

Inhibitive Performance of Bitter Leaf Root Extract on Mild Steel Corrosion in Sulphuric Acid Solution

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Abstract Cost of organic and some inorganic inhibitors are relatively low but many of the effective inhibitors such as chromate, arsenate and ethanolamine are very toxic, harmful to human health and their environment. The inhibitive ability of Bitter leaf (*Vernonia amygdalina*) root extract was investigated on corrosion of mild steel in 1.5 M Sulphuric acid solution using weight loss, hydrogen evolution and thermometric measurements at temperature ranges of 30-60°C. The root extract was characterized for phytochemical screening using Gas Chromatography Mass Spectroscopy (GCMS) and Fourier Transformation Infra-Red Spectroscopy (FTIS). The result showed the extracts contained some organic compounds which are responsible for the inhibitive ability. The corrosion rate of mild steel in the presence of inhibitors decreases and increase as the temperature increases. The inhibitor exhibit excellent inhibition efficiency on mild steel corrosion in H₂SO₄ solution as 90 %, 84.82 %, 79.65 % and 76.90 % of inhibition efficiency achieved with addition of 0.5 g/l concentration of bitter leaf root extract (BLRE) at 30°C, 40°C, 50°C and 60°C temperature respectively. The inhibition efficiency increase with in concentration of inhibitor and decreases with rise in temperature. The adsorption parameters also obeyed the Langmuir adsorption isotherm and the result of Gibbs free energy of adsorption (ΔG_{ads}) showed spontaneous process of adsorption that is consistent with physical adsorption mechanism.

Keywords: bitter leaf root, inhibitive performance physical adsorption, and mild steel

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1. Introduction

Corrosion is an electrochemical phenomenon by which metallic structures are damaged slowly through anodic dissolution [1,2]. The damage is chemically induced on a metal which leads to deterioration of its properties and finally fail under construction. The failure of mild steel as construction materials can be dangerous to both human health and economy. Mild steel is much prone to corrosion when exposed to the action of bases or acids in the industries [3]. The use of inhibitors during acid pickling, acid descaling, oil well acidizing are practical methods for protection against corrosion in acidic media [3]. Among the several methods of corrosion control and prevention, the use of corrosion inhibitors, is very popular [4]. Corrosion inhibitors are used to protect metals from corrosion. It has been documented that most of the efficient inhibitors are organic compounds that contain in their structures mostly nitrogen, sulphur or oxygen atoms and function via adsorption of the molecules on the metal surface creating a barrier to corrosion attack [4]. Some organic inhibitors had been found effective to control corrosion attack but toxic to human aggressive media

attributed to the type of organic compounds that constitute their phytochemistry [5,6]. Extracts of many plants have been investigated and reported by several authors as having the potentiality to reduce metal dissolution in various aggressive acids [5]. In recent times, studies have been carried out to identify more useful applications of this abundant noxious weed and certain active compounds with antioxidant activities such as chlorophylls and carotenoids, phenols, alkaloids and terpenoids which was reported present in bitter leaf extract [7]. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its geographical location and the efficiency is justified by the phytochemical compounds present therein with molecular and electronic structures bearing close similarity to conventional organic inhibitor molecules [8]. Bitter leaf plant (*Vernonia amygdalina*) is a commonly available plant in most parts of the tropical nations in Africa and Asia. The plant leaves, root and stem are edible in which the leaves is taking as vegetable soup and the root/stem is usually taking as chew stick in some parts of west African countries (Nigeria). As shown in Figure 1, the root of bitter leaf is non toxic and cheap. *Vernonia amygdalina* leaf extract has been reported to have inhibitory effect on mild steel and stainless steel in acidic

media [9,10,11,12]. The leaves extract has been reported to contained tannin and saponins that contribute to the inhibitory action via physical adsorption mechanism [9,13]. The present study intends to investigate the performance of the root extract on mild steel in sulphuric acid solution.



Figure 1. 250 g Root samples of Bitter leaf

2. Materials and Methods

2.1. Preparation of Inhibitor (BLRE)

The Bitter Leaf Root (BLR) sample was sourced at Gidan kwano campus, Federal University of Technology, Minna, Niger State. The plants parts were washed thoroughly with water to remove unwanted material. The samples were shade dried, pulverized, and weighed. The weighed inhibitor was stored in desiccator prior used. 60 g of ground sample was mixed with ethanol, tightly cover to prevent evaporation and kept for 48 hours the extracts were filtered to obtain high yield of the concentration. The filtered solution was heated in rotary evaporator setup to expel the ethanol at 78°C for 20 min.

2.2. Phytochemical Analysis

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

Fourier Transformation Infrared (FTIR) analyses: BLRE was characterized by FTIR spectroscopy for identification of all active functional groups with FTIR-8400S instrument.

Gas Chromatography Mass Spectrometer (GCMS) analyses: BLRE also analyzed on GCMS-QP2010 PLUS SHIMADZU instrument, to detect all organic species present quantitatively.

2.3. Preparation of Test Solution

The solution of 1.5 M Sulphuric acid was prepared by dilution of 98 % H₂SO₄ with distilled water. The inhibitors were accurately weighed dissolve in prepared 1.5 M sulphuric 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.

2.4. Preparation of Metal Specimen

The mild steel sample obtained has chemical composition of carbon 0.053 %, Silicon 0.14%, Aluminium 0.2 %, Calcium 0.1 %, Manganese 0.48 %, Iron 97.48 %, Copper 0.057 % and Chromium 0.018 %.

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 to sufficiently remove any mill scale on the sample mild steel as also done by reference [14]. The specimen were washed thoroughly with distilled water, degreased with absolute ethanol, dipped into acetone and dried in air. The dried specimens were stored in desiccators before used.

2.5. Weight Loss (WL) Measurement

Weight loss measurements were conducted under total immersion using 250 ml capacity beakers containing 200 ml prepared solution at 30°C to 60°C which was maintained in a thermostated water bath. The mild steel coupons were weighed and dropped in 1.5 M sulfuric acid solution with the aid of acid resistance plastic clip. The coupons were retrieved at 3 hours interval progressively for 15 hours. After each exposure time, the mild steel coupons were removed, washed thoroughly to remove the corrosion product (Rust Stain) with emery paper, rinsed with distilled water and dried in acetone as previously reported [4,14]. 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 inhibitors were determined.

