Research Article

Cuminum cyminum Extracts as Eco-Friendly Corrosion Inhibitor for Mild Steel in Seawater

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1. Introduction

Recently, plant extracts have again become important as an environmentally acceptable, readily available, and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. However, synergistic (and antagonistic) effects are often expected with these mixtures of inhibitors that may affect their inhibition efficiency. Several investigations have been reported using such economic plant extracts. El Hosary et al. [1] studied the corrosion inhibition of aluminium and zinc in 2 N HCl using naturally occurring Hibiscus sabdariffa (Karkade) extract. The inhibition of corrosion of steel, aluminium, and copper in HCl, H₂SO₄, and citric acid by molasses was also studied [2], and 83% and 13% inhibition efficiencies were obtained for HCl and H₂SO₄ solutions, respectively, containing 0.75% molasses. Loto reported the inhibitive action of Vernonia amygdaлина (bitter leaf) on the corrosion of mild steel in 0.5 M HCl at 28°C [3]. Arviri and Igbo studied the inhibitive action of V. amygdaлина on the corrosion of aluminium alloys in HCl and HNO₃ at concentrations of 0.2 and 0.4 g/L at 29°C [4]. They showed that the solution extract of the leaves serves as an excellent inhibitor. The inhibition effect of Zanthoxylum alatum plant extract on the corrosion of mild steel in 20%, 50%, and 88% aqueous orthophosphoric acid has been investigated by weight loss and electrochemical impedance spectroscopy (EIS). Plant extract was found to reduce the corrosion of steel more effectively in 88% than in 20% phosphoric acid [5]. An inhibition efficiency of 75.11% was observed with the extract of the leaves of Nypa fruticans Wurmb [6] for the corrosion of mild steel in hydrochloric acid solutions. El-Etre et al. examined some naturally occurring substances as corrosion inhibitors for different metals in various environments [7–11].

The application of extracts of henna, thyme, bgugaine, and irrini was investigated for their anticorrosion activity [12–15]. The effect of addition of bgugaine on steel corrosion in HCl is patented [16]. Saleh and El-Hosary studied the peel of pomegranate [17] and beetroot [18, 19] as corrosion inhibitor for mild steel in acid media. Sanghvi et al. have investigated the anticorrosion activity of Emblica officinalis, Terminalia chebula, Terminalia bolivia [20], Sapindus trifoliatus, and Acacia concinna [21]. Corrosion inhibition has also been studied for the extracts of Swertia angustifolia [22], Eucalyptus leaves [23], Eugenia jambolana [24], Pongamia
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total dissolved salts (mg/L)</td>
<td>8000 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>8.1</td>
</tr>
<tr>
<td>Calcium as Ca (mg/L)</td>
<td>160 ppm</td>
</tr>
<tr>
<td>Total hardness (CaCO₃ equivalent)</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Magnesium as Mg (mg/L)</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Sodium as Na (mg/L)</td>
<td>0</td>
</tr>
<tr>
<td>Chloride as Cl (mg/L)</td>
<td>17600 ppm</td>
</tr>
<tr>
<td>Sulphate as SO₄ (mg/L)</td>
<td>3254 ppm</td>
</tr>
</tbody>
</table>

2. Experimental

2.1. Preparation of Plant Extract of Jeera Extract. An aqueous plant extract was prepared by grinding 10 g of *Cuminum cyminum* extract, filtering, and making up to 100 using double distilled water.

2.2. Preparation of Specimens. Carbon steel specimens (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.

2.3. Weight Loss Method. Relevant data of seawater used in the study are given in Table 1.

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor for one day. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY 62. The corrosion products were cleaned with Clarke's solution [42]. The inhibition efficiency (IE) was then calculated using

\[
\text{IE} = 100 \left(1 - \frac{W_2}{W_1}\right)\% \tag{1}
\]

where \(W_1\) = corrosion rate in the absence of the inhibitor, and \(W_2\) = corrosion rate in the presence of the inhibitor.

2.4. Surface Examination. The carbon steel specimens were immersed in various test solutions for a period of one day, taken out, and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

2.4.1. FTIR Spectra. FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed and mixed thoroughly with KBr made in to pellets, and FTIR spectra were recorded.

The fluorescence spectra of the film formed on the CS samples recorded with a Hitachi F-4500 fluorescence spectrophotometer.

