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CORROSION INHIBITION EFFICIENCY, ADSORPTION BEHAVIOR, KINETICS AND THERMODYNAMIC STUDIES OF *LANNEA ACIDA* ETHANOL LEAVES EXTRACT ON MILD STEEL IN HYDROCHLORIC ACID

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ABSTRACT

The corrosion inhibition potential of *lannea acida* (LA) ethanol leaves extract was investigated using mild steel in 1.0 M HCl solution. The leaves extract was characterized using FT- IR Spectroscopy. The surface analysis of the mild steel was also studied using scanning electron microscopy. The study was carried out at an ambient temperature and selected high temperatures. The LA leaves extract concentration ranges from 0.1- 0.9g/L. The data obtained from weight loss measurements show that the leaves extract repressed the corrosion rate of mild steel. The increase in temperature with a corresponding increase or decrease in the inhibitor efficiency of LA leaves extract shows that the adsorption mechanism obeyed comprehensive adsorption. The value of activation energies (Ea) obtained which ranged from 15.32 to 17.63 kJ mol^{-1} agrees with the physical adsorption mechanism. The values of enthalpy of activation (ΔH*) obtained were positive and ranged from 38.29 to 59.00 KJ mol^{-1} is an indication that the dissolution of the mild steel is an endothermic reaction and requires less energy in the presence of LA leaves extract. The values of entropy of activation (ΔS*) obtained which were negative indicate that the activated complex in the rate-determining step is associative rather than dissociative. The kinetics study shows the adsorption process follows first-order kinetics. The adsorption isotherm data fitted best into Freundlich adsorption isotherm.

Keywords: Corrosion rate, mild steel, HCI, *Lannea acida* (LA), adsorption, efficiency, temperature

INTRODUCTION

One of the challenges around the world today is how to prevent and manage the corrosion of metals. This is a common condition that affects metals and their alloys. Metals have become an integral part of human life. The discovery of metals has been of great assistance to mankind for centuries now. It has created alternative materials for use instead of woods, stones, etc. The use of metals has become encompassing as its found its uses in the building of houses, bridges construction, kitchen utensils, industrial equipment, automobile, pieces of jewelry etc. But it was soon found out that these metallic materials over the time of usage exhibit changes in their chemical composition. This results in a reduction in their life span and the expected performance of these metallic materials and this are due to a phenomenon known as corrosion (Eddy et al,.2009; Kumar and Vikas, 2013)

Corrosion is a naturally occurring process generally defined as the deterioration of metallic materials as a result of the chemical reaction between the metals and their

Most of these inhibitors are synthesized and some are chosen from compounds having heteroatoms such as N, O, S, P with hydrocarbon parts attached to the polar group. However, some of these synthetic corrosion inhibitors are not only expensive but are toxic, non-degradable, and not eco-friendly

environment (Popoola et al., 2013). The effect of corrosion can be felt in virtually every work of life (Bradford, 1993; Perez, 2004). Therefore corrosion needs to be checked. Researches have been in a bid to find preventive measures to curtail and manage corrosion since it can't be eradicated (Omotosho, 2016). One of the best methods available involves the use of corrosion inhibition. Corrosion inhibitor is defined as a substance which when added to a corrosive solution in a small concentration will lower the corrosion rate of metals or it alloys. This effect of inhibition is due to the interaction between the inhibitor molecules or particles and the metal surface. There is adsorption of inhibitor particles on the metal surface, which forms a protective coherent layer on it (Eddy et al., 2015). This inhibition can also occur when the vacant orbital of the metal, mostly the d-orbital received the transferred electron from the inhibitor molecule (Bradford, 1993; Eddy et al., 2009; 2015). Corrosion inhibitors can be an organic compound or inorganic compounds and their inhibition potentials can be correlated to their chemical composition and structure.

(Ita, 2004). In a bid to find a substitute for the synthetic corrosion inhibitors an era of green inhibitors emerges. Green Inhibitors are of plant origin and biodegradable and are void of heavy metals or other toxic substances. They contain heterocyclic compounds (Riggs and Hurd, 1967). Several plants extract have been reported to have inhibited corrosion rate and their corrosion inhibition properties are often attributed to their phytochemical constituents (Umoren and Ebenso, 2008). In this present work, the ethanol leaves extract of *lannea acida (LA)* plant is studied in detail for its corrosion inhibition potentials on mild steel in 1.0 M HCI solution.

Experimental techniques

Materials

The study was performed with a mild steel sheet which was purchased commercially with the chemical compositions as determined by the quantiometric method as follows; Si: 3.420, Mg: 0.630, P: 0.0370, Zn: 0.0047, S: 0.0336, As: 0.0045, Ca: 0.2948, Cr: 0.0299, C: 0.15, and the remainder is Fe. The mild steel sheet was mechanically cut into coupons of the dimension of 4 x 2 x 0.1 cm each. Each coupon was subjected to chemical treatments, degreased in absolute ethanol, and dried in acetone. Then coupons are stored in a desiccator before the commencement of the work. All chemicals used in this research were purchased and of analytical graded quality. The corrodents' solution for the weight loss test was acid solutions of 1.0 M HCl.

Preparation of plant extract

The leaves of *Lannea acida* were collected from the Kankia Community of Katsina State, Nigeria. The plant leaves were dried under-ventilated cover. The leaves were ground into fine powder. 300g of powdered LA leaves were soaked in 1.25 L of ethanol which serves as an extraction solvent for 48 hrs. The stock of the extracts so obtained was used after obtained its crude form in preparing different concentrations of the extract by dissolving 0.1, 0.3 0.5, 0.7, 0.9g in 1L of the acids solution

Gravimetric method

The pretreated mild steel (coupons) measuring 4 cm by 2 cm x 0.1 cm were weighed and subsequently immersed in the test media consisting of varying concentrations of the inhibitor and control solution (1.0 M HCl without inhibitor) The washed coupon was rinsed in acetone and air-dried before re-weighing. The difference in weight for a period of 168 hours was taken as total weight loss (Eddy and Odoemelam, 2009). All experiment was carried out in triplicates. The result obtained from the weight loss test; the and covered with the aluminum fold. The weight loss was measured at intervals of 24 hours - 168 hours. After every 24 hours, the corrosion product was removed by washing each coupon with a solution containing 50% NaOH and 100g L-1 of zinc dust

inhibition efficiency(%) of the inhibitor, the degree of surface coverage, and corrosion rates (CR in g) were calculated using equations 1, 2, 3,4 respectively (Omotosho, 2016).

$$W = Wi - W_f \qquad (1)$$

$$\text{Inhibition Efficiency (\%IE)} = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} x\ 100 \qquad (2)$$

$$\text{Surface coverage } (Q) = \frac{Wc - W}{Wc} \qquad (3)$$

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \text{ x } W}{A \text{ x } T \text{ x } D} \qquad (4)$$

Where T is immersion time in an hour, W is weight loss in grams, A is an area of the sample (coupon) in square cm (cm^2) and D is the density of metal in g per cm^3. CR_{blank} is the corrosion rate of sample in an acid medium (HCl) and CR_{inh} is the corrosion rate of metal sample in inhibitor and the acid. W_i is the weight before immersion and W_f is the weight after immersion.

Temperature study

The weight loss test on the mild steel also studied under a selected higher temperature apart from the ambient temperature. The thermostat was set to the temperature of 313k, 323k, and 333k. The experiment was carried out as done at ambient temperature and the immersion period was 3 hours.

FT-IR analysis

The FT-IR analysis of the LA leaves extract and the corrosion product (in the absence and presence of inhibitor) were carried out using Fourier Transform Infrared Spectrophotometer. The samples were scanning through a wave number range of 400-4500 cm^{-1}(Ita and offiong,1999).

