Corrosion Inhibition of Mild Steel in Acidic Medium by Jathropha Curcas Leaves Extract

Jamiu K. Odusote1,* and Olorunfemi M. Ajayi2
1Department of Materials and Metallurgical Engineering, University of Ilorin, Ilorin, Nigeria
2Department of Mechanical Engineering, University of Ilorin, Ilorin, Nigeria

ABSTRACT:
Inhibition of corrosion of mild steel in sulphuric acid by acidic extract of Jatropha Curcas leaves has been studied using weight loss and thermometric measurements. It was found that the leaves extract act as a good corrosion inhibitor for mild steel in all concentrations of the extract. The inhibition action depends on the concentration of the Jatropha Curcas leaves extract in the acid solution. Results for weight loss and thermometric measurements indicate that inhibition efficiency increase with increasing inhibitor concentration. The adsorption of Jatropha curcas leaves extract on the surface of the mild steel specimens obeys Langmuir adsorption isotherm. Based on the results, Jatropha curcas leaves extract is recommended for use in industries as a replacement for toxic chemical inhibitors.

Keywords: Mild steel, Corrosion inhibitor, Jathropha Curcas, Surface coverage and Langmuir adsorption isotherm

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1. Introduction

Corrosion is a naturally occurring process generally defined as the deterioration of a material because of reaction with its environment.1 Corrosion can also be defined as the destructive attack of a metal by chemical or electrochemical reaction with the environment.2 Corrosion is a naturally occurring phenomenon which affects our society daily, and it results into damage, destruction and degradation to household gadgets, automobiles, airplanes, highway bridges, energy production and distribution systems, among others. Mild steel is a material of choice, which has found wide application in many industries like automobile, petrochemicals, construction, metallurgical and refineries, and so on. This is due to its low cost, availability and excellent mechanical properties.3 However, it suffers corrosion in hostile aggressive environment.

The rate of metallic corrosion can be reduced by addition of inhibitors. Some of these inhibitors are synthetic in nature and therefore not eco-friendly because of the toxic products released to the environment after usage.4 Green inhibitors are naturally occurring and are eco-friendly, non-toxic and readily available. These inhibitors have been found to be effective in retarding the corrosion rate of metals exposed to aggressive environment and have continued to receive attention as replacement for synthesized organic inhibitors. These inhibitors have also been reported in recent studies to exhibit good inhibition efficiencies in acidic and other aggressive media.5-20 The inhibitory action of some of these natural plant products has been found to be due to the presence of organic compounds such as tannins, alkaloids, steroids, amino acids, flavanoids etc.21-23 Some researchers have also reported that the inhibitive effect of some plants solution extract is due to the formation of pro-
tective film on the metal surface as a result of adsorption of molecules of phytochemicals present in the pl
ant on the surface of the metal.\textsuperscript{24-26}

\textit{Jatropha curcas}, is a valuable multipurpose plant, that belongs to the family of Euphorbiaceae. Its seeds have been reported to be highly beneficial for the production of bio-diesel and for generating electrical energy.\textsuperscript{27} \textit{Jatropha curcas} seed husk extract has been found to be an effective eco-friendly and good corrosion inhibitor for mild steel in hydrochloric acid solution.\textsuperscript{28} Alcoholic leaf extract of \textit{Jatropha curcas} has also been reported to inhibit the corrosion of brass (Cu-40Zn) in 1N hydrochloric acid and natural sea water.\textsuperscript{29} However, the aim of this study is to produce corrosion inhibitor from \textit{Jathropha curcas} leaves extract with a view of determining the effectiveness of the corrosion inhibitor produced on mild steel in concentrated tetraoxosulphate (vi) acid solution.

2. Experimental

2.1. Specimen preparation

Rectangular specimens of mild steel were mechanically press cut into 1.5×2 cm coupons. The specimens were mechanically polished using LINN MAJOR STRUER-ITALY (Model No. 224732) with emery papers of different grades. Specimens were prepared by degreasing in ethanol and cleaning in acetone. It was then allowed to dry and kept in a desiccator. The composition of the mild steel samples was analyzed using Optical Emission Spectrometer (OES) and the result is presented in Table 1.

