Corrosion Inhibition of Medium carbon steel in the acidic medium using \textit{Salsola.} \textit{L.} plant extract

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\section*{ABSTRACT}

This study included the corrosion inhibition of metal corrosion process of medium carbon steel using (1M H\textsubscript{2}SO\textsubscript{4}), The weight los\textsuperscript{s} method has been applied pieces of carbon steel divided to Cubans with dimension (0.4*2*2.4)cm, the samples were polished using carbide silicon paper with dimensions of (180,200, 400,600, 800,1000). The samples were immersed in alcoholic medium at temperature (20\degree C) for 3 hours. natural inhibitor (\textit{Salsola.}L.) was used which extracted in aqueous and alcoholic medium, different concentrations (1000,2000)ppm have been used, the results indicated that highest degree of inhibition for aqueous extract is 93.3\% with concentration of (2000)ppm and 90.5\% with (1000)ppm at (20\degree C). While the alcoholic inhibitor showed the highest efficiency 92.4\% with concentration of (2000)ppm and 88.6\% with concentration of (1000)ppm respectively. The structure of inhibitor was studied by infrared spectroscopy and the tested samples were studied by scanning electron microscope

Key words: \textit{Salsola.} \textit{L.}, Corrosion, Inhibition, Medium Carbon Steel,

\section*{HOW TO CITE THIS ARTICLE}


\section*{INTRODUCTION}

Corrosion is defined as damage to metals and alloys due to their chemical or electrochemical reaction with the surrounding environment. Metals and alloys gradually change into compounds such as oxides, hydroxides, carbonates and sulphides\textsuperscript{1}. Corrosion is the atmospheric oxidation/degradation of metals. It is an electrochemical process by which metallic surfaces react with their environment causing the metal to lose its material properties due to surface deterioration\textsuperscript{2}, as defined by scientists in the year (1830 A.D) as a complex phenomenon has been studied physically, chemically, electrochemically, kinetically or thermodynamically, the studies proved that to be entirely dependent on mechanical properties of metal\textsuperscript{3}. In general, the driving force for the completion of the corrosion reaction is the change in the free energy of the material as a result of their transformation into compounds with a generally lower free energy than their constituent metals\textsuperscript{4}, therefore they are automatically formed if exposed to the appropriate conditions, the resulting compounds are more stable than the metal which is naturally composed of them\textsuperscript{5}. Process of corrosion of the metal leads to ions generation with some electrons that are consumed by a secondary reaction. When the metal is placed in pure water, some ions will be transferred directly to the solution\textsuperscript{6}.

\begin{equation}
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-} \quad E^{0} = 0.44 \text{ v} \quad \ldots(1.1) \quad \text{oxidation}
\end{equation}
Accumulation of the negative charge on the metal and presence of metal ions in the solution makes the reaction go back:

\[ \text{Fe}^{+2} + 2e^- \rightarrow \text{Fe} \quad \text{E}^\circ = -0.44 \text{ V} \quad \ldots \ldots (1.2) \]  

shorthand \[4\]

at the end, the equilibrium obtained

\[ \text{Fe} \rightarrow \text{Fe}^{+2} + 2e^- \quad \ldots \ldots \ldots (1.3) \]

The potential difference depends on the type of metal and the composition of the solution \[5,6\].

The inhibitors effect on the electrochemical reaction kinetics in the corrosion process, and fixed on the inhibitors on the metal surface, thus the process easy the electrical double layer changes, if same active inhibitors used in the industry is organic compounds, as containing oxygen, nitrogen and sulfur atoms which can lead to adsorption of compounds on the surface of the metal\[6\].

Also biodegradable green inhibitors that do not contain heavy metals or other toxic compounds are used. Corrosion inhibitors generally control corrosion through the mechanism of these inhibitors, which are applied to the surface of the metal, which acts on the basis of adsorption, on the metal surface \[7\]. Adsorption depends on the charge nature of the metal surface, electronic properties and, properties of solvents, temperature the electrochemical potential\[8,9\].

This study aimed to estimate the ability of a plant extract to inhibit the corrosion of using metal and to find the difference in the corrosion rate for the static phase at time and different temperatures.

**EXPERIMENTAL**

1- **Samples preparation**

The samples were divided to small Cubans with dimensions (2 cm) length and (2.4 cm) width and (0.4 cm) thickness\[10\].

