Abstract: The inhibition property of Pisonia Alba Extract (PAE) on the corrosion of carbon steel in 1N HCl was investigated using potential dynamic, electrochemical impedance study (EIS), weight loss technique. Weight loss study reveals that the formulation consisting of 3nL of Pisonia Alba (PSA) and 50ppm of Zn²⁺ offers 91% inhibition efficiency to carbon steel immersed in 1N HCl solution. The results of Polarization study reveals that this system functions as a mixed type of inhibitor. The AC impedance study reveals that a protective film formed on the metal surface. FT-IR spectrum reveal that the protective film consists of Fe²⁺-PAE complex and Zn(OH)₂. Scanning electron microscopy (SEM) observation, confirmed the existence of an inhibitor molecules on the metal surface.

Keywords: Pisonia Alba, inhibition efficiency, Corrosion rate, protective film

I. INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely [1]. The use of inhibitors is one of the best options of protecting metals against corrosion in various fields of application as acid pickling and acid descaling [2]. Corrosion inhibition of steel in hydrochloric acid solution by Rosemary oil has been studied by Chaieb [3]. Naturally occurring henna (Lawsona inermis L) has anti-inflammatory, antipyretic and analgesic effect [4-5]. Henna has inhibitory action on aluminium and steel in aggressive solution [6]. Henna has been used as corrosion inhibitor for iron in hydrochloric acid [7]. The inhibitors employed are varied and some have been found to be severe to health and the environment at large.

Thus efforts are now directed towards formulation of modern environmentally safe inhibitors in which plant extracts have become important as eco-friendly, economical, readily available and renewable sources of effective corrosion inhibitors. Pisonia alba (Nyctaginaceae), commonly known as Lettuce Tree, is an evergreen tree 9-12 m high found sparsely wild in the beach forests of Andaman Islands, cultivated to a small extent in India and Ceylon. The fresh leaves moistened with Eau-de-Cologne are used to subdue inflammation of a filariosis nature in the legs and other parts [8]. They are used as diuretic. The root is purgative. A survey of literature revealed that Pisonia Alba is an untapped candidate for antidiabetic activity though it is extensively used in traditional healing of diabetes in Kerala (Anonymous, 1969) [9]. The present study aimed at investigating the inhibitive properties of extract of Pisonia Alba plant leaves on the corrosion of carbon steel in 1N HCl solution.

II. EXPERIMENTAL

A. Preparation of Specimen

Carbon steel specimen [0.0267 % S, 0.06 % P, 0.4% Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.
B. Preparation of plant extract

Table 1: Main constituents of Pisonia Alba Extract (PAE) are shown below:

<table>
<thead>
<tr>
<th>Pisonia Alba Extract (PAE)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl phthalate:</td>
<td>Phytol:</td>
</tr>
<tr>
<td>Molecular formula: C_{12}H_{14}O_{4}</td>
<td>Molecular formula: C_{20}H_{40}O</td>
</tr>
<tr>
<td>Molecular weight: 222.089</td>
<td>Molecular weight: 296.308</td>
</tr>
<tr>
<td>IUPAC: Diethyl benzene-1,2-dicarboxylate</td>
<td>IUPAC: (2E,7R,11R)-3,7,11,15,-tetramethyl-2-hexadecen-1-ol</td>
</tr>
</tbody>
</table>

An aqueous extract of Pisonia Alba Extract (PAE) was prepared by grinding 10 g of Pisonia Alba with double distilled water, filtering the suspending impurities, and making up to 100 mL. The extract was used as corrosion inhibitor in the present study.

C. Corrosion Medium

The corrosion solution of 1N HCl used was prepared by dilution of analytical reagent grade 37% HCl with distilled water. From this stock solution 100 mL each of standard solutions are prepared with and without different concentrations of the inhibitor. The 1 N HCl also served as the blank solution in the experiments.

