ABSTRACT
The performance of a fatty acid amide inhibitor synthesized from the coffee bagasse oil has been evaluated by electrochemical techniques such as potentiodynamic polarization curves, open circuit potential measurements, linear polarization resistance, and electrochemical impedance spectroscopy. Inhibitor concentrations included 0, 5, 10, 25, 50, and 100 ppm. Inhibitor efficiency was evaluated on an X70 steel in a CO2-saturated brine at 60°C. All the different techniques have indicated a decrease in the cathodic current density and inhibitor efficiency values as high as 96%. The inhibitor was chemically adsorbed on to the steel according to the analysis of the inhibitor adsorption process.

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Introduction
The corrosion of carbon steel due to dissolved carbon dioxide (CO2) is commonly known as “sweet corrosion” and it is a serious problem in the different stages of hydrocarbon transport (1). It is known that CO2 when dissolved in water promotes the formation of carbonic acid (H2CO3). In this way, the carbonic acid reacts with the carbon steel causing its degradation and assisting in the formation of cracks which can evolve to fractures (2). This is a serious problem because the rupture of the hydrocarbon transport lines causes great economic and material losses, as well as damage to the environment.

The mechanism of CO2 corrosion is extremely complex because it is affected by various factors such as temperature, pressure, pH, flow rate, dissolved salts, water composition, and so on (3). Various methods have been used to mitigate the problems caused by the CO2 corrosion process, being the injection of corrosion inhibitors one of the most extensively investigated (4). A corrosion inhibitor can be defined as a compound that, when added in small quantities in an aggressive environment, decreases the corrosion rate without modifying the composition of the corrosive medium (5). The corrosion inhibitors can be classified depending on the source and the way in which they affect the different corrosive processes that are carried out onto metal surface. Different parameters influence the choice of a corrosion inhibitor, being the main ones, its inhibition efficiency and its impact on the environment (5).
The corrosion inhibitors of organic origin have taken great relevance in the field of corrosion control due to their excellent performance which makes them a good choice from the cost–benefit point of view (6). Most corrosion inhibitors of organic origin have the ability to be adsorbed on the metal surface forming layers of hydrophobic films that limit the mass transport of aggressive species. The adsorption capacity of this type of inhibitors is related to the presence of heteroatoms such as N, O, P and S in the molecular structure (5, 7, 8).

Currently, new sources of organic corrosion inhibitors have been investigated due to their low or no toxicity and excellent performance. One of the most studied sources are the vegetable oils with high content of unsaturated fatty acids, this type of oils when reacting with amines-type compounds can form corrosion inhibitors as amines, amides and imidazolines of fatty acids (5, 7, 8). A particularity of these compounds is that their molecule is formed by the following main components: a polar group (integrated by oxygen, nitrogen, phosphorus or sulfur atoms) which interacts strongly with the metal surface by means of dipolar forces or a coordinated type bond, and a non-polar group (hydrophobic hydrocarbon chain) which acts as a barrier between the metal surface and electrolyte (7, 9). Nowadays it is of great interest the search of new sustainable sources as renewable raw materials that allow to take advantage of the photosynthetic activities of the plants. In particular, the use of both waste and agroindustrial byproducts is an excellent source for obtaining vegetable fats and oils, which can be used for the synthesis of products with greater added value. These actions contribute to a sustainable use of natural resources because the food chain is not affected and new croplands are not required to obtain this type of vegetable fats and oils.

Coffee is one of the most consumed grains in the world, and its processing generates large amounts of waste (bagasse). The coffee bagasse contains 13–15% (dry base) of oil with a high content of linoleic acid as the most abundant fatty acid (7). These characteristics make this agroindustrial waste attractive in order to contribute to a sustainable use of natural resources. Therefore, the objective of this work is to take advantage of the oil content of the coffee bagasse for its use in the synthesis of a green corrosion inhibitor. The inhibitor synthesized from the coffee bagasse oil was a fatty acids amide, and its performance was evaluated on an API X70 steel using electrochemical techniques in CO₂-saturated brine (3.5% wt NaCl) at 60°C. The electrochemical techniques used include open-circuit potential (OCP) measurements, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves.

