

Type of article: Original Paper

Title: *Lannea Microcarpa* Leaves Extract as Corrosion Inhibitor for Aluminium Metal in Acid Medium

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Abstract

The inhibitive action of the leaves extract of *Lannea microcarpa* was studied using weight loss, electrochemical, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) techniques. The weight loss results revealed that the inhibition efficiency of the plant extract increases with increase in concentration of the extract and decreases with increasing temperature and concentration of the HCl acid used. The highest inhibition efficiency of the extract (76.19%) was observed when 0.6g/L of extract in 0.2M HCl at 303K was used. The electrochemical results showed that the plant extract inhibitor functions via mixed type mechanism, inhibiting the rates of both anodic metal dissolution and cathode hydrogen ion reduction reactions. The values of activation energies calculated were found to be greater in inhibited systems than uninhibited systems, indicating physisorption process, while the negative values of ΔG suggest feasible and spontaneous adsorption process. FTIR spectra showed that the inhibition mechanism was an adsorption process through the functional groups present in the phytochemicals of the plant extract onto the aluminium metal surface. Surface morphology analysis through SEM also revealed that corrosion product confirmed the protection offered by the extract on metal surface. Kinetic studies revealed that the adsorption process follows first order reaction and the half-lives of the inhibited metal are relatively longer than those of the uninhibited metal. The adsorption data were found to be more consistent and fitted well the Langmuir isotherm relative to other isotherm models tested.

Keywords: Aluminium, Lannea microcarpa, Weight loss, Inhibition efficiency

INTRODUCTION

Aluminium and its alloys are used in various industries at different capacities due to its light weight, recyclability, high strength, low cost, corrosion resistance, ductility, formability, durability and conductivity (Ayuba *et al.*, 2018). Though aluminium facilitates the formation of a compact adherent passive oxide film for its corrosive immunity in various environments, the surface film is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acid or base that makes it prone to corrosion (Khaled and Al-Qahtani, 2009; John and Joseph, 2013). Therefore, the use of inhibitors is inevitable under these circumstances. The synthetic inhibitors are now generating greater environmental concerns due to the toxic effect of the synthetic compounds on human and animal life during their production and use. Phyto-inhibitors now attract more attention in the research world over the synthetic counterparts due to the eco-friendliness, availability, affordability and efficient nature of this class of inhibitors (Al-Otaibi *et al.*, 2012).

The African grape, *Lannea microcarpa* is a dioecious species of the Sudanian zone which belongs to the family of Anacardiaceae (Arbonnier, 2002). It can reach up to 15m in height and 70cm in diameter. It has a rounded parasol like crown with some descending branches with thick leafy foilage (Marquet and Jansen, 2005). The species occurs in the western part of Sahel including many parts of Nigeria (often in Rocky areas in pockets of sand) (Awodoyin *et al.*, 2015). We have discovered paucity of literature on the use of *Lannea microcarpa* as aluminium metal corrosion inhibitor. This report focuses on the use of the leaves extract of *Lannea microcarpa* as a corrosion inhibitor for aluminium metal in acid solutions through weight loss, electrochemical, FITR and SEM techniques.

MATERIALS AND METHODS

Plant Sample Collection

Fresh leaves of *Lannea microcarpa* were obtained from Bayero University Kano (Old campus), Gwale local government area, Kano state, Nigeria. They were identified by a botanist in the Department of

Plant Biology, Bayero University Kano, with herbarium registration number: BUK HAN 280 for documentation and referencing. The leaves were then washed, air dried, ground into powder form and sieved to pass through 250nm meshed sieve.

Plant Extraction

500g of the sieved powdered sample of the plant was soaked in 1.5 liters of ethanol (95%) for two weeks with constant shaking. The mixture was then filtered and concentrated to free the extract from ethanol using rotavapor (BUCHI Labortechnik AG/9230 Flawil/Switzerland). The concentrated extract was then air dried for one week, weighed and labelled for subsequent use.

Aluminium Coupons Preparation

The aluminium sheet used for this study has the following composition: Al₂O₃ (99.36%), SiO₂ (0.02%), Fe₂O₃ (0.14%), SO₃ (0.04%), Cl (0.03%), K₂O (0.03%), CuO (0.02%), TiO₂ (0.01%), Ga₂O₃ (0.01%) and MnO (0.01%). The sheets were mechanically pressed-cut into coupons, each of dimensions 4 x 3 x 0.11cm. Each coupon was de-greased by washing with ethanol, dipped in acetone and allowed to dry in air and then preserved in a dessicator (Bereket and Yurt, 2001).

Preparation of Plant Extract Solutions

0.2, 0.4, and 0.6 gL⁻¹ of the extract in 0.2M HCl were prepared by weighing 0.2, 0.4 and 0.6g of the extract and dissolving each in 5ml of ethanol and then transferred into 1litre of 0.2M HCl separately and made to the make using 0.2M HCl solution. The same procedure was repeated (but with different extract weights) in preparing 0.4 and 0.6 gL⁻¹ in 0.4 and 0.6M HCl solutions respectively. Blank corrodent solutions were also prepared by adding 5ml of ethanol each to 0.2, 0.4 and 0.6M HCl solutions respectively.

Phytochemical Analysis of the Plant Extract

Phytochemical analysis of the ethanolic extract of *Lannea microcarpa* leaves was carried out according to the method reported by Tiwari *et al.* (2011). The secondary metabolites tested include: alkaloid, saponins, phytosterols, phenols, flavonoids, proteins and amino acids, triterpenes respectively.

