LEAVE EXTRACT OF Syzygium malaccense AS GREEN INHIBITOR OF MILD STEEL IN ACIDIC MEDIUM

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ABSTRACT
Corrosion inhibition of mild steel in 1N hydrochloric acid medium was investigated in the presence of Syzygium malaccense leaves extract (SMLE) as a green corrosion inhibitor. The inhibition effect of the extract was studied by weight-loss method, potentiodynamic polarization, Fourier transform infrared spectroscopy, x-ray diffraction and scanning electron microscopy. The inhibition efficiency increased with increasing inhibitor concentration and temperature. The temperature effect on inhibition process in 1N hydrochloric acid solution at temperature range 303 – 333 K. The results showed that the highest inhibition efficiency 88.11% was observed in the presence of 7 g/L SMLE in 1N hydrochloric acid solution at high temperature. The adsorption of SMLE was found to obey the Langmuir adsorption isotherm model. A mixed-type inhibitor of SMLE was confirmed from the potentiodynamic polarization. Thermodynamic and kinetic parameters were assessed on the corrosion and inhibition process.

Keywords: Green Corrosion Inhibitor, Syzygium malaccense, Mild Steel, Weight Loss, SEM, Isotherm Langmuir.

INTRODUCTION
Mild steel is commonly used in the construction of tanks, refinery equipment, pipelines, etc., due to its low cost and easy availability. However, mild steel also has disadvantages, such as it tends to be susceptible to corrosion. The use of inhibitors is one of the best methods of protecting metal from corrosion. It slows down the rate of metal corrosion when it is in a corrosive medium of suitable concentration. Synthetic organic compounds are often used as corrosion inhibitors, but most are toxic, not environmentally friendly, and expensive. The development of “green inhibitors” is currently increasingly attractive because these alternative corrosion inhibitors are non-toxic, cheap, renewable, and biodegradable. These green inhibitors are usually compounds containing atoms such as oxygen, nitrogen, sulfur atoms, and aromatic rings. The green inhibitors that have been studied are Xanthium strumarium leaf extract, Gnetum gnemon. L bark extract, neem leaf extract, and Mangifera odorata seed extract. This compound can protect corrosion by inhibiting the corrosion’s active side by adsorbing or forming a protective layer on the steel surface.

In the present work, Syzygium malaccense leaves extract (SMLE) was used as a corrosion inhibitor of mild steel in 1N hydrochloric acid medium. In a separate study, SMLE contains glycoside flavonoids such as myricetin 3-O-L-rhamnoside (myricitrin), myricetin 3-alpha L arabinofuranoside and myricetin 3'-glucoside is expected can decrease the rate of corrosion by formed complexes with steel and adsorb on the steel surface. The inhibition effect of the SMLE on the corrosion of mild steel in 1N hydrochloric acid medium was investigated using a weight-loss method, potentiodynamic polarization, Fourier transform infrared (FTIR) analysis, UV-Vis spectroscopy, x-ray diffraction (XRD) and scanning electron microscopy (SEM).

EXPERIMENTAL

Material and Methods
Preparation of Syzygium malaccense Leaves Extract
Syzygium malaccense leaves were dried and mashed by grinding, then weighed as much as 300 g. Samples were macerated with 1L methanol for three days. The extract obtained was filtered, and the solvent was...
evaporated using a rotary evaporator to obtain concentrated extract. The concentrated extract was weighed 2 g and diluted with distilled water into a 100 mL volumetric flask, then made in various concentrations.

**Preparation of Specimens**
Mild steel specimens were cut of 2.0 x 1.0 cm and a thickness of 1 mm containing 0.0149 P; 0.0715 Si; 0.001Ni; 0.141 Mn; 0.189 C; 0.019 Se; 0.0018 Cr, and remaining Fe. The specimens were then cleaned and mashed on the surface by using iron emery, rinsed with aquadest and acetone. After dried, the mild steels were weighed and kept in desiccators.

**Phytochemical Studies**
The SMLE phytochemical studies were carried out using the method described in the literature. The Frothing, Shinoda, and Braemer tests were used to identify saponins, flavonoids, and phenolics, respectively. Alkaloids were determined by the Dragendorf test, whereas steroids and terpenoids were examined by the Liebermann-Burchard test.

