

The Corrosion Inhibition of Mild Steel in Sulphuric Acid Solution by Adsorption of African *Perquetina* Leaves Extract

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ABSTRACT: The inhibition of mild steel corrosion in sulphuric acid solution was studied with application of Africa *parquetina* leaves extract (APLE) using Gravimetric, Gasometric and Thermometric measurements. The phytochemical characterization of the leaves extract were also carried out using Gas chromatography mass spectroscopy (GCMS) and Fourier transformation Infra Red (FTIR) analysis. The result showed the presence of phytochemical compounds and functional groups greatly contributed to the inhibitive strength. The inhibition efficiency at optimum concentration 0.5 g/l was 87.78 % and it was increased with the increase in concentration of APLE but decreased with increase in temperature. The adsorption of inhibitor obeyed Langmuir adsorption isotherm and the free energy of adsorption suggested that it was physisorption. Finally, the Dubinnin-Radushkevich isotherm model also suggested the techniques adopted in the corrosion measurement were in good agreement.

KEYWORDS: Mild steel, adsorption, Sulphuric acid solution, PNLE, Characterization

I. INTRODUCTION

Mild steel is a material commonly used in industries due to its low cost, availability and excellent mechanical properties [1]. Mild steel and alloys react chemically/electrochemically with corrosive medium (acid solutions) to form stable compound, in which the loss of metal occurs [2]. Acid solutions are widely used for the removal of undesirable scale and rust in many industrial processes [3]. In this process metal surface become more corroded due to acidic attack and inhibitors is added in the acidic solutions to control the metals dissolution as well as consumption of the acid [2, 4]. The use of synthetic inhibitors has been seriously discouraged due to its high cost, non-biodegradability and harmfulness. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors [5]. Recent researches have shown that green inhibitors are more environmental friendly than any form of inhibitors known to man [6]. It is therefore pertinent to us to explore the number of green leaves that are available for the betterment of our survival. Most green inhibitors are organic compounds that contain heteroatom's (S, N, O, and P) or those that have long carbon chains or aromatic ring systems [7].

African Parquetina is a shrub that is commonly found in West African countries especially Nigeria and Ghana [8]. The plant flourishes in equatorial climate and it is commonly used in different parts of West and East Africa for the treatment of several ailments which includes diarrhoea, gonorrhoea, menstrual disorders, insanity, intestinal worm infections, skin lesions and erectile dysfunction [9-11]. Phytochemical screening PNLE confirmed the presence of phytochemical compounds like folic acid, vitamin B₁₂, alkaloids, saponins, glycosides, tannins and anthraquinones. It was also reported that the plant contained flavonoids and the antioxidant vitamins A and C [12]. Most of these phytochemical are organic compounds that have center for π electron in which the adsorption of the inhibitor on the surface of mild steel is enhanced by their presence [13]. It has been reported that major constituents in plant extracts that enhance the inhibition potential are Saponins, alkaloids, lipids and some vitamins [14]. The present work intends to investigate the inhibitive strength of PNLE on corroded mild steel in 2M sulphuric acid solution.

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II. MATERIALS AND METHOD

Preparation of Metal Specimen

The mild steel coupon used in this study has the chemical composition shown in the Table 1.

Table 1: Chemical composition of the mild steel

Element	C	Si	Al	Ca	S	Mn	P	Fe	Cu	Cr
Composition %	0.053	0.14	0.2	0.1	-	0.48	-	97.48	0.057	0.018

Test was carried out at National Geological Survey Agency (NAGSA), Kaduna.

The mild steel specimens were mechanically cut in to dimension of 2.0 x 0.2 x 2.5 cm (with a surface area of 11.8 cm²). Prior to all, the mild steel coupons were mechanically polished with series of emery paper from 400 to 1200 grades. The specimen are washed thoroughly with distilled water, degreased with absolute ethanol, dipped into acetone and dried in air. The dried specimens stored in desiccators before used.

Preparation of Inhibitors (Extracts)

The samples were abundantly collected at Pakata Area, Ilorin kwara state, Nigeria. The leaves were washed thoroughly with water to remove unwanted material. The samples were shield dried, grinded in to powder, and weighed. Each weighed ground leaves were stored in desiccators prior to usage. 60 g of ground samples was mixed with ethanol, tightly covered to prevent evaporation and kept for 48hours to obtained high yield of the extract concentration then filtered. The filtered solution was heated in rotary evaporator set-up to expel the ethanol.

Phytochemical Analysis

The extracts analysis were carried out at National Research Institute of Chemicals Technology (NARICT), Zaria and results were printed from spectroscopy. The extracts obtained were analyzed to determine the compounds and their functional groups. These tests were;

Fourier Transformation Infrared (FTIR) analyses: Both of the extracts obtained were characterized by FTIR spectroscopy for identification of all active functional groups. The analysis was carried out with FTIR-8400S instrument.

Gas Chromatography Mass Spectrometer (GCMS) analysis: The extracts were also analyzed on GCMS-QP2010 PLUS SHIMADZU instrument, to detect all organic species present in the extracts quantitatively.

Preparation of test solution

The solution of 2M Sulphuric acid was prepared by dilution of 98 % H₂SO₄ with distilled water. The inhibitors were accurately weighed dissolve in prepared 2M H₂SO₄ acid solution to obtain different inhibitors concentrations (0.1, to 0.5 g/l). The test solutions were prepared in different containers to carry out the corrosion experiment.

