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Assessment of Locust Bean Pod Extract (*Parkia Biglobosa*) as Corrosion Inhibitor for Mild Steel in Acidic Media

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Abstract: The corrosion characteristic of Mild Steel in 1.0 molar HCl using Locust Bean Pod extract as corrosion inhibitor was investigated employing gravimetric measurement. The research was carried out at a constant time of twenty-four (24) hours and varying inhibitor concentrations and temperature in the range of 0.5 - 2.5% v/v and 40 - 60^oC respectively. Results obtained revealed that Locust Bean Pod is a moderate corrosion inhibitor for Mild Steel with maximum concentration and inhibition efficiency of 2.5% v/v and 72.86% respectively at 40^0C. Thermodynamic parameters such as heat of adsorption, free energy and activation energy were obtained from experimental data. The inhibitor was physically absorbed unto the surface of Mild Steel blocking more active sites thereby inhibiting corrosion.

Key Words: Corrosion Inhibitor, Hydrochloric Acid, Locust Beans Pod Extract, Mild Steel

I. INTRODUCTION

Mild steel is one of the most important widely used engineering materials particularly for the structural and automobile application. However, it undergoes rusting easily in the humid atmosphere and its rate of corrosion is quite high in acid environment. Thus, protection of mild steel from corrosion is important studies that need urgent attention. Out of several methods, use of chemical inhibitor is one of the most practical methods for the prevention of corrosion particularly in acidic media. Acid solutions are widely used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid de-scaling and oil wet cleaning etc[1, 2]. Corrosion inhibitors are generally used to reduce the corrosion rates. Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulphur, oxygen in their functional groups with aromatic and heterocyclic rings. These compounds have been reported by several researchers[1, 3-4]. Most of the corrosion inhibitors act by adsorption of their molecules on metal surface. Their action depends on the nature and surface charge of the metal, nature of the medium and the chemical structure of the inhibitor[5]. Corrosion inhibitors are of great practical importance, being extensively employed in minimizing metallic waste in engineering materials[6]. Many current corrosion control methods use coating and conversion layers which contain toxic and environmentally hazardous material. There is a great need to find a non toxic replacement that is compatible with current industrial technologies. Well known as non toxic compound and due to their availability and relatively low cost, naturally substances find various applications in many fields. Like tannin, beet root[7,8], saponin[9], tamarind, tea-leaves, pomegranate juice peels[10,11] and the mixture of the later three sapindus, trifolianus and acacia concianna[12], swertiw aungustefolia[13] and prosopis juliflora[14] which have been evaluated as effective corrosion inhibitor. Recent awareness of the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids as well as organic dyes[15-19] has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin. Such investigation is of great importance because in addition to being environmentally friendly and ecologically acceptable, plants products are inexpensive, readily available and renewable sources of materials. The use of natural products as corrosion inhibitors have been widely reported by several authors[20-27]. The corrosion inhibitor of mild steel in different acid media has been studied by various authors[28-31]. In view of above, this research is aimed at investigating the inhibiting effect of Locust Bean Pod extract of mild steel in 1M HCl acid.

II. MATERIALS AND METHODS

Preparation of Specimens: The chemical analysis of the mild steel used in this study was carried out at National Metallurgical Development Center, (NMDC) Jos, Nigeria. The mild steel was machined into standard corrosion coupons. The surface preparation of the mechanically polished coupons were carried out using different grades of emery papers, degreased with acetone dried at room temperature, weighed using digital weighing balance, recorded and stored in a desiccators.

Preparation of Plant Extract: The locust beans pod were collected dried at room temperature and converted into powder form and chemical analysis carried out at Biochemical Laboratory of the National Research Institute for Chemical Technology (NARICT), Bassawa, Zaria, Kaduna State, Nigeria.

