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Corrosion Inhibition and Adsorption Properties of Ethanolic Extract of *Lannea Microcarpa* Leaves on Carbon Steel and Zinc Metal in Acidic Medium

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Abstract: Corrosion of materials such as mild steel and or zinc metal causes big losses in the economy of many countries due to the great amount of funds required in order to be minimized. The aim of the research is to investigate the corrosion of carbon steel and zinc metal in acidic medium using *Lannea microcarpa* leaves extract by weight loss method. It was observed that the inhibition efficiency increase with temperature for both carbon steel and zinc metal. The adsorption of *Lannea microcarpa* leaves were found to obey Langmuir isotherm model for zinc metal with R^2 value close to unity and that of carbon steel obeys Freundlich isotherm model.

Key words: Corrosion, *Lannea microcarpa*, Carbon Steel, Zinc Metal, Langmuir isotherm, Freundlich isotherm

I. Introduction

Corrosion is the disintegration of a material or its properties by reaction when interacting with its surrounding environment such as moisture, acids, bases, salts, aggressive metal polishes and many other liquid chemicals. Corrosion of materials such as mild steel and or zinc metal causes big losses in the economy of many countries due to the great amount of funds required in order to be minimized. Mild steel and of course low-alloy steels are the most widely used materials in the marine environment, lightly stressed component (studs, bolts, gear, shaft etc.), and constructions purposes due to its excellent mechanical properties, low cost, and availability. Applications of mild steel are also for the fabrication of number reaction vessels, tanks, pipelines and underground structures [1]. Acid solutions are widely used in industries for lots of purposes, such as acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Due to the general aggressive nature of acid solutions, inhibitors are commonly used to reduce the corrosive attack of acid solutions to the contacted metallic materials, among which steel is extensively used [2]. The use of inhibitors is one of the most practical approaches for protecting metals against corrosion, especially in acidic media. These compounds can be adsorbed on metal surfaces, block the active sites, and decrease the corrosion rate. The adsorption ability of inhibitors onto the metal surface depends on the nature and surface charge of metal, chemical composition of electrolytes, and molecular structure and electronic characteristics of inhibitor molecules. Organic compounds containing functional electronegative groups and p electrons in triple or conjugated double bonds such as nitrogen, sulfur, and oxygen are usually good inhibitors since these compounds are easily adsorbed on metal surfaces [3]. Despite continuing advances in the formulation of corrosion resistance materials, the use of chemical inhibitors often remains the most practical and cost effective means of preventing corrosion. The use of sulphuric acid in such processes predominates. A large number of organic compounds containing polar functional groups in their molecules have been reported as effective corrosion inhibitors for mild steel in H_2SO_4 solutions [4]. Corrosion inhibitors are used in eliminating the undesirable destructive effect and in preventing the metal dissolution. In the past few years, the inhibition of mild steel corrosion in acid solutions by various types of organic inhibitors has attracted more attention. Most of the available inhibitors are the toxic compounds that should be replaced by new inhibitors in the environmental protection [5]. The industrial application of nonmetallic materials is almost always precluded because of problems arising from the severity of the environment and the aggressive conditions of temperature, pressure and wear. On the other hand, in several industrial environments most metals and alloys are affected by different forms of corrosion attack, particularly dangerous if localized. For these reasons the industrial use of corrosion inhibitors is often a good solution to prevent corrosion phenomena and to provide a more acceptable lifetime of metallic structures [6].

Many reseachers have applied plant extract to inhibit the corrosion of carbon steel and Zinc metal such as *Prosofis juliflora* [1]. *Parkia biglobosa* [7]. *Dacryodis edulis* extract [8]. *Salsola oppositifolia* extract [9]. *Murraya koenigii* leaves [10]. *Osmanthus fragrance* leaves [11]. *Carica papaya* leaves [12]. *Punica granatum* [13]. Bamboo leaf extract [14].

Lannea microcarpa commonly known as African grapes or “Faaru” in Hausa is a tropical deciduous tree that grow up to about 16 m tall and 70 cm in diameter. It’s located in most regions of West Africa and largely distributed in the dry forest re-growth areas. Ethanol extract of the leaves shows the presence of: Alkaloid, tannins, sugars, phenol, flavonoid, Terpenoid, glycoside, quinines, coumarins, Resins, phlobotanins, and carbohydrate but absence of Anthraquinones [15].