**Figure 1.** Fatty amide derivatives from coffee oil: (a) linoleic N-[[2-(2-hydroxyethyl) amino] ethyl]-amide, (b) palmitic N-[[2-(2-hydroxyethyl) amino] ethyl]-amide, (c) oleic N-[[2-(2-hydroxyethyl) amino] ethyl]-amide, and (d) stearic N-[[2-(2-hydroxyethyl) amino] ethyl]-amide.

**Experimental procedure**

As testing material, cylindrical samples of X70 steel of 8 mm in diameter and 12 mm in length were used. These cylindrical samples acted as a working electrode (WE) and before each test they were grinded with 1200 grade abrasive paper, washed with distilled water, ethanol, and acetone.

As a corrosion inhibitor, a fatty acid amide synthesized from coffee bagasse oil was used. The synthesis procedure was according to the procedure reported in the literature (5, 8). The details of the synthesis and the characterization of the inhibitor have been reported by the authors in a previous publication (10). According to the studies carried out, the monitoring of the synthesis process (by thin layer chromatography) confirmed the complete conversion of the triglycerides to fatty acid amide. After the purification of the products and their characterization by FTIR spectroscopy, a yield of the synthesis process of 96.9% was obtained. Based on these results, it was established that the molecular structure...
of the fatty amides synthesized is as shown in Figure 1 in a proportion similar to that of the fatty acid content of the oil used for its synthesis (44.2% linoleic acid, 34.41% palmitic acid, 8.53% oleic acid, 7.56% stearic acid) (10).

Tests were performed in a 500-ml electrochemical cell (the electrolyte volume was 400 ml) using a three-electrode arrangement. The X70 steel cylinders were used as the WE, as a reference electrode a saturated calomel electrode (SCE) (SCE = 0.242 V vs standard hydrogen electrode, SHE), and as an auxiliary electrode a graphite bar with an area greater than that of the WE. As corrosive electrolyte, a CO₂-saturated brine (3.5% wt NaCl) at a temperature of 60°C was used (pH ≈ 4.8) (11). The performance of the synthesized inhibitor was evaluated at various concentrations, namely, 5, 10, 25, 50, and 100 ppm. In a typical test, before introducing the electrode array, the brine was allowed to saturate with CO₂ for at least 1 hour. Due to the test temperature, it was necessary to use a Luggin capillary filled with a KCl-saturated solution. OCP measurements were performed at 1-hour intervals measuring the potential between WE and SCE. LPR measurements were made by polarizing the specimen ± 15 mV with respect to the OCP at a scanning rate of 1 mV s⁻¹ (12–14). EIS measurements were obtained using an AC signal with amplitude of 10 mV in a frequency range of 10⁵–10⁻² Hz at the OCP value. Potentiodynamic polarization curves were obtained after 10 h of immersion of the WE into the corrosive electrolyte in order to allow the inhibitor to achieve its maximum surface coverage. After this stabilization period, WE was polarized from −400 mV to 1200 mV with respect to its equilibrium potential at a scanning speed of 1 mV s⁻¹. In the case of the OCP, LPR, and EIS measurements, the inhibitor was added 1 h after initiated the tests. EIS, LPR and OCP measurements were performed on a Gamry Interface 1000 potentiostat-galvanostat, whereas for the polarization curves a GilIAC potentiostat-galvanostat was used.

**Result and discussion**

**Potentiodynamic polarization curves**

Figure 2 shows the potentiodynamic polarization curves of the X70 steel evaluated in the CO₂-saturated brine in absence and presence of inhibitor after 10 h of stabilization at 60°C. In absence of inhibitor, an active behavior of the X70 steel is observed at potentials slightly above its corrosion potential, which suggests the inability of the material to form a layer of protective corrosion products on its surface that prevents the continuous dissolution of Fe according to the next reaction:

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

On the other hand, the cathodic branch shows the typical behavior of a CO₂-saturated systems (low or no dissolved oxygen content) with a limit current density value. In this case, the degradation process of the materials is assisted by the dissolved CO₂ which forms carbonic acid according to following reaction:

\[
\text{CO}_2(g) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3.
\]

