CORROSION INHIBITION OF \textit{Caesalpinia coriaria} (DIVI-DIVI) PODS EXTRACT ON MILD STEEL IN 1M SOLUTIONS OF HCl AND H2SO4

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Abstract
The Corrosion inhibition effect of antioxidants from \textit{Caesalpinia coriaria} (Divi-Divi) pods extract on Mild Steel in 1M HCl and H2SO4 has been investigated extensively by weight loss. The effect of media (acids) to extract on the corrosion inhibition of Mild Steel at the room temperature of 303K was satisfactorily analysed. The results obtained indicated that \textit{Caesalpinia coriaria} extract contains antioxidants and acted as effective inhibitor in the acid media, having inhibition efficiencies of 1.44\% at 0.1g/l and 9.96 at 0.2g/l of inhibitor concentration in HCl and H2SO4 respectively. The inhibition efficiency of the antioxidants from the extract increases with the increase in concentrations but decreases with the increase in temperature. The inhibitor achieves its inhibition through physical adsorption of the antioxidants from the extract on the surface of the Mild Steel. The experimental data also, revealed that the adsorption of the antioxidants occurred according to the Langmuir adsorption isotherm.

Keywords: Corrosion, Antioxidants, \textit{Caesalpinia coriaria}, Mild Steel.

Introduction
Corrosion is a primary means by which metals deteriorate because of its reaction with environment and hence a major industrial and economical problem. Both direct and indirect losses due to corrosion are huge. The deterioration occurs due to contact between metals and corrosive media or agents such as; oxygen, moisture, acids, bases, salts, acid vapours, formaldehydes, ammonia and sulphur containing gases and other liquid chemicals. Corrosion inhibitors reduce the rate of either anodic oxidation or cathodic reduction or both[1,2]. Considerable efforts are being deployed to find suitable compounds to be used as corrosion inhibitors in various corrosive media to stop or delay, to the maximum, the degradation of metal and metallic materials. Many metals and alloys that are used in different human activities are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media. The study of mild steel corrosion phenomena has become important particularly in acidic media because of the increased industrial applications of acid solutions. For instance, refining of crude oil usually involves a variety of strong acid attacking the equipment surface and industrial cleaning processes such as pickling and acid de-scaling [3, 4]. The antioxidiant property of the plant material is due to the presence of many active phytochemicals including vitamins, flavonoids, terpenoids, carotenoids, cumarins, curcumins, lignin, saponin, plant sterol etc which are believed to be in different parts of the green plants e.g fruits, leaves, stem, roots etc as reported by different researches[1,5,6]. The aim of this study is to use naturally occurring, cheaply available, environmentally safe and economical material for the extraction of corrosion inhibitor and hence, inhibit the corrosion of mild steel exposed to corrosion media (acids). To obtain corrosion rate, corrosion inhibition efficiency and degree of surface area coverage of the inhibitor on the applied mild steel and to ascertain the type of adsorption (physisorption or chemisorption) between the antioxidants (inhibitors) and surface of the mild steel by applying the adsorption principle.

Materials and Methods
Preparation of mild steel specimen
The Mild steel strips used in the study were mechanically pressed-cut into coupons, each of dimensions, 4.0 × 2 × 0.2cm with the following composition as determined by quotiometric method, wt (%): C (0.14), Mn (0.6), Si (0.03), S (0.025), P (0.36), and the rest Fe. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a moisture free desiccator. All reagents used in this study were of analar grade and double distilled water was used for their preparation[2, 7, 8].

Preparation of \textit{C. coriaria} Pods Extract
A large quantity of \textit{Caesalpinia coriaria} pods were collected from its trees within the premises of the Nigerian Institute of Leather and Science Technology, Samaru-Zaria. The pods were identified at the herbarium, Department of Biological Science, Ahmadu
Bello University, Zaria. The sample was then, room-dried for a period of three (3) weeks, and ground into powder with 0.4mm mesh size. The sample was soaked into methanol for 48 hours. The extract was then filtered carefully, the filtrate was concentrated using water-bath until it dried completely from which the working concentrations of *Caesalpinia coriaria* pods extract were prepared, and the concentration of the working solution is expressed in terms of % (w/v). The lowest inhibitor concentration used in this experiment was 0.1 g/L in 0.5M HCl and H2SO4 while the highest was 0.5 g/L in 1M HCl and H2SO4 [6, 8].

