Int. J. Electrochem. Sci., 11 **(2016)** 8132 – 8144, doi: 10.20964/2016.10.46

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Use of a Palm Oil-Based Imidazoline as Corrsion Inhibitor for Copper in 3.5% NaCl Solution

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Received: 3 March 2016 / *Accepted:* 6 April 2016 / *Published:* 6 September 2016

A palm-oil modified hydroxyethyl imidazoline has been used as corrosion inhibitor for Cu in 3.5 % NaCl solution by using potectiodynamic polarization curves, linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) measurements. Results showed that modified imidazoline acts as good inhibitor for Cu and its efficiency increases with increasing its concentration and exposure time. It was found that modified imidazoline contains compounds with heteroatoms within their molecular structure which act as sites to be chemically adsorbed on to the Cu surface, by following a Langmuir type of isotherm, to form protective corrosion products.

Keywords: copper, corrosion, imidazoline.

1. INTRODUCTION

Due to its good electrical and thermal conductivities, mechanical properties, copper is one of the most important metals used in the industry and it is widely used in industries such as electrical power lines, pipelines and domestic and industrial facilities including sea water, heat conductors, heat exchangers, among others [1, 2]. Therefore, corrosion of copper and its inhibition in a wide variety of environments, particularly when they include chloride ions, has been widely studied by many researchers [3-8]. According to these studies, the corrosion resistance of these alloys in neutral or near neutral conditions is due to the formation of highly protective copper oxides or hydroxides on the metal surface. However, in presence of chloride ions, the formation of such oxide or hydroxide films can be more difficult [9-10].

The use of organic inhibitors containing polar groups including nitrogen, sulphur and oxygen [11–16] is one of the most important methods in the protection of copper against corrosion. It has been reported that heterocyclic compounds with polar functional groups and conjugated double bonds [17–20] can be used to inhibit copper corrosion. Amongst the most used inhibitors, organic ones and their derivatives such as azoles [21-24], amines [25-29], amino acids [30, 31] and many others are the most widely used.

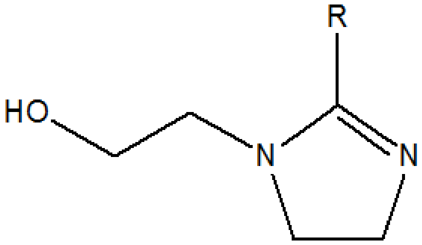

Figure 1. General structure of a hydroxyethyl imidazoline, where R is an alkyl chain derivatives.

Imidazolines or their salts have been used successfully as corrosion inhibitors for the CO_2 corrosion of carbon steel in the oil and gas industries nitrogen-based organic inhibitors, [32-34]. An imidazoline has a molecular structure as shown in Fig. 1, which is composed of a five member ring containing nitrogen elements, where R is a C-14 saturated hydrophobic head group and OH a pendant hydrophilic group attached to one of the nitrogen atoms. Yoo et al. [35] evaluated 2-(2-alkyl-4,5-dihydro-1H-imidazol-1-yl)ethanol, a bio-diesel-based imidazoline, as corrosion inhibitor of mild steel in 1.0 M hydrochloric acid and compared with the same imidazoline but prepared with petroleum-based chemicals. It was found that, for a concentration higher than 100 ppm, the bio-diesel-based imidazoline acted as an effective corrosion inhibitor. Thus, the goal of this manuscript is to evaluate the use of a palm oil-modified imidazoline as corrosion inhibitor for Cu in 3.5 % NaCl solution.

2. EXPERIMENTAL PROCEDURE

2.1 Material

As working electrode, cylinders made of Cu with 25 mm in length and 5.0 mm diameter were used in this work. Electrodes were polished by using 600 grade emery paper, cleaned with alcohol, acetone and distilled water.

2.2 Testing solution.

A commercial hydroxyetyl-imidazoline modified with palm oil was used as nhibitor used in this work. For the imidazoline modification, a mixture of distilled palm oil biodiesel (59-120 °C/0.05

mmHg) 2.22 g and 0.936 g of 2-(2-aminoethylamino)ethanol were heated and magnetically stirred at 140 ° C during 9 hours at atmospheric pressure and 3 hours at a reduced pressure (20 mm Hg). The reaction mixture was distilled at the Kugelrohr apparatus under reduced pressure (235 °C /0.05 mmHg) to obtain 1.42 g of palm imidazoline mixture. Resulting inhibitor is not water soluble, so, it was dissolved in pure 2-propanol and then added to the corrosive solution, which consisted of 3.5 % sodium chloride solution. Concentrations used in this work were 0, 5, 10, 25, 50 and 100 ppm at room temperature.

