Study of the Electrochemical Behavior of Mango Extract as a Corrosion Inhibitor of Carbon Steels by varying the PH of the electrolytic medium

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ABSTRACT
The corrosion at industrial level produces a great economic loss, it is then when the necessity in the industry to apply technologies that mitigate this phenomenon, one of these technologies is the use of corrosion inhibitors. Commercial inhibitors are major environmental pollutants, so in the last decade, there have been numerous studies using various plant extracts, which act as corrosion inhibitors with high efficiency. Electrochemical tests were carried out to evaluate the inhibitory effect of mango extract in electrochemical medium of 3.5 % NaCl and 1 % H2SO4 on AISI 1045 steel. The corroded surface was analyzed with scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX) techniques. It was obtained that the mango extract presented efficiencies above 80 %, in the study media, being the highest efficiency (96.5 %) in acid medium. Scanning electron microscopy (SEM) corroborated the results obtained and allowed establishing that the inhibition mechanism is by physiadsorption.

Keywords: Electrochemical testing, inhibitors, mango extract, corrosion, SEM

INTRODUCCIÓN
Currently, it’s common to observe metal parts, equipment, installations and structures that show signs of corrosion (oxides, pitting, thickness loss, etc.). This is associated with the fact that metallic materials, when interacting with the environment, try to take the form similar to that of which they were obtained from nature. In this sense, the phenomenon of corrosion is presented as the destruction or deterioration of the material due to the interaction with the surrounding environment, being this the general cause

RESUMEN del Comportamiento Electroquímico de Extracto de Mango como Inhibidor de Corrosión de Aceros al Carbono variando el PH del medio electrolítico

La corrosión a nivel industrial produce de grandes pérdidas económicas, es entonces cuando surge la necesidad por parte de la industria de aplicar tecnologías que mitiguen este fenómeno de corrosión, entre estas tecnologías está el empleo de inhibidores de corrosión. Los inhibidores comerciales son grandes contaminantes del medio ambiente, por lo que, en la última década, se han realizado numerosos estudios con diversos extractos vegetales, los cuales actúan como inhibidores de la corrosión con una alta eficiencia. Se realizaron ensayos electroquímicos para evaluar el efecto inhibidor del extracto de mango en medio electroquímico de NaCl al 3.5 % y H2SO4 al 1 % sobre el acero AISI 1045. Se analizó la superficie corroída mediante las técnicas de microscopía electrónica de barrido (MEB) y espectroscopía de energía dispersiva (EDX). Se obtuvo que el extracto de mango presentó eficiencias por encima del 80 %, en los medios de estudio, siendo la mayor eficiencia (96.5 %) en medio ácido. Por medio de la microscopía electrónica de barrido (MEB) se pudo corroborar los resultados obtenidos y establecer que el mecanismo de inhibición es por fisiasdorsción.

Palabras claves: Ensayos electroquímicos, inhibidores, extracto de mango, corrosión, MEB.
of alteration or degradation of most of the metallic materials manufactured [1]. Before their commercial and industrial applications, the metallic surface often requires removal of rusts and scales using strong acid such as H₂SO₄, HCl, HNO₃ and H₃PO₄. This process of acid cleaning is generally known as acid pickling, being HCl and H₂SO₄ the most used [2].

The importance of the corrosion study and the way to avoid or control it, is linked to a high economic and social impact. According to studies [3], it has been estimated that the amount of material damaged or affected in total or partial form is considerable worldwide and leads to significant economic losses. The great economic losses generated by this phenomenon, has been of great importance for the industry and society, that is why many studies have been conducted on the corrosion rate on the metallic materials exposed to several environment and different technological applications have been developed to mitigate this phenomenon; among these technologies there is the use of corrosion inhibitors.

In recent years, research on corrosion inhibitors has been focused on the evaluation of plant extracts as corrosion inhibitors on different types of steel. Corrosion inhibitors based on plant extracts are compounds obtained from natural substances, synthesized in a safe and energy-efficient manner, with minimal or no toxicity, rapidly biodegradable and do not generate any type of environmental impact [4,5]. Research about corrosion bioinhibitors has been focused on the study of natural polymers, aminoacids, vitamins and, more recently, soluble plant extracts [4]. The use of corrosion bioinhibitors has been gaining importance because the vegetable kingdom is an abundant and sustainable source of naturally synthesized compounds that can be extracted through procedures with a low associated cost [6,7].