Corrosion Testing: The cleaned and dried coupons were immersed in the test solutions of 1.0 M HCl with constant time (24 hours) but varying temperatures of 40^{o}C, 50^{o}C and 60^{o}C. The first set of tests was carried out without inhibitor to serve as control, then in solutions containing Locust Bean Pod extracts of concentrations, 0.5, 1.0, 1.5, 2.0 and 2.5% v/v. The weight losses of each coupon after 24 hours were measured. From the data obtained, corrosion rate, inhibitor efficiency, degree of surface coverage, free energy of absorption, activation energy and heat of absorption were determined.

Corrosion Rate: The weight loss was determined by finding the difference between the initial weight of the coupons and the new weight after 24 hour using the relationship[32].

$$W = W_o + W_f \tag{1}$$

Where: W = Weight loss, W_o = Initial Weight, W_f = Final weight.

The corrosion rate was determined from standard expression for measurement of corrosion rate in millimeter per year (mmpy)[33].

$$mmpy = \frac{87.6W}{DAT} \tag{2}$$

Where W = Weight loss (mg), D = Density of material (g/cm^3), T = Time of exposure (hours), A = Total surface area (in^2).

Inhibitor Efficiency (%): The inhibitor efficiency (IE) were computed using the relationship[33].

$$Inhibitor\ Efficiency\ (IE) = \frac{CR_o - CR}{CR_o} \times 100\% \tag{3}$$

Where CR and CR_o are the corrosion rates with and without the inhibitors present respectively.

Degree of Surface Coverage: The degree of surface coverage was calculated from the equation.

$$Degree\ of\ Surface\ Coverage\ (\theta) = \frac{CR_o - CR}{CR_o} \tag{4}$$

Reaction Kinetics: The activation energy E_a of the corrosion reaction was calculated using the Arrhenius equation given by[34].

$$\log \frac{R_1}{R_2} = \frac{E_a}{2.303R} \tag{5}$$

R_1 and R_2 are the corrosion rates at any given two different temperatures T_1 and T_2.

Free Energy of Adsorption (ΔG_{ads}): Free energy of adsorption was determined using the given relationships.

$$\Delta G_{ads} = -RT\ln(55.5K) \tag{6}$$

$$where \qquad K = \frac{\theta}{C(1-\theta)}$$

Where C is concentration of inhibitor (% v/v), K equilibrium constant and θ is the degree of surface coverage.

Heat of Adsorption (ΔH_{ads}): The heat of adsorption of the inhibitor was calculated using the equation

$$\Delta H_{ads} = 2.303R\left\{\log\left(\frac{\theta_2}{1-\theta_1}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right\}\left(\frac{T_2T_1}{T_2-T_1}\right) \text{(J/mol)} \tag{7}$$

Where θ_1 and θ_2 are degree of surface coverage at any two temperatures T_1 and T_2

III. RESULT AND DISCUSSION

Results: The phytochemical analysis of Locust Bean Pod carried out revealed the presence of Tannin (9.11mg/100g), Saponin (7.87mg/100g), Alkaloids (3.71mg/100g), Phenol (0.06mg/100g) and Flavonoids (0.27mg/100g). The chemical composition of the mild steel is shown in Table 1.

Table 1: Chemical Composition of Mild Steel

S/NO	ELEMENTS	COMPOSITION IN WEIGHT (%)
1.	Carbon	0.078%
2.	Phosphorus	0.06
3.	Silicon	0.024
4.	Manganese	0.192
5.	Chromium	0.049
6.	Copper	0.0134
7.	Aluminium	0.023
8.	Nickel	0.050
9.	Iron	Remainder

The variation of the corrosion rate with concentration of inhibitor (Locust Bean Pod) is shown in Figure 1, Figure 2 show the variation of inhibitor efficiency with concentration of inhibitor at three different temperatures while, Figures 3, 4, and 5 shows the variation of Free Energy of Absorption (ΔG_{ads}), Activation Energy (Ea) and Heat of Absorption (ΔHads) respectively with concentration of inhibitor.