Then, the degradation of the X70 steel can occur by the contact of the dissociated species of carbonic acid with the metallic surface according to following reactions (15–18):

\[
2\text{H}_2\text{CO}_3 + 2\text{e}^- \rightarrow 2\text{HCO}_3^- + \text{H}_2,
\]
The above anodic and cathodic reactions as a whole promote the formation of iron carbonate with limited protective characteristics; in addition to this, it has been reported that its precipitation onto metal surface occurs above 50°C and at long exposure times (19):

\[
\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3. \tag{6}
\]

In presence of the inhibitor, a shift of the \(E_{\text{corr}}\) values towards nobler potentials is observed, together with a displacement of the whole polarization curves towards lower current densities. It is also observed that the cathodic limit current density decreases with an increase in the inhibitor concentration. The foregoing is more noticeable at inhibitor concentrations above 10 ppm. The observed changes in presence of the inhibitor indicate a decrease in the corrosion rate of the steel due to the inability of the aggressive ions to interact with the steel surface due to the adsorption of a protective inhibitor film (20).

Table 1 shows the electrochemical parameters obtained from the polarization curves. These parameters were obtained from the potentiodynamic polarization curves as indicated in Figure 3. According to data given in Table 1, it is observed that the addition of the inhibitor caused a significant change in the values of \(E_{\text{corr}}, i_{\text{corr}}\) and \(B_c\) due to a decrease in the available cathodic sites on the metal surface as a consequence of the adsorption of the inhibitor.

Inhibition efficiency, \(E\), was determined according to the following equation:

\[
E(\%) = \frac{i_{\text{corr}}^b - i_{\text{corr}}^i}{i_{\text{corr}}^b} \times 100, \tag{7}
\]

where \(i_{\text{corr}}^b\) and \(i_{\text{corr}}^i\) are the corrosion current density in the absence and presence of the inhibitor respectively. According to the calculated values, inhibition efficiency higher than 95% was observed for concentrations greater than 10 ppm.

### OCP measurements

Figure 4 shows the evolution of the OCP value as a function of time for X70 steel immersed in \(\text{CO}_2\)-saturated brine at 60°C with and without the addition of inhibitor. It is observed that in absence of the inhibitor X70 steel shows a constant increase in its OCP values towards nobler values as the immersion time increases. This response can be associated with the formation and accumulation of corrosion products on the steel surface (21, 22), as can be seen in Figure 5, where the surface morphology of specimens exposure at 2 and 16 h of immersion in to the corrosive solution are shown. By comparing both superficial aspects, it is evident that the amount of corrosion products on the steel surface increases with the immersion time, which contributed

![Figure 3. Schematic representation of the electrochemical parameters from the potentiodynamic polarization curves.](image-url)
to decrease the active sites which causes a shift of the OCP values in to the noble direction. In presence of inhibitor, in all cases, the evolution of the OCP values indicates nobler potential values than those observed without the addition of inhibitor. An abrupt increase in the OCP values is observed in the first 2 h of testing, which may indicate a strong affinity of the inhibitor towards the metal surface. This behavior has been observed when there is the adsorption of inhibitor molecules on the metal surface which can modify the kinetics of the anodic, cathodic or both reactions (1). The fluctuations in the OCP values observed at concentrations greater than 10 ppm may be due to the reorganization of the inhibitor adsorbed molecules due to the existence of repulsion forces caused by their high concentration in the electrolyte.

**LPR measurements**

Figure 6 shows the evolution of the polarization resistance value, $R_p$, as a function of time for X70 steel immersed in...
CO₂-saturated brine at 60°C with and without the addition of inhibitor. It is known that the polarization resistance values are inversely proportional to the corrosion current density according to the following equation:

\[ i_{corr} = \frac{B_a B_c}{B_a + B_c} \times \frac{1}{R_p}, \]  

where \( B_a \) and \( B_c \) are the anodic and cathodic Tafel slopes respectively, obtained from the polarization curves (1). Therefore, the polarization resistance values can be used to infer the corrosion rate of the material under study. The variation in the polarization resistance values observed for X70 steel in the absence of inhibitor shows an almost constant value during the first 12 h of immersion and subsequently a slight decrease is observed until the end of the test. This behavior may be associated with the formation of a corrosion products layer that was not able to prevent the metal dissolution possibly due to the presence of imperfections on its surface such as porosity or cracks.

