Use of an amide-type corrosion inhibitor synthesized from the coffee bagasse oil on the corrosion of Cu in NaCl

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ABSTRACT

An amide, namely \(N-[2-\{(2-hydroxyethyl) amino\} ethyl]-amide\), extracted from the fatty acids contained in the coffee bagasse, has been investigated as a possible green corrosion inhibitor for copper in 3.5\% NaCl by using potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements. Results were complemented by detailed scanning electronic microscopy, FTIR and gas chromatography studies. Results have shown that \(N-[2-\{(2-hydroxyethyl) amino\} ethyl]-amide\) is a good, mixed type of corrosion inhibitor, with an efficiency that increases with its concentration but it decreases with a rise in the temperature. It adsorbs chemically onto the copper surface by following a Langmuir type of adsorption isotherm.

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1. Introduction

Due to its good properties such as electrical and thermal conductivity, weldability, mechanical properties and corrosion resistance (1, 2), copper and its alloys are candidates to be used to store drinkable water as well as some other fluids in a wide range which includes oil and chemical processes as well as marine industries (3–5). Despite its high resistance towards uniform type of corrosion, pitting of copper and its alloys is still of concern in environments containing ammonia, steam containing \(\text{CO}_2\), \(\text{NH}_3\), sulfides and chlorides (6–8). Some of the methods used to improve the copper alloys corrosion resistance include the use of coatings (9), alloying elements (10) and corrosion inhibitors (11–26). Among these, fatty acids have been used as very effective corrosion inhibitors (27–32). Some of the most effective corrosion inhibitors are those which contain within their structure heteroatoms such as N, O, P and S, due to their ability to be adsorbed onto the metal surface to form protective corrosion products. In the last years, there has been a lot of interest in the scientific community for the naturally occurring inhibitors in fruits, roots or...
leaves which contain compounds with nitrogen, sulfur and oxygen which have been used as naturally occurring corrosion inhibitors since they are much less toxic, inexpensive and readily available (33–44). Natural extracts contain phytochemical constituents such as tannins, flavonoids, ascorbic acid, amino acids, phenolic acid and alkaloids with an electronic structure similar to the above-mentioned synthetic organic inhibitors. Coffee is one of the most consumed grains in the world which contains alkaloids (caffeine and trigonelline mainly), sugars (sucrose, fructose, lactose) and organic acids such as acetate, formate, malate and oxalate (45). Different researchers have evaluated coffee solid paste extracts by decoction and infusion (46), by maceration in water (47) or in sulfuric acid (48) as a corrosion inhibitor for steel in hydrochloric acid. However, the world widespread consumption of coffee produces big amounts of residues that make necessary the development of technological uses for food residues may reduce the volume of waste discarded and increase the economic viability of appropriate waste management options. Thus, the goal of this research goal is to use the coffee residues to obtain fatty acids contained in an essential oil, which could be used as a green corrosion inhibitor for copper in a chloride-containing solution.

2. Experimental procedure

2.1 Inhibitor synthesis

The working oil was extracted from coffee residue. The type of coffee was a mixture of Organic Arabic coffee beans (maragogipe and natural), from the Chiapas region, southern part of Mexico. The bagasse was dried in an oven at 60°C during 72 h. The oil extraction was performed by two conventional methods: Soxhlet (hexane at reflux, 4 h) and non-assisted extraction with hexane. For the latter, the oil content was studied as a function of time at room temperature, every 24 h during 8 days and the optimal solvent–bagasse ratio (ml g⁻¹) was determined at room temperature with solvent/bagasse of 4:1, 6:1, 8:1 and 10:1. The saponification index for the coffee oil was determined in KOH. The reagents used in this work were purchased from Sigma Aldrich. The solvents used were analytical-grade Fermont. The fatty amide was prepared through the aminolysis direct of coffee oil and hydroxyethyl ethylene diamine, as shown in Figure 1 (49). The synthesis was performed by placing in a ball flask 10 g of coffee oil and 3.63 g of N-(2-hydroxyethyl) ethylene diamine in a mole ratio of 1:3. The mixture was stirred during 2 h at 140°C. The progress of the reaction was confirmed by using thin layer chromatography (TLC). The TLC conditions were using silica as a support and a heptane-ethyl acetate (9:1) solution as an eluent; after 2 h of reaction, it was observed the complete formation of amide. The crude of reaction was purified: first, a wash with a hot brine solution was performed to eliminate the glycerol. It was obtained 12.18 g of the amide mixture as a brown paste, a 96.9% of yield. After that, the organic phase was recrystallized in acetone. This product was recrystallized in chloroform-hexane to give a slightly yellow solid compound. As a corrosive electrolyte, a 3.5% NaCl solution was used.

