LOCUST BEAN (*PARKIA BIGLOBOSA*) POD EXTRACT AS CORROSION INHIBITOR ON ALUMINIUM IN ACIDIC MEDIA ITS ADSORPTION ISOTHERM MODELS

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ABSTRACT

This work investigated the use of locust bean pod extract as an inhibitor to mitigate corrosion of aluminium metal in an acidic environment. Gravimetric weight loss method was used to study the corrosion process with a view to evaluating the weight loss, and adsorption isotherms parameters in the presence of the plant extract inhibitor. Phytochemical analysis was carried out on the locust bean pod extract, this revealed the presence of tannin, flavonoids and saponins compounds which suggest that the locust bean pod extract is a good green corrosion inhibitor. It was observed that the corrosion inhibition occurred by an attribute of inhibitor molecules adsorption on the surface of the aluminium metal which is seen to best fit to Langmuir adsorption isotherm model with the R^2 value of 0.9982 in comparison to the other coefficient of determination values obtained from the other isotherms model used. However, more than one active sites of inhibitor were adsorbed on the surface of aluminium metal. The Gibb's free energy (ΔG^o)values obtained ranges between (-0.072 – -19.735 kJ/mol) which confirmed the spontaneity, feasibility, and physical adsorption mechanism. This also indicates a strong spontaneous adsorption of the locust bean pod extract on the aluminium metal surface.

Keywords: Adsorption, Hydrochloric acid, Inhibition, Weight loss.
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INTRODUCTION

Corrosion is the gradual deterioration of a material by electrochemical reaction due to its interaction with its environment. It has been an everyday challenge in all sectors of the economy particularly the manufacturing industry [1]. One of the major causes of aluminium corrosion is the corrosion of its electrode which causes severe hydrogen evolution problems. Seawater environment are extensively used in the industries such as; gas production and offshore oil, shipping, coastal industrial plant that is mainly used for cooling and power plant, desalination plant and oil field water and injection. The presence of (Cl^-) is the main cause of corrosion in the environments. Corrosion causes damage in marine industries due to exposure of vessel to chloride medium, corrosion cost has geometrically increased yearly with an approximately cost of 60-80 billion dollars worldwide [2]. Aluminum is the second most used metal after iron, it is used in a large number of applications such as alloys. Because of the low atomic mass and the negative value of the standard electrode potential, aluminium potentially attracts as an anode material for power sources with high energy densities [3].

The unique combinations of properties provided by aluminum and its alloys make aluminum one of the most versatile, economical, and attractive metallic materials for a broad range of uses from soft, highly ductile wrapping foil to the most demanding engineering applications. Aluminum alloys are second only to steels in use as structural metals [4]. The significance of this metal protection process in different areas of application has necessitated the keen interest in research of corrosion inhibition by various corrosion scientists [5]. Metals (aluminium) corrode because they move to a thermodynamically stable state. For metals to corrode, they have to react with their environment. Damage due to corrosion is responsible for fluid leakage, structural weakness and eventual failure of the metal. This is responsible for the high cost for inspection/monitoring, repair/replacement and high cost of industrial end product. In efforts to mitigate aluminum metal corrosion, the main tactic is to separate the metal from corrosive environments, this can be achieved using corrosion inhibitors. Recently, the use of chemical inhibitors has been limited due to environmental regulations; however, plant extracts have again become important because their source is renewable and environmentally friendly for a wide range of these needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures that is low cost. A lot of natural products were previously used as corrosion inhibitors for different metals in various environments as reported by these authors [6 – 15] but limited research work has been reported in literature on the use of this pod in mitigating corrosion which this study seeks to explore. This study focused on the phytochemical screening, fourier transform infrared spectroscopy (FTIR), and adsorption isotherms on corrosion of aluminium metal in hydrochloric acid.

