Coriandrum sativum leaves extract (CSL) as an eco-friendly green inhibitor for corrosion of carbon steel in acidic media

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Abstract
The inhibition efficiency of coriandrum sativum leaves extract (CSL) have been studied as an eco-friendly green inhibitor for corrosion of carbon steel in 1 M HCl and 0.5 M H2SO4 solutions using the potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), weight loss techniques and scanning electron microscopy analysis. The inhibition efficiency increased with the increase of the concentration of the extract and decreased with the increase in temperature. The results obtained showed that CSL extract inhibited the corrosion process by a physical adsorption mechanism that followed the Langmuir adsorption isotherm model. The adsorption thermodynamic parameters that were calculated include, free energy of adsorption (ΔG° ads), enthalpy of adsorption (ΔH° ads), and entropy of adsorption (ΔS° ads) revealed that the adsorption process are spontaneous and exothermic. All the results show that the CSL extract can act as an inhibitor for the corrosion of carbon steel in the acidic medium.

Keywords: Carbon steel, Hydrochloric acid, Corrosion inhibition, coriandrum sativum leaves, Adsorption.

1. Introduction:
The study of corrosion inhibition of carbon steel using inhibitors in acidic media, particularly hydrochloric acid and sulfuric acid, is one of the most important topics that study corrosion resulting from chemical cleaning and descaling in different industries. The dangerous effects known for most industrial corrosion inhibitor is the motivation for the use of natural products, which are non-toxic, biodegradable and readily available and renewable source as needed. There are several studies that illustrated the efficiency of some natural products as inhibitors to corrosion, and the study was performed on several metals and alloys in the acidic media. Recent studies have focused on the use of environmentally friendly inhibitors, specially plant extracts such as seed extract, root extracts, peel extract, Juice extract, leaves extract [1].

Many studies have proven the efficiency of plant extracts as corrosion inhibitors for carbon steel, such as Petroselinum Crispum (Parsley), Eruca Sativa (Arugula) and Anethum Graveolens (Dill) extracts [2,3], Actinidia delicosa (Kiwi fruit) [4], Cucumis sativus peel extract [5].

Few investigation has focused on the study of the efficiency of coriandrum sativum seeds extract [6], and there are no previous studies indicate the use of coriandrum sativum leaves extract in the carbon steel corrosion inhibition in acidic medium.

In this study, electrochemical measurements and weight loss method were used to study the coriandrum sativum leaves extract efficiency as corrosion inhibition for carbon steel in both 1 M HCl and 0.5 M H2SO4 acid.
2. Materials and Methods

2.1. Specimen preparation:
Tests were performed on SABIC carbon steel specimens with the following composition (in wt. %) C 0.143%, Mn 0.897%, Si 0.004%, P 0.008%, Cr 0.009%, Cu 0.003%, V 0.004%, Ni 0.011%, Ti 0.001%, Al 0.044%, Nb 0.011%, Ca 0.003%, N 0.003%, Mo 0.001%, Sn 0.0001%, CEQ 0.296%, Tres 0.024%, and Fe balance. Carbon steel circular strips of the same composition with an exposed area of 1 cm$^2$ were used. Before each test, the specimens were ground with 800 and 1200 grit grinding papers, cleaned by distilled water and acetone.

2.2. Preparation of plant extract:
CSL dried in an electric furnace for 10 – 20 min at 50°C then ground to powder. CSL dried powder (5 g) were mixed with 500 ml of test solutions 1 M HCl and 0.5 M H$_2$SO$_4$, and refluxed at 50°C for 2 h. The extracts were left to cool-down, and were then filtered using Whatman filter paper. The filtrate (35% (wt.%)) was then kept as the stock solution. Working solutions of different concentrations ranging from 20 to 60 % (v/v) were prepared from the stock solutions by dilution with 1 M HCl and 0.5 M H$_2$SO$_4$ solutions.

2.3. Fourier transform infrared spectroscopy (FT-IR):
A KBr pellet was made from the dried extract and was characterized using FT-IR (Nicolet's auxiliary experiment module - AEM, Omnic software).

