

Research Article

Thermodynamic Investigation of *Leptadenia Hastata* (Yadiya) Leaves Extract on Corrosion Inhibition of Mild Steel in Acidic Media

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ABSTRACT

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The inhibiting effect of *Leptadenia hastata* (Yadiya) leaves extract on corrosion inhibition of mild steel in acidic media was studied by thermo gravimetric techniques. Three temperatures ranging from 313 K – 333 K with interval of 10 °C were used to study the effect of temperature on corrosion behavior of mild steel. The thermodynamic parameters and the values of free energy of adsorption for investigated extract were calculated and discussed. The results show that inhibition efficiency increases with increasing the inhibitor concentration, which is attributed to the presence of phyto-compounds in the extract. On the other hand, the decrease of inhibition efficiency with increase in temperature indicates the adsorption to be chemisorption. The adsorption of the extract on the mild steel surface obeys the Langmuir adsorption isotherm. It was found that the adsorption increases, in the same direction as inhibition efficiency. The results obtained depict the influences of temperature and its effects on corrosion control in acidic medium.

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INTRODUCTION

The advent and improvement of today's metallurgy, developing ferrous alloys of distinct grades which are more easily affected by corrosion than the iron produced in ancient times, has made the Iron Age a remarkable one (Khanna, 2002). The most important of these alloys is Steel (an alloy of iron and carbon, which has low carbon content, especially mild steel is the most commonly, used metal due to its cheapness, availability and excellent mechanical properties). Financial losses have been assessed in several studies which conclude that premature materials degradation costs industrialized nations approximately 3 % of their gross domestic product (GDP) (Angst, 2018). Despite this, an estimate shows that 25-30 % of this could be avoided if corrosion prevention technologies are put in place (NACE, 2002). Corrosion may be defined broadly as the destruction or deterioration of metal by direct chemical and electrochemical reactions with its environment (Buchweishaija, 2009). Most simply stated, metallic corrosion is the reverse of electroplating. The metal being corroded forms the anode while the cathode is that being electroplated. Metallic corrosion occurs because in many environments most metals are not inherently stable and tend to revert to some more stable combination which the metallic ores as found in nature are familiar with (Uzorh, 2013). Generally, the dissolution of metal can be suppressed by the action of adsorptive inhibitors which may prevent the assays.

MATERIALS AND METHODS

Materials

The materials used for this study include:

The low carbon steel with chemical compositions shown in Table 2 was analysed at Spectral Laboratory Service, Kaduna by the XRF method. This was done to determine the

adsorption of the aggressive ions, and by the formation of a more resistant film on the metallic surface (El Maghraby, 2009). However, the secondary environmental effect of severe hazard inflicted on the ecosystem due to the carcinogenic and non-biodegradable nature of synthetic inorganic inhibitors, has made the scientific community begin to search for eco-friendly inhibitors like the green organic inhibitors, which are biodegradable and poses no advance environmental effect (Abdel-Gaber *et al.*, 2011). Green organic inhibitors of corrosion are those derived from some plant's extract or biodegradable material and cause the reduction of dissolved metal, reducing its corrosion rate. The natural plant extract contains a variety of organic compounds, for example, amino acids, alkaloids, steroids, flavonoids, proteins and tannins as a green alternative for toxic and hazardous compounds (Anbarasi and Vasudha, 2014). Moreover, the use of organic inhibitors is specifically interesting due to their cheapness, availability, non-toxic, renewability and eco-friendliness whereas *Leptadenia hastata* (*Yadiya*) is one of these inhibitors and has never been used as a corrosion inhibitor. This research work is aimed at investigating the corrosion inhibiting effect of *Leptadenia Hastata* (*Yadiya*) leaves extract using mild steel in an acidic medium. The objectives are to formulate the extract through the soxhlet method and to carry out a corrosion test using the thermodynamics method.

elements present and their percentage in the steel. *Leptadenia Hastata* (*Yadiya*) leaves, Masking tapes, cotton wool, burette, dropper, hand gloves, thread, plastic container and abrasive papers were used.