MATERIALS AND METHODS

Materials

Locust bean (*Parkia Biglobosa*) pods were obtained from Ogbomoso Community in Oyo State, Nigeria. Aluminium metals were procured from accredited iron sheet dealer in Effurun, Delta State, Nigeria. It was machined into 40 mm × 20 mm × 2 mm in Mechanical Engineering Department Workshop at Federal University of Petroleum Resources, Effurun, Delta State. The surface preparation of the mechanically polished coupons were carried out using sand papers, washed with 100 ml ethanol, degreased with 50 ml acetone and dried at room temperature. JENWAY model meter (pH – 3510), vacuum drying oven (DZF 6021), digital weighing balance (JJ 224BC), and beakers, were utilized for this corrosion study. Hydrochloric acid, acetone, and ethanol solutions used were of analytical grades and were procured from a qualified chemical dealer in Effurun, Delta State, Nigeria.

Methods

Pre-treatment of sample and sample characterization

The locust bean pod samples were thoroughly washed thereafter sun dried and pulverized into powdery form with the aid of laboratory blender. This was then sieved with a sieve of 0.143 µm mesh. The sample was later stored in a desiccator prior to use.

Phytochemical analysis

The phytochemical screening of the locust bean pod extract was done to identify the main groups of active chemical constituents present in the extract like the presence of tannin, saponin, alkaloids, phenol and flavonoids [16].

Fourier Transform Infrared Spectroscopy (FTIR)

Locust bean pod extract of 0.143 µm particle size was observed with Fourier Transform Infrared Spectroscopy (Buck Scientific model 530) with the range 500 – 4000 cm^{-1} (wavelength). The background material used in the analysis is potassium bromate (KBr).

Extraction of Locust Bean extracts (*Parkia Biglobosa*) pod

The locust bean (*Parkia Biglobosa*) pods were washed thoroughly with running water to remove debris at room temperature. 300 g of the pulverized locust bean pod powder was macerated in 96 % ethanol at room temperature in preparation for extraction in 500 mL Sohxlet extractor. 300 mL of 96 % ethanol was reflux continuously for 3 hours at 78 ^{o}C. Locust bean pod extract of 2 g was weighed and dissolved in different molar concentration of hydrochloric acid used for the corrosion study.

Procedure of the experiment

The gravimetric method was used. Each aluminium steel coupon was sized 40 mm × 20 mm × 2 mm. Before polishing, a hole of 0.1 cm was drilled on each coupon. The coupon was weighed initially before been suspended with the aid of a nylon thread in a 100 ml beaker containing 50 ml of 0.5 M, 1 M, 1.5 M, and 2 M HCl solution at different inhibitor concentrations. The mechanism of inhibition and thermodynamic parameters were studied at 303 K temperature at contact time. Each of the aluminium steel metal coupons immersed in different inhibitor concentrations and without inhibitor concentration after the corrosion process was dipped in both distilled water and ethanol solutions. The corroded coupon was scrubbed to remove any remaining residual inhibitor concentration and HCl. Thereafter, the coupon was then washed thoroughly with washing liquor, rinsed with distilled water and later dried in an acetone before been reweighed.

Determination of weight loss

The weight loss of the aluminium metal coupon was determined using equation 1 below;

$$Weight\ loss, (g) = W_1 - W_2 \quad (1)$$

Where, W_1 is the initial weight of the aluminium metal coupon, W_2 is the final weight of the aluminium coupon after corrosion study.

Free Energy of Adsorption (ΔG_{ads})

Free energy of adsorption was determined using the given relationships.

$$\Delta Gads = -2.303RTlog(55.5 \times K) \quad (2)$$

Where T = absolute temperature in Kelvin, R = Universal gas constant (8.3145J/mol K), K_{ads} is the equilibrium constant of adsorption. The constant value of 55.5 is the concentration of water in solution in mol/K.

RESULTS AND DISCUSSION

Characterization of aluminium metal and locust bean (*Parkia Biglobosa*) pod extract