D. Weight-Loss Method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke’s solution [10]. The inhibition efficiency (IE) was then calculated using the equation:

\[
IE \, (\%) = \left( \frac{W_1 - W_2}{W_2} \right) \times 100
\]

where \(W_1\) is the weight loss value in the absence of inhibitor and \(W_2\) is the weight loss value in the presence of inhibitor.

E. Analysis of Variance (F-Test)

F-Test was carried out to investigate whether synergistic effect existing between inhibitor systems is statistically significant [11, 12]. If F-value is above 5.32 for 1, 8 degrees of freedom, it was proved to be at statistically significant. If it is below the value of 5.32 for 1, 8 degrees of freedom, it was statistically in significant at 0.05 level of significance confirmed.

F. Polarization Study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The inhibition efficiency (IE) values were calculated from \(i_{corr}\) values using the equation [13].
\[
IE \% = \left( \frac{i_{corr}^0 - i_{corr}^{in}}{i_{corr}^0} \right) \times 100
\]

Where \(i_{corr}^0\) and \(i_{corr}^{in}\) are the corrosion current densities in case of uninhibited and inhibited solutions respectively.

G. AC impedance Spectra
The instrument used for polarization study was also used for AC impedance spectra. The cell set up was the same as that was used for polarization measurements. The real part (\(Z'\)) and the imaginary part (\(Z''\)) of the cell impedance were measured in ohms at various frequencies. AC impedance spectra were recorded with initial \(E(v) = 0\) V, high frequency limit was 1x105 Hz, low frequency limit was 1 Hz, amplitude = 0.005 V and quiet time \(t_q = 2s\). The values of charge transfer resistance, \(R_{ct}\), and the double layer capacitance, \(C_{dl}\), were calculated.

\[
R_{ct} = (R_s + R_{ct}) - R_s
\]

Where, \(R_s\) is solution resistance and

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

where \(f_{max}\) is maximum frequency.

H. Surface Examination Study
The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

1) Fourier Transform Infrared Spectra (FT-IR): The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

2) Scanning electron microscopy: The surface morphology of the formed layers on the carbon steel surface after its immersion in control solutions containing 1N HCl solution in the absence and in the presence of the inhibitor were carried out. After one day, the specimens were taken out, washed with distilled water and dried. The SEM photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

III. RESULTS AND DISCUSSION

A. Weight-Loss Method
Table 2: Corrosion rates (CR) of carbon steel immersed in 1N HCl solution containing in the presence and absence of inhibitor system at various concentrations of inhibitors and the inhibition efficiencies (IE) obtained by weight loss method:

Inhibitor system: Zn\(^{2+}\)-PAE Immersion period: one day

<table>
<thead>
<tr>
<th>PAE (mL)</th>
<th>Zn(^{2+}) (0 ppm)</th>
<th>Zn(^{2+}) (25 ppm)</th>
<th>Zn(^{2+}) (50 ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IE %</td>
<td>CR (mmpy)</td>
<td>IE %</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>0.5978</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>48</td>
<td>0.4760</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>55</td>
<td>0.4117</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>0.3663</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>0.4209</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>51</td>
<td>0.4481</td>
<td>59</td>
</tr>
</tbody>
</table>
The inhibition efficiency (IE) of Pisonia Alba Extract (PAE) in controlling corrosion of carbon steel immersed in 1N HCl solution for a period of one day in the absence and presence of Zn\(^{2+}\) is given in Table 2. It is observed that when the carbon steel is immersed in 1N HCl solution of Pisonia Alba Extract (PAE) only shows (60%) good inhibition efficiency (IE) (in the absence of Zn\(^{2+}\)). This inhibition efficiency is found to be enhanced in the presence of Zinc ion. When Zn\(^{2+}\) (50 ppm) is added IE also increases and gives maximum 91% IE at 3mL of Pisonia Alba Extract (PAE) and 50 ppm of Zn\(^{2+}\) this shows that synergistic effect exists between Zn\(^{2+}\) and the active principles present in PSA. When the concentration of Zn\(^{2+}\) increases from 25 ppm to 50 ppm the IE slightly increases. This may be due to the fact that, when the concentration of Zn\(^{2+}\) increases, the Zn\(^{2+}\)-PAE complex formed in the bulk of the solution. When the concentration of PAE was increased the IE decreased. This due to the fact that when higher concentrations of PAE are added the protective film (Fe\(^{2+}\)-PAE Complex) formed on the metal surface goes into solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken [14]. Hence the IE decreases, similar observation was made with Hibiscus Rosa-Sinensis Al at pH 12 [14], Euphorbia [16], Henna [17].