2.3 Electrochemical techniques.

Open circuit potentials (OCP) readings, potentiodynamic polarization curves, linear polarization resistance, LPR, and electrochemical impedance spectroscopy, EIS were the electrochemical techniques employed. A conventional three electrodes glass cell with a Pt rode as auxiliary and a saturated calomel electrode (SCE) as reference electrodes respectively. To carry out the polarization curves, they were recorded from -300 to +300 mV respect to the open circuit potential, E_{corr}, at a constant sweep rate of 1 mV/s. LPR measurements were carried out by polarizing the specimen from +10 to –10 mV respect to E_{corr}, at a scanning rate of 1 mV/s every hour during 24 hours. Polarization resistance values, R_p, were calculated from these measurements. Impedance measurements were carried out at the open-circuit potential by applying a signal with an amplitude of +10 to -10 mV in the frequency range 100 kHz to 1.0 mHz. All experiments were carried out using Interface 1000 Gamry Potentiostat/Galvanostat/ZRA analyzer.

3. RESULTS AND DISCUSSION

3.1 Open circuit potentials.

The effect of palm oil-modified imidazoline concentration on the variation of the open circuit potential value, OCP, with time for Cu exposed to 3.5 % NaCl solution is given in Fig. 2.

It can be seen that at all the inhibitor concentrations, the OCP value shifts towards more active values during the first hours of testing and then it shifts towards less negative potential values until it reaches a steady sate value. However, the shift towards more active values is less pronounced for the uninhibited solution, since it shifted from -280 to -300 mV during the first hour, it remains at this value during more or less 5 hours, and then it shifts towards -280 mV and remains around this value during the rest of the testing time. It has been reported [36] that this shift towards more active values is due to the dissolution of any pre-formed protective film, and consequently this increases the kinetic of the anodic dissolution reaction, whereas the shift towards more positive potential values corresponds to the formation of protective copper oxide films.

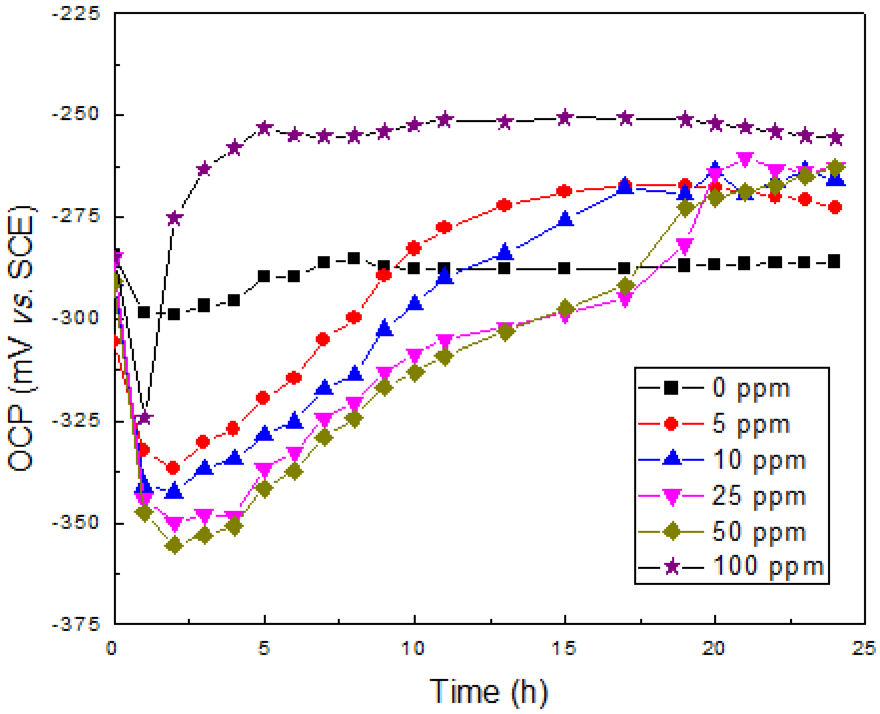

Figure 2. Effect of oil palm-modified hydroxyethyl imidazoline concentration in the variation of the OCP value with time for Cu in 3.5 % NaCl solution.