However, in presence of the inhibitor, the \( R_p \) values tend to monotonically increase during the first 10 h of immersion, but they remain practically constant at longer times. This behavior is more evident with the addition of 25, 50, and 100 ppm of inhibitor. The increase in \( R_p \) values (greater than 1 order of magnitude) is due to the adsorption of the inhibitor on the metal surface which forms a protective barrier between the electrolyte and the active sites of the alloy (21).

Based on the results shown in Figure 6, inhibition efficiencies were calculated for the different concentrations of inhibitor according to the following relationship:

\[ E(\%) = \frac{R_{p,i} - R_{p,b}}{R_{p,i}} \times 100, \]

where \( R_{p,b} \) and \( R_{p,i} \) are the \( R_p \) values in the absence and presence of the inhibitor respectively. Based on the calculated inhibition efficiencies (Figure 7), it can be observed that there is an increase in the inhibition efficiency as a function of the concentration of inhibitor, obtaining values as high as 90% for inhibitor concentrations greater than 10 ppm, which reached after 10 h of testing. The performance observed for inhibitor concentration higher than 25 ppm was very similar, so 25 ppm is the optimal.

**Electrochemical impedance spectroscopy (EIS)**

Figure 8 shows the evolution of the impedance spectra for X70 steel evaluated in CO₂-saturated brine in the absence of inhibitor. From the Nyquist diagram, the presence of a depressed, capacitive semicircle whose diameter tends to decrease with the immersion time is observed. This behavior indicates that the corrosion products formed are not protective and, therefore, the corrosion rate tends to increase. At low frequencies, it is possible to observe the presence of a small capacitive semicircle that refers to the adsorption of intermediate species produced by the hydrolysis of Fe during the metal dissolution. This can be explained according to the following reactions (23, 24):

\[ Fe + H_2O \leftrightarrow FeOH_{ad} + H^+ + e^-, \]

\[ FeOH_{ad} \rightarrow FeOH^+ + e^-, \]
FeOH$^+$ + H$^+$ ↔ Fe$^{2+}$ + H$_2$O,  \hspace{1cm} (12)

where FeOH$_{ad}$, an intermediate product before the formation of the Fe$^{2+}$ ion, is the species adsorbed on the surface. From the Bode diagrams, in the different regions of high, medium, and low frequencies, it is possible to observe different behaviors associated to a component with a real physical meaning, for example: a resistor has the shape of a plateau with a phase angle of 0°, an ideal capacitive behavior shows a phase angle of $-90^\circ$, and a slope of $-1$, and an element associated with diffusion shows a phase angle of $-45^\circ$ and a slope of $-0.5$ (25). However, when a behavior showing a phase angle less than $-90^\circ$ is observed, it indicates a not entirely capacitive process, which may suggest that charge and mass transfer processes are carried out simultaneously on the WE surface. Based on this, it can be seen that in the intermediate frequency region (Figure 8), X70 steel shows both a slight increase and displacement of its maximum phase angle towards lower frequencies as a function of time. This indicates an increase in the capacitive behavior of X70 steel surface, and it can be attributed both to the accumulation or formation of the intermediate species due to the hydrolysis of Fe previously explained (21). On the other hand, in the low frequency region a second time constant is observed, this is associated with the second semicircle observed in the Nyquist diagram, in addition the low frequency plateau is not completely defined. These characteristics can be associated with mass transfer limitations due to the presence of species adsorbed on the surface of the electrode.

Figure 9 shows the evolution of the impedance spectra for X70 steel in CO$_2$-saturated brine as a function of the inhibitor concentration after 24 h of immersion. From the
Nyquist diagrams, it is possible to observe a capacitive semicircle whose diameter increases as a function of the inhibitor concentration. This behavior indicates that the metal dissolution process is affected by the presence of the inhibitor adsorbed on the surface of the electrode (26). The decrease in the diameter of the capacitive semicircle observed at 100 ppm may be due to a supersaturation of inhibitor molecules present on the surface of the WE. This can cause the presence of repulsion forces between the inhibitor molecules that leads to desorption processes, thereby increasing the number of active sites exposed to the electrolyte. In addition to this, the absence of the small capacitive semicircle observed at low frequencies in the absence of the inhibitor is evident (Figure 8). This suggests that by the action of the inhibitor the adsorbed species are removed or the formation of intermediate species is interrupted (27). From the Bode diagrams, it is possible to observe the presence of two time constants from the high frequency region to the intermediate frequency region. The first time constant (high frequency) is the typical response due to the formation of an inhibitor film with hydrophobic characteristics on the surface of the WE. This type of characteristics has been previously reported in the presence of both amide and imidazoline fatty acid inhibitors (7, 8, 18, 28). On the other hand, the second time constant observed in the intermediate frequency region corresponds to the capacitive response of the metal surface (29).