**Chemical analysis**

The carbon steel samples and the Salsola. L. extract of plant (aqueous and alcoholic) were analyzed spectroscopic ally (Table1), using the atomic absorption spectrophotometer device. *(Note: The device has no ability to measure all elements in the metal and extract).*

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
<th>Mn</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>1.8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.11</td>
<td>17.0</td>
</tr>
</tbody>
</table>

*(Table 2) Elements analysis data of the leaves of the plant (aqueous and alcoholic)*

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Fe</th>
<th>K</th>
<th>Cu</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>0.003</td>
<td>0.03</td>
<td>0.5</td>
<td>0.03</td>
<td>99</td>
<td>0.01</td>
<td>0.045</td>
<td>0.032</td>
</tr>
</tbody>
</table>

2- **Preparation of Salsola.L. extracts (inhibitor)**\[11\]:

The plant extract was prepared using tap water so as to wash the plant and freeing him from the dust suspended in it limit to (40-60%) and polar solvents (aqueous and ethanol) as follows: \[10\].

3-1- The organic extract was prepared as follow (50)gm of the Salsola.L. plant powder in a conical flask(500ml) was mixed with 250 ml of petroleum ether, the mixture was stirred for 72hr using magnetic stirrer and, then the solution was filtered off and dried in oven at (20-30\(^{\circ}\)C), the filtrate was saved in a glass container and placed in the refrigerator at a temperature of (4)\(^{\circ}\)C.

3-2- The alcoholic extract of the Salsola.L. plant was prepared by following procedure (50)gm from the powder that prepared in (3-1) was mixed with 250 ml ethanol 99.9% and stirred for 72hr using the
magnetic stirrer, then the solution filtered and evaporated the filtrate under low pressure using rotary evaporator at (4) °C and the remaining extract (50%) is reserved until use\textsuperscript{[11,12]}.

3-3- Prepare aqueous extract: the aqueous extract was prepared as mentioned in (3-2), was mixed (50gm) with 250 ml of water and stirred for 72hr using the magnetic stirrer. The solution is then filtered off and the filtrate was evaporated under vacuum at (4) °C and the remaining extract (50%) \textsuperscript{[11,12]}.

Preparation of the corrosion solution:
By dilution method, 1M concentration of sulfuric acid was prepared\textsuperscript{[8]}

4- Measurement of the weight loss:
All metal samples were placed in 100 ml of (1)M H\textsubscript{2}SO\textsubscript{4} and then transferred to a water bath at the required temperature and concentration to the inhibitor for 3hr, then the samples were cleaned and washed with deionized water, and dried with a tissue paper or smoothened paper (type 180-1000 P) and then washed with acetone and dried again. The weight loss was determined in the presence of the inhibitor at concentrations 2000, 1000 ppm at (20, 30, 40 °C)\textsuperscript{[13]}.

RESULTS AND DISCUSSION

1. Method of weight loss
Corrosion rates (CR) were determined in the presence and absence of inhibitor using the following Equation\textsuperscript{[14]}:

\[
(CR) = \frac{\Delta W}{A \times t} \quad \text{......... (1.4)}
\]

Where \(\Delta W\) weight loss (gm), \(A\): surface area of sample (m\textsuperscript{2}), \(t\): time of sample exposure for day.

Corrosion rates were obtained in g / m\textsuperscript{2} . day (g.m\textsuperscript{2}d).

The inhibition efficiency was calculated using the equation:

\[
\% \text{ IE} = \frac{CR_u - CR_i}{CR_u} \times 100 \quad \text{......... (1.5)}
\]

Where \(CR_u\) and \(CR_i\) are the corrosion rates in the absence of different concentrations of inhibitors, respectively.

The inhibition efficiency (IE\%) can be also calculated using the following equation\textsuperscript{[15]}:

\[
\% \text{ IE} = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \quad \text{..... (1.6)}
\]

Where \((i_{corr})_a\) and \((i_{corr})_p\) is the density of the corrosion current (μA.cm\textsuperscript{2}) in the absence of inhibitors, respectively.

Surface cover (\(\theta\)) can be calculated by the following equation\textsuperscript{[16]}:

\[
\theta = \frac{\text{IE}}{100} \quad \text{................. (1.7)}
\]

Where: \(\theta\) surface coverage, (IE) inhibition efficiency\textsuperscript{[17]}.