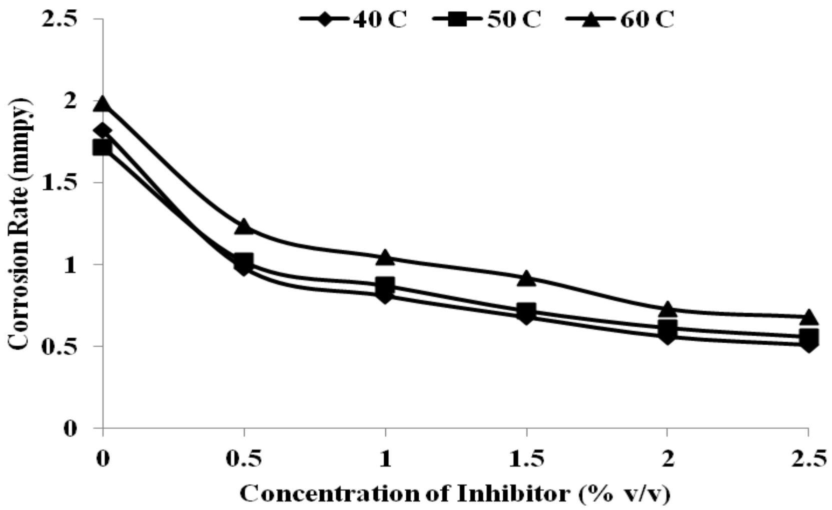

Figure 1: Variation of corrosion rate with concentration of inhibitor at 40°C, 50°C and 70°C

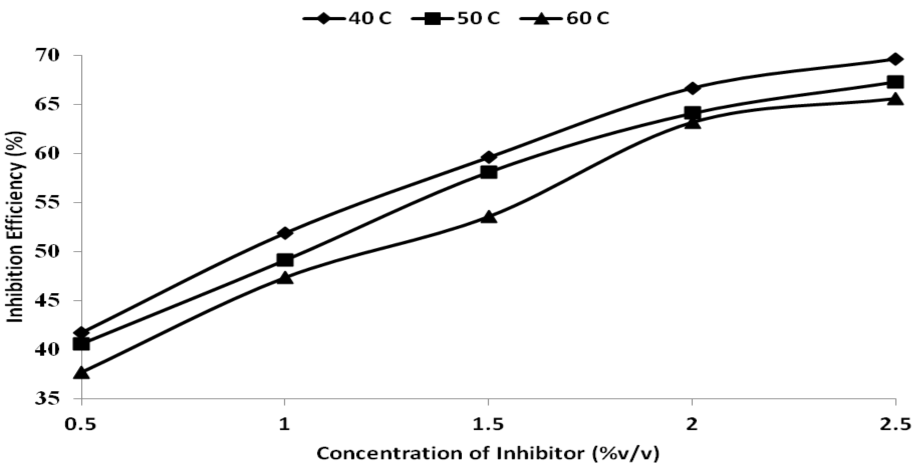

Figure 2: Variation of inhibitor efficiency with concentration of inhibitor at 40°C, 50°C and 60°C