2.5. Potentiodynamic Polarization. A three-electrode cell consisting of mild steel as working electrode (WE), a platinum wire counter electrode (CE), and a saturated reference electrode was used for measurements. All the potential values reported here were VSSCE. The working electrode was mechanically polished on various grades of emery sheet, rinsed with double distilled water, and degreased with trichloroethylene. Potentiodynamic polarization curves were recorded using an H and CH electrochemical work station impedance analyzer model CHI 660A provided with iR compensation option. Polarization curve measurements were carried out at scan rate of 0.01 V s⁻¹. The exposed area (1 cm²) was mechanically polished with a series of emery sheets of variable grades. The samples were washed thoroughly with double distilled water before insertion in the cell. During the polarization study, the scan rate was 0.01 V s⁻¹, hold time at \(E_f\) was 0 s, and quiet time was 2 s.

2.6. AC Impedance Measurements. The instrument used for polarization was used for AC impedance study also. The cell set-up was the same as that had been used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms at various frequencies. The values of charge transfer resistance, \(R_{ct}\), and the double layer capacitance, \(C_{dl}\), were calculated. The equivalent electrical circuit diagram is shown in Figure 7.

3. Result and Discussion

3.1. Analysis of Results from Weight Loss Method. Table 2 shows the values of corrosion rates and inhibition efficiencies obtained from weight loss measurements of different concentrations of Jeera extract. 4 mL of the Jeera extract offered 93% corrosion inhibition efficiency to carbon steel immersed in 100 ml solution containing seawater. When the
Table 2: Corrosion rates (milligram per square decimeter per day) (Mdd) of carbon steel immersed in seawater in the presence and absence of inhibitors and the inhibition efficiencies (IE) obtained by mass loss method. Inhibitor: Jeera extracts (Cuminum cyminum). Period of immersion: 1 day.

<table>
<thead>
<tr>
<th>Jeera extract</th>
<th>CR/mdd</th>
<th>Inhibition efficiency IE%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.52</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>18.49</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>2.35</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>4.37</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>14.46</td>
<td>51</td>
</tr>
</tbody>
</table>

Concentration of Jeera extract was increased, the inhibition efficiency decreased, and the corrosion rate increased, and this is due to the fact that when higher concentrations of Jeera extract are added, the protective film (Fe$^{2+}$ - Cuminum cyminum complex) formed on the metal surface goes into the 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 [43].

3.2. Analysis of Polarization Curves. A polarization study has been used to detect the formation of protective film on the metal surface [44]. When a protective film formed on the metal surface, the linear polarization resistance (LPR) increases, and the corrosion current ($I_{corr}$) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solution are shown in Figure 1. The curves show the effects of different inhibitors on the corrosion behavior of carbon steel. The inhibition efficiencies (IE) obtained by the mass loss method are given in Table 1. The inhibition efficiency increases with the concentration of the inhibitor. The LPR value increases from 51.67 $\times$ 10$^{-2}$ to 63.67 $\times$ 10$^{-2}$ ohm cm$^2$. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 7.963 $\times$ 10$^{-6}$ to 6.295 $\times$ 10$^{-6}$ Acm$^2$ [45, 46].

3.3. Analysis of Ac Impedance Spectra. AC impedance spectra have been used to detect the formation of the film formed on the metal surface. If the protective film is formed, the charge transfer resistance increases, and double layer capacitance value decreases [40]. The AC impedance spectra of carbon steel immersed in various solutions are shown in Figure 2 (Nyquist) and Figure 3 (impedance-Bode plots). The AC impedance parameter, namely, charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$) are given in Table 4.

When carbon steel is immersed in aqueous solution containing seawater, the $R_{ct}$ value is 88 ohm cm$^2$, and $C_{dl}$ value is 1.027 $\times$ 10$^{-7}$ F/cm$^2$. When 4 ml of (Cuminum cyminum) extract is added, the $R_{ct}$ value increases from 88 ohm cm$^2$ to 116 ohm cm$^2$, and $C_{dl}$ value decreases from 1.027 $\times$ 10$^{-7}$ F/cm$^2$ to 0.7817 $\times$ 10$^{-8}$. This suggest that a protective film is formed on the metal surface of the metal. Further there is increase in impedance log (Z/ohm), value from 2.02 to 2.12 (derived from Bode plot shown in Figure 3).