2.4. Electrochemical measurements:
Electrochemical measurements were carried out using ACM instruments model 1783. The electrochemical cell consisted of a conventional three-electrode configuration with graphite as the counter electrode and a saturated calomel electrode (SCE) coupled with a Luggin-Haber capillary as the reference electrode. The tip of the Luggin capillary was placed very close to the surface of the working electrode in order to minimize the ohmic contribution. The working electrode was cut from a carbon steel rod with a cross-sectional area of one cm$^2$ and embedded in a Teflon holder. It was immersed in test solutions of 1 M HCl and 0.5 M H$_2$SO$_4$ with and without 20, 30, 40, 50, 60% of the inhibitor at 25°C, the open circuit potential was measured after 10 minutes to attain a steady state.

2.4.1. Potentiodynamic polarization measurements:
In Potentiodynamic polarization studies, the polarization curves performed with a scan rate of 0.2 mVs$^{-1}$ in the potential range of ± 250 mV with respect to the potential of corrosion. All the potentials recorded with respect to the SCE. Then, corrosion current density (I$_{corr}$) is determined from the intercept of extrapolated cathodic and anodic Tafel slopes. The inhibition efficiency (E$_{inh}$ %) are calculated using Eq. 1:

$$E_{inh} \% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (1)$$

Where I$_{corr}$ and I$_{corr(inh)}$ are referred to as the corrosion current density without and with inhibitor, respectively.

2.4.2. Electrochemical impedance spectroscopy:
EIS measurements performed at corrosion potentials, E$_{corr}$, over a frequency range of 10 kHz to 10 MHz with an AC signal amplitude perturbation of 10 mV peak to peak. The inhibition efficiency (E$_{inh}$ %), are calculated using Eq. 2:

$$E_{inh} \% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (2)$$

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Where $R_{ct}$ and $R_{ct(inh)}$ referred to as the charge transfer resistance without and with the addition of the inhibitor, respectively.

2.5. Gravimetric (weight loss) method
In the gravimetric experiment, a previously weighed carbon steel specimens was completely immersed in 100 mL of 1 M HCl and 0.5 M H$_2$SO$_4$ solutions with and without the inhibitor for a period of 3 h. Then, the specimens were washed, dried and weighed. The weight loss was calculated. The experiments were repeated at different concentrations of inhibitor (20 - 60%) at 25°C and 60°C. From the weight loss results, corrosion rates (C.R), degree of surface coverage ($\theta$), and the inhibition efficiency ($E_{inh\%}$) of the inhibitor were calculated using Eq. (3)–(5), respectively [3]:

\[
C.R = \frac{W}{At} \quad (3)
\]

\[
\theta = \frac{W_o - W_{inh}}{W_o} \quad (4)
\]

\[
E_{inh\%} = \frac{W_o - W_{inh}}{W_o} \times 100 \quad (5)
\]

where $A$ is the area of the carbon steel specimens (in cm$^2$), $t$ is the immersion time (in hours) and $W$ is the weight loss of carbon steel after time, $t$, $W_o$ and $W_{inh}$ are the weight losses (mg) for carbon steel.

2.6. Scanning electron microscope (SEM):
Scanning microscopy was performed using a JSM-6380 LA model scanning electron microscope with a high resolution of 3.0nm and an accelerating voltage of 0.5 to 30 kV for carbon steel surface after immersion in 1 M HCl in the absence and presence of 50% of CSL extracts for 3 h at room temperature.

3. Results and Discussion
3.1. FTIR results of CSL extracts:
The important IR absorption bands of inhibitors are in Fig. 1 and their respective FT-IR peaks are in Table 1. These results showed that the inhibitors containing functional groups with O and N atoms and other attached to aromatic ring, which are commonly gathered in corrosion inhibitors [2,5].