2.2 Spectroscopic characterization

The oil and fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide were characterized by FTIR spectroscopy on film at a Bruker Tensor 27 FT-IR spectrometer (Pike Miracle Single-Bounce ATR Cell). To know fatty acid profile contained in the coffee oil, it was analyzed by gas chromatography (GC) (150302-ext-01 STE 4981) with a flame ionization detector (FID). Fatty acid methyl ester was prepared as follows: 5 g of coffee oil and a KOH–methanol solution (0.076 g in 2 ml) were placed in a flask drop by drop at 70°C under stirring conditions during 30 min. The glycerol was separated and the methyl ester was neutralized. One microliter of this sample was injected into the equipment operated with a split of 50, flow 1.8 ml min⁻¹, and separation was carried out on an AT-FAME capillary column (30 m × 0.25 mm, 0.25 µm), using helium as the carrier gas. The oven temperature was kept at 180°C during 15 min, followed by a temperature gradient of 10°C min⁻¹ up to 230 °C and held during 3 min. Both injector and detector temperatures were kept at 250°C. Peaks of fatty acid methyl esters were identified by matching their relative times with those of commercial standards (FAME).

2.3 Testing material

Material used for this investigation was a commercial 6.00-mm diameter rod made of Cu. Specimens measuring 20 mm in length were spot welded to a copper wire, encapsulated in a commercial, polymeric resin, abraded with 600 grade emery paper, washed and dried.

2.4 Electrochemical techniques

Electrochemical techniques such as potentiodynamic polarization curves, linear polarization resistance and electrochemical impedance spectroscopy (EIS) were used. A three-electrode glass cell with a saturated calomel and a graphite rod as reference and counter electrodes, respectively. Before starting the tests,
working electrode was left to start a steady state free corrosion potential value, $E_{\text{corr}}$, normally 2 h. For polarization curves, specimen was polarized from the cathodic branch up to the anodic branch, starting in a value of $-400$ mV and finishing in a potential value of $+800$ mV with respect to the $E_{\text{corr}}$ value at a scan rate of $1$ mV s$^{-1}$. Tafel extrapolation method was used to calculate corrosion current density values, $I_{\text{corr}}$. EIS measurements were carried out at the $E_{\text{corr}}$ value and a sinusoidal signal with an amplitude of $15$ mV was applied within a frequency interval of $0.05$–$30,000$ Hz. Tests were carried out at $25$, $40$ and $60^\circ$C, three times, by using a hot plate. Corroded surfaces were analyzed in a low-vacuum LECO scanning electronic microscope (SEM) whereas the chemical analysis of the corrosion products was carried out with an energy dispersive x-ray (EDX) analyzer attached to it.

