A Study of *Eruca vesicaria*, *Bromelia hemisphaerica* and *Erythrina americana* as Green Corrosion Inhibitors for Carbon Steel in Sulfuric Acid

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Abstract

A study of *Eruca vesicaria*, *Bromelia hemisphaerica* and *Erythrina americana* as eco-friendly corrosion inhibitors for 1018 carbon steel in 0.5 M H₂SO₄ has been carried out by using weight loss tests, potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements. Results have shown that the three extracts performed as good corrosion inhibitors, but the *Eruca vesicaria* exhibited the best performance followed by *Erythrina americana*. The three inhibitors formed a protective, passive film which protected the steel from corrosion. This was because they contain antioxidants present in their molecular structure with heteroatoms such as N, C and O like phenols, amino acids, etc., which react with metal and environment to form the protective film.

Keywords

Acid Corrosion, Green Inhibitors, Electrochemical Techniques

1. Introduction

Corrosion causes big economic losses to the industry and is a cause of big accidents. In industrial processes such...
as acid pickling, well oil acidizing, metals and alloys are exposed to corrosive environments such as sulfuric acid (H₂SO₄), hydrochloric acid (HCl) and phosphoric acid (H₃PO₄) among others, which causes corrosion [1]-[3]. Among the different ways to protect metals against corrosion, the use of corrosion inhibitors is one of the most widely used methods [4]-[6]. However, most of the used, synthetic inhibitors are toxic, expensive and harmful for living species [7] [8]. Some plants had been studied as corrosion inhibitors such as Salvia officinalis [9], Musa paradisica [10], Capsicum anum [11], Adhotada vasica [12], and many others [13]-[22]. It was found that all these plant extracts act as good corrosion inhibitors for metal corrosion in acidic media. The corrosion inhibition of these compounds has been attributed to the presence of active compounds present in their structure. These organic compounds usually contain polar functions with nitrogen, sulphur or oxygen atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, which are the major adsorption centres to protect metal form further corrosion [23].

Eruca vesicaria subsp. sativa (syn. E. sativa), Bromelia hemisphaerica and Erythrina americana are plants widely used in Mexico because they are excellent source of antioxidants, enzymes or sedative and calming effects [24]-[26]. For instance, Eruca vesicaria contains phenolic compounds, carotenoids, glucosinolates, whereas Eruca vesicaria contains enzymes such as proteases which have been increased in their use in pharmaceutic, photographic, waste disposal, medicine, and the food industry. Finally, Erythrina americana contains alkaloids such as Erisopine, Erisodine, α-Erythridine, β-Erythridine, and non-proteins aminoacids, lectines and trispenes [26]-[29] containing heteroatoms such as C, O and N, with good antioxidant properties. Since corrosion is an oxidative process, the use of these plants and their antioxidants properties make them good candidates to be used as corrosion inhibitors for 1018 carbon steel in 0.5 M H₂SO₄.

2. Results and Discussion

Material tested in this work was 1018 carbon steel containing 0.14% C, 0.90% Mn, 0.30% S, 0.030% P and as balance Fe, encapsulated in commercial epoxic resin with an exposed area of 1.0 cm². The aggressive solution, 0.5 M H₂SO₄ was prepared by dilution of analytical grade chemical in distilled water. Eruca vesicaria, Bromelia hemisphaerica and Erythrina americana were obtained from a local market. For the extraction, dried leafs of the plants were soaked in methanol during 21 days obtaining a solid, which was weighted and dissolved in methanol and used as a stock solution and used then for preparation of the desired concentrations by dilution. Used concentrations included 0, 200, 400, 600, 800 and 1000 ppm. To characterize the obtained extracts, FTIR technique was used. The IR spectra were recorded with KBr pellets on a Tensor 27 Bruker spectrophotometer between 400 and 4000 cm⁻¹. For the corrosion tests, both gravimetric and electrochemical techniques were used.

Weight loss experiments were carried out with carbon steel rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After a total time of exposition of 72 hours, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Tests were performed by triplicate at room temperature (25°C). Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

\[ \Delta W = \left( m_1 - m_2 / A \right) \]  

(1)

where \( m_1 \) is the mass of the specimen before corrosion, \( m_2 \) the mass of the specimen after corrosion, and \( A \) the exposed area of the specimen. For the weight loss tests, inhibitor efficiency, I.E., was calculated as follows:

\[ \text{I.E.}(\%) = 100 \left( \Delta W_1 / \Delta W_2 - \Delta W_1 / \Delta W_2 \right) \]  

(2)

where \( \Delta W_1 \) is the weight loss without inhibitor, and \( \Delta W_2 \) the weight loss with inhibitor. Specimens were weighed in an analytical balance with a precision of 0.1 mg.

Electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value, \( E_{\text{corr}} \). Polarization curves were recorded at a constant sweep rate of 1 mV/s at the interval from \(-1000\) to \(+1000\) mV respect to the \( E_{\text{corr}} \) value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically distributed and a saturated calomel electrode (SCE) as reference. Corrosion current density values, \( i_{\text{corr}} \), were obtained by using Tafel extrapolation. Electrochemical impedance spectroscopy tests were carried out at \( E_{\text{corr}} \) by using a signal with an amplitude of 10 mV in a frequency interval of 100 mHz - 20 kHz. An ACM potentiostat controlled by a desk top computer was...
used for the polarization curves, whereas for the EIS measurements, a model PC4 300 Gamry potentiostat was used.

3. Results and Discussion

3.1. Weigh Loss Tests

The effect of *Eruca vesicaria*, *Bromelia hemisphaerica* and *Erythrina americana* concentration on the weight loss of 1018 carbon steel in 0.5 M H₂SO₄ is shown in Figure 1, where it can be seen that in all cases, the weight loss decreases as the inhibitor concentration increases. The lowest weight loss was obtained with the addition of *Eruca vesicaria*, whereas with the addition of *Bromelia hemisphaerica* the steel had highest weight loss values. In a similar way, the inhibitor efficiency increased with increasing its concentration, obtaining the highest values, between 40% and 80%, when *Eruca vesicaria* was added, whereas the lowest values were obtained with the addition of *Bromelia hemisphaerica*, obtaining values between 18% and 50%, Figure 2. This decrease in the corrosion rate is due to the adsorption of the different inhibitors on the steel surface, and the fact that its efficiency values increase with an increase in its concentration is due to an increase in the surface area covered by the inhibitor.

3.2. Polarization Curves

The effect of *Eruca vesicaria* concentration in the polarization curves for 1018 carbon steel in 0.5 M H₂SO₄ is given in Figure 3, where it can be seen that with or without inhibitor, steel displays an active-passive behaviour. The E_corr value shifts towards nobler values as soon as the *Eruca vesicaria* is added to the solution, and the i_corr values decrease with the addition of the inhibitor for one order of magnitude up to 800 ppm, Table 1, and then it decreases with a further increase in the inhibitor concentration. This could be because *Eruca vesicaria* reacts with iron ions released during the corrosion process to form corrosion products which can be either protective or non-protective. For concentrations lower than 800 ppm, these corrosion products are protective and adherent, whereas for doses higher than 800 ppm, the formed corrosion products could be non-adherent, non-protective, which are detached from the metal surface, increasing, thus, the corrosion rate of the steel. Inhibitor efficiency values increase with the increase in the inhibitor concentration, reaching its highest value, 86%, when 1000 ppm of *Eruca vesicaria* was added to the solution. Both anodic and cathodic Tafel slopes were decreased with the addition of the inhibitor, especially the cathodic one, indicating that *Eruca vesicaria* is a mixed type of inhibitor, decreasing both the anodic dissolution of iron and the cathodic hydrogen evolution reaction, since in an acidic environment, it is the dominant cathodic reaction. The potential where the passivation starts,
Figure 2. Effect of *Eruca vesicaria*, *Bromelia hemisphaerica* and *Erythrina americana* concentration on the inhibitor efficiency values for 1018 carbon steel in 0.5 M H$_2$SO$_4$.

Figure 3. Effect of *Eruca vesicaria* concentration on the polarization curves for 1018 carbon steel in 0.5 M H$_2$SO$_4$.

Table 1. Electrochemical parameters obtained from polarization curves in *Eruca vesicaria*.