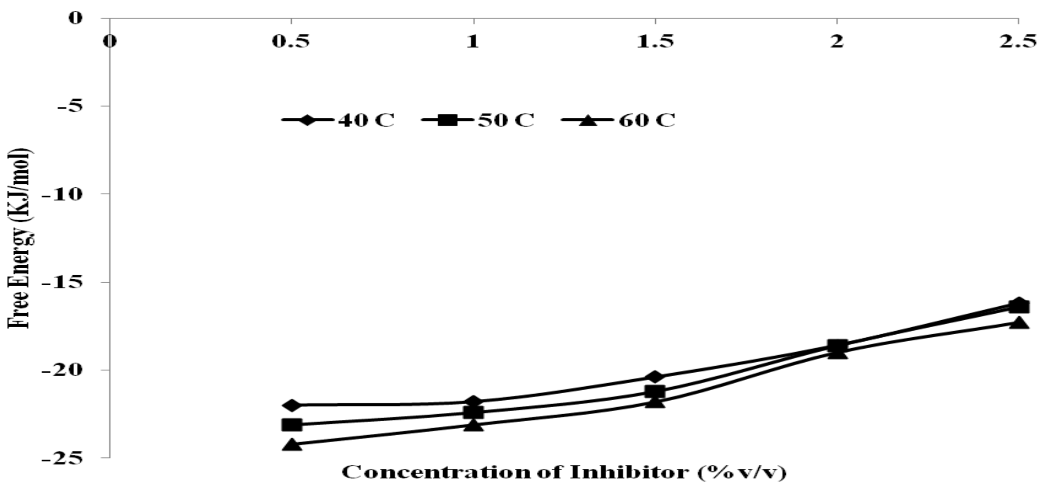

Figure 3: Variation of free energy of absorption with concentration of inhibitor at 40^{o}C, 50^{o}C and 60^{o}C

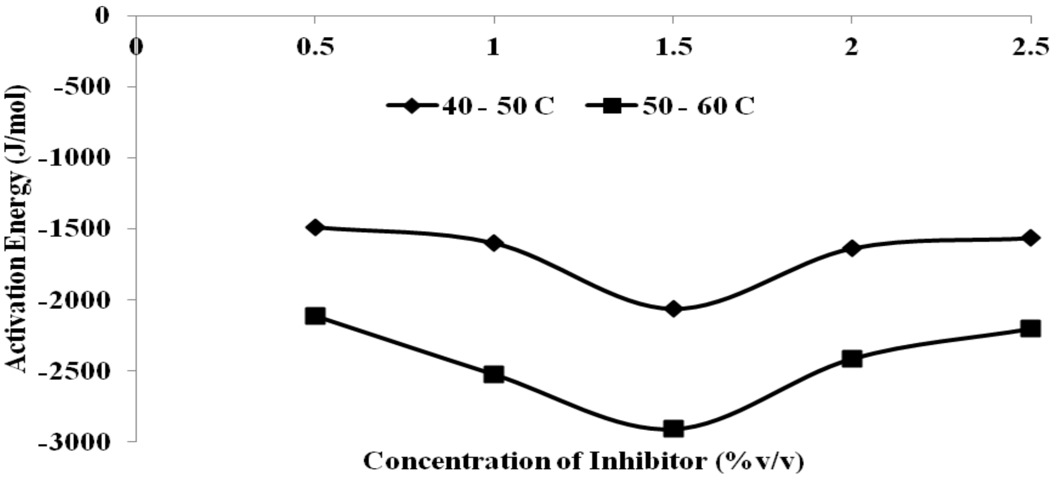

Figure 4: Variation of activation energy with concentration of inhibitor at 40-50^{o}C, 50-60^{o}C

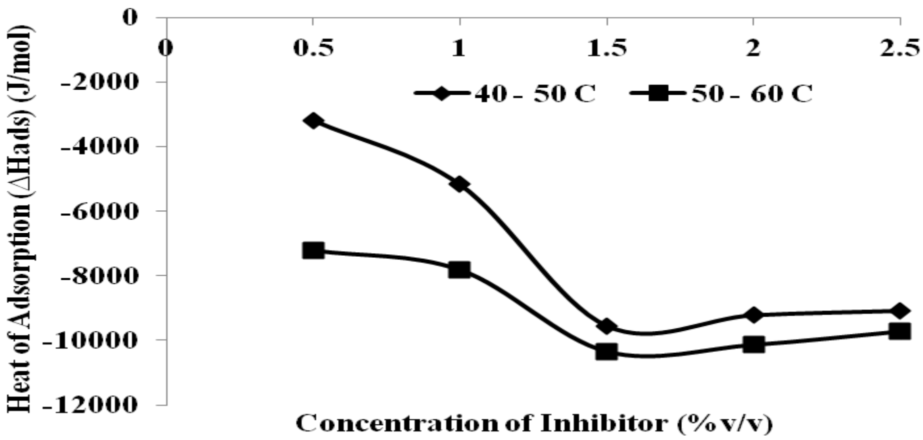

Figure 5: Variation of heat of adsorption with concentration of inhibitor at 40-50^{o}C, 50-60^{o}C