Weight loss was calculated by finding the difference between weight of each coupon before and after immersion [12,15]

$$\Delta W = W_b - W_a \quad (1)$$

W_b is the weight before immersion, W_a is the weight after immersion. While the corrosion rate (g/cm²h) in absence and presence of inhibitors was calculated using equation 2 [4].

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

Where Δw is the weight loss (g) after exposure time t (h), A is the area of the specimen (cm²), t is time of exposure in hours and CR is the corrosion rate at each exposure time. The corrosion rate obtained in the absence and presence of inhibitor was used to calculate inhibitor efficiency (IE %) as in equation 3 [14].

$$IE(\%) = \left(\frac{CR_1 - CR_2}{CR_1} \right) \times 100 \quad (3)$$

Where $IE(\%)$ is inhibition efficiency, CR_1 is the corrosion rate of mild steel in absence of inhibitors, CR_2 is the corrosion rate of mild steel coupons in presence of concentration of inhibitors.

2.6. Hydrogen Evolution (HE) measurement

Hydrogen evolution measurement was carried out using gasometric assembly similar to the gasometric setup described by [16]. The assembly was setup to measure the volume of hydrogen gas evolved from mild steel corrosion in test solution. This apparatus consists of two necked

conical flask (reaction vessel) which contained the corrodent and metal coupons. Others are separating funnel, 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 an 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 3 minutes interval, progressively for 27 minutes and the difference in the level of water was recorded as the volume of hydrogen gas. From obtained values of hydrogen gas evolved, the inhibition efficiency (IE %) was calculated using equation 4 [4,16].

$$\text{Slope} = \frac{V_f - V_i}{t_f - t_i} \quad (4)$$

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.

$$\text{IE}\% = 1 - (\text{CR}_{\text{inh}} / \text{CR}_{\text{blank}}) \quad (5)$$

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.

2.7. 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 into test tube as described by [16] and shown in

Figure 2. The flask was filled with 1.5 M H_2SO_4 solution and mild steel coupons were carefully dropped in the test solution and quickly closed while the thermometer probe was pierced through the cock that covers the test tube. The temperature variation on thermometer was monitored at 15 minutes interval until maximum temperature was reached and recorded. The experiment was repeated in the presence of different concentrations of studied inhibitors. Computation reaction number was calculated as obtained in the past literature [16,17] and this was used to evaluate the inhibition efficiency (IE %) as in equations 6 and 7:

$$R(\text{C min}^{-1}) = \frac{T_m - T_i}{t} \quad (6)$$

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 (IE %) was computed from the value of percentage reduction in reaction number as below:

$$\text{IE}\% = \frac{R_{aq} - R_{wi}}{R_{aq}} \times 100 \quad (7)$$

Where R_{aq} is the reaction number of the aqueous 1.5 M H_2SO_4 and R_{wi} is the reaction number in the presence of each inhibitors.



Figure 2. Thermometric setup

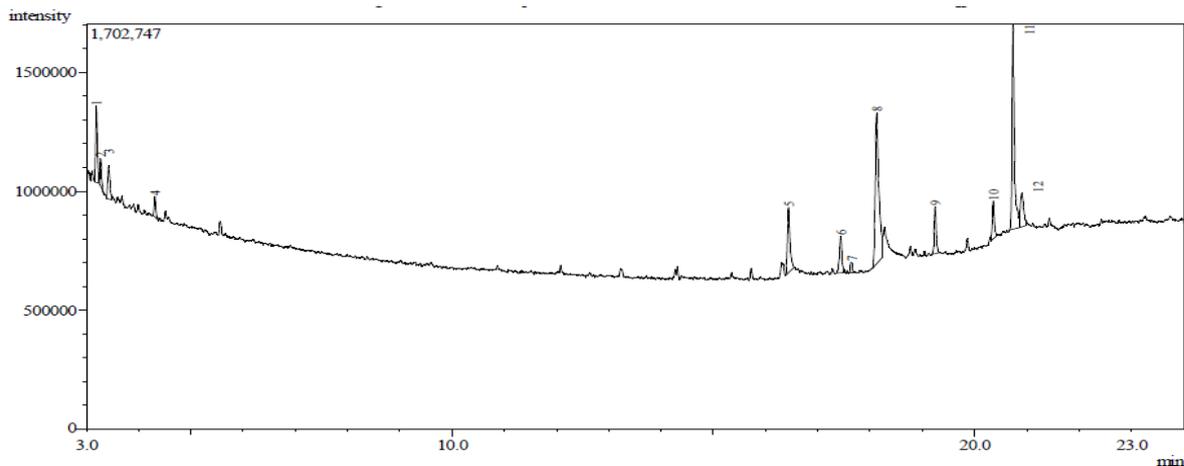


Figure 3. Chromatogram of Bitter leaf root extracts (BLRE)

3. Results and Discussion

3.1. Properties of Inhibitors in Inhibition Efficiency

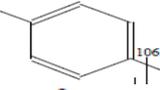
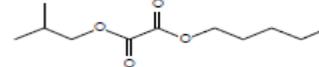
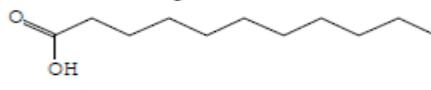
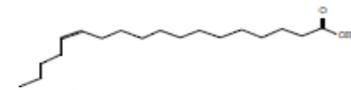
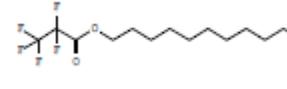
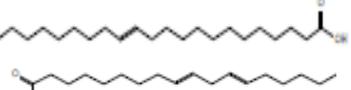
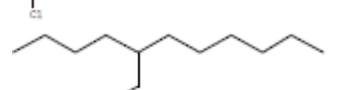
The role of inhibitors is to form a barrier of one or several molecular layers against acid attack and this

depends on phytochemical compounds which vary widely on the part of the plant and its geographical location [18]. The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process [19]. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent, and efficiency of inhibition depends on the mechanical, structural, and

chemical characteristics of the adsorption layers formed under particular conditions [19]. It was previously reported that bitter leaves extract in the literature that they contained many phytochemical compounds like tanins, saponins, alkaloids, and flavanoids [9]. Figure 3 is Gas

Chromatography Mass Spectroscopy (GCMS) of bitter leaf root extract (BLRE) to confirm the number of organic compounds in each extract. The chromatogram is plot of intensity (Relative abundance of each organic compound) against the minute (min) each organic compounds detected.