Scanning electron microscopy

Surface analysis of the mild steel coupons in the inhibited and uninhibited acid mediums was studied using Scanning Electron Microscope. The snapshots of the specimens were taken to investigate their surface morphologies.

Determination of the thermodynamic and activation parameters:

Activation energy (Ea): Activation energy was calculated using the following Arrhenius equation (5) (Umoren et al., 2008).

$$\text{Log CR} = \text{Log A} - \frac{(\text{Ea})}{2.303\ \text{RT}} \qquad (5)$$

Where A is the Arrhenius pre-exponential factor, CR is corrosion rate, T is the absolute temperature in Kelvin and R is the universal gas constant. The slope of the graph plotted between log CR and 1/T gives the values of activation energy at various studied temperatures.

Enthalpy of activation (ΔH*) and entropy of activation (ΔS*)

The values of enthalpy of activation (ΔH*) and entropy of activation (ΔS*) were obtained from transition state equation (6) (Umoren et al., 2016).

$$\text{LogCR/T} = [\log(R/hN) + (\Delta S^*/2.303R)] - [\Delta H^*/2.303RT] \qquad (6)$$

Where CR is corrosion rate, N is Avogadro`s number, T is the absolute temperature and R is the universal gas constant, h is Planck`s constant. A plot between log (CR/T) and (1/T) gives a straight line with a slope of (- ΔH*/2.303) and intercept of [Log(R/N h) + ΔS*/2.303)] from which the values of enthalpy of activation (ΔH*) and entropy of activation (ΔS*) were calculated

Kinetics study

The corrosion reaction is more or less a heterogeneous reaction composed of anodic reactions at the same or different rate (Olasehinde et al., 2013). It kinetics process of LA extract was studied using the first-order kinetics with the integral method of analysis. The first-order equations are given in equations 8 and 9

$$-\text{Log (W)} = K_1t/2.303 \qquad (8)$$

$$t_{1/2} = 0.693/K_1 \qquad (9)$$

Where W is the weight loss in (g), k_1 is the first-order rate constant per hour, and t is the immersion time also in (hour). The $t_{1/2}$ is the half-life of the studied corrosion process obtainable from equation (9)

Absorption Isotherms:

Langmuir adsorption isotherm: This is used to study the mechanism of adsorption of leaves extracts of LA on the surface of the mild steel. The mathematical expression for Langmuir adsorption isotherm is according to equation (10) below;

$$C_{inh}/\theta = 1/k_{ads} + C_{inh} \qquad (10)$$

Where C_{inh} is the inhibitor concentration in (g/L) and K_{ads} is the equilibrium constant of adsorption, θ is the degree of surface coverage and is equal to IE% /100. A straight line is obtained between log (C_{inh}/θ) and log C_{inh} values if the adsorption process follows Langmuir adsorption isotherm.

Freundlich adsorption isotherm

This is given by the following equation (11) and (12)

$$\theta = K_{ads}.\ C_{inh} \qquad (11)$$

$$\text{Log}\theta = \text{Log}\ (K_{ads}) + 1/n\ \text{Log}\ C_{inh} \qquad (12)$$

Where <n<1, θ is the degree of surface coverage and C_{inh} is the concentration of the inhibitor, K_{ads} is the equilibrium constant in the adsorption process. A straight line is obtained between the logarithm of the degree of surface coverage (θ) and the logarithm of inhibitor concentration C_{inh} in Freundlich isotherm. Log K_{ads} is the intercept, 1/n is equated to the slope of the plot and n is a positive Freundlich exponent which is the intensity of the adsorption process on the surface.

RESULTS AND DISCUSSION

Phytochemical Analysis

The phytochemical analysis of different parts of the LA plant such as the bark, stem, and leaves in different extraction solvents had been performed (Alfred, 2018; Etuk et al., Manzo et al., 2017). The compounds identified include alkaloids, cardiac glycosides, phenols, saponins, steroids, tannins, and terpenoids (Onoshe et al., 2018; Manzo et al., 2017). Lannea acida leaves were also analyzed by (Leung et al., 1968) for their calcium, carbohydrates, energy, fat, fiber, phosphorous, and protein contents (Alfred, 2018).

Effect of concentration of Lannea acida

Fig. 1a shows the variation of weight loss with time (hour) with the presence or absence of LA leaves extract and Fig 1b shows the variation of inhibition efficiency with a concentration of LA for the corrosion of mild steel in 1.0 M HCI at ambient temperature. Table 1a shows the results for weight loss and inhibition efficiencies and Table 1b the corrosion rate from the weight loss measurement at ambient temperature. The results show a decrease in the corrosion rate of mild steel in inhibited medium compared to uninhibited medium and as the concentration of the LA extract increases. Figure 1b shows the variation of the inhibition efficiency (IE%) with inhibitor concentration. The inhibition efficiency increases with increased inhibition concentration but decreases with increased time of immersion. The inhibition efficiency of the LA extract was best at 0.9 g/L at 24 hours immersion with 57.3%.

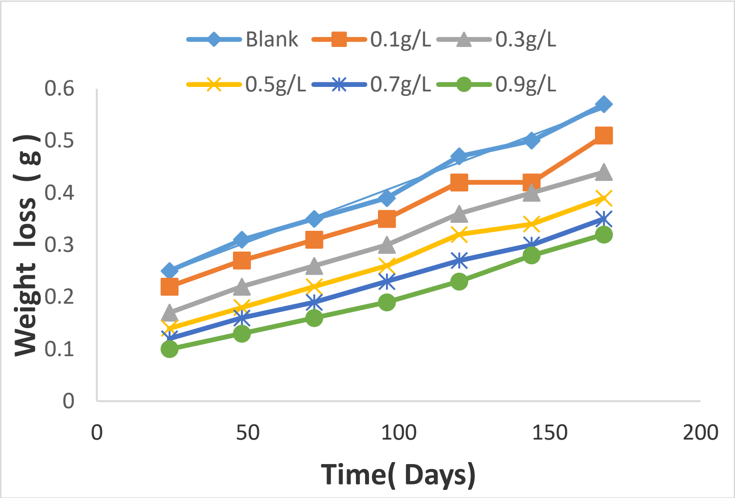


Fig 1a. Variation of weight loss (g) with time (hour) for the corrosion of mild steel in 1.0 M HCl in the presence and absence of various concentrations of LA extract at ambient temperature.

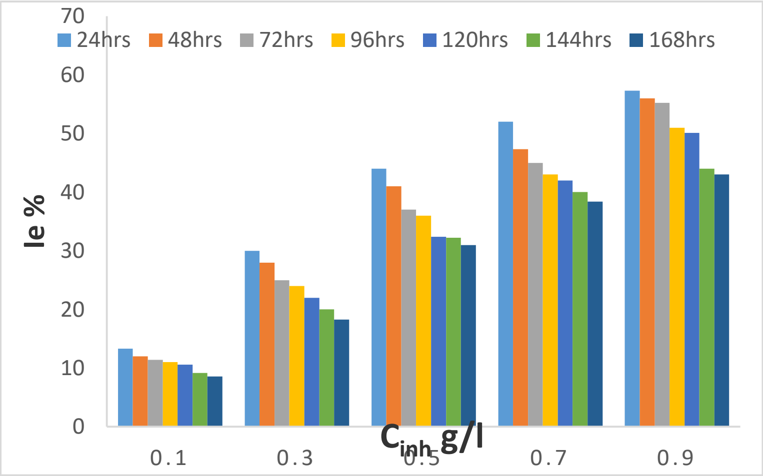


Fig 1b Variation of inhibition efficiency with concentration (g/L) for the corrosion of mild steel in 1.0 M HCl in the presence of various concentrations of LA leaves extract at ambient temperature.