When the modified imidazoline is added, the potential shifts towards more active values is more pronounced that for the uninhibited solution, since it shifts from a value of -280 mv down to -360 mV. The potential value remains there more or less a few hours, and then it moved towards more positive values, and it reaches a steady state value after 10 hours of exposure to the 3.5 % NaCl solution. When 100 ppm of inhibitor are added, the time to achieve the steady state value was the shortest, around 5 hours, and at this inhibitor concentration the potential value achieved had the most positive value, -250 mV.

3.2 Polarization curves.

The effect of modified imidazoline concentration in the polarization curves for Cu in 3.5 % NaCl solution is given in Fig. 3. For the uninhibited solution, a cathodic limit current density can be seen probably die to the diffusion of oxygen either through the solution or through the preformed oxide films [37]. A cathodic peak can be observed at a potential value of -250 mV, which could be due to the reduction of any corrosion products formed when copper was immersed into the solution at the free corrosion potential [38]. On the anodic branch, an increase in the anodic current density can be seen until it reaches a maximum, decreases, and then increases once again. The increase in the anodic current density is due to the formation of CuCl, Cu_2O, and/or Cu(OH) film [39] that protect the copper from a further dissolution. The following increase in the current density after the small passive zone is due to the film passive film dissolution and the copper oxidation into cupric ions [40]. The addition of modified imidazoline decreased both the cathodic and anodic current density values, the cathodic peak disappeared and the passive zone appeared at much lower potential values. Electrochemial parameters are given in table 1. It can be seen that the I_{corr} value was decreased for almost two orders of magnitude and the inhibitor efficiency value increased in presence of the inhibitor. Inhibitor efficiency values were calculated with following equation:

$$I.E\,(\%) = \left(\frac{I_{corr} - I'_{corr}}{I_{corr}} \right) x\,100 \qquad (1)$$

where I'_{corr} and I_{corr} are the corrosion current density values with and without inhibitor respectively. Anodic Tafel slope was increased whereas the cathodic one was lowered with the addition of modified imidazoline, indicating that this inhibitor acts as a mixed type one.

3.3 Linear polarization resistance.

The effect of the palm oil-modified hydroxyethyl imidazoline concentration in the change of the R_p value with time is given in Fig. 4.

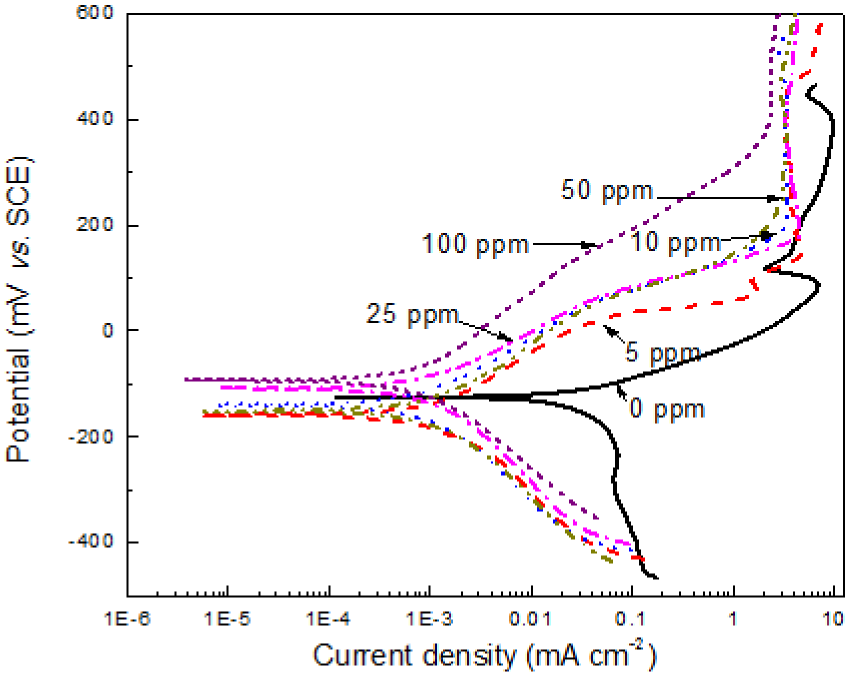

Figure 3. Effect of oil palm-modified hydroxyethyl imidazoline concentration in the polarization curved for Cu in 3.5 % NaCl solution.