Table 1. Phytochemical Compounds name and their structure obtained from GCMS

S/N	Compounds Name	Structure
1	Ethylbenzen	
2	Decane	
3	1, 4-dimethylbenzen	
4	Isobutyl pentyl ester	
5	Nonadecanoic acid	
6	Methyl ester	
7	Methyl tridecanoate	
8	13-Docosenoic acid	
9	Pentafluoropropionic acid	
10	13-Docosenoic acid	
11	9, 12-Octadecandienyl chloride	
12	2-Buthyl-1-octanol	

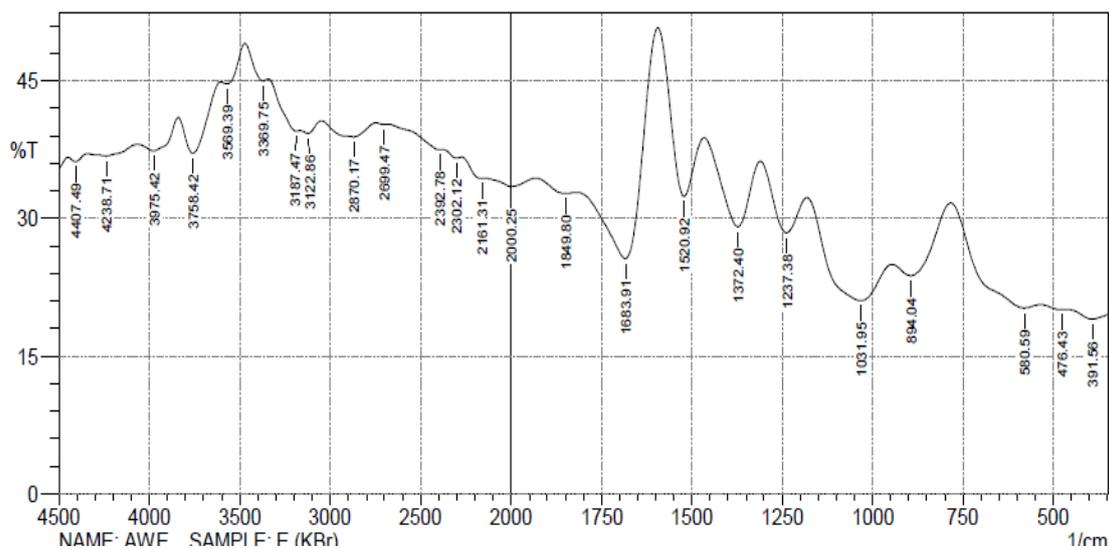


Figure 4. Infrared spectrogram of BLRE

The result from Figure 3 showed twelve peaks and it was reported that the peaks were proportional to the amount of the organic compounds formed [20]. It was observed from the chromatogram that bitter leaf root extract (BLRE) contained twelve organic compounds. The detail of the organic compounds names with their

structures are shown in Table 1. The presence of these compounds and their structures contribute to the inhibition efficiency due to the many functional groups that was found present in compounds as shown cleared in Table 1 and these functional groups were analyzed with Fourier transformation infrared spectrum (FTIS) in Figure 4.

The spectrum is the plot of percentage of intensity (Relative abundance of each functional group) and frequency values that depicts the surface coverage of each functional group in inhibition process. It has been established that the strength of the adsorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group [19]. When an H atom attached to the C in the ring is replaced by a substituent group (NH₂, OH, NH, NO₂, CHO, or COOH) and these improves inhibition [21]. Since large amount of saponin compounds was reported present in Bitter leaf root extracts, highest peak with frequency value of 1683.91 cm⁻¹ from Figure 4 is attributed to hydroxyl (OH) group which is the largest functional groups in saponin compounds according to [22].

Therefore, this protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors [19].

3.2. Corrosion Evaluation of Test Specimen without and with Inhibitor.

Reference [9] reported the evaluation of corrosion on mild steel in corrosive media without and with inhibitor by visual inspection and evaluation of corrosion parameters (corrosion rate, inhibition efficiency and surface coverage) from experimental corrosion measurement..

3.2.1. Visual Inspection

Visual inspection was investigated on the corroded mild steel specimen without and with addition of inhibitor in 1.5 H₂SO₄ solutions to compare the degree of their corrosion rates as shown in Figure 5. Image a, b, c, d, and e from Figure 5 represent the mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.5 g/l, 0.4 g/l, 0.3 g/l, 0.2 g/l, and 0.1 g/l concentration of BLRE inhibitor after 15 hours exposure time. It could be observed from the image a, b, c, d, and e in Figure 5 that the influence of BLRE as corrosion inhibitor in H₂SO₄ solution with mild steel samples reduced the formation of rust from 0.5 g/l to 0.1 g/l concentration of BLRE and this means surface specimens were protected by adhesive layer formation. The image (f) depicts mild steel sample immersed in 1.5 M H₂SO₄ solution without inhibitor after 15 hours exposure time and this gives the evidence that the sample without corrosion inhibitor corrodes uniformly as reported by [9] with increased thickness of corrosion products.

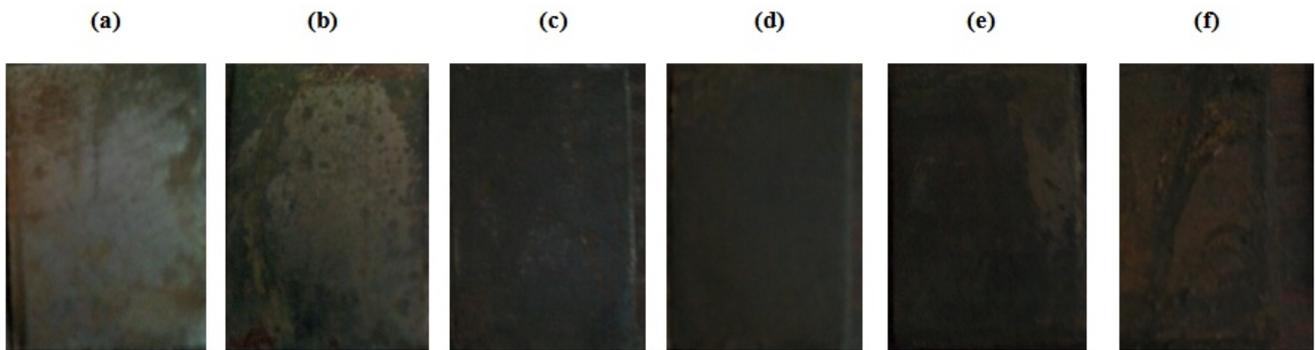


Figure 5. Immersed Mild steel specimen in 1.5 M H₂SO₄ solution for 15 hours exposure time at 30°C temperature