2.2. Phytochemical analysis of \textit{Jatropha curcas} leaves

The phytochemical composition of \textit{Jatropha curcas} leaves is shown in Table 2. As shown in the table, the extract contains high contents of alkaloids (1.610 mg/L) and flavonoids (0.672 mg/L), along with tannins, saponins and phenols. Ahirraon \textit{et al.} 2011 reported similar experimental results to the current work. Previous studies\textsuperscript{21-23} have also reported that saponins, tannins and alkaloids are active constituents of most green inhibitors.

2.3. Preparation of \textit{Jatropha curcas} leaves extract

The acidic extracts of \textit{Jatropha curcas} (JC) were prepared from fresh leaves which were washed, cut into pieces, air dried and then grounded well and sieved into powdery form. 10 g each of the powdery leaf was put into flat bottom flask containing 200 cm$^3$ of 2 M sulphuric acid (H$_2$SO$_4$) solution as shown in Figure 1. The resulting solutions were refluxed for 2 hr and left overnight before it was carefully filtered. The stock solution was prepared from the filtrate and prepared into the desired concentrations as reported elsewhere.\textsuperscript{30}

2.4. Weight loss measurement

The pretreated mild steel specimens of size 1.5×2.0

\begin{table}  
\centering  
\caption{Chemical composition of the investigated mild steel sample}  
\begin{tabular}{ll}  
\hline  
Element & Composition (wt.\%) \\
\hline  
Carbon & 0.17 \\
Silicon & 0.21 \\
Manganese & 0.55 \\
Phosphorus & 0.02 \\
Sulphur & 0.02 \\
Copper & 0.18 \\
Nickel & 0.01 \\
Tin & 0.02 \\
Iron & 98.81 \\
\hline  
\end{tabular}  
\end{table}

\begin{table}  
\centering  
\caption{Major phytochemical constituents of \textit{Jatropha curcas} leaves extract}  
\begin{tabular}{lllll}  
\hline  
Phytochemical & Alkaloids & Flavonoids & Saponins & Tannins & Phenol \\
\hline  
Composition (mg/L) & 1.610 & 0.672 & 0.412 & 0.124 & 0.465 \\
\hline  
\end{tabular}  
\end{table}

\begin{figure}  
\centering  
\includegraphics[width=0.5\textwidth]{plant_extraction_process.png}  
\caption{Plant extraction process.}  
\end{figure}
×0.2 cm were completely immersed in 50 mL of the test solution of 2 M sulphuric acid in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions for weight measurement after 24, 48, 72, 96 and 120 hr, washed thoroughly with distilled water, and dried completely. The weight loss was taken as the difference in weight of the specimens before and after immersion determined using digital balance with sensitivity of ±1 mg. From the weight loss measurements, the corrosion rate, inhibition efficiency (IE)\% and surface coverage (θ) of the plant extract were calculated using Equations 1, 2 and 3,\textsuperscript{31,32} respectively.

Corrosion rate (g cm\(^{-2}\) h\(^{-1}\)) = \(\frac{\Delta W}{A T}\) \hspace{2cm} (1)

where \(W\) is the weight loss (g), \(A\) is the surface area of the mild steel coupon (cm\(^2\)), and \(T\) is the time of exposure (hr).

Inhibition Efficiency (\%) = \(\left(\frac{CR_B - CR_W}{CR_B}\right) \times 100\) \hspace{2cm} (2)

Surface Coverage (θ) = \(\frac{CR_B - CR_W}{CR_B}\) \hspace{2cm} (3)

where \(CR_B\) and \(CR_W\) are the corrosion rates in the absence and presence of the inhibitor.

2.5. Thermometric method measurements

Thermometric analysis was carried out according to the method described by Ejikeme \textit{et al.}\textsuperscript{33} The mild steel coupons of dimension 4×2×0.2 cm were immersed in 50 mL of test solutions of 4 M sulphuric acid in the presence and absence of the inhibitor. The initial temperature in all experiments was kept at 30°C. The process of the corrosion reaction was monitored by determining the change in temperature with time using a standard digital thermometer. From the rise in temperature per minute, the reaction number (RN), inhibition efficiency and surface coverage were calculated using Equations 4, 5 and 6, respectively.