Table 1a. Weight loss and inhibition efficiencies of mild steel in the presence and absence of LA leaves extract in 1.0 M HCl at ambient temperature. (Values of inhibition efficiency (IE%) in parenthesis).

Conc g/L	Weight Loss (g)						
	24hrs	48hrs	72hrs	96hrs	120hrs	144hrs	168hrs
Blank	0.2500	0.3100	0.3500	0.3963	0.4663	0.4996	0.5696
0.1 g/L	0.2167(13.3)	0.2734(12.0)	0.3101(11.4)	0.3504(11.0)	0.4171(10.6)	0.4271(9.2)	0.5071(8.6)
0.3 g/L	0.1733(30.0)	0.2233(28.0)	0.2633(25.0)	0.3016(24.0)	0.3649(22.0)	0.4016(20.0)	0.4466(18.3)
0.5 g/L	0.1400(44.0)	0.1833(41.0)	0.2200(37.0)	0.2552(36.0)	0.3152(32.4)	0.3385(32.2)	0.3935(31.0)
0.7 g/L	0.1200(52.0)	0.1633(47.3)	0.1933(45.0)	0.2276(43.0)	0.2709(42.0)	0.3009(40.0)	0.3509(38.4)
0.9 g/L	0.1067(57.3)	0.1367(56.7)	0.1567(55.2)	0.1961(51.0)	0.2328(50.1)	0.2795(44.0)	0.3245(43.0)

Table 1b. The corrosion rate of mild steel in the presence and absence LA leaves extract at various hour in 1.0 M HCI at ambient temperature

Conc (g/L)	Corrosion rate (g)						
	24hrs	48hrs	72hrs	96hrs	120hrs	144hrs	168hrs
Blank	0.1451	0.1799	0.2031	0.2300	0.2707	0.2900	0.3306
0.1 g/L	0.1258	0.1587	0.1800	0.2033	0.2421	0.2479	0.2944
0.3 g/L	0.1005	0.1296	0.1528	0.1751	0.2118	0.2331	0.2592
0.5 g/L	0.0812	0.1064	0.1277	0.1481	0.1830	0.1965	0.2284
0.7 g/L	0.0697	0.0948	0.1122	0.1321	0.1572	0.1747	0.2037
0.9 g/L	0.0619	0.0794	0.0909	0.1138	0.1351	0.1622	**0.1884**

Effect of Temperature

The values of weight loss, corrosion rate (g), inhibition efficiencies (IE%), surface coverage (θ) of the mild steel at higher temperatures from weight loss measurement are shown in Table 2. The obtained results show that the weight loss of mild steel increases with increased temperature in all the systems. This result is because an increase in temperature does increase the average kinetic energy of the reacting molecules and therefore corrosion rate increased (Ehteram, 2007). But, with an increase in the concentration of LA extract weight loss reduced drastically. The mitigating effect of the extract of LA was responsible for the decreased weight loss in the inhibited system. Fig 2 also shows that the inhibition efficiency IE% of leaves extract of LA increased or decreased with increased temperatures at different studied extract concentrations. This shows that comprehensive adsorption (physical and chemical adsorption) is obeyed. This type of observation was reported in previous studies by several researchers (Ehteram, 2007; Abd-El-Nabey et al., 1996). The best inhibition efficiency of 51% was observed at 0.9 g/L concentration of inhibitor at 60^{0}.

Table 2: Weight loss, inhibition efficiency, corrosion rate, and surface coverage of mild steel in the presence and absence of LA leaves extract in 1.0 M HCI at 313k, 323k, and 333k

Conc(g/L)	Weight Loss (g)		
	313k	**323k**	**333k**
Blank	**0.1800 (0.8359)**	**0.2200 (1.0216)**	**0.3050 (1.4163)**
0.1 g/L	**0.1550 (14.0) (0.7198) (0.1389)**	**0.1813 (18.0) (0.8419) (0.1759)**	**0.2400 (21.0) (1.1145) (0.2131)**
0.3 g/L	**0.1400 (22.0) (0.6501) (0.2222)**	**0.1715 (20.4) (0.8127) (0.2045)**	**0.2100 (31.2) (0.9751) (0.3115)**
0. 5 g/L	**0.1200 (33.0) (0.5573) (0.3333)**	**0.1500 (32.0) (0.6960) (0.3182)**	**0.1850 (39.3) (0.8591) (0.3934)**
0.7 g/L	**0.1150 (36.1) (0.5340) (0.3611)**	**0.1438 (35.0) (0.6678) (0.3464)**	**0.1750 (43.0) (0.8123) (0.4262)**
0.9 g/L	**0.1050 (42.0) (0.4876) (0.4167)**	**0.1313 (40.3) (0.6097) (0.4032)**	**0.1500 (51.0) (0.6966) (0.5082)**

Values of inhibition efficiency (IE%), corrosion rate(CR) and surface coverage(θ) in parenthesis respectively.

Thermodynamics parameters

The activation energy (Ea) for the corrosion of mild steel in 1.0 M HCI was calculated using the Arrhenius equation. Log CR= Log A- (Ea /2.303 RT). The plots of log CR versus 1/T for the corrosion of mild steel in the presence of various concentrations of LA yielded straight lines (Fig. 2). From the slope of the Arrhenius plot, the values of Ea were obtained. The values of Ea obtained ranged from 15.32 to 17.63 kJ mol^{-1} and are lower than what is obtained in the uninhibited acid medium (29.94 KJ mol-1). This lower Ea is attributed to the chemical adsorption of inhibitors on the surface of mild steel. This conclusion is validated by the finding of other researchers (Mansfeld, 1995; Morad, 2006; De Souza, 2009). The values of Ea agree with the mechanism of physical adsorption in which the value of Ea is expected to be less than 80.00 KJ mol-1(Chuhul et al., 2015; Omotosho and Ajayi, 2012; Fontana, 1987).

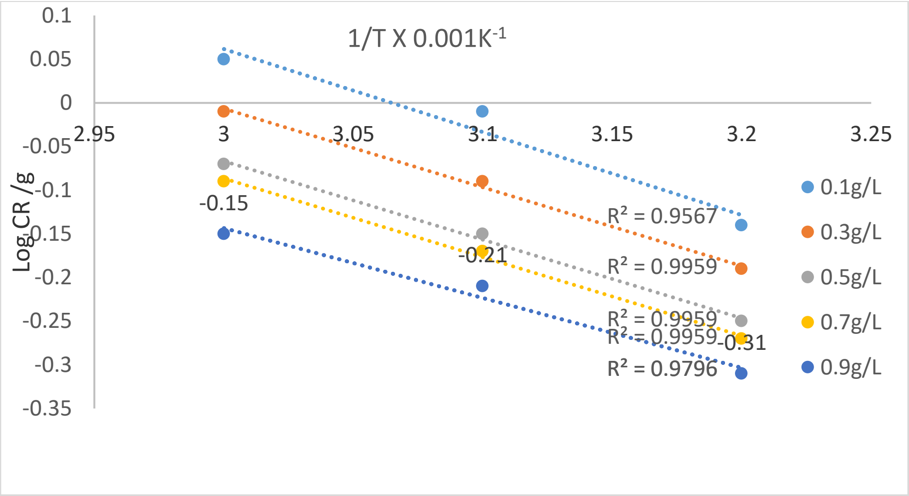


Fig. 2. Variation of log CR versus 1/T for the corrosion of mild steel in 1.0 M HCI containing various concentrations of LA leaves extract.

