Leucas Martinicensis as an Inhibitor of Carbon Steel Corrosion in Acidic Medium

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Abstract:

The inhibitory potentials of aqueous leave extract of Leucas Martinicensis (LM) for the corrosion of carbon steel in 1 M HCl solution was studied using gravimetric method, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and scanning electron microscopy (SEM). The effect of temperature on the corrosion rate and inhibition efficiency was investigated, and some thermodynamic parameters were calculated. The result of the study revealed that the extract act as a potent inhibitor on carbon steel in the acid medium. The corrosion inhibition efficiency increases with increase in concentration and decreases with temperature. Maximum inhibition efficiency of 97 % was achieved at 250 ppm LM in 1M HCl and 303 K temperature. The potentiodynamic studies revealed that investigated LM extract act as mixed type inhibitor. Inhibitor adsorption characteristics were approximated by Langmuir adsorption isotherm at all the concentrations and temperatures studied. The result of SEM analysis was found to be consistent with the gravimetric and electrochemical results.

Keywords

Leucas Martinicensis, Corrosion, Carbon steel, EIS, Potentiodynamic polarization, SEM

1. Introduction

The oil and gas industry use a lot of carbon steel for casing, flow lines, oil tubing and transmission pipelines. They are also used for various industrial applications due to their excellent structural and mechanical strength [1]. Acidic solutions particularly HCl, are widely used in industries and the areas of application are acid cleaning, acid pickling, ore production, acid descaling and oil well acidification. These industrial processes lead to corrosion of the metal. There are many approaches that may be applied to protect or minimize the corrosion of metals, which include metal coating, painting, inorganic coating, as well as use of chemical inhibitors. The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media. Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosion attack. For the protection of steel in acidic media, organic corrosion inhibitors are more effective than inorganic compounds [2].

Organic compounds with heterocyclic rings, π electrons and heteratoms like nitrogen, sulfur, oxygen, or phosphorous were successfully utilized as corrosion inhibitors. Such compounds function via adsorption of the molecules on the metal surface, creating barrier against corrosion attack [3-6]. However, in the application of these inhibitors for corrosion control, factors such as toxicity, cost, availability and environmental friendliness are very important. In recent years, researchers have been working on the concept of green inhibitors with negligible harmful effects to the environment, to avoid the toxic effect of synthetic corrosion inhibitors. Naturally occurring substance such as Argemone mexicana [7]; Annona Muricata [8]; Lanvandula stoechas, Musa sapientum peels [9, 10], Balanites aegyptiaca [11], Camellia sinensis [12], red onion skin extract [13] have been used as corrosion inhibitors at different environmental conditions. Leucas martinicensis is an annual herb which is used for repellant of mosquito due to minty odor; it is an erect plant which is usually unbranched, with length of up to 1 m, which is finely hairy. They possess opposites leaves, ovate to ovate lanceolate with the margin coarsely serrate-crenate inflorescence of several space with many flowered verticals having long thistle-like calyx teeth [14]. The current study presents the experimental assessment of the adsorption and corrosion inhibiting efficacy of aqueous leave extracts of Leucas Martinicensis (LM) on the corrosion of carbon steel in 1 M HCl solution using gravimetric method, potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy (SEM).
2. Experimental

2.1. Preparation of metals and test solution

The carbon steel samples used in the present study had a chemical composition in wt%: C 0.076%, Cu 0.135%, P 0.012%, Si 0.026%, Mn 0.192%, Cr 0.050%, Ni 0.050%, P 0.012%, Al 0.023%, balance Fe. Each sample, which was 0.12 cm in thickness, was mechanically press-cut into coupons of dimension 3 x 2.5 cm for gravimetric measurement. Carbon steel samples with dimension 1 x 2 cm were embedded in araldite with an exposed steel area of 1 cm² for potentiodynamic polarization and electrochemical impedance measurements. The specimens were polished successively using 400, 600 and 800 gritted emery papers, degreased by washing with ethanol, dried with acetone, and preserved in a desiccator before the corrosion tests. A 1 M HCl solution (test solution) was prepared using triple-distilled water and analar-grade (AR) HCl.

2.2. Preparation of LM extract

Fresh leaves of Leucas martinicensis (LM) were collected around “Otouke” river bank in Bayelsa state Nigeria, in the Month of August, 2019. The plant was identified and authenticated in the herbarium of the Department of Botany, University of Port Harcourt, Nigeria. The leaves were washed under running water, cut into small pieces, shade dried and powdered. Stock solution of the plant extract was prepared by boiling weighed amount of the dried and ground leaves of LM under reflux for 4 h in 1 M HCl. The resulting solution was cooled, filtered and stored. Inhibitor test solutions of the extract were prepared in the concentration range of 50 – 250 ppm.