Reaction Number (RN) (\(^{\circ}\)C min\(^{-1}\)) = \(\frac{(T_m - T_i)}{t}\) \hspace{2cm} (4)

Inhibition Efficiency (\%) = \(\left(\frac{RN_{aq} - RN_{wi}}{RN_{aq}}\right) \times 100\) \hspace{2cm} (5)

Surface Coverage (θ) = \(\frac{RN_{aq} - RN_{wi}}{RN_{aq}}\) \hspace{2cm} (6)

where \(T_m\) and \(T_i\) are the maximum and initial temperatures (\(^{\circ}\)C), respectively, and \(t\) is the time (min) taken to reach the maximum temperature. \(RN_{aq}\) is the Reaction Number in the absence of inhibitor (control) and \(RN_{wi}\) is the Reaction Number in the presence of inhibitor.

3. Results and Discussion

Figure 2 shows the weight loss of mild steel in the absence and presence of different concentration of Jatropha curcas leaves extract in 2 M sulphuric acid at different time interval. The figure clearly shows a reduction in weight loss of the metal coupons in the presence of these inhibitors compared to the blank solution. The figures also revealed that the loss in weight of the coupons decreases as the concentration of the inhibitors increases, indicating good corrosion inhibition performance of JC leaves extract at all concentrations. The 2 mL extract concentration recorded a weight loss value of 0.45 g after 120 hr exposure, while 4 mL extract concentration addition gave a weight loss value of 0.30 g after the same period. 0.15 g were lost at 6 mL extract concentration, 0.08 g weight lost was recorded for the 8 mL extract concentration and the 10 mL concentration of the JC extract in sulphuric acid test solution gave a weight loss of 0.05 g.

The Jatropha curcas leaf extract showed significance inhibitory properties at all concentration when the mild steel specimens were immersed in sulphuric acid possibly due to formation of passive film on the metal surface. The synergistic combination of all the phytochemical constituents could be responsible for the passivity and hence very good inhibition in the test medium. Salami \textit{et al.}\textsuperscript{34} observed that as the concent-
tration of Musa Sapientum extract (inhibitor) in 2.0 M H$_2$SO$_4$ increases, the weight loss of mild steel decreases. This is in agreement with the findings in the current study.

The calculated values of corrosion rate for the mild steel samples in 2 M H$_2$SO$_4$ in the absence and presence of JC leaves extract of different concentrations at different immersion time are shown in Figure 4. The result shows that the corrosion rate for the mild steel samples was lower in the presence of the extracts compared to the acid solution without inhibitor. The corrosion rate decreases as the concentration of the JC leaves extract increases, indicating that the rate of corrosion is dependent on the amount of inhibitor present. This result also showed that the JC leaves extract actually inhibited the corrosion of mild steel in sulphuric acid solution.

However, at lower JC leaves extract concentration, the corrosion rate increases with increase in exposure time for both the blank solution and the acidic solution with JC extract up to 4 mL concentration. Although, the corrosion rate was fluctuating and it decreases between 24 and 48 hr immersion period, but later increased and reached its maximum at 72 hr immersion of the mild steel sample in the test solution. This observation may be due to formation of discontinuous passive film on the surface of the metal due to lower concentration of the JC leaves extract in the acid. However, the period between 24 hr and 72 hr immersion periods may be referred to as transient or incubation period, which is associated with the breakdown of the discontinuous passive film on the surface of the immersed metal.

Above this immersion period, the corrosion rate decreased and nearly became constant in the test solution containing JC leaves extract, indicating inhibiting effect of the extract. However, this trend was not similar with the observation in the test solution with higher concentration of JC leaves extract, that is, between 6 mL and 10 mL concentrations. The corrosion rate decreased with increased immersion period from 24 hr to 48 hr, and later became nearly independent of the immersion period above 48 hr immersion period, possibly due to faster rate of adsorption of the phytochemical constituents onto the surface of the metal and

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**Table 3.** Inhibition efficiency of mild steel in different concentrations of Jatropha Curcas leaves extract in 2M H$_2$SO$_4$ at different time of immersion

