Inhibiting Effect of Seeds Extract of Pithecellobium Dulce on Corrosion of Mild Steel in 1N HCL Medium

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Abstract:
The inhibition of the corrosion of mild steel in hydrochloric acid solution by the leaves Extract of Pithecellobium Dulce Seeds (PDS) has been studied using weight loss, electrochemical impedance spectroscopy and Potentiodynamic polarization technique. Inhibition was found to increase with increasing concentration of the extract. Results indicated that PDS Extract could be served as an efficient natural corrosion inhibitor in the acidic solution. Polarization measurements showed that the studied extract acts as mixed type inhibitor in 1N HCl acid with significant reduction of cathodic and anodic current densities. The electrochemical impedance study further confirms the formation of an adsorbed film on the mild steel. The Scanning Electron Microscopy morphology of the absorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extract.

Keywords: Mild Steel, Corrosion Inhibition, Weight Loss Method, Electrochemical Technique, Scanning Electron Microscopy (SEM).

I. Introduction
The study of mild steel corrosion is theoretical and practical importance 1. Mild steel is commonly used in industries because of cost-effective and easy fabrication, but it is prone to undergo corrosion in aggressive environmental conditions. Usually, sulphuric acid and hydrochloric acid are used in acid pickling, chemical cleaning to eliminate detrimental rust and scale in several industries. One of the significant methods of dealing with this problem is the usage of corrosion inhibitor in the aggressive media2. Severe corrosion attack is known to occur on metals in such aggressive environments. Aqueous solutions of acids are among the most corrosive media. The inhibition of corrosion on iron based alloys by organic additives has been studied widely 3,6. A considerable work has been done on the study of organic compounds as corrosion inhibitors 7,8. Most acid corrosion inhibitors are N, O, and S containing organic compounds 9,11. But, unfortunately most of them are highly toxic to both human being and environment. Most of the synthetic organic compounds showed good anticorrosive activity, which are highly toxic to cause severe hazards to both human being and the environment during its application 12. The recent and growing trend is the use of medicinal plant extract as corrosion inhibitors. Hence use of natural products which are eco-friendly and are being used as corrosion inhibitors has become need of the time. Now the development of corrosion inhibitor of natural source and nontoxic type has been considered more important and desirable 13,12. Plant extracts contain mixtures of proteins, polysaccharides, polycarboxylic acids, tamin, alkaloids, and terpinoids and so forth 13. Some investigators studied the plant extract and the derived organic species become more important as an environmentally benign, easily available and acceptable source for a wide range of inhibitor 24,25. A large number of research studies have been devoted to the inhibitive performance of natural corrosion inhibitors on the corrosion of metals in various aggressive solutions showing that these extracts could act as potential corrosion inhibitors 26,42. The plant extract are rich source of organic molecules which have appreciably high inhibition efficiency and hence termed as eco-friendly or green inhibitor 43. Medicinal values of PDS plants lie in some chemical substances that produce a definite physiological action on human body 14. Different parts of PDS have wide variety of uses especially in traditional system of medicine. The present study aims at broadening the application of plant extracts for mild steel corrosion inhibition by investigating the inhibitive properties of PDS extract for mild steel corrosion in 1N HCL using weight loss method, potentiodynamic polarization and electrochemical impedance technique.

II. MATERIALS AND METHODS

2.1. Preparation of mild steel specimen
Mild steel strips were mechanically cut into strips of size 4 cm x 2 cm x 0.1 cm containing the composition of (C - 0.030%, Mn - 0.169%, Si - 0.015%, P - 0.031%, S - 0.029%, Cr - 0.029%, Ni - 0.030%, Mb - 0.016%, and Cu - 0.017%) and the remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of 1cm² were used. Mild steel strips were polished by using emery paper of (400, 600, 800, 1000, and 1200) grade, subsequently degreased with acetone and finally washed with deionized water, and stored in the desiccators. Accurate weight of the metal was taken using four digital electronic balances model (Shimadzu ay220).