**Weight Loss Measurement**
The corrosion rate was determined based on the weight loss method by immersing steel in 50 mL of 1N HCl medium with various SMLE concentrations. Temperature variations done were 30°, 40°, 50°, and 60°C for 7 hours using a water bath. Then mild steels were cleaned, washed, and dried in the oven. After drying, they were weighed, and the weighing result is expressed as the final weight ($m_2$). The corrosion rate was determined using equation (1):

\[ C_R = \frac{m_1 - m_2}{A \times t} \]  

Where $A$ represents an area in cm$^2$ and $t$ is time in h. From the corrosion rate (CR) obtained, it can be determined the degree of coverage ($\theta$) and inhibition efficiency (IE) using equations (2) and (3):

\[ \theta = \frac{CR_0 - CR_1}{CR_0} \]  

\[ IE(\%) = \frac{CR_0 - CR_1}{CR_0} \times 100\% \]

Where $CR_0$ and $CR_1$ are the corrosion rates in the absence and presence of extract, IE is inhibition efficiency.

**Potentiodynamic Polarization Measurement**
Potentiodynamic polarization experiments were conducted using a potentiostat DAQ 466 with a three-electrode system. Mild steel is used as the working electrode (surface area 0.0221 cm$^2$ open), Ag / AgCl, and platinum (Pt) are used as reference and auxiliary electrodes. Potentiodynamic polarization measurements were carried out in 1N HCl medium containing various concentrations of inhibitors. Three electrodes were immersed in a container containing corrosive media without and in different inhibitor concentrations. The potential used is from -450 mV to -200 mV to obtain a potentiodynamic polarization curve. The inhibition efficiency (IE) is calculated using equation (4):

\[ IE(\%) = \frac{I_0 - I_1}{I_0} \times 100\% \]

$I_0$ and $I_1$ are current density values in the absence and presence of extract. They were calculated from the intersection of the cathodic and anodic Tafel lines.

**Fourier Transforms Infrared Measurement (FTIR)**
FTIR measurements were carried out by taking corrosion products attached to steel, which were immersed in 1N HCl medium without and in inhibitors. The corrosion product was then dried and analyzed by FTIR spectrophotometer (Nicolet IS10 FT-IR, Thermo Scientific).
Analysis of X-ray Diffraction (XRD)
Analysis of x-ray diffraction was performed on steels immersed for 6 days in the corrosive medium of 1N HCl without, and in the presence of 5 g/L SMLE, then the steel plate was dried and analyzed by XRD (ProAnalytical).

Analysis of Scanning Electron Microscopy (SEM)
The mild steel was dipped in 1N HCl without and in the presence of 5 g/L SMLE for 6 days. The mild steel was then dried and analyzed on the steel surface by SEM (HORIBA EMAX x-act).

RESULTS AND DISCUSSION
Phytochemical Analysis of SMLE
The phytochemical constituent of SMLE is shown in Table-1. The result indicates that SMLE contains several secondary metabolite compounds such as phenolic, steroids, alkaloids, flavonoids, and saponins. Some of the compounds contained in SMLE are thought to function as corrosion inhibitors.

Table-1: Phytochemical constituent of SMLE

<table>
<thead>
<tr>
<th>Phytochemical</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolics</td>
<td>+</td>
</tr>
<tr>
<td>Steroids</td>
<td>+</td>
</tr>
<tr>
<td>Alkaloids</td>
<td>+</td>
</tr>
<tr>
<td>Flavonoids</td>
<td>+</td>
</tr>
<tr>
<td>Saponins</td>
<td>+</td>
</tr>
<tr>
<td>Triterpenoids</td>
<td>-</td>
</tr>
</tbody>
</table>

Weight Loss Measurement
Corrosion Rate and Inhibition Efficiency
Corrosion rates and inhibition efficiency values can be calculated using weight loss data for various SMLE concentrations at different temperatures. Figure-1 shows a decrease in corrosion rate with increasing SMLE concentration and an increase in corrosion rate with increasing temperature with immersion time for 7 hours.
The decrease in corrosion rate shows a good inhibitory efficiency of SMLE in 1N HCl acid medium. This inhibitory effect is associated with the adsorption of extracts on the steel surface. Increased inhibition efficiency with increasing SMLE concentration shows that the inhibitory efficiency is increasing because more extracts are adsorbed with increasing concentration of inhibitors.