Weight Loss Experiments

Previously treated and weighed aluminium coupons were separately and completely immersed in 100ml beakers containing the test solutions of different concentrations with or without the inhibitor. The beakers were closed and inserted into a thermostatic water bath maintained at a particular temperature. The coupons were withdrawn from the test solutions at an interval of 1hour for a total period of 4hours where they were washed with distilled water and light brush, dried in acetone and reweighed. The differences in weight were taken as weight loss (Yousoufi *et al.*, 2013), while the differences in weight for a period of 4hours was taken as the total weight loss. The weight loss experiment was conducted by varying temperature (303, 313 and 323K), corrodent concentration (0.2, 0.4 and 0.6M HCl) and extract concentrations (0.2, 0.4 and 0.6g/L) respectively.

From the weight loss results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and corrosion rate of aluminium metal coupon (CR) were calculated using equations (1 – 3) respectively (Okafor *et al.*, 2010):

$$\%I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{W_1}{W_2} \quad (2)$$

$$CR(gh^{-1}cm^{-2}) = \frac{\Delta w}{At} \quad (3)$$

Where W_1 and W_2 are weight loss in gram of aluminium in presence and absence of inhibitor in HCl solutions respectively, θ is the degree of surface coverage, CR is the corrosion rate, Δw is the weight loss (g), A is the area of the specimen (cm^2) and t is the period of immersion (h).

Electrochemical Measurements

Aluminium metal samples for electrochemical experiments were of dimension 1.0cm x 1.0cm. These were subsequently sealed with epoxy resin in such a way that only one square surface of area 1.0cm²

was left uncovered. The exposed surface was de-greased in acetone, rinsed with distilled water and dried in warm air. Linear polarization studies were carried out on uninhibited and inhibited (0.2, 0.4 and 0.6g/L) sample in 0.2M HCl in the potential range of -1000 to -2000 mV at a scan rate of 0.333 mV per second at a temperature of 298K (Awe *et al.*, 2015).

Kinetic Study

The kinetics of corrosion inhibition of aluminium metal in HCl solutions were studied by immersing aluminium coupons in 0.2M HCl and 0.0, 0.2, 0.4 and 0.6g/L of the plant extract at 323K for 24h at some interval for 6hours. The graph of $-\log(\Delta w)$ against time was plotted for first order kinetics as shown in the equations (4) and (5) (Fadare *et al.*, 2016):

$$-\log(\Delta w) = k_1 t / 2.303 \quad (4)$$

Where k_1 from the equation (4) was calculated from the slope of the graph and substituted into equation (5) in order to calculate the half lives:

$$t_{1/2} = \frac{0.693}{k_1} \quad (5)$$

Fourier Transform Infrared Spectrophotometry (FT-IR) Analysis

FT-IR instrument model Cary 630 FTIR Spetrophotometer (Agilent Technologies) was used to identify the major functional groups present in leaves extract of *Lannea microcarpa* and corrosion product of inhibited aluminium metal in HCl solution. The analysis was done by scanning the sample through a wave number range of 650 – 4000 cm^{-1} ; 32 scans at 8 cm^{-1} resolution (Eddy *et al.*, 2008).

Scanning Electron Microscopy (SEM) Analysis

Morphological studies of the aluminium coupons surfaces exposed to uninhibited and inhibited corrosion systems containing 0.6M HCl for 4hours at 323K were taken using a prox Scanning Electron Microscope (Phenom World Eindhoven). In the sample preparation for SEM analysis, a thin layer of adhesives serving as carbon glue was attached onto a stub, and very small amount of the

materials to be viewed were spread on the stub materials and subsequently viewed in the instrument to obtain micrographs at an accelerating voltage of 15.00 kV and x500 magnification (Awe *et al.*, 2015).

RESULTS

a. Phytochemical Screening

The phytochemical investigation of ethanolic extract of *Lannea microcarpa* leaves revealed the presence of flavonoids, Tannins, phenols, proteins, sterols and saponins (table1). Presence of secondary metabolites in plant extracts has been identified to be responsible for the corrosion inhibitory properties on metal surfaces (Awe *et al.*, 2015). The chemical structures of most of these phytoconstituents contained electron rich bond or heteroatoms that facilitates their electron donating ability; hence, the inhibition of corrosion of aluminium by ethanolic extract of *Lannea microcarpa* leaves is attributed to the phytoconstituents of the extract. Similar inferences have been reported by some researchers for the inhibition of corrosion of metals by extracts of some plants (Bendahou *et al.*, 2006; Ebenso *et al.*, 2008). Also, possession of π - electrons or suitable functional groups may facilitate the transfer of charge from the inhibitor's molecule to the charged metal surface (physical adsorption) or transfer of electron from the inhibitor's molecule to the vacant orbitals of the metal (chemical adsorption) as reported by Obi-Egbedi and Obot (2013).

Table1: Phytochemical screening of leaves extract of *Lannea microcarpa*

Bioactive agent	Qualitative analysis
Flavonoids	+
Phenols	+
Proteins/amino acids	+
Alkaloids	-
Saponins	+
Triterpenes	-

Phytosterols	+
Tannins	+

Note: + indicates the presence of phytochemicals, - indicates the absence of phytochemicals.

b. Weight Loss Experimental Results

i. Effect of HCl Concentration and Temperature on Weight Loss of Al in Blank Solutions

The effect of corrodent concentration on weight loss of aluminium has been studied at 0.2, 0.4 and 0.6M HCl solutions for 4h immersion time in uninhibited aluminium at 303, 313 and 323K. The results showed that increase in concentration of acid and/or temperature increases the weight loss as well as corrosion rate in the uninhibited aluminium (figure 1). As can be seen from table 2 also, the corrosion rate of aluminium in blanked 0.2MHCl is $0.0875\text{mgh}^{-1}\text{cm}^{-2}$ while that of blanked 0.6MHCl under the same condition temperature of 303K is $1.8229\text{mgh}^{-1}\text{cm}^{-2}$. The above observation is due to the fact that the rate of chemical reaction increases as the concentration of active species increases (Mohammad *et al.*, 2012). Generally, corrosion process is attributed to the presence of water, air and H^+ which accelerate the process, therefore as the concentration of acid increases, the active species H^+ increases which in turn increases the corrosion rate. The observation may also be due to increase in the rate of diffusion and ionization of active species in the corrosion reactions (Iloamoeke *et al.*, 2012).