- (a) Mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.5 g/l concentration of BLRE inhibitor after 15 hours exposure time
- (b) Mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.4 g/l concentration of BLRE inhibitor after 15 hours exposure time
- (c) Mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.3 g/l concentration of BLRE inhibitor after 15 hours exposure time
- (d) Mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.2 g/l concentration of BLRE inhibitor after 15 hours exposure time
- (e) Mild steel sample immersed in 1.5 M H₂SO₄ solution with 0.1 g/l concentration of BLRE inhibitor after 15 hours exposure time
- (f) Mild steel sample immersed in 1.5 M H₂SO₄ solution without inhibitor after 15 hours exposure time.

Table 2. Corrosion Parameters for Weight loss and Hydrogen evolution Methods

Methods		Weight loss						Hydrogen Evolution					
Temp	Conc. (g/l)	0	0.1	0.2	0.3	0.4	0.5	0	0.1	0.2	0.3	0.4	0.5
30	CR	0.029	0.0082	0.0068	0.0057	0.0036	0.0029	0.353	0.103	0.087	0.067	0.045	0.033
	IE %		71.72	76.55	80.34	87.58	90		70.82	75.35	81.02	87.25	90.65
	θ		0.717	0.766	0.803	0.876	0.9		0.708	0.753	0.81	0.872	0.906
40	CR	0.0323	0.0097	0.0088	0.0078	0.0059	0.0049	0.485	0.151	0.136	0.125	0.096	0.079
	IE %		69.96	72.75	75.85	81.73	84.82		68.87	71.96	74.23	80.21	83.71
	θ		0.7	0.728	0.759	0.817	0.848		0.689	0.72	0.742	0.802	0.837
50	CR	0.0344	0.0119	0.0101	0.009	0.008	0.007	0.593	0.212	0.183	0.163	0.147	0.121
	IE %		65.41	70.64	73.83	76.74	79.65		64.25	69.14	72.51	75.21	79.59
	θ		0.654	0.706	0.738	0.767	0.797		0.642	0.691	0.725	0.752	0.796
60	CR	0.0368	0.015	0.0131	0.0109	0.0097	0.0085	0.634	0.258	0.231	0.191	0.173	0.145
	IE %		59.23	64.4	70.38	73.64	76.9		59.31	63.57	69.87	72.71	77.12
	θ		0.592	0.644	0.704	0.736	0.769		0.593	0.636	0.699	0.727	0.771

3.2.2. Evaluation of Corrosion Parameters.

The parameters of corrosion include corrosion rates (CR), inhibition efficiency (IE %), and surface coverage

(θ) obtained from weight loss and hydrogen evolution experimental methods are listed in Table 2 at different temperatures and concentrations of inhibitor.

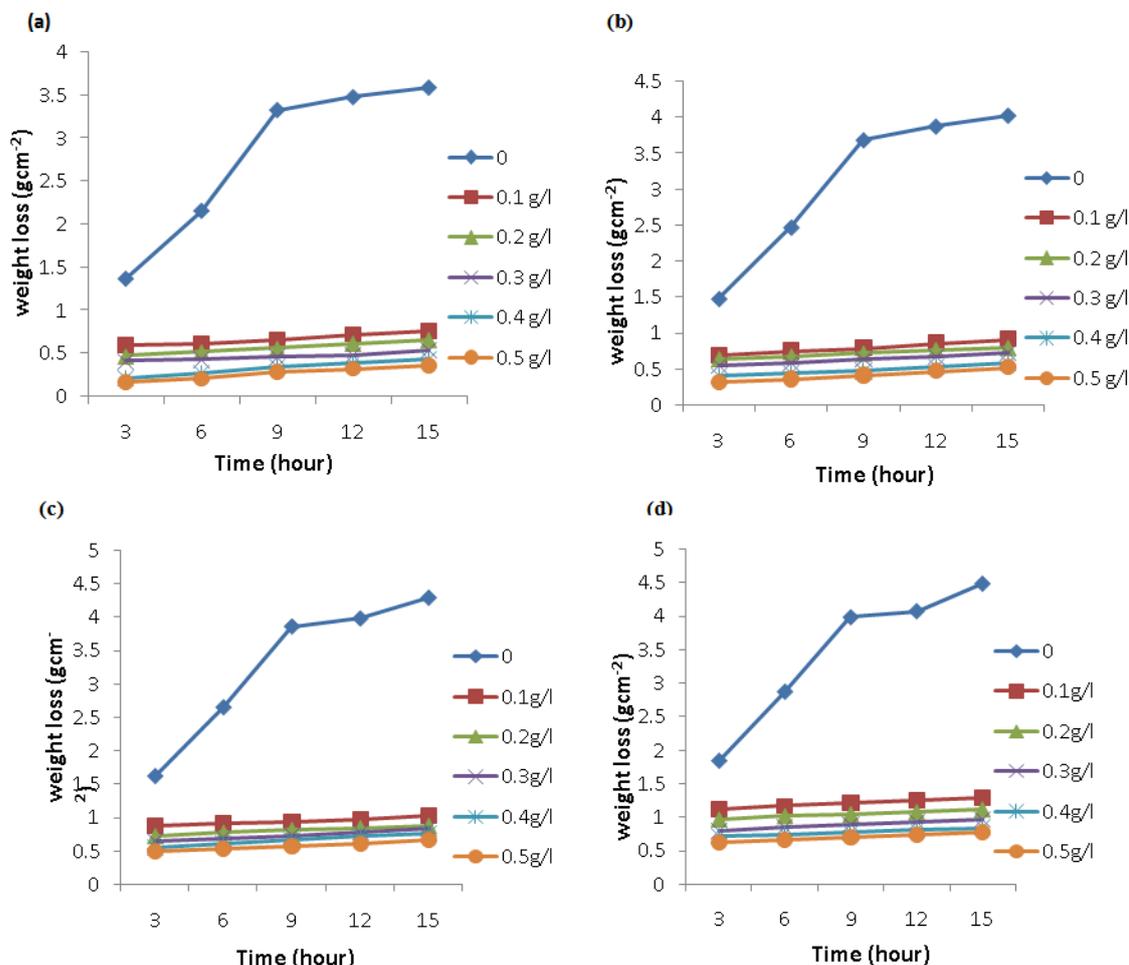


Figure 6. Plot of Weight loss against Time for mild steel in 1.5 M H₂SO₄ in absence and presence of BLRE at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C respectively

The various corrosion rates obtained decreased with addition of different concentrations of inhibitor (BLRE) and lowest values were obtained at addition of highest concentration (0.5 g/l) of the studied extracts at all investigated temperature. It is also noticed that corrosion rate of mild steel in the presence of inhibitor (BLRE) increases with rise in temperatures.