![Figure 1. FTIR spectra of CSL extracts.](image)

3.2. Potentiodynamic polarization
The polarization curves for carbon steel in 1M HCl and 0.5 M H$_2$SO$_4$ solution without and with different concentrations (20% – 60%) of CSL at 25°C are shown in Figs. 2. The electrochemical parameters, anodic
Tafel constant ($\beta_a$), cathodic Tafel constant ($\beta_c$), corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), and the corresponding inhibition efficiencies are illustrated in Table 2.

**Table 1. FT-IR peaks of CSL extract.**

<table>
<thead>
<tr>
<th>Peaks from FT-IR spectra</th>
<th>Possible functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>403.20</td>
<td>C–C (aliphatic)</td>
</tr>
<tr>
<td>617.89</td>
<td>–C=C stretch</td>
</tr>
<tr>
<td>1068.10</td>
<td>P–O–C stretch</td>
</tr>
<tr>
<td>1247.46</td>
<td>O–SO$_2$–O</td>
</tr>
<tr>
<td>1411.10</td>
<td>X–SO$_2$–X</td>
</tr>
<tr>
<td>1614.22</td>
<td>C=N stretch</td>
</tr>
<tr>
<td>2927.20</td>
<td>C–H (aromatic)</td>
</tr>
<tr>
<td>3339.39</td>
<td>N–H stretch</td>
</tr>
</tbody>
</table>

Figs. 2 showed affected of both anodic and cathodic reactions in the presence of different concentrations of CSL extract, the cathodic appeared to be more pronounced and the corrosion current densities of the additives decreased significantly compared to the blank. It is clear from Table 2 that the Tafel slopes of the anodic ($\beta_a$) and cathodic ($\beta_c$) are significantly changed in the presence of CSL as result of adsorption the molecules of inhibitor. The corrosion process decrease as a result to both metallic dissolution and hydrogen evolution at the metal surface [8] which can be explained by the adsorption of organic compounds such as heteroatoms (oxygen, sulfur, phosphorus and nitrogen) found in CSL at the carbon steel surface. Those aromatic rings or multiple bonds, found in organic compound acted as mixed type inhibitor [7], and the inhibition is due to geometric blocking mechanism.

![Figure 2](image_url)

**Figure 2.** Polarization curves for carbon Steel in (a) 1 M HCl (b) 0.5 M H$_2$SO$_4$ with and without 20%, 30%, 40%, 50% and 60% of CSL extract at 25°C.

The result in 1 M HCl solution containing 60% of CSL at 25°C indicate decrease of the corrosion current density of carbon steel from 3.24 mA/cm$^2$ to 0.48 mA/cm$^2$ and increase in the corrosion inhibition efficiency to 85.19%, similar results have been obtained in 0.5 H$_2$SO$_4$ and this behavior is due to the good coverage of the metal surface by CSL molecules that block the active sites on the metal surface [5].
From the results, it is clear that the CSL extract was good inhibitor for carbon steel corrosion in both 1 M HCl and 0.5 M H₂SO₄ solutions.

Table 2. Electrochemical parameters for Carbon Steel in (a) 1M HCl (b) 0.5 M H₂SO₄ with and without 20, 30, 40, 50% and 60% of CSL extract at 25ºC.