2.3. Polarization and EIS measurements

A potentiostat/galvanostat Autolab 302N (Eco Chemie, Netherlands) supported by a frequency response analyzer FRA-2 and Nova 1.9 software was used for Potentiodynamic polarization and EIS tests. The electrolytic cell consists of three electrodes: the platinum foil acts as the counter electrode, the saturated calomel acts as the reference electrode and the carbon steel acts as the working electrode. The electrochemical tests order was EIS and afterward polarization technique. Before starting the experiments, a time interval of about 30 min is given for the system to reach a steady state and the open circuit potential is noted. Electrochemical impedance spectroscopy measurements were carried out under potentiostatic condition in a frequency range of 100 kHz to 0.01 Hz, with amplitude of 10 mV AC signal. The potentiodynamic curves were recorded by changing the electrode potential from -1.0 to 0.0 V versus SCE with scan rate of 1 mV s⁻¹.

2.4. Gravimetric measurements

After accurate weighing, the carbon steel coupons were dipped in a 150 mL beaker, which contained 100 mL of HCl with and without addition of different concentrations of LM, maintained at 303 K. The coupons were retrieved from their corroding solution after 4 h, washed with 1.0 M NaOH containing 4.0 g of Zinc dust, rinsed in acetone, dried in air and reweighed [5]. The corrosion rate (CR) was computed from the following equation:

\[
CR = \frac{8.76w}{DA\tau} \tag{1}
\]

where \(w\) is the average weight loss of carbon steel coupons, \(A\) represents the total surface area of one carbon steel coupon, \(\tau\) is the immersion time (4 h) and \(D\) is the density of carbon steel in g cm⁻³. From the corrosion rate, the surface coverage (\(\theta\)) and inhibition efficiency (\(%IE_{WL}\)) were determined using equations (2) and (3), respectively.

\[
\theta = \frac{CR^0 - CR^i}{CR^0} \tag{2}
\]

\[
%IE_{WL} = \theta \times 100 \tag{3}
\]

where \(CR^0\) and \(CR^i\) are the corrosion rates in the absence and presence of the inhibitor respectively.

2.5. SEM measurements

The surface analysis of the carbon steel coupons was conducted by immersion of the cleaned sample in 1 M HCl solution without and with 250 ppm LM inhibitor for 5 h and washing and drying the coupons. The corroded carbon steel surfaces were examined using a scanning electron microscope (SEM, JOEL, JSM-T20, Japan).

3. Results and Discussion

3.1. Polarization Measurements

Figure 1 illustrates the polarization curves of carbon steel in 1 M HCl solution without and with selected concentrations of Leucas martinicensis extract at 30°C. Essential corrosion parameters such as corrosion potential (\(E_{corr}\)), corrosion current density (\(I_{corr}\)) and anodic and cathodic Tafel slopes (\(\beta_a\) and \(\beta_c\) respectively) were calculated by linear extrapolation of the cathodic and anodic Tafel plots. The inhibition efficiency (%IE_{PDP}) was calculated from the \(I_{corr}\) values using equation 4 [15].

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\[ \% IE_{PDP} = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100 \quad (4) \]

were \( I_{corr}^0 \) represents the corrosion current density in the absence of inhibitor and \( I_{corr}^i \) is the corrosion current density at any particular concentration of inhibitor. The polarization parameters along with calculated \( % IE_{PDP} \) are presented in Table 1. It is apparent from the polarization curves and Table 1 that both anodic and cathodic currents of the corrosion reactions were reduced after the addition of the different concentrations of the inhibitor to the acidic solution. This action suggested that the LM extract may be classified as a mixed type inhibitor. Furthermore, the increase in LM concentration slightly shifted the values of \( E_{corr} \). The maximum shift in the value of \( E_{corr} \) in the present study was 49.3 mV which is less than 85 mV, confirming the suggestion that the studied LM inhibitor is a mixed type inhibitors, which implies the inhibitor reduce the anodic mild steel dissolution and also retard the cathodic hydrogen evolution reactions [16, 17]. Also, from Table 1, it is clear that the corrosion current density (\( I_{corr} \)) values decrease from 2.038 mA cm\(^{-2}\) to 0.101 mA cm\(^{-2}\) with the addition of various concentrations of LM, revealing that the inhibitor molecules protect the carbon steel from corrosion. The inhibition efficiency (\( % IE_{PDP} \)) values in Table 1 increase with increase in concentration of the studied inhibitor.