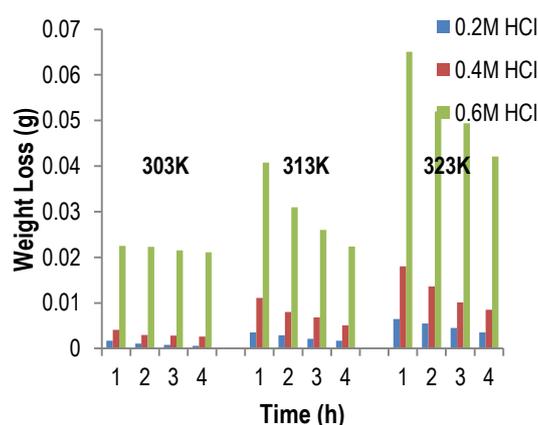


Fig.1: Variation of weight loss with time for the corrosion of aluminium in blank HCl at varying temperatures

ii. Effect of HCl Concentration on Weight Loss of Al in Plant Extract Solutions

The effect of inhibitor (*Lannea microcarpa*) of different concentrations (0.2, 0.4 and 0.6g/L) on the corrosion process of aluminium in 0.2, 0.4 and 0.6M HCl has been studied at 303, 313 and 323K. Figure (2a-c) show the variation of weight loss with time of aluminium immersed in 0.2, 0.4 and 0.6M HCl containing various concentrations of extract at 303, 313 and 323K. It is evident from the figures that, the weight loss of aluminum decreases with increase in concentration of inhibitor but increases with increasing period of contact in all the three concentrations of HCl and at all temperatures. It is also clear from the figures that all the three concentrations of *Lannea microcarpa* inhibited the corrosion of aluminium in all the concentrations of HCl and at all the studied temperatures. Table 2 revealed that the corrosion rate of aluminium decreases with increase in concentrations of inhibitor while surface coverage and inhibition efficiency increase with increasing concentrations of inhibitor. When the concentration of inhibitor varies from 0.2g/L to 0.6g/L in 0.2M HCl the inhibition efficiency increases from 57.14% to 76.19%. This shows that extract of *Lannea microcarpa* can serve as inhibitor retarding the corrosion of aluminium in HCl solution. The decrease in weight loss and corrosion rate with increasing concentrations of extract is attributed to the adsorption of extract molecules onto the aluminium metal which decreases the area of contact between aluminium metal and corrosive medium. Similar results were reported by Thilagavathy and Saratha (2015).

Moreover, the increase in weight loss as a result of increase in concentration of acid on inhibited aluminium, may be attributed to the rupture of bond between extract compound and aluminium surface by acid molecules at higher concentrations to form hydrogen-aluminium bond. These results in higher accumulation of the active sites by acid molecules which prevents the penetration of extract molecules to the surface of the aluminium (Krishnaveni and Ravichandran, 2014).

Nevertheless, it can observe from table 2 that, the inhibition efficiency of the extract decreases with increase in temperature, the inhibition efficiency of extract (0.6g/L) in 0.2M HCl at 303K was 76.19% but when the temperature was raised to 323K under the condition, the inhibition efficiency decreased to 47% (table 2). This effect suggests that the adsorption of extract of *Lannea microcarpa* on

aluminium metal is consistent with the mechanism of physical adsorption as reported by Awe *et al.* (2015).