Chemicals, Solvents and Reagents

1M HCl and 1M H₂SO₄ were the chemicals used for the preparation of the medium needed for the corrosion process. Distilled Water, Ethanol and Acetone were the solvents used for extract preparation and Ferric chloride, 1 M

NaOH, silica gel, Molish, Mayers and Fehling's reagents were used for phytochemical screening obtained from Emmicon scientific supplies chemical store, Adjacent Mara-Zain Hotel Bama Road Maiduguri.

Table 1: The equipment used for this research include the following

INSTRUMENT/ EQUIPMENT	USE
Bench vice, hack saw, metal scraper:	Used to cut and prepare the steel bar into required dimension (coupons).
Xenometrix XRF Machine (Model: Genius IF)	For determining the elemental composition of the steel bar.
Analytical mass balance (Newacalox: Mode 8068, 100×0.001g): Desiccator:	For measuring the mass of samples. used for drying and keeping the prepared samples air tight
Soxhlet extractor Separating funnel and filter paper:	for preparation of extracts For filtration of mixture of ethanol and leave or from their chaff.
Conical flask, water bath (Gulfex Medical and Scientific: HH-420	Used for conducting thermodynamics test

Methods**Preparation of the leaves sample**

The *Leptadenia hastata* (Yadiya) leaves collected from Ramat Polytechnic School Farm were washed with tap water to remove dirt, and shade dried to remove the moisture content. The leaves were then pulverized into a fine powder and weighed on the analytical mass balance to 700 g (Loto *et al.*, 2012).

Extraction

The powdered sample of 30 g was placed inside a thimble made from filter paper, which is loaded into the extraction chamber of the Soxhlet apparatus, and further attached to a round bottom flask containing a solvent (methanol) and a condenser. The solvent 400 ml was heated causing it to evaporate at 65 °C.

The hot solvent vapour travels up to the condenser, where it cools and drips down onto the dry powder. The chamber containing the powder slowly fills with warm solvent until, when it is almost full, which was emptied by siphon action, back down to the flask. This cycle was allowed to repeat many times. During each cycle, a portion of the material dissolves in the solvent until the entire leaching is carried out. Concentrate and excess solvent were removed using a vacuum rotary evaporator, leaving behind only the crude extracts material and scrap with the use of a metal scraper into a beaker, covered with Aluminum foil and stored in a desiccator for further use (Adam *et al.*, 2019).

Preparation of mild steel specimen

The mild steel used for this research was obtained from Maiduguri Monday Market opposite NEPA headquarters. The steel was sectioned for elemental analysis using X-Ray Fluorescence. However, the steel material was obtained in form of pipe, sectioned by a cutting machine and mechanically pressed into a flat bar and later cut into straight square rods, which were further turned into a cylindrical cross-section for further processing. Samples for Thermo-gravimetric analysis was prepared.

According to ASTM G1-03, as adopted by Ibrahim and Habbab (2011), low carbon steel rods mechanically cut into a cylindrical shape with a diameter of 10 mm and a thickness of 10 mm was polished to mirror surface with abrasive papers of 80 to 800 grades. The specimens were first washed with water, then degreased in ethanol, followed by water and finally in acetone. The samples were allowed to dry in the air before preservation in a desiccator to avoid re-oxidation.

Table 2: Elemental Analysis

Elements	Composition (%)
C	0.394
Si	1.538
Ba	0.039
Pb	0.015
S	0.07
Cl	0.092
Rb	0.092
Cr	0.028
Al	1.344
Ca	0.093
Cu	0.019
Ti	0.032
Mn	0.48
Sn	0.005
Ag	0.002
Sb	0.009
Fe	93.401
Mg	2.436

Experimental Procedure

Previously conditioned weighed specimens were immersed in 100 ml of 1M HCl and 1M H₂S₄ acid respectively with constant time (1 hour) but varying temperature viz; 313 K, 323 K, 333 K. The first sets of tests carry out without an inhibitor to serve as a control, subsequently in a test solution containing

$$\log \frac{R_1}{R_2} = \frac{-Ea}{2.303RT}$$

proprietary extract concentrations ranging from 0 – 1000 ppm. The thermodynamic parameters such as heat of adsorption of the inhibitor on the metal surface (Q), change in free energy of the reaction, corrosion rate and energy of activation for corrosion reaction of low carbon steel (E) calculated using the Arrhenius equation (Yaro *et al.*, 2010):