2.2. Preparation of the plant extract
The medicinal plants PDS were taken and cut into small pieces, and dried in room temperature and ground well in to powder. 20 g of the powder from each was refluxed in 200 ml distilled water kept at overnight. The refluxed solution was then filtered carefully, the filtrate volume was made up to 500ml using double distilled water which is the stock solution, and the concentration of the stock solution is expressed in terms of ppm. From the stock solution, 5 - 20 ppm
concentration of the extract was prepared using 1N hydrochloric acid \(^{45}\).

2.3. Weight loss method

Mild steel specimens were immersed in 200 ml of 1N HCl solution of various concentration of the inhibitor in the absence and presence of mild steel for 24 hours. The weights of the specimens before and after immersion containing determined using four digit model (Shimadzu ay220). From the mass loss measurements, the corrosion rate was calculated using the following relationship

\[
CR \text{ (mmpy)} = \frac{K \times \text{Weight Loss}}{D \times A \times t \text{ (in hours)}}
\]

Where, \(K = 8.76 \times 10^6\) (constant), \(D\) is density in gm/cm\(^3\) (7.86), \(W\) is weight loss in grams and \(A\) is area in cm\(^2\). The inhibition efficiency (%) was calculated using equation (2) respectively,

\[
\text{IE} \% = \frac{W_0 \times W_i}{W_0 \times 100}
\]

Where, \(W_0\) and \(W_i\) are the weight loss in the absence and presence of the inhibitor.

2.4. Potentiodynamic polarization methods

Potentiodynamic polarization measurements were carried out using CHI660 E electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential from Tafel slope. Experiment were carried out in a conventional three electrode cell assembly with mild steel specimen of 1cm\(^2\) area which was exposed and the rest being covered with red lacquer, was used as working Electrode, a rectangular Pt foil as the counter electrode and a saturated calomel state open circuit potential (OCP). The polarization was carried from a cathodic potential of -800 mV (vs SCE) to an anodic potential of -200 mV (vs. SCE) at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential, and corrosion current were calculated. The inhibitor efficiency was calculated using the formula:

\[
\text{IE} \% = \frac{l_{corr} - l_{corr}^*}{l_{corr}} \times 100
\]

Where \(l_{corr}\) and \(l_{corr}^*\) are corrosion current in the absence and presence of inhibitors.

2.5. Electrochemical impedance method

The electrochemical AC-impedance measurements were also performed using CHI660E electrochemical analyzer. Experiments were carried out in a conventional three electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10 mV was superimposed on the steady state open circuit potential. The real part (\(Z'\)) and the imaginary part (\(Z''\)) were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of \(Z'\) versus \(Z''\) was made. From the plot, the charge transfer resistance (\(R_{ct}\)) was calculated, and the double layer capacitance (\(C_{dl}\)) was then calculated using the formula:

\[
C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}
\]

Where \(R_{ct}\) is charge transfer resistance, and \(C_{dl}\) is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

\[
\text{IE} \% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100
\]

Where \(R_{ct}\) and \(R_{ct}^0\) are the charge resistance values in the inhibited and uninhibited solution respectively.

2.7. Scanning electron microscopy

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of mild steel were examined using (JEOL) computer controlled scanning electron microscope.

III. RESULTS AND DISCUSSION

3.1. Weight loss method

Weight loss method was done for mild steel in 1 N HCl with various concentrations of PDS extract ranging from 5 to 20 ppm, and the corresponding values of inhibition efficiency and corrosion rate are given in Table 1. It is observed from the table that the corrosion rate decreased and thus the inhibition efficiency increased as increasing concentration of PDS extract (5 ppm to 20 ppm). The maximum inhibition efficiency of about 79.76 % was achieved at 15 ppm of PDS extract. This result indicated that PDS extract could act as an excellent corrosion inhibitor.

<table>
<thead>
<tr>
<th>Conc. Of PD seeds Extract (ppm)</th>
<th>Weight loss (g)</th>
<th>Corrosion rate (mmpy)</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0.0939</td>
<td>206.47</td>
<td></td>
</tr>
<tr>
<td>05</td>
<td>0.0381</td>
<td>026.41</td>
<td>59.53</td>
</tr>
<tr>
<td>10</td>
<td>0.0285</td>
<td>022.57</td>
<td>69.64</td>
</tr>
<tr>
<td>15</td>
<td>0.0194</td>
<td>020.00</td>
<td>79.76</td>
</tr>
<tr>
<td>20</td>
<td>0.0280</td>
<td>027.77</td>
<td>70.59</td>
</tr>
</tbody>
</table>