![Figure 1](https://journals.pen2print.org/index.php/ijr/)

**Figure 1.** Tafel polarization plots of carbon steel in 1 M HCl solution with various concentrations of LM.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>(-E_{corr}) (mV vs SCE)</th>
<th>(I_{corr}) (mA cm(^{-2}))</th>
<th>(b_a) (mV dec(^{-1}))</th>
<th>(b_c) (mV dec(^{-1}))</th>
<th>(IE_{PDP}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>495.4</td>
<td>2.038</td>
<td>139</td>
<td>156</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>528.3</td>
<td>0.943</td>
<td>94</td>
<td>116</td>
<td>53.8</td>
</tr>
<tr>
<td>150</td>
<td>527.5</td>
<td>0.528</td>
<td>105</td>
<td>119</td>
<td>74.1</td>
</tr>
<tr>
<td>250</td>
<td>544.7</td>
<td>0.101</td>
<td>91</td>
<td>98</td>
<td>95.0</td>
</tr>
</tbody>
</table>

### 3.2. EIS Measurements

The EIS measurements were performed on carbon steel in 1 M HCl without and with selected concentrations of LM. Nyquist impedance plots in the absence and presence of the inhibitor are presented in Figure 2. The EIS spectra in the absence and presence of LM show similar shapes suggesting that the studied inhibitor is controlling the corrosion reaction without modifying the mechanism of carbon steel [18]. The Nyquist plots show depressed semicircles, having one capacitive loop. This observation indicates that the corrosion of carbon steel was controlled by a charge transfer process. The diameter of semicircle increases with the increase of the investigated compounds concentration. The deviation of the capacitive loop from a complete semi-circle can be referred to the heterogeneity and micro-roughness of the working electrode surface [19, 20]. Figure 4 shows a one-time constant equivalent electrical circuit that is used for fitting the measured EIS data of a uniformly corroding electrode in an electrolyte [21]. The equivalent circuit consists of a solution resistance (\( R_s \)), a charge transfer resistance (\( R_{ct} \)) and a constant phase element (CPE). The CPE is introduced in the circuit instead of a pure double layer capacitor to give a more accurate fit [22]. The inhibition efficiency (\( % IE_{EIS} \)) was calculated from the \( R_{ct} \) values using the following relation:

\[ \% IE_{EIS} = \frac{R_{ct}^0 - R_{ct}^i}{R_{ct}^0} \times 100 \quad (5) \]

where \( R_{ct}^0 \) and \( R_{ct}^i \) are the charge transfer resistance in absence and presence of LM, respectively. The impedance of the CPE is expressed as:

\[ Z_{CPE} = \left( \frac{1}{Y_0} \right) \left[ (j\omega)^{-\alpha} \right] \quad (6) \]

where \( Y_0 \) is the amplitude comparable to a capacitance, \( j \) is the square root of –1, \( \omega \) is angular
frequency \((\omega = 2\pi f_{\text{max}})\) at which the imaginary part of the impedance \((-Z_{im})\) is maximal and \(f_{\text{max}}\) is AC frequency at maximum, \(n\) is the phase shift. The double layer capacitance \((C_{dl})\) can be calculated using the following equation [17, 23]:

\[
C_{\text{eff}} = Y_0\omega^{(n-1)} = \left(\frac{Y_0 R_{ct}}{R_{\text{ct}}^n}\right)^{\frac{1}{n}}
\]  

(7)

Various impedance parameters of the Nyquist plots are given in Table 2.

### Table 2. Electrochemical impedance parameters obtained from Nyquist plots of Leucas martinicensis

<table>
<thead>
<tr>
<th>Conc. of Inhibitor (ppm)</th>
<th>(R_s) (Ω cm(^2))</th>
<th>(R_{ct}) (Ω cm(^2))</th>
<th>(Y_{ct}) (μΩs(^2)/cm(^2))</th>
<th>(C_{dl}) (μF/cm(^2))</th>
<th>(n)</th>
<th>(\text{IE}_{\text{EIS}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.047</td>
<td>30.5</td>
<td>383.1</td>
<td>347.2</td>
<td>0.947</td>
<td>50.7</td>
</tr>
<tr>
<td>50</td>
<td>1.385</td>
<td>61.9</td>
<td>254.8</td>
<td>182.9</td>
<td>0.952</td>
<td>75.9</td>
</tr>
<tr>
<td>150</td>
<td>1.529</td>
<td>126.4</td>
<td>236.0</td>
<td>168.5</td>
<td>0.959</td>
<td>75.9</td>
</tr>
<tr>
<td>250</td>
<td>1.481</td>
<td>391.0</td>
<td>218.6</td>
<td>137.7</td>
<td>0.964</td>
<td>92.2</td>
</tr>
</tbody>
</table>

Figure 2: (a) Nyquist plots of corrosion inhibition of mild steel in 0.5 M HCl in the absence and presence of different concentrations of LM, (b) Equivalent Circuit Diagram.