The aim of this paper is to investigate the effect of *Lannea microcarpa* leaves extract as an effective and eco-friendly source of corrosion inhibitor for the inhibition of carbon steel and zinc metal in acidic medium using weight loss method at different temperatures.

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II. Materials and Methods

Extraction of *Lannea microcarpa*

Lannea microcarpa Leaves was collected from Alh. Yushau Farm at Dawanau, Dawakin Tofa Local Government Area, in Kano State which was then authenticated by prof. L. D. Fagwalawa and accessed by M. A. Abbas at the department of Biological Sciences, Aliko Dangote University of Science and Technology Wudil, Kano State. The leaves was spread out in a laboratory for two weeks so as to dried and then transferred to an electric oven at 100 ^{0}C for an hour for it to be properly dried, and then grounded to powder. The powdered leaves was then soaked in a beaker and ethanol was added on to it, and left at room temperature for 6 days and the dark green sample was filtered and the resulting filtrate was transferred to rotatory evaporator for some hours in order to make the sample free from ethanol until a thick sticky greenish was obtained, the extract obtained was used to prepared various concentration of inhibitor. 1 M HCl stock solution was used as blank solution.

Material Preparation

The material used for the study were mild carbon steel and zinc metal. The sheets were mechanically pressed cut to form different coupons. Each of dimension 3 cm by 4 cm and 0.306 mm thickness having an approximate weight of 3.10 g with density of 8.44 g/cm^3.the coupons were degrease by washing with methanol and dried in an oven. All reagent used for the study were analar grade and distilled water was used for their preparation.

Weight loss experiment

Weight loss is simple method to evaluate the effectiveness of a corrosion inhibitor [16].

A previously weighed coupon was completely immersed in the test solution using 250 Ml open beaker. Containing 0.5 g, 1.0 g, 1.5 g, 2.0 g and 2.5 g of extracts into 10 ml of 1 M HCl Solution. The beaker was then covered with Aluminium foil and inserted into a water bath maintained at 303 K for 2 hours. The corrosion product was then removed from the solution and washed each coupon with distilled water and then in a solution containing 0.1 M NaOH in order to quench the reaction. The washed coupons was rinsed in acetone and dried in oven and kept in desiccator before reweighing. The experiment was repeated at 313 K and 323 K for 2 hours each respectively.

III. Result and Discussion

The role of the inhibitor is to form a barrier of one or several molecular layers against acid attack and this depends on phytochemical compounds which vary widely on the part of the plant and its geographical location [1]. It was reported that ethanol extract of *Lannea microcarpa* leaves shows the presence of: Alkaloid, tannins, sugars, phenol, flavonoid, Terpenoid, glycoside, quinines, coumarins, Resins, phlobotanins, and carbohydrate but absence of Anthraquinones. [16] Weight loss measurement were carried out at different temperatures ranging from 303-323 K. From the average weight loss result. The corrosion rate (CR), the degree of surface coverage (θ). As well as the % inhibition of the inhibitor, were calculated using the equation below

$$CR = \frac{\text{w x } 87.6}{A\ x\ D\ x\ T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\theta = \frac{\text{w1}-\text{w2}}{w1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

$$\text{I.E} = \frac{\text{w1}-\text{w2}}{w1} x100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where W1 and W2 are the weight loss (g) for the coupons in the absence and presence of the inhibitor, θ is the surface coverage of the inhibitor, A is the area of the coupons in cm^2, T is the time of immersion in hour and w is weight loss of the coupons after time T and D is the density of the coupons. The result were shown in tables below:

Table 1. Gravimetric Analysis for Carbon Steel in 1 M HCl at different Temp. in the Absence and Presence of the various Conc. of the extract

Temp (K)	Conc.(g/l)	%I.E	Θ	CR	Log C	C/ Θ	Log Θ
303	Blank	…..	…..	0.0549	…..	…..	…..
	0.5	22.04	0.2204	0.0428	-0.3010	2.2686	-0.6568
	1.0	30.78	0.3078	0.0380	0	3.2489	-0.5117
	1.5	41.71	0.4171	0.0320	0.1761	3.5962	-0.3798
	2.0	48.09	0.4809	0.0285	0.3010	4.1589	-0.3179
	2.5	59.74	0.5974	0.0221	0.3979	4.1848	-0.2237
313	Blank	…..	…..	0.0709	…..	…..	…..