The organic compounds of the extracts are adsorbed on the surface of metals and alloys through bonds and heteroatoms such as oxygen, sulfur, nitrogen and phosphorus in the form of functional polar, aliphatic and aromatic remains, which can act as adsorption centers forming a barrier on the surface, thus protecting the metals from corrosive degradation [3].

Generally, there are heteroatoms of organic inhibitors in functional polar groups, such as CN⁻, NO₂⁻, NH₂⁺, COOH⁻, COOCH₃⁻, OCH₃⁻, etc., which act as adsorption centers on metal surfaces [1, 8]. In addition, these functional polar groups improve the solubility of compounds in polar electrolyte media such as H₂O, HCl, H₂SO₄, H₃PO₄, HNO₃, etc. [3, 9].

Studies have been conducted in acidic electrolyte media such as HCl, where it has been found that mango extract obtained from the peel give adequate protection to steel in 5 % and 10 % HCl at 25 and 40 °C [8-10]. Also it has been found that the increase of mango extract concentration the inhibition efficiency significantly increased and reached the maximum value of about 92 %. In the presence of 1000 mg/L mango extract the iron surface damage decreased and the inhibitor molecules adsorption provide a hydrophobic surface [9]. C.A. Loto [11-12] evaluated the effect of mango leaf and peel extract separately and combined as an inhibitor of steel samples in H₂SO₄ 0.2 M, and a good efficiency of 70.15 % was obtained when combined at room temperature.

In neutral media, such as NaCl, it has been found that the mango extract presents a good efficiency at room temperature and this depends on the microstructure and roughness of the samples [6, 7, 13]. Diaz W. [6] studied the effect of the microstructure of two steels 1010 and 4140 on the efficiency of mango extract mixed with alkyd resin through potentiodynamic tests in a 5 % NaCl
solution, obtaining an efficiency of 92.18 % in 1010 steels and 0 % for 4140 steels. Tarazona J. [7] evaluated the efficiency of mango extracts on steel surfaces with roughness grades 80 and 600 through weight loss tests in 5 % NaCl media, finding that 600 grade finishes had the highest efficiency of 80.34 % at immersion times of 168 hours. The possibility of using this extract as a corrosion inhibitor is very interesting from the point of view of economy and environment areas. Therefore, the aim of this research is to evaluate the inhibitory effect of mango extract on carbon steels in NaCl and H₂SO₄ media.

MATERIALS AND METHODS
Initially, a chemical analysis was carried out on the steel samples in order to corroborate their composition. Then, in order to evaluate the mango extract as a possible inhibitor of corrosion processes, a chemical analysis of the mango extract was carried out in order to know the present elements. The analysis was performed in an atomic absorption spectrophotometer, PERKIN ELMER model Analyst 300. Subsequently, the test samples were prepared with the dimensions of 1.00 cm × 1.00 cm × 0.15 cm approximately, which were prepared metallographically according to the ASTM G-1 standard [14].

To perform the electrochemical tests, the samples were embedded in epoxy resin in order to provide a surface with an area of 1.00 cm × 1.00 cm approximately, which will be exposed to the electrolytic medium. Finally, the mango extract solution was applied with a concentration of 2 % v/v [6, 7, 13], through the immersion and drying method: 24 h of immersion and 4 h of drying at 45 °C in a stove.

The potentiodynamic polarization curves were carried out according to the procedure indicated in the ASTM G59-97 standard [15]. A potentiostat EG&G, model 272 A was used. The open circuit potential (Eoc) was determined during 30 min for each sample tested. Tafel extrapolation curve was started at a potential of \(E_0 = -300 \text{ mV vs } E_{oc}\), and the \(E_f = 300 \text{ vs } E_{oc}\), a Saturated Calomel electrode (SCE) was used as reference electrode and graphite rods as reference electrodes, at a scanning potential rate of 0.167 mV/s. The electrolyte solutions used in the tests were 3.5 % NaCl and 1 % H₂SO₄.

The microstructural characterization and corrosion products analysis of the samples tested were carried out through the Scanning Electronic Microscopy (SEM) technique, in a Hitachi equipment, model S-2400 and by Energy Dispersion X-Ray Spectroscopy (EDX).