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

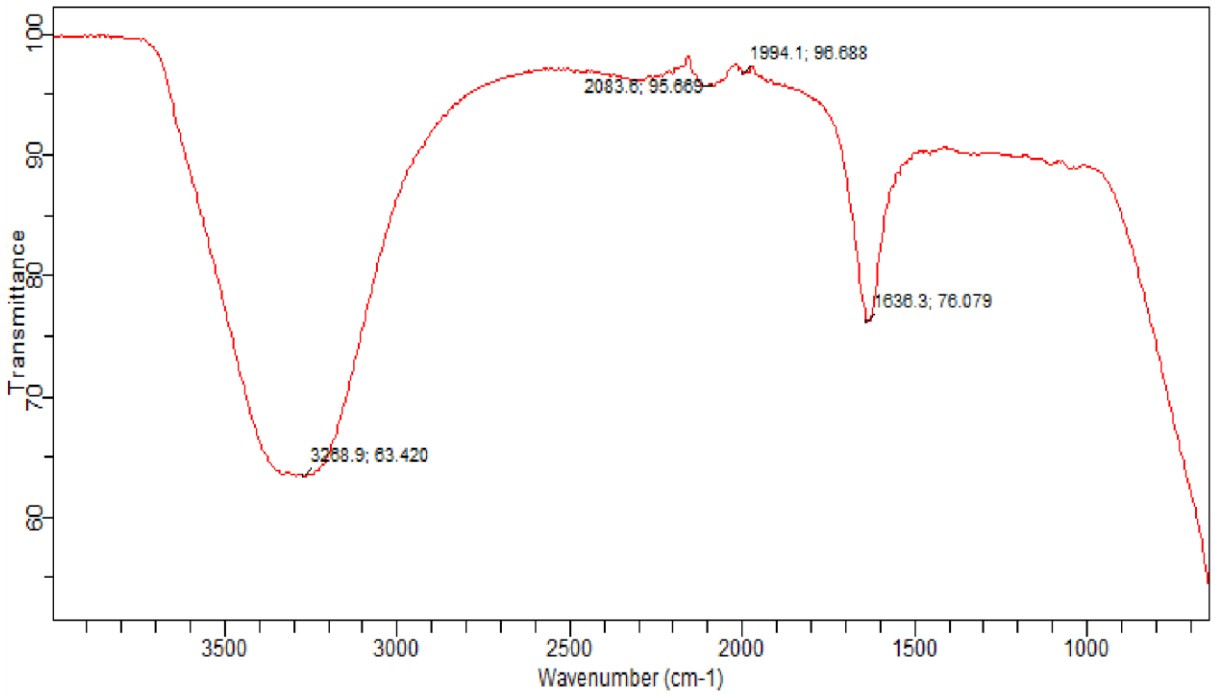

Figure 1: FTIR Spectra for locust bean pod extract.

Figure 1 gives the FTIR result of the locust bean pod extract. It can be seen that frequency (3269.9 cm^{-1}) depict RO-H (Alcohol) wide rounded broad band [17; 18]. The band with a very weak wave length number 2083.6 cm^{-1} corresponds to ($C \equiv C$) stretch, the broad band 1994.1 cm^{-1} revealed the alkene group, ($C = C$). The sharp band (1636 cm^{-1}) corresponds to C = O stretch ketone, and $R_2C = O$. The presence of aromatic, and carbonyl double bond groups in the extract suggest that locust bean pod extract can be used as a corrosion inhibitor on aluminium in acidic medium.

Table 1: Phytochemical Analysis of Locust Bean Pod Extract

Constituent	Parameter indicator
Saponin	+
Reducing sugar	-
Alkaloids	+
Protein (Amino acids)	+
Steroids	+
Tannins	+
Flavonoid	+
Anthraquinones	-
Phenolic compound	+
Terpenoids	+
Carbohydrates	+

Keys: (+) indicates present, (-) indicates absent

Phytochemical screening.
It can be noted that, locust bean pod extract is composed of many organic naturally occurring compounds and revealed the presence of alkaloids, phenolic compounds, tannins, flavonoids, steroids, terpenoids, protein, and steroids as depicted in Table 1 [19 – 21]. Consequently, the corrosion inhibitive action noticed in locust bean pod extract can be ascribed to the components of the extract that is adsorbed on the aluminium steel surface. The core constituents of the locust bean pod extract contain O - N atoms in functional groups (RO–H, $C \equiv C$, C═O, R_2C═O, and N–H) as seen in figure 1. The O-heterocyclic rings, as observed in locust bean pod extract meet the descriptive qualities of typical corrosion inhibitors [19]. Hence, it is logical to infer that the flavonoids, alkaloids, and amino acids in locust bean pod extract display the inhibition performance. When protonated chemical molecules in locust bean pod extract are adsorbed on the aluminium metal surface, a Vander Waal coordinate bond might be created by limited transfer of electrons from O, and N atoms to the vacant d- orbital of Al. These core chemical compounds inherent in locust bean pod extract may be protonated in HCl solution.