The values of inhibition efficiency (IE %) and surface coverage (θ) for each investigated inhibitors were listed in the Table 1 and it can be observed that the inhibition efficiency and surface coverage increases with increase in inhibitors concentrations. Reference [18] shows the corrosion inhibition is initiated by the displacement of adsorbed water molecules by inhibitor species leading to specific adsorption of inhibitor on the metal surface. The inhibition efficiency was found to be decreasing with rise in temperatures. Some non uniformity of inhibition efficiency values was as a result of dimeric film formed on the surface of mild steel [23]. Therefore, the inhibition decrease with increase in temperature which result to gradual desorption of the outer layer of the dimeric inhibitor film on mild steel surface.

Figure 6 and 7 depict the graphs of weight loss and volume of hydrogen gas evolved against time for mild

steel corrosion in 1.5 M H₂SO₄ in absence and presence of different concentrations of inhibitors at 30°C to 60°C respectively. It was observed from the Figure 5 that the weight loss of mild steel increase with increase in time and temperature but decrease with increase in concentration of inhibitor (BLRE).

Similar behaviour was observed in Figure 7 where liberation of hydrogen gas evolved decreased on introduction of different concentration of inhibitor (Bitter leaves root extract) compared to the liberation of hydrogen gas in solution of mild steel and sulphuric acid without inhibitor. This showed that the inhibitors slow the reaction of mild steel and 1.5M H₂SO₄. The volume of hydrogen gas evolved also observed increasing with rise in temperatures and time but decreasing with increase in concentration of inhibitors. It can be seen clearly from the Tables that hydrogen evolution rate values decrease with addition of inhibitors compared with uninhibited system. Reference [4] reported the values of hydrogen evolution rate can be correlated to the corrosion rate of mild steel coupons without and with inhibitor (BLRE) used to obtain inhibition efficiency as in Table 2. The increasing values of hydrogen evolution rate were observed with rise in temperature which is equivalent to

decreasing values of inhibition efficiency but increases with increase in the concentration of inhibitor.

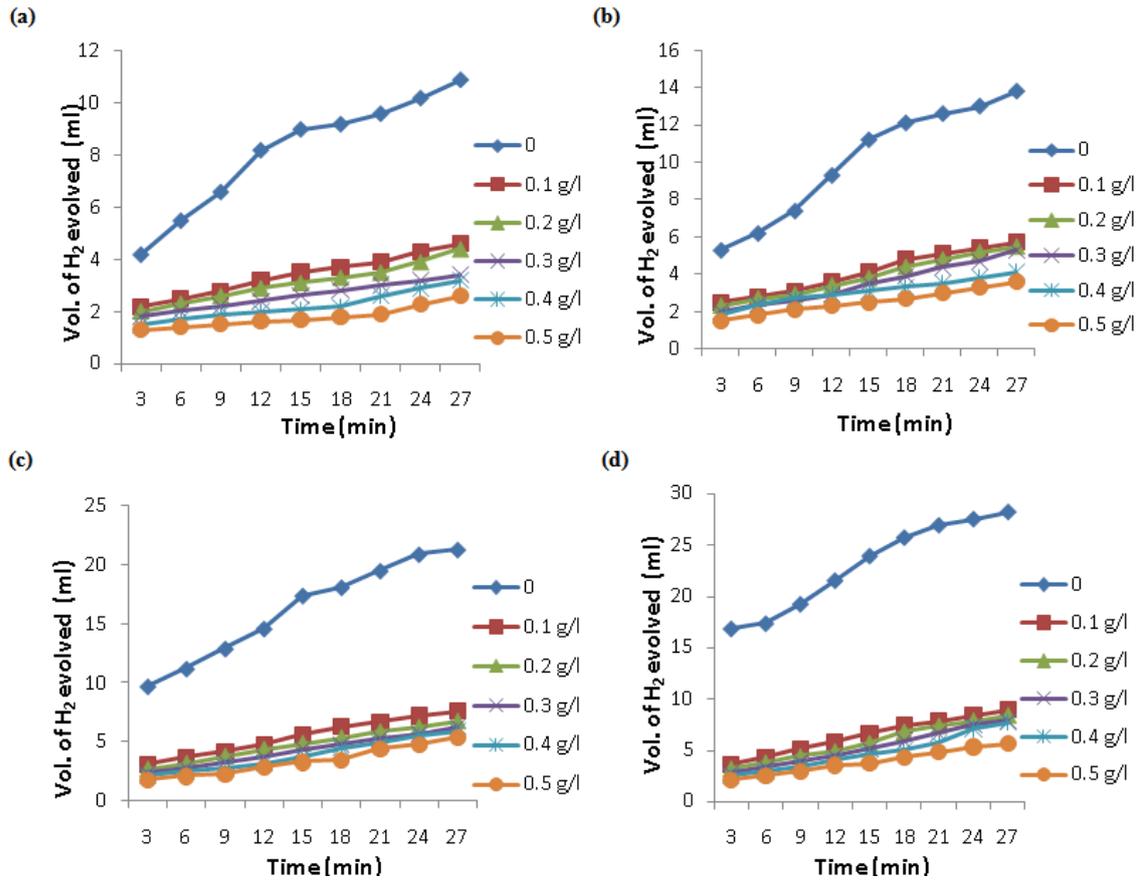


Figure 7. Plot of Volume of Hydrogen gas evolved against Time for mild steel in 1.5 M H₂SO₄ in absence and presence of BLRE at (a) 30°C, (b) 40°C, (c) 50°C and (d) 60°C respectively

3.2.2. Thermometric Measurement Corrosion Analysis.

Corrosion reaction was also investigated through digital thermometric readings obtained by inserted the thermometer in the test solution in absence and presence of studied inhibitors. According to [18,24] the significance of using this method has been proved in evaluating corrosion of metals and alloys in various corroding agents. The application of this method also showed the different behaviour of corrosion reaction on mild steel in absence

and presence of studied inhibitors. Table 3 below gives the obtained corrosion parameter for the measurement.