RESULTS AND DISCUSSION

Chemical analysis.
Table I shows the results obtained in the chemical analysis of the carbon steel samples. According to the carbon content present in the samples, the steel used is a 1045 according to the classification in the AISI/SAE nomenclature [16].

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% C</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>0.49 ±0.01</td>
</tr>
<tr>
<td>AISI 1045</td>
<td>±0.01</td>
</tr>
</tbody>
</table>

Table II shows the elements present in the mango extract, obtained in the chemical analysis by the atomic absorption technique, highlighting the presence of the following elements: Copper, Calcium, Magnesium, Zinc and Sodium.

<table>
<thead>
<tr>
<th>Extract</th>
<th>% Cu</th>
<th>% Ca</th>
<th>% Zn</th>
<th>% Mg</th>
<th>% Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mango</td>
<td>0.09 ±0.01</td>
<td>1.33 ±0.02</td>
<td>7.42 ±0.04</td>
<td>1.17 ±0.02</td>
<td>0.08 ±0.02</td>
</tr>
</tbody>
</table>
Electrochemical Tests.

In order to evaluate the mango extract as an inhibitor of corrosion processes, polarization curves of the AISI 1045 steel samples were carried out with and without the application of the mango extract, at different pH conditions of the electrolytic medium.

Figure 1 shows the electrochemical behavior of the samples exposed to the 3.5 % NaCl electrolyte medium at 25 °C. Note that the corrosion current density ($i_{corr}$) decreases significantly with the addition of the extract. In addition, a change in the anodic shift of the $E_{corr}$ values from -780 mV (blank) to -870 mV (mango) is observed, the tafel slopes value ($\beta_a$), indicates that the mango extract probably inhibits the cathodic reaction more than the anodic reaction for AISI 1045 steel in 3.5 % NaCl, due to the adsorption of the organic components of the extract on the active cathodic sites of the metal surface, probably preventing the hydrogen evolution reactions from occurring on it, while the slopes of anodic tafel ($\beta_a$) don’t present great changes in the slope, so it is assumed that the extract acts as an inhibitor cathode [17-19].

![Fig. 1. Electrochemical behavior of steel samples with and without mango extract in 3.5 % NaCl solution.](image)

It can be seen that the corrosion current density ($i_{corr}$) decreases significantly with the addition of mango extract. While the $i_{corr}$ values, present an approximate value of -575, in both curves.

This means that the extract probably acted blocking cathodic and anodic sites, due to the adsorption of organic compounds in the active sites of the sample surface, delaying both the metal dissolution and the hydrogen release reactions, and consequently decreasing the corrosion rate, so it is assumed that the extract acts as a mixed type inhibitor.

![Fig. 2. Electrochemical behavior of steel samples with and without mango extract in 1% H₂SO₄ solution.](image)

Saleh et al. [17], had similar results in the inhibition of low carbon steel, with mango extract in HCl media, these results are consistent with those obtained by Cardozo da Rocha and collaborators. [18-21]

Tables III and IV show the results of corrosion rate ($V_{corr}$), Tafel slopes ($\beta_a$, $\beta_c$), as well as the efficiency (E), of the mango extract as an inhibitor of the corrosion processes in AISI 1045 steel samples, in electrolytic solutions of H₂SO₄ and NaCl, respectively. It can be noted that mango extract, presented a higher efficiency in acidic media than neutral media.
Table II

<table>
<thead>
<tr>
<th>Sample in NaCl</th>
<th>$V_{corr}$ (g/cm$^2$ year)</th>
<th>$\beta_a$</th>
<th>$\beta_c$</th>
<th>$E$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pattern</td>
<td>0.12</td>
<td>0.020</td>
<td>0.030</td>
<td>-</td>
</tr>
<tr>
<td>Mango Ex.</td>
<td>0.15</td>
<td>0.028</td>
<td>0.050</td>
<td>87.47</td>
</tr>
</tbody>
</table>

Table IV

<table>
<thead>
<tr>
<th>Sample in H$_2$SO$_4$</th>
<th>$V_{corr}$ (g/cm$^2$ year)</th>
<th>$\beta_a$</th>
<th>$\beta_c$</th>
<th>$E$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pattern</td>
<td>7.16</td>
<td>0.030</td>
<td>0.027</td>
<td>-</td>
</tr>
<tr>
<td>Mango Ex.</td>
<td>0.25</td>
<td>0.023</td>
<td>0.019</td>
<td>96.50</td>
</tr>
</tbody>
</table>

The efficiency values were calculated according to equation (1):

$$E (%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

(1)

Where, $i^0_{corr}$ and $i_{corr}$, are the corrosion current density without and with inhibitor respectively [3]. A reduction of the corrosion rate respect the standard sample can be observed, having high efficiency values in the media under study, with percentages of efficiency of 87.47 % and 96.50 % for 3 % NaCl and 1 % H$_2$SO$_4$, respectively.