B. Influence of Immersion period on the Inhibition efficiency of Pisonia Alba extract (pae)

The influence of duration of immersion on the IE of PAE (3 mL) - Zn\(^{2+}\) (50 ppm) system is given in Table 3. When the immersion period increases the inhibition efficiency decreases and the corrosion rate increases this shows that the protective film formed on the metal surface, was broken by the corrosive environment and the film was dissolved, this same result is shown in Phyllanthis amarus extract [18], Banana Peel Extract [19].

<table>
<thead>
<tr>
<th>Immersion Period (days)</th>
<th>Corrosion Rate (CR) in the absence of the inhibitor (mmpy)</th>
<th>Corrosion Rate (CR) in the presence of the inhibitor PAE (3ml) + Zn(^{2+}) (mmpy)</th>
<th>Inhibition Efficiency (IE%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5978</td>
<td>0.0912</td>
<td>91</td>
</tr>
<tr>
<td>3</td>
<td>0.6635</td>
<td>0.1645</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>0.7305</td>
<td>0.3860</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>0.8014</td>
<td>0.4963</td>
<td>66</td>
</tr>
</tbody>
</table>

C. Synergism Parameter (S\(_I\))

Table 4: Synergism parameters for PAE - Zn\(^{2+}\) (25 ppm) system in carbon steel immersed in 1N HCl for a period of one day.
Table 5: Synergism parameters for PAE-Zn\textsuperscript{2+} (50 ppm) system in carbon steel immersed in 1N HCl for a period of one day

<table>
<thead>
<tr>
<th>PAE (mL)</th>
<th>Zn\textsuperscript{2+} (50 ppm)</th>
<th>I\textsubscript{1}</th>
<th>I\textsubscript{2}</th>
<th>(I\textsubscript{1+2})</th>
<th>S\textsubscript{I}</th>
<th>IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.48</td>
<td>0.22</td>
<td>0.64</td>
<td>1.1266</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.54</td>
<td>0.22</td>
<td>0.79</td>
<td>1.7085</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.60</td>
<td>0.22</td>
<td>0.91</td>
<td>3.4466</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>0.55</td>
<td>0.22</td>
<td>0.78</td>
<td>1.5954</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0.51</td>
<td>0.22</td>
<td>0.67</td>
<td>1.1581</td>
<td>67</td>
</tr>
</tbody>
</table>

Synergism Parameter (S\textsubscript{I}) has been calculated to know the synergistic effect existing between two inhibitors [20, 21]. The values of S\textsubscript{I} > 1 suggest a synergistic effect. S\textsubscript{I} approaches 1 when no interaction exists between the inhibitor compounds. In case of S\textsubscript{I} < 1, the negative interaction of inhibitors prevails (i.e., corrosion rate increases). Synergism parameter is calculated using the relation.

\[ S_{I} = \frac{(1-I_{1+2})}{(1-I_{1+2})} \]

Where, I\textsubscript{1} is the surface coverage of inhibitor (PAE), I\textsubscript{2} is the surface coverage of inhibitor (Zn\textsuperscript{2+}) and I\textsubscript{1+2} is the combined surface coverage of inhibitors (PAE) and (Zn\textsuperscript{2+}). The calculated synergism parameter values for Pisonia Alba Extract (PAE) and Zn\textsuperscript{2+} synergism are given in the table 4 and 5.

Synergism Parameter (S\textsubscript{I}) for the formulation consisting of 3mL of PAE and 50 ppm of Zn\textsuperscript{2+} ions are 3.4466 which is greater than one. This shows that the synergistic effect exists between PAE and Zn\textsuperscript{2+}.