Experimental Procedure

Weight loss measurement

Weight loss measurements were conducted under total immersion using 250 ml capacity plastic containing prepared solution at 30 to 60 °C which was maintained in a thermostated water bath. The mild steel coupons were weighed and dropped in the corrodent with the aid of acid resistance plastic clip. The coupons were retrieved at 3 h interval progressively for 15 h. After each exposure time, the mild steel coupons were removed, washed thoroughly to remove the corrosion product with 400-1200grade emery paper, rinsed with distilled water and dried in acetone. The mild steel was re-weighed to determine the weight loss, in gramme by the difference of mild steel weight before and after immersion. The corrosion rates (g/cm²h) in the absence and presence of the studied inhibitors were determined.

Weight loss was calculated by finding the difference between weight of each coupon before and after immersion;

$$W = W_b - W_a$$

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W_b is the weight before immersion, W_a is the weight after immersion. While the corrosion rate (g/cm^2h) in absence and presence of inhibitors was calculated using equation 2:

$$CR = \frac{\Delta w}{At} \quad 2$$

Where Δw is the weight loss (g) after exposure time t (h), A is the area of the specimen (cm^2) and t is time of exposure in hours, and CR is the corrosion rate at each exposure time.

$$I(\%) = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) \times 100 \quad 3$$

Where $I(\%)$ is inhibition efficiency, ρ_1 is the corrosion rate of mild steel in absence of inhibitors, ρ_2 is the corrosion rate of mild steel coupons in presence of concentration of inhibitors.

Hydrogen evolution measurement

Hydrogen evolution measurement was carried out using gasometric assembly similar to the gasometric setup described by [15]. The assembly was setup to measure the volume of hydrogen gas evolved from mild steel corrosion in test solution. This apparatus consist of two necked conical flask (reaction vessel) where the corrodent and metal coupons contained. Others are separating funnel, inverted calibrated tube with taps, water bath and retort stand. The measurement was carried out with different test solutions that were introduced into the reaction vessel that was connected to a inverted calibrated tube through a delivery tube. Initial volume of water in the calibrated tube was recorded and mild steel coupons were carefully dropped in the test solution then quickly closed. The volume of hydrogen gas evolved from corrosion reaction was monitored by the downward displacement of water. This displacement was monitored at 2 minutes interval, progressively for 18 minutes and the different in the level of water was recorded as the volume of hydrogen gas. From obtained values of hydrogen gas evolved, the inhibition efficiency ($I\%$) was calculated using equation 4

Corrosion rate is the Hydrogen evolution rate = Slope

$$\text{Slope} = \frac{V_f - V_i}{T_f - T_i} \quad 4$$

Where V_f (cm^3) is the Volume of hydrogen gas evolved at final time taken, V_i (cm^3) is the volume of hydrogen gas evolved at initial time taken, T_f (min) is the final time recorded and T_i (min) is the initial time recorded for each experiment.

$$CR = \text{Slope} = (V_2 - V_1) / (t_2 - t_1) \quad 5$$

$$I\% = 1 - (CR_{inh}/CR_{blank}) \quad 6$$

Where CR_{blank} is the hydrogen evolution rate in absence of inhibitors and CR_{inh} is the hydrogen evolution rate in the presence of different concentration of inhibitors.

Thermometric measurement

The thermometric measurement was conducted using digital thermometer having probe to take temperature reading in the reaction system. The temperature probe was inserted in to test tube as described by [15] and shown in Figure 1. The flask was filled with 2 M H_2SO_4 solution and mild steel coupons were carefully dropped into the test solution and quickly closed while the thermometer probe was pierced through the cock that cover the test tube. The temperature variation was monitored at ten minutes interval until maximum temperature was reached and recorded. The experiment was repeated in the absence and presence of different concentrations of studied inhibitors. Computation reaction number was calculated as obtained in the past literature ([15-16]. As below:

$$R (\text{°Cmin}^{-1}) = \frac{T_m - T_i}{t} \quad 7$$

Where T_m is the maximum temperature, T_i is the initial temperature of the system and t is time (min) taken to reach the maximum temperature. The inhibition efficiency ($\%I$) is going to compute from the value of percentage reduction in reaction number as below:

$$\%I = \frac{R_{aq} - R_{wi}}{R_{aq}} \times 100 \quad 8$$

Where R_{aq} the reaction is number of the aqueous $2MH_2SO_4$ and R_{wi} is the reaction number in the presence of each inhibitor.



Figure 1: Photograph of thermometric setup

III. EXPERIMENTAL RESULTS

Inhibition and adsorption mechanism

The power of the inhibition depends on the molecular structure of the inhibitor [17]. Organic leaf extracts were investigated to contained some functional groups like hydroxyl (OH), carboxyl (COOH), amino (NH₂), carbonyl oxygen (C=O) aromatic groups oxygen and halide groups that inhibits mild steel corrosion in H₂SO₄ by simple blocking effect mechanism. According to Abdulrahman [18-19] have reported that organic inhibitors that functioned by the simple blocking effect are mixed type inhibitor (plant extracts). Figure 2 and 3 represent the Fourier transformation infra red (FTIR) and Gas chromatography mass spectroscopy results for APLE respectively.