*Scanning Electron Microscopy (SEM)*

The following figures are the micrographs corresponding to the AISI 1045 steel samples, with and without mango extract, where the electrochemical behavior of the steel in the electrolytic media studied is observed, and how this behavior was modified in the presence of mango extract.

Figure 3a shows the micrograph of the standard sample of AISI 1045 steel, which shows a fairly rough surface possibly due to the attack of the medium and the formation of iron oxide on the metal surface, a product of the corrosive process of the sample exposed to the medium of 3.5 % NaCl without any protection.

As for the sample with mango extract (fig. 3b), it can be observed a surface with small areas without damage and others with irregular deposits. This morphology possibly corresponds to a non-uniform film of mango extract adsorbed on the surface, which evidences that the inhibitor extract was not able to maintain its uniform adsorption on the surface under this study condition.

Figure 4a shows three types of textures formed on the surface (points 1, 2 and 3). A smooth surface (point 1) in the presence of non-uniform areas possibly formed by the mango extract film. Analyzing the respective EDX (fig. 4b, table V), it is clear that in point 1, the carbon content is slightly higher than that corresponding to the steel substrate, which could mean that there is a thin film of mango extract adsorbed to prevented the attack of the 3.5 % NaCl medium on the surface, since the roughness of the attack on the surface is lost, as in the standard sample (fig. 3a). As for points 2 and 3 (P2, P3), deposits with a high...
carbon content in the presence of a low iron content (fig. 4b, table V), which corresponds to deposits of the mango extract.

**Fig. 4.** (a) SEM in SE mode of surface the AISI 1045 steel coupons at 500X and (b) their respective point EDX made in different areas of the surface with mango extract.

**Table V.** EDX analysis of different areas from the surface with mango extract.

<table>
<thead>
<tr>
<th>Pt</th>
<th>%C</th>
<th>%O</th>
<th>%Na</th>
<th>%Si</th>
<th>%S</th>
<th>%Ca</th>
<th>%Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.79</td>
<td>3.34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>87.02</td>
</tr>
<tr>
<td>2</td>
<td>17.94</td>
<td>7.01</td>
<td>1.15</td>
<td>1.84</td>
<td>13.92</td>
<td>13.18</td>
<td>44.96</td>
</tr>
<tr>
<td>3</td>
<td>16.94</td>
<td>14.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67.51</td>
</tr>
</tbody>
</table>

Figure 5a presents the micrograph of the standard sample of steel AISI 1045, which shows a fairly rough surface, probably with a layer of iron oxide on the metal surface due to corrosive process of the sample exposed to the 1% H2SO4 medium. Figure 5b shows the presence of a uniform layer on the surface, possibly corresponding to the superficial adsorption of mango extract. This shows that the mango extract exhibited an excellent inhibition behavior against the corrosion process, thus achieving the protection of the metal surface under these study conditions.

**Fig. 5.** SEM in SE mode of surface at 100X of AISI 1045 steel coupons: (a) Sample without inhibitor and (b) sample with mango extract, exposed in a 1% H2SO4 medium.

Figure 6 shows the micrographs of the AISI 1045 steel samples at 500X magnification (fig. 6a) and the representative points with their respective EDX analysis, taken in different areas of the surfaces once exposed in the study medium (fig. 6b, table VI). In the mango extract sample a layer can be observed on the metal surface possibly formed by the mango extract. Analyzing the respective EDX, it can be said that in the three points studied, the carbon content is quite high and other elements such as Cu and Mg, which are characteristics of organic inhibitors, appear, and evidences the presence of a mango extract film, this is observed quite pronounced in points 1 and 2 (pts 1, 2). Also, it was observed that the mango extract achieved the formation of a sufficiently uniform and adherent layer on the metal surface, preventing the sample from being severely attacked by the electrolytic medium, which is consistent with the high values of efficiency as an inhibitor of mango extract obtained (96.5%).
Fig. 6. (a) SEM in SE mode of surface the AISI 1045 steel coupons with mango extract at 500X and (b) their general EDX made on the surface of the samples exposed in a 1% H₂SO₄ medium.