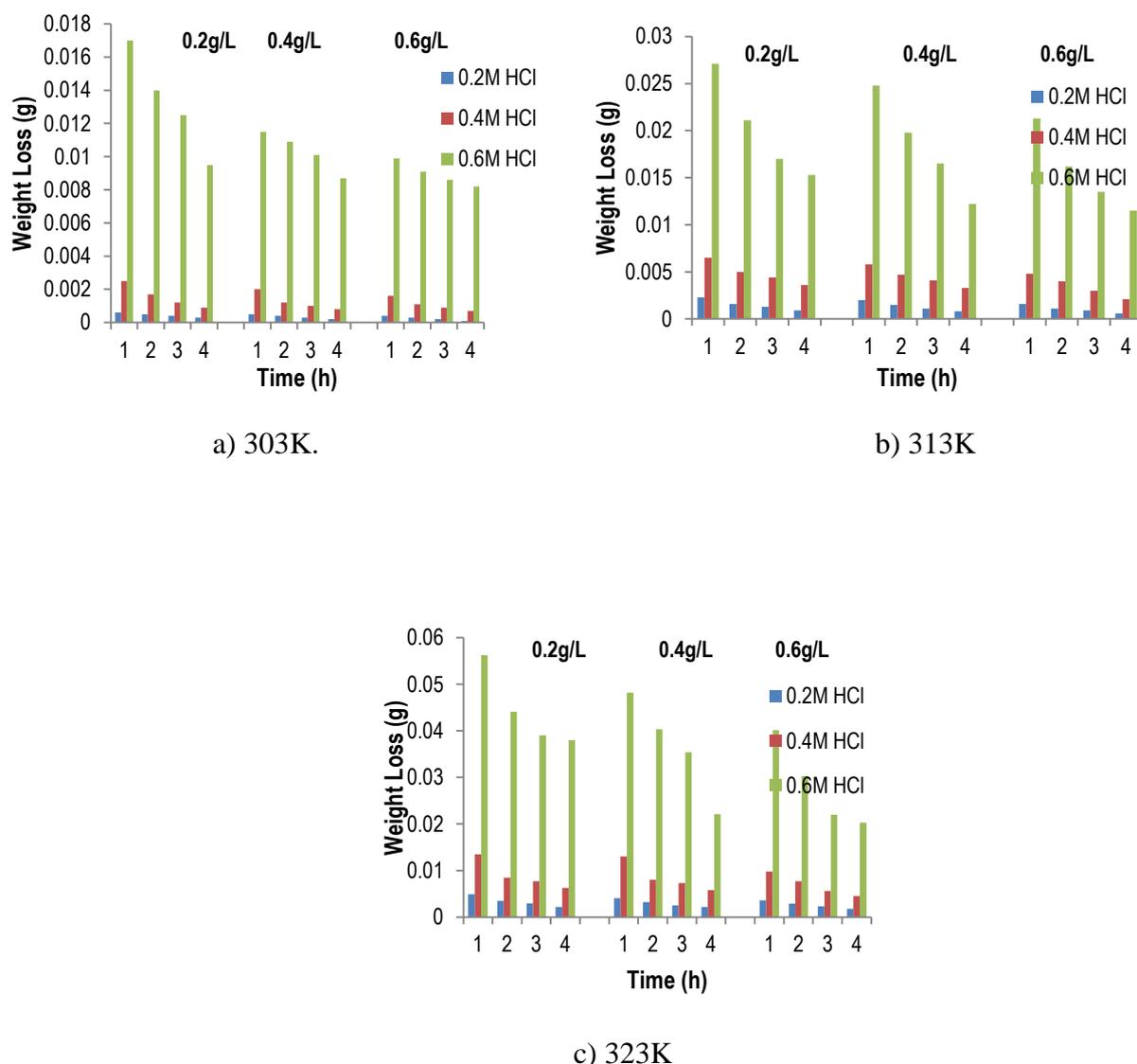
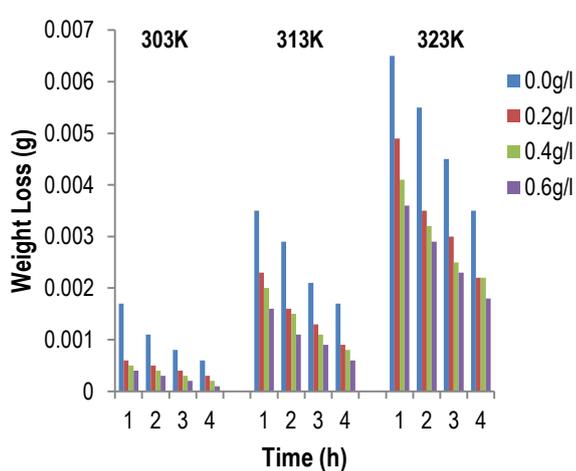


Fig. 2: Variation of weight loss with time of aluminium immersed in different concentrations of extract in 0.2-0.6M HCl at Varying Temperatures.

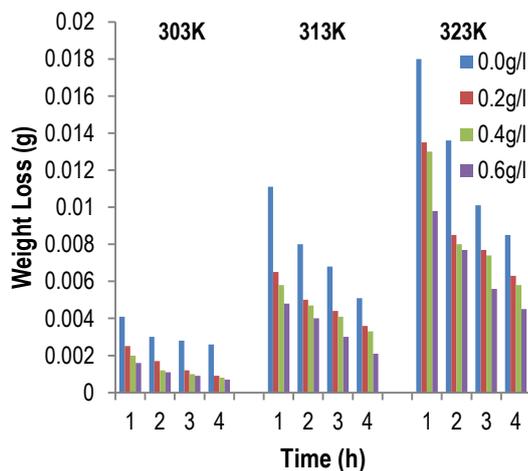
ii. Effect of Temperature and Plant Extract Concentration

The effect of temperature on weight loss and corrosion rate of inhibited aluminium metal immersed in 0.2, 0.4 and 0.6M HCl for 4h was studied by varying the temperature (303, 313 and 323K) and the results are presented in figures (3a-c). From the figures, it is clear that the weight loss of the inhibited aluminium metal increases with increase in temperature in all the three concentrations of acid. It is also observed from table 2 that the corrosion rate of inhibited and uninhibited aluminium metal increases

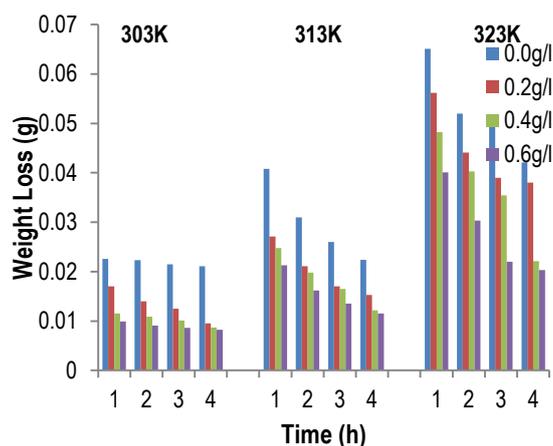
with increasing temperature in all the three concentrations of the acid. The corrosion rates of blank and 0.6g/L of extract in 0.2M HCl at 303K are 0.0875 and 0.0208mg/h.cm² respectively, while at 323K the corrosion rates raised to 0.4167mg/h.cm² for the blank and 0.2208mg/h.cm² for 0.6g/L inhibited aluminium metal (table 2). This observation shows that increase in temperature increases the reactivity of active constituents of the corrosion medium. A rise in temperature usually increases the rate of hydrogen evolution reaction on the cathode which results in a higher metal dissolution rate. It is also supported by the fact that chemical reactions increase with increasing temperature (general rule guiding the rate of chemical reactions). Also, increase in temperature increases the kinetic energy of molecules of the corrosion medium which leads to overcoming of energy barrier for corrosion more rapidly. It is also observed from table 2 that inhibition efficiency decreases with increase in temperature. This can be attributed to increase in solubility of protective films on the metal thereby increasing the susceptibility of the metal to corrosion (Udom *et al.*, 2017). This observation also suggests weak adsorption interaction between aluminium surface and the inhibitor (physical adsorption) due to the higher desorption of molecules at higher temperature (Zhao *et al.*, 2017).



a) 0.2M HCl



b) 0.4M HCl



c) 0.6M HCl

Fig. 3c: Variation of weight loss with time of aluminium immersed in various concentrations of extract at Varying HCl Concentration at 303-323K.