From table 2, it shows that the activation energies for the corrosion of mild steel decreased with an increase in the concentration of LA leaves extract. The decrease in Ea values is attributed to an increase in the degree of adsorption of the inhibitor on the mild steel surface which decreased the reaction rate. The lower Ea has also been reported in inhibited solutions compared to the uninhibited ones by (Putilova et al; Martinez and Stern, 2001; Abd- El- Rehim et al., 2001). The phenomenon is said to be an indication of the chemical adsorption mechanism due to the formation of a film on the surface area of the mild steel by inhibitor species as temperature rises (Mansfeld, 1995; Morad, 2006). These further support the occurrence of both physical and chemical adsorption for LA leaves extract on mild steel surfaces in HCl solutions.

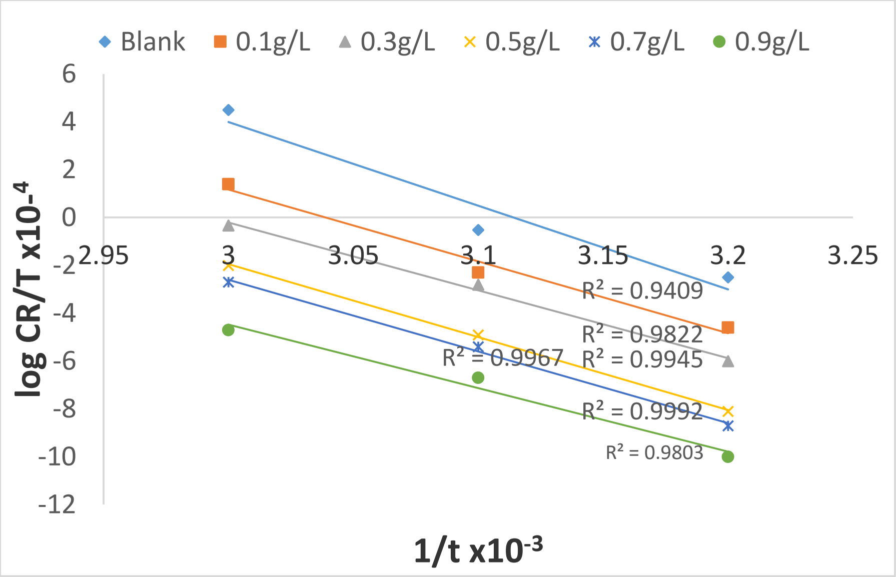


Fig. 3: Variation of log CR/T versus 1/T for the corrosion of mild steel in 1.0 M HCI containing Various concentration of LA leaves extract.

The plots of log CR/T versus 1/T of the Transition State equation yielded straight line (Fig 3). The slope and the intercept are equated to $-\Delta H^*/2.303R$ and $[\mathrm{Log}(R/Nh)+\Delta S^*/2.303)]$ respectively. The values of ΔH* calculated from the slope were positive except for the blank. The ΔH* values ranged from 38.29 to 59.00 KJ mol-1. The positive ΔH* values are an indication that the dissolution of the mild steel is an endothermic reaction and requires less energy in the presence of Lannea acida extract (Okafor et al., 2007, 2010).

Table. 3 Thermodynamics parameters for the adsorption of LA leaves extract on mild steel surface

C x10^{-3}M	**Ea (KJmol^{-1})**	**R2**		**ΔH*(KJmol^{-1})**	**ΔS*(KJmol^{-1})**	**R2**
Blank	26.94	0.9968	-	-67.01	-77.91	0.9409
0.1	17.63	0.9567		59.00	-144.03	0.9822
0.3	17.23	0.9959		57.15	-174.5	0.9945
0.5	16.80	0.9959		58.37	-206.19	0.9992
0.7	16.71	0.9959		38.29	-220.56	0.9967
0.9	15.32	0.9796		47.87	-261.71	0.9803

The values of the entropy of activation (ΔS*) calculated from the intercept were negative. This is an indication that the activated complex in the rate-determining step represents an association rather than dissociation. It equally means a decrease in disordering occurred as the reaction proceeds from reactants to the activated complex (Abd- El-Rehim et al., 2001b; Gomma and wahdan, 1995). Table 2 shows that the ΔS* shifts to more negative values as the concentration of inhibitor increased (Ehteram, 2007).

Kinetics study.

Fig 4 shows the plot of –log W (weight loss) against immersion time in (hour) in the presence and absence of LA leaves extracts. The rate constant, and half-life parameters are shown in Table 6. From the table, the corrosion rate constant values increased with an increase in the concentration of LA leaves extract. The values of half-life decreased as the concentration of LA extract increases. There is also a corresponding decrease in half-life values as the rate constant increases. This confirmed the first-order kinetics for the corrosion of mild steel in 1.0 M HCI. The correlation coefficient values obtained which were close to unity showing that the experimental value fitted well to the first-order kinetics. Similar results had also been reported by (Ijuo et al., 2016; Olasehinde et al., 2013).

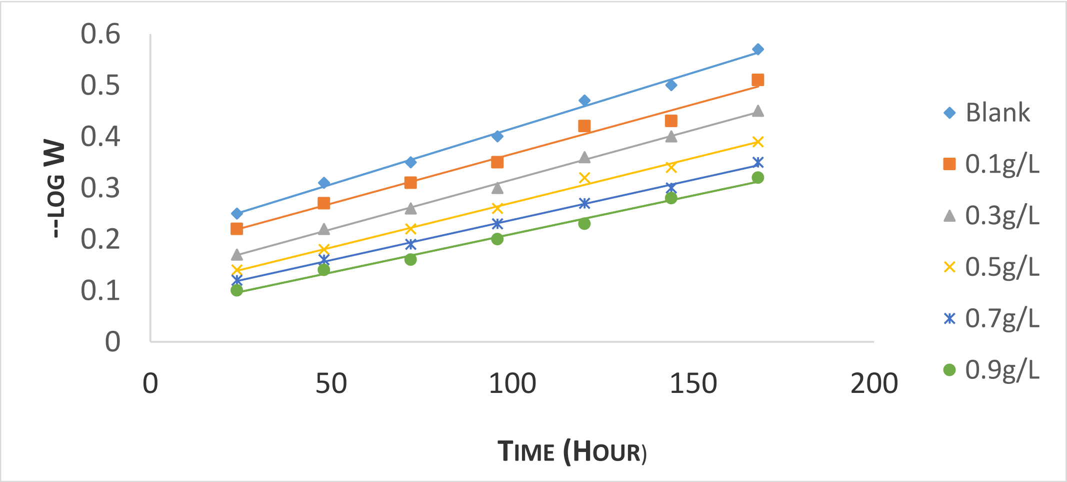


Fig. 4 Variation of –Log W (weight loss) versus Time (hour) in the presence or absence of LA leaves extract.

Table 4. Half-life and rate constant parameters at various concentration leaves extract of LA at ambient temperature.

Conc.	**Rate constant K_i (hrs^{-1})**	**Half- life (hour)**	**R^2 value**
Blank	0.0578	11.99	0.9946
0.1 g/L	0.0637	10.88	0.9848
0.3 g/L	0.0730	9.45	0.9979
0.5 g/L	0.0819	8.46	0.9943
0.7 g/L	0.0883	7.85	0.9972
0.9 g/L	0.0932	7.44	0.9908

Adsorption studies

Langmuir adsorption equation relates the degree of the surface coverage to the concentration of the inhibitor according to equation (8)

$$C_{inh}/\ \theta = \ 1/kads + C_{inh} \qquad (8)$$

A plot of C_{inh}/θ versus C_{inh} from weight loss data yielded a straight line as shown in Fig 5. The values of the parameters obtained were shown in Table 5. From the results, the slopes and R^2 values were close to unity which indicate strong adherence to Langmuir adsorption isotherm. These indicate an interaction among the adsorbed species on the surface of the mild steel (Okafor et al., 2008; Oguzie, 2008). The values of ΔG_{ads} obtained were negative, ranged from -6.30 to -6.56 kJ mol^{-1} and less than the threshold values of -40 KJ mol^{-1} which is required for the chemical adsorption mechanism. Therefore this shows the spontaneous nature of the adsorption of inhibitor on the mild steel surface and the stability of the adsorbed layer on the surface of the mild steel. This complied with the physical adsorption mechanism.

