroded. It is also noted that the inhibition process of the Paw-Paw extract prevents the corrosion attack on the metal even at very high temperature when Paw-Paw extract is used as an inhibitor as agreed with literature (Okafor *et al.*, 2020; Uwah *et al.*, 2013). The inhibition properties of Paw-Paw are better at increased time even with temperature change (Ikeuba *et al.*, 2015). At a higher time, the corrosion rate values are higher compared those at 24hrs and 48hrs respectively. The degree of inhibition is of such CR at 72hrs > CR at 48 > CR at 24hrs, also, CR at 5g/L > CR at 10g/L > CR at 15g/L > CR at 20g/L.

3.1.3 Effect of Temperature on Corrosion Rate with Extracts Concentrations

Figures 3a and 3b explain the effect of temperature on the corrosion rate due to extracts variation

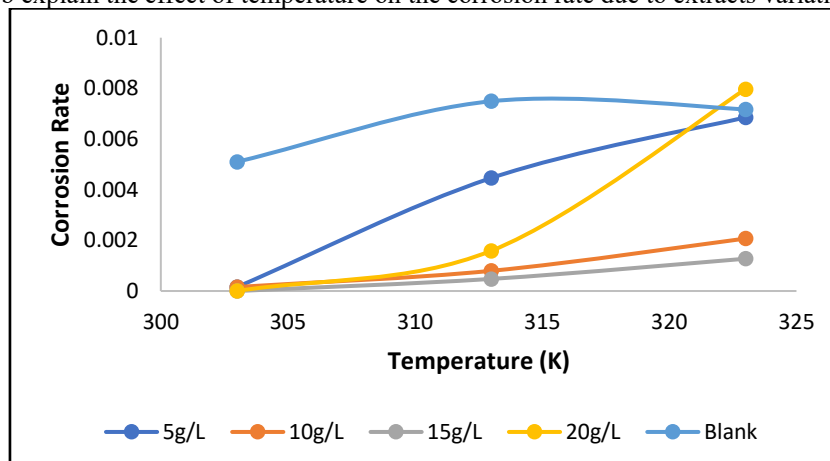


Figure 13: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Guava Extract) on the Rate of Corrosion after 24hrs

Temperature increase affects corrosion rate of mild steel in acidic environment, as evidence in Figure 3ai. The Figure shows that inhibitor concentration reduces the rate of corrosion as the blank (corrosion taking place without an inhibitor). The guava extract agrees with the claim that temperature increase weakens its performance and corrosion attacks on the surface of the metal because at highest temperature, the corrosion rate value is highest even though the concentration of the inhibitor is very high. Thus, temperature rise is a major factor that affects corrosion on metal. This may be due to the fact that higher temperatures are as a result of lower activation energies, which are easily broken for new bonds to form. The corrosion rates values are generally low, which indicates the effect of inhibition efficiency of the guava extract at 24hrs time.

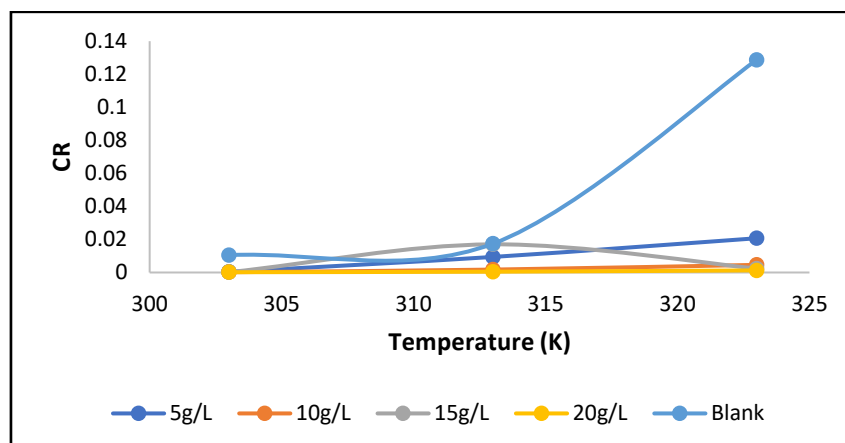


Figure 14: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Guava Extract) on the Rate of Corrosion after 48hrs

The corrosion rates (CR) values at varying concentrations profiles, increase in temperatures and at 48hrs of time are generally higher compared to those at 24hrs. Similarly, Figure 14 showed the same trend of corrosion effect on the mild steel metal. This is evidence from literature works (Oshomogho *et al.*, 2020; Gupta *et al.*, 2019). The degree of corrosion rate using Guava extract is such that, $CR_{48hrs} > CR_{24hrs}$. This showed that time is also a factor that affect corrosion inhibition as higher time reduces the performance of the inhibitor thereby favouring CR.

