Inhibitive Action of Capparis Spinosa Extract on the Corrosion of Carbon Steel in an Aqueous Medium of Hydrochloric Acid

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Abstract: Capparidaceae (Capparis spinosa), is a common perennial shrub and woody plant, typically Mediterranean, largely used in folk medicine in the Mediterranean countries including Morocco. The effect of Capparis Spinosa (CSE) on the corrosion inhibition of carbon steel in 1 M hydrochloric acid (HCl) solution was evaluated by several analytical methods, among these are weight loss method, potentiodynamic polarization and impedance spectroscopy (EIS). Results showed that CSE inhibits the corrosion of steel and the inhibition is more efficient at high concentration of CSE. Results also showed that, the inhibition decrease at higher temperature. Potentiodynamic polarization studies clearly reveal that CSE acts as a cathodic inhibitor. The adsorption of Capparis Spinosa on carbon steel was found to obey the Langmuir adsorption isotherm. The activation energies and enthalpies of the corrosion process of carbon steel in acidic medium of CSE were also calculated.

Keywords: Inhibition; Carbon steel; Polarisation; Capparis Spinosa extract; Adsorption.

1. INTRODUCTION

Capparis Spinosa known traditionally in Morocco as Al-Kabara (CSE), is a common perennial shrub with medicinal and aromatic properties. It belongs to the family Capparidaceae, it grows in the wild in the Mediterranean region like Morocco, Italy, Spain and other countries [1]. The first recorded medical application for Capparis was by the Sumerians in 2000 BC. The ancient Romans also used the plant for the same purpose. All of the roots, stems and leaves of spinosa are used as food [2]. Capparis spinosa has been also known to have anti-inflammatory [3], antioxidant [4,5], anti-hepatotoxic [6], anti-bacterial [7] antidiabetic activities [8]. The medical effectiveness of this plant was related to the fact that the plant contains a significant amount of antioxidants bioflvinoids and Vitamine C. The importance of these compounds is related to their biological and free radical scavenger activities. The presence of these antioxidants in the extract of CSE makes it an attractive source for natural metal corrosion inhibitor.

The technology of metal corrosion inhibitor has recently received a considerable amount of attention [9]. Plant extracts considered to-be excellent for corrosion metals against acidic media [10-22]. Plant extracts are low-cost and biodegradable. These values make plant extracts valuable in both economic and environmental point of view. In our labs we did several studies for using extracts for corrosion inhibition agains acidic media. One of those studies Chamomile extract [23], Argan oil [24, 25], Argan extract [26], Verbena extract [27], Thymus capitatus [28,29], Thymus oil [30,31], Artemisia [32-33], Hibiscus sabdariffa [34], Citrus paradise [35], Jojoba oil [36], Lavender oil [37], Penryoyal Mint oil [38], Oxandra asbeckii [39] and Piperanine [40] All of those previous studies gave excellent results as corrosion inhibitors for metals in acidic medium. This work aimed to study the use of Capparis Spinosa extract as carbon steel corrosion inhibitor in 1 M HCl solution.

2. MATERIALS AND METHODS

2.1. Solutions Preparation

The aerial parts of Capparis Spinosa (CSE) were obtained from a special production field in the region of Souss Massa Valley (Morocco). A stock solution of Capparis Spinosa extract was prepared as follows: A known weight of dried and pulp fruits of Capparis Spinosa plant were crushed in a blender and soaked for 24 h at room temperature in 1 M HCl solution. After solution preparation and filtration, the solution kept as stock solution. All corrosion measurements were done in triplicate to assure accuracy.
2.2. Materials

A carbon steel with a composition (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe) was used for the experiment.

2.3. Gravimetric, Polarization and Impedance Spectroscopy Measurements

2.3.1. Gravimetric Analysis

The carbon steel used for experiment was rectangular with a dimension (2cmx 2cm x 0.08 cm) and was placed in a solution of 1 M HCl at different concentration of Cappars Spinosa for 6 h. Gravimetric analysis were done using a glass cell with a controlled cooling condenser. The specimen was abraded with glass paper of different grades and after that washed with ethanol and distilled water.