Table 1. Percentage of inhibition efficiency and corrosion rate at different concentration of inhibitor in 1N HCl medium

3.2. FT-IR measurement

The FTIR spectra have been used to analyze the protective film formed on metal surface. Although various compounds present in the PDS extract which contributed in effective working of the inhibitor, it was very difficult to identify each compound separately to know the group present in the PDS extracts. FTIR spectrum of the PDS extract is shown in Fig. 1. It was observed from the figure, broad peak obtained at 3299.42 cm\(^{-1}\) can be assigned to N-H or O-H stretching. C-H stretching was observed at 2920.47 cm\(^{-1}\). Other strong peak obtained at 1642.57 cm\(^{-1}\) correspond to C=O (may be aldehyde or ketone). The peak at 1096.64 cm\(^{-1}\) due ring oxygen atom. Mild steel has co-ordinated with the O – atom of the OH group, -C = O group and the ring oxygen atom. On the basis of the result, it can be said that PDS extract contain Nitrogen and Oxygen (N-H, C=O, C-N, C-O, C=O, C-O) in the extract containing the OH group, aldehyde or ketone. The peak at 1096.64 cm\(^{-1}\)}
impedance measurements were performed to evaluate the charge transfer resistances ($R_{ct}$) and double layer capacitance ($C_{dl}$) and through these parameters the inhibition efficiency was calculated. Fig. 3 shows the Nyquist plots for mild steel in 1N HCl with different concentration of PDS extract and the impedance parameters derived from these investigations are given in Table 3. It is observed from Fig. 3, the obtained impedance diagrams are almost in a semi-circular appearance, indicating that the charge transfer process mainly controls the corrosion of mild steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. In fact, the presence of PDS extracts enhanced the values of $R_{ct}$ in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in values of $C_{dl}$ follows the orders similar to that obtained $I_{corr}$ in this study. The decrease in $C_{dl}$ shows that the adsorption of this inhibitor takes places on the metal surface in acidic solution. Moreover, the increase in the values of $R_{ct}$ with the inhibitor concentration leads to the increase in inhibition efficiency. The maximum $R_{ct}$ values of 66.854 (ohm cm$^2$) and minimum $C_{dl}$ value of 9.830 x 10$^{-5}$ (µF/cm$^2$) are obtained at an optimum concentration of 15 ppm with maximum inhibition of 86.42%.

Table 3. Impedance parameter for mild steel in 1N HCl acid solution in the absence and presence of varied concentration of inhibitor.

<table>
<thead>
<tr>
<th>Conc. PD seeds (ppm)</th>
<th>$R_{ct}$ (ohm cm$^2$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>IE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8.937</td>
<td>7.266x10$^{-3}$</td>
<td>*</td>
</tr>
<tr>
<td>5</td>
<td>22.713</td>
<td>1.002x10$^{-3}$</td>
<td>60.65</td>
</tr>
<tr>
<td>10</td>
<td>24.901</td>
<td>6.870x10$^{-4}$</td>
<td>64.10</td>
</tr>
<tr>
<td>15</td>
<td>65.854</td>
<td>9.830x10$^{-5}$</td>
<td>86.42</td>
</tr>
<tr>
<td>20</td>
<td>31.568</td>
<td>4.460x10$^{-4}$</td>
<td>71.68</td>
</tr>
</tbody>
</table>

3.5. Scanning Electron Microscopy

Scanning electron microscopy was used to examine the morphology of the inhibited mild steel specimens in 1N HCl. SEM images for the mild steel specimens exposed to 1N HCl in the absence and presence of PDS extract are shown in Fig. 4A and 4B. From SEM images, it can be concluded that PDS extract inhibited mild steel dissolution in acid by covering the surface area with protective film which has found absent in case of acid interaction with mild steel. Examination of Fig. 4A revealed that the specimen immersed in 1N HCl was rough and highly damaged due to the attack of aggressive acids. Fig. 4B clearly showed that the mild steel surface was covered with the protective layer formed by inhibitor which prevents the metal from further attack of acid medium thus inhibiting corrosion.