Fig.-1: Effect of SMLE Concentration on Corrosion Rate (CR) and Inhibition Efficiency (%IE) in 1N HCl for 7 hours with Different Temperature

Isotherm Adsorption and Thermodynamic Parameters
The adsorption isotherm method is one of the methods used to determine the inhibitors' interaction on the steel surface. The degree of surface coverage (θ) of various concentrations got from the measurement of weight loss is used to determine the isotherm that is most suitable for explaining the adsorption inhibitor
process. In this study, the good correlation coefficient obtained from the straight line between C/θ and C inhibitors was obtained using the Langmuir adsorption isotherm by the equation:

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]  

(5)

Where C is the inhibitor's concentration, K_{ads} is the adsorption equilibrium constant, and θ is the degree of surface coverage. The C/θ plot against C presents a straight line at different temperatures shown in Fig 2.

Some linear regression parameters between C/θ and C were calculated and displayed in Table 2, where the correlation coefficient (R^2) obtained is almost equal to 1. It indicates that this inhibitor follows the Langmuir adsorption isotherm in the corrosive medium 1N HCl.

The value of the equilibrium constant, K_{ads} was computed from the intercept of the straight line. The equilibrium constant associated with the energy of the free standard adsorption (ΔG_{ads}^o) can be calculated through by equation:

\[
(\Delta G_{ads}^o) = -RT \ln (C_{H_2O} \cdot K_{ads})
\]

(6)

Where C_{H_2O} is the concentration of water in solution in 1000 gL^{-1} and R is the gas constant. From Table 2, it can be found the (ΔG_{ads}^o) values were negative. The negative value of Gibbs energy (ΔG_{ads}^o) indicates spontaneous and stable the extracted layer is adsorbed on the steel surface.\(^{1,9-12}\). Generally, values of ΔG_{ads}^o around − 20 kJ/mol or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), whereas those around − 40 kJ/mol or higher involve charge sharing or transferring from molecules to the metal surface to form a coordinate type of bond. The calculated free energy values shown in Table xx are around -20 kJ/mol and are more negative which showed the adsorption of extracts that occur physisorption and chemisorption (mixed adsorption) and more towards chemisorption.\(^{1,9-12}\).

From the listed value of K_{ads} and (ΔG_{ads}^o) in Table-2, standard enthalpy (ΔH_{ads}^o) and entropy (ΔS_{ads}^o) of adsorption can be determined using the equation:

\[
\ln K_{ads} = -\frac{\Delta H_{ads}^o}{RT} + \frac{\Delta S_{ads}^o}{R} - \ln C_{H_2O}
\]

(7)

The value of ΔH_{ads}^o and ΔS_{ads}^o were assessed from the slope and intercept of the plot of lnK_{ads} versus 1/T (Fig.-3) and the results can be seen in Table-2. The positive value of ΔH_{ads}^o suggest that the adsorption of inhibitor molecules to the metal surface is an endothermic process. The positive value of ΔS_{ads}^o indicates a substitution process that is associated with an increase in solvent entropy wherein the increase in entropy is caused by adsorption of inhibitor molecules replaced more absorbed water molecules and desorption entropy.\(^{11,13}\)
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Thermodynamic Activation Parameters
Thermodynamic parameters such as activation energy (Eₐ), enthalpy of activation (ΔH*), and activation entropy (ΔS*) for mild steel corrosion in 1N HCl solution absence and presence of SMLE at 303-333K were calculated from the Arrhenius equation:

$$\ln \frac{C_R}{T} = -\frac{E_a}{R} + \ln A$$

(8)

Where Eₐ is the activation energy, CR is the corrosion rate, A is constant, T is the absolute temperature and R is the universal gas constant.

The positive values of ΔH* for SMLE suggest the endotherm nature of the mild steel corrosion process. Also, the negative values of ΔS* imply that the reaction was spontaneous and the activated complex in the reaction is unstable.

Table-3 indicates that the lower value of Eₐ with the addition of extracts. The decrease of Eₐ may be related to the chemisorption of the inhibitor on the mild steel surface. So it can reduce the rate of corrosion of mild steel in 1N HCl medium and the need for energy for the corrosion reaction is low. The enthalpy (ΔH*) and entropy (ΔS*) was obtained from the transition state equation:

$$\ln \frac{C_R}{T} = \ln \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S^*}{R} \right) - \frac{\Delta H^*}{RT}$$

(9)

The positive values of ΔH* for SMLE suggest the endotherm nature of the mild steel corrosion process. Also, the negative values of ΔS* imply that the reaction was spontaneous and the activated complex in the reaction is unstable.