2.3.2. Potentiodynamic Polarization

Polarization measurements were carried out using Volta lab (PGZ 100) potentiostate that was controlled by software model (Voltamaster 4) under static condition. This potentiostat is connected to a cell with three electrode thermostats with double wall (Tacussel Standard CEC/TH). The working electrode is a rectangular disk from carbon steel. A saturated calomel electrode (SCE) and a platinum electrode were used, respectively, as reference and auxiliary electrode. All potentials were referred to this reference electrode. Each reading has a 30 min of stabilization time to hav a stable value for $E_{corr}$. The electrochemical was studied for both inhibited and uninhibited and were recorded for anodic and cathodic potentiodynamic polarization curves. The experiments were done at scan range of potential -800 to -200 mV/SCE with 1mV/s scan rate. To obtain the corrosion current densities ($I_{corr}$) a segment of extrapolation from by Tafel slopes for both cathodic and anodic were taken.

2.3.3. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) experiments were done in the frequency range of 100 kHz to 0.1 Hz using open circuit potential, of 10 points /decade, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. The best semicircle used to fit through the data points in the Nyquist plot using a non-linear least square fit with the interaction with the x-axis.

3. RESULTS AND DISCUSSION

3.1. Polarization Results

The effect of different concentration of Spinosa on corrosion is shown in Figure 1. Extrapolation of Tafel straight line shown in Figure 1, which helps us to calculate the values of electrochemical parameters, such as corrosion potential ($E_{corr}$), cathodic Tafel slopes ($b_c$), corrosion current density ($I_{corr}$). All these value are summarized in Table 1.

![Figure 1: Summary of the potentiodynamic polarization of C38 steel at different concentration.](image)

The inhibition efficiencies were calculated from $I_{corr}$ values according to equation 1:

$$E_i \% = \left( \frac{I_{corr} - I'_{corr}}{I_{corr}} \right) \times 100$$

(1)

where $I_{corr}$ and $I'_{corr}$ are uninhibited and inhibited corrosion current densities, respectively.

Careful evaluation of polarization curves and electrochemical parameter indicates that the inhibition efficiency increased, and the corrosion current density decreased when the concentration of the inhibitor is increased. The results indicate that, the adsorption of inhibitor molecules on the carbon steel surface increase with increasing the inhibitor concentration.

Table 1: Electrochemical Parameters of C38 Steel at Various Concentrations of CSE in 1M HCl and Corresponding Inhibition Efficiency

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$-E_{corr}$ (mV/SCE)</th>
<th>$I_{corr}$ (µA/cm²)</th>
<th>$b_c$ (mV/dec)</th>
<th>$E_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>469</td>
<td>588</td>
<td>168</td>
<td>-</td>
</tr>
<tr>
<td>5.0 g/l</td>
<td>520</td>
<td>40</td>
<td>165</td>
<td>93.19</td>
</tr>
<tr>
<td>4.0 g/l</td>
<td>507</td>
<td>62</td>
<td>156</td>
<td>89.45</td>
</tr>
<tr>
<td>2.0 g/l</td>
<td>495</td>
<td>72</td>
<td>149</td>
<td>87.75</td>
</tr>
<tr>
<td>1.0 g/l</td>
<td>494</td>
<td>121</td>
<td>142</td>
<td>79.42</td>
</tr>
<tr>
<td>0.5 g/l</td>
<td>478</td>
<td>134</td>
<td>140</td>
<td>77.21</td>
</tr>
</tbody>
</table>
From the above table we can see the slopes of the cathodic Tafel lines changed with increasing inhibitor concentration, which effect the presence of the CSE on the kinetics of hydrogen evolution and this shift Ecorr towards more cathodic values. This shift in Ecorr values towards more negative potential. This indicate that the inhibitor is cathodic [41,42]. The inhibition efficiency of Capparis Spinosa was observed at 5g/L.