**Gravimetric Experiment**
The sample coupons of mild steel were weighed using a digital weighing balance, labelled and immersed in the test solutions (1M HCl and 1M H2SO4) with and without inhibitor for as long as 1 day (24 hrs) at room temperature. Before immersion, the pieces of coupon were degreased in ethanol, washed with mixture of 50g Zinc dust with 25 ml of 0.1M NaOH, dried with acetone and weighed. The duration for the process was 5 days (120 hours). The weight loss of the metal in the corrosive solutions, the inhibition efficiency (%I) of the inhibitor, and the degree of surface coverage (θ) and the corrosion rate of the mild steel (CR) were calculated using equation 1, 2, 3, and 4 respectively [1, 8, 9, and 10]:

\[
\Delta W = W_1 - W_2 
\]

\[
\%I = (1 - W_1/W_2) \times 100 
\]

\[
\theta = 1 - W_1/W_2 
\]

\[
CR = \frac{\Delta W}{AT} 
\]

Where; W1 and W2 are the weight of metal before and after exposure to the corrosive solution respectively. 

\[
\Delta W = \text{Weight loss of the mild steel in g after time “t”} 
\]

\[
W = \text{Weight loss in g.} 
\]

\[
T = \text{Exposure time in hours.} 
\]

\[
A = \text{Exposed area of coupon in cm}^2. 
\]

**Results and Discussion**
The weight loss study, corrosion rate and inhibition efficiency for mild steel was carried out in 1M HCl & H2SO4 acids in the absence and presence of various concentrations of the *Caesalpinia coriaria* extract ranging from 0.1 g/l to 0.5 g/l. Using the weight loss data, inhibition efficiency, surface coverage of the inhibitor and the corrosion rate have been calculated. The results obtained in the weight loss method are summarised in Table and figures below;

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>Inhibition Efficiency (%I)</th>
<th>Surface Coverage (θ)</th>
<th>Corrosion Rate (g/cm²h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HCl</td>
<td>H₂SO₄</td>
<td>HCl</td>
</tr>
<tr>
<td>Blank</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.1</td>
<td>1.44</td>
<td>4.90</td>
<td>0.0144</td>
</tr>
<tr>
<td>0.2</td>
<td>1.25</td>
<td>9.96</td>
<td>0.0125</td>
</tr>
<tr>
<td>0.3</td>
<td>0.71</td>
<td>5.76</td>
<td>0.0071</td>
</tr>
<tr>
<td>0.4</td>
<td>0.70</td>
<td>3.64</td>
<td>0.0070</td>
</tr>
<tr>
<td>0.5</td>
<td>1.17</td>
<td>3.02</td>
<td>0.0116</td>
</tr>
</tbody>
</table>

Fig. 1: Variation of weight loss with time for the corrosion of mild steel in 1M HCl in the presence for various concentrations of inhibitor

Fig. 2: Variation of weight loss with time for the corrosion of mild steel in 1M HCl in the absence of inhibitor
Adsorption Considerations

As presented in Table 1, there is notable decrease in the value of corrosion rate with increase extract concentration due to higher degree of surface coverage, because of enhanced inhibitor adsorption. The adsorption characteristics of methanol extract of Caesalpinia coriaria pods was also investigated by fitting data obtained for the degree of surface coverage using Langmuir adsorption isotherm. The assumptions of Langmuir adsorption isotherms can be expressed as follows [13]:

\[
\frac{C}{\theta} = \frac{1}{K} + C
\]

where; \(C\) is the concentration of the inhibitor in the bulk electrolyte, \(\theta\) is the degree of surface coverage of the inhibitor and \(K\) is the adsorption equilibrium constant. Taking logarithm of equation yields,

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

Values of adsorption parameters were tested graphically for fit to Langmuir adsorption isotherm. As depicted in Fig. 3, a straight line are obtained when \(\log\left(\frac{C}{\theta}\right)\) is plotted against \(\log C\) and the linear correlations coefficient of the fitted data are considerably good for inhibitor.

References