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>2 mL</th>
<th>4 mL</th>
<th>6 mL</th>
<th>8 mL</th>
<th>10 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.5</td>
<td>50.00</td>
<td>62.50</td>
<td>75.00</td>
<td>87.5</td>
</tr>
<tr>
<td>2</td>
<td>53.85</td>
<td>61.54</td>
<td>69.23</td>
<td>76.92</td>
<td>84.62</td>
</tr>
<tr>
<td>3</td>
<td>30.43</td>
<td>69.57</td>
<td>84.78</td>
<td>91.30</td>
<td>93.48</td>
</tr>
<tr>
<td>4</td>
<td>30.00</td>
<td>60.00</td>
<td>80.00</td>
<td>88.00</td>
<td>92.00</td>
</tr>
<tr>
<td>5</td>
<td>40.00</td>
<td>60.00</td>
<td>80.00</td>
<td>89.30</td>
<td>93.33</td>
</tr>
</tbody>
</table>
subsequently formation of continuous and protective passive film. This film serves as a strong barrier which inhibited the penetration of sulphuric acid solution onto the metal surface and thereby inhibited the corrosion of the metal in the acidic medium in the presence of higher concentration of the JC leaves extract.

Table 3 shows the inhibition efficiency of mild steel in different concentrations of Jatropha Curcas leaves extract in 2 M \( \text{H}_2\text{SO}_4 \) at different time of immersion. The results show that the inhibition efficiency increases with increase in the concentration of the extract of Jatropha curcas, probably due to an increase in the metal surface area covered by the extract. The optimum inhibition efficiency was found to be 93.33% at the maximum concentration of the inhibitor. The inhibitive effect of the JC leaves extract could be attributed to the presence of some phytochemical constituents in the extract as shown in Figure 2.

Previous studies\textsuperscript{21-23} have revealed that the inhibitory action of some of natural plant products is due to the presence of organic compounds such as tannins, alkaloids, steroids, amino acids and flavanoids. Some of these compounds are present in the JC leaves extract, and are adsorbed onto the surface of the metal to inhibit its corrosion in the acidic medium. However, as the concentration of the inhibitor increases, the amount of phytochemical constituents absorbed onto the surface of the metal also increases, thereby increasing the efficiency of the inhibitor at higher concentrations. Rani and Selvaraj\textsuperscript{29} have shown that alcoholic leaf extract of \textit{Jatropha curcas} inhibited the corrosion of brass (Cu-40Zn) in 1 N hydrochloric acid and natural sea water. In another study, \textit{Jatropha curcas} seed husk extract was found to be an effective eco-friendly and alternate corrosion inhibitor for mild steel in hydrochloric acid solution.\textsuperscript{28} These observations are in agreement with the results of the current study.

Figure 5 shows a plot of temperature versus time for the corrosion of mild steel in 4 M \( \text{H}_2\text{SO}_4 \) in the absence and presence of different concentrations of Jatropha curcas leaf extract. The results obtained revealed that maximum temperature was attained in the blank solution. This value corresponds to 0.696°C/min as shown in Table 4. Figure 5 also revealed that as the concentration of the inhibitor increases reaction number of \( \text{H}_2\text{SO}_4 \) decreases from 0.440 to 0.10°C/min. This observation shows the JC extract inhibit the corrosion of mild steel in the acidic medium, probably by adsorption on the metal surface. As the concentration of the extract increases, the degree of metal surface coverage increases, and thus the inhibition efficiency also increases as shown in Table 4. Formation of protective film on the metal surface as a result of adsorption of molecules of phytochemicals compounds in green inhibitors on the metal surface has been reported to be responsible for their inhibitory action.\textsuperscript{24-26} Thus, the inhibitory action of the JC leaves extract may be due to adsorption of molecules of phytochemical compounds such as saponins, tannins and alkaloids onto

<table>
<thead>
<tr>
<th>Concentration of JC extract (mL)</th>
<th>Reaction Number ((^\circ\text{C/min}))</th>
<th>Inhibition Efficiency (%)</th>
<th>Surface Coverage ((\theta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.696</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.00</td>
<td>0.440</td>
<td>36.78</td>
<td>0.3678</td>
</tr>
<tr>
<td>10.00</td>
<td>0.380</td>
<td>45.40</td>
<td>0.4540</td>
</tr>
<tr>
<td>15.00</td>
<td>0.280</td>
<td>59.77</td>
<td>0.5977</td>
</tr>
<tr>
<td>20.00</td>
<td>0.240</td>
<td>65.52</td>
<td>0.6552</td>
</tr>
<tr>
<td>25.00</td>
<td>0.100</td>
<td>85.63</td>
<td>0.8563</td>
</tr>
</tbody>
</table>
the metal surface. The results obtained using thermometric method is in agreement with those obtained using the weight loss measurements.