Table-2: Adsorption Parameter of SMLE in 1N HCl on Mild Steel Surface

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>K_{ads} (Lg⁻¹)</th>
<th>ΔG_{ads} (kJ/mol)</th>
<th>ΔH_{ads} (kJ/mol)</th>
<th>ΔS_{ads} (J/mol)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>4.0747</td>
<td>-20.94</td>
<td>24.23</td>
<td>149.07</td>
<td>0.995</td>
</tr>
<tr>
<td>313</td>
<td>5.5279</td>
<td>-22.42</td>
<td>24.23</td>
<td>149.05</td>
<td>0.999</td>
</tr>
<tr>
<td>323</td>
<td>7.4053</td>
<td>-23.92</td>
<td>24.23</td>
<td>149.08</td>
<td>0.999</td>
</tr>
<tr>
<td>333</td>
<td>9.7664</td>
<td>-25.43</td>
<td>24.23</td>
<td>149.13</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Fig.-3: The Plot between ln K_{ads} and 1/T for Adsorption of SMLE on Mild Steel Surface

Fig.-4: Arrhenius Plots of SMLE at Different Concentrations in 1N HCl Medium
rate-determining step represents an association rather than a dissociation step and that the reaction was spontaneous\(^1,10\).

Table-3: Activation Parameters of Mild Steel in 1N HCl at Different Concentration

<table>
<thead>
<tr>
<th>SMLE Concentration (g/L)</th>
<th>(E_d) (kJ/mol)</th>
<th>(\Delta H^*) (kJ/mol)</th>
<th>(\Delta S^*) (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.44</td>
<td>58.80</td>
<td>-53.48</td>
</tr>
<tr>
<td>2</td>
<td>45.11</td>
<td>42.47</td>
<td>-116.49</td>
</tr>
<tr>
<td>3</td>
<td>43.57</td>
<td>40.93</td>
<td>-122.00</td>
</tr>
<tr>
<td>5</td>
<td>43.46</td>
<td>40.82</td>
<td>-122.79</td>
</tr>
<tr>
<td>6</td>
<td>43.31</td>
<td>40.67</td>
<td>-123.65</td>
</tr>
<tr>
<td>7</td>
<td>41.03</td>
<td>38.76</td>
<td>-130.79</td>
</tr>
</tbody>
</table>

**Potentiodynamic Polarization Studies**

Analysis of SMLE concentration’s effect on the polarization behavior of mild steel in 1N HCl was carried out, and Tafel plots were recorded for different inhibitor concentrations shown in Fig.-5. Electrochemical measurements are carried out to understand the reactions of anodic and cathodic kinetic processes. Potential starts ranged from -425 mV to -200 mV with a scan speed of 1 mV / s. Table-4 shows the parameters analyzed, namely corrosion current density (\(I_{corr}\)), corrosion potential (\(E_{corr}\)), anodic and cathodic Tafel slopes (\(\beta_a\) and \(\beta_c\)), and inhibition efficiency (% \(IE\)) were calculated by equation (4).\(^{15-17}\)

![Image of Tafel plot]

The corrosion potential \(E_{corr}\) values of SMLE shifted to anodic and cathodic directions. The inhibitor is classified as a cathodic or anodic inhibitor when the corrosion potential shift is more than 85 mV. The change in the \(E_{corr}\) with the presence of an extract of less than 85 mV, then it is indicated as a mixed type inhibitor. According to Table-4, it can be seen that SMLE means a mixed-type inhibitor and inhibits the rate of corrosion at anodic and cathodic simultaneously.\(^{16,18}\)

Table-4: Potentiodynamic Curve Polarization Parameters of SMLE on Mild Steel in 1N HCl Medium

<table>
<thead>
<tr>
<th>C (g/L)</th>
<th>(E_{corr}) (V)</th>
<th>(I_{corr} \times 10^{-2}) ((\mu)A/cm(^2))</th>
<th>(\beta_a) (V/dec)</th>
<th>(\beta_c) (V/dec)</th>
<th>% (IE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.295</td>
<td>4.74</td>
<td>6.666</td>
<td>-8.825</td>
<td>0.00</td>
</tr>
<tr>
<td>2</td>
<td>-0.280</td>
<td>0.76</td>
<td>9.354</td>
<td>-6.428</td>
<td>83.97</td>
</tr>
<tr>
<td>3</td>
<td>-0.290</td>
<td>0.67</td>
<td>9.032</td>
<td>-9.285</td>
<td>85.72</td>
</tr>
<tr>
<td>5</td>
<td>-0.300</td>
<td>0.63</td>
<td>8.750</td>
<td>-8.852</td>
<td>86.51</td>
</tr>
<tr>
<td>6</td>
<td>-0.304</td>
<td>0.54</td>
<td>9.602</td>
<td>-8.059</td>
<td>88.52</td>
</tr>
<tr>
<td>7</td>
<td>-0.310</td>
<td>0.53</td>
<td>8.673</td>
<td>-9.223</td>
<td>88.77</td>
</tr>
</tbody>
</table>