3. Results and discussion

3.1 Inhibitor characterization

The residual oil yield in the coffee bagasse determined by the Soxhlet method was $17.6\%$. The oil yield studied by non-assisted extraction with hexane showed that the highest performance was at $24$ h ($14\%$). The thin particle of the coffee bagasse allows the highest yield in a short time. The optimum solvent/bagasse ratio was determined as $8:1$. The saponification index of coffee oil was $190.084$. The content of fatty acids contained in the coffee oil determined by GC is shown in Table 1. The oil extracted by the two methods presents a content of fatty acids as a function of time. Linoleic and palmitic acids have the highest concentration in the coffee oil. The total concentration of unsaturated fatty acids is higher ($53.06\%$) than the total concentration of saturated fatty acids ($42.49\%$). The triglyceride characterization by IR spectroscopy, Figure 2, shows three absorption characteristics frequencies for ester group. At $1743$ cm$^{-1}$ appears a very strong signal for the C=O stretching vibration. Two strong bands are observed at lower frequency, $1159$ and $720$ cm$^{-1}$, for C–O–C antisymmetric stretching and O–C–O bend vibration. For the fatty N-[2-[(2-hydroxyethyl) amino] ethyl]-amide derived from the coffee oil, the carbonyl frequency of the amide is lower ($1642$ cm$^{-1}$) compared to triglyceride ($1743$ cm$^{-1}$) because nitrogen is less electronegative than oxygen. Two medium bands are observed at $3300$ and $1555$ cm$^{-1}$ corresponding to the N-H amide group for stretch and bend vibration, respectively. For the amine group, the N-H stretch appears at $3300$ cm$^{-1}$ and the N-H deformation at $715$ cm$^{-1}$. The C–N stretch

![Figure 1. Synthesis of fatty acid N-[2-((2-hydroxyethyl) amino) ethyl]-amide. R = alkyl chains of coffee oil fatty acids.](image1)

![Figure 2. IR spectra of N-[2-((2-hydroxyethyl) amino) ethyl]-amide and triglyceride.](image2)

| Fatty acids     | Type of fatty acid | Soxhlet (wt%) | Non-assisted extraction (wt%) |
|----------------|-------------------|--------------|-------------------------------|
| Palmitic acid  | Saturated         | 34.41        | 32.98                         |
| Stearic acid   | Saturated         | 7.56         | 6.62                          |
| Oleic acid     | Unsaturated       | 8.53         | 6.73                          |
| Linoleic acid  | Unsaturated       | 44.2         | 41.19                         |
| Arachidic acid | Unsaturated       | 0.33         | 0.24                          |
| Behenic acid   | Saturated         | 0.52         | 0.66                          |
of the amide group appears at a higher frequency (1461 cm\(^{-1}\)) than the C–N stretch (1120 cm\(^{-1}\)) of secondary amine group by the electronegativity influences of this group. The strong and broad band from 3400 to 3100 cm\(^{-1}\) was assigned to O–H stretch. Medium strong and broad band at 1052 cm\(^{-1}\) corresponds to the C–OH bond in-plane bend and the out-of-plane deformation at 700 cm\(^{-1}\). Finally, for C-H\(_3\) stretch of the methyl and methylene groups turned up at 2920 and 2852 cm\(^{-1}\) and about of 1461 and 1373 cm\(^{-1}\) the asymmetric and symmetric deformation, respectively.

### 3.2 Open circuit potential

The evolution of the open circuit potential (OCP) value for Cu in 3.5% NaCl solution at different fatty amide concentrations during a 24-h period time is given in Figure 3. This figure shows that the OCP value for the uninhibited solution was the most active one, oscillating between −400 and −420 mV during the whole period of testing. Regardless of the inhibitor concentration, the OCP value increased during the first 2 h but after this time it reached a steady-state value. As soon as the inhibitor was added, the OCP value shifted towards nobler values, reaching the highest value with an addition of 100 ppm of inhibitor. It has been established that the shift of the OCP value towards nobler values is due to the formation of a protective film on the metal surface, containing probably CuCl, Cu\(_2\)O and/or Cu(OH) (50–53) which protects the metal, reaching a maximum or critical value, \(I_{corr}\), after which a decrease in the current density value is observed due to the establishment of a passive zone at a potential value of −50 mV. This passive zone is very narrow, since it finishes when a pitting potential, \(E_{pit}\), is reached at −30 mV. After this value, an increase in the anodic current density value can be seen once again due to the dissolution of the passive film. On the cathodic branch, a limiting current density value can be seen due to the oxygen reduction reaction at a potential value of −800 mV; for potential values lower than this, an increase in the cathodic current density due to the hydrogen evolution reaction is observed. Obtained electrochemical parameters are given in Table 2. When the fatty amide is added, the \(E_{corr}\) value is shifted towards more active values with small doses of inhibitor, i.e. 5 and 10 ppm. However, for inhibitor concentrations equal or higher than 25 ppm, the \(E_{corr}\) value shifts towards nobler values. The corrosion current density value, \(I_{corr}\), decreases as the inhibitor concentration increases, reaching its lowest value when 100 ppm of inhibitor was added. The passive zone is achieved at a potential value much lower than that in the absence of inhibitor, and the passive current density value is decreased with the addition of fatty amide. On the cathodic branch, there is no presence of a limit current density when the inhibitor was added and the cathodic current density was much less affected than the anodic one. Inhibitor efficiency (IE) values were calculated by