Corrosion rate, inhibition efficiency, corrosion current efficiency and surface coverage were assessed under different conditions. The results were collected in (Table 3,4). It is clear that the rate of corrosion increases with increasing temperature and concentration of sulfuric acid and decreases with increasing of inhibitory concentrations.
Table 3: Temperature effect upon corrosion rate, density of the corrosion current of medium carbon steel in 1M of H₂SO₄ and surface coverage in presence of aqueous extract inhibitor

<table>
<thead>
<tr>
<th>Sample</th>
<th>C₁ (ppm)</th>
<th>T (°C)</th>
<th>Corrosion rate (g.m⁻².d)</th>
<th>I_corr (μA.cm⁻²)</th>
<th>θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>20</td>
<td>530</td>
<td>450.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>0</td>
<td>30</td>
<td>900</td>
<td>497.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.</td>
<td>0</td>
<td>40</td>
<td>1440</td>
<td>682.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.</td>
<td>1000</td>
<td>20</td>
<td>50</td>
<td>42.7</td>
<td>0.905</td>
<td>90.5</td>
</tr>
<tr>
<td>5.</td>
<td>1000</td>
<td>30</td>
<td>135</td>
<td>74.6</td>
<td>0.850</td>
<td>85</td>
</tr>
<tr>
<td>6.</td>
<td>2000</td>
<td>40</td>
<td>240</td>
<td>114</td>
<td>0.833</td>
<td>83.3</td>
</tr>
<tr>
<td>7.</td>
<td>2000</td>
<td>20</td>
<td>35</td>
<td>30.1</td>
<td>0.933</td>
<td>93.3</td>
</tr>
<tr>
<td>8.</td>
<td>2000</td>
<td>30</td>
<td>100</td>
<td>55.7</td>
<td>0.888</td>
<td>88.8</td>
</tr>
<tr>
<td>9.</td>
<td>2000</td>
<td>40</td>
<td>210</td>
<td>99.6</td>
<td>0.854</td>
<td>85.4</td>
</tr>
</tbody>
</table>

Table 4: Temperature effect upon corrosion rate, density of the corrosion current of medium carbon steel in 1M of H₂SO₄ and surface coverage in presence of alcoholic extract inhibitor

<table>
<thead>
<tr>
<th>Sample</th>
<th>C₁ (ppm)</th>
<th>T (°C)</th>
<th>Corrosion rate (g.m⁻².d)</th>
<th>I_corr (μA.cm⁻²)</th>
<th>θ</th>
<th>% IE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0</td>
<td>20</td>
<td>530</td>
<td>450.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>0</td>
<td>30</td>
<td>900</td>
<td>497.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3.</td>
<td>0</td>
<td>40</td>
<td>1440</td>
<td>682.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4.</td>
<td>1000</td>
<td>20</td>
<td>60</td>
<td>51.3</td>
<td>0.886</td>
<td>88.6</td>
</tr>
<tr>
<td>5.</td>
<td>1000</td>
<td>30</td>
<td>140</td>
<td>77.6</td>
<td>0.844</td>
<td>84.4</td>
</tr>
<tr>
<td>6.</td>
<td>2000</td>
<td>40</td>
<td>310</td>
<td>147.4</td>
<td>0.784</td>
<td>78.4</td>
</tr>
<tr>
<td>7.</td>
<td>2000</td>
<td>20</td>
<td>40</td>
<td>34.2</td>
<td>0.924</td>
<td>92.4</td>
</tr>
<tr>
<td>8.</td>
<td>2000</td>
<td>30</td>
<td>130</td>
<td>72.1</td>
<td>0.855</td>
<td>85.5</td>
</tr>
<tr>
<td>9.</td>
<td>2000</td>
<td>40</td>
<td>280</td>
<td>133.1</td>
<td>0.805</td>
<td>80.5</td>
</tr>
</tbody>
</table>

Evaluation of corrosion rate

The weight loss method was used to calculate the corrosion rates in non-inhibitory acid solutions at different temperatures (20, 30, 40°C). The average carbon steel corrosion rate in 1M H₂SO₄ increased from 530 to (1440 g.m⁻².d) with increasing temperature (20 - 40°C). And the density of the Corrosion current of the medium carbon steel was increased from (450.5 - 682.7) (μA.cm⁻²) with an increase in temperature (20 – 40°C). (Figure 1) shows the increased in the rate of corrosion with increased of temperature, the relationship between temperature as variable and the rate of corrosion and (Figure 2) shows the increased of the density of the corrosion current with increased temperature.

Effect of acid in presence an inhibitor at different temperatures
From (Figures3,4) we notice the effects of temperature on corrosion rate that was expressed for the different inhibitor concentrations The two forms show that the corrosion rate increases with rise of temperature and inhibitor
concentration. When using (1000) ppm an inhibitor at temperatures (20-40°C), the highest corrosion rate was (310) g.m⁻².d⁻¹ at (40°C) when (1000, 2000 ppm) concentration of alcoholic Salsola.L. extract been used. While the lowest corrosion rate was (50) g.m⁻².d⁻¹ at 20°C with the aqueous extract.