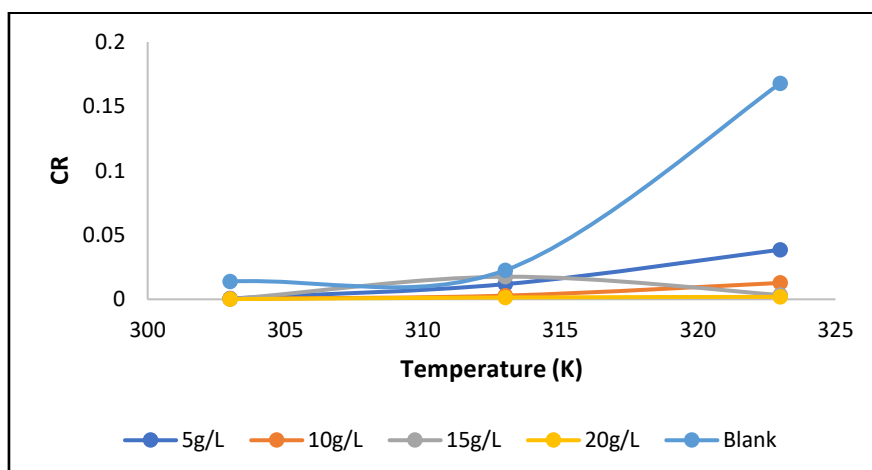


Figure 15: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Guava Extract) on the Rate of Corrosion after 72hrs

Highest corrosion rate occurs at 72hrs for increasing temperature and reducing concentration of the Guava extract, as shown in Figure 15. The order of degree of corrosion based on performance of inhibitor showed that $CR_{72} > CR_{48} > CR_{24}$, and that $CR_{5g/L} > CR_{10g/L} > CR_{15g/L} > CR_{20g/L}$. This is in line with literatures (Ikeuba *et al.*, 2015; Ojong *et al.*, 2023).

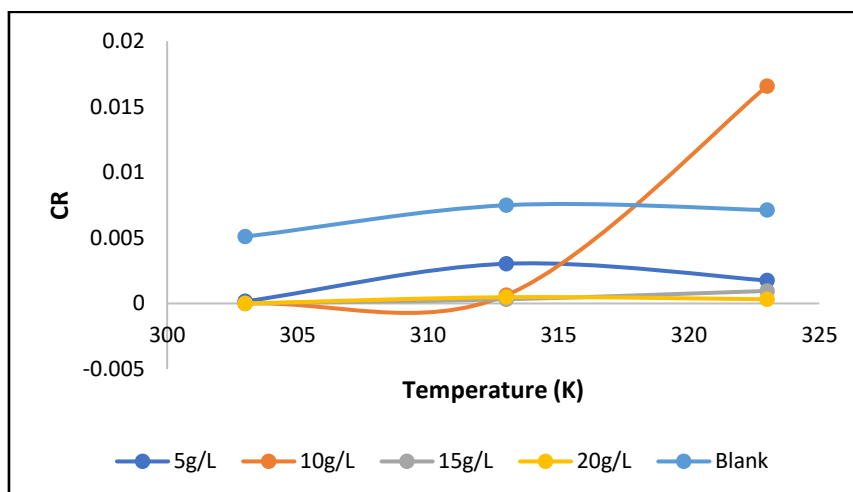


Figure 16: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Paw-Paw Extract) on the Rate of Corrosion after 24hrs

The corrosion rate of mild steel in acidic environment at varying concentration of pawpaw extract with increasing temperature for 24hrs is generally lower compared to that of Guava extract at same condition as shown in Figure 3bi. The reason is the fact that pawpaw extract seems to be a better inhibitor than Guava extract, as explained earlier. There is an abnormality as at extract concentration of 10g/L, the corrosion rate is very high, this may be due to the fact that there are some errors emanated from experiment and measurement. Hence, CR guava extract > CR pawpaw.