Table 2: Weight loss calculated parameters for various concentrations of *Lanena microcarpa* extract

Te mp . (K)	Conc. of extrac t (g/L)	0.2MHCl			0.4MHCl			0.6MHCl		
		CR (mg/cm. h) $\times 10^{-2}$	θ	% I (%)	CR (mg/cm. h) $\times 10^{-2}$	θ	% I (%)	CR (mg/cm. h) $\times 10^{-2}$	θ	% I (%)
303	0.0	8.8	-	-	26.0	-	-	182.2	-	-
	0.2	3.8	0.5	57.	12.9	0.5	50.	100.0	0.4	45.
	0.4	2.9	0.6	66.	10.6	0.5	59.	85.8	0.5	52.
			7	7		9	2		3	9
	0.6	2.1	0.7	76.	10.0	0.6	61.	74.6	0.5	59.
			6	2		2	6		9	1
313	0.0	21.3	-	-	64.6	-	-	250.4	-	-
	0.2	12.7	0.4	40.	40.6	0.3	37.	167.7	0.3	33.
	0.4	11.3	0.4	47.	37.3	0.4	42.	152.7	0.3	39.
			7	1		2	3		9	0
	0.6	8.8	0.5	58.	28.9	0.5	55.	130.2	0.4	48.
			9	8		5	2		8	0
323	0.0	41.7	-	-	104.6	-	-	434.6	-	-
	0.2	28.3	0.3	32.	77.1	0.2	26.	369.4	0.1	15.
	0.4	25.0	0.4	40.	70.8	0.3	32.	317.1	0.2	27.
			0	0		2	3		7	0
	0.6	22.1	0.4	47.	57.5	0.4	45.	269.2	0.3	38.
			7	0		5	0		8	1

c. Polarization Measurements

Figure 4 shows Tafel's polarization curves of aluminium electrode in 0.2M HCl in presence and absence of various concentrations of *Lannea microcarpa* extract. It can observe from the figure that the cathodic and anodic reactions in blank HCl follow Tafel's law, the plots also show that both cathodic and anodic reactions were suppressed with the addition of various concentrations of *Lannea microcarpa*, implying that the plant extract functioned as mixed-type inhibitor, reducing the rates of both anodic dissolution and cathodic hydrogen evolution reactions.

Moreover, it follows from the figure that the shapes of polarization plots for the inhibited electrodes are not substantially different from the uninhibited electrode, suggesting that the presence of *Lannea microcarpa* extract merely decreases the rate of corrosion but does not alter the electrochemical reactions responsible for the corrosion process (Khaled and Amin, 2009).

The electrochemical parameters such as inhibition efficiency (IE), corrosion rate (C_r), corrosion potential (E_{corr}), Cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density (i_{corr}) obtained by extrapolating Tafel lines are presented in table 3. The inhibition efficiencies were calculated according to the equation (6) (Zhaoet al., 2017) and they were found to increase with increase in extract concentration.

$$IE(\%) = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100 \quad (6)$$

Where i_{corr}^o and i_{corr} are the corrosion current densities obtained from uninhibited and inhibited solutions respectively.