Adsorption Isotherms
Four different adsorption isotherms were examined so as to have an understanding on the interface between the inhibitor and aluminium metal surface. The isotherms employed were Langmuir, Freundlich, Temkin, and El - Awady adsorption isotherms. The linear regression determination coefficient (R^2) was used to determine the model that fitted best to the experimental values.

Langmuir adsorption isotherm
Langmuir relationship is represented by equation (3)

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (3)$$

where K is the equilibrium constant of adsorption (M^{-1}) which was employed to obtain the Gibb's free energy, C is the inhibitor concentration ppm, and Θ is the degree of surface coverage [22 – 24]. A plot of C/Θ against C as shown in figure 2 gave a reciprocal of intercept as the adsorption constant.

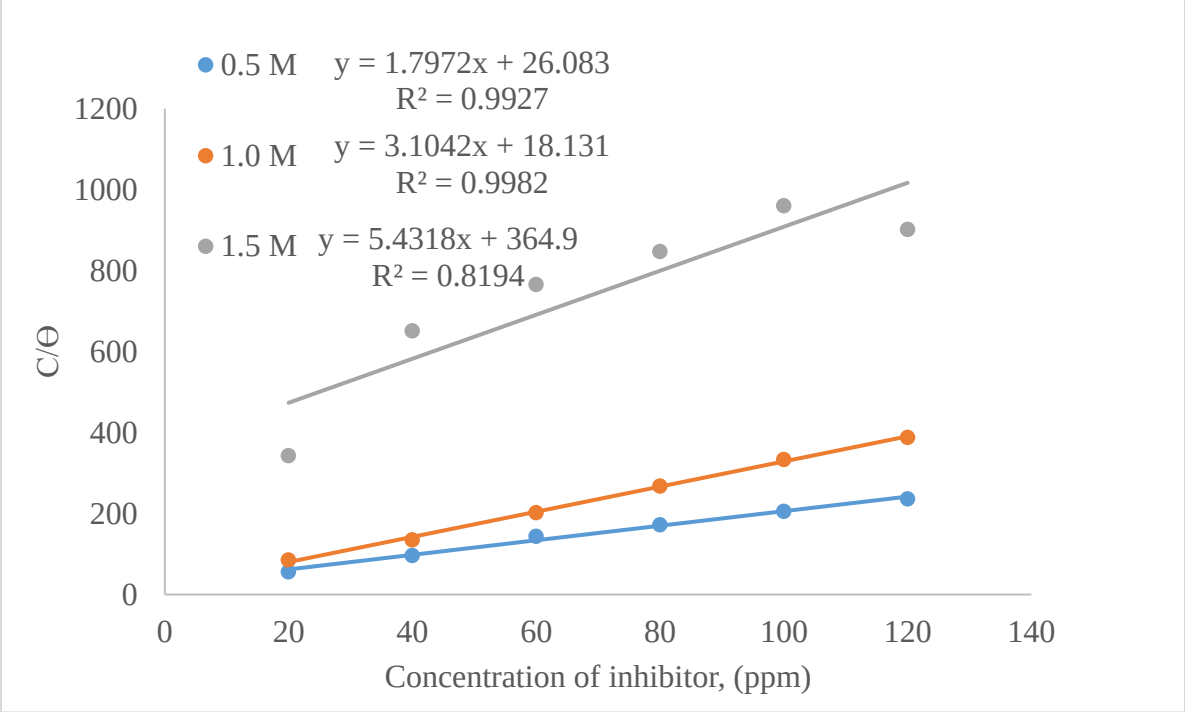

Figure 2: Langmuir isotherm for adsorption of inhibitor on aluminium metal surface at 303K