Table 5 Langmuir adsorption parameters for mild steel in the presence of leaves extract of LA at 313,323 and 333 K.

Temp (K)	R^2	K_{ads}	ΔGads KJmol^{-1}
313	**0.9679**	**0.2020**	**-6.3**
323	**0.9679**	**0.2000**	**-6.5**
333	**0.9087**	**0.1923**	**-6.7**

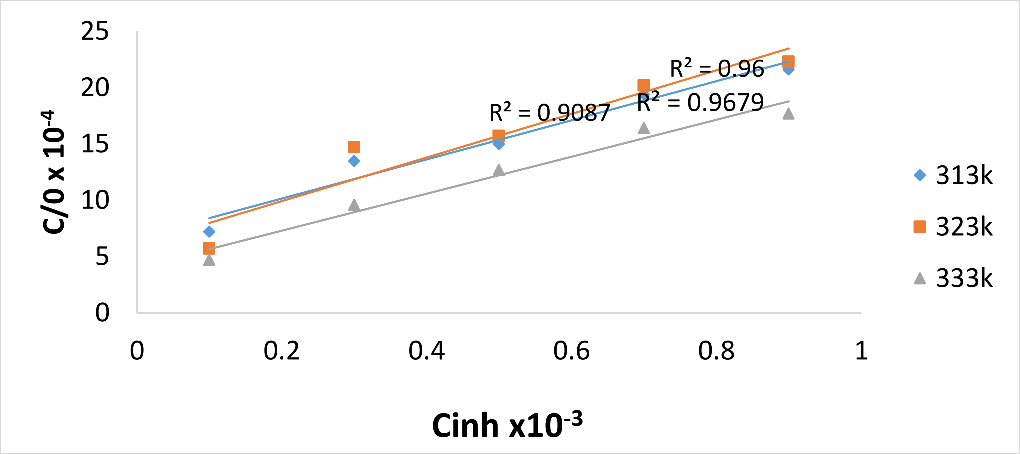


Fig. 5. Variation of C/θ versus C_{inh} for Langmuir isotherm adsorption of LA leaves extract on the surface of mild steel.

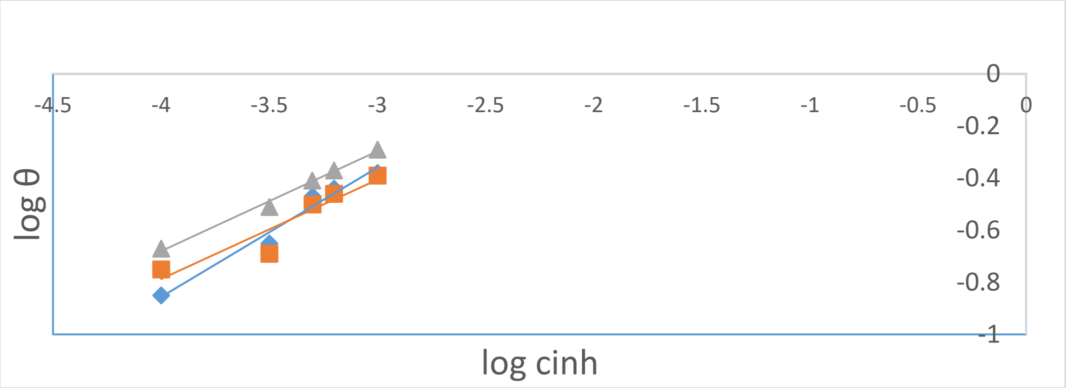


Fig. 6. Variation of Log θ versus Log C_{inh} for Freundlich isotherm adsorption of LA leaves extract on the surface of mild steel.

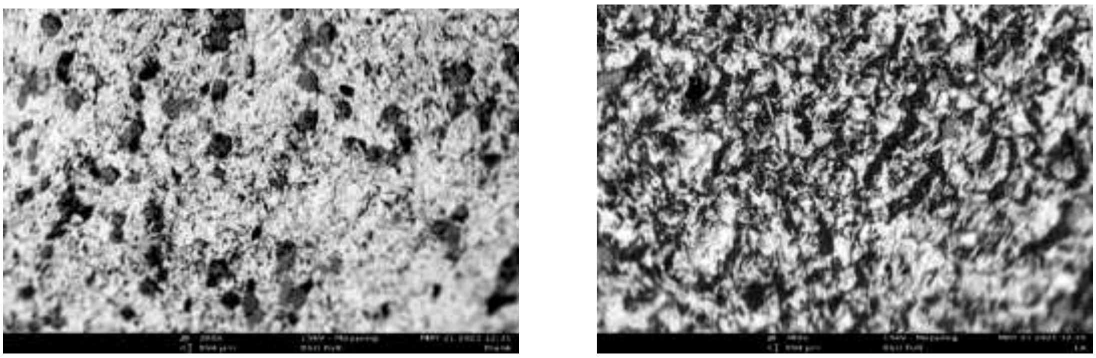
The plot of Log θ versus C_{inh} from weight loss data yielded straight lines as shown in Fig 6 and the parameters obtained in Table 6. From the results, R^2 values were close to unity which indicates strong adherence to Freundlich adsorption isotherm. The values of ΔG_{ads} obtained were also negative, ranged from -8.32 to -10.14 kJ mol^{-1} which is also less than -20.00 kJ mol^{-1} and this supports the physical adsorption mechanism. The values of 1/n obtained which is the intensity of the adsorption process of mild steel surface shown in Table 6 are less than unity which indicates favorable adsorption (Okewale and Adesina, 2020). The values of 1/n also speak of the degree of heterogeneity of the adsorption surface. At 333k temperature, the surface of the mild steel becomes more heterogeneous as the 1/n value (0.3985) gets closer to zero (Itodo et al., 2018; Abdulrahman et al., 2008). The comprehensive adsorption mechanism suggested in the work is thought to occur in succession. First by physical adsorption due to the effective adsorption of molecules of water on the surface of mild steel, then complemented by a chemical interaction between the mild steel surface and the unused part of the water molecules which initiates the chemical adsorption process (Okewale and Adesina, 2020).

Table 6. Freundlich isotherm adsorption parameters for mild steel in the presence of leaves extract of LA at 313,323 and 333 K

Temp (K)	n	1/n	R2	K_{ads}	ΔGads KJmol^{-1}
313	2.3809	0.42	0.9927	0.8869	-10.14
323	1.8130	0.5516	0.9728	0.3985	-8.32
333	2.6062	0.3837	0.8820	0.4232	-8.74

Surface morphology

Plate 1a shows the SEM image of mild steel coupon in uninhibited acid solution, while plate 1b is the SEM image of the mild steel coupon in the presence of the inhibitor at a magnification of 300x. Mild steel specimen dipped in 1.0 M HCI solution in the absence of inhibitor appears to be very light and damaged with patches as the surface is much corroded. This is due to the dissolution of metal in the solution. However, the presence of 0.9 g/L of the inhibitor inhibited the corrosion rate. The surface of the coupon tends to be dark in comparison to the one in the uninhibited medium. This suggests the formation of a protective film on the mild steel surface which in turn minimizes the attack of the acid.