D. Analysis of F-values (analysis of variance ANOVA)

To investigate whether, the influence of Zn\textsuperscript{2+} on the inhibition efficiencies of Pisonia Alba Extract (PAE) is statistically significant, F-test was carried out [22]. The results are given in Table 8. The results of Analysis of variance (ANOVA) shows the influence of 25 ppm and 50 ppm of Zn\textsuperscript{2+} on the inhibition efficiencies of 1mL, 2mL, 3mL, 4mL, 5mL, extract of Pisonia Alba.

Table 8: Distribution of F – value between the inhibition efficiencies of various concentrations of PAE (0 ppm of Zn\textsuperscript{2+}) and the inhibition efficiencies PAE in the presence of 25 ppm and 50 ppm of Zn\textsuperscript{2+}.

<table>
<thead>
<tr>
<th>Zn\textsuperscript{2+} (ppm)</th>
<th>Source of variance</th>
<th>Sum of squares</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F - value</th>
<th>Level of Significance of F</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Between</td>
<td>185</td>
<td>1</td>
<td>185</td>
<td>7.12</td>
<td>P &lt;0.05</td>
</tr>
<tr>
<td></td>
<td>Within</td>
<td>208</td>
<td>8</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Between</td>
<td>1210</td>
<td>1</td>
<td>1210</td>
<td>18.84</td>
<td>P &gt;0.05</td>
</tr>
<tr>
<td></td>
<td>Within</td>
<td>513.4</td>
<td>8</td>
<td>64.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The obtained F-value 7.12 for 25 ppm Zn\textsuperscript{2+} was not statistically significant, since it was less than the critical F-value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it was concluded that the influence of 25 ppm Zn\textsuperscript{2+} on the inhibition efficiencies of various concentrations of PAE was not statistically significant.
The obtained F-value 18.84 for 50 ppm Zn$^{2+}$ was statistically significant, since it was greater than the critical F-value 5.32 for 1, 8 degrees of freedom at 0.05 level of significance. Therefore, it was concluded that the influence of 50 ppm Zn$^{2+}$ on the inhibition efficiencies of various concentrations of PAE was statistically significant.

### E. Potentiodynamic Polarization Study

The potentiodynamic polarization curves of carbon steel electrode in 1N HCl solution in the absence and presence of inhibitor formulations are shown in figure 2. The electrochemical parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), Tafel slopes ($b_{c}$-cathodic and $b_{a}$-anodic) and linear polarization resistance (LPR) are derived from these curves and the inhibition efficiency value are listed in table 6.

#### Table 6: Tafel polarization values for the corrosion of carbon steel in 1N HCl in the absence and presence of inhibitor formulation:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>PAE (mL)</th>
<th>Zn$^{2+}$ (ppm)</th>
<th>$E_{corr}$ (mV vs SCE)</th>
<th>$i_{corr}$ (A/cm$^2$)</th>
<th>$b_{c}$ (mV/dec)</th>
<th>$b_{a}$ (mV/dec)</th>
<th>LPR (Ω cm$^2$)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-500</td>
<td>$4.284 \times 10^{-4}$</td>
<td>68.1</td>
<td>118.4</td>
<td>48.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>-465</td>
<td>$1.204 \times 10^{-4}$</td>
<td>81.3</td>
<td>147.2</td>
<td>134.7</td>
<td></td>
<td>72</td>
</tr>
</tbody>
</table>

When carbon steel is immersed in 1N HCl solution, the corrosion potential ($E_{corr}$) is -500 mV vs SCE. The formulation consisting of 50 ppm of Zn$^{2+}$ and 3 mL of PAE shifts the corrosion potential to -465 mV vs SCE. In general, an inhibitor can be classified as an anodic type or cathodic type, when the displacement in corrosion potential ($E_{corr}$) of inhibitor formulation is larger than 85 mV with respect to the corrosion potential ($E_{corr}$) of the control [23,24]. In this present study, the maximum displacement exhibited by the Pisonia Alba Extract (PAE) is <35 mV, from which it can be concluded that PAE acts as a mixed type inhibitor. The inhibitor formulation control the both anodic and cathodic reaction [25]. This observation was also reported by several authors, who studied the inhibitory effects of plant extract based inhibitor formulations in acidic media are mixed type inhibitor [26-29]. The inhibition efficiency obtained from polarization studies is found to be 72%.