Conc. of Inhibitor	Reaction Number	Inhibition Efficiency
0	0.0212	
0.1 (g/l)	0.0111	47.61
0.2 (g/l)	0.0100	52.85
0.3 (g/l)	0.0094	55.48
0.4 (g/l)	0.0089	58.09
0.5 (g/l)	0.0083	60.71

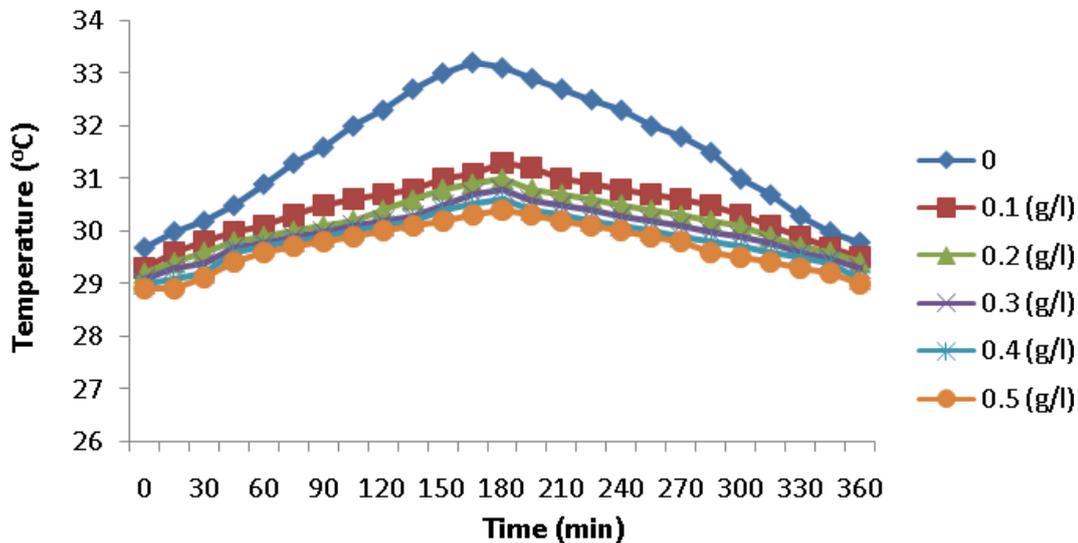


Figure 8. Graph of Temperature against time for Bitter leaf root extract

The corrosion rate in this method is the calculated reaction number listed in the Table 3 with the corresponding inhibition efficiency computed from the values of reaction number obtained. Introduction of different concentrations of inhibitors reduced the maximum temperature compared with uninhibited system reaction as showed in Figure 8.

This is an indication that the studied inhibitors inhibit corrosion of mild steel in acidic solution. It has been reported that the inhibition process depend on the degree of surface coverage of adsorbed molecules on metals. It was observed from the reaction number obtained that at highest concentration (0.5 g/l) of inhibitors added and lower valued of reaction number obtained (0.0083 for BLRE).

From the reaction numbers (RN) evaluated, it is much cleared that RN decreases with increase in concentrations of inhibitors. The inhibition efficiency increase with increase in concentration of inhibitors as 60.71% was obtained at 0.5 g/l concentration.

3.3. Adsorption Considerations

Adsorption is the process in which atoms, ions or molecules from chemical substances adhere to a surface of the adsorbent. Adsorption behaviour is usually described and analyzed with adsorption isotherm model like Freundlich, Flory-Huggins, Temkin, Bockris-swinkles, Langmuir and Frumkin adsorption isotherms [18].

The degree of surface coverage was obtained for different concentrations of the studied extract from weight loss and hydrogen evolution measurement with expression $IE \% = \theta \times 100$ and the obtained values of inhibitors concentration upon the surface coverage (C/θ).

The adsorption was achieved by fitting the degree of surface coverage data into various adsorption isotherms or models and the correlation coefficients (highest) used to determine the best fit isotherm which can then be used to describe the inhibitor adsorption mechanism [6]. The evaluated values obtained for ratio of inhibitor concentration to surface coverage was applied on adsorption isotherm using Langmuir adsorption model which relates the degree of surface coverage to the different concentrations of the studied inhibitor with equation 8 [18]

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (8)$$

Where θ is the surface coverage and is division of inhibition efficiency (IE %) by 100, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. Figure 9 represent the plots of Langmuir adsorption model for mild steel in 1.5M H_2SO_4 containing bitter leaf root extract (BLRE), obtained from weight loss and hydrogen evolution measurement in which the values were plotted against the concentration of inhibitors (C).

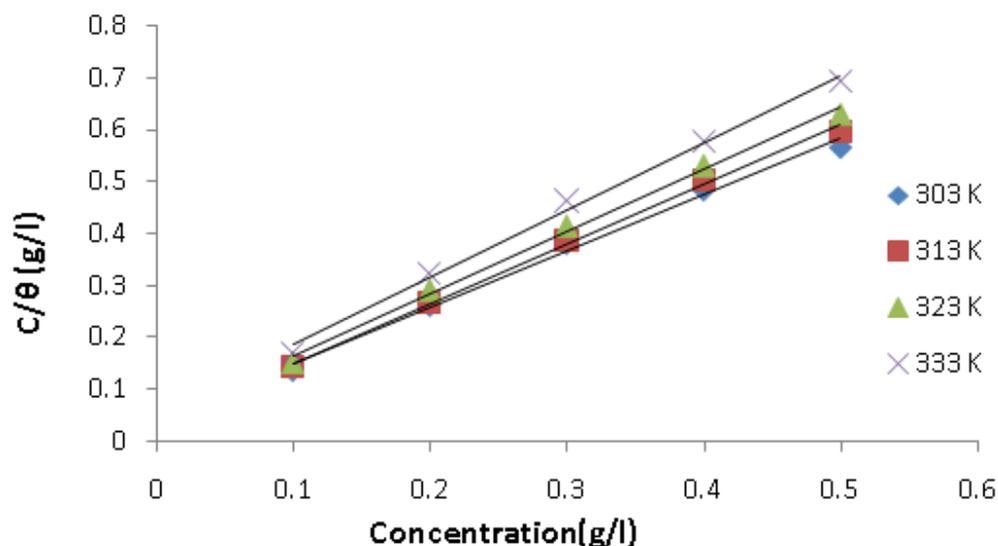


Figure 9. Langmuir adsorption isotherm model for mild steel in 1.5M H_2SO_4 containing BLRE at different temperatures