Table 2: Langmuir Adsorption Isotherm Model Values at 303K, Temperature

Concentration	K_{ads}	R^2	slope	ΔG(kJ/mol
0.5 M	0.0384	0.9982	1.7972	-1.907
1.0 M	0.0552	0.9982	3.1042	-2.821
1.5 M	0.0027	0.8194	5.4318	4.782

Freundlich isotherm

The non – ideal system fitting can be done at times by fixing the experimental data to Freundlich adsorption isotherm as seen in figure 3 [25]. This is expressed in equation 4 with the linear of equation 4 written as equation 5:

$\theta = KC^n$ (4)

Equation 4 can be re – written

$$log\theta = logK + nlogC \quad (5)$$

A plot of log Ɵ against log C should give a straight line as noticed in fig. 3. Where Ɵ is the degree of surface coverage, C is the concentration of inhibitor, in ppm, K is the adsorption equilibrium constant which is a measure of capacity of adsorption, (mL/g), and n is the positive constant called the Freundlich exponent which is obtained from the slope of equation 5 this talks about the intensity of adsorption process on the aluminium metal surface.

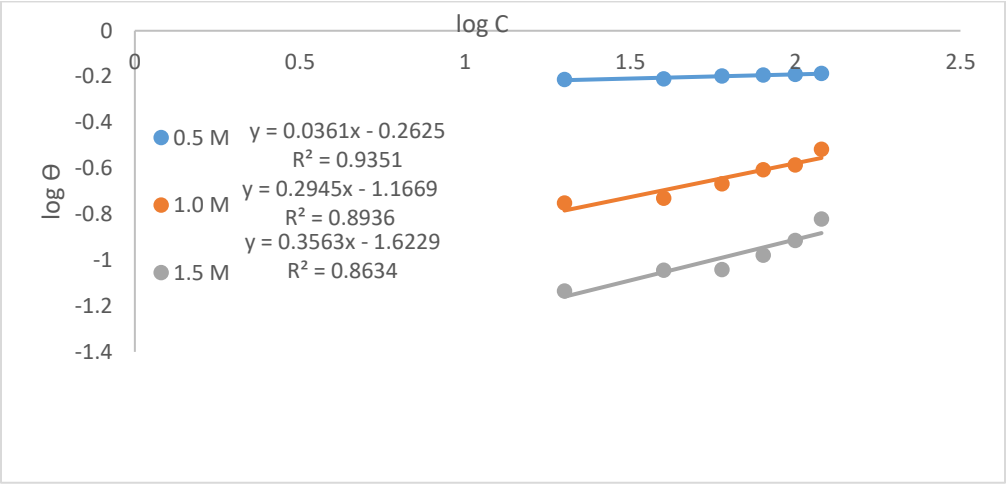

Figure 3: Freundlich isotherm for adsorption of inhibitor on aluminium metal surface at 303K

Table 3: Freundlich Adsorption Isotherm Model Values at 303K, Temperature

Concentration	K_{ads}	R^2	n	ΔG(kJ/mol
0.5 M	0.546	0.9351	0.0361	-8.596
1.0 M	0.068	0.8936	0.2945	-3.349
1.5 M	0.024	0.8634	0.3563	-0.722

Temkin isotherm

This is expressed in equation (6) with the linear form written as equation (7);

$\Theta = \frac{1}{f}\ln(K_{ads}C)$ (6)

Equation 10 can be re - written as $\Theta = \frac{1}{f}logC + \frac{1}{f}logK$ (7)

where Ɵ is a linear function of ln C [26], K is the equilibrium constant of adsorption, (mL/g), C is the inhibitor concentration, (ppm), and f is a coefficient of inhomogeneity. A plot of Ɵ against log C gives a straight line as indicated in figure 4, if Temkin isotherm is followed.