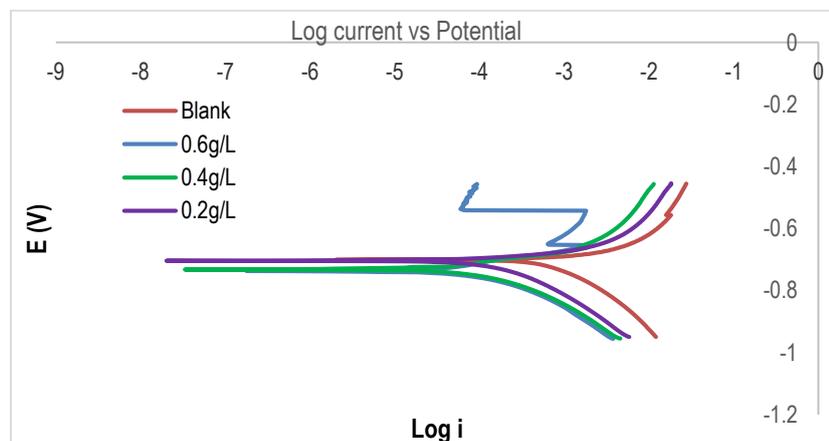


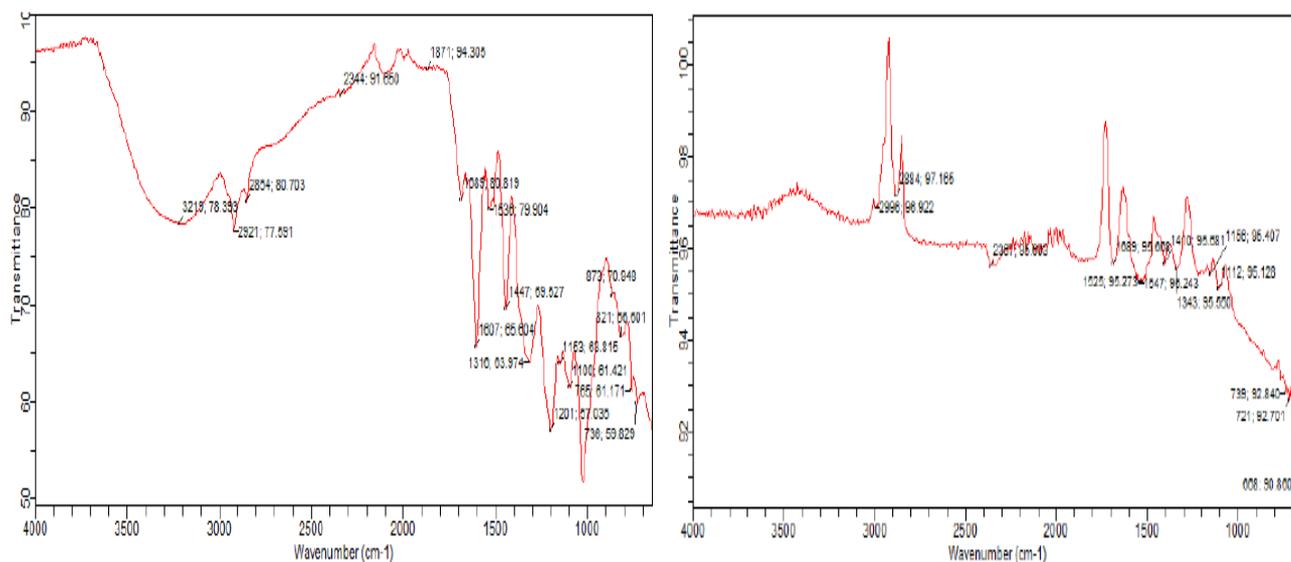
Fig. 4: Overlaid Tafel Polarization Curves Recorded for Al in 0.2M HCl Solutions in Varying Concentrations of *Lannea microcarpa*.

Table 3: Electrochemical parameters obtained from Tafel polarization technique for Al in 0.2M HCl solutions in varying concentrations of extract at 25°C

Extract concentration (gL ⁻¹)	i_{corr} (μAcm^{-2})	E_{corr} (mV)	β_a (mV dec ⁻¹)	β_c (mV dec ⁻¹)	C.R (mmpy)	% I (%)
0.0	-389.197	-701.151	29.996	102.27	4.2362	-
0.2	-37.571	-737.556	56.091	50.156	0.43597	90.35
0.4	-28.892	-730.858	37.206	53.955	0.33525	92.58
0.6	-22.704	-703.843	14.729	36.837	0.26346	94.17

d. Fourier Transform Infrared (FT-IR) Spectroscopic Results

The IR spectra of powdered extract of *Lannea microcarpa* leaves and corrosion product with inhibitor are shown in figures (5 a-b). By comparing the spectrum of extract and corrosion product with inhibitor, it can observe that the C-N stretch at 1100cm⁻¹ was shifted to 1112 cm⁻¹, C-O stretch at 1153 cm⁻¹ was shifted to 1156 cm⁻¹, N-O stretch at 1316 cm⁻¹ was shifted to 1343 cm⁻¹, C-C stretch in ring at 1447 cm⁻¹ was shifted to 1410 cm⁻¹, N-H bend at 1607 cm⁻¹ was shifted to 1547 cm⁻¹. The shift in the frequencies indicates that there is an interaction between the metal and the plant extract (Okafor *et al.*, 2007).



a) Ethanol Leaves Extract of *Lannea Microcarpa*
Fig. 5: FTIR Spectra of the studied specimens.

b) Corrosion Product of Aluminium in Extract

e. Scanning Electron Microscopy

Morphological studies of the surfaces of uncorroded aluminium specimen, and corroded (inhibited and uninhibited acids) were carried out by scanning electron microscopy (SEM) after immersion in the test solutions for 4h at 323K, the images are presented in figure (6). The most severely corroded surface is observed in the uninhibited system (fig. 6a) which is damaged by presence of cracks, pits and patches all over the surface, followed by the metals in inhibited acid figure(6b-d) which are visibly less damaged compared to the uninhibited metal. The surface of uncorroded aluminium metal contains no surface defect (fig.6e). This implies that addition of extract of *Lansea microcarpa* leaves to acid solutions protected the aluminium metal from undergoing severe corrosion by formation of protective layer on the surface through adsorption of the extract on the aluminium surface.