![Fig.1. Polarization curves of carbon steel immersed in various test solutions](image-url)
1) 1N HCl solution
2) 3mL Pisonia Alba Extract (PAE) + 50 ppm of Zn$^{2+}$ + 1N HCl solution

The corrosion current density value and LPR value for 1N HCl solution are $4.284 \times 10^{-4}$ A/cm$^2$ and 48.9 Ω cm$^2$. For the inhibitor formulation of 3mL Pisonia Alba Extract (PAE) and 50 ppm of Zn$^{2+}$, the corrosion current density value has decreased to $1.504 \times 10^{-4}$ A/cm$^2$ and the LPR value has increased to 134.7 Ω cm$^2$. The fact that the LPR value increases with decrease in corrosion current density indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit the corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface [30-34].

F. AC impedance Spectra

Electrochemical impedance spectroscopy (EIS) has been widely used in investigating corrosion inhibition processes since it provides more information on both the resistive and capacitive behavior at metal solution interface [34]. The corrosion behavior of mild steel in 1N HCl solution in the absence and presence of the extract was investigated using this technique. In the equivalent circuit, $R_s$ represents the solution resistance, $R_p$ represents the charge transfer resistance, and CPE represents the constant phase element describing the interface double layer. CPE is used instead of double layer capacitance to describe deviations induced by surface roughness and dispersion effects. The impedance of CPE can be represented as follows:

$$Z_{\text{CPE}} = A^{-1} (j\omega)^n$$

where $A$ is a proportionality coefficient, $\omega$ is the sine wave angular frequency ($\omega=2\pi f$, the frequency in Hz) and $j$ is the imaginary number ($j^2 = -1$), $n$ has a meaning of a phase shift and can be used as a measure of the surface inhomogeneity. For $n=0$, $Z_{\text{CPE}}$ represents a resistance with $R= A^{-1}$, for $n = 1$ a capacitance with $C= A$, for $n = 0.5$ a Warburg element and for $n = -1$ an inductance with $L= A^{-1}$ [36]. The value range of a real electrode of $n$ is often between 0 and 1. The smaller the value of $n$, the rougher the electrode surface and the more serious the corrosion of the electrode [37].

In the present study in the presence of the control alone, a small semicircle with an $R_s$ value of 34.5 Ω cm$^2$. When the combination of 50 ppm of Zn$^{2+}$ and 3 mL of PAE, is considered in the presence of control, a large depressed semicircle is observed. The $R_p$ value is $597 \Omega$ is greater than that observed in case of the control. The CPE value at the metal/solution interface is found to decrease from 127 μF/cm$^2$ in the case of the control to 17.21 μF/cm$^2$ in the case of the inhibitor formulations. The value of $n$ is increased from 0.78 to 1 in the presence of 50 ppm of Zn$^{2+}$ and 3 mL of PAE, suggesting a decrease of inhomogeneity of interface during inhibition. These results indicate that there is formation of non-porous and protective film. The inhibition efficiency obtained from impedance studies is found to be 74%. Several authors who studied the inhibiting effects of plant extract based corrosion inhibitors also reported that there is formation of thick and less permeable protective film on the metal surface [38-40]. A significant observation related to the inhibition efficiency values is to be noted. If the inhibition efficiency values obtained from weight loss, polarization and EIS studies are compared, differences are observed. It is suggested that the inhibition efficiency values obtained from various methods may not be strictly comparable when the immersion times used in these methods are not the same[41].