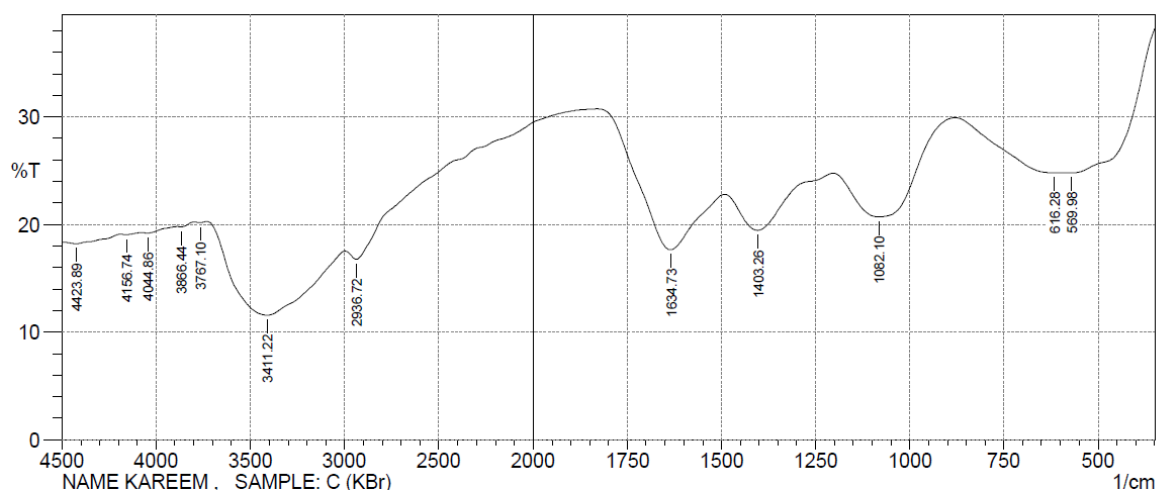


Figure 2: Fourier Transformation Infrared for APLE

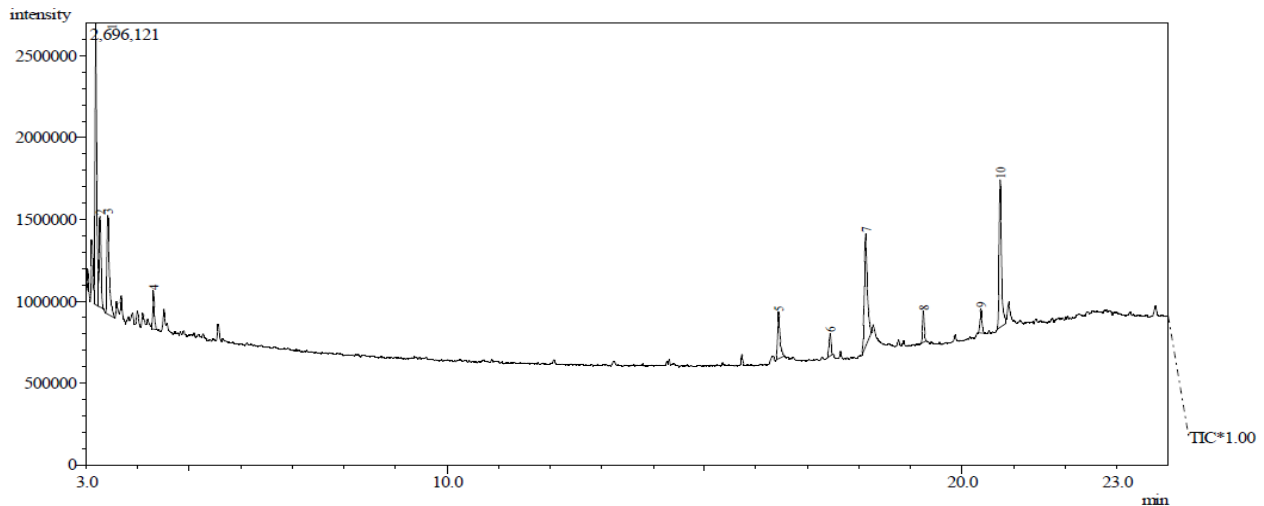
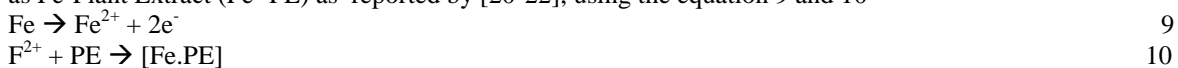


Figure 3: Gas Chromatography Mass Spectroscopy (GCMS) for APLE

It has been established that FTIR spectrophotometer is a powerful tool that can be used to identify the type of bonding particularly functional group(s) present in the organic compound. Extract contained organic compounds and these organic compounds were adsorbed on the metal surface providing protection against corrosion [20]. The presence of organic compound can be explained from the GCMS analysis carried out on the studied plant extract with their chemical structures. It is very clear from the graph that PNLE has 10 organic compounds and comprises of functional groups in their chemical structures. This presence of the functional groups was depicted with broad peaks as presented from the plate 4.1 and dissolved in the acidic solution to react with mild steel and from organometallic complex such as Fe-Plant Extract (Fe- PE) as reported by [20-22], using the equation 9 and 10



These complexes might get adsorbed onto steel surface by van der Waals force to form a protective film to isolate mild steel from corrosion. This assumption could be further confirmed by the FTIR results obtained by [23].

Inhibitor adsorption abilities are due to their molecular properties for different kinds of organic compounds present which contribute to high inhibition efficiency [24-26].

Gravimetric Measurement

Corrosion of mild steel involved chemical or electrochemical reaction with corrosive media to form a stable compound and the compounds formed are called corrosion product. The continue formation of this compound on the surface of mild steel result in deterioration of mild steel properties and consequently losing weight. It could be observed from the table that, the weight loss was also found decreasing with increase in concentration of inhibitor and decreasing with rise in temperatures.

The values of corrosion rate and inhibition efficiency listed in table 4.1 at 30 and 60 0C temperatures, showed the studied plant extracts act as good corrosion inhibitors and the obtained corrosion rate result decreased with addition of sample leaves extract and increase with rise in temperature . In fact, in some researches, weight loss was referred to corrosion rate because it determines the level of corrosion rate of mild steel in corrosion reaction. It can be found that weight of mild steel decreases with rise in temperature leading to increase in corrosion rate.