For the uninhibited solution, a slight increment in the R_p value can be seen during the first 4 hours of testing, due to the establishment of a protective barrier made of corrosion products, but after that time, a decrease in the R_p value, and thus, an increase in the corrosion rate can be observed. In natural fresh waters, protection of copper is given by the formation of Cu_2O and $Cu(OH)_2$, but in presence of chloride ions, the formation of unstable CuCl film and soluble chloride complexes such as

$CuCl_2^-$ and $CuCl_3^{2-}$ increase the anodic dissolution of copper [41, 42]. As soon as the inhibitor is added, the R_p value increases almost one order of magnitude, decreasing thus the corrosion rate. However, for low inhibitor concentrations such as 5, 10 or 25 ppm, the R_p value increases during the first 2-3 hours, indicating an unstable formed film by the inhibitor. After this time, the R_p value has a slight decrease during more or less 5 hours, and then it increases once again and reaches a steady state value. For inhibitor concentrations higher than 50 ppm, the R_p value increases monotonically with time, reaching a steady state value 2 orders of magnitude higher than that for the uninhibited solution, indicating the formation of a very stable protective film. It has been suggested the existence of two different corrosion protection mechanism of copper by organic inhibitors: one establishes that organic inhibitors such as imidazoline are chemically absorbed on top of copper surface forming a protective film [43]. The second one indicates that the inhibition of inhibitors arise from the formation of a complex between Cu^{2+} ions released during the copper dissolution and the inhibitor on top of copper [44].

The variation in the inhibitor efficiency values with time for the different concentrations is given in Fig. 5. Inhibitor efficiency values were calculated by using

$$I.E.\ (\%) = 100\ (R_{p1} - R_{p2}) / R_{p1} \qquad (2)$$

where the polarization resistance with inhibitor and without inhibitor are R_{p1} and R_{p2} respectively. It can be seen that the inhibitor efficiency rapidly increases to reach values between 70-80% within the first two hours.

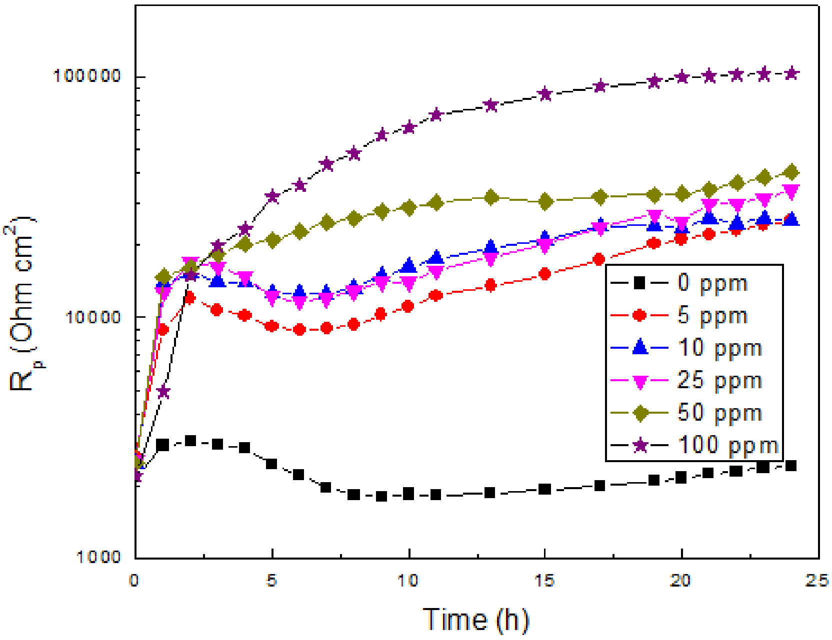

Figure 4. Effect of oil palm-modified hydroxyethyl imidazoline concentration in the variation of the R_p value with time for Cu in 3.5 % NaCl solution.

However, for inhibitor concentrations of 5, 10 and 25 ppm, efficiency values have a slight decrease after two hours, indicating an unstable formed film, but after 8 hours, efficiency values increase once again end reaches a steady state value. For inhibitor concentrations higher than 50 ppm, efficiency values increased all time, indicating a more stable formed film on top of copper surface. It can be seen that an increase in the inhibitor concentration brought an increase in the efficiency values, indicating that the decrease in the corrosion rate is due to the inhibitor adsorption. When more inhibitor molecules are available to cover the metal surface due to an increase in the inhibitor concentration, then an increase in the inhibitor efficiency with increasing the inhibitor concentration will occur [36].

3.4 Electrochemical impedance spectroscopy.

Nyquist diagrams for Cu in 3.5 % NaCl with and without different concentrations of the modified imidazoline is given in Fig. 6.

