CORROSION INHIBITIVE PROPERTIES OF EXTRACT OF JATROPHA CURCAS LEAVES ON MILD STEEL IN HYDROCHLORIC ACID ENVIRONMENT

J. K. Odusote1* and O. M. Ajayi2

* jamiukolavole@gmail.com

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1 Department of Materials and Metallurgical Engineering, University of Ilorin, Ilorin, Nigeria.
2 Department of Mechanical Engineering, University of Ilorin, Ilorin, Nigeria.

Abstract: Jatropha curcas leaves extract was tested as a green corrosion inhibitor for mild steel in aqueous hydrochloric acid solution using gravimetric and thermometric techniques. The results reveal that the inhibition efficiency vary with concentration of the leaf extract and the time of immersion. Maximum inhibition efficiency was found to be 95.92% in 2M HCl with 0.5 g/l concentration of the extract in gravimetric method, while 87.04% was obtained in thermometric method. The inhibiting effect was attributed to the presence of alkaloids, flavonoids, saponins, tannins and phenol in the extract. The adsorption processes of the Jatropha curcas leaves extract onto the mild steel is consistent with the assumptions of Langmuir isotherm model and also found to be spontaneous. From the results, a physical adsorption mechanism is proposed for the adsorption of Jatropha curcas leaves extract onto mild steel surface.

Keywords: Mild Steel, Green Inhibitor, Corrosion, Weight Loss, Thermometric, Adsorption Isotherms.

1. INTRODUCTION

The word corrode is derived from the Latin word corrode, meaning to eat into or wear gradually. Corrosion is a naturally occurring process generally defined as the deterioration of a material and/or its properties because of reaction with its environment [1]. Corrosion is a naturally occurring phenomenon which affects our society daily, and it results into damages, destruction and degradation to household gadgets, automobiles, airplanes, highway bridges, energy production and distribution systems, among others [2].

Corrosion is one of the major global problems in industries and resulting to losses each year in hundreds of billions of dollars. Corrosion studies have been carried out in several countries and their finding showed that annual corrosion costs ranged approximately from 1 to 5% of the Gross National Product (GNP) of those nations [3]. The consequences of corrosion are many, and the effect of these on safe, reliable and efficient operation of equipment or structure is often more serious than simple loss of a metal. Some of the major harmful effects of corrosion include reduction of metal thickness, hazards or injuries to people arising from structural failure, loss of time, reduced value of goods, contamination of fluids in vessels and pipes, etc. [4].

Mild steel is a material of choice and it finds wide application in many industries like automobile, petrochemicals, construction, metallurgical, refineries, and so on. This is due to its low cost, availability and excellent mechanical properties [5]. However, it suffers corrosion in hostile aggressive acidic or alkaline environment. Acids are used to remove oxides and other contaminants from metal surfaces. Acids are also used for derusting and pickling, cleaning of refinery equipment, oil well acidizing, descaling, removal of calcareous deposits from boilers, pipelines carrying petroleum products, etc. [6].

There are various forms of controlling corrosion of metals such as appropriate material selection, coatings, cathodic protection, design and use of inhibitors. However, the use of inhibitors is one of the best methods of protecting metals against corrosion [4]. An inhibitor is a chemical that when added to corrosive environment in small concentration reduce the rate of metal corrosion [7]. These inhibitors are classified either as interface inhibitors or environmental conditioners as shown in Figure 1 [8]. Most of the corrosion inhibitors are synthetic
chemicals, which are expensive and very hazardous to the environment. Therefore, it is desirable to source for environmentally safe and green inhibitors, which are non-toxic, biodegradable and readily available [9].

Several researchers have reported the use of plant extracts as effective corrosion inhibitor for mild steel in acidic media [10-23]. These plant extracts include Rosemarinus Officinalis [10], Carica Papaya [11, 14], Azadirachta Indica [12], Vernonia Amydalina [13], Allium Sativum [15], Phyllanthus Amarus [16], Telfaria Occidentalis [17], Sansevieria Trifasciata [18], Hibiscus Subdariffa [19], Lawsonia [20], Musa Sapientum [21], Prosopis Cineraria [22], Gossipium Hirsutum [23] among others. In a recent study, Jatropha Curcas leaves extract was reported to act as a good corrosion inhibitor for mild steel in both aqueous sulphur and hydrochloric acid solutions using gasometric technique [24]. Previous report by Odusote and Ajayi [25] also revealed that the inhibition efficiency of Jatropha Curcas leaves extract on mild steel in sulphuric acid solution increased with increasing inhibitor concentration. The results indicated that the inhibition action of the extract was dependent on the concentration of the leaves extract in the acid solution [24, 25]. The present study is aimed at investigating the effectiveness of the leaves extract of Jatropha Curcas as corrosion inhibitor of mild steel in aqueous hydrochloric acid environment using gravimetric and thermometric methods.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