1

Where: R₁ and R₂ are the corrosion rates at any given two different temperatures,

R = Gas constant

Ea = Activation energy

T = Absolute Temperature

The free energy of absorption of inhibitors was calculated according to equation below (Zhang and Hua., 2009).

$$\Delta G (\text{ads}) = -RT \ln 55.5K \quad 2$$

Where:

$\Delta G (\text{ads})$ = Gibbs energy of absorption (KJ/mole)

R = Universal Gas Constant (KJ)

T = Absolute temperature (K)

K = Equilibrium constant

To study the absorption characteristics of leaves extracts on low carbon steel surfaces, values from the degree of surface coverage were used to fit curves for Langmuir adsorption isotherms.

The Langmuir adsorption isotherms equation relates the degree of surface coverage with the concentration of the inhibitor in the bulk electrolyte as follows:

$$K = \frac{\theta}{C(1-\theta)} \quad 3$$

θ = Degree of surface coverage,

C = Concentration of inhibitor

Enthalpy (ΔH) and Entropy (ΔS) of Adsorption

Enthalpy is defined as a measure of the total energy of a thermodynamics system and entropy is the degree of disorder of a body. The enthalpy (heat) (ΔH) and the entropy (ΔS) of adsorption of the inhibitors were calculated from the transition state equation (Umoren *et al.*, 2009).

$$C.R = \frac{RT}{Nh} \exp \frac{(\Delta S)}{R} \exp \frac{(\Delta H)}{RT} \quad 4$$

Where; C.R is corrosion rate, h is plank constant ($6.62606957 \times 10^{-34} \text{ m}^2 \text{ Kg/s}$), N is the Avogadro's number ($6.02214129 \times 10^{23}$) and R is the gas constant ($0.00831447 \text{ KJ/ mol}$). The values of ΔH and ΔS were obtained from the slope and intercept of $\text{Log} \frac{CR}{T}$ VS $\frac{1}{T}$ respectively, with the slope equal

$(\frac{-\Delta H}{2.303R})$ and intercept equal

$$\left(\text{Log} \frac{R}{NH} + \frac{\Delta S}{2.303R} \right) \quad 5$$

RESULTS AND DISCUSSION

Thermo gravimetric Analysis of Coupons in HCl

The temperature tendency of the inhibitor's efficiency was analysed by weight loss measurements in the temperature ranging from 313-333 K for different inhibitor concentrations. The results portrayed in figure 1 shows that an increase in the temperature of the corrosive environment from 313-323 K enhances the corrosion rate which leads to the decline in the efficiency from 36 %, 69 %, 87 % and 82 %, to 26 %, 40 %, 83 % and 55 % for

250 ppm, 500ppm, 750 ppm and 1000 ppm concentration of *Leptadenia Hastata* (*Yadiya*) extract. Although there is an increment of inhibition efficiency from temperature 323-333 K for 250 ppm, 500 ppm and 1000 ppm the efficiency is still less than the initial obtained. The reduction in inhibition efficiency can be due to the increased effect of temperature on the low carbon steel dissolution process and partial desorption of the adsorbed inhibitor molecules from the metal surface. The low inhibition efficiencies at elevated temperatures revealed that inhibitor adsorption occurs through chemisorption (Kalaiselvi *et al.*, 2018).