Modeling of the impedance spectra was performed based on the equivalent circuits shown in Figure 10. The equivalent circuit used to describe the behavior of the X70 steel in absence of the inhibitor is shown in Figure 10(a). In this case, $R_s$ represents the resistance of the solution, $CPE_{dl}$ is the constant phase element of the electrochemical double layer, $R_{ct}$ is the resistance to charge transfer, and $W_s$ is the Warburg element representative of the phenomenon of diffusion in a finite layer. Modification of the Randless circuit, with the inclusion of a constant phase element and a Warburg element ($W_s$), is commonly used for the description of species adsorbed on the metal surface considering the combination of mass transfer phenomena and irregularities caused by surface irregularities (8, 21, 28). The impedance of the CPE is defined by

$$Z_{CPE} = Q^{-1}(j\omega)^{-n},$$  

where $Q$ is a constant, $\omega$ is the angular frequency (rad/s), $j$ is the imaginary number $\sqrt{-1}$, and $n$ is an exponent that describes the phase variation. For the modeling of the

\[\text{Figure 9. Evolution of the impedance spectra for X70 steel in CO}_2\text{-saturated brine as a function of the inhibitor concentration after 24 h of immersion.}\\
\text{Figure 10. Equivalent circuits proposed to model the evolution of the impedance spectra: (a) in the absence of inhibitor and (b) with the addition of inhibitor.}\]
impedance spectra in the presence of inhibitor, the equivalent circuit of Figure 10(b) was used, where CPE\(_f\) and \(R\) are the capacitive response produced by the inhibitor film adsorbed on the steel surface and its resistance respectively. This type of equivalent circuit has been used to model the presence of an inhibitor film on the surface of the WE (8, 21, 28, 30).

Table 2 shows the values used to simulate the EIS data by using the equivalent circuits in the absence and presence of inhibitor. Analysis of the data obtained clearly shows that the calculated \(R_{ct}\) values are practically the same in all cases to those reported in the LPR measurements. This indicates that the proposed equivalent circuits perfectly fit the surface processes that occur at the WE surface. In general, it is observed that in presence of inhibitor the CPE\(_{dl}\) values are lower than those obtained in absence of inhibitor. It has been indicated that this may be due either to a decrease in the dielectric constant or an increase in the thickness of the electrochemical double layer due to the adsorption of the inhibitor molecules which cause a decrease in the corrosion rate (12, 31).

**Surface analysis by SEM**

Figure 11 shows morphological aspects of the surface of the API X70 steel corroded during 24 h in the CO2-saturated brine with and without inhibitor addition at 60°C. According to Figure 11(a), it is observed that the morphology of the X70 steel surface evaluated in the absence of inhibitor shows a corroded surface with the