From Figure 9 represent Langmuir adsorption model for mild steel in 1.5M H_2SO_4 containing BLRE. The intercept 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 free energy of adsorption ΔG_{ads} as employed by many researchers [6,25,26]

$$K_{ads} = (1/55.5) \text{Exp}(-\Delta G_{ads} / RT) \quad (9)$$

Where 55.5 is the water concentration, R is the universal gas constant and T is the thermodynamic temperature.

Table 4 represent the Langmuir adsorption parameters obtained for both studied inhibitors at all investigated temperatur

Table 4. Some parameters from Langmuir isotherm in method

Methods	Temp.	ΔG_{ads} (KJ/mol)	Slope	K_{ads} (g/l)	R^2
Weight Loss	30°C	-17.71	1.020	20.36	0.99
	40°C	-17.57	1.100	19.23	0.99
	50°C	-18.10	1.186	23.78	0.99
	60°C	-17.14	1.195	16.25	0.99
Hydrogen Evolution	30°C	-17.50	1.020	18.72	0.99
	40°C	-17.41	1.130	18.07	0.99
	50°C	-17.36	1.140	17.40	0.99
	60°C	-16.63	1.150	13.24	0.99

The adsorption parameters derived from value indicate the binding power of the inhibitor to the metal surface is decreasing with increase in temperature [27]. The same values was obtained in K_{ads} value from the Table 4 and this behavior was reported increase in temperature results in desorption of some absorbed components of the extract on the metal surface which is consistent with the physisorption mechanism [4,6].

It was observed from the correlation coefficient (R^2) obtained that strong inhibitive and adsorption behaviour was acquired using the investigated extracts. The linearity of Langmuir isotherm plots depict by R^2 value (0.99) and the inhibitor adsorbed on anodic/cathodic sites resulting to the deviation of unit gradients of correlation coefficient [28].

The free energy of adsorption of (ΔG_{ads}) obtained from equation 4.3 and given in the Table 4. The result obtained were negatives and this implied spontaneous process of adsorption of studied inhibitor via physical adsorption process. It was also observed that the free energy of adsorption decrease with increase in temperature. Reference [18] reported this phenomenon that the adsorption of inhibitor on to mild steel surface was unfavorable with increase in experimental temperatures which result to desorption of adsorption inhibitor from the metal surface. Many researcher have reported the values of free energy of adsorption (ΔG_{ads}) is around -20 KJ/mol or less as obtained in the present study is consistent with physisorption adsorption and when it is around -40

KJ/mol or higher is consistent with chemical adsorption mechanism.

3.4. Effect of Temperature on Corrosion Rate

The influence of temperature on corrosion of mild steel showed in the relationship between corrosion rate and inhibition efficiency as reported previously. This effect contributed to rapid corrosion of mild steel and reduces the inhibition efficiency of any inhibitors applied to protect the surface of the metal. Further analysis was carried out with Arrhenius equation to obtain the kinetic corrosion parameters for the temperature influence on mild steel in H_2SO_4 in absence and presence of BLRE. The equation to analyze this, is given in equation 10 [14].

$$\text{LogCR} = \log A - \left(\frac{E_a}{2.303RT} \right) \quad (10)$$

Where CR 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 10a and 10b represent the Arrhenius graph for weight loss (wl) and hydrogen evolution (he) measurements where log of corrosion rate (LogCR) was plotted against the inverse of temperature ($1/T$) values for mild steel in 1.5M H_2SO_4 in absence and presence of inhibitors (BLRE).

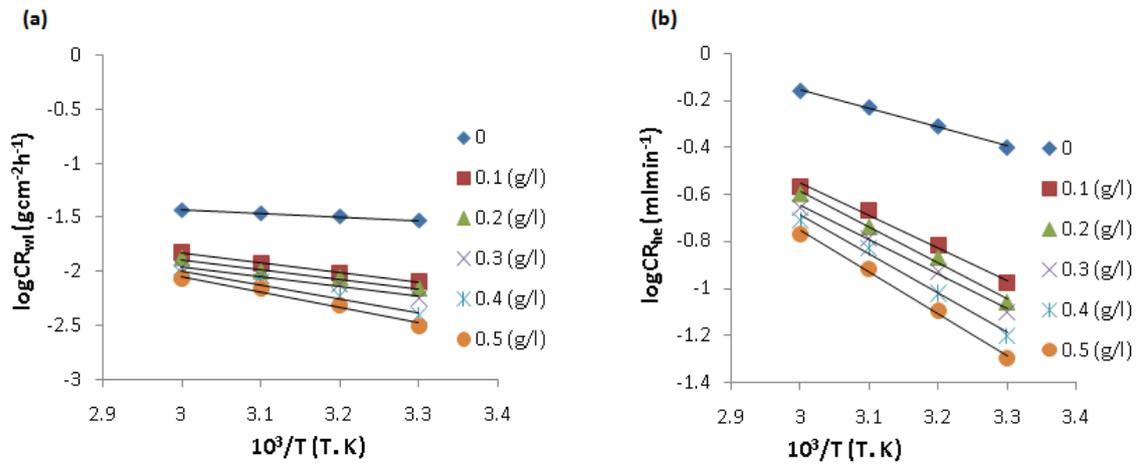


Figure 10. a and b: Arrhenius graph for mild steel corrosion in 1.5M H_2SO_4 in the presence and absence of BLRE using weight and hydrogen evolution methods respectively