<table>
<thead>
<tr>
<th>C$_{inh}$ (ppm)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (mA/cm$^2$)</th>
<th>$\beta$$_a$ (mV/dec)</th>
<th>$\beta$$_c$ (mV/dec)</th>
<th>I.E. (%)</th>
<th>$E_{pas}$ (mV)</th>
<th>$i_{pas}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$-426$</td>
<td>$1.94 \times 10^{-4}$</td>
<td>36</td>
<td>177</td>
<td>---</td>
<td>680</td>
<td>$7.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>200</td>
<td>$-384$</td>
<td>$3.5 \times 10^{-3}$</td>
<td>27</td>
<td>142</td>
<td>82</td>
<td>536</td>
<td>$5.94 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>$-384$</td>
<td>$3.1 \times 10^{-3}$</td>
<td>24</td>
<td>136</td>
<td>84</td>
<td>535</td>
<td>$3.94 \times 10^{-4}$</td>
</tr>
<tr>
<td>600</td>
<td>$-403$</td>
<td>$2.63 \times 10^{-5}$</td>
<td>22</td>
<td>131</td>
<td>86</td>
<td>678</td>
<td>$2.44 \times 10^{-4}$</td>
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<tr>
<td>800</td>
<td>$-424$</td>
<td>$1.9 \times 10^{-3}$</td>
<td>21</td>
<td>122</td>
<td>90</td>
<td>760</td>
<td>$7.64 \times 10^{-3}$</td>
</tr>
<tr>
<td>1000</td>
<td>$-356$</td>
<td>$2.8 \times 10^{-3}$</td>
<td>20</td>
<td>120</td>
<td>65</td>
<td>--</td>
<td>$8.74 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
$E_{\text{pas}}$, as well as the passive current density value, $i_{\text{pas}}$, were decreased with the addition of *Eruca vesicaria*, indicating that a better passive film is formed on top of steel when *Eruca vesicaria* is present. Thus, *Eruca vesicaria* helps to improve the passive film properties of the steel.

Polarization curves for 1018 carbon steel at different concentrations of *Bromelia hemisphaerica* is shown in Figure 4, where it is clear the active-passive behaviour of the steel. The free corrosion potential value was only marginally shifted towards nobler values and the corrosion current density was decreased as the *Bromelia hemisphaerica* concentration increased obtaining its lowest value with the addition of 800 ppm, Table 2. Both the anodic and cathodic Tafel slopes were decreased, especially with the highest inhibitor concentrations, indicating the mixed character of *Bromelia hemisphaerica*. Inhibitor efficiency values increased with increasing the *Bromelia hemisphaerica* concentration, between 64% and 74%, but these values were smaller than those obtained with *Eruca vesicaria*. The $E_{\text{pas}}$ and $i_{\text{pas}}$ values were lowered with the addition of *Bromelia hemisphaerica*, lower even than those obtained with the addition of *Eruca vesicaria*, improving, thus, the film passive properties of the steel, even in a better way than *Eruca vesicaria* did.

Finally, the effect of *Erythrina americana* concentration on the polarization curves for 1018 carbon steel in 0.5 M H$_2$SO$_4$ is shown in Figure 5. In this figure it can be seen that steel display an active-passive behaviour regardless of the *Erythrina americana* concentration. This time, the $E_{\text{corr}}$ value was shifted towards nobler values as the *Erythrina americana* concentration increased, Table 3, but the $i_{\text{corr}}$ value, although was decreased with the addition of the inhibitor, it reached its lowest value when 400 ppm of inhibitor were added, and it increased once again with a further increase in the *Erythrina americana* concentration. Thus, the inhibitor efficiency reached its

### Table 2. Electrochemical parameters obtained from polarization curves in *Bromelia hemisphaerica*.

<table>
<thead>
<tr>
<th>$C_{\text{inh}}$ (ppm)</th>
<th>$E_{\text{corr}}$ (mV)</th>
<th>$i_{\text{corr}}$ (mA/cm$^2$)</th>
<th>$\beta_a$ (mV/dec)</th>
<th>$\beta_c$ (mV/dec)</th>
<th>L.E. (%)</th>
<th>$E_{\text{pas}}$ (mV)</th>
<th>$i_{\text{pas}}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>−426</td>
<td>$1.94 \times 10^{-4}$</td>
<td>36</td>
<td>177</td>
<td>---</td>
<td>680</td>
<td>$7.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>200</td>
<td>−414</td>
<td>$7.1 \times 10^{-5}$</td>
<td>34</td>
<td>155</td>
<td>64</td>
<td>530</td>
<td>$5.94 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>−394</td>
<td>$7.4 \times 10^{-5}$</td>
<td>32</td>
<td>146</td>
<td>62</td>
<td>635</td>
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</tr>
<tr>
<td>600</td>
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<td>$6.7 \times 10^{-5}$</td>
<td>30</td>
<td>134</td>
<td>65</td>
<td>615</td>
<td>$2.94 \times 10^{-4}$</td>
</tr>
<tr>
<td>800</td>
<td>−431</td>
<td>$5.0 \times 10^{-5}$</td>
<td>29</td>
<td>128</td>
<td>74</td>
<td>570</td>
<td>$1 \times 10^{-4}$</td>
</tr>
<tr>
<td>1000</td>
<td>−407</td>
<td>$6.8 \times 10^{-5}$</td>
<td>20</td>
<td>123</td>
<td>65</td>
<td>570</td>
<td>$2.54 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
highest value, 84%, at 400 ppm of *Erythrina americana*, value slightly lower than the highest efficiency obtained with *Eruca vesicaria*, 90%. Both anodic and cathodic Tafel slopes were lowered by the addition of *Erythrina americana*, indicating that it acts as a mixed type of inhibitor, decreasing both the anodic iron dissolution and cathodic hydrogen evolution reactions. The $E_{\text{pas}}$ value was lowered only with the addition of 200 ppm of *Erythrina americana*, whereas the passive current density value, $i_{\text{pas}}$, was lowered by the addition of 200, 800 and 1000 ppm of *Erythrina americana*, forming, at these concentrations, a better passive film on top of the steel, improving, thus, the film passive properties.