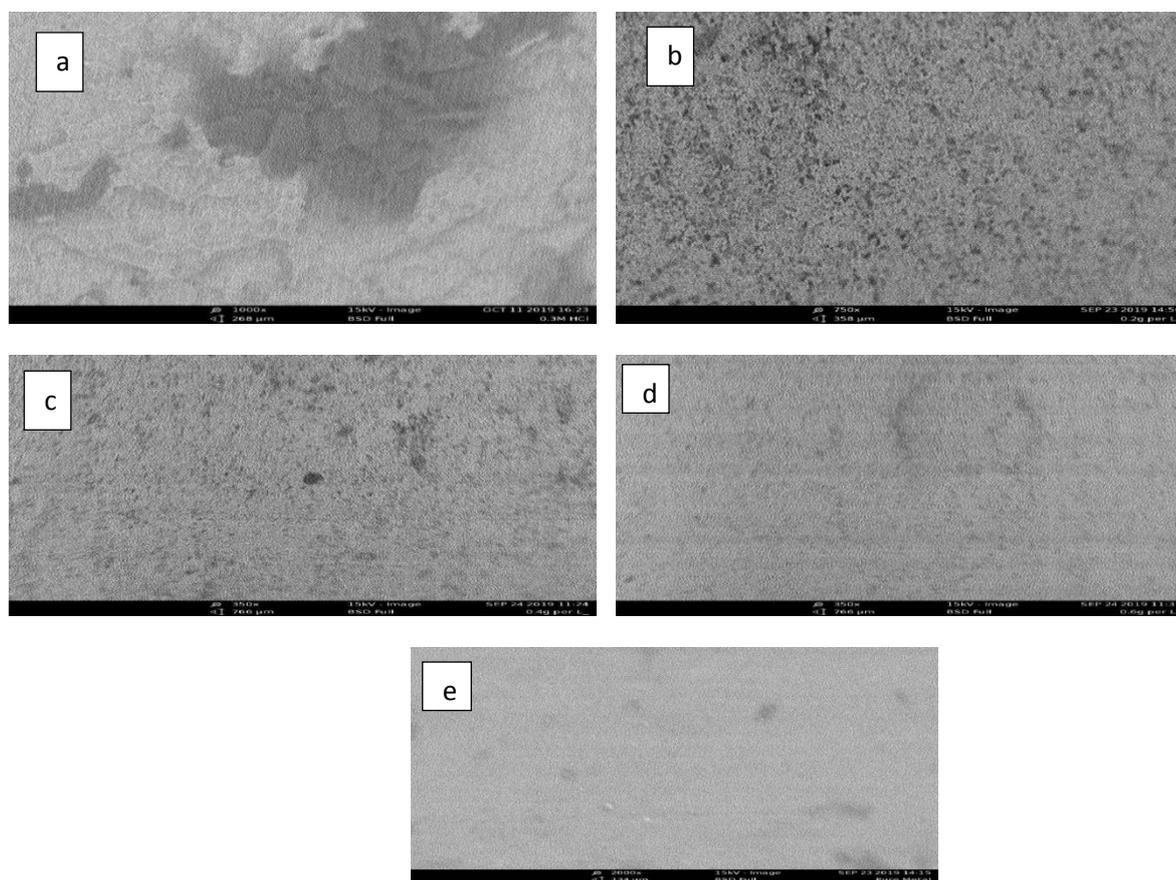


Fig. 6: SEM Micrographs of Aluminium Dipped in 0.6M HCl for (a) 0.0g/L (Blank) (b) 0.2g/L (c) 0.4g/L (d) 0.6g/L of *Lansea microcarpa* Extract, (e) Uncorroded Aluminium.

f. Adsorption Isotherm

Inhibitors protect metals from corrosion by adsorbing onto the surface by forming a thin adsorption layer. The efficiency of an inhibitor is largely dependent on the extent of adsorption of the inhibitor molecules on the metal surface. The nature of corrosion inhibitors has been deduced in terms of the adsorption characteristics of the inhibitor (Thilagavathy and Saratha, 2015). The adsorption characteristic of inhibitor can be evaluated with the help of surface coverage (θ) and the inhibitor concentrations. There are many isotherm models to describe the inhibitor/metal interactions. Five of these models were used namely: Langmuir, Freundlich, Temkin, Florry-Huggins and El-Awady isotherm. Their correlation coefficients (R^2) were used to determine the best fit isotherm among them. Table4 shows the parameters obtained from the plot of each isotherm at different temperatures (303-323K) and the best fit was assigned by taking into consideration the values of R^2 at all the temperatures. From the values of R^2 of the tested isotherms at all temperatures, the extract of *Lannea microcarpa* leaves showed strong adherence of inhibition process to Langmuir adsorption isotherm due to its closeness to unity when compared to the other isotherms.

Langmuir adsorption isotherm describes quantitatively the formation of monolayer adsorbate on the outer surface of the adsorbent. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Fadare *et al.*, 2016). Langmuir equation is an ideal isotherm for physical and chemical adsorption (Eddy and Ebenson, 2008). From table4 the values of equilibrium constants K_{ads} are all positive, indicating a favourable adsorption (Nnanna *et al.*, 2010). The Langmuir isotherm is presented by the equation(7):

$$C/\theta = 1/K_{ads} + C \quad (7)$$

Where C is the concentration of inhibitor, θ is the surface coverage and K_{ads} the adsorption equilibrium

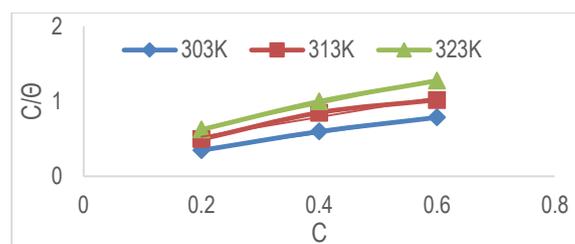


Figure 7. Langmuir adsorption isotherm for aluminium metal in HCl at different temperatures.

Table 4: Adsorption parameters for the adsorption of *LanneaMicrocarpa* extract on aluminium surface

Isotherm	Temperature(K)	Slope	$\Delta G_{ads}(KJmol^{-1})$	R^2	K_{ads}
Langmuir	303	1.09	-15.043	0.9932	7.06
	313	1.38	-13.894	0.9690	3.75
	323	1.63	-13.885	0.9925	3.17
Freundlich	303	0.26	-9.738	0.9883	0.86
	313	0.33	-9.428	0.9395	0.67
	323	0.35	-9.214	0.9968	0.56
Temkin	303	0.39	-22.579	0.9777	140.48
	313	0.37	-20.919	0.9122	55.74
	323	0.31	-21.442	0.9876	52.81
Flory-Huggins	303	1.35	-15.460	0.9286	8.33
	313	1.75	-14.268	0.7913	4.33
	323	2.87	-14.921	0.9686	4.66
EL-Awady	303	0.77	-13.894	0.9635	4.47
	313	0.66	-12.043	0.9138	1.84
	323	0.57	-11.187	0.9914	1.16