Table VI. EDX analysis of the surface from samples exposed in H₂SO₄.

<table>
<thead>
<tr>
<th>Pt</th>
<th>% C</th>
<th>% O</th>
<th>% Al</th>
<th>% S</th>
<th>% Mn</th>
<th>% Fe</th>
<th>% Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.63</td>
<td>2.07</td>
<td>3.41</td>
<td>0.69</td>
<td>52.04</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>39.14</td>
<td>8.25</td>
<td>1.32</td>
<td>3.56</td>
<td>47.39</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>18.04</td>
<td>13.67</td>
<td>1.52</td>
<td>79.3</td>
<td>0.44</td>
<td>58.41</td>
<td></td>
</tr>
</tbody>
</table>

SEM of the steel samples AISI 1045 transverse session with mango extract.

Figure 7a shows the micrographs of the cross section made to the AISI 1045 steel sample at 500X exposed in 3.5% NaCl. In this case, the formation of an adherent layer of mango extract on the metal surface can be seen.

Figure 7b shows in a more detailed way the layer formed on the surface and when analyzing the points EDX, it can be observed that point 3 (extract film) presents a high carbon and a low iron contents in comparison with points 1 and 2 (metal surface), which present a high iron content, which evidences the presence of the inhibitor on the metal surface, assuming that the inhibition mechanism is by physiadsorption [6,7,19].

Table VII. EDX analysis percentage at respects points of the surface with mango extract (fig. 7b).

<table>
<thead>
<tr>
<th>Pt</th>
<th>% C</th>
<th>% O</th>
<th>% Na</th>
<th>% Mg</th>
<th>% Al</th>
<th>% K</th>
<th>% Ca</th>
<th>% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16.90</td>
<td>21.46</td>
<td>1.51</td>
<td>0.11</td>
<td>0.16</td>
<td>59.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.73</td>
<td>11.09</td>
<td>0.36</td>
<td>1.50</td>
<td>0.45</td>
<td>95.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>23.51</td>
<td>11.09</td>
<td>0.36</td>
<td>1.50</td>
<td>0.45</td>
<td>63.09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inhibition mechanism.

It is quite difficult to establish which components of mango extract inhibit the corrosion processes, because mango is a fruit with antioxidant compounds such as polyphenols, carotenoids and vitamins C and E, as well as phenolic compounds such as flavonoids. Another element that mango contains in great quantity is pectin which is a structural heteropolysaccharide [18], although probably the content of polyphenols and flavonoids are those that inhibit the processes of corrosion since it has been demonstrated that there are vegetable extracts without pectin but with flavonoids and polyfenoles that inhibit the corrosion processes [3,18,22].

These components have hydroxyl and carbonyl functional groups, with antioxidant properties, which interact with
the metal surface forming an amorphous oxyhydroxide (FeO.OH) layer. This layer separates the electrolyte and the metal surface, behaving as a barrier against diffusion and could also interact with some component of the electrolyte medium, modifying the inhibitory characteristics of the layer of product formed [22]. Finally, it is inferred according to the results obtained, that the mechanism of inhibition of the mango extract varies according to the pH; in NaCl media it is an anodic type inhibitor, while in acidic media it is a mixed type, and the mechanism of adsorption is by physiadsorption.

CONCLUSIONS
Mango extract proved to be very effective in its application as a corrosion inhibitor in 3.5 % NaCl and 1 % H₂SO₄ media, due to the fact that a remarkable reduction in the corrosion rate is achieved with respect to the values obtained in the standard sample. The inhibition mechanism of the mango extract in the 3.5 % NaCl solution was anodic, while in the H₂SO₄ electrolyte medium it acted as a mixed inhibitor. Mango extract obtained a higher inhibition efficiency in acidic medium. By means of SEM technique, it was proved the formation of a film of mango extract on the metallic surface, in both studied media, establishing that probably the inhibition mechanism is by physiadsorption of the extract on the steel surface.

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