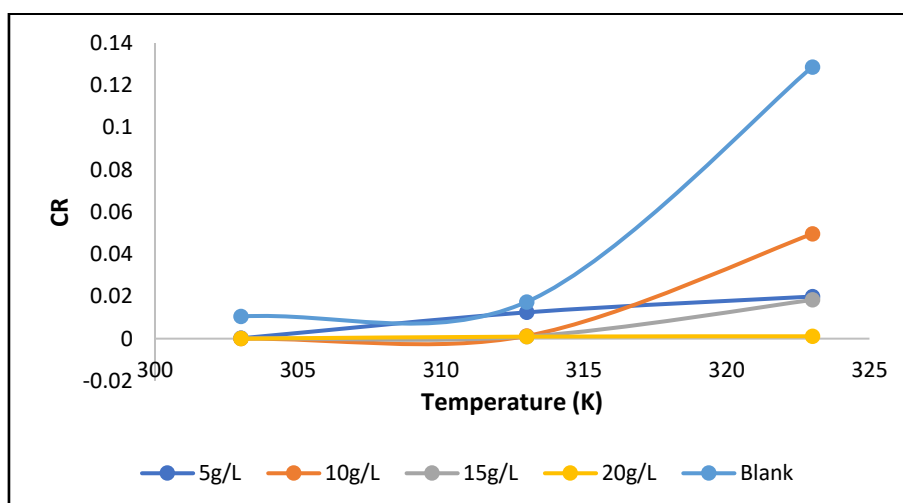


Figure 17: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Paw-Paw Extract) on the Rate of Corrosion after 48hrs

Corrosion rate here for 48hrs time the extract spent in the beaker at varying temperature for different pawpaw extract concentration is a little bit high compared to CR for 24hrs time spent, as shown in Figure 17. The result presented is okay as agreed with literatures (Ojong *et al.*, 2023; Ikeuba *et al.*, 2015). Generally, corrosion rate against pawpaw extract is low compared to Guava extract and also, agreed that corrosion rate decreases with increasing extract concentration but with decreasing temperature. This shows that concentration of the inhibitor (extract), time and temperature affect corrosion inhibition of mild steel metal in acidic environment.

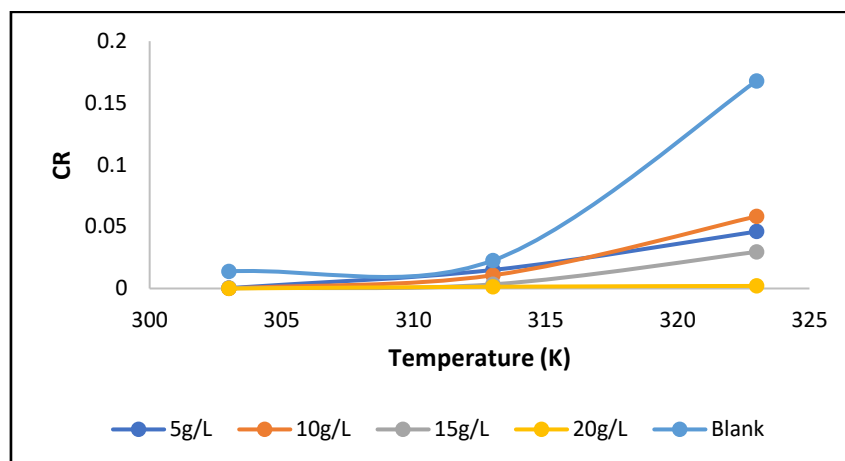


Figure 18: Effects of Increasing Temperature with Increasing Concentration of Inhibitor (Paw-Paw Extract) on the Rate of Corrosion after 72hrs

Corrosion rate on inhibited mild steel metal in acidic environment with extract of pawpaw for 72hrs is highest compared to that for 48hrs and 24hrs accordingly. This is shown in Figure 18, and when compared to corrosion rate at the same condition using Guava extract, the CR is generally lower. This shows that $CR_{72} > CR_{48} > CR_{24}$ and also, CR_{24} for Guava $> CR_{24}$ for pawpaw and so on.

3.2 Corrosion Inhibition Mechanism Explained

Kinetic Parameters Determination such as the activation energies, the adsorption kinetic constants and Gibb's free energy help explain the corrosion inhibition of the extracts on the metal surface.