<table>
<thead>
<tr>
<th>Inhibitor CSL in</th>
<th>Concentration (v/v)%</th>
<th>E_{corr} (mV)</th>
<th>β_{a} (mV)</th>
<th>β_{c} (mV)</th>
<th>I_{corr} (mA cm⁻²)</th>
<th>C_rate (mm/year)</th>
<th>E_{inh} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCl</td>
<td>0</td>
<td>-555.08</td>
<td>131.31</td>
<td>149.12</td>
<td>3.24</td>
<td>37.28</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-525.77</td>
<td>120.30</td>
<td>119.23</td>
<td>0.66</td>
<td>7.61</td>
<td>79.63</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-524.07</td>
<td>112.88</td>
<td>116.51</td>
<td>0.65</td>
<td>7.57</td>
<td>79.94</td>
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<tr>
<td></td>
<td>40</td>
<td>-523.38</td>
<td>104.81</td>
<td>116.00</td>
<td>0.64</td>
<td>7.41</td>
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</tr>
<tr>
<td></td>
<td>50</td>
<td>-519.56</td>
<td>111.03</td>
<td>119.75</td>
<td>0.59</td>
<td>6.81</td>
<td>81.79</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-524.3</td>
<td>115.38</td>
<td>116.74</td>
<td>0.48</td>
<td>5.53</td>
<td>85.19</td>
</tr>
<tr>
<td>0.5 M H₂SO₄</td>
<td>0</td>
<td>-560.00</td>
<td>115.8</td>
<td>135.97</td>
<td>16.17</td>
<td>116.63</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-527.70</td>
<td>76.69</td>
<td>119.28</td>
<td>4.51</td>
<td>51.86</td>
<td>72.11</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>-522.62</td>
<td>73.72</td>
<td>124.45</td>
<td>3.76</td>
<td>43.28</td>
<td>76.75</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-519.88</td>
<td>65.9</td>
<td>123.51</td>
<td>3.46</td>
<td>39.79</td>
<td>78.60</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-516.27</td>
<td>67.95</td>
<td>118.34</td>
<td>2.89</td>
<td>33.25</td>
<td>82.13</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-516.22</td>
<td>74.58</td>
<td>120.89</td>
<td>2.58</td>
<td>29.69</td>
<td>84.04</td>
</tr>
</tbody>
</table>

3.3. Electrochemical impedance spectroscopy (EIS)

The effect of CSL extract concentration in the Nyquist plots for carbon steel in 1 M HCl, and in 0.5 M H₂SO₄ at 25ºC is shown in Figs. 3. Most of the impedance spectra obtained for the corrosion of carbon steel in 1 M HCl and 0.5 M H₂SO₄ solutions with the inhibitor consist of two capacitive loops, with their centers at the real axis and their diameters increase with the increase of the inhibitor concentration, which indicates that the surface covered by CSL increases with the increase of CSL concentration. The presence of two capacitive loops may be attributed to the relaxation process obtained by adsorption species like Cl⁻_{ads}, SO₄²⁻_{ads} and H⁺_{ads} on the electrode surface. It may also be caused by adsorption of inhibitor on the electrode surface or by the re-dissolution of the passivated surface at low frequencies. In other words, the inductive behavior at low frequency is probably due to the adsorption of the products of the corrosion on the electrode surface (for example, [FeOH]_{ads} and [FeH]_{ads}) [9], all parameters were obtained from the high capacitive loops. This is manifested in the increase in R_{ct} values and with a simultaneous decrease in the values of C_{dl} (Table 3). The increase in double layer thickness resulted in the decrease in C_{dl} that will lead to decrease in dielectric constant as a result of displacing the adsorbed water molecules and adsorption of extract (organic matter) on to the surface of the carbon steel. These results suggest that the resistance increased in the charge transfer process at the electrode–electrolyte interface due to the formation of a protective layer on the metal surface due to adsorption of inhibitor molecules [10], thus isolating the metal from the corrosive ions attack present in the solution.