**Analysis of FTIR**

Analysis of FTIR aims to understand the possible interactions between the adsorbed compound and mild steel through the FTIR spectrum shift. Fig.-6(a) shows strong broadband at 3343.59 cm\(^{-1}\), attributed to O-
H stretching. The bands at 2928.24 cm\(^{-1}\), 1689.20 cm\(^{-1}\), and 1615.06 cm\(^{-1}\) are characteristic of C-H, C=O, and C=C stretching vibration. The band at 1363.42 cm\(^{-1}\) is assigned to C-O stretching vibration.\(^1\) In Fig.-6(b), the FTIR spectrum of product corrosion shows the stretching bands shifting to 3320.01 cm\(^{-1}\), 1621.28 cm\(^{-1}\), 1443.14 cm\(^{-1}\), and 1367 cm\(^{-1}\) for O-H, C-H, C=O, C=C, and C-O vibrations, respectively. This shift in the bands indicates an interaction between SMLE and steel, which forms a barrier layer on mild steel surfaces. This layer can reduce the corrosion rate of steel.\(^1\)

**X-ray Diffraction Analysis**

The X-ray diffraction method was used to characterize the protective layer formed on mild steel in the presence of SMLE. Figure-7 shows the XRD pattern on mild steel immersed in the test medium. The XRD pattern on the surface of mild steel immersed in 1N HCl medium is shown in Fig.-7(a). The peaks at 2\(\theta\) = 22.91°, 33.71°, 65.46°, and 82.74° indicate the presence of iron oxides such as Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\), and Fe. A peak at 2\(\theta\) = 45.16° with high intensity indicates a corrosion product showing a high corrosion rate.\(^9\) Figure-7 (b) shows the XRD pattern on mild steel 2\(\theta\) = 44.87°, 65.21°, 82.53° immersed in the test medium with 5 g/L SMLE. XRD patterns in SMLE presence show a decrease in peak intensity, indicating SMLE inhibitory action as a corrosion inhibitor.\(^9,21\) From this, it is clear that a protective film on the mild steel surface in the presence of SMLE has been formed.\(^22\)

**SEM Analysis**

The surface morphology of mild steel in 1 N HCl medium in the absence and presence of 5 g/L SMLE was examined using SEM. Fig.-8 (a) shows the surface morphology of untreated mild steel. It can be seen that the surface of mild steel is still smooth because mild steel has not interacted with 1N HCl. Fig.-8(b) is the surface morphology of mild steel immersed in 1N HCl for 7 days. The steel surface was damaged due to corrosion in 1N HCl medium. Fig.-8(c) shows the surface morphology of mild steel immersed in 1N HCl.
medium with the addition of 5 g / L SMLE. It can be seen that the morphology of mild steel is flatter and smoother than mild steel immersed in 1N HCl medium. The resulting flat surface is caused by the formation of a protective layer on the steel surface. This protective layer resists the attack of corrosive media against the steel surface.  

![Fig.-8: SEM Images of Unexposed and Exposed Mild Steel in 1N HCl in the Presence and Absence of Extracts](a) Unexposed Mild Steel, (b) 1N HCl (d) 1N HCl with 5 g/L SMLE.]

**CONCLUSION**

SMLE acts as green inhibitor corrosion for the corrosion of the mild steel in 1N HCl solution were studied. The inhibition efficiency increases with increasing SMLE concentration and temperature. The highest inhibition efficiency value of SMLE was 88.11% by the weight loss method. The adsorption of different concentrations of the extract on the surface of the obeyed Langmuir adsorption isotherm and adsorption is spontaneous. Polarization studies showed that SMLE acted as a mixed-type inhibitor. FTIR spectra provided evidence for adsorption inhibitor on the surface of the mild steel. XRD and SEM analysis confirmed protective film formation against acid attack.

**REFERENCES**