| Table 2. Values obtained from the modeling of the impedance spectra for X70 steel in CO2-saturated brine at different inhibitor concentrations. |
|---|---|---|---|---|---|---|
| \(t\) (h) | CPE\(_f\) (\(\mu\)F-cm\(^{-2}\)) | \(n\) | \(R\) (\(\Omega\)-cm\(^2\)) | CPE\(_{dl}\) (\(\mu\)F-cm\(^{-2}\)) | \(n\) | \(R_{ct}\) (\(\Omega\)-cm\(^2\)) | \(R_{W}\) (\(\Omega\)-cm\(^2\)) |
| 0 ppm | | | | | | | |
| 0 | – | – | – | 5.05E-04 | 0.79 | 98.2 | 9.9 |
| 3 | – | – | – | 5.93E-04 | 0.82 | 88.7 | 5.6 |
| 6 | – | – | – | 6.94E-04 | 0.86 | 91.1 | 6.3 |
| 9 | – | – | – | 7.03E-04 | 0.87 | 91.1 | 4.6 |
| 12 | – | – | – | 7.88E-04 | 0.88 | 87.7 | 6.2 |
| 18 | – | – | – | 9.77E-04 | 0.89 | 79.7 | 3.7 |
| 24 | – | – | – | 1.19E-03 | 0.89 | 79.4 | 4.9 |
| 5 ppm | | | | | | | |
| 0 | – | – | – | 7.19E-04 | 0.77 | 66 | – |
| 3 | 8.99E-04 | 0.76 | 0.03 | 1.16E-04 | 0.89 | 79 | – |
| 6 | 9.49E-04 | 0.78 | 0.01 | 1.38E-04 | 0.90 | 85 | – |
| 9 | 7.48E-04 | 0.86 | 0.01 | 9.30E-05 | 0.91 | 79 | – |
| 12 | 6.17E-04 | 0.89 | 0.126 | 2.18E-04 | 0.86 | 107 | – |
| 18 | 6.08E-04 | 0.90 | 0.150 | 2.93E-04 | 0.88 | 114 | – |
| 24 | 6.87E-04 | 0.89 | 0.102 | 2.77E-04 | 0.88 | 114 | – |
| 10 ppm | | | | | | | |
| 0 | – | – | – | 7.48E-04 | 0.75 | 72 | – |
| 3 | 6.27E-04 | 0.81 | 0.239 | 2.25E-04 | 0.79 | 111 | – |
| 6 | 3.60E-04 | 0.84 | 1.40 | 4.25E-04 | 0.81 | 124 | – |
| 9 | 2.39E-04 | 0.87 | 0.112 | 5.09E-04 | 0.81 | 129 | – |
| 12 | 2.42E-04 | 0.86 | 0.123 | 4.81E-04 | 0.83 | 132 | – |
| 18 | 1.88E-04 | 0.88 | 0.116 | 5.97E-04 | 0.85 | 130 | – |
| 24 | 1.46E-04 | 0.90 | 1.05 | 5.99E-04 | 0.86 | 139 | – |
| 25 ppm | | | | | | | |
| 0 | – | – | – | 6.00E-04 | 0.78163 | 68 | – |
| 3 | 2.66E-04 | 0.82 | 0.8 | 3.13E-05 | 0.81 | 330 | – |
| 6 | 1.85E-04 | 0.80 | 1.4 | 3.61E-05 | 0.88 | 667 | – |
| 9 | 1.47E-03 | 0.79 | 14 | 2.64E-05 | 0.92 | 1163 | – |
| 12 | 1.20E-04 | 0.79 | 23 | 2.46E-05 | 0.91 | 1582 | – |
| 18 | 1.31E-04 | 0.77 | 30 | 2.31E-05 | 0.92 | 1775 | – |
| 24 | 1.37E-04 | 0.75 | 41 | 2.35E-05 | 0.92 | 1886 | – |
| 50 ppm | | | | | | | |
| 0 | – | – | – | 6.67E-04 | 0.77 | 62 | – |
| 3 | 2.98E-04 | 0.82 | 11 | 2.18E-05 | 0.71 | 379 | – |
| 6 | 9.02E-05 | 0.84 | 14 | 6.94E-05 | 0.81 | 1040 | – |
| 9 | 8.77E-05 | 0.81 | 35 | 6.52E-05 | 0.80 | 1531 | – |
| 12 | 9.35E-05 | 0.80 | 51 | 6.61E-05 | 0.79 | 1702 | – |
| 18 | 7.32E-05 | 0.80 | 49 | 8.70E-05 | 0.78 | 1775 | – |
| 24 | 8.13E-05 | 0.79 | 58 | 7.82E-05 | 0.82 | 1744 | – |
| 100 ppm | | | | | | | |
| 0 | – | – | – | 6.17E-04 | 0.78 | 68 | – |
| 3 | 8.39E-04 | 0.77 | 2.3 | 2.07E-07 | 0.74 | 169 | – |
| 6 | 1.04E-04 | 0.92 | 2.1 | 2.18E-04 | 0.70 | 594 | – |
| 9 | 7.16E-05 | 0.89 | 2.9 | 1.59E-04 | 0.73 | 1218 | – |
| 12 | 3.02E-06 | 0.75 | 72.8 | 1.36E-05 | 0.94 | 1234 | – |
| 18 | 1.19E-05 | 0.78 | 83.9 | 7.86E-05 | 0.79 | 1303 | – |
| 24 | 1.11E-05 | 0.77 | 117.5 | 7.19E-05 | 0.81 | 1434 | – |
presence of localized attack (pitting). It has been suggested that the presence of this localized type of attack is possible when steel is not able to form fully protective scales (32). According to this, it is clear that the steel is unable to develop a protective layer of corrosion products that limit the corrosive attack of the electrolyte. However, when the inhibitor is added to the corrosive medium it was observed that the surface appearance of the X70 steel changed depending on the amount of inhibitor added. With 5 ppm of inhibitor (Figure 11b), a surface with less surface damage was observed but the presence of a localized attack is still observed; this is because the amount of inhibitor was not enough to form a continuous protective film on the steel surface. With the addition of 10 ppm of inhibitor (Figure 11c), a less rough surface was observed and the presence of localized attack was not observed. However, with the addition of 25, 50, and 100 ppm (Figure 11d–f), a homogeneous surface was observed and it is still possible to detect the presence of some lines due to the surface finish made prior to the corrosion tests. The surface aspects are consistent with the reported inhibition efficiencies above, that is, the optimal inhibitor concentration is 25 ppm.