Following both the polarization and EIS studies, it was observed that inhibition efficiency increased with the increase in the concentration of CSL (Tables 2 and 3) reaching the maximum values of 85.62% and 83.05% at 60% CSL extract in 1 M HCl and 0.5 M H₂SO₄, respectively, due to the increase of the adsorption of inhibitor molecules at the active sites on the carbon steel surface under such condition. The efficiency of CSL was good compared to the previous studies like Cucumis sativus peel extract [5], Coffee Ground extracts [11], Watermelon Rind extract [12] and Pipali (Piper longum) Fruit Extract [13].
3.4. Gravimetric (weight loss) method
The inhibition efficiency of carbon steel in the absence and presence different concentrations of CSL extract in 1 M HCl and 0.5 M H₂SO₄ were studied at two different temperatures (25, 60°C) during 3 h of immersion. The results indicate that the corrosion rate of carbon steel has decreased with the increase of inhibitors concentration. The values of corrosion rates (C.R), and the inhibition efficiency (E_{inh}%) obtained from the weight loss for different inhibitor concentrations at two different temperatures in 1 M HCl and 0.5 M H₂SO₄ are given in Table 4. It is obvious that there is a decrease in the corrosion rate of carbon steel proportion with the increase in concentration of CSL. This indicates that the CSL in the solution inhibits the corrosion of carbon steel in both acids and that the extent of corrosion inhibition depends on the amount of CSL present. From Fig. 4, it is clear that inhibition efficiency increased with increasing the inhibitor concentration, and decreased at higher temperatures. The maximum value of inhibition efficiency (E_{inh}%) was obtained for 60% of CSL is 85.90% in 1 M HCl and 84.56% in 0.5 M H₂SO₄ at 25°C. Due to the complex compounds or high phytochemical constituents of CSL, it is difficult to assign the inhibiting action to a particular constituent or group of
constituents. The inhibitor molecules present in the extract block the surface of carbon steel via adsorption mechanism [14]. While the decrease in inhibition efficiency due to the increased rate of dissolution of carbon steel and partial desorption of the inhibitor from the metal surface with temperature [15,16]. On other hand, the decrease in inhibition efficiency with the increase in temperatures, reveals physical adsorption mechanism (physisorption) and may be due to increase in solubility of the protective film formed rapidly on carbon steel surface, which is believed to inhibit the process of corrosion [17].

![Figure 4](image_url)

**Figure 4.** Effect of CSL extract concentrations on inhibition efficiency (E\textsubscript{inh}%). for carbon Steel in (a) 1M HCl (b) 0.5 M H\textsubscript{2}SO\textsubscript{4} at 25\textdegree C and 60\textdegree C.

**Table 4:** The values of C.R, and E\textsubscript{inh}% for different inhibitor concentrations at 25\textdegree C, and 60\textdegree C in acidic media.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>25\textdegree C</th>
<th>60\textdegree C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acidic medium</strong></td>
<td><strong>Concentration (v/v)%</strong></td>
<td><strong>Corrosion Rates (C.R mg/cm\textsuperscript{2}.h)</strong></td>
</tr>
<tr>
<td>1 M HCl</td>
<td>Blank</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.12</td>
</tr>
<tr>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
<td>Blank</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.23</td>
</tr>
</tbody>
</table>

3.5. Adsorption Isotherms and thermodynamic parameters

The mode and extent of the interaction between the CSL inhibitors and the carbon steel surfaces were investigated by applying adsorption isotherms. The Langmuir, Freundlich, and Temkin approach were used to determine the adsorption mechanisms of the inhibition reaction. The isotherms were best described by the adsorption behavior of the CSL extracts on the surface of carbon steel. Langmuir adsorption isotherm can be expressed according to Eq. 6 [18-20]:

\[
\frac{C}{C_0} = \frac{1}{q_{\text{m}}} + \frac{1}{q_{\text{m}}}Kc
\]
\[
\theta = \frac{K_{ads} C_{inh}}{1 + K_{ads} C_{inh}} \quad (6)
\]
where \(C_{inh}\) is the inhibitor concentration, \(K_{ads}\) is the adsorption equilibrium constant. Rearranging this Eq. 6 gives Eq. 7:

\[
\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (7)
\]

The linear variation of \(C_{inh}/\theta\) vs. \(C_{inh}\) of the CSL in 1 M HCl and 0.5 M H\(_2\)SO\(_4\) solutions showed that the adsorption is well fitted by the Langmuir adsorption isotherm (Figs. 5. A), the slope and \(R^2\) presented in Table 5.

**Figure 5:** Langmuir (A), Freundlich (B), Temkin (C) isotherms for the adsorption of CSL extract on the surface of the carbon steel.
The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient (the degree of compatibility between the experimental data and the isotherm equation) at different temperatures. The $R^2$ values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm [21].