Inspection of the results in Table 2 revealed that the addition of LM into the acid solution increased appreciably the value of charge transfer resistance \((R_{ct})\) and reduced the value of double layer capacitance \((C_{dl})\). This condition is due to the increasing of the surface coverage by the inhibitor, which can lead to higher inhibition efficiency. The corrosion inhibition efficiencies obtained from EIS results are in good agreement with those from potentiodynamic polarization curves.

### 3.3. Gravimetric Measurements

Figure 3 displayed the variation of corrosion rate against Leucas martinicensis (LM) concentration at different temperature. It is evident from the Figure, that corrosion rates of mild steel for the blank solution are higher than those obtained for solutions containing various concentrations of LM. The CR decreases with increase in the concentration of LM but increase with increasing temperature. These indicate that the rate of corrosion of mild steel increases with increase in temperature and that LM inhibited the corrosion of mild steel in 0.5 M HCl solution. The variation of inhibition efficiency of LM against inhibitor concentration for the corrosion of mild steel is given in Figure 4. From the results, it can be seen that the inhibition efficiency (%IE\(_{\text{EIS}}\)) increases with increasing concentration for LM in 0.5 M HCl and decreases with increase in temperature. This is an indication that the extract is effective in suppressing the corrosion on the surface of the metal and that the inhibition is concentration dependent.
where C is the concentration of LM, θ is the surface coverage and $K_{ads}$ is the adsorptive equilibrium constant [24]. Figure 5 show that a plot of $C/θ$ versus C yields a straight line with good correlation coefficient, which indicates that the plot obeys Langmuir adsorption isotherm.

$$\Delta G_{ads}^0 = -RT \ln (55.5K_{ads})$$  \hspace{1cm} (9)$$

where R is the gas constant (8.314 kJ/mol) and T is the absolute temperature. The value 55.5 is the concentration of water in solution in mol/L. The adsorption parameters from Langmuir adsorption isotherms are estimated and given in Table 3.

Table 3: Adsorption parameters deduced from Langmuir isotherm.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>$R^2$</th>
<th>Slope</th>
<th>$K_{ads}$ (ppm$^{-1}$)</th>
<th>$-\Delta G_{ads}^0$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>0.9984</td>
<td>0.9682</td>
<td>0.1058</td>
<td>29.01</td>
</tr>
<tr>
<td>313</td>
<td>0.9951</td>
<td>1.1092</td>
<td>0.0856</td>
<td>29.66</td>
</tr>
<tr>
<td>323</td>
<td>0.9907</td>
<td>1.0346</td>
<td>0.0791</td>
<td>30.14</td>
</tr>
</tbody>
</table>

Table 3 showed that the adsorption equilibrium constant ($K_{ads}$) values decreases with increasing temperature, which indicates that the inhibitor is easily and strongly adsorbed on to the mild steel.

3.4. Adsorption Consideration

Basic information on the interaction between the inhibitor and mild steel can be provided by the adsorption isotherm. The manner of adsorption (physisorption or chemisorption) is determined by the electronic structure of the metal, nature of the corrodent and the chemical nature of the inhibitor. The experimental data from gravimetric measurements were applied to different adsorption isotherm equations to fit the values of surface coverage (θ) to get an isotherm with highest regression coefficient ($R^2$). However, the Langmuir adsorption isotherm was found to be the most suitable, which could be presented as follows:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$  \hspace{1cm} (8)$$
The free energy of adsorption, $G_{ad}$, are negative and less than the threshold value of -40 kJ mol$^{-1}$, required for chemical adsorption, indicating that the adsorption of LM on mild steel surface is spontaneous and occurred according to the mechanism of physical adsorption [26].