(a) (b)

Plate 1: SEM Image of Mild Steel in 1.0 M HCI Solution without Inhibitor (a) and with Inhibitor (b) after 5 days immersion at ambient temperature 300X Magnification

FT-IR analysis

The FT-IR Spectral for the LA leaves extract, corrosion product both in the inhibited and uninhibited medium were shown in Fig. 5-8. Their spectral characteristics were also shown in Table 6-8. Fig 7 indicates the spectrum of corrosion product with LA extract shows that some of the peaks in LA leaves extract spectrum shifted in its spectrum. The Alcohol peak in LA spectrum at 3260 cm^{-1} shifted to 3339 cm^{-1}, C=C stretch at 1607 cm^{-1} shifted to 1611 cm^{-1}, C-O stretch at 1205 cm^{-1} shifted to 1201 cm^{-1}. The shift in the frequencies indicates that there is the interaction between the mild steel and the inhibitor (Eddy et al., 2010b; Awe, 2015). However, N-O stretch at 1536 cm^{-1}, C=C bend at 877 $cm^{-1,}$ and C-CI bend at 736 were missing from the corrosion product spectrum, this suggests that probably these bonds were used for adsorption of the inhibitor on the surface of the mild steel (Awe, 2015). The spectrum of corrosion product of mild steel in the uninhibited medium in Figure 8 shows that the spectrum is IR active. O-H stretch was observed at 3648 cm^{-1},C=C stretch at1611 cm^{-1},C-O stretch at 1033 cm^{-1} and C-H bend at 840 cm^{-1} .

Table 6. FT-IR Spectrum Characteristics of *LA* Leaves extract.

Vibrational frequency cm^{-1}	Functional group	Frequency of leaves cm^{-1}	Assignment
3400 -3200	O-H stretch	3260, 67.888	Alcohols, phenols
3000-2850	C-H stretch	2925, 66.627	Alkanes
2960-2850	C-H	2854, 72.437	Alkanes
1660-2000 C-H	1998	Allene	
1670-1780	C=O stretch	1689	Carbonyl compounds
1620-1610	C=C stretch	1607	Ketone
1550-1500 N=O stretch	1536	Nitro compounds	
1450-1470 C-H bend	1447	Alkyl group	
1342-1266	C-N stretch	1316	Aromatic amine
1125-1205 C-O stretch	1149	Alcohol	
1125-1205 C-O stretch	1205	3° Alcohol	
1230-1030 C-N stretch	1030	Amine	
885-895	C=C bend	877	Alkene
810-840	C=C bend	825	Alkene
750-810	C- CI	769	Alkyl halide
735-770	C-CI	736	Alkyl halide

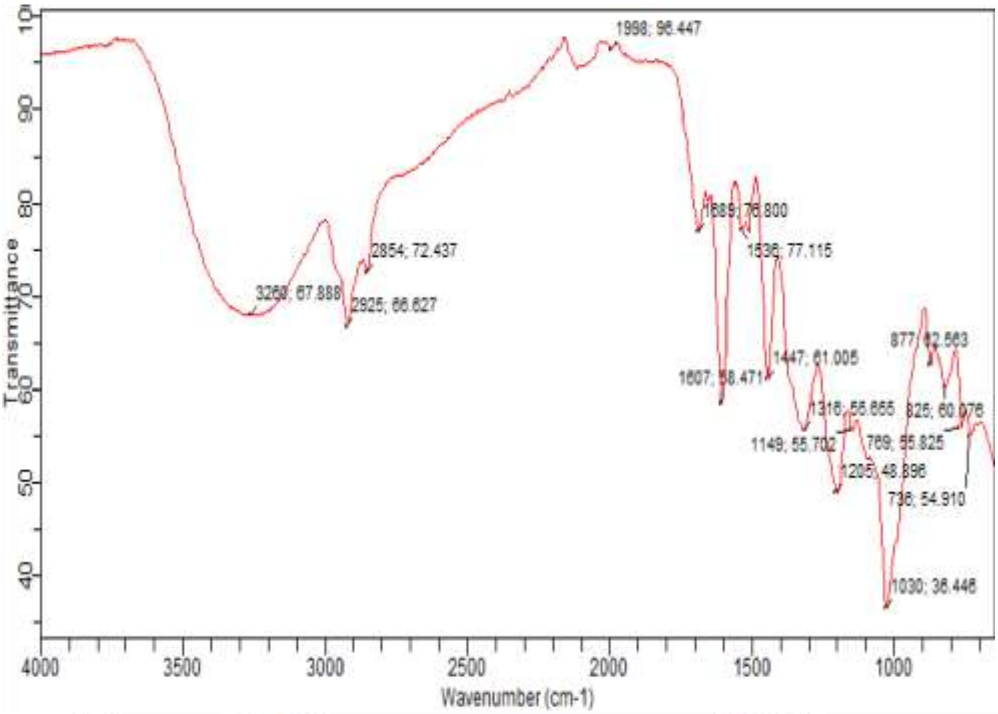
Table 7. FT-IR Spectrum of the Corrosion Product from the Corrosion of Mild Steel in 1.0 M HCl inhibited system

Vibrational Frequency cm^{-1}	Functional group	Frequency of leaves cm^{-1}	Assignment
3400- 3200	O-H stretch	3339, 58.945	Alcohols, phenols
3000-2850	C-H stretch	2925, 73.682	Alkanes
2900-2850	C-H stretch	2854, 76.636	Alkanes
1667-1780	C=O stretch	1689	Carbonyl compound
1620-1610	C=C stretch	1611	Ketone
1450-1470	C-H bend	1447	Alkyl group
1342-1266	C-H stretch	1316	Aromatic amine
1125-1205	C-O stretch	1201	Alcohol
1125-1205	C-O stretch	1149	Alcohol
1230-1030	C-N bend	1030	Amine
810-840	C=C bend	825	Alkene
750-810	C-CI bend	769	Alkyl halide

Table 8 FT- IR Spectrum of the corrosion product from the corrosion of mild steel in 1.0 M HCl uninhibited System

Vibrational frequency cm^{-1}	Functional group	Frequency of leaves cm^{-1}	Assignment
3700-3584	O-H stretch	3648, 94.842	Alcohol
2500-3500	O-H stretch	3335, 74.005	Alcohol
1620- 1611	C=C stretch	1611	Ketone
1035-1050	C-O stretch	1033	Alcohol
810-840	C-H Bend	840	Aromatic compound

.



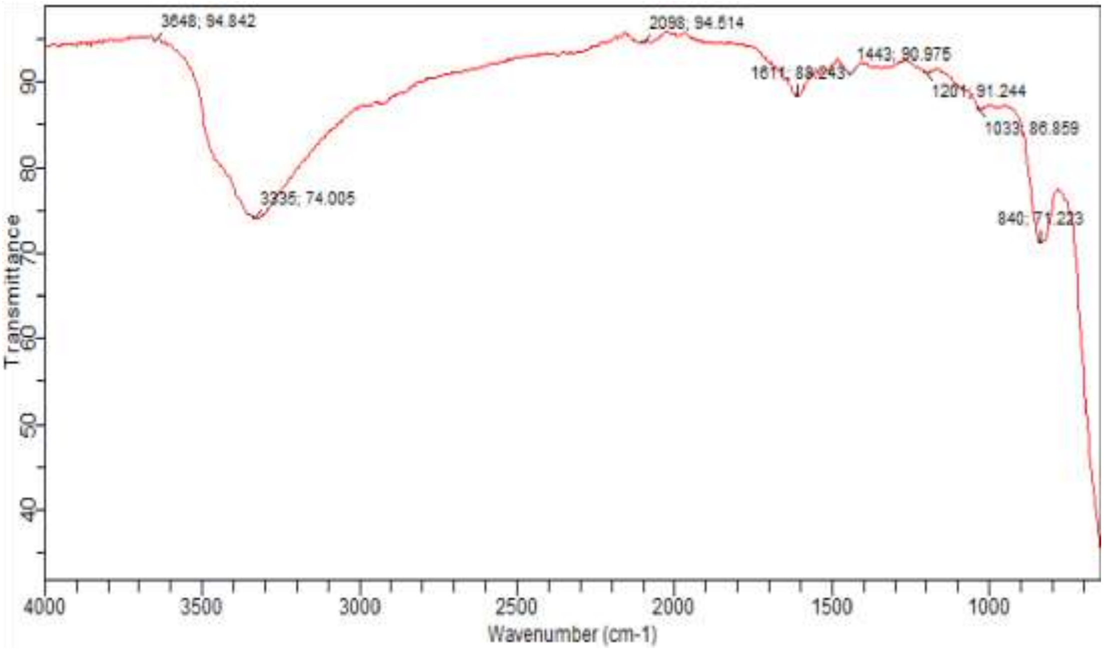


Fig 6. : FT-IR Spectrum of LA the leaves extract.