Fig. 1. Equivalent Circuit (EC) model used to fit the experimental data. In which $R_s$ represent the solution resistance, $R_p$ charge transfer resistance CPE are constant phase elements for double layer
Information:

**Fig. 2.** AC impedance spectra of carbon steel immersed in various test solutions

**Table 7:** Analysis of AC impedance parameters of carbon steel immersed in 1N HCl in the presence and absence of inhibitor formulation:

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>$R_\text{ct}$ (Ω cm$^2$)</th>
<th>CPE (µF/cm$^2$)</th>
<th>Constant Exponent (n)</th>
<th>IE %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAE (mL)</td>
<td>Zn$^{2+}$ (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>34.65</td>
<td>127</td>
<td>0.78</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>131.5</td>
<td>17.21</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
</tbody>
</table>

**G. Fourier Transform Infrared Spectra (FT-IR)**

FT-IR spectra have been used to analyze the protective film found on the metal surface [42,43]. The FTIR spectrum (KBr) of pure PAE is shown in Fig. 3a. The pure PAE shows C=O stretching frequency at 1628 cm$^{-1}$ and $\text{-OH}$ stretching frequency at 3403 cm$^{-1}$. The peak appears at 1432 cm$^{-1}$ due to C-H bending vibration. The as symmetric C-O-C stretching frequency appears at 1248 cm$^{-1}$. The symmetric C-O-C stretching frequency appears at 1058 cm$^{-1}$. The FT-IR spectrum of protective film formed on the surface of the metal immersed in 1N HCl solution containing 3mL of Pisonia Alba Extract (PAE) and 50 ppm of Zn$^{2+}$ is shown in Figure 3b. The C=O stretching frequency decreased from 1628 cm$^{-1}$ to 1624 cm$^{-1}$ and $\text{-OH}$ stretching frequency decreased from 3403 cm$^{-1}$ to 3399 cm$^{-1}$. The C-H bending vibration shifted from 1432 cm$^{-1}$ to 1421 cm$^{-1}$. The asymmetric C-O-C stretching frequency shifts from 1248 cm$^{-1}$ to 1233 cm$^{-1}$. The symmetric C-O-C stretching frequency shifts from 1058 cm$^{-1}$ to 1039 cm$^{-1}$. This suggested that PAE is coordinated with Fe$^{2+}$ on the anodic sites of the metal surface also resulting in the formation of PAE-Fe$^{2+}$ complex. The
peak appears at 1384 cm$^{-1}$ indicate the presence of zinc hydroxide. The IR results indicate the formation of a protective film on the metal surface and may consists of Fe$^{2+}$-PAE complex and Zn(OH)$_2$.
1) polished mild steel
2) mild steel immersed in 1N HCl solution
3) mild steel immersed in 3mL of Pisonia Alba Extract (PAE) + 50 ppm of Zn$^{2+}$ + 1N HCl solution

IV. CONCLUSIONS

From the overall experimental results the following conclusions can be deduced:

The formulation consisting of 3mL of Pisonia Alba Extract (PAE) and 50 ppm of Zn$^{2+}$ offers 91% inhibition efficiency to carbon steel immersed in 1N HCl solution.

The synergism parameter ($S_{ij}$) and F-test confirms that synergistic effect exists between the Pisonia Alba Extract (PAE) - Zn$^{2+}$ system in controlling the corrosion of carbon steel immersed in 1N HCl solution in the absence and presence of Zn$^{2+}$.

When immersion period increases corrosion rate also increases.

Potentiodynamic polarization study reveals that Pisonia Alba Extract (PAE) is good inhibitor and act as mixed type inhibitor for carbon steel corrosion in 1N HCl solution.

AC impedance spectra reveal that double layer capacitances decrease with respect to blank solution when the plant extract is added. This fact confirms the absorption of plant extract molecules on the carbon steel surface.

The FTIR spectra reveal that the protecting film consists of Fe$^{2+}$- PAE (active ingredient) complex.

SEM studies confirm that protective film formed on the carbon steel surface and the corrosion process inhibited.

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