The chemical composition of the mild steel (0.17 wt% C) sheet sample specimens used for this work has been reported earlier [25]. The sample specimens were ground, polished and degreased in ethanol. This was followed by drying in acetone before they were stored in a desiccator.

2.2. Preparation of Jatropha Curcas leaves Extract

Fresh leaves of Jatropha Curcas (JC) plant was obtained, washed under running water, cut into pieces, air dried and then grounded well and sieves into powdery form. Then, 10g each of the powdery leaf was put into flat bottom flask containing 200 cm³ of 2M HCl solution. The resulting solution was refluxed for 2 hours and left overnight before it was carefully filtered. The stock solution was prepared from the filtrate and prepared into the desired concentrations as earlier reported [24, 25].

2.3. Weight Loss Measurement

Mild steel specimens of uniform dimension of approximately 1.5cm X 2cm X 0.2cm was used for the weight loss study. The specimens were weighed using an electronic weighing balance and then immersed completely in 50 ml of 2M HCl for 5 days. The mild steel specimens were taken out of the solution every 24 hours, washed thoroughly with distilled water, and dried completely. This was followed by taking the final weights of the immersed specimens. From the initial and final weights of the specimens for each day, the loss in weight was calculated.

From the weight loss, the corrosion rate, inhibition efficiency (IE) % and surface coverage (θ) of the plant extract were calculated using the Equations 1, 2 and 3 [26, 27]:

\[
\text{Corrosion rate (g cm}^{-2} \text{ h}^{-1}) = \frac{\Delta W}{AT} \tag{1}
\]

\[
\text{Inhibition Efficiency (IE %) =} \frac{(CR_B - CR_W)}{CR_B} \times 100\tag{2}
\]

\[
\text{Surface Coverage (θ) =} \frac{CR_B - CR_W}{CR_B} \tag{3}
\]

where CR_B and CR_W are corrosion rates in the absence and presence of the inhibitor, W is the weight loss (g), A is the surface area of the mild steel coupon (cm²) and T is the time of exposure (hours).
2.4. Thermometric Method

Thermometric analysis was carried out according to the method described by Ejikeme et al. [28]. The mild steel coupons of dimension 4cm X 2cm X 0.2cm were immersed in 50 ml of 4M HCl solution as shown in figure 1. The initial temperature was recorded. The process of the corrosion reaction was monitored by determining the change in temperature with time using a standard digital thermometer shown in figure 2.

From the rise in temperature per minute, the reaction numbers (RN), inhibition efficiency (IE) and surface coverage (θ) were calculated using equations 4, 5 and 6 respectively:

\[
RN \, (^{o}C \, min^{-1}) = \frac{T_{m} - T_{i}}{t} \quad (4)
\]

\[
\%IE = \left( \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \right) \times 100 \quad (5)
\]

\[
\theta = \left( \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \right) \quad (6)
\]

where

- \( RN \) = Reaction Number
- \( RN_{aq} \) = Reaction Number in the absence of inhibitor (Control)
- \( RN_{wi} \) = Reaction Number in the presence of inhibitor
- \( T_{m} \) = Maximum Temperature attained by the system
\[ T_i = \text{initial temperature} \]
\[ T = \text{Time (minutes)} \]

2.5. Adsorption Isotherm

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) permeates or is dissolved by a liquid or solid (the absorbent) [29]. Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

Adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction [30].

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. It is very important in knowing the mechanism of inhibition of corrosion reaction of metals. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Flory Huggins, Langmuir isotherm etc.

2.5.1. Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is represented by equation 7 [31], and a linearly fit curve of \( \frac{C}{\theta} \) against C indicates that the adsorption of the extracts onto the metal surface obeys Langmuir isotherm model.