Adsorption of molecules of phytochemical constituents present in the plant extracts on the surface of the metal is responsible for the inhibitive properties of some natural inhibitors. Therefore, it is critical to determine the mechanism of interaction between the phytochemicals in the JC leaves extract and the mild steel sample surfaces in the current study. Adsorption isotherms such as Langmuir, Freundlich, Frumkin and Temkin have been used by various authors for the description of adsorption equilibrium.

Febrianto et al. reported that Temkin isotherm is superior in the prediction of gas phase equilibira, while Freundlich isotherm has the ability to fit nearly all experimental adsorption data. Langmuir adsorption isotherm is used when it is assumed that the inhibitors adsorbed on the metal surface decrease the surface area available for metallic corrosion.

The observed data are tested graphically with different adsorption isotherms and was found to be best fitted to Langmuir isotherm, which can be expressed by the Equation 7.

\[
\log \frac{C}{\theta} = \log C - \log K \tag{7}
\]

The degree of surface coverage, \( \theta \) was determined from the inhibition efficiencies for the different inhibitor concentrations; \( C \), and \( K \) is an adsorption coefficient. The plot of log \( \frac{C}{\theta} \) versus log \( C \) is shown in Figure 5, which clearly revealed that the experimental adsorption data fitted with the Langmuir adsorption isotherm for the adsorption of JC leaves extract on mild steel surface. The results show a clear linear relationship with a regression close to unity of 0.989 for the adsorption of the JC leaves extract in sulphuric acid solution. This proves that Langmuir isotherm model is appropriate for the adsorption of the extract of Jatropha Curcas leaves onto the metal surface in \( H_2SO_4 \) solution. Plant extract contains organic compounds having polar atoms or groups which are absorbed on the metal surface. The compounds interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slopes values from unity. 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. Similar result was reported by Ebenso et al. when methyl red and halide ions were used as corrosion inhibitor on aluminium in sulphuric acid.

Table 5 shows the values of Langmuir adsorption isotherm parameters of Jatropha curcas leaves extract in \( H_2SO_4 \) solution. As shown in the table, the value of standard free energy of adsorption for J. Curcas leaves extract in \( H_2SO_4 \) is negative, indicating that the adsorption process was spontaneous and stable. The result also shows that adsorption of the inhibitor on the surface of the mild steel is exothermic. The value, \(-13.6\) KJ/mol, showed that the extract was physically adsorbed on the surface of the metal, and thus the mechanism of inhibition is by physisorption.

4. Conclusions

Based on the results from the determination of the effectiveness of JC leaves extract as an inhibitor of corrosion of mild steel in sulphuric acid solution, the following conclusions can be drawn.

Jatropha curcas leaves extract contains active phytochemical constituents such as tannins, alkaloids, flavonoids, saponins and phenols, which make it to be a very effective inhibitor of the corrosion of mild steel in sulphuric acid solution. The inhibition efficiency increases with increase in the concentration of the extract of Jatropha curcas leaves, up to an optimum inhibition efficiency of 93.33% in gravimetric study.

The adsorption of the inhibitor onto the metal surface is an exothermic and spontaneous process. The value of free energy suggested the physical adsorption of the inhibitor on the metal surface and it obeys Langmuir adsorption isotherm.

Jatropha curcas leaves extract has a promising potential as an alternative eco-friendly, non-toxic, readily available inhibitor to replace the non-biodegradable, toxic and expensive synthetic chemicals, which are currently being in use.

Table 5. Calculated values of Langmuir Adsorption isotherm parameters of Jatropha Curcas leaves extract in \( H_2SO_4 \)

<table>
<thead>
<tr>
<th>Plant Extract</th>
<th>Intercept</th>
<th>Slope</th>
<th>Log K</th>
<th>( R^2 )</th>
<th>( \Delta G_{ads}(KJ/mol) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>JC in 2M ( H_2SO_4 )</td>
<td>0.599</td>
<td>0.475</td>
<td>0.273</td>
<td>0.989</td>
<td>-13.6</td>
</tr>
</tbody>
</table>
References