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	0.5	45.13	0.4513	0.0389	-0.3010	1.1079	-0.3455
	1.0	52.47	0.5247	0.0337	0	1.906	-0.2801
	1.5	64.03	0.6403	0.0255	0.1761	2.3427	-0.1936
	2.0	69.53	0.6953	0.0216	0.3010	2.8765	-0.1578
	2.5	81.10	0.8110	0.0134	0.3979	3.0826	-0.0910
323	Blank	.....	.....	0.0947	**…..**	**…..**	**…..**
	0.5	59.87	0.5987	0.0380	-0.3010	0.8351	-0.2228
	1.0	67.16	0.6716	0.0311	0	1.4890	-0.1729
	1.5	74.87	0.7487	0.0238	0.1761	2.0035	-0.1257
	2.0	78.99	0.7899	0.0199	0.3010	2.5320	-0.1024
	2.5	87.65	0.8765	0.0117	0.3979	2.1913	-0.0572

Table 2. Gravimetric Analysis for Zinc metal in 1M HCl at different Temp. in the Absence and Presence of the Various Conc. Of the Extract.

Temp (K)	Conc.(g/l)	%I.E	Θ	CR	Log C	C/ Θ	Log Θ
303	Blank	…..	…..	0.0414	…..	…..	…..
	0.5	35.29	0.3529	0.0267	-0.3010	1.4168	-0.4523
	1.0	46.85	0.4685	0.0222	0	2.1345	-0.3293
	1.5	60.38	0.6838	0.0164	0.1761	2.4843	-0.2191
	2.0	72.94	0.7294	0.0112	0.3010	2.7420	-0.1370
	2.5	85.50	0.8550	0.0069	0.3979	2.9240	-0.0680
313	Blank	…..	…..	0.0402	…..	…..	…..
	0.5	50.74	0.5074	0.0198	-0.3010	0.9854	-0.2946
	1.0	63.68	0.6368	0.0146	0	1.5704	-0.1960
	1.5	74.37	0.7437	0.0103	0.1761	2.0169	-0.1286
	2.0	84.40	0.8440	0.0064	0.3010	2.3697	-0.0737
	2.5	92.03	0.9203	0.0032	0.3979	2.7165	-0.0361
323	Blank	…..	…..	0.0410	…..	…..	…..
	0.5	72.68	0.7268	0.0112	-0.3010	0.6880	-0.1386
	1.0	83.33	0.8333	0.0064	0	1.2000	-0.0792
	1.5	89.75	0.8975	0.0042	0.1761	1.6713	-0.0470
	2.0	94.87	0.9487	0.0021	0.3010	2.1081	-0.0229
	2.5	99.51	0.9951	0.0002	0.3979	2.5123	-0.0021

Adsorption consideration

Adsorption isotherm are very vital and helpful which shows the mechanism of the interaction between inhibitor and the metal surface.[17] The most usually used adsorption isotherms are Langmuir, Temkin, Freundlich and some other various isotherms. [16] However Freundlich and langmuir isotherm model were tested in these present study. Which can be expressed by the following equation:[9]

$$log\theta = logKads + nlogC \quad \text{(4)}$$

Where 0<n<1; θ–surface coating; C-inhibitor concentration; Kads-Equilibrium constant of Cads-adsorption-desorption process. A correlation between θ and inhibitor concentration in acidic medium for Langmuir's adsorption model is reported

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By various workers. [18] and is represented by equation.(5)

$$\frac{C}{\theta} = \frac{1}{Kads} + c \quad \text{..... (5)}$$

The equilibrium constant of adsorption (K_{ads}) was related to free energy of adsorption ΔG_{ads} as given in below equation. [19]

$\Delta G_o = -2.303RT\log (55.5K_{ads})$ ..... (6)

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

It was observed that the extract obeys Freundlich adsorption isotherm at 303 K with a degree of linearity at 0.9876 which is also close to unity indicating strong adherence of the adsorption of Lannea Microcarpa Leaves extract on the surface of the carbon steel. In contrast the adsorption of *Lannea microcarpa* on Zinc metal in 1 M HCl obeys the Langmuir adsorption isotherm at 323 K with a degree of linearity at 0.997 as shown in Fig: 4&6.