3.4. Fourier Transfer-Infrared Spectra. The main constituent of Jeera extract is cuminaldehyde [47]. The structure of cuminaldehyde is shown in Scheme 1. It contain carboxylic group, cumin structure.

The Cuminum cyminum extract was evaporated to dryness to a solid mass. Its FTIR spectrum is shown in Figure 4(a). $\nu$-C=C stretching frequency appeared at 2141 cm$^{-1}$.
Table 3: Corrosion parameters of carbon steel immersed in seawater in the absence and presence of inhibitors.

<table>
<thead>
<tr>
<th>System</th>
<th>$E_{corr}$ mV versus SCE</th>
<th>$b_1$ mV/decade</th>
<th>$b_2$ mV/decade</th>
<th>$LPR$ Ohm cm$^2$</th>
<th>$I_{corr}$ A/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>−926</td>
<td>152</td>
<td>236</td>
<td>$65.32 \times 10^{-2}$</td>
<td>$6.164 \times 10^{-6}$</td>
</tr>
<tr>
<td>Seawater + (Cuminum cyminum) extract (4 mL)</td>
<td>−883</td>
<td>153</td>
<td>247</td>
<td>$51.67 \times 10^{-2}$</td>
<td>$0.7963 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 4: AC impedance parameters of carbon steel immersed in various solutions. Inhibitors: Jeera extract.

<table>
<thead>
<tr>
<th>System</th>
<th>$R_{ct}$ ohm cm$^2$</th>
<th>$C_{dl}$ F/cm$^2$</th>
<th>Impedance value log (Z/ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater</td>
<td>88</td>
<td>$1.027 \times 10^{-7}$</td>
<td>2.02</td>
</tr>
<tr>
<td>CC (4 mL) + Seawater</td>
<td>128</td>
<td>$7.0703 \times 10^{-9}$</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Figure 3: Bode plot of carbon steel immersed in various solutions (Bode plots). (a) Seawater, (b) Seawater + 4 ml Jeera extract.

Figure 4: FTIR spectra. (a) Aqueous solution of Jeera extract, (b) Aqueous solution of seawater + Jeera extract 4 mL.
The aromatic –CH stretching frequency appeared at 2927 cm\(^{-1}\), –C=O stretching frequency appeared at 1607 cm\(^{-1}\) [48, 49].

The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the aqueous solution containing seawater and Seawater containing 4 mL of Jeera extract is shown in Figure 4(b). –OH stretching frequency appeared at 3402 cm\(^{-1}\) to 3435 cm\(^{-1}\). –C=C stretching frequency appeared at 2141 cm\(^{-1}\) to 2091 cm\(^{-1}\). The aromatic –CH stretching frequency appeared at 2927 cm\(^{-1}\) to 2923 cm\(^{-1}\). –C=O stretching frequency appeared at 1607 cm\(^{-1}\) to 1638 cm\(^{-1}\).

3.5. Fluorescence Spectra. The UV-visible adsorption spectrum of aqueous solution of Cuminum cyminum and Fe\(^{2+}\) is shown in Figure 5. Peaks appear at 228 nm, 268 nm. When the Fe\(^{2+}\) is added to the aqueous solution of Cuminum cyminum, peak appears at 225 nm and 265 nm [46].

The fluorescence spectrum (\(\lambda_{ex} = 225\) nm) of an aqueous solution of Fe\(^{2+}\)-Cuminum cyminum is shown in Figure 6(a). A peak appears at 252 nm. This due to that Fe\(^{2+}\)-active principle complex is formed in solution [40].

The fluorescence spectrum (\(\lambda_{ex} = 225\) nm) of the film formed on the surface of the metal after immersion in the solution containing seawater and 4 mL of Cuminum cyminum extract is shown in Figure 6(b). The peaks appeared at 252 nm confirming the presence of Fe\(^{2+}\)-Cuminum cyminum extract complex formed on the metal surface.

4. Conclusion

The corrosion inhibition by aqueous solution of Jeera extract in the presence and absence of inhibitor was studied by weight-loss study and electrochemical measurements. The results show that inhibitor has the ability of reducing the corrosion rate of carbon steel in aqueous solution containing Jeera extract, and it acts as an anodic inhibitor. This effectiveness is confirmed by electrochemical impedance spectra and potential polarization analysis.

Acknowledgment

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References