**Adsorption isotherms**

A parameter that contributes to the understanding of the adsorption process, of the inhibitor molecules on a metal surface exposed to an aggressive environment, are the adsorption isotherms. It is known that the adsorption process occurs by the displacement of one or more molecules of water adsorbed on the surface and which are replaced by an inhibitor molecule (33).

\[
\text{Org}_{(\text{sol})} + x\text{H}_2\text{O}_{(\text{ads})} \leftrightarrow \text{Org}_{(\text{ads})} + x\text{H}_2\text{O}_{(\text{sol})}.
\]

The adsorption can be carried out in two different ways, either physical or chemical adsorption. Physical adsorption or physisorption occurs by means of electrostatic forces (Van Der Waals forces or London forces), whereas chemical adsorption or chemisorption is carried out due to the formation of a coordinate bond between the \(\pi\) electrons of the N atoms contained in the inhibitor.

![Figure 11. Surface aspect of X70 steel corroded in CO\(_2\)-saturated brine with and without addition of inhibitor after 24 h of immersion: (a) 0 ppm, (b) 5 ppm, (c) 10 ppm, (d) 25 ppm, (e) 50 ppm, (f) 100 ppm.](image-url)
molecule and the Fe$^{2+}$ ions present on the metal surface, forming a metal–inhibitor complex (34, 35).

$$\text{Fe}^{2+} + \text{Inh}_{\text{ads}} \rightarrow [\text{Fe} - \text{Inh}]_{\text{ads}} \text{tr}, \quad (15)$$

where the complex formed may or may not protect the steel depending on its stability and solubility in the system under study (27). In order to define the type of adsorption of the inhibitor under study, in this work the Langmuir model was used. The description of a chemisorbed monolayer according to the Langmuir model is given by (35)

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C, \quad (16)$$

where $C$ is the molar concentration of the inhibitor, $\theta$ is the degree of coverage, and $K_{\text{ads}}$ is the adsorption constant. The degree of coverage can be obtained by dividing the inhibition efficiency values by 100. The inhibition efficiencies obtained from the EIS measurements were calculated according to the following relationship:

$$E(\%) = \frac{R_{\text{ct},i} - R_{\text{ct},b}}{R_{\text{ct},i}} \times 100, \quad (17)$$

where $R_{\text{ct},i}$ and $R_{\text{ct},b}$ are the $R_{\text{ct}}$ values in the absence and presence of the inhibitor respectively. In the case of LPR and EIS measurements, the average of the inhibitor efficiency value obtained during the last 12 h was used to determine the degree of coverage. Based on the $i_{\text{corr}}$ data (Table 1), $R_p$ and $R_{\text{ct}}$ (Table 3), the graph shown in Figure 12 was obtained, and the values of the adsorption constant shown in Table 4 were obtained from the adjustment lines. It should be noted that the polarization resistance based on EIS measurements is the sum of $R_\text{ct}$ and $R_p$, however, since $R_p$ is small compared to $R_{\text{ct}}$ it is acceptable to consider $R_{\text{ct}}$ as $R_p$ for EIS.