3.2.1 Corrosion Rate Parameters

Corrosion rate parameters include the rate constant, Arrhenius constant and activation energy (see Table 2).

Table 2 indicates the kinetic corrosion rate constants generated for the green corrosion of mild steel coupon in acidic environment using guava and pawpaw leaves extracts. The values show variation of the kinetic constants' values with temperature and time. It is observed from the coefficient of determination (R^2) values that at higher temperatures and time, the corrosion rates data obtained from the experiment fitted well and thus, better values of kinetic constants. Also, the kinetic constant from pawpaw leaf extract is better than those obtained from guava leaf extract. This is because the R^2 values from pawpaw are $> R^2$ values for guava leaf extracts. As the R^2 values tend towards unity, the better the performance of the inhibitor. The higher the k_i values, the difficulties the corrosion effect on the mild steel coupon. So, the kinetic constants for pawpaw leaf extracts are $>$ than the kinetic constants obtained from guava leaf extract. Thus, $k_{50} > k_{40} > k_{30}$ and that k_i values for pawpaw extract $> k_i$ values for guava leaf extract.

Table 2: Rate Constant Values from Inhibition of Corrosion using Guava and Paw-Paw Extracts

Time (hr.)	Temperature ($^{\circ}$ C)	Inhibition Parameters			
		Guava Extract		Paw-Paw	
		k_i	R^2	K_i	R^2
24	30	0.4278	0.166	0.41098	0.624
48		0.21294	0.089	0.2059	0.667
72		0.14259	0.167	0.13730	0.668
24	40	0.4391	0.772	0.41156	0.660
48		0.21895	0.731	0.21634	0.625
72		0.14589	0.734	0.13985	0.753
24	50	0.43687	0.728	0.42101	0.665
48		0.21821	0.725	0.2261	0.794
72		0.14503	0.722	0.16122	0.734

3.2.2 Determination of Arrhenius Constants and Activation Energies of Extracts in Corrosion of Mild Steel Metal

Table 3 shows the Arrhenius constants and activation energies obtained from the rate law for both guava and pawpaw leaves extract as stated in equation (7) to (8). The A_{is} and E_{ai} values for pawpaw leaf extract are higher, increases with time and also have higher R^2 -values than those obtained from guava leaf extract. This proved that higher E_{ai} values ensure difficulty in corrosion rate to take place and vice versa. Thus, pawpaw leaf

extract is a better inhibitor compared to guava leaf extract. According to Ikeuba *et al.* (2015) and (2013), the adsorption process is a physical one since the E_{ai} values are below 80kJ/mol for both extracts. The increase in apparent activation energies in the inhibited solution of pawpaw extract may be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature and time (Uwah *et al.*, 2013). The activation energy for pawpaw extract increased gradually from 1.421kJ/mol to 9.491kJ/mol with increase in concentration and time, an indication that an increased tendency towards chemical adsorption while an opposite tendency was observed in the presence of guava leaf extracts suggesting that an increased tendency towards physical adsorption of the extracts unto the mild steel surface at higher concentration.

Table 3: Arrhenius Constant and Activation Energy Values at varying Temperatures and Time for the Inhibition of Corrosion of Mild Steel with Extracts

Time (hr.)	Inhibition Parameter					
	Ea (kJ/mol)	Guava Extract A(m/day)	R ²	Ea (kJ/mol)	Paw-Paw Extract A(m/day)	R ²
24	1.27	0.606	0.597	1.421	0.602	0.779
48	1.48	0.3192	0.668	5.570	0.932	0.9998
72	1.029	0.189	0.529	9.491	2.272	0.821

3.3 Adsorption Kinetic Parameters

The kinetic adsorption constant further explained the corrosion inhibition mechanism of the extract on to the adsorption principles on the surface of the metal, thereby providing protective layer for the prevention of corrosion attack on the metal surface.

Table 4a is used to determine the adsorption kinetics via surface coverage and concentration of the extracts to generate adsorption kinetic isotherm constants for Langmuir and Temkin adsorption isotherms at varying extract concentrations, temperatures and for 24hrs, 48hrs, and 72hrs the extracts stayed in the acidic solution.