The corrosion rate value obtained was used to determine the inhibition efficiency of the studied leaves extract in corrosion process. It is much cleared from the table 2 that the inhibition efficiency increases with increase in concentration of inhibitor and decrease with rise in temperatures. The decrease in inhibition efficiency was as a result of desorption of some inhibitor substituent as lower value is obtained at 60⁰C (75.82 %) compared to the inhibition efficiency at 30⁰C (87.78 %). It has been established that increase in temperature leads to gradual desorption of the outer layer of dimeric inhibitor film and at the same time the underlying layer effectively protect the metal surface from acid attack [16]. Furthermore, the complex effect of temperature on the inhibited acid-metal reaction result from the changes in the metal surface such as rapid etching, desorption of inhibitor itself and inhibitor undergoing

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decomposition/ or rearrangement which contribute to this observed effect/ behavior [16]. Therefore exposure of mild steel to acidic media for longer period of time results in high corrosion rate and fall of inhibition efficiency at elevated temperature.

Table 2: Corrosion parameters obtained from Gravimetric measurement at 30 and 60 °C

Temp.	Conc. CP	Time (h)	0	0.1 (g/l)	0.2 (g/l)	0.3 (g/l)	0.4 (g/l)	0.5 (g/l)
30 °C	WL	2	1.36	0.52	0.41	0.31	0.28	0.22
		4	2.15	0.56	0.45	0.38	0.32	0.26
		6	3.32	0.59	0.47	0.45	0.35	0.3
		8	3.47	0.64	0.49	0.53	0.38	0.36
		10	3.58	0.67	0.52	0.59	0.44	0.42
	CR		0.0434	0.0109	0.0086	0.0076	0.0063	0.0053
60 °C	WL	2	2.16	1.17	1.05	0.84	0.77	0.68
		4	2.78	1.21	1.08	0.87	0.81	0.72
		6	3.86	1.25	1.12	0.9	0.85	0.76
		8	4.27	1.28	1.17	0.94	0.88	0.79
		10	4.62	1.32	1.21	0.98	0.92	0.83
	CR		0.0579	0.0235	0.0212	0.017	0.0157	0.014
	I %		74.88	80.18	82.25	85.54	87.78	
	I %		59.41	63.38	70.63	72.88	75.82	

Gasometric Measurement

The reaction of acid solution on mild steel in the absence and presence of inhibitor results in liberation of hydrogen gas. Figure 4 represents Graph of hydrogen gas evolved versus time at 30 and 60°C temperatures to obtain slopes which were taken as the hydrogen evolution rate or corrosion rate.

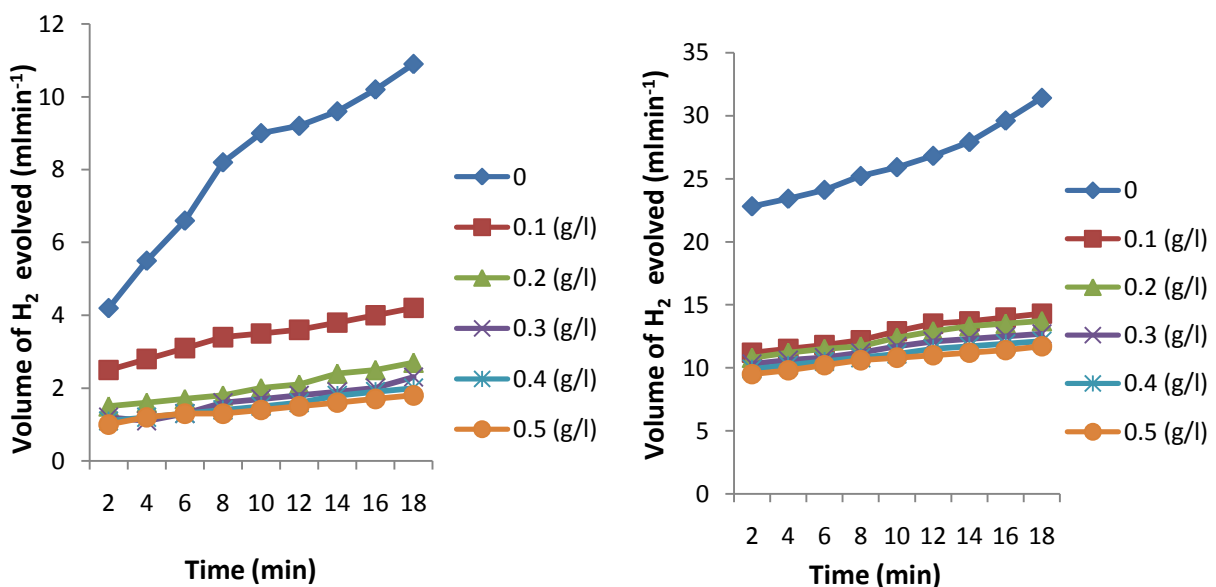


Figure 4: Graph of hydrogen gas evolved against time at 30 and 60 °C temperatures

From Figure 4 explore, it was observed that the volume of the hydrogen gas evolved in absence and presence of inhibitor increase with increase in temperature and decrease with addition of different concentrations of studied inhibitors has established that the non uniformity and non linearity of the plots as well as the differences in inhibition

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efficiency is due to the presence of mill scale on the mild steel specimen used in the corrosion study [16]. Gasometric parameters obtained which include volume of hydrogen gas evolved, the slope (hydrogen evolution rate), and inhibition efficiency are listed in Table 4 at all investigated temperature.