Temperature Effect on Inhibition efficiency

The inhibition efficiency of the extract has been evaluated at different temperature for the study of corrosion on carbon steel and zinc metal and the results were shown in fig. 1 & 2. It is clear that increase in temperature leads to the increase in inhibition efficiency.

Inhibition Efficiency Effect on Inhibitor Concentration.

As shown from table 1 & 2 above inccrease in concentration of the inhibitor increase the inhibition efficiency. As its reported by [20]. Increase in I.E as concentration increases can be attributed to adsorption of inhibitor. [21].

Thermodynamic Studies

The effect of temperature for the corrosion of carbon steel and zinc metal at various temperature of *Lannea microcarpa* can also be calculated using Arrhenius equation below [22].

Log CR= logA-(Ea/2.303RT)……(7)

Where

CR is the rate of corrosion on mild steel and zinc metal. A is The Arrhenius constant. Ea activation energy, R is the universal gas constant which is ($8.314KJMOL^{-1}K^{-1}$), T is Temperature.

Log CR was plotted against the inverse of temperature (1/T) values for Carbon steel and Zinc metal in 1 M HCl in absence and presence of inhibitors.

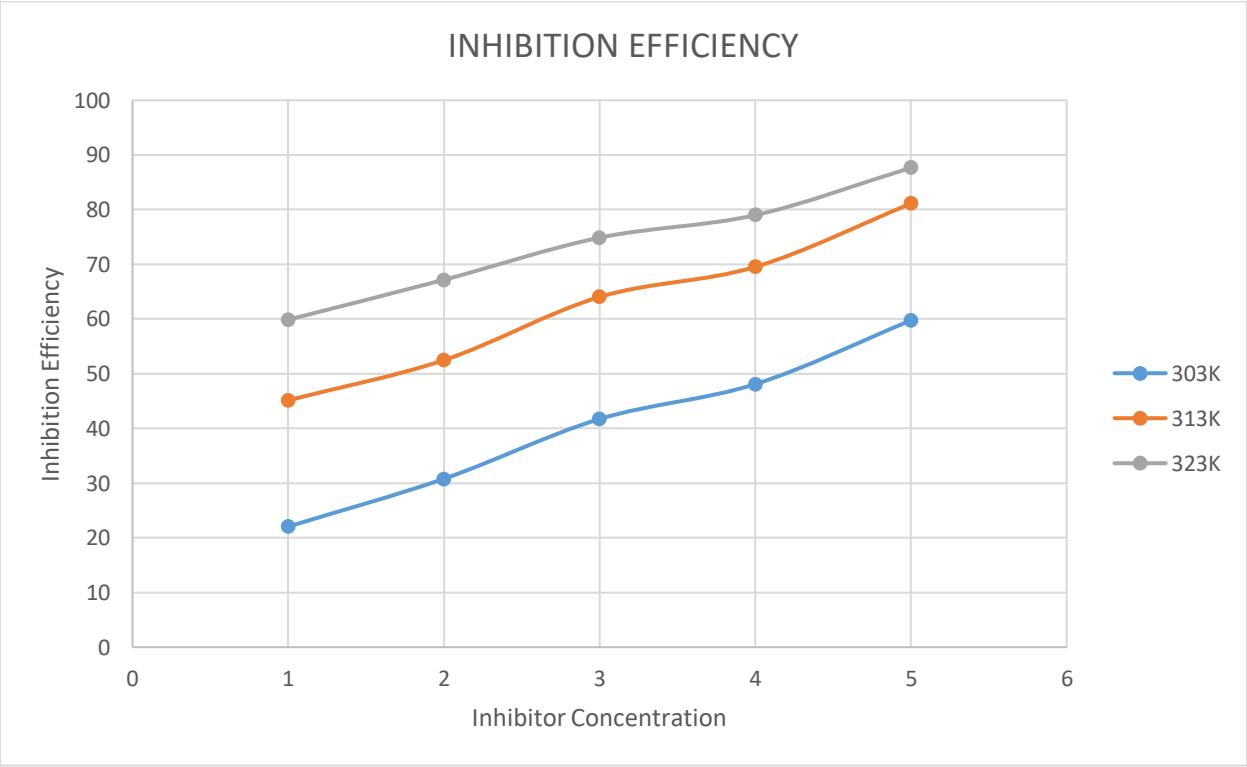


Fig 1: Variation of Inhibition Efficiency for the Corrosion of Carbon Steel at 303 K, 313 K and 323 K