![Figure 3](image)

**Figure 3.** Effect of N-[2-((2-hydroxyethyl) amino) ethyl]-amide concentration on the OCP value for Cu exposed to 3.5% NaCl at different exposure times.

### 3.3 Potentiodynamic polarization curves

Polarization curves for Cu in 3.5% NaCl solution at different fatty amide concentrations are given in Figure 4. At 25°C, Figure 4(a), a rapid increase in the anodic current density value can be seen in the absence of inhibitor, corresponding to the anodic dissolution of Cu, probably with the formation of CuCl, Cu\(_2\)O and/or Cu(OH) film (50–53) which protects the metal, reaching a maximum or critical value, \(I_{corr}\), after which a decrease in the current density value is observed due to the establishment of a passive zone at a potential value of −50 mV. This passive zone is very narrow, since it finishes when a pitting potential, \(E_{pit}\), is reached at −30 mV. After this value, an increase in the anodic current density value can be seen once again due to the dissolution of the passive film. On the cathodic branch, a limiting current density value can be seen due to the oxygen reduction reaction at a potential value of −800 mV; for potential values lower than this, an increase in the cathodic current density due to the hydrogen evolution reaction is observed. Obtained electrochemical parameters are given in Table 2. When the fatty amide is added, the \(E_{corr}\) value is shifted towards more active values with small doses of inhibitor, i.e. 5 and 10 ppm. However, for inhibitor concentrations equal or higher than 25 ppm, the \(E_{corr}\) value shifts towards nobler values. The corrosion current density value, \(I_{corr}\), decreases as the inhibitor concentration increases, reaching its lowest value when 100 ppm of inhibitor was added. The passive zone is achieved at a potential value much lower than that in the absence of inhibitor, and the passive current density value is decreased with the addition of fatty amide. On the cathodic branch, there is no presence of a limit current density when the inhibitor was added and the cathodic current density was much less affected than the anodic one. Inhibitor efficiency (IE) values were calculated by

![Table 2.](image)

### Table 2. Electrochemical parameters obtained from polarization curves.

| \(C_{inh}\) (ppm) | \(E_{corr}\) (mV) | \(\beta_\alpha\) (mV/Dec) | \(\beta_\beta\) (mV/Dec) | \(I_{corr}\) (mA cm\(^{-2}\)) | IE (%) | \(\theta\) |
|------------------|------------------|------------------|------------------|------------------|---------|---------|
| 0                | −398             | 40               | −355             | 0.0367           | −       | −       |
| 5                | −488             | 164              | −152             | 0.005            | 86      | 0.86   |
| 10               | −424             | 142              | −128             | 0.0032           | 91      | 0.91   |
| 25               | −350             | 146              | −148             | 0.0025           | 93      | 0.93   |
| 50               | −336             | 105              | −170             | 0.0020           | 94      | 0.94   |
| 100              | −304             | 102              | −142             | 0.0015           | 95      | 0.95   |
using the following equation:

\[ IE \% = \left( \frac{I_{corr} - I'_{corr}}{I_{corr}} \right) \times 100, \]  

[1]

where \( I_{corr} \) and \( I'_{corr} \) are the corrosion current density values in the absence and presence of the fatty amides, respectively. Table 2 clearly shows an increase in the inhibitor efficiency value when its concentration increases. The metal fraction surface covered by the inhibitor, \( \theta \), which is given by dividing the inhibitor efficiency value by 100, also increases with the inhibitor concentration. This implies that the reduction in the \( I_{corr} \) value is due to the adsorption of the fatty amide type of inhibitor and to an increase in the area of the metal covered by it (54). Finally, anodic Tafel slope increased whereas the cathodic one decreased by adding the inhibitor, indicating that both anodic and cathodic reactions are affected by the inhibitor; therefore, it can be said that it is acting as a mixed type of inhibitor.