Table 3: Hydrogen evolution parameters obtained using PNLE

Temperature (°C)	30						60						
	Concent. (g/l)	0	0.1	0.2	0.3	0.4	0.5	0	0.1	0.2	0.3	0.4	0.5
Time (min)	2	4.2	2.5	1.5	1.2	1.1	1	22.8	11.2	10.8	10.3	9.9	9.5
	4	5.5	2.8	1.6	1.1	1.2	1.2	23.4	11.5	11.2	10.6	10.2	9.8
	6	6.6	3.1	1.7	1.3	1.3	1.3	24.1	11.8	11.5	10.8	10.5	10.2
	8	8.2	3.4	1.8	1.6	1.4	1.3	25.2	12.2	11.7	11.2	10.8	10.6
Slope	10	9	3.5	2	1.7	1.5	1.4	25.9	12.9	12.4	11.7	11.1	10.8
	12	9.2	3.6	2.1	1.8	1.6	1.5	26.8	13.5	12.9	12.1	11.5	11
	14	9.6	3.8	2.4	1.9	1.8	1.6	27.9	13.7	13.3	12.3	11.7	11.2
	16	10.2	4	2.5	2	1.9	1.7	29.6	14	13.5	12.5	11.9	11.4
	18	10.9	4.2	2.7	2.3	2	1.8	31.4	14.3	13.7	12.7	12.1	11.7
I %		0.399	0.1	0.077	0.07	0.058	0.046	0.518	0.208	0.194	0.16	0.142	0.133
			74.93	80.7	82.45	85.46	88.47		59.85	62.54	69.11	72.59	74.32

From the Table 3 the value of hydrogen evolution rate obtained as the slope from Figure 4 showed the addition of different concentration of inhibitors really reduced the rate of the gas evolved and this is corresponded to the increase in the inhibition efficiency as low value were obtained at elevated temperature but the hydrogen evolution rate increased. Similar behavior was reported by [20, 27] that the value of hydrogen evolution rate (ml/min) evaluated from the slope of volume- time plots and the inhibition efficiency increase with rise in temperature in inhibited and uninhibited system as obtained for the present study.

Thermometric Measurement

The corrosion of mild steel was investigated using thermometric readings. This method was also investigated by [16] to obtain inhibition efficiency with plot of temperature against time in the absence and presence of the different concentrations of inhibitors.

As shown in Figure 5, It was observed from the plots that the temperatures increase with increase in time as long as thermometer stays in the solution till it reaches maximum at 110 minute and then decreases. According to Solomon et al., [16] reported, the reason for this observation is not clear, but El-Etre [28] has attributed it to decreasing corrosion concentration with increasing reaction time which correspond to decrease in corrosion rate; leading to decrease in the quantity of heat evolved. At inhibited system, the maximum temperature was attained at very short time as similar behavior was obtained by Solomon et al., [16] in Figure 5 with addition of APLE in the acidic solutions resulted to reduction of maximum temperature. And this is an indication that APLE inhibit the corrosion of mild steel in the acidic medium probably by adsorption on the metal surface.

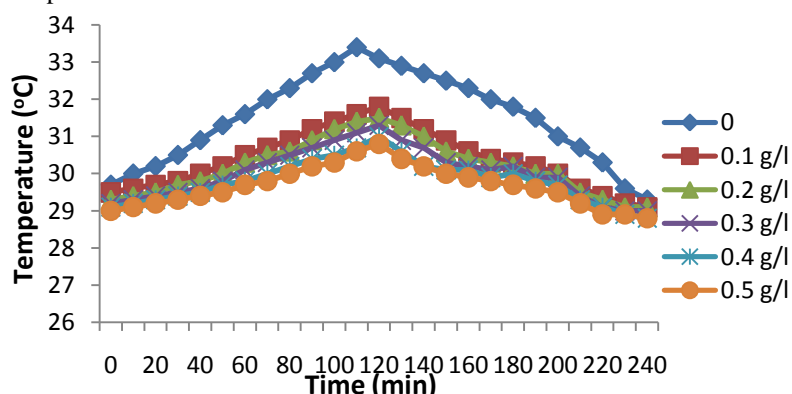


Figure 5: Graph of Temperature against time for PNLE

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Table 4: Corrosion Parameters for Thermometric measurement using APLE

Conc. of Inhibitor	0	0.1 (g/l)	0.2 (g/l)	0.3 (g/l)	0.4 (g/l)	0.5 (g/l)
Reaction Number	0.0336	0.0192	0.0183	0.0175	0.0158	0.015
Inhibition Efficiency		43.01	45.5	47.97	52.93	55.4

It has established that the extent of inhibition depends on the degree of surface coverage of the metal by the adsorbed molecules [16]. Potential adsorption is noted at the highest concentration of inhibitor which corresponds to decrease in reaction number R as showed in Table 4. The result of inhibition efficiency increased with increase in concentration of studied inhibitors.

3.5 Adsorption consideration

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption Isotherms [20]. The degree of surface coverage (θ) was evaluated for different concentrations of the studied extract from weight loss and hydrogen evolution measurement with expression $I \% = \theta \times 100$ which showed the relationship between surface coverage (θ) and inhibition efficiency (I %). The Langmuir adsorption isotherm was adopted in this work with relationship between surface coverage (θ) and inhibitors concentrations by the expression / equation 11 [16, 23]

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C \tag{11}$$

Where θ is the surface coverage, c is the concentration, K_{ads} is the equilibrium constant of adsorption process. Figure 6 represent Langmuir adsorption model for mild steel in 2M H_2SO_4 containing APLE.