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### 3.3. Potentiodynamic polarization methods

![Fig. 2. Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of PDS extracts.](https://example.com/fig2)

**Table 2.** Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency. The electrochemical polarization parameter for mild steel in the absence and presence of various concentrations of PDS extract in 1N HCl solution is given in Table 2 and their polarization curves are shown in Fig. 2. It was observed from the Fig. 2 that the presence of PDS extracts decreases both cathodic and anodic slopes with the increased inhibitor concentration. This may be ascribed to adsorption of inhibitor over the corroded metal surface. Since both anodic and cathodic reactions were suppressed, the PDS extracts act as a mixed type inhibitor. The results of the polarization measurement are tabulated in Table 2. It is observed that $I_{corr}$ decreases significantly with increasing concentration of PDS extracts, and the maximum inhibition efficiency of 98.45% was achieved at 10 ppm. This is because of increase in the blocked portion of the metal surface by adsorption. Further, the concentration of PDS has less effect on the $E_{corr}$ which shows that PDS acts as a mixed inhibitor. Shivakumar et al. reported that, if the deviation in the $E_{corr}$ is greater than 85 mV in the presence of inhibitor with respect to blank, the inhibitor could be recognized as cathodic and anodic type inhibitor. However, the deviation in $E_{corr}$ is less than 85 mV it could be recognized as mixed type of inhibitor. In the present investigation, the maximum deviation range is 47 mV which reveals that PDS extracts act as a mixed inhibitor.

### 3.4. Electrochemical impedance methods

![Fig. 3. Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of PDS extract.](https://example.com/fig3)

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**Fig. 2.** Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of PDS extract. The corrosion behavior of mild steel in 1N HCl solution is absent and presence of PDS extracts was also investigated by EIS method. Impedance measurements were studied to evaluate the charge transfer resistances ($R_{ct}$) and double layer capacitance ($C_{dl}$) and through these parameters the inhibition efficiency was calculated. Fig. 3 shows the Nyquist plots for mild steel in 1N HCl with different concentration of PDS extract and the impedance parameters derived from these investigations are given in Table 3. It is observed from Fig. 3, the obtained impedance diagrams are almost in a semi-circular appearance, indicating that the charge transfer process mainly controls the corrosion of mild steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. In fact, the presence of PDS extracts enhanced the values of $R_{ct}$ in acidic solution. Values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decrease in values of $C_{dl}$ follows the orders similar to that obtained $I_{corr}$ in this study. The decrease in $C_{dl}$ shows that the adsorption of this inhibitor takes places on the metal surface in acidic solution. Moreover, the increase in the values of $R_{ct}$ with the inhibitor concentration leads to the increase in inhibition efficiency. The maximum $R_{ct}$ values of 66.854 (ohm cm$^2$) and minimum $C_{dl}$ value of 9.830 x 10$^{-5}$ (µF/cm$^2$) are obtained at an optimum concentration of 15 ppm with maximum inhibition of 86.42%.

**Table 3.** Impedance parameter for mild steel in 1N HCl acid solution in the absence and presence of varied concentration of inhibitor.
Fig. 4. SEM image of the surface of mild steel after immersion for 24 hours in 1N HCl solution in the absence (4A) and in the presence (4B) of optimum concentration of the PD plant Seeds extracts.

IV. Conclusion

The effect of acid concentration and the effect of addition the aqueous extract of PDS on the corrosion of mild steel have been studied. The following conclusion may be drawn: Pithecellobium Dulce Seeds acts as efficient corrosion pickling inhibitor on mild steel in 1 N HCl acid. The use of PDS plants as corrosion inhibitor is environmentally safe, nontoxic, eco-friendly, cost effective and easily available. The extracts of PDS showed maximum efficiency of 79.76 % at the optimum concentration of 15 ppm for one day immersion time at room temperature. Results obtained in non-electrochemical methods (weight loss method) have good agreement with the electrochemical methods. The PDS plants extracts act as a mixed type inhibitor on the metal surface. SEM examination showed that there was an improvement in the surface morphology of the as corroded inhibited mild steel compared to uninhibited samples. The results suggest that PDS could act as corrosion inhibitor for mild steel in HCl and they can be used to replace toxic and non-bio gradable inhibitors.

V. References