Freundlich adsorption isotherm is given by Eq. 8:

$$\theta = K_{ads} C_{inh}^{1/n} \quad (8)$$

and the linearized version by Eq. 9:

$$\ln \theta = \ln K_{ads} + \frac{1}{n} \ln C_{inh} \quad (9)$$

where $n$ is the measure adsorption intensity. Values of $\ln \theta$ are plotted against $\ln C_{inh}$ (Fig. 5. B). The slope and $R^2$ data are presented in Table 3. From the slope of the Freundlich plot, $1/n$ is above 1, which indicates that it is cooperative adsorption.

Temkin adsorption isotherm assumes a uniform distribution of adsorption energy that increases with the increase in the surface coverage. This is given by Eq. 10:

$$\theta = \frac{1}{f} \ln K_{ads} + \frac{1}{f} \ln C_{inh} \quad (10)$$

where $f$ determines the adsorbent-adsorbates interaction. However, the plot of surface coverage $\theta$ against the natural logarithm of the concentration of the extract, $\ln C_{inh}$, is shown in Fig. 5. C, the slope and $R^2$ are presented in Table 3.

From the Langmuir, Freundlich and Temkin isotherms in Table 5, the degrees of linearity $R^2$ were also close to unity indicating that the CSL extracts were strongly adsorbed on the surface of the carbon steel.

From the intercept of straight lines, $K_{ads}$ values can be obtained and related to the free energy of adsorption, $\Delta G^\circ_{ads}$ by Eq. 11

$$\Delta G^\circ_{ads} = - R T \ln (55.5K_{ads}) \quad (11)$$

where $R$ is the universal gas constant, $T$ is the absolute temperature and 55.5 is the molar heat of adsorption of water. Results obtained show that the values of $\Delta G^\circ_{ads}$ are negative in all cases, which indicate that the reaction is spontaneous [17], and that the CSL extracts are strongly adsorbed on the carbon steel surface. The values of $\Delta G^\circ_{ads}$ are less negative than -20 kJ/mol in the Langmuir and Freundlich isotherms, which means physical adsorption occurred on the surface of carbon steel in both 1 M HCl and 0.5 M H$_2$SO$_4$ acids, while it were more negative than -20 kJ/mol in the Temkin isotherm, that means the both physical adsorption and chemical adsorption (mixed adsorption) occurred on the surface of carbon steel in both 1 M HCl and 0.5 M H$_2$SO$_4$ acids.

Generally, the values of $\Delta G^\circ_{ads}$ of up to -20 kJ/mol are consistent with electrostatic interaction between charged inhibitor molecules and the carbon steel surface (physical adsorption) and those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecule to carbon steel surface to form a coordinate bond (chemisorption).

The Langmuir, Freundlich, and Temkin isotherms being followed confirmed a mixed adsorption mechanism owing to the spontaneity of the process. Thus, the CSL extract can be used to inhibit the carbon steel corrosion in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions.

The enthalpy of adsorption ($\Delta H^\circ_{ads}$) for the corrosion of carbon steel in 1 M HCl and 0.5 M H$_2$SO$_4$ solutions in the presence of CSL were calculated from the Gibbs–Helmholtz equation, which is defined as follows:

$$\left[ \frac{\partial (\Delta G^\circ_{ads}/T)}{\partial T} \right]_p = \frac{\Delta H^\circ_{ads}}{T^2} \quad (12)$$

Which can be arranged to give the following equation:
\[
\frac{\Delta G^\circ_{ads}}{T_2} - \frac{\Delta G^\circ_{ads}}{T_1} = \Delta H^\circ_{ads} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \tag{13}
\]

The entropy of adsorption (\(\Delta S^\circ_{ads}\)) for the corrosion of carbon steel in 1 M HCl and 0.5 M H\(_2\)SO\(_4\) solutions in the presence of CSL were calculated from the Gibbs free energy equation:

\[
\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \tag{14}
\]

from which the values of \(\Delta S^\circ_{ads}\) and \(\Delta H^\circ_{ads}\) were calculated and listed in Table 5. In both the systems, the negative signs of enthalpies \(\Delta H^\circ_{ads}\) reflect the exothermic behavior of inhibitor on the carbon steel surface.