Polarization curves had a very similar behavior to that observed at 25°C was observed when the temperature increased up to 40°C and 60°C, Figure 4(b) and (c), where it can be seen that the \( E_{corr} \) value shifted towards nobler values and the \( I_{corr} \) value decreased with the addition of the inhibitor. For the uninhibited solution, the passive behavior was still observed at 40°C but it was absent at 60°C. However, the passive behavior was observed at both temperatures in the presence of the \( N \)-[2-{[(2-hydroxyethyl) amino] ethyl}-amide. Table 3 shows the effect of temperature on the \( I_{corr} \) and efficiency values at 0 and 100 ppm of inhibitor as obtained from these plots. It is clear the corrosion current density values increase and the inhibitor efficiency decreases as the temperature increases, indicating that the desorption of the inhibitor is aided with increasing the temperature. The apparent activation energy for the corrosion rate of copper in 3.5% NaCl solution containing different doses of \( N \)-[2-{[(2-hydroxyethyl) amino] ethyl}-amide can be calculated by using an Arrhenius-type equation as

Figure 4. Effect of \( N \)-[2-{[(2-hydroxyethyl) amino] ethyl}-amide concentration on the polarization curves for Cu exposed to 3.5% NaCl at (a) 25, (b) 40 and (c) 60°C.
follows:

\[
\ln I_{\text{corr}} = -\frac{E_a}{2.303RT} + \ln F,
\]

where \( R \) is the molar gas constant, \( T \) is the absolute temperature and \( F \) is the frequency factor. Arrhenius plots of \( \ln I_{\text{corr}} \) against \( 1000/T \) for copper in 3.5% NaCl solution in the absence and presence of \( N-[2-[(2\text{-hydroxyethyl)} \text{ amino}] \text{ ethyl}]\)-amide are shown in Figure 5. The apparent activation energy obtained for the corrosion process in the NaCl solution was found to be 10.46 and 17.1 kJ mol\(^{-1}\) in the absence and presence of the inhibitor, respectively. Notably, the energy barrier of the corrosion reaction increased in presence of the inhibitor, indicating that the corrosion process is more difficult in the presence of the inhibitor because the inhibition process is mainly controlled by the activation energy, hence the corrosion rate decreases, most probably due to the adsorption of the inhibitor on the copper surface.

### 3.4 Adsorption isotherms

Since it has been assumed that the decrease in the corrosion rate of Cu in NaCl solution is due to the adsorption of the inhibitor on the metal surface, it is necessary to understand the adsorption mechanism. For this, experimental data were fit to different adsorption isotherms, and as it can be seen in Figure 6, the best fit was obtained with a Langmuir type of adsorption isotherm, with a correlation coefficient of 0.99, which can be formulated as:

\[
\frac{C_{\text{inh}}}{\theta} = C_{\text{inh}} + \frac{1}{K_{\text{ads}}},
\]

where \( K_{\text{ads}} \) is the adsorption–desorption constant and is related with the Gibbs energy, \( \Delta G_{\text{ad}} \) as follows:

\[
\Delta G_{\text{ad}}^0 = -RT\ln K_{\text{ads}}.
\]

By fitting the data, a value of 3.82 was obtained for \( K_{\text{ads}} \) whereas for \( \Delta G_{\text{ad}} \) a value of −43.17 kJ mol\(^{-1}\) was obtained. The negative value of adsorption-free energy suggests the spontaneity of the adsorption of \( N-[2-[(2\text{-hydroxyethyl)} \text{ amino}] \text{ ethyl}]\)-amide molecules and the stability of the adsorbed layer on the copper surface. In general, values for \( \Delta G_{\text{ad}} \) of −20 kJ mol\(^{-1}\) or lower suggested that electrostatic interaction between charge of inhibitor molecules and the metal surface resulted in physical adsorption. Whereas, when \( \Delta G_{\text{ad}} \) is −40 kJ mol\(^{-1}\) or lower, it involves the sharing or transfer charge from inhibitor molecule on the metal surface to form covalent bond coordination which then promotes chemical adsorption. The adsorption process is chemical adsorption due to the value of \( \Delta G_{\text{ad}} \) that was below −40 kJ mol\(^{-1}\) (49–51).