3.2. Electrochemical Impedance Spectroscopy Measurements

The Nyquist representations of impedance behavior of carbon steel in 1M HCl solution in the absence and the presence of Capparis Spinosa at different concentrations plotted at open circuit potential (E corr) at 298 K after 30 min of contact time is shown in Figure 2. The diameter of Nyquist plots increased when increasing concentration of Capparis Spinosa, and this cause formation of inhibition film on the surface. It is also clear that the impedance diagrams show depressed semicircles at the center under the real axis, generally referred to the frequency dispersion of interfacial impedance due to roughness, inhomogeneity of the solid surfaces and adsorption of inhibitor [43,44].

To calculate inhibition efficiency using the EIS measurements, eq. 2 was used.

\[ E_{Rt} \% = \left( \frac{R_t - R_0}{R_t} \right) \times 100 \]  

(2)

were \( R_t \) and \( R_0 \) are the charge transfer resistances in inhibited and uninhibited solutions respectively.

The values of the polarization resistance were calculated by subtracting the high frequency intersection from the low-frequency intersection [45]. The double-layer capacitance (\( C_{dl} \)) and the frequency at which the imaginary component of the impedance is maximal (\( -Z_{max} \)) are found using eq.3.

\[ C_{dl} = \frac{1}{2 \pi f_m R_t} \]  

(3)

with \( C_{dl} \): Double layer capacitance (\( \mu F.cm^{-2} \)); \( f_{max} \): maximum frequency (Hz) and \( R_t \): Charge transfer resistance (\( \Omega.cm^{-2} \)).

The values of charge transfer resistance \( R_t \), double layer capacitance \( C_{dl} \) derived from Nyquist plots and inhibition efficiency \( E_{Rt} \), for the corrosion of carbon steel in 1M HCl with different concentration of inhibitors are listed in Table 2. It can be seen that the presence of Capparis Spinosa enhances the values of \( R_t \) and reduces the \( C_{dl} \) values. The decrease in the \( C_{dl} \) was a result of the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [46] indicating that Capparis Spinosa extract adsorbed at the metal surface preventing metal/solution interface.

### Table 2: Parameters of the Electrochemical Impedance of Corrosion of Steel in Acid Medium at Various Concentrations of CSE

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Conc. (g/l)</th>
<th>( R_t(\Omega.cm^2) )</th>
<th>( C_{dl}(\mu F/cm^2) )</th>
<th>( E_{Rt} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>18</td>
<td>221</td>
<td>-</td>
</tr>
<tr>
<td>CSE</td>
<td>5.0</td>
<td>306</td>
<td>20.81</td>
<td>94.12</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>284</td>
<td>22.43</td>
<td>90.66</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>276</td>
<td>23.08</td>
<td>87.48</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>232</td>
<td>27.45</td>
<td>79.20</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>222</td>
<td>28.69</td>
<td>77.01</td>
</tr>
</tbody>
</table>

3.3. Adsorption isotherm

Adsorption isotherm was used to understand the interaction between inhibitor and the electrode surface. The adsorption isotherm was best fit with Langmuir isotherm using eqs 4-5 [47].

\[ \frac{C}{\epsilon} = \frac{1}{K} + C \]  

(4)

\[ K = \frac{1}{55.5} \exp(-\frac{\Delta G_{abh}}{RT}) \]  

(5)

where \( C \) is the inhibitor concentration, \( \epsilon \) the fraction of the surface covered determined by \( E/100 \), \( K \) the
equilibrium constant, $\Delta G_{ads}$ is the standard free energy of adsorption reaction, $R$ is the universal gas constant, $T$ is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution in mol/L. Fig. 14 shows the dependence of the ratio $C/\theta$ as function of $C$.

![Figure 3: Langmuir adsorption isotherm of CSE on the steel surface at 298K.](image)

From Figure 3 we obtained almost straight line with correlation value close to 1. The thermodynamic constants obtained from Figure 3 are summarized in Table 3.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Slope</th>
<th>$K_{ads}$ (M$^{-1}$)</th>
<th>$R^2$</th>
<th>$\Delta G_{ads}^o$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSE</td>
<td>1.06</td>
<td>50.84</td>
<td>0.99</td>
<td>-19.675</td>
</tr>
</tbody>
</table>

The value $\Delta G_{ads}^o$ is calculated as -19.675 kJ mol$^{-1}$. From the negative sign of $\Delta G_{ads}^o$ which indicates spontaneity of the adsorption process and the stability of the adsorbed layer on the electrode surface [48, 49].