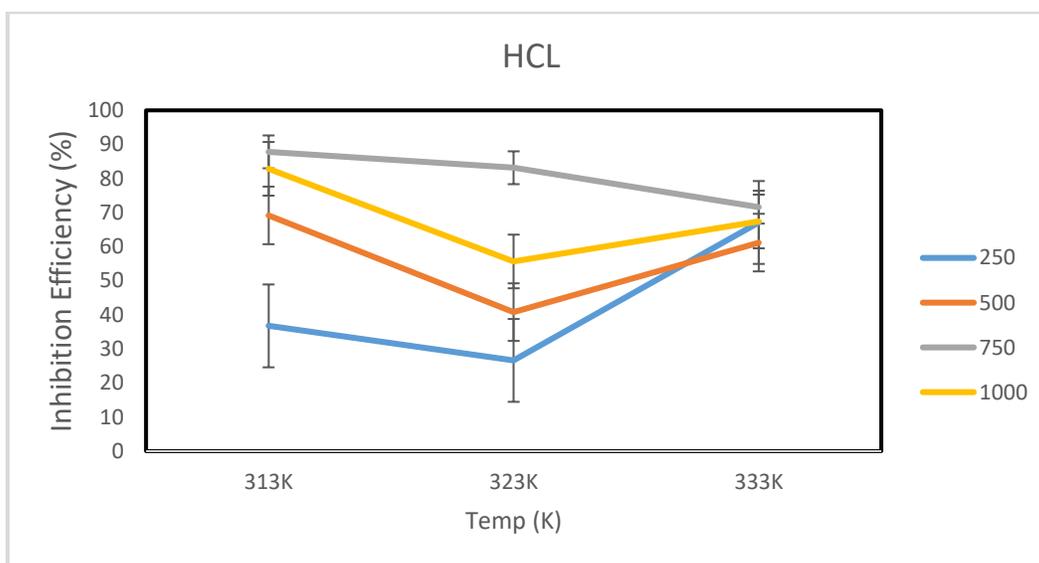


Figure 1: Effect of Temperature on the percentage inhibition efficiency of Leaves Extract Concentration in 1 M HCl Solution

Thermo gravimetric Analysis of Coupons in H₂SO₄

The effect of temperature on the inhibition efficiency of *Leptadenia hastata* (*Yadiya*) leaves extract on corrosion of low carbon steel in 1 M H₂SO₄ was studied. Different concentrations from 250 ppm - 1000 ppm at 250 ppm intervals were tested by Thermo gravimetric measurement over a temperature range of 313 – 333 K. The results from figure 2 revealed that on increasing concentration temperature there is a decrease in

inhibition efficiency for all concentrations showing physisorption adsorption except for 250 ppm which happened to be chemisorption from the beginning up till the end of the experiment. Moreover, an increase in inhibition efficiency was noticed from temperatures 323 – 333 K for 500 ppm, 750 ppm and 1000 ppm indicating the reaction to be chemisorption at this temperature which was similarly reported by (Kalaiselvi *et al.*, 2018).

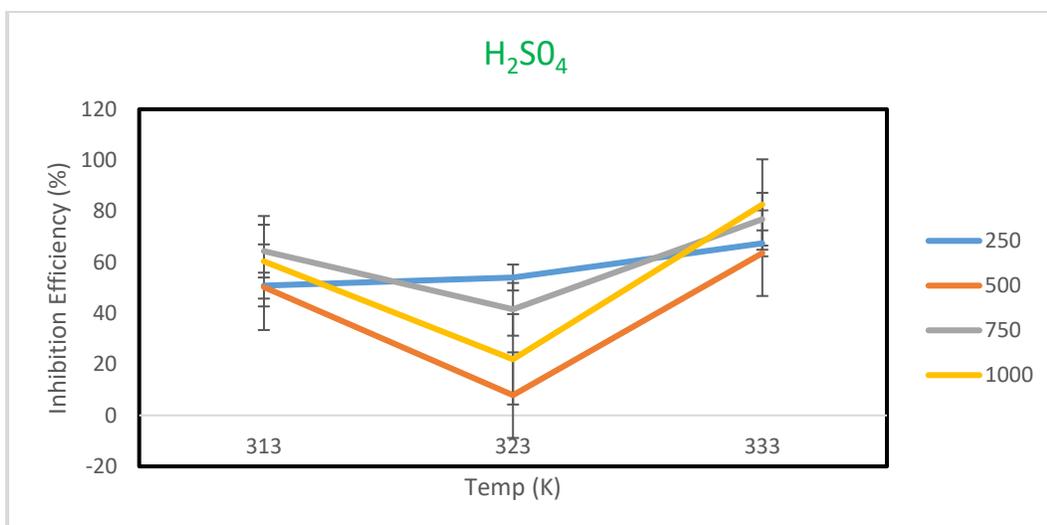


Figure 2: Variation of percentage inhibition efficiency with temperature at different concentration of Leaves Extract in 1 M H₂SO₄ Solution.