Fig. 7: FT-IR Spectrum of the Corrosion Product from Corrosion product of mild steel in uninhibited System.

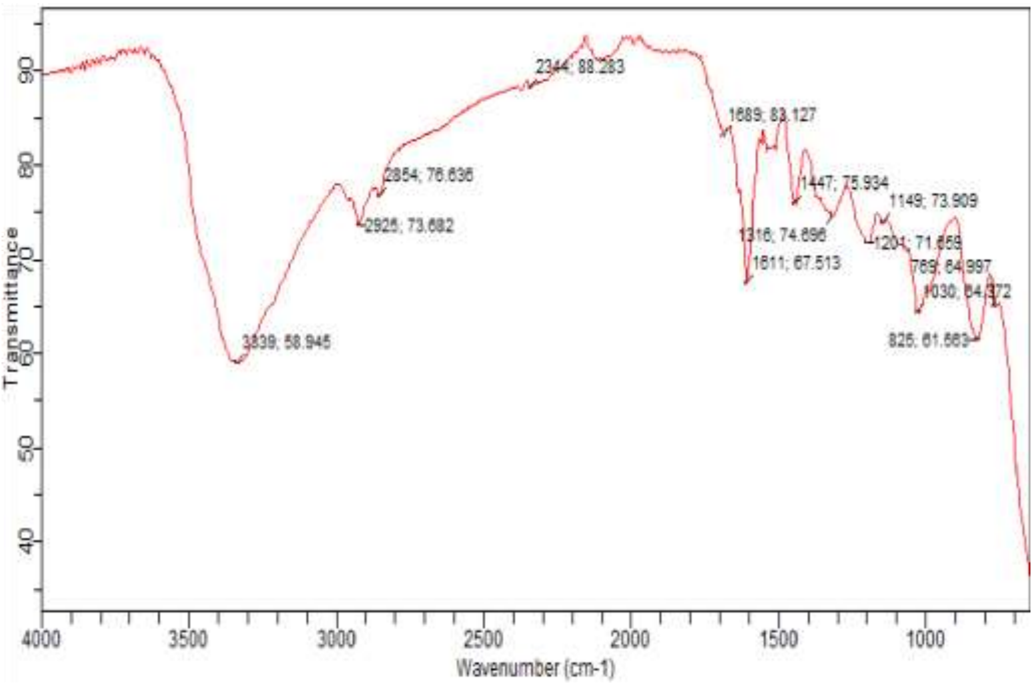


Fig. 7: FT-IR Spectrum of the Corrosion Product from the Corrosion of Mild Steel in 1.0 M HCl in inhibited System.

CONCLUSIONS

From the research study, the following conclusions have been arrived at.

- *Lannea acida* leaves extract is a good inhibitor for mild steel in an acidic environments both at ambient and higher temperatures.
- The inhibition efficiency of *LA* leaves extract increases with the increased concentration of the extract and decreases with increased time of immersion. However, at increased temperature, there is an increase or decrease in the inhibitor efficiency as certain concentrations which suggested comprehensive adsorption (physical and chemical adsorption) for the *LA* leaves extract adsorption on mild steel.
- The results from the FT-IR spectral showing the peaks of most of the functional groups in leaves extract in the corrosion product film spectral confirmed that adsorption of LA leaves extract on the mild steel surface occurred.
- The positive ΔH* values are an indication that the dissolution of the mild steel is an endothermic reaction and requires less energy in the presence of *Lannea acida* extract.
- The adsorption of the leaves extracts of LA on mild steel surface base on the R^2 values best fitted into Freundlich adsorption isotherm at all studied temperatures.
- The rate of corrosion reaction (specific reaction rate) of the mild steel in 1.0 M HCI follows first-order Kinetics as an increase in rate constant resulted in the corresponding decrease in half-life values. The half- lifetime on the other hand decreases with an increased in concentration.

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REFERENCES

Abdulrahman F W, Hassan L G, Itodo A U, Maigandi S A (2008). Freundlich Adsorption Isotherms of Adsorbent from H_3PO_4 and $ZnCI_2$ Treated Irish Potato Peels. Nigerian journal of Basic and applied Science, vol 16 No 2.

Abd El-Rehim S.S, Hassan H.H and Amin M.A,(2001b) Mater. Chem. Phys. 70 - 64. 33.

Abd El-RehimS.S , Ibrahim M.A.M and Khalid K F,(2001) Mater. Chem. Phys. 70- 268.

Abd-El-Nabey B A, Khamis E, Ramadan E. Sh and El-Gindy, (1996).A Corrosion (NACE) 52- 671.

Alfred M. (2018). *Lannea acida*: a review of its medicinal uses and phytochemistry and pharmacological Properties. Medicinal Plants and Economic Development (MPED) Research Centre, Department of Botany, University of Fort Hare, Private Bag X1314, Alice 5700, South Africa..

Ayeni, F.A., Aigbodion, V.S., & Yaro, S.A. (2007). Non-toxic Plant Extract as Corrosion Inhibitor for Chill Cast Al-Zn-Mg Alloy in Caustic Soda Solution. Eurasian Chemico Technological Journal, 9 (2), 91-96.

Awe F E., 2015 Experimental and computational studies of corrosion inhibition potential of selected plant extracts on corrosion of mild steel and aluminum in acid medium. Phd thesis

Bradford, S A., Corrosion Control, (1993).p. 1, Van Nostrand Reinhold, New York.

Chahul H F, Ayuba .M and Nyior S. (2015). Adsorptive, kinetic, thermodynamic and inhibitive properties of *Cissus populnea* stem extract on the corrosion of aluminum in acid medium. Chemsearch journal,6 (1):20-30.

De Souza F.S, Spinell A, Caffeic Corros. Sci SI, 642 (2009).

Eddy N O, Ebenso E E, Ibok U J (2009).Adsorption, synergistic inhibitive effect and quantum chemical studies of ampicillium (AMP) and halides for the corrosion of mild steel in H_2SO_4.. J Appl Electrochem (2010) 40; 445-456.

Eddy, N. O., Ebenso, E. E. and Ibok, U. J. (2010). Adsorption, synergistic inhibitive effect and quantum chemical studies of ampicillin (AMP) and halides for the corrosion of mild steel in H_2SO_4. *Journal of Applied Electrochem*istry, **40**: 445-456

Eddy. N. O., Momoh, Y. H., and Oguzie, E. E. (2015). Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. Journal of Advanced Research, **6:** 203-217.

Eddy, N. O (2009b). Ethanol Extract of *Phyllanthus Amarus* as a Green Inhibitor for the Corrosion of Mild Steel in H2SO4. *Portugaliae Electrochimica Acta,* **27**(5):579-589.

Eddy, N. O. (2009b). Inhibitive and adsorption properties of ethanol extract of *Colocasia esculenta* leaves for the corrosion of mild steel in H_2SO_4. *International Journal of Physical Sci*ence, **4(3)**: 1-7.