IV. DISCUSSION

Visual observation of coupons (without and with inhibitor) after 24 hours of exposure reveals changes in colour of the coupons from bright shiny surfaces to dull ones which indicates uniform corrosion. Pits were observed on the samples which are indications of corrosion attack by the hydrochloric acid. However, the changes in colour of the coupons were more intense with the solutions without inhibitor so was the presence of pits.

Figure 1 show the variation of corrosion rate with concentration of inhibitor in the presence of locust bean pod extract as corrosion inhibitor at temperatures of 40^0C, 50^0C and 60^0C. The trend shows a decrease in corrosion rate with increase concentration of the extract from 0.5-2.5%v/v. The corrosion inhibition of locust bean pod extract could be attributed to the presence of tannin and alkaloid in its composition[32] which resulted in absorption of the extract onto the surface of the mild steel. It was evident from Figure 1 that the corrosion rates of the mild steel increases with increase in temperature. At higher temperature, the protective bonds of the inhibitor dissociate[35]. This can be attributed to the decrease in the efficiency of inhibitor due to the fact that at lower temperature the inhibitor molecules adsorb onto the mild steel surface, while at a higher temperature desorption of the molecules from the mild steel surface occur as a result of dissociation of constituents of the inhibiting substance[36], and increase in electrochemical activity.

Figure 2 shows the variations of inhibitor efficiency with concentration of inhibitor. The inhibitor efficiency of locust bean pod extract increased for concentration up to 2.5% v/v with the optimum obtained at 40^oC. The increase in inhibitor efficiency could be attributed to the adsorption of locust bean pod extract on the surface of the mild steel thereby blocking the active site on ht e surface, therefore reducing the corrosion rate.

Free Energy of Adsorption (ΔG_{ads}) from Figure 3 revealed negative values that suggest a strong interaction of the inhibitor molecules on the surface of the mild steel. The values of ΔG_{ads} become less negative as the temperature increased from 40–60^oC. The negative values of ΔG_{ads} imply state of spontaneity, and it was observed that any values around -40Jmol^{-1} or higher are consistent with the electrostatic interaction (physisorption) while those around -40Jmol^{-1} or lower involve chemisorptions[37-38]. This revealed that the adsorption of the inhibitor on mild steel surface is spontaneous and confirm physical adsorption mechanism[39].

Activation energy (Ea): Activation energies of the inhibited system were found to be higher than those of the uninhibited system (Figure 4), this revealed the presence of inhibitors which cause a change in the values of the apparent activation energies and furthermore, it indicates a change in the rate determining step brought about by the presence of various chemical components of the inhibitors[40].

Figure 5 revealed the heat of adsorption (∆Hads) which clearly show negative values as the inhibitor increases. The nature of absorption depends on the values of ∆Hads that is, if $|\Delta Hads| < 10$kJ/mol the adsorption is physical adsorption and if $|\Delta Hads| > 10$kJ/mol the adsorption is chemical[37] which confirms this research as physical adsorption.

V. CONCLUSION

From the analysis of the results obtained in this research, the following are drawn:

1. The characterization of locust bean pod extract which revealed the presence of tannin, alkaloid, saponins and flavonoids. The absorption of these species onto the mild steel surface reduces the corrosion rate in 1M HCl solution.
2. The adsorption of the inhibitor on the surface of mild steel was observed to be by physical adsorption mechanism.
3. Corrosion inhibition efficiency of locust bean pod extract increases with the increase in concentration of inhibitor to an optimum at 2.5% v/v. The inhibition efficiency was highest at 40^oC at an optimum inhibition efficiency of 2.5% v/v.

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