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]  

(7)

\( C \) is the concentration of aqueous extract; \( \theta \) is the surface coverage, while \( K_{ads} \) is the equilibrium constant for the absorption process.

The standard Gibbs free energy value which reveals the type of interaction existing between inhibitor molecules and metal/alloy surface was calculated with Equation 8 [32].

\[
\Delta G_{ads} = -RT \ln (55.5 K_{ads})
\]  

(8)

where \( R \) is the universal gas constant 8.314 J mol\(^{-1}\) K\(^{-1}\), \( T \) the thermodynamic temperature in K, 55.5 represents the molar concentration of water in the solution.

2.5.2. Flory –Huggins Isotherm

The Flory-Huggins adsorption isotherm can be expressed according to equation 9 as reported by [33].

\[
\log(\frac{\theta}{C}) = x \log(1-\theta) + \log K
\]  

(9)

where \( x \) = size parameter and is a measure of the number of adsorbed water molecules substituted by given inhibitor molecules.

2.5.3. Freundlich Isotherm

Freundlich adsorption isotherm was tested using Equation 10, which could be written as equation of a straight line (Equation 11) [34].

\[
\theta = KC^n \quad (\text{where } 0 < n < 1)
\]  

(10)

\[
\ln \theta = \ln K + n \ln C
\]  

(11)

where \( K \) represents the equilibrium constant of adsorption and \( C \) is the extract concentration.
3. RESULTS AND DISCUSSION

3.1. Chemical Composition of the Mild Steel and Phytochemical Composition of the JC Leaf Extract

The chemical composition analysis result has been reported earlier [24, 25]. The results showed that the investigated material is mild steel based on its carbon content [35]. Although, mild steel has relatively good mechanical properties, but its corrosion resistance has been reported to be poor especially in acidic environment [5]. In a previous study by Ajayi et al. [24] and Odusoke and Ajayi [25], the phytochemical composition of Jatropha curcas leaves extract has been found to contain tannins, saponins, alkaloids, phenol and flavonoids]. Saponins, tannins and alkaloids are the active constituents of most green inhibitors [36].

3.2. Weight Loss Data

The curves for the variation of weight loss with exposure time for the mild steel specimens immersed in 2M HCl solution with varied concentrations of Jatropha Curcas leaves extract are presented in figure 3. From the figure, it was

![Graph showing variation of weight loss with time for the corrosion of mild steel in 2M HCl.]

Fig. 3. Variation of weight loss with time for the corrosion of mild steel in 2M HCl.

Table 1. Inhibition efficiency of mild steel in different concentrations of Jatropha Curcas leaves extract in 2M HCl at different time of immersion.

<table>
<thead>
<tr>
<th>Time(days)</th>
<th>Inhibition efficiency (I.E. %) of J.C. leaves extract in HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 g/l</td>
</tr>
<tr>
<td>1</td>
<td>79.59</td>
</tr>
<tr>
<td>2</td>
<td>73.42</td>
</tr>
<tr>
<td>3</td>
<td>80.00</td>
</tr>
<tr>
<td>4</td>
<td>77.71</td>
</tr>
<tr>
<td>5</td>
<td>74.60</td>
</tr>
</tbody>
</table>
found that the weight loss of the mild steel specimens increased with the period of exposure but decreased as the concentration of the inhibitor increases. This indicates that the rate of corrosion of mild steel increases with increase in the period of exposure, and that Jatropha Curcas leaves extract inhibited the corrosion of mild steel in 2M HCl. The order of increasing corrosion inhibition performance was: 0.5 g/l>0.4 g/l>0.3 g/l>0.2 g/l>0.1 g/l concentration of the extract of Jatropha Curcas leaves. Undoubtedly, the constituents of Jatropha Curcas leaves extract exhibited a reasonable degree of electrochemical corrosion inhibition activity that was dependent on the concentration. Loto [37] reported that the corrosion inhibition performance could be attributed to the presence of alkaloids and synergistic combination of other phytochemical constituents which form a barrier on the surface of mild steel as observed when Camellia Sinensis extract was used as corrosion inhibitor for mild steel in dilute sulphuric acid.