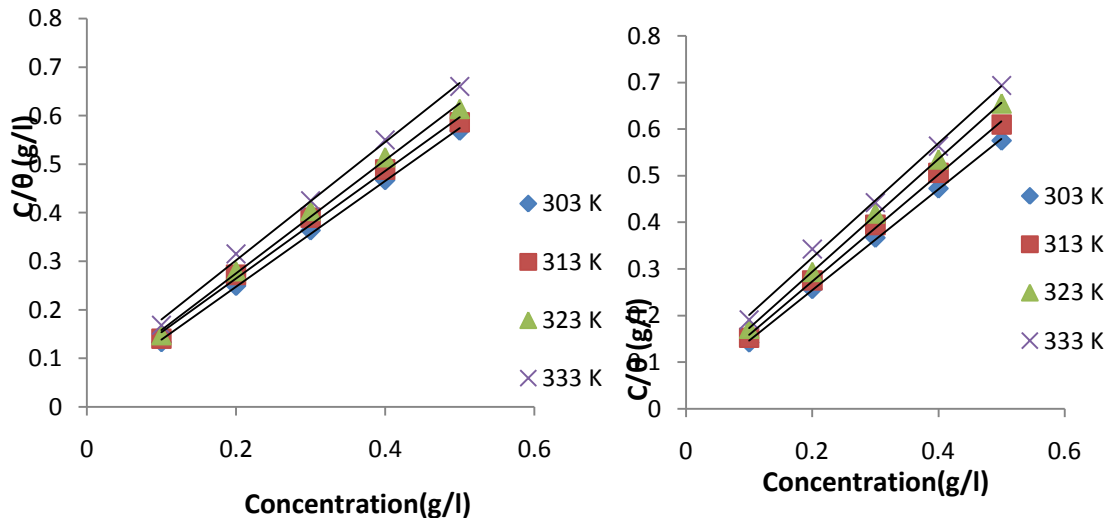


Figure 6: Langmuir adsorption isotherm model for mild steel in 2M H_2SO_4 containing APLE at different temperatures. From Figure 6 represent Langmuir adsorption model for mild steel in 2M H_2SO_4 containing APLE and the slope obtained from the graph was related with inverse of equilibrium constant of adsorption (K_{ads}) to compute the values of K_{ads} . K_{ads} was related to the free energy of adsorption (ΔG_{ads}) by the equations 12 [29].

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \tag{12}$$

Where ΔG_{ads} is the free energy of adsorption, R is molar gas constant, T is the temperature and K_{ads} is the equilibrium constant of adsorption.

The adsorption parameters derived from the Langmuir plots are listed in Table 5. The behavior of equilibrium constant of adsorption (K_{ads}) was noticed increasing with increase in temperature as the same behavior was reported by [20] that resulted in the desorption of some absorbed components of the extract on the metal surface which is consistent with the proposed physisorption mechanism

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Table 5: Adsorption parameters for inhibitors at all investigated temperatures

Methods	Temperature	slope	Intercept	K _{ads}	ΔG _{ads}	R ²
Gravimetric	30 °C	1.089	0.0300	33.3	-18.9	0.99
	40 °C	1.108	0.0432	23.14	-18.03	0.99
	50 °C	1.168	0.0418	23.93	-18.1	0.99
	60 °C	1.218	0.0583	17.14	-17.3	0.99
Gasometric	30 °C	1.08	0.0308	32.49	-18.89	0.99
	40 °C	1.09	0.0417	23.96	-18.12	0.99
	50 °C	1.18	0.0415	24.11	-18.1	0.99
	60 °C	1.24	0.0562	17.81	-17.36	0.99

From the values of free energy of adsorption obtained indicated the studied inhibitor (APLE) function by physical adsorption on mild steel surface. It has been established that the value of free energy of adsorption up to - 20 KJmol⁻¹ are consisted with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than - 40 KJmol⁻¹ involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorptions) [20]. The result obtained for free energy of adsorption (ΔG_{ads}) for studied inhibitor lie between (-18.9) and (-17.3) KJmol⁻¹ signifying spontaneous adsorption of the additives via physisorption mechanism.

Although it was reported by Solomon et al., [16] that the plots are linear as depicted by correlation coefficient (R²) values (0.99) as value of unity from the slopes are expected from ideal Langmuir adsorption equation. It has been postulated in the deviation of Langmuir isotherm equation that adsorbed molecules does not interact with one another which [16] claimed not to be true due to large organic molecule in plant extract having polar atoms or groups which can be adsorbed on the cathodic and anodic site of the metal resulting in deviation from unit gradient which also reported by other researcher [30].

Dubinnin-Radushkevich isotherm model

Experimental result obtained was also applied on Dubinnin – Radushkevich Isotherm Model (D-RIM). This model was initially used to distinguish between physical and chemical adsorption for removal of some pollutants from aqueous solution by adsorption on various adsorbents [16, 31]. It was reported that [32] applied this model in explaining the mechanism of adsorption of corrosion inhibition on to the metal surface in acidic medium and can also be used to obtain the viability of experimental methods for corrosion. The equation for the isotherm model are in equation 13, 14 and 15

$$\ln\theta = \ln\theta_{max} - a\delta^2 \tag{13}$$

where θ_{max} is the maximum surface coverage and (polany potential) and can be expressed by equation 14

$$\delta = RT \ln \left(1 + \frac{1}{C_{lin}} \right) \tag{14}$$

Where R is Molar gas constant T is the absolute temperature and such is the concentration of the inhibitor. The constant a gives the mean adsorption energy E which is the transfer energy of 1mol of adsorbate from infinity (bulk solution) to the surface of the adsorbent

$$E = \frac{1}{\sqrt{2a}} \tag{15}$$

The magnitude of E gives information about the type of adsorption and when the value of E less than 8 KJmol⁻¹ indicates physical adsorption [16, 32]. Figure 7 showed the relationship between $\ln\theta$ and δ^2 for the data obtained for the different method. From the Dubinnin – Radushkevich model as the parameters are listed the Table 6. It was observed that the values of E indicated physical adsorption mechanism and values of maximum surface coverage (θ_{max}) for the three measurements are in good agreement as similar to the range of inhibition efficiency obtained value.