The \(\Delta S^\circ_{ads}\) value is negative in the Langmuir and Temkin isotherms, but it is positive in the Freundlich isotherm. A negative \(\Delta S^\circ_{ads}\) is an indication that the corrosion process is controlled by activation complex \([22-24]\). Also, the positive values of \(\Delta S^\circ_{ads}\) reflect the fact that the adsorption process is accompanied by an increase in entropy, which is the leading force for the adsorption of the inhibitor onto the carbon steel surface.

**Table 5**: Langmuir, Freundlich, Temkin adsorption isotherms and thermodynamic parameters for adsorption of CSL extract on the surface of the carbon steel.

<table>
<thead>
<tr>
<th>Adsorption Isotherm</th>
<th>T (K)</th>
<th>1 M HCl</th>
<th>0.5 M H(_2)SO(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(R^2)</td>
<td>(K_{ads})</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>0.987</td>
<td>0.933</td>
</tr>
<tr>
<td>Freundlich</td>
<td>298</td>
<td>0.906</td>
<td>0.095</td>
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<td>333</td>
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<td>0.951</td>
<td>0.256</td>
</tr>
</tbody>
</table>

3.6. **Scanning electron microscope (SEM):**

The scanning electron microscope (SEM) study of the carbon steel surface after immersion in 1 M HCl solution in the absence and presence 50% CSL extract, and in 0.5 M H\(_2\)SO\(_4\) solution in the absence and presence 50% CSL extracts for 3 h at 25°C. Are shown in Fig. 6 (A-Blank), and (B-Blank) the carbon steel was severely damaged with pitted areas and observed weak films on some places in surface believed to be ferrous chloride, which indicates the dissolution of iron in acid solution. It is clear from Fig. 6 (A-CSL) and (B-CSL), that the protective inhibitor layer deposited on the surface blocks the dissolution of iron from carbon steel. The results indicate that CSL extract is more effective in 1M HCl solutions than in 0.5 M H\(_2\)SO\(_4\) because inhibition efficiency depends on the type of inhibitor and the corrosion products. This explains the lower corrosion rate of carbon steel in 1 M HCl.
Figure 6. SEM photograph of carbon steel immersed in 1 M HCl (A) and in 0.5 M H₂SO₄ (B-Blank), and in the presence 50% of inhibitor A-CSL), and (B-CSL) for 3h at 25°C.

Conclusion

- The results obtained from the potentiodynamic polarization, EIS measurements, and gravimetric (weight loss) method demonstrated that the CSL extract acts as an effective inhibitor of carbon steel corrosion in the 1 M HCl, and 0.5 M H₂SO₄ solutions.
- The results obtained from the gravimetric (weight loss) method demonstrated that the CSL extracts acts as an effective inhibitor of carbon steel corrosion in 1 M HCl, and 0.5 M H₂SO₄ solutions.
- Inhibition efficiency increases with the increase in the concentration of CSL, and decreases with rise in temperature. Also, the effective inhibitor of carbon steel corrosion in 1 M HCl more than in 0.5 M H₂SO₄.
- The adsorption of CSL on the carbon steel surface from 1 M HCl, and 0.5 M H₂SO₄ solutions follows the Langmuir, Freundlich, and Temkin adsorption isotherms.
- The calculated values of ΔG°_ads, ΔH°_ads, and ΔS°_ads revealed that the adsorption process are spontaneous and exothermic, and the inhibitor molecules were adsorbed on the metal surface through physical adsorption and chemical adsorption (mixed adsorption) mechanism.
- The results of the SEM study showed that the corrosion of carbon steel in 1 M HCl and 0.5 M H₂SO₄ inhibited by CSL extracts.
- Therefore, all the results show that the CSL extracts can act as an inhibitor for the corrosion of carbon steel in the 1 M HCl and 0.5 M H₂SO₄ solutions.

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Reference

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