### 3.5. Corrosion activation parameters

Temperature can affect mild steel corrosion in acidic media in the presence and absence of inhibitor. To calculate activation thermodynamic parameters of the corrosion reaction such as the apparent activation energy $E_a$, the entropy ($\Delta S^*$) and the enthalpy ($\Delta H^*$) of activation, Arrhenius equation and its alternative formulation called transition state equation were used [27]:

$$\log CR = \log A - \frac{E_a}{2.303RT}$$  \hspace{1cm} (10)

$$CR = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right)$$  \hspace{1cm} (11)

T is the absolute temperature, A is the pre-exponential factor and R is the universal gas constant, h is Planck’s constant, N is Avogadro’s number. A plot of log of corrosion rate obtained by weight loss measurement versus 1/T gave a straight line as shown in Figure 6 for mild steel in 0.5 M HCl in the presence of different concentrations of LM; the activation energy was calculated from the slope ($-E_a/R$). To obtain $\Delta H^*$ and $\Delta S^*$, log CR/T versus 1/T are plotted at different concentrations of LM corrosion inhibitor as displayed in Figure 7. Straight lines were obtained with a slope of $(\Delta H^*/2.303R)$ and an intercept of $[\log (R/Nh) + (\Delta S^*/2.303R)]$, from which the values of $\Delta H^*$ and $\Delta S^*$ were calculated. The corrosion activation parameters compiled in Table 3.

The presence of LM inhibitor increased the activation energies ($E_a$), indicating strong adsorption of the inhibitor molecules on the metal surface. In addition, the value of activation energy is around 40 to 80 kJ mol$^{-1}$ which can be suggested to obey the physical adsorption (physisorption) mechanism [28]. The positive values of activated enthalpy, $\Delta H^*$ means that the process is an endothermic process and it needs more energy to achieve the activated state or equilibrium state [29]. The values of change in activation entropy, $\Delta S^*$ in the presence of the inhibitor are large and negative indicating that the activated complex in the rate-determining step is associative in nature, and therefore, the activated complex has more orderly structure [29, 30].

### Table 4. Activation parameters for mild steel in 0.5 M HCl in the absence and presence of various concentrations of LM

<table>
<thead>
<tr>
<th>Conc. (ppm)</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H^*$ (kJ/mol)</th>
<th>$\Delta S^*$ (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>39.30</td>
<td>28.81</td>
<td>-264.32</td>
</tr>
<tr>
<td>50</td>
<td>41.55</td>
<td>35.29</td>
<td>-261.83</td>
</tr>
<tr>
<td>100</td>
<td>56.27</td>
<td>51.04</td>
<td>-283.50</td>
</tr>
<tr>
<td>150</td>
<td>63.73</td>
<td>58.58</td>
<td>-291.53</td>
</tr>
<tr>
<td>200</td>
<td>69.41</td>
<td>66.28</td>
<td>-301.08</td>
</tr>
<tr>
<td>250</td>
<td>75.82</td>
<td>72.52</td>
<td>-317.36</td>
</tr>
</tbody>
</table>

**Figure 6.** Arrhenius plots for the corrosion of mild steel in 0.5 M HCl without and with LM inhibitor.

**Figure 7.** Transition state plots for mild steel in 0.5 M HCl without and with LM inhibitor.

### 3.6. Scanning Electron Microscopy (SEM)

Scanning electron microscopy images were taken to justify that the corrosion inhibition behaviour of the studied LM is due to the formation of protective film on the mild steel surface. Figure 8 shows the SEM images of mild steel samples immersed in 0.5 M HCl without and with maximum concentration of
the studied inhibitor after 5 h immersion time. The surface of the mild steel specimen retrieved from the blank 0.5 M HCl solution (Figure 8a) suffered significant damage and marked with series of deep pits due to uninhibited acid corrosion. However, in the presence of the studied LM inhibitor (Figure 8b) the mild steel surface is smoother and protected, which confirms their inhibition action [31, 32].

![SEM images of (a) mild steel in 0.5 M HCl, (b) mild steel in 0.5 M HCl + 250 ppm LM](image)

Figure 8. SEM images of (a) mild steel in 0.5 M HCl, (b) mild steel in 0.5 M HCl + 250 ppm LM

4. Conclusion

Leave extract of *Leucas Martinicensis* (LM) have been investigated for its corrosion inhibition potentials on mild steel in 0.5 M HCl. The extract showed appreciable corrosion inhibition performances for mild steel in 0.5 M HCl solution and their inhibition efficiency increases with increasing concentrations of the inhibitor. The shift in $E_{corr}$ (≤85 mV) from potentiodynamic polarization studies showed that the studied extract is mixed-type inhibitor. EIS data revealed that the extract adsorbed on mild steel surface and exhibit non-ideal capacitive behaviour. The adsorption of LM on mild steel obeyed the Langmuir adsorption isotherm and occurred via physisorption mechanism. SEM images proved that the mild steel surface immersed in the aggressive media in the presence of LM is protected from direct acid attack.

5. References