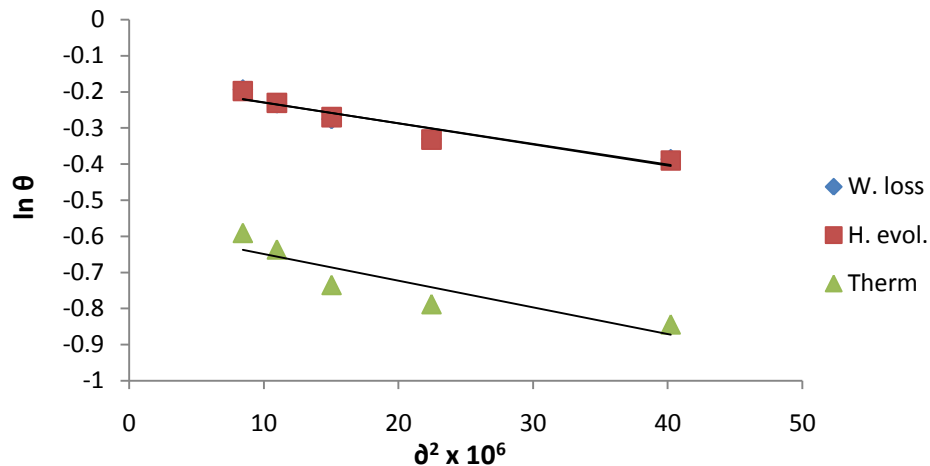


Figure 7: Dubinnin-Radushkevich isotherm model for mild steel in 2M H₂SO₄ containing APLE for different methods

Table 6: Some parameters of linear regression from Dubinnin-Radushkevich isotherm model

methods	θ_{max}	a	E	R ²
Weight loss	0.842	0.0057	7.35	0.9
Hydrogen evol.	0.8428	0.0058	7.27	0.92
Thermometric	0.563	0.0074	7.21	0.82

Effect of temperature and activation parameters of inhibition process

The effect of temperature on corrosion inhibition efficiency for mild steel in 2M H₂SO₄ in the absence and presence of different concentrations of APLE at all investigated temperature was verified with application of Arrhenius and transition state equation to evaluate activation and other kinetic corrosion parameters. The influence of this temperature in corrosion process affects the corrosion rate of mild steel and the values was used to obtained this parameters.

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation

$$\text{Log} p = \text{log} A_f - \left(\frac{E_a}{2.303 RT} \right) \tag{16}$$

Where is the corrosion rate E_a is the apparent activation energy of the mild steel dissolution, R is the molar gas constant T is the absolute temperature, and A is the frequency factor. Figure 8 depicts Arrhenius plot as log of corrosion rate (Logp) was plotted against the reciprocal of temperature (1/T) for mild steel in 2M H₂SO₄ in absence and presence of different concentrations of APLE. The plots obtained are straight lines and the activation energy was evaluated from the slope of the straight lines plots.

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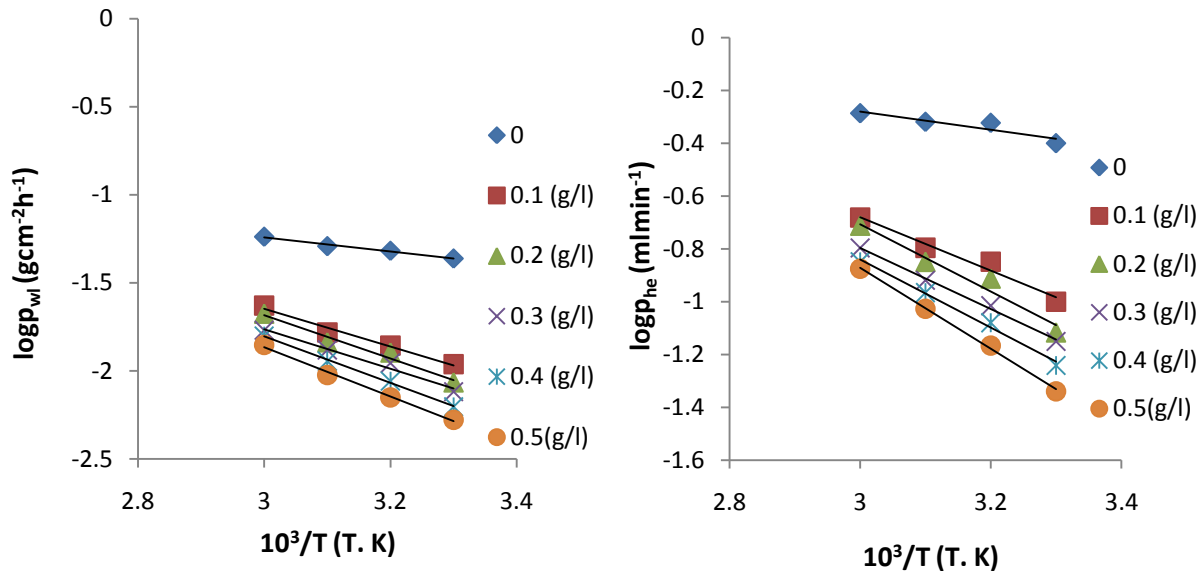


Figure 8: Arrhenius graph for mild steel corrosion in 2M H₂SO₄ in the absence and presence of APLE, for Gravimetric and Gasometric measurements

In order to calculate the enthalpy and entropy of activation for the corrosion process, the alternative formulation of Arrhenius equation, also called transition state equations was used as given in equation 17

$$\text{Log}(\rho) = \left[\left(\log\left(\frac{R}{Nh}\right) + \frac{\Delta S}{2.303R} \right) \right] - \frac{\Delta H}{2.303RT} \tag{17}$$

Where h is the Planck's constant, N is the Avogadro's number ΔS is the entropy of activation, T is the absolute temperature and R is the universal gas constant. The linear plots of $\log(\rho/T)$ against $1/T$ deduced from Equation (17) was applied in the computation of ΔH and ΔS from the slope of $(-\Delta H/2.303R)$ and intercept of $(\log(R/Nh) = \Delta S/2.303R)$ as shown in Figure 9 for both inhibitor (APLE).