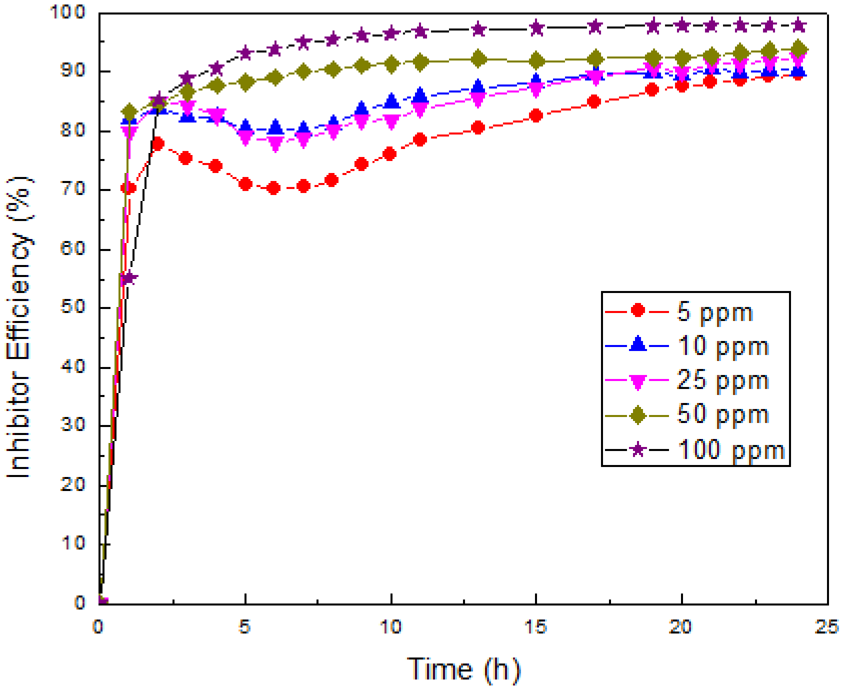

Figure 5. Dependence of the inhibitor efficiency value with time for Cu in 3.5 % NaCl solution with the oil palm-modified hydroxyethyl imidazoline.

For the uninhibited solution, it is clear the formation of two capacitive loops as published elsewhere [37,38], with the high frequency semicircle associated to the charge transfer process, due to the oxidation of copper, whereas the low frequency loop is associated to the formation of a corrosion products film [37, 38]. As soon as the inhibitor is added, the shape of the Nyquist diagram did not change in shape but only in size, which is an indication that the corrosion mechanism remained unaltered, with the total impedance increasing with an increase in the inhibitor concentration. The increase in the charge transfer resistance with the increase in the imidazoline concentrations, table 2, has been related with an increase in the protection effect given by the inhibitor.