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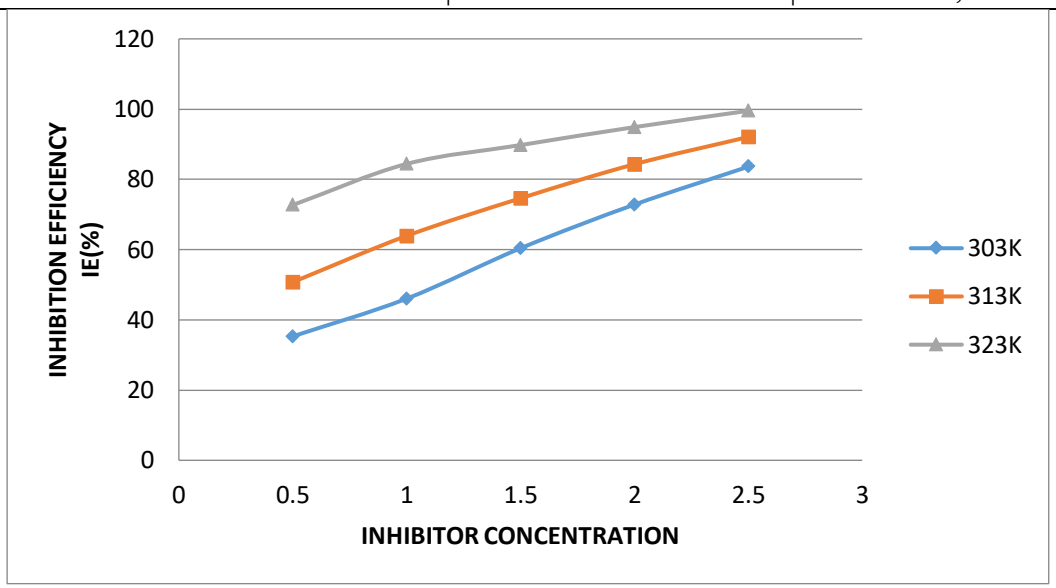


Fig 2: Variation of Inhibition Efficiency with Inhibitor Concentration for the Corrosion of Zinc Metal at 303 K, 313 K and 323 K

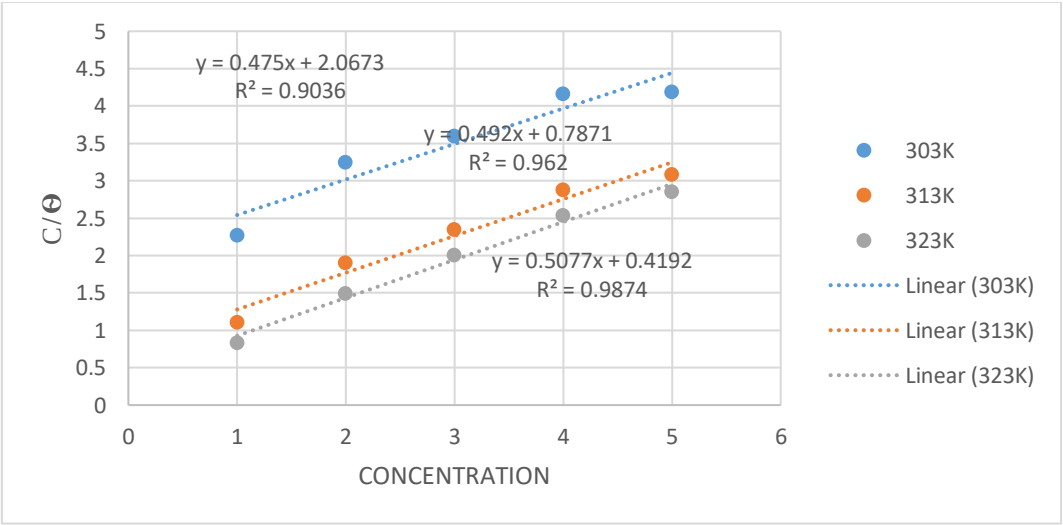


Fig 3: Langmuir Isotherm plot for Carbon Steel in 1 M HCl Solution Containing *Lannea microcarpa* extract at 303 K – 323 K