### 3.5 EIS measurements

EIS diagrams, in both Nyquist and Bode formats, for Cu in 3.5% NaCl solution containing different concentrations of \( N-[2-[(2\text{-hydroxyethyl)} \text{ amino}] \text{ ethyl}]\)-amide are shown in Figure 7. Nyquist diagrams, Figure 7(a), show the presence of two depressed, capacitive semicircles, regardless of the inhibitor concentration. The high-
frequency semicircle corresponds to the accumulation of corrosion products that form a film, whereas the low-frequency one corresponds to the double electrochemical layer. The diameter of the high-frequency semicircle corresponds to the film resistance, $R_f$, whereas that for the low-frequency semicircle corresponds to the charge transfer resistance, $R_{ct}$. The sum of $R_f + R_{ct}$, which gives the polarization resistance, $R_p$, increases with an increase in the $N$-[2-((2-hydroxyethyl) amino) ethyl]-amide concentration, probably due to its adsorption on the metal surface and to the formation of a protective film. Bode plots, Figure 7(b), indicate an increase in the total impedance with increasing the inhibitor concentration, and the existence of two peaks. The shape of Nyquist diagrams did not change with the exposure time, as shown in Figure 8, which shows the evolution of

![Figure 7](image.png)

**Figure 7.** Effect of $N$-[2-((2-hydroxyethyl) amino) ethyl]-amide concentration on the (a) Nyquist and (b) Bode plots for Cu exposed to 3.5% NaCl at 25°C.
Nyquist diagrams with time for Cu in 3.5% NaCl solution containing 0 and 100 ppm, respectively, indicating that the corrosion mechanism remains the same either with the inhibitor concentration or with the exposure time. For uninhibited solution, Figure 8(a) shows that the total impedance decreases during most of the exposure time, indicating the desorption of any formed film on the metal surface. On the other hand, for solution containing 100 ppm of \(N\)-[2-[(2-hydroxyethyl) amino] ethyl]-amide, Figure 8(b), the total impedance increases during the first 12 h, decreasing with a further increase in the exposure time due to the desorption of the film formed by the inhibitor.

EIS data were simulated by using an electric circuit shown in Figure 9, where \(R_s\) is the solution resistance, \(R_{ct}\) the double layer resistance where the charge transfer takes place. \(CPE_{dl}\) is a constant phase element related to capacitance of the double electrochemical layer. This \(CPE_{dl}\) is placed instead of an ideal double layer capacitor, \(C_{dl}\), to take into account the dispersion effects due to surface roughness and other surface heterogeneities. \(R_f\) corresponds to the resistance of the film formed by the inhibitor and corrosion products, whereas that \(CPE_f\) is
the constant phase element related to the capacitance of the film formed by the inhibitor and the corrosion products. Electrochemical parameters obtained from the fitting of EIS data by using electric circuits shown in Figure 9 are given in Table 4. It can be seen that both $R_{ct}$ and inhibitor efficiency values increase whereas the value of $C_{dl}$ decreases with an increase in the $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide concentration.