### 3.3. EIS Measurements

The effect of *Eruca vesicaria* concentration in the Nyquist diagrams for 1018 carbon steel in 0.5 M H$_2$SO$_4$ is given in Figure 6, where it can be seen that data display a single, capacitive-like, depressed semicircle at all frequency values, with its centre at the real axis, indicating that the corrosion process is under charge transfer control from the metal to the solution through the double electrochemical layer. The semicircle diameter, equivalent to the charge transfer resistance, which is inversely proportional to the $i_{\text{corr}}$ value, increases with increasing the *Eruca vesicaria* concentration up to 800 ppm, decreasing with a further increase in the inhibitor concentration, Table 4, as explained above. This way, the lowest corrosion rate is obtained with the addition of 800 ppm of *Eruca vesicaria*. The double layer capacitance, $C_{\text{dl}}$, decreases with increasing the *Eruca vesicaria* concentration reaching its lowest value at 800 ppm, increasing once again with a further increase in the *Eruca vesicaria* concentration. This decrease in the $C_{\text{dl}}$ value is due to the adsorption of *Eruca vesicaria* on to the steel.
Figure 6. Effect of *Eruca vesicaria* concentration on the Nyquist diagrams for 1018 carbon steel in 0.5 M H$_2$SO$_4$.

Table 4. Electrochemical parameters obtained from Nyquist plots in *Eruca vesicaria*.

<table>
<thead>
<tr>
<th>C$_{inh}$ (ppm)</th>
<th>R$_s$ (Ohm cm$^2$)</th>
<th>R$_ct$ (Ohm cm$^2$)</th>
<th>C$_{dl}$ (F/cm$^2$)</th>
<th>I.E. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.7</td>
<td>46</td>
<td>8.5 x 10$^{-5}$</td>
<td>---</td>
</tr>
<tr>
<td>200</td>
<td>1.8</td>
<td>214</td>
<td>3.7 x 10$^{-5}$</td>
<td>78</td>
</tr>
<tr>
<td>400</td>
<td>3.6</td>
<td>298</td>
<td>3.3 x 10$^{-5}$</td>
<td>84</td>
</tr>
<tr>
<td>600</td>
<td>2.4</td>
<td>386</td>
<td>2.6 x 10$^{-5}$</td>
<td>88</td>
</tr>
<tr>
<td>800</td>
<td>2.4</td>
<td>731</td>
<td>2.4 x 10$^{-5}$</td>
<td>93</td>
</tr>
<tr>
<td>1000</td>
<td>1.8</td>
<td>314</td>
<td>3.5 x 10$^{-5}$</td>
<td>85</td>
</tr>
</tbody>
</table>

The effect of the three extracts concentration on the R$_{ct}$ values for 1018 carbon steel in 0.5 M H$_2$SO$_4$ is shown in Figure 9, where it can be seen that the highest R$_{ct}$ values, and thus, the lowest corrosion rates, were obtained with the addition of *Eruca vesicaria*, whereas the lowest R$_{ct}$ values, and thus, the highest corrosion rates, were obtained with the addition of *Bromelia hemisphaerica*. It can be seen, however, that each extract has an optimum concentration where the highest R$_{ct}$ value is obtained. Thus, this optimum inhibitor concentration was 800 ppm for *Eruca vesicaria* and *Bromelia hemisphaerica*, whereas for *Erythrina americana* was 400 ppm. The addition of an inhibitor concentration higher than this optimum value increases the corrosion rate.
It is generally accepted that the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules absorbed on the metal surface:

\[
\text{Inh}_{\text{sol}} + x\text{H}_2\text{O}_{\text{ads}} \rightarrow \text{Inh}_{\text{ads}} + x\text{H}_2\text{O}_{\text{sol}}
\]  