Adsorption Mechanism:

The values of θ at different concentrations of *Leptadenia hastata* (Yadiya) leaves extracts in 1 M HCl, and 1 M H₂SO₄ at a temperature of 313, 323, and 333 K were used to explain the adsorption process. Data were tested graphically by fitting to Langmuir isotherm by plotting C/θ vs. C (figures 3- 4), linear plot exhibited strong positive regression coefficient

(R^2) values of 0.99 %, 0.59 % and 0.95 % for HCL and 0.98 %, 0.73 % and 0.53 % for H₂SO₄ respectively. This suggests that the experimental data fit the Langmuir adsorption isotherm which reveals that there is no interaction between adsorbate and adsorbent. It indicates clearly that the inhibitor is displacing water from the metal surface (Chung *et al.*, 2018).

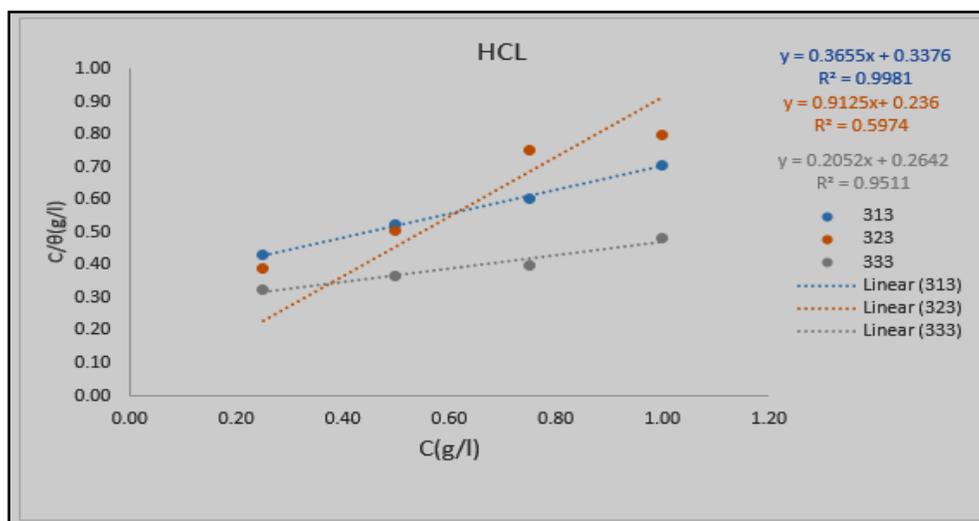


Figure 3: Plot of C/θ versus C of leaves extract for the corrosion of low carbon steel in 1 M HCl at different Temperature

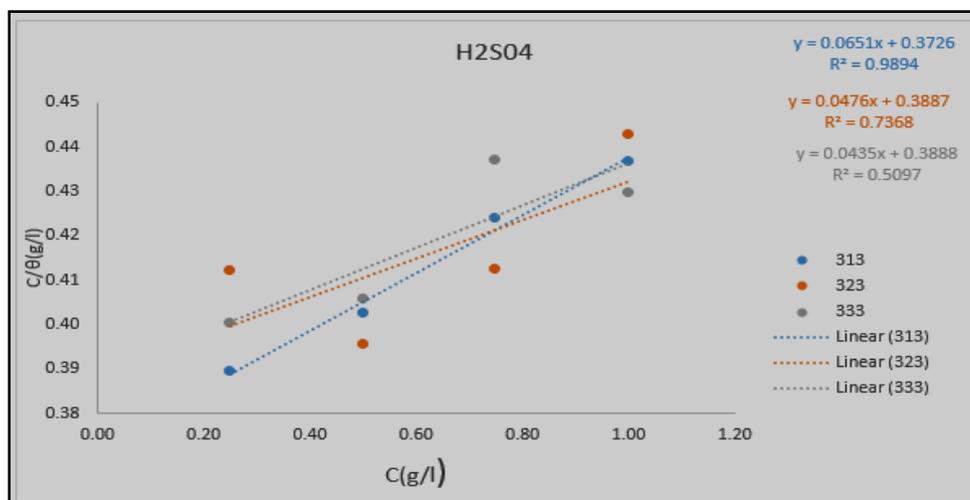


Figure 4: Plot of C/θ versus C of leaves extract for the corrosion of low carbon steel in 1 M H_2SO_4 at different Temperature