The concentration of 2000 ppm of the inhibitor at different temperatures gave the highest corrosion rate (280) g.m⁻².d⁻¹ at (40°C) when using extract of the alcoholic. The lowest value of the corrosion rate was (35) g.m⁻².d⁻¹ at (20°C) with the aqueous extract.

Figure (3) The effect of Temperature on the corrosion rate of medium Carbon steels in (1) M H₂SO₄ with the presence of aqueous extract

Figure (4) The effect of Temperature on the corrosion rate of medium carbon steels in (1) M H₂SO₄ with the presence of alcoholic extract.

Figure (5) Effect of temperature on the density of the corrosion current in (1) M H₂SO₄ with a aqueous extract

Figure (6) Effect of temperature on the density of the corrosion current in (1) M H₂SO₄ in presence of the alcoholic extract.

Figure (7) Effect of Temperature on the inhibition efficiency in (1) M H₂SO₄ in presence of alcoholic extract

Figure (8) Effect of Temperature on the inhibition efficiency (1) M H₂SO₄ in presence of aqueous extract.
Figure (9) Effect of concentration on inhibition efficiency in (1) M H₂SO₄ in presence of aqueous extract

Figure (10) Effect of concentration on inhibition efficiency in (1) M H₂SO₄ with an alcoholic extract

Figure (11) Effect of concentration on density of the erosion current in (1) M H₂SO₄ with a aqueous extract

Figure (12) Effect of concentration on density of the erosion current in (1 M H₂SO₄) with the presence of the alcoholic extract

Figure (13) Effect of Concentration on Corrosion rate in (1) M H₂SO₄ with aqueous extract

Figure (14) Effect of Concentration on Corrosion rate in (1) M H₂SO₄ with alcoholic extract.

Scanning electron microscopy studies
The microscopic examination of the surface of the eroded sample in the acid medium showed dark color and that are indicating to corrosion products result from corrosion due to direct exposure to the acid medium. However, with the inhibitors, the damage is much smaller on the surface with clear color. And that because of formation protective layer on the steel surface which prevents the contact between the surface and medium.
Studies of inhibitory structures and infrared radiation

FTIR study of inhibitor composition for the purpose of metal surface protection, plant extract was used and the FT-IR spectra were recorded in order to elucidate the potential interactions between the adsorbed inhibitor (Salsola L.) and the surface of carbon steel which are immersed in (1M)H$_2$SO$_4$. FT-IR results (Table 5) and figure(21) showed that the stretching frequencies of the inhibitor were shifted to lower values in comparison with the frequencies of the free extract and that maybe as a result of the reaction between the extract molecules and the surface of the metal.
Theses stretching frequencies are assigned to the presence of the alkaloids and flavone's compounds which are responsible for such surface pro

For the purpose of protecting the surface of the metal using plant extracts and finding the best plant that provides protection [18].

Table 5: The important bands for the extract(Cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>ν-NH</th>
<th>ν-CH₃aliph</th>
<th>ν-CH₂aliph</th>
<th>ν-C=O</th>
<th>ν-C=C Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free inhibitor</td>
<td>3298b</td>
<td>2920w</td>
<td>2853w</td>
<td>1739s</td>
<td>1560s</td>
</tr>
<tr>
<td>inhibitor</td>
<td>3282b</td>
<td>2918w</td>
<td>2850w</td>
<td>1736s</td>
<td>1560s</td>
</tr>
</tbody>
</table>

B=bond , w=weak , s=strong

Figure 21: FT-IR spectra of the Salsola. L. extract (1) M H₂SO₄

Figure (22) FT-IR spectrum of the extract for the protective layer formed on the metal surface after immersion in 1M H₂SO₄

CONCLUSIONS
1- Salsola.L. extract acts as a good inhibitor for the corrosion of Carbone-steel in 1 M H₂SO₄ solution.
2- Inhibition efficiency increases with rise the inhibitor concentration but decreases with rise the temperature.
3- The results obtained from polarization measurements revealed that Salsola.L. extract behaves as a mixed type of inhibitor.
4- Salsola.L. alcoholic extract is better than an aqueous extract at lower concentration.
5-FT-IR show the layers of corrosion inhibition with iron ions on the Carbone medium steel surface especially for the compounds that present in the plant extract.

ACKNOWLEDGEMENT

This work was supported by Tikrit university / college of education pure sciences / chemistry department, our great thanks goes to professor Modher Mohammed for this support and reading the manuscript.

REFERENCES