From the adsorption constant, the standard adsorption energy ($\Delta G^\circ_{\text{ads}}$) can be obtained by the following equation (36):

$$\Delta G^\circ_{\text{ads}} = -R \ln (55.5 \cdot K_{\text{ads}}). \quad (18)$$

With $R$ being the universal constant of the gases ($8.314472 \text{ J mol}^{-1} \text{ K}^{-1}$), $T$ the temperature (K), and the value of 55.5 corresponds to the molar concentration of the water in the solution. A negative value of the standard adsorption energy indicates that the inhibitor adsorption process occurs spontaneously. In addition, several authors report that a physical adsorption process occur when $\Delta G^\circ_{\text{ads}}$ values close to $-20$ KJ mol$^{-1}$ are obtained, and a chemical adsorption process when $\Delta G^\circ_{\text{ads}}$ values of at least $-40$ KJ mol$^{-1}$ are obtained (37). Therefore, according to the values reported in Table 4, it can be asserted that the inhibitor molecules are chemisorbed on the surface of X70 steel. This suggests the formation of a possible metal–inhibitor complex that protected the metal surface by reducing the active sites exposed to the aggressive environment.

### Conclusion

The amide-type inhibitor synthesized from coffee bagasse oil showed an excellent performance at concentrations greater than 10 ppm. The optimal inhibition concentration was 25 ppm with inhibition efficiencies greater than 95% according to the results of the different electrochemical techniques evaluated. Polarization curves showed that the inhibitor exhibits a cathodic behavior. The adsorption of the inhibitor molecules on the metal surface caused a shift in the OCP values of the X70 steel towards nobler potentials because to the strong affinity of the inhibitor towards the metal surface. LPR and EIS tests showed that with the addition of the inhibitor, a protective barrier is formed between the metal surface and the aggressive medium, which causes an increase in both $R_p$ and $R_{\text{ct}}$ values of greater than 1 order of magnitude. The adsorption of the inhibitor molecules was adjusted to the Langmuir model and, according to the

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**Table 3.** Average values of $R_p$ and $R_{\text{ct}}$, inhibition efficiencies and degrees of coverage from LPR and EIS measurements.

| Inhibitor concentration (ppm) | LPR | EIS |
|------------------------------|-----|-----|
|                             | $R_p$ | $R_{\text{ct}}$ | $R_p$ | $R_{\text{ct}}$ |
| 0                           | 86   | 82  | -    | -    |
| 5                           | 141  | 111 | 0.3872 | 26.44 | 0.2644 |
| 10                          | 158  | 134 | 0.4530 | 38.57 | 0.3857 |
| 25                          | 1801 | 1747| 95.18  | 95.29 | 0.9529 |
| 50                          | 1710 | 1740| 94.93  | 95.27 | 0.9527 |
| 100                         | 1313 | 1323| 93.39  | 93.78 | 0.9378 |

**Table 4.** Values of $K_{\text{ads}}$ and $\Delta G^\circ_{\text{ads}}$ obtained from Tafel, LPR and EIS measurements.

| Method | $K_{\text{ads}}(\text{M}^{-1})$ | $\Delta G^\circ_{\text{ads}}(\text{KJ mol}^{-1})$ | $R^2$ |
|--------|---------------------------------|---------------------------------|-------|
| LPR    | 4.61E+04                        | -40.87                          | 0.9877 |
| Tafel  | 4.40E+04                        | -40.74                          | 0.9845 |
| EIS    | 2.95E+04                        | -39.63                          | 0.9737 |

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**Figure 12.** Adsorption isotherms obtained from the values of $i_{\text{corr}}$, $R_p$ and $R_{\text{ct}}$. 

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Gibbs free energy values, it is concluded that are spontaneously adsorbed by a chemical adsorption process.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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