Generally, values of $\Delta G_{ads}^o$ up to -20 kJ. mol$^{-1}$ or lower are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); while the values around -40 kJ/mol or lower involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [50]. In the present work, the value of $\Delta G_{ads}^o$ is found to be around -20 kJ.mol$^{-1}$; means that the adsorption mechanism of Capparis Spinosa on carbon steel surface is mainly the physisorption.

### 3.4. Effect of Temperature

The study of temperatures effect on the corrosion behavior of carbon steel using polarization methods in the range of 298–328 K in the absence and the presence of CSE at 5 g/l in 1M HCl were studied and shown in Figures 4 and 5.

![Figure 4: Nyquist diagrams for C38 steel in 1 M HCl at different temperatures.](image)

![Figure 5: Nyquist diagrams for C38 steel in 1 M HCl + 5g/l of CSE at different temperatures.](image)

In the studied temperature range (298–328 K) both the $R_{ct}$ values and the inhibition efficiency decrease with increasing temperature in uninhibited and inhibited solutions. The $R_{ct}$ value of C38 steel increases more rapidly with temperature in the presence of the inhibitor; these results confirm that Capparis Spinosa acts as an efficient inhibitor in the range of temperature studied.

The corrosion rate is inversely proportional to $R_t$ values and the parameters of of $E_a$, $\Delta H_a$ and $\Delta S_a$ were
estimated from the slopes of the straight lines in Figures 6 and 7.

Table 4: Thermodynamic Parameters for the Adsorption of CSE in 1 M HCl on the C38 Steel at Different Temperatures

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>T (K)</th>
<th>R_t (Ω.cm²)</th>
<th>C_dL (µF/cm²)</th>
<th>E_{rel} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>298</td>
<td>18</td>
<td>221</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>11</td>
<td>229</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>318</td>
<td>8</td>
<td>199</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>5</td>
<td>201</td>
<td>-</td>
</tr>
<tr>
<td>CSE</td>
<td>298</td>
<td>306</td>
<td>21</td>
<td>94.12</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>200</td>
<td>20</td>
<td>94.50</td>
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<td></td>
<td>318</td>
<td>135</td>
<td>18</td>
<td>94.07</td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>118</td>
<td>21</td>
<td>95.76</td>
</tr>
</tbody>
</table>

Table 5: The Value of Activation Parameters $E_a$, $\Delta H_a$, $\Delta S_a$ and $\Delta G_{ads}$ for Steel in 1M HCl in the Absence and Presence of 5g/l of CSE

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$E_a$ (kJ/mol)</th>
<th>$\Delta H_a$ (kJ/mol)</th>
<th>$\Delta S_a$ (J/mol)</th>
<th>$E_a$-$\Delta H_a$ (K J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>36.39</td>
<td>33.79</td>
<td>-191.53</td>
<td>2.60</td>
</tr>
<tr>
<td>CSE</td>
<td>29.14</td>
<td>26.55</td>
<td>-239.06</td>
<td>2.60</td>
</tr>
</tbody>
</table>

The values of $E_a$ from the solution having Capparis Spinosa is lower than the blank. Also, the positive signs of $\Delta H_a$ indicates that the endothermic nature of the Carbon steel dissolution process. The value of $\Delta S_a$ is lower for inhibited solution than that for the uninhibited solution. This phenomenon suggested that a decrease in randomness occurred on going from reactants to the activated complex.

4. CONCLUSION

There was a direct relation between inhibition efficiency and the concentration of Spinosa and it appeared mostly at 5 g/L. While increasing temperature decreased inhibition efficiency. The extracts of Capparis Spinosa in HCl acts as cathodic type inhibitor. The adsorption of the Capparis Spinosa extract is a spontaneous process as indicated by the negative value of the $\Delta G_{ads}$ indicates that and obeys the Langmuir isotherm model.

ACKNOWLEDGEMENTS

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