| $C_{in}$ (ppm) | $R_s$ (ohm cm$^2$) | $R_{ct}$ (ohm cm$^2$) | $C_{dl}$ (μF cm$^2$) | $n_{dl}$ | $R_f$ (ohm cm$^2$) | $C_f$ (μF cm$^2$) | $n_f$ | IE (%) |
|---------------|-------------------|----------------------|---------------------|---------|-------------------|-------------------|------|--------|
| 0             | 12.5              | 8.66E + 1            | 4.7E − 5            | 0.76    | 4.95E + 3         | 2.8E − 3          | 0.46 | --     |
| 5             | 13.79             | 3.1E + 2             | 7.7E − 6            | 0.88    | 1.25E + 4         | 7.6E − 4          | 0.62 | 71     |
| 10            | 14.06             | 3.20E + 2            | 6.2E − 6            | 0.89    | 1.50E + 4         | 4.4E − 4          | 0.67 | 74     |
| 25            | 12.26             | 7.02E + 2            | 5.7E − 6            | 0.86    | 2.03E + 4         | 3.22E − 5         | 0.76 | 87     |
| 50            | 13.27             | 1.32E + 3            | 4.3E − 6            | 0.88    | 2.23E + 4         | 2.3E − 5          | 0.88 | 93     |
| 100           | 9.789             | 2.44E + 3            | 2.9E − 6            | 0.96    | 3.22 + 4          | 1.21E − 5         | 0.91 | 96     |

Figure 11. EDX spectra of copper surface immersed in 3.5% NaCl solution containing (a) 0 and (b) 100 ppm of $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide at 25°C.
reducing the corrosion rate, probably due to the adsorption of the inhibitor which brings a decrease in the local dielectric constant or an increase in the thickness of the double electrochemical layer. Thus, the increase in the $R_{ct}$ and inhibitor efficiency values as well as a decrease in the $C_{dl}$ value with an increase in the inhibitor concentration are due to the $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide molecules adsorption on the metal surface and a gradual replacement of the water molecules and a decrease in the extent of dissolution reaction. On the other hand, the value of $R_t$ increases also with the inhibitor concentration, decreasing the film-formed inhibitor conductivity, which shows that the protectiveness of the film increases in the presence of the inhibitor. As the $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide concentration increases and the corrosion rate decreases, the $n_{dl}$ value increases, due to a decrease in the metal surface roughness because the corrosion rate has been lowered. It can be noted also that the $R_t$ values are higher than those for $R_{ct}$, which shows that the corrosion resistance is given by the corrosion products film.

### 3.6 Surface characterization

The SEM images of copper surface corroded in 3.5% NaCl solution in the absence and presence of 100 ppm of $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide are shown in Figure 10. It is clear that in the uninhibited solution, Figure 10(a), the surface shows a high density of pits due to the attack by the chloride-containing solution. The pits density is clearly reduced when $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide is added to the solution, indicating a decrease in the corrosion rate. On the other hand, EDX analysis of the corroded copper surface in the absence of $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide, Figure 11(a), shows only the presence of Cu and O, whereas in the presence of $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide, the peak corresponding to C appears, which is an indication that the inhibitor molecules have been observed on the copper surface which provides corrosion protection to copper. Thus, it seems that the inhibition mechanism begins with the adsorption of the inhibitor. Adsorption of inhibitor is influenced by the chemical structure and donor atom of the molecule (N, O, S, etc.). It also depends on the nature or charge on the surface of the metal and vacant d-orbitals of the metal (55). In NaCl solutions, the metal surface gets a negative charge due to specific adsorption of chloride ions and metal attract positively charged species in the medium. The inhibitor molecule is adsorbed onto the copper surface by the replacement of surface adsorbed water molecules through a chemical adsorption mechanism as established in Section 3.4. Inhibitor molecule can also be adsorbed on the metal surface through the donor acceptor interaction with vacant d-orbitals of copper and π-electron center and hetero atoms such as oxygen and nitrogen (56). The presence of heteroatoms atoms such as N and O enhances the availability of π-electrons to get bonded to the vacant d-orbital of Cu. Hence, the adsorption of these components on the surface of copper is enhanced by the presence of these heteroatoms, mainly in the amine and amide groups.

### 4. Conclusions

Following conclusions can be withdrawn from this work:

a) $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide extracted from fatty acids contained in the coffee bagasse is a good, mixed inhibitor for the corrosion of copper in 3.5% NaCl affecting both the anodic metal dissolution and cathodic oxygen reduction reactions.

b) Inhibitor efficiency increases with its concentration but decreases with an increase in the temperature.

c) Adsorption of $N$-[2-[(2-hydroxyethyl) amino] ethyl]-amide on copper is chemical in nature and it follows a Langmuir type of adsorption isotherm.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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