Table 4a: Calculated Values of Corrosion Rates, Surface Coverage, and Inhibition Efficiency for the Green Corrosion Experiment Conducted

Inhibitor	Time (hr.)	Conc. (g/L)	Corrosion Rate (m/day)			Surface Coverage, θ		
			30°C	40°C	50°C	30°C	40°C	50°C
Paw-Paw Extract	24	Blank	0.0051	0.00749	0.00717	-	-	-
		5	0.00016	0.00303	0.00175	0.969	0.596	0.924
		10	0.0000	0.00064	0.016578	1.000	0.915	0.945
		15	0.0000	0.0032	0.000956	1.000	0.957	0.959
		20	0.0000	0.00048	0.000319	1.000	0.976	0.986
	48	Blank	0.01052	0.017375	0.128636	-	-	-
		5	0.000159	0.012433	0.019925	0.985	0.284	0.845
		10	0.0000	0.001275	0.049573	1.00	0.927	0.850
		15	0.000159	0.000956	0.018331	0.985	0.945	0.852
		20	0.0000	0.000956	0.0016	1.00	0.945	0.991
	72	Blank	0.013868	0.022635	0.167848	-	-	-
		5	0.000319	0.014984	0.04061	0.977	0.338	0.726
		10	0.000	0.01068	0.0583	1.00	0.528	0.752
		15	0.000159	0.003347	0.02965	0.989	0.852	0.823
		20	0.0000	0.001435	0.00207	1.00	0.937	0.988

The Langmuir and Temkin isotherm were investigated by testing and experimental data obtained which further explained the understanding of the corrosion inhibition mechanism based on the equations (9) and (10). It is suspected that the inhibition of metal corrosion occurred as a result of the adsorption of the active principles of the extracts into the metal surface. The experimental data from guava and pawpaw leaves extracts used for corrosion inhibition of mild steel fitted well in the Langmuir isotherm than Temkin isotherm. Also, the K_{ad} (adsorption kinetic constant) for the pawpaw leave extract are better than that obtained from guava leaf extract based on the R^2 values for pawpaw are $>$ than those for guava leaf extract. The K_{ad} values for pawpaw extracts based on the R^2 values are better fitted at 40°C compared to 50°C and 30°C, hence, $R^2_{40} > R^2_{50} > R^2_{30}$. This trend is also followed for Langmuir K_{ad} values obtained from guava leaf extract. It is also noticed that using Temkin isotherm, R^2 values for guava leaf extract fitted well than those for pawpaw extract and that $R^2_{40} > R^2_{50} > R^2_{30}$ for guava compared to $R^2_{30} > R^2_{50} > R^2_{40}$ for pawpaw leaf extract.

The R^2 values for the Langmuir at 40°C and 50°C are closed to unity at varying time (0.9999, 0.9997, 0.9999), and (0.999, 0.976 and 0.954) for pawpaw extract, and (0.9997, 1 and 1) and (0.9973, 0.9993 and 0.9991), suggesting that the Langmuir isotherm for guava extract strictly adheres to the principles underlying the

deviation of Langmuir isotherm. However, these values are not up to 1 for some cases, indicating that there is a slight deviation from the Langmuir theory of adsorption (Ikeuba *et al.*, 2015; Okafor *et al.*, 2007). The R^2 -values which are very close to unity, indicate that there is formation of monolayer of Langmuir adsorption and there is no interaction between the adsorbed species.

Table 4b: Adsorption Isotherm Parameter Values

Time (hr.)	Temp. ($^{\circ}\text{C}$)	Inhibition Adsorption Isotherm Parameters									
		Guava Extract					Paw-Paw Extract				
		Langmuir			Temkin		Langmuir			Temkin	
		K_{ad}	R^2	a	K_{ad}	R^2	K_{ad}	R^2	A	R^2	K_{ad}
24	30	0.1291	0.810	-1.199	1.612	0.874	0.3148	0.9761	-1.943	0.818	0.406
48		0.16186	0.9065	-1.340	1.240	0.870	0.081	0.225	-1.029	0.796	2.243
72		0.1821	0.9326	-1.466	1.041	0.868	0.0736	0.750	-1.104	0.950	2.550
24	40	3.0998	0.9997	-19.380	2.984E-16	0.740	6.120	0.9999	-21.834	0.776	1.691E-18
48		12.626	1	-45.045	4.555E-38	0.776	13.004	0.9997	-72.463	0.222	3.74E-62
72		4.127	1	-19.011	8.165E-16	0.949	769.321	0.9999	-36.765	0.554	2.447E-31
24	50	0.446	0.9973	-2.612	0.111	0.911	1.778	0.999	-12.019	0.924	1.232E-9
48		0.9557	0.9993	-4.513	2.214E-3	0.889	0.5845	0.976	-6.039	0.5001	2.495E-4
72		0.559	0.9991	-3.054	0.041	0.946	0.2929	0.954	-2.976	0.735	0.083