The log values of corrosion rate upon the temperature ($\text{Log}(\rho/T)$) estimated were plotted against the inverse of the investigated temperatures showed in Figure 9 to obtain their slopes and the intercepts for computation of enthalpy (ΔH) and entropy (ΔS) of activation.

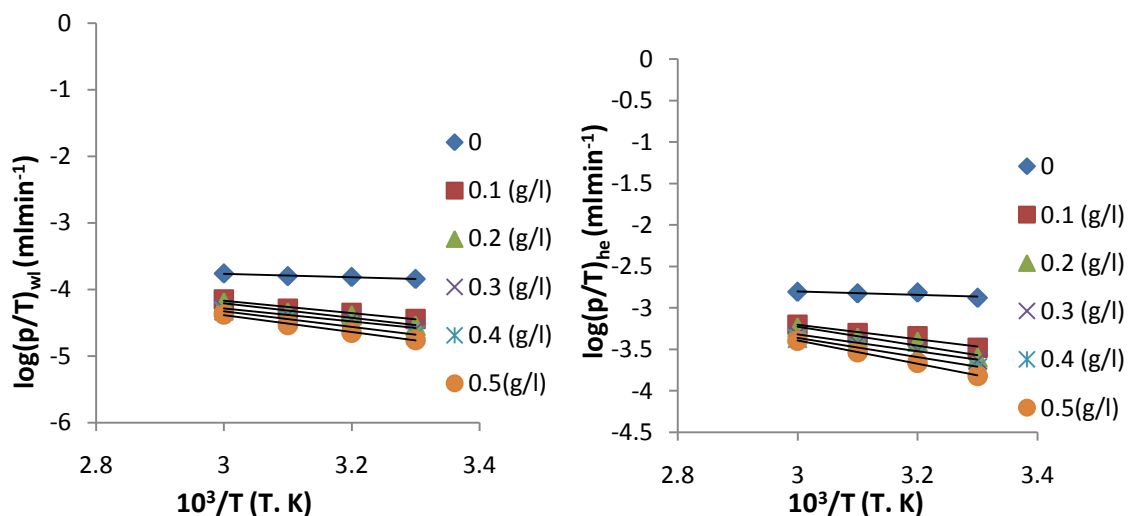


Figure 9: Transition state graph for mild steel corrosion in 2M H₂SO₄ in the absence and presence of different concentrations of PNLE for Gravimetric and Gasometric measurements.

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It can be seen in the table that E_a is higher in the presence of the inhibitors than in their absence. The modification in the values of E_a may be attributed to the geometric blocking effect of adsorbed inhibitive species on the metal surface [33]. This observation further supports the proposed physisorption mechanism as reported by [34]

The values of ΔH and ΔS are given in Table 7. The positive values of ΔH both in the absence of additives reflect the endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult [35].

Table 7: Activation parameters for mild steel corrosion in 2M H₂SO₄ in the presence and absence of different concentration of inhibitors using gravimetric and gasometric methods

Methods	Concentration (g/l)	E_a (KJ/mol)	ΔH (KJ/mol)	ΔS (Jmol ⁻¹ K ⁻¹)
Gravimetric	2M H ₂ SO ₄ Only	7.66	5.05	-254.51
	0.1 g/l of APLE	20.53	17.91	-223.65
	0.2 g/l of APLE	23.49	20.88	-215.48
	0.3 g/l of APLE	21.41	18.79	-223.26
	0.4 g/l of APLE	25.21	22.59	-212.64
	0.5 g/l of APLE	26.8	24.18	-209.03
Gasometric	2M H ₂ SO ₄ Only	6.59	3.97	-239.3
	0.1 g/l of APLE	19.32	16.71	-208.78
	0.2 g/l of APLE	24.39	21.77	-194.07
	0.3 g/l of APLE	22.18	19.56	-202.41
	0.4 g/l of APLE	24.68	22.06	-195.78
	0.5 g/l of APLE	29.31	26.68	-182.5

It is also seen in Table 7 that E_a and ΔH vary in the same manner but however, the values of ΔH are lower than that of E_a . The values of ΔS in the absence and presence of the extract are negative (Table 7). This indicates that the activated complex in the rate of determining step represents an association rather than dissociation meaning that a decrease in disordering takes place on going from reactants to activated complex. Similar observations have been reported in the literature for mild steel dissolution in the absence and presence of inhibitors in H₂SO₄ solution [27, 35]. Also the ΔS values tend to more negative values as the extract concentration increases showing more ordered behavior leading to increase inhibition efficiency.

IV. CONCLUSION

The effect of APLE as corrosion inhibitor in sulphuric acid really minimized the corrosion rate on mild steel, as lower corrosion rate obtained on addition of 0.5 g/l concentration of inhibitors. The inhibition efficiency increased in the presence of APLE but decreased with rise in temperature as 87.78 % and 75.82 % obtained for 30 and 60 °C respectively. The adsorption of APLE on mild steel obeyed the Langmuir adsorption isotherm while the Dubinin-Radushkevich isotherm model showed the adopted measurement in this work are in good agreement.

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