Eddy, N. O. and Odoemelam, S. A. (2009); Inhibition of the corrosion of mild steel in H2SO4 by ethanol extract of *Aloe vera. Resin and Pigment Technology,* **38**(2): 111-115.

.Etuk EU, Ugwah MO, Ajagbonna OP, Onyeyili PA.(2009). Ethnobotanical survey and preliminary evaluation of medicinal plants with antidiarrhoea properties in Sokoto State, Nigeria. J Med Plants Res.3763- 6.

Eddy, N. O., Ebenso, E. E. and Ibok, U. J. (2010). Adsorption, synergistic inhibitive effect and quantum chemical studies of ampicillin (AMP) and halides for the corrosion of mild steel in H2SO4. *Journal of Applied Electrochem*istry, **40**: 445-456.

Fontana, M.G. (1987), *Corrosion Engineering*, 3rd edition, McGraw-Hill, New York.

Gomma M K and Wahdan,M H.,(1995). Mater. Chem. Phys. 39 -209.

Ita, B. I. (2004a). 4-Formylmorpholine hydrazone and 4-formymorpholine: New corrosion inhibitors for mild steel in 0.1M hydrochloric acid solution. *Proccurement of the Chemical Society of Nigeria.*

Ijuo, GA; Chahul, HF; Eneji, IS; (2016). Corrosion inhibition and adsorption behaviour of *Lonchocarpus laxiflorus* extract on mild steel in hydrochloric acid. *Ew. J. Chem. Kine*.1:21-30.

Ita B.I. and Offiong O.E., (1999).“Corrosion inhibitory properties of 4- phenylsemicarbazide and semicarbazide on mild steel in hydrochloric acid”, Materials Chemistry and Physics, 5(2) 179–184.

Itodo A.U., Aondofa B.G. and Iorungwa M.S (2018**).** Retarding Mild Steel Corrosion using a Blend of Schiff Base Metal

Complex and Neem Plant Extract. *Chem Search Journal 9(2): 45 – 63*

Jia-J F., Suning Li., Ying W., Lin-Hua C and Lu-de L,(2010) Computational and electrochemical studies of some amine acid compounds as corrosion inhibitors for mild steel in hydrochloric acid solution”, Journal of Materials science, 45(22) , 6255-6265.

Kumar.H and Vikas Y,(2013) “Corrosion characteristics of mild steel under different atmospheric Conditions by Vapour Phase Corrosion Inhibitors,” *American Journal of Materials Science and Engineering*, vol. 1, no. 3, pp. 34–39.

Leung WT, Busson F, Jardin C.(1968). Food Composition Tables for use in Africa. Rome: Food and Agriculture Organization (FAO) of the United Nations.

Mansfeld F, (1995) J.Appl.Electrochem. 25,187.

Morad M.S, Kamal El-Dean A.M, Corrs. Sci 48, 3.398, (2006).

Manzo LM, Moussa I and Ikhiri K. (2017) Phytochemical screening of selected medicinal plants used against diarrhea in Niger, West Africa. Int J Herbal Med; 532-8.

Martinez S and Stern I, J. Appl Electrochem. 31 (2001) 973

Njoku, VO; Oguzie, EE; Obi, C; Ayuk, AA; (2014). Baphia nitida Leaves extract as a Green Corrosion Inhibitor for the Corrosion of Mild

Steel in Acidic Media. *Advances in Chemistry* 2014:1–10.

Oguzie, E. E. (2008). Corrosion Inhibitive Effect and Adsorption Behaviour of *Hibiscus Sabdariffa* Extract on Mild Steel in Acidic Media. *Portugaliae Electrochimica Acta* **26**: 303-314.

Oguzie, E. E., Mejeha, I. M., Nwandu, M. C., Okeoma, K. B., Nnanna, L. A., Chidiebere, M. A. and Eze, F. C. (2012b). Experimental and theoretical assessment of the inhibiting action of *Aspilia africana* extract on corrosion of aluminium alloy AA3003 in hydrochloric acid. *Journal of Materials Science,* **47:** 2559-2572.

Okafor, P. C., Ebenso, E. E and Ekpe, U. J.,(2010). Azadirachta Indica Extracts as corrosion inhibitor for mild steel in acid medium. International Journal of Electrochemical Science, (5): 978-993.

Okafor, P. C., Osabor, V. I and Ebenso, E. E.,(2007a.) Eco-friendly corrosion inhibition: The inhibitive action of ethanol extracts of Garcinia Kolar for the corrosion of mild steel in H_2SO_4 Solutions Pigment and Resin Technology, 36, (5): 299 305.

Okewale A O and Adesina O A**,** (2020**)** Kinetics and Thermodynamic Study of Corrosion Inhibition of Mild Steel in 1.5M HCI Medium using Cocoa Leaf Extract as Inhibitor. J. Appl. Sci. Environ. Manage. Vol. 24 (1) 37-47.

Olasehinde, E.F; Olusegun, S.J; Adesina, A.S; Omogbehin, S.A; Momoh-Yahayah, H; (2013).Inhibitory action of *Nicotiana tobacum* extracts on the corrosion of mild steel in HCl: adsorption and thermodynamic study. *Nat. Sci*. 11:83 – 90.

Omotosho, O.A., & Ajayi, O.O. (2012). Investigating the acid failure of aluminum alloy I 2 M hydrochloric acid using *Vernonia amygdalina*. ITB Journal of Engineering Science, 44, (1), 77-92.

Omotosho O A .2016. Inhibition evaluation of chemical and plant extracts on the corrosion metallic alloys in acidic environment.

Onoshe S, Azubuike MM, Hitler L, Oghenekevwe IE, Mary MA, Amos PI.(2018) Free radical scavenging activity and preliminary

Phytochemical screening of ethylacetate fraction of stem bark of *Lannea acida* (A. Rich). J Nat Prod Resource; 4:182-4.

Palmer E, Pitman N. (1972).Trees of Southern Africa covering all Known Indigenous Species in the REPUBLIC of South Africa, South-West Africa, Botswana, Lesotho and Swaziland. Cape Town: Balkema;.

Perez N, (2004) Electrochemistry and corrosion science, p. 1, Kluwer Academic Publishers, New York.

Priya B, (2017) Studies on potential green corrosion inhibitors for mild steel in different media Ph.D. thesis. University of Kota, Kota.

Popoola, L.T., Grema, A.S., Latinwo, G.K., Gutti, B., & Balogun, A.S. (2013). Corrosion Problems during Oil and Gas Production and its Mitigation. International Journal of Industrial Chemistry, 4(35), 1-15. Potgieler.

Putilova I. N, Balezin S. A and Barannik V P,(1960) Metallic Corrosion Inhibitors, Pergamo Press, New York-31.

Riggs O.L Jr. and Hurd R M, (1967) Corrosion 23 -252.

Schmidt E, Lotter M, McCleland W. (2002).Trees and shrubs of Mpumalanga and Kruger National Park Johannesburg: Jacana Media;

Umoren S.A., Eduok U.M., Solomon M.M. and Udoh A.P.,(2016) "Corrosion inhibition by leaves and stem extracts of *Sida acuta* for mild steel in 1 M H2SO4 solutions investigated by chemical and spectroscopic techniques". Arabian Journal of Chemistry, 9, S209-S224.

Umoren, S.A., Obet, I.B., Akpabio, L.E., & Etuk, S.E. (2008). Adsorption and corrosive inhibitive properties of Vigna unguiculata in alkaline and acidic media. Pigment and Resin Technology, 37 (2), 98-105.

Umoren, S. A. and Ebenso, E. E. (2008). Studies of anti-corrosive effect of *Raphia hockeri* exudates gum-halide mixtures for aluminium corrosion in acidic medium. *Pigment and Resin Technol*ogy, **37(3):**173-182.