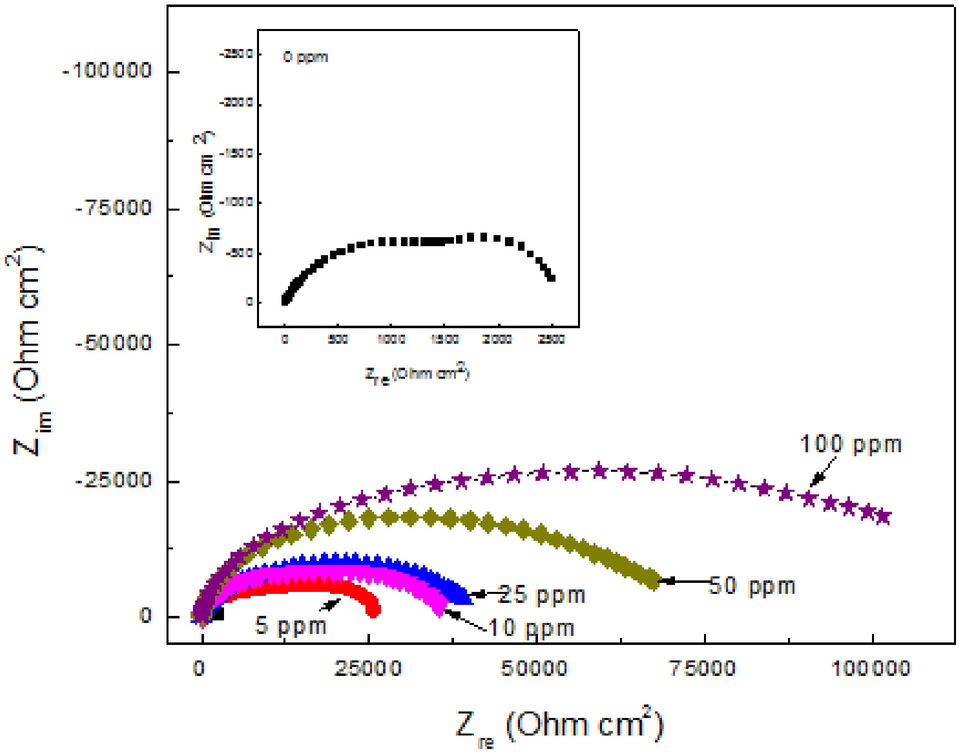

Figure 6. Effect of oil palm-modified hydroxyethyl imidazoline concentration in the Nyquist diagrams for Cu in 3.5 % NaCl solution.

The decrease in the double layer capacitance is due to the absorption of the inhibitor on to the metal surface and replacing the water molecules. The corrosion products or film resistance, R_f, and film capacitance, C_f, are also shown in table 2. It can be seen that the film resistance values are higher than those values for the double layer, due to its passive characteristics. The addition of the modified imidazoline increases both the charge transfer and the corrosion products resistance. The presence of the oxide film induced an increase in the charge transfer resistance, and this oxide stops the ingress of the electrolyte to the metal surface, whereas the corrosion products resistance increase due the incorporation of a complex formed by copper ions, $Cu^{2+,}$ and the modified imidazoline. Additionally, the presence of this oxide film induces a decrease in the capacitance of the double layer, C_{dl}, which makes more difficult the contact of the 3.% % NaCl solution with the copper surface. Inhibitor efficiency values were higher than 90% and increased with the inhibitor concentration, similar to the values obtained from the polarization curves, table 1.

The evolution in the time of the Nyquist diagrams for the uninhibited 3.5 % NaCl solution is given in Fig. 7, where it is evident the formation of two capacitive loops during the whole testing time; the semicircles diameter increased during the first 6 hours, but after that, it decreased with a further increase in the testing time, Fig. 7.

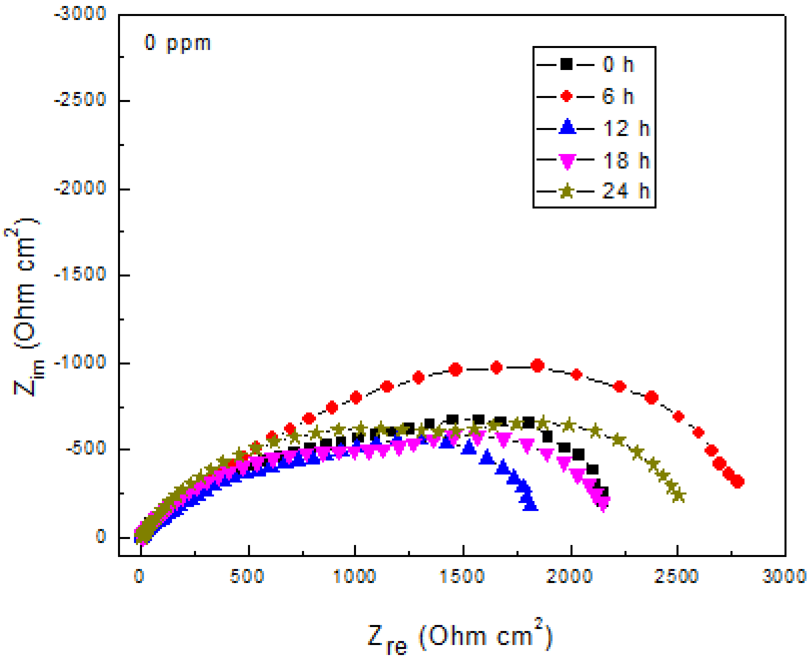

Figure 7. Evolution of Nyquist diagrams with time for Cu exposed to uninhibited 3.5 % NaCl solution.