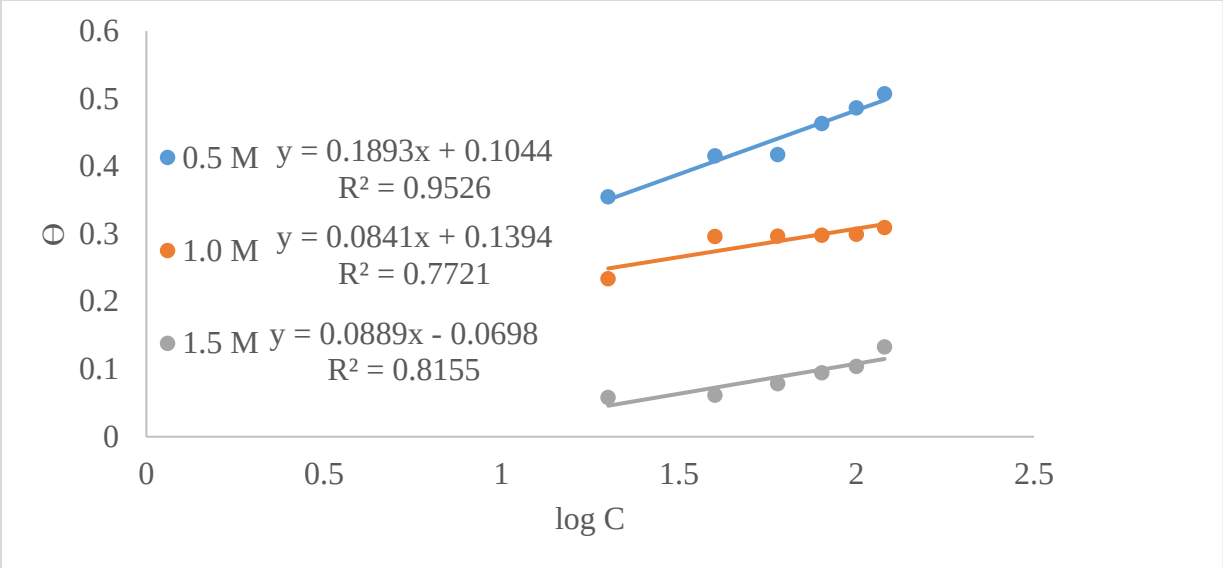

Figure 4: Temkin isotherm for adsorption of inhibitor on aluminium metal surface at 303K

Table 4: Temkin Adsorption Isotherm Model Values at 303K, Temperature

Concentration	K_{ads}	R^2	f	ΔG(kJ/mol
0.5 M	3.56	0.9526	5.83	-13.318
1.0 M	45.45	0.7721	11.89	-19.735
1.5 M	0.164	0.8155	11.25	-5.564

El-Awady isotherm

This model is also referred to as the kinetic/thermodynamic model and is written as follows;

$$\log\left(\frac{\theta}{1-\theta}\right) = logk + ylog\ C \qquad (8)$$

where y represents the number of inhibitor molecules occupying one active site of the metal surface, Ɵ is the degree of surface coverage, C is the inhibitor concentration, ppm. A plot of log (Ɵ/1-Ɵ) against log C as shown in figure 5 can be applied to determine the associated parameters such as the reciprocal of y which is used to illustrate the number of active sites on the .

aluminium metal surface occupied by one molecule of the locust bean pod extract. It can be related to the binding constant, B, according to equation (9) [27].

$$B = k^{1/y} \qquad (9)$$

When 1/y>1, each locust bean pod extract molecule is considered to adsorb more than one active site on the aluminium metal surface and vice – versa. As seen in Table 5 it can be confirmed that more of the locust bean pod extract is adsorb on more than one active site of the surface of aluminium metal in acidic environment