3.3. Inhibition Efficiency

Table 1 shows the result of inhibition efficiencies of Jatropha Curcas leaves extract on corrosion of mild steel specimens in 2M HCl at different time of immersion. From the table, it is observed that inhibition efficiency increases as the concentration of the extract of JC increases at all the exposure times. At 120 hours of exposure, the inhibition efficiency was 74.60% for 0.1 g/l extract concentration while for 0.5 g/l concentration, the inhibition efficiency was 89.42%. The inhibition efficiency of the leaves of Jatropha Curcas extract could be associated with its complex chemical compound which include alkaloid as reported earlier [36]. The phytochemical constituents act as inhibitive passive film formers on the mild steel. Umoren et al. [34] reported similar experimental results when Aningeria robusta extract was used as green inhibitor in HCl solution and observed that as the concentration of the inhibitor increases, the inhibition efficiency increases. They also reported that the adherent film of the inhibitor on the surface of immersed specimens hindered active corrosion reactions, and hence the penetration of the Cl- reacting species through film barrier. The synergistic action of the constituents promote more stable passive film formation on the surface of the mild steel and thereby increasing the inhibition efficiency of the plant extract as reported by Patel et al. [38].

3.4. Corrosion Rate

Figure 4 shows the variation in corrosion rate with time of exposure with varying concentration of Jatropha Curcas leaves extract. For the control experiment, the figure showed that the rate of corrosion increased from 0g/cm² at the beginning of the experiment to a value of $6.80 \times 10^{-3}$g/cm²h.

![Fig. 4. Variation in corrosion rate against time of immersion of the extract in 2M HCl.](image-url)
after 24 hours possibly due to faster corrosion rate at the early stage. Subsequently, the corrosion rate decreased to a value of 5.49 g/cm²h after 48 hours exposure. This may be due to the formation of protective films, which tend to shield the metal surface from corrosion attack, thereby reducing the rate of corrosion as observed by Nnanna et al. [39]. Above 48 hours exposure, the corrosion rate increases up to a value of 6.94 g/cm²h, probably due to breaking down of the initial protective films, and thus leading to faster corrosion rate. From 72 to 120 hours immersion period, the rate of corrosion decreases possibly due to formation of more adherent passive film.

For 0.1 g/l inhibitor concentration, the corrosion rate slightly increases from 1.40 g/cm²h at 24 hours exposure time to 1.46 g/cm²h after 48 hours exposure which could possibly be due to surface corrosion attack. However, above 48 hours of exposure, the corrosion rate decreases to a value of 1.33 g/cm²h and started to level off at 120 hours, indicating the formation of protective oxide film. This can be attributed to the adsorption of the molecules of the inhibitor on the surface of mild steel [40]. Amita and Bharathi [41] reported that green inhibitors contain phytochemical constituents which act as physical barrier that restrict the diffusion of ions and then prevent metals from corrosion attack.

Similar observations were made at 0.2 g/l inhibitor concentration. The corrosion rate increased gradually up to 72 hours exposure at Jatropha curcas leaves extract concentration of 0.3-0.4 g/l but later decreased at higher exposure times. However, there was a slight increase after 96 hours exposure possibly due to breakway of protective film [36].

3.5. Thermometric Data

Figure 5 reveals the results obtained from the variation of the temperature with time of immersion for mild steel corrosion in 4M HCl with and without extract of Jatropha curcas leaves at different concentrations of the inhibitor. The results revealed that maximum temperature was attained in the blank solution. This corresponds to a reaction number of 0.633°C/min (Table 2). Further inspection of Figure 5 revealed that on addition of the extract, the temperature decreased with increased extract concentrations. Similar results have been reported, and these have been attributed to the formation of a barrier layer when the extract adsorbed on the surface of the metal [6, 28, 42]. This is in agreement with the observation in the current study. The calculated values of reaction number (RN), percentage reduction in reaction number (inhibition efficiency) and surface coverage for
Table 2. Calculated values of reaction number, percentage inhibition efficiency and the degree of surface coverage at different concentration of J. Curcas leaf extract in 4M HCl