Thermodynamic parameters of Corrosion in 1 M HCl and 1 M H_2SO_4

According to Table 1 for inhibited and uninhibited 1 M HCl and H_2SO_4 , the E_a values are greater than 20 KJ/mol which shows that the entire process is controlled by the surface reaction. For the uninhibited system, the values of E_a were found to be 33.71 KJ/mol and 19.91 KJ/mol. The addition of different concentrations of the *Leptadenia hastata* (*Yadiya*) extract raises the E_a in the range from

34.71 KJ/mol to 48.80 KJ/mol for HCl and 21.84 KJ/mol to 37.11 KJ/mol suggesting physical adsorption of inhibitor on the low carbon steel surface with the temperature rise. A decrease in absorption enhances more desorption of inhibitor molecules as these two processes are in equilibrium. As a result of enhanced desorption, more surface area of the low carbon steel was exposed to acid attack which leads to the increase in corrosion rate at elevated temperatures (Singh, 2010).

Table 3: Values of Activation Energy, Enthalpy and Entropy of *Leptadenia hastata* (*Yadiya*) on Medium Low Carbon Steel in 1 M HCl and 1 M H_2SO_4

%Concentration	E_a (KJ/mol)		ΔH (KJ/mol)		$-\Delta S$ (KJ/mol)	
	HCL	H_2SO_4	HCL	H_2SO_4	HCL	H_2SO_4
0	33.71	19.91	24.16	14.16	69.3	72.44
250	34.78	21.84	33.68	21.44	40.9	69.72
500	38.73	24.59	35.12	23.76	36	58.84
750	41.93	30.07	37.28	25.68	28.5	42.87
1000	48.80	37.11	40.32	34.24	17.5	34.06

Free Energy (ΔG_{ads})

The values of free energy of adsorption (ΔG_{ads}) for all the temperatures shown in Table 2 were negative suggesting natural adsorption of inhibitor on the surface of the low carbon steel. Generally, values of ΔG_{ads} up to -20 KJ/mol are consistent with physisorption while those around -40 KJ/mol or higher are chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond. Based on the results, the values obtained for ΔG_{ads} at

temperature 313 K were - 22.84 KJ/mol for 1 M H_2SO_4 and - 32.53 KJ/mol for 1 M HCl. This suggests physisorption, therefore, it can be said that the absorption mechanism of molecules of *leptadenia hastata* (Yadiya) on the low carbon steel at 313 K was proposed to be physisorption. Similarly, at 333 K the values obtained for ΔG_{ads} were - 76.14 KJ/mol and - 37.10 KJ/mol for 1 M H_2SO_4 and 1 M HCl solutions indicating the absorption of inhibitor molecules to be chemisorption (Chung *et al.*, 2018).

Table 4: Thermodynamic parameters from Langmuir adsorption isotherm for the adsorption of *leptadenia hastata* (Yadiya) extracts on low carbon steel in 1M H_2SO_4 and 1 M HCL from 313-333 K.

H_2SO_4	K_{ad} (mol^{-1})	$\Delta G(KJmol^{-1})$	R^2
313	0.0004	-22.8444	0.8008
323	0.0023	-52.0924	0.8519
333	0.0119	-76.1367	0.8839
HCL			
313	0.0149	-32.5335	0.82
323	0.0063	-2.4145	0.7556
333	0.0082	-37.1015	0.8244

CONCLUSION

The leaf extracts of *leptadenia hastata* (Yadiya) act as a good and efficient inhibitor of carbon steel. The results show that inhibition efficiency increases with increasing the inhibitor concentration, which is attributed to the presence of phyto-compounds in the extract. On the other hand, the decrease of inhibition efficiency with an increase in

temperature indicates the adsorption to be chemisorption. The values of activation energy and enthalpy of adsorption were higher in the presence of the inhibitor suggesting the physisorption mechanism of the extracts and that the process is endothermic. The leaf extract obeys Langmuir adsorption isotherm which revealed that there is no interaction between the adsorbate and adsorbent.

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