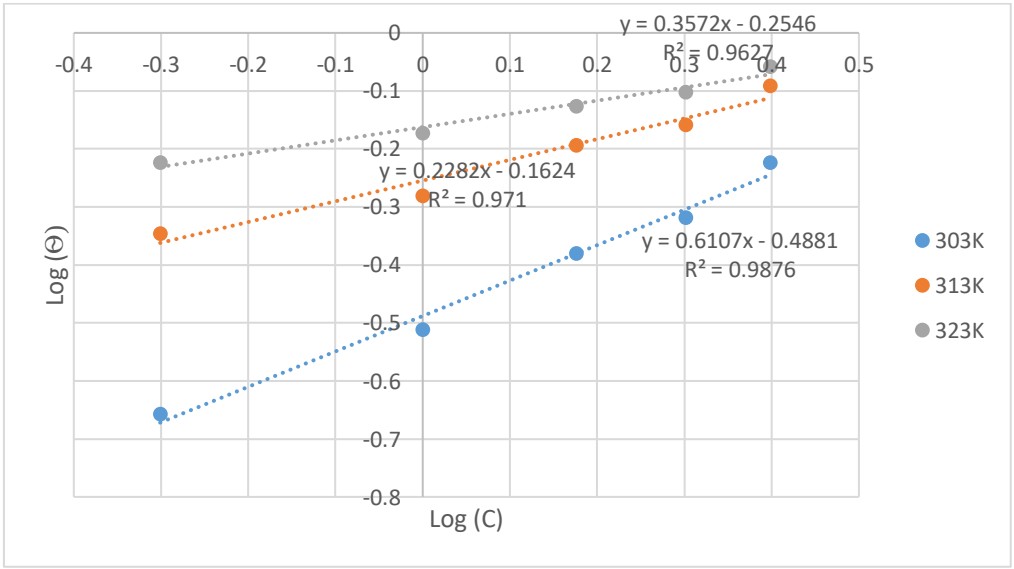


Fig 4: Freundlich Isotherm plot for Carbon Steel Corrosion in 1 M HCl Solution on *Lannea microcarpa* Leaves extract

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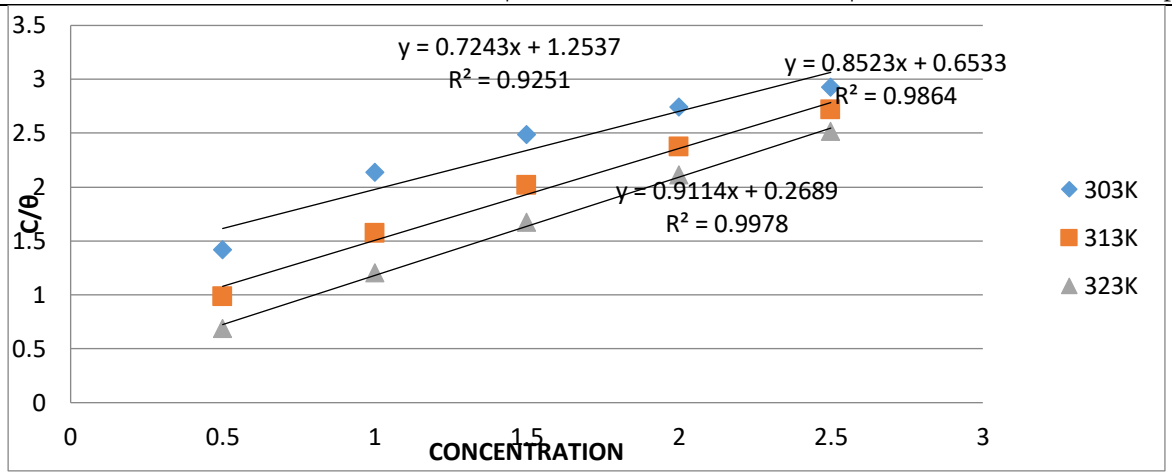


Fig 5: Langmuir Isotherm plot for Zinc steel Corrosion in 1 M HCL Solution Containing *Lannea macrocapa* Extract at 303 K, 313 K, 323 K.