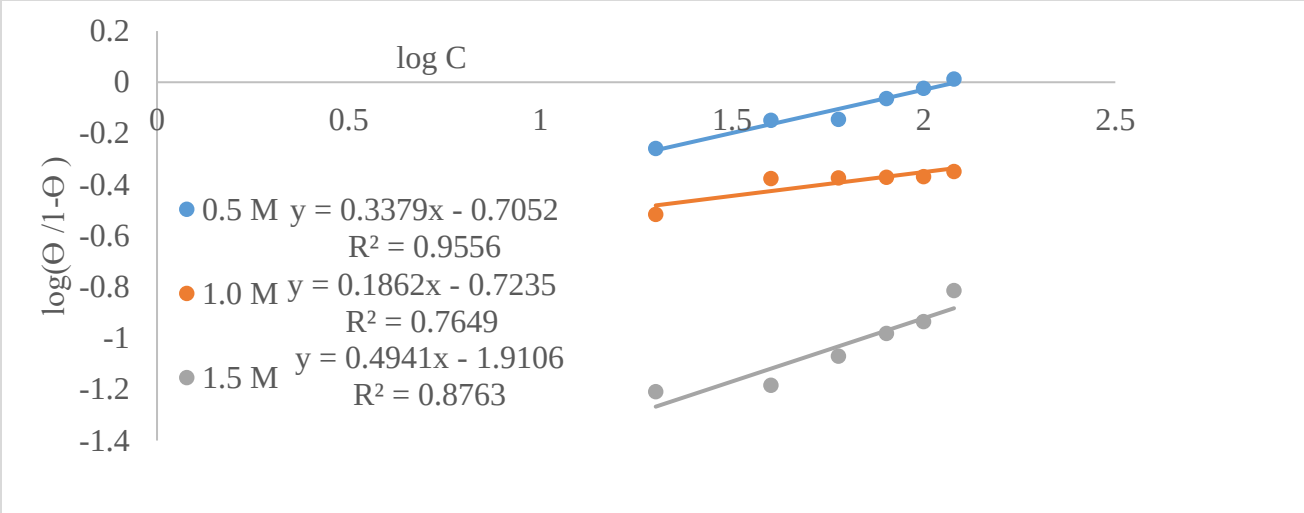

Figure 5: El - Awady isotherm for adsorption of inhibitor on aluminium metal surface at 303K

Table 5: El - Awady Adsorption Isotherm Model Values at 303K, Temperature

Concentration	K_{ads}	R^2	y	1/y	ΔG(kJ/mol
0.5 M	0.197	0.9556	0.3379	2.959	-6.026
1.0 M	0.189	0.7649	0.1862	5.371	-5.921
1.5 M	0.0123	0.8763	0.4941	2.024	0.961

Tables 2 – 5 shows the various parameters of adsorption isotherms studied. The adsorption equilibrium constant (K_{ads}) value was seen to decrease with increase in acid concentration, this indicates that, the locust bean pod extract (inhibitor) is easily adsorbed on the aluminium metal surface at lower acid concentration. But when the acid concentration was higher, the adsorbed inhibitor tends to desorbs from the aluminium metal surface. The negative value of the Gibb's free energy (ΔG^o) obtained for both 0.5 and 1. 0 M indicates that the adsorption is spontaneous, feasible, and indication of stability of adsorbed locust bean pod extract inhibitor but at 1.5 M the value of (ΔG^o) obtained is positive as seen in tables 2 and 5 which revealed that the locust bean pod extract adsorption is becoming non spontaneous and non-feasible as this acid concentration. The result obtained in this work is similar to that reported by [28]. ΔG^o Value of $-20\ \text{kJ mol}^{-1}$ or lower indicates electrostatic interaction (physical adsorption), while those around $-40\ \text{kJ mol}^{-1}$ or higher are generally accepted to form a coordinate type of bond (chemisorption) [29]. In the case of our study, values obtained revealed a physisorption in nature except for 1.5 M concentration of HCl in Tables 2 and 5 which clearly show that the adsorption is not physical at this concentration of HCl. Langmuir adsorption isotherm indicated that the locust bean pod extract contains organic compounds having polar atom or groups which are adsorbed on the metal surface and may interact by mutual repulsion or attraction [30, 31].

CONCLUSION

Adsorption isotherms, phytochemical screening, and Fourier transform infrared spectroscopy on weight loss of aluminium metal in the presence of locust bean pod extract inhibitor were carried out in this study. As acid concentration is increase the weight loss of the aluminium metal increase as well. Gibb's free energy (ΔG^o_{ads}) values obtained suggest a strong interaction of the inhibitor molecules on the surface of the aluminium metal this also show that the adsorption of locust bean pod extract on aluminium metal surface is spontaneous and feasible. Adsorption isotherm experimental data was best fitted to Langmuir model which implied a monolayer of adsorption of the inhibitor on the aluminium metal surface. However, more than one active sites of inhibitor was adsorbed on the surface of aluminium metal.

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