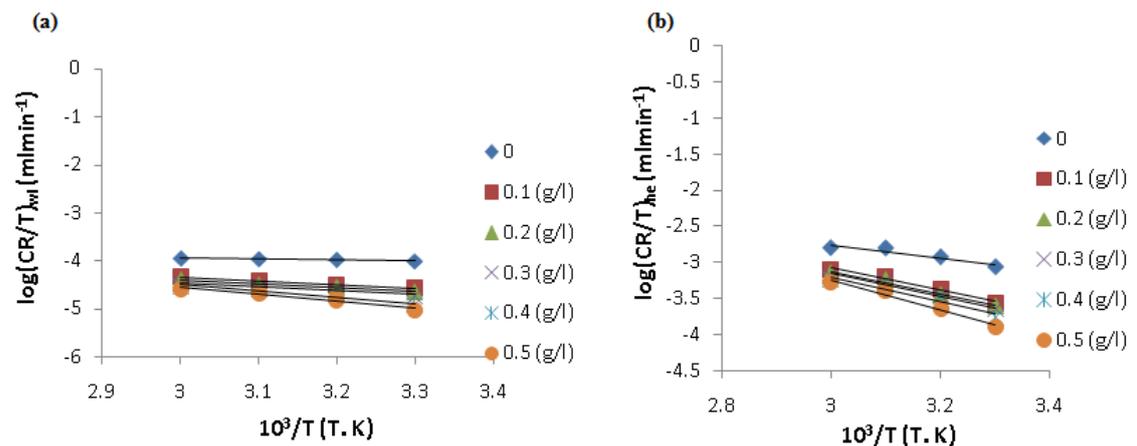


Figure 11. Transition state graph for mild steel corrosion in 1.5 M H_2SO_4 in the presence and absence of BLRE using weight loss and hydrogen evolution methods

Straight lines graphs were obtained and the activation energy was evaluated from the slope of the straight line plots

In order to calculate enthalpy and entropy of activation for the corrosion process, the alternative formulation of Arrhenius equation, also called transition state equations was given in equation 11 [14].

$$\text{Log}(\text{CR}) = \left[\log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{2.303R}\right) \right] - \frac{\Delta H}{2.303RT} \quad (11)$$

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 $\log(\text{CR}/T)$ against $1/T$ deduced from Equation (11) 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 11 for both measurements and this represent Transition state graph for mild steel in 1.5M H_2SO_4 in the presence and absence of inhibitors using both measurement values.

The slopes and intercept obtained from Figure 11a and 11b were used to evaluate enthalpy and entropy change of the system and the values obtained are presented in Table 5. Table 5 give the activation parameters of temperature influence on corrosion rate of mild steel in the absence and presence of inhibitor with 1.5 M sulfuric acid.

Table 5. Activation parameters where values of E_a , ΔH and ΔS are given

Methods	Concentration (g/l)	E_a (KJ/mol)	ΔH (KJ/mol)	ΔS ($\text{Jmol}^{-1}\text{K}^{-1}$)
Weight Loss (wl)	1.5M H_2SO_4 Only	6.31856	3.89376	-261.59
	0.1 g/l of BLRE	17.2324	14.2987	-238.02
	0.2 g/l of BLRE	17.2324	14.9570	-237.16
	0.3 g/l of BLRE	17.4239	14.9690	-238.35
	0.4 g/l of BLRE	24.3169	24.3592	-210.82
	0.5 g/l of BLRE	27.5719	27.7193	-201.66
Hydrogen Evolution (he)	2M H_2SO_4 Only	15.3177	13.6600	-208.16
	0.1 g/l of BLRE	26.4231	22.9172	-187.97
	0.2 g/l of BLRE	28.9122	23.9602	-185.80
	0.3 g/l of BLRE	27.9548	25.8370	-181.26
	0.4 g/l of BLRE	31.7843	34.1937	-156.68
	0.5 g/l of BLRE	33.8904	37.5548	-147.94

Increased activation energy (E_a) in inhibited solutions compared to the uninhibited 1.5 M H_2SO_4 suggests that the inhibitor adsorbed on the corroding mild steel surface is consistent with physical adsorption mechanism while either unchanged or lower E_a in the presence of inhibitor suggest chemisorptions [29]. It is seen from Table 5 that E_a values were lower in the presence of studied leaves extract compared to that in their absence hence leading to reduction in the corrosion rates.

However, It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [3,30]. The apparent activation energy (E_a) values obtained in Table 5 occur primarily through physisorption mechanism on the mild steel surface in the presence of inhibitor (BLRE).

The positive values of ΔH both in the absence and presence of inhibitors reflect the endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult [31]. It was observed in Table 5 that E_a and ΔH vary in the same manner but however, the values of ΔH are lower than that of E_a . This has been reported that the corrosion process must involve a gaseous reaction, simply hydrogen evolution reaction associated with decrease in total reaction volume [29,32]. The values of ΔS in the absence and presence of the extract are negative (Table 5). 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 H_2SO_4 solution [4,31]. Also the ΔS values tend to more negative values as the extract concentration increases showing more ordered behavior leading to increase inhibition efficiency. The gradual increase in negative entropy (ΔS) in the presence of the inhibitor signifies the formation of more ordered stable layer of active molecules of the extracts on the mild steel surface as extract concentration increase [33].

3.5. Conclusion

The main conclusion drawn from the corrosion inhibition potential of studied plant extract (Inhibitors) on mild steel in 1.5M H_2SO_4 examined by weight loss, hydrogen evolution and thermometric measurement studies are:

1. The presence of functional groups in phytochemical compounds structure confirmed from GCMS and FTIR analyses increased the inhibitive action of the inhibitors
2. The inhibitor exhibit excellent inhibition efficiency on mild steel corrosion in H_2SO_4 solution than the leaf samples. The inhibition efficiency increase with increase in concentration of inhibitors as 90 % obtained at 30°C compared with 69 % inhibition efficiency obtained for bitter leaf extract on stainless steel, 80 % inhibition efficiency for *Sida acuta* leaves extract from the literature at same temperature but the root samples are scarce to obtained compared to the leaf samples.
3. The result of free energy of adsorption decrease with increase in temperature. The values obtained for free

energy of adsorption were negatives and this implied spontaneous process of adsorption that is consistent with physical adsorption process.

- The positive values of ΔH both in the absence and presence of inhibitors reflect the endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult. Finally, the ΔS values tend to more negative values as the extract concentration increases showed more ordered behavior that result to increase inhibition efficiency.

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