<table>
<thead>
<tr>
<th>Concentration of JC extract (g/l)</th>
<th>Reaction Number (°C/min)</th>
<th>Inhibition Efficiency (%I.E.)</th>
<th>Surface Coverage (θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.633</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>0.387</td>
<td>38.8</td>
<td>0.3880</td>
</tr>
<tr>
<td>0.50</td>
<td>0.316</td>
<td>50.08</td>
<td>0.5008</td>
</tr>
<tr>
<td>0.75</td>
<td>0.269</td>
<td>57.50</td>
<td>0.5750</td>
</tr>
<tr>
<td>1.0</td>
<td>0.164</td>
<td>74.09</td>
<td>0.7409</td>
</tr>
<tr>
<td>1.25</td>
<td>0.082</td>
<td>87.04</td>
<td>0.8704</td>
</tr>
</tbody>
</table>

various concentrations of Jatropha Curcas extract is presented in Table 2. The result showed that the reaction number which corresponds to the rate of corrosion of mild steel decreased in the presence of J. Curcas leaves extract compared to the blank solution. In addition, the percentage inhibition and the degree of surface coverage increase with increase in J. Curcas extract concentration. Similar observations have been reported by several authors, which supported the results in the present study [43, 44].

3.6. Adsorption Isotherm

The standard Gibbs free energy values were determined for Langmuir, Flory-Huggins and Freundlich isotherm models using the experimental data obtained from weight loss measurements. The equilibrium constant for the absorption process, $K_{ads}$ values were calculated from the linear fits. The plots showed that the fitting of the isotherm data for Flory-Huggins and Freundlich adsorption isotherm did not give a perfect straight line as compared to the Langmuir parameters. Thus, indicating that adsorption processes of the leaves extract of Jatropha curcas leaves extract does not perfectly obeys Flory-Huggins and Freundlich adsorption isotherm. Langmuir adsorption isotherm was found to give the best fit of the experimental data with a regression coefficient $R^2$ of 0.999, while the $R^2$ for Flory-Huggins and Freundlich isotherms are 0.924 and 0.960, respectively. These results revealed that the Langmuir isotherm model is the most suitable for describing the adsorption process of Jatropha Curcas leaf extracts on mild steel surface in the hydrochloric acid environment. This is similar to observation of Olusegun et al. [45] during the investigation of the inhibitive effect of the acid extract of jatropha curcas leaves on the corrosion inhibition of mild steel using mass loss method.
The values of standard Gibbs free energy determined by the three isotherm models are -10.9 kJ mol\(^{-1}\) for Langmuir, -13.78 kJ mol\(^{-1}\) for Flory-Huggins and -9.40 kJ mol\(^{-1}\) for Freundlich. The calculated values of the standard free energy of adsorption from all the three models have negative values, indicating the spontaneity of the corrosion reaction. The results also revealed that the adsorption of inhibitor molecules on the mild steel surface takes place due to electrostatic interactions between the JC leaf extract molecules and metal electrode surface. Furthermore, since all the values of the standard free energy from the three isotherm models are less negative than -40 kJ mol\(^{-1}\), thus the adsorption processes of JC leaf extract onto the mild steel surface occurred by physical absorption [46]. In addition, the values of the size of parameters (x) are positive, indicating that the adsorbed species of Jatropha Curcas leaves extract is bulky since it could displace more than one molecule of water from the mild steel surface.

Plant extract contains organic compounds having polar atoms or groups which are absorbed on the metal surface. Obot and Obi-Egbedi [43] reported that compounds interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slopes values from unity when Ipomoea Involcrlata was used as plant extract. The application of Langmuir isotherms to the adsorption of Jatropha curcas leaves extract on mild steel indicated that there is no interaction between the adsorbate and the adsorbent. The application of Langmuir adsorption isotherm suggests that there is no interaction between the adsorbed species as reported by some authors [26, 27].

4. CONCLUSIONS

On the basis of this study, the following conclusions are drawn:
1. The leaves extract of Jatropha Curcas acts as a good and efficient inhibitor for corrosion of mild steel in HCl medium.
2. The inhibition of the corrosion of mild steel by acid extract of JC is due to the phytochemical constituents in the plant extract.
3. The negative sign of free energy of adsorption indicates that the adsorption of Jatropha curcas leaves extract on mild steel surface was a spontaneous process and the mechanism of inhibition was found to be physorption.
4. The adsorption of different concentrations of the Jatropha curcas leaves extract on the surface of mild steel in HCl solution fits into Langmuir adsorption isotherm model. However, Flory-Huggins and Freundlich isotherms were found not to be suitable.
5. Results obtained in weight loss method were in good agreement with thermometric method.

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