(3)

The inhibitor may then combine with freshly generated Fe\(^{2+}\) ions on steel surface, forming metal inhibitor complexes [30] [31]:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e
\]  

(4)

\[
\text{Fe}^{2+} + \text{Inh}_{\text{ads}} \rightarrow \left[\text{Fe} - \text{Inh}\right]^{2+}_{\text{ads}}
\]  

(5)

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution. At low concentrations the amount of inhibitor is not enough to form a compact complex with the metal.
ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher inhibitor concentrations, more inhibitor molecules become available for the complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion. Thus, it has been shown that the decrease in $i_{corr}$ and the increase in the $R_{ct}$ values is due to the protective character of the inhibitors. Micrographs of corroded surfaces after being corroded in $H_2SO_4$ shown in Figure 10 are an evidence of this. For steel corroded in the uninhibited solution, Figure 10(a), micrograph shows a
film formed on top of steel, which gives some protection to the steel as evidenced by polarization curves in Figure 3 for the blank, uninhibited solution. This film, however, contains micro cracks and porous, sites where the aggressive solution can penetrate and corrode the underlying metal. When the three inhibitors were added, however, these porous and micro cracks disappeared, improving the film protectiveness, as evidenced by polarization curves, Figures 3-5, and evidencing that the addition of either \textit{Eruca vesicaria}, \textit{Bromelia hemisphaerica} or \textit{Erythrina americana} are the responsible for the steel improved corrosion resistance.

### 3.4. FTIR Results

The good corrosion inhibition properties shown by \textit{Eruca vesicaria}, \textit{Bromelia hemisphaerica} and \textit{Erythrina americana} is due to the presence of antioxidants present in their molecular structure containing heteroatoms such as N, C and O. For instance, \textit{Eruca vesicaria} and \textit{Erythrina americana} contain amino acids, and phenols. Infrared diagram for the pure \textit{Eruca vesicaria}, 0.5 M H$_2$SO$_4$ + 800 ppm of \textit{Eruca vesicaria} before and after the polarization curve are shown in Figure 11. For the pure extract, four peaks can be distinguished: the one at 3340 cm$^{-1}$, which corresponds to the hydroxyl group, O-H, whereas the peak at 2900 cm$^{-1}$ has been assigned to the amine, NH$_2$, group. The peak found at 1740 cm$^{-1}$ corresponds to the carboxile, C=O, group, Table 5, whereas the one at 1050 cm$^{-1}$ has been assigned to the C-O group. It is well known that OH$^{-1}$ can passivate the steel protecting it against corrosion, reacting with Fe$^{2+}$ ions to form Fe(OH)$_2$ responsible for the steel passivation. Amine is also well known to form a good passive film on metals to protect steel from corrosion, and it can be protonated to give NH$^{3+}$ to react with Fe(OH)$_2$ to give FeONH$^{2+}$ + H$_2$, and probably the FeONH$^{2+}$ complex, equations [3] and [5] is the one which remains on the steel surface to protect it.

![FTIR for pure Eruca vesicaria and 0.5 M H$_2$SO$_4$ + 800 ppm Eruca vesicaria before and after the corrosion test.](image)

\textbf{Figure 11.} FTIR for pure \textit{Eruca vesicaria} and 0.5 M H$_2$SO$_4$ + 800 ppm \textit{Eruca vesicaria} before and after the corrosion test.

<table>
<thead>
<tr>
<th>Wave number (cm$^{-1}$)</th>
<th>Assigned functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3340</td>
<td>O-H</td>
</tr>
<tr>
<td>2900</td>
<td>NH$_2$</td>
</tr>
<tr>
<td>1740</td>
<td>C=O</td>
</tr>
<tr>
<td>1050</td>
<td>C-O</td>
</tr>
</tbody>
</table>
4. Conclusion

It has been shown that *Eruca vesicaria*, *Bromelia hemisphaerica* and *Erythrina americana* acted as good corrosion inhibitors for 1018 carbon steel in 0.5 M H$_2$SO$_4$ with the best efficiency exhibited by *Eruca vesicaria*, 80%, whereas the worst efficiency, 40%, was exhibited by *Bromelia hemisphaerica*. The three inhibitors improved the protective properties of the formed passive film on top of the steel by reducing both the passivation potential and current density values. The protection given by the different extracts is due to the presence of antioxidants like phenols and amino acids, which contain heteroatoms in their structure such as C, N, or O, which react with metal and environment to form a complex which adsorbs on to the steel and protect it from the environment.

References