3.4 Gibb's Free Energy Values

The spontaneity and stability of the adsorption of the extracts on to surface of the metal depends on the free energy of the process.

The standard adsorption free energy ΔG values shown in Table 5 were obtained based on the equation (11).

Negative values of the Gibb's free energies from the Langmuir isotherm considered range from -16.5kJ/mol to -34.2kJ/mol for guava extract indicate spontaneity and stability of the adsorption layer for the process using both extracts. The values of the free energy as shown in Table 5 at varying temperature, were far below -40kJ/mol, for both extracts, except for pawpaw extract at 30 $^{\circ}\text{C}$ at time of 48hrs and 72hrs where the free energies are above -40kJ/mol. This suggests that the adsorption process is a physical adsorption mechanism as reported in works of Singh *et al.*, (2010), Ikeuba *et al.*, (2015), and Gupta *et al.*, (2020).

The exception having free energies above -40kJ/ml shows that the adsorption lends to chemisorption mechanism (Ikeoba *et al.*, 2015, Ogbobe *et al.*, 2018). The free energy values for both extracts obtained using Temkin isotherm, showed that the adsorption process is not feasible for temperatures of 40 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$ at time 24hrs, 48hrs and 72hrs and 24hrs, and 48hrs respectively but took place at 30 $^{\circ}\text{C}$ for both extracts.

Except for temperature of 50 $^{\circ}\text{C}$ where adsorption process occurs at 24hrs and 72hrs, for guava extract. Generally, based on Gibb's free energy values, the process does not follow Temkin adsorption isotherm but Langmuir as claimed earlier with the study of other parameters discussed.

Table 5: Change in Gibb's Free Energy for the Adsorption Isotherms of the Extracts

Guava Extract		Paw-Paw Extract		Temperature ($^{\circ}\text{C}$)	Time (hr.)
$\Delta G T$ (kJ/mol)	$\Delta G L$ (kJ/mol)	$\Delta G L$ (kJ/mol)	$\Delta G T$ (kJ/mol)		
-109.223	-47.8617	-69.526	-75.7095	30	24
-102.846	-53.3582	-36.5323	-117.252		48
-98.5947	-56.2219	-34.2037	-120.37		72
796.692	-129.244	-146.323	926.5741	40	24
2057.921	-164.505	-165.246	3450.342		48
771.4194	-136.43	-267.689	1668.843		72
-47.1071	-83.1415	-118.972	427.4574	50	24
54.32063	-102.888	-90.1483	110.8831		48
-21.3026	-88.9926	-72.2469	-39.5756		72

Conclusion

Aguma *et al.*, 2025 has proven that paw-paw extracts perform better, efficiently and effectively in coping corrosion attacks in mild steel equipment conveying oil and gas for processing. However, the mechanistic and kinetics examined in this study showed the following;

- (i) That the effect of the factors such as time, temperature, and concentration of the inhibitors have adverse consequences on mild steel, which could reduce the attacked rate on the metal due to extract concentration and the type of extract used.
- (ii) The adsorption characteristics of Paw-Paw and Guava extract on mild steel corrosion in acidic medium solutions followed Langmuir monolayer adsorption isotherm and physical adsorption mechanism proposed for the adsorption process based on the values of E and ΔG (more negative values).
- (iii) The surface interaction between the mild steel coupons and the inhibitor (Paw-Paw and Guava extracts) estimated by Langmuir and Tempkin adsorption isotherms revealed that Langmuir fitted better with the experimental data obtained with a higher regression value.
- (iv) Increasing the temperature of the corrosion medium was also observed to result increase in corrosion rate but with corresponding increase in inhibition efficiency indication that some of the extract components become more adsorbed at lower temperature and so contribute more to the overall inhibiting effect.

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