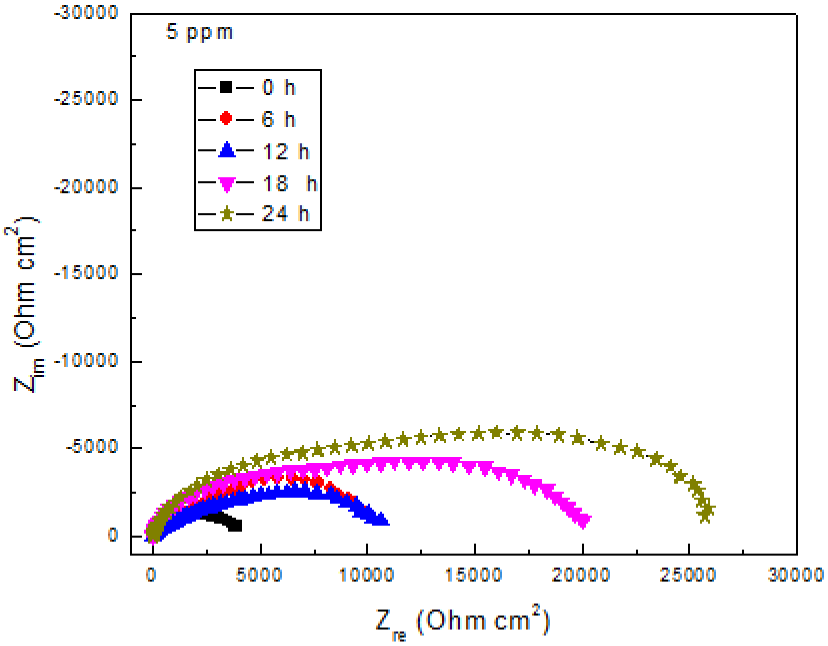

Figure 8. Evolution of Nyquist diagrams with time for Cu exposed to 3.5 % NaCl solution containing 5 ppm of oil palm-modified hydroxyethyl imidazoline.

This decrement in the total impedance with time indicates that the corrosion products formed on top of copper surface exposed to the uninhibited solutions has been detached form it, allowing the electrolyte to penetrate the film and corrode the underlying metal. The presence of the two loops during the whole experiment shows that the corrosion mechanism did not change during the testing time. For solution containing 5 ppm, Fig. 8, Nyquist diagrams exhibited one semicircle at high and intermediate frequency values, and a second one at lower frequency values, which correspond to the charge transfer resistance and to the formation of protective corrosion products by the modified Imidazoline and copper ions respectively.

The semicircles diameter increase with time reaching its maximum value after 24 hours of exposure to the electrolyte. Table 3 gives the change in the evolution in the R_{ct} and C_{dl} values with time for the Cu in 3.5 NaCl without and 5 ppm of imidazoline respectively. In this table inhibitor efficiency values were calculated by using

$$\mathrm{I.E.}\ (\%) = 100\ (R_{ct1} - R_{ct2}) / R_{ct1} \qquad (3)$$

where R_{ct1} is the charge transfer resistance with inhibitor and R_{ct2} the charge transfer resistance without inhibitor. It is clear that while the charge transfer resistance value for the uninhibited solution practically remained constant during the whole testing time, fluctuating around 1 kohm cm^{-2}, that for inhibited solution increased from 2 to 12 kohm cm^{-2},indicating that the protectiveness given by the inhibitor formed film increases as time elapses. Capacitance values were always decreased in presence of modified imidazoline, due to the adsorption of the inhibitor on to the Cu surface and the displacement of water molecules [42, 43].

3.5 Adsorption isotherms.

In order to get more information on the adsorption mechanism of the used inhibitor, efficiency values obtained from EIS data were fitted to different adsorption isotherms, but the best fit was obtained with the Langmuir type of isotherm a shown in Fig. 9. Langmuir isotherm is given by:

$$C_{inh}/\Theta = 1/K_{ads} + C_{inh} \qquad (3)$$

where C_{inh} is the inhibitor concentration, Θ the metal fraction covered by the inhibitor, equal to the inhibitor efficiency divided by 100, and K_{ads} the adsorption constant, which were calculated from the intercepts in Fig. 6. Standard free energy of adsorption, ΔG^0_{ads} can be calculated by using following expression:

$$K_{ads} = 1/55.5\ \exp\ (\Delta G^0_{ads}/RT) \qquad (4)$$

obtaining a value for ΔG^0_{ads} of -41.5 kJ mol^{-1}. It has been established that values of ΔG^0_{ads} lower than -40 kJ mol^{-1} are related with physisorption, whereas if the ΔG^0_{ads} value lies around -40 kJ mol^{-1} then we are talking about chemisorption [32]. We have a spontaneous process due to the negative value of the free-energy of adsorption, and we can also say that the oil palm modified imidazoline was chemically adsorbed on the steel surface because the ΔG^0_{ads} value lied around -40 kJ mol^{-1}. The formation of links between the d orbital of iron atoms and the lone π electron pairs present on the N, S and/or O atoms of the inhibitor [39, 40] are the responsible for the chemisorption of the inhibitor molecules involving the displacement of water molecules from the metal surface