g. Thermodynamic Studies

The free energy of adsorption, ΔG_{ads} was calculated according to the equation (8):

$$\Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \quad (8)$$

Where ΔG_{ads} is the Gibbs free energy, K_{ads} is the adsorption equilibrium constant obtained from the intercept of each adsorption isotherm, R is the universal gas constant, T is the temperature of the system, 55.5 is water concentration. The calculated values of ΔG_{ads} for all the tested isotherms ranges between -2.238 to -22.579KJmol⁻¹ which are negatively less than the threshold value -40KJmol⁻¹ required for the mechanism of chemical adsorption to take place (Awe *et al* 2015). Therefore the adsorption of extract of *Lannea microcarpa* leaves on aluminium surface is spontaneous and consistent with the mechanism of physical adsorption (Loto, 2011). The calculated values of ΔG_{ads} and K_{ads} for

the tested isotherms at 303, 313 and 323K are presented in table 4. The activation energy for the corrosion process was calculated by using the Arrhenius equation (9):

$$\log CR = \log A - E_a / 2.303RT \quad (9)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius pre-exponential factor, E_a is the activation energy (minimum energy needed before the corrosion reaction of the metal proceed), R is the universal gas constant and T is the temperature of the system.

Plot of logCR against reciprocal of absolute temperature from equation (9) above gives a straight line with slope equals to $-E_a / 2.303R$ from which the activation energies were calculated and presented in table5. The calculated values of E_a ranges from 53.363 to 54.340KJmol⁻¹ for the extract, while the E_a obtained for the blank is 36.121KJmol⁻¹. The values of E_a calculated were found to be greater in inhibited aluminum than those obtained in blank, suggesting the formation of an adsorption film of physical electrostatic nature (Award, 2006; Oguzie *et al.*, 2012; Rao and Prabhu, 2013; Cookey *et al.*, 2018).

The values of enthalpy and entropy of corrosion process were calculated according the transition state equation (10):

$$\log(CR/T) = \{\log R/N_A h + \Delta S_a / 2.303R\} - \Delta H_a / 2.303RT \quad (10)$$

Where ΔH_a is the enthalpy of the corrosion process, ΔS_a is the entropy of activation for the corrosion process, N_A is avogadro's number and h is plank's constant.

Plot of CR/T Vs recipocal of absolute temperature gives a straight line with slope equals to $-\Delta H_a / 2.303R$ and intercept equals to $\{\log R/N_A h + \Delta S_a / 2.303R\}$ from which enthalpy and entropy of activation for the corrosion process were calculated as presented in table5. The positive values of enthalpy of activation both in presence and absence of extract reflects the endothermic nature of aluminium dissolution process (Awe *et al.*, 2015). While the negative values of entropies of adsorption indicate that the activated complex in the rate determining step represents association rather

than dissociation, which means that there is reduction in disorderliness on going from reactant to activated complex (Oguzie, 2008).

Table 5: Energy parameters for the dissolution of aluminium in HCl in absence and presence of different concentrations of *Lanneamicrocarpa*

Extract Conc. (gL ⁻¹)	E_a (KJmol ⁻¹)	ΔH_a (KJmol ⁻¹)	ΔS_a (KJmol ⁻¹)
0.0 (blank)	36.121	33.575	-0.1296
0.2	54.330	51.544	-0.0754
0.4	54.340	51.726	-0.0759
0.6	53.363	50.711	-0.0804

h. Kinetic Study

The kinetic of aluminium corrosion in the solution of HCl was studied by fitting data obtained from weight loss measurements into different kinetic equations. The test revealed that the corrosion of aluminium in solutions of HCl is consistent with a first order kinetic model which can be derived as follows. If the initial concentration of aluminium is a_0 and after time, t , x mole of the corrosion product is formed, then the kinetic equation of the reaction can be represented according to the equation (11):

$$dx/dt = k_1(a_0 - x) \quad (11)$$

where k_1 is the first order reaction rate constant. Rearrangement of equation(11) yields equation (12) and upon integration, equation (13) and equation 4.9 are obtained

$$dx/(a_0 - x) = k_1 dt \quad (12)$$

$$-\ln(a_0 - x) = k_1 t \quad (13)$$

$$-\log(\Delta w) = k_1 t / 2.303 \quad (14)$$

Also, for a first order reaction, the half-life is related to the rate constant as follows

$$t_{1/2} = 0.693/k_1 \quad (15)$$

The plots of $-\log$ (weight loss) versus time were linear. Values of kinetic parameters deduced from the plots are presented in Table6. From the results obtained, it is evident that the half-life of aluminium in solutions of HCl containing various concentrations of the inhibitors are greater than the half-life of

aluminum in the blank solution. Therefore, the extract of *Lannea microcarpa* increases the half-life of aluminium in HCl solutions.

Table 6: Kinetic parameters for the corrosion of aluminium in 0.6M HCl containing various concentrations of *Lanneamicrocarpa*

Extract Conc. (gL ⁻¹)	R ²	K ₁	t _{1/2} (h)
0.0 (blank)	0.9863	0.198	3.500
0.2	0.9922	0.141	4.915
0.4	0.9943	0.098	7.071
0.6	0.9829	0.089	7.787

CONCLUSION

This study revealed that extract of *Lannea microcarpa* effectively inhibited the corrosion of aluminium at the studied conditions using weight loss, electrochemical, SEM, FTIR and kinetic studies. The inhibitive process was found to be the mixed type through adsorption due to the presence of some phytochemicals present there in the extract. Thermodynamic parameters revealed that the adsorption of the extract onto the aluminium surface was spontaneous, endothermic and also supported the physical adsorption process.

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