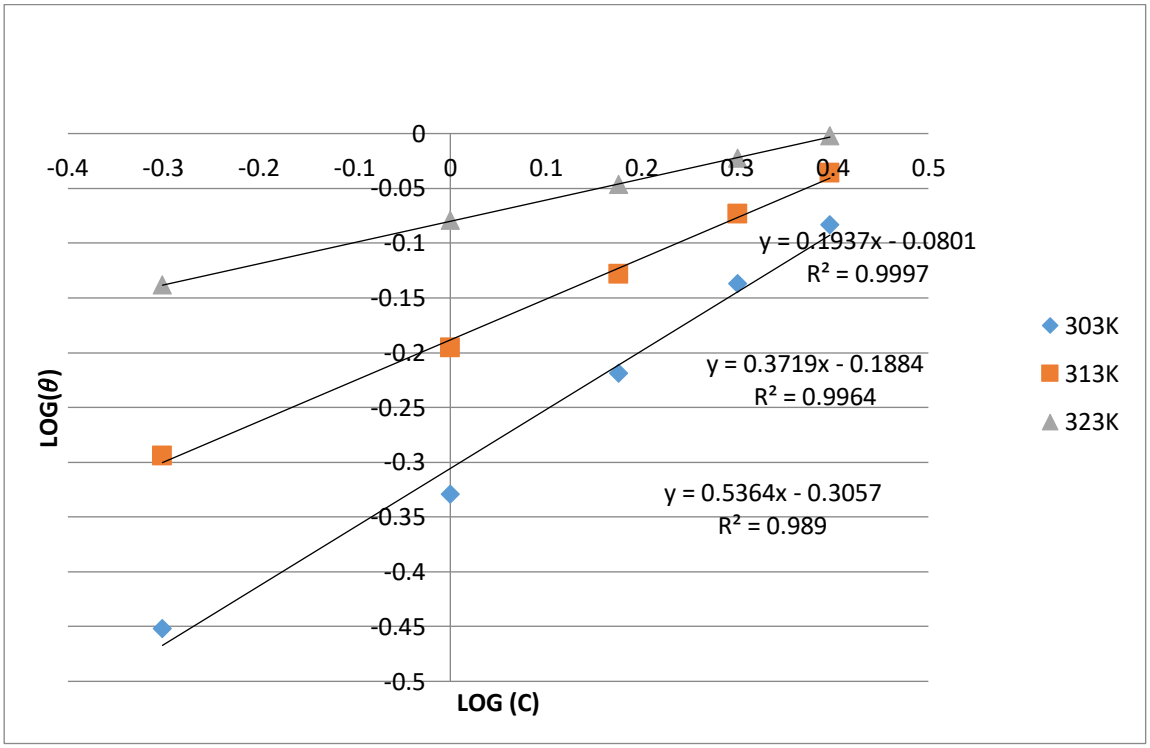


Fig 6: Freundlich Isotherm plot for Zinc Metal in 1 M HCl solution Containing *Lannea macrocapa* Extract at 303 K, 313 K, 323 K.

IV. Conclusion

According to the result presented above. The ethanol extract of *Lannea microcarpa* leaves on carbon steel and zinc metal in acidic medium were examine using weight loss method at different temperatures. Inhibition efficiency was found to be 87.65% at 323 K for carbon steel and that of zinc metal was 99.51% at 323 K also. The extract was found to obey Langmuir adsorption isotherm for zinc metal and in contrast the plant extract obeys Freundlich isotherm for carbon steel. Conclusively the leaf extract of the plant could be serve as eco-friendly and effective source of corrosion inhibition for carbon steel and zinc metal in acidic medium.

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Conflict of interest

Authors have declared that no conflict of interest exist.

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