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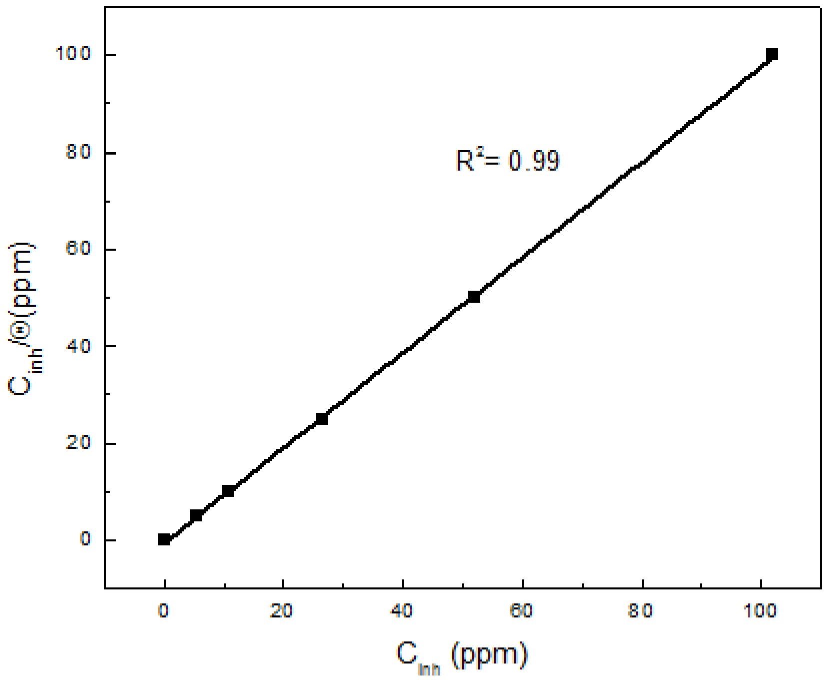

Figure 9. Langmuir adsorption isotherm for Cu exposed to 3.5 % NaCl solution containing various concentrations of inhibitor at 25 ^{0}C obtained from Nyquist diagrams.

Thus, all the results suggest that palm oil-modified imidazoline acts as corrosion inhibitor for Cu in neutral NaCl solutions being adsorbed on to the copper surface. This adsorption can be either physical or chemical. It was shown that imidazoline is adsorbed on copper surface by displacing water molecules from the metal, which involves the shearing of electrons between the nitrogen atoms and copper surface [41]. Similarly, there can be adsorption by the hydrogen bond formation between heteroatoms such as N and O present in the imidazoline and the corrosion products on top of copper surface, mainly Cu_2O [39, 40]. The adsorption occurs through the N and O atoms through their π-electrons and to the aromatic rings electron from the imidzoline to get linked to the unoccupied d-orbital of Cu is increased. El-Lateef et al. [46] use some fatty acids surfactants derived from a palm oil and used them as inhibitors for the CO_2 corrosion of carbon steel in a NaCl solution at 50 ^{0}C. Surfactants synthetized included Sodium sulfonatooxy, Potassium sulfonatooxy and Ammonium sulfonatooxy fatty acids, together with Sulfonatooxy fatty acidemonoethanolamine and acidediethanolamine complexes. It was found that these fatty acids acted as good corrosion inhibitors because disposition of the molecules to donate orbital electrons to an appropriate acceptor with empty molecular orbitals, in this case, Cu, to be adsorbed on to the metal surface and to form protective corrosion products. The sites were this adsorption could occur were always heteroatoms present in the molecules, such as N, C, O, S, present in the inhibitor structure.

4. CONCLUSIONS

A imidazoline modified with palm oil has been evaluated to inhibit the corrosion of Cu in 3.5 % NaCl solution. Resulting modified imidazoline acted as a good corrosion inhibitor, and its efficiency increased with increasing its concentration and in the elapsing time. It is thought that corrosion inhibition is due to the adsorption of imidazoline, chemical in nature, on to the Cu surface accordidng to an adsorption isotherm Langmuir-type. The inhibition of this imidazoline was due to the presence heteroatoms within the molecular structure of compounds and act as sites to form bonds with Cu to be adsorbed and to form protective corrosion products.

ACKNOWLEDGEMENTS
Financial support from Consejo Nacional de Ciencia y Tecnología (CONACYT, México) (Projects 196205, 159898, and 159913) is gratefully acknowledged.

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