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Genoveva BustosRivera-Bahena

FCQel, Universidad Autónoma del Estado de Morelos

A. M. Ramírez-Arteaga

FCQel, Universidad Autónoma del Estado de Morelos

Hugo A. Saldarriaga-Noreña

Centro de Investigaciones Químicas-IICBA, Universidad Autónoma del Estado de Morelos

A.K. Larios-Gálvez

CIICAp-IICBA, Universidad Autónoma del Estado de Morelos

José G. González-Rodríguez

CIICAp-IICBA, Universidad Autónoma del Estado de Morelos

M. Romero-Aguilar

FCQel, Universidad Autónoma del Estado de Morelos

R. López-Sesenes (✉ rlopez@uaem.mx)

FCQel, Universidad Autónoma del Estado de Morelos

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Genoveva BustosRivera-Bahena², A.M. Ramírez-Arteaga², ³Hugo A. Saldarriaga-Noreña, A.K. Larios-Gálvez¹, José G. González-Rodríguez¹, M. Romero-Aguilar² and R. López-Sesenes^{2*}

¹ CIICAp-IICBA, Universidad Autónoma del Estado de Morelos, Cuernavaca, México; Av. Universidad 1001, Chamilpa, 62209, Cuernavaca, México.

² FCQeI, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Chamilpa, 62209, Cuernavaca, México.

³ Centro de Investigaciones Químicas-IICBA, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Chamilpa, 62209, Cuernavaca, México.

Corresponding author: Roy López Sesenes, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Cuernavaca, 62209 Morelos, México. Email: rlopez@uaem.mx

Abstract

The hexane extract of *Persea Schiedeana* Ness (PSN) was analyzed as corrosion inhibitor for the brass surface immersed in 0.5 M HCl. Fourier-transform infrared spectroscopy and a gas chromatographic (GC) and mass spectrometric (MS) were used to identify the PSN extract's functional groups and compound constituents. The functional groups identified were CH₃ and CH₂ functional alkyl groups, C=O stretching vibration of aldehydes, ketones, and carbonyl groups found in flavonoids and fatty acids. The GC-MS determined the presence of fatty acids in the PSN extract, where palmitic acid, oleic acid, and ethyl oleate were the major constituents. Electrochemical characterizations were conducted to observe the effect of the hexane extract of PSN as corrosion inhibitor on the brass surface. The R_p and R_n calculated from EIS and ENA give the same behavior with magnitude values near each one. Based on the OCP behavior, it was determined that the PSN works as a mix inhibitor affecting both anodic and cathodic reactions. The corrosion current density (I_{corr}) determined with the Potentiodynamic test suggests that the extract of PSN reduces the corrosion rate of the brass with efficiencies above 90 % for all concentrations. The efficiency obtained for each PSN concentration was attributed to forming a corrosion scale of CuO and Cu₂O, which reacted with the carboxyl group to form copper carboxylates on the metal surface.

Keywords: corrosion inhibitor, brass, electrochemical analyses, *Persea Schiedeana* Ness, natural extract.

1. Introduction.

Natural product extracts have been proposed in the last years as an alternative to be used as corrosion inhibitors due to having their chemical compounds such as aromatic rings, OH- groups, and heteroatoms (N, O, S, and P) [1, 2] which make them an excellent alternative to replace the synthetic organic and inorganic compounds currently used as corrosion inhibitor since well know that they can reduce the corrosion rate due to in their chemical structure exist the compounds mentioned before [3]. Also, the extraction methods used to obtain the active compounds are cheap and easy to carry out, such as Soxhlet, maceration, hydro distillation, and so on [4-6].

Several metal surfaces are exposed to corrosive environments. Some modifications in their microstructure have been developed to reduce the aggressive effect on their surface by adding intermetallic elements, heat treatments, coating applications, organic and inorganic inhibitors, and so on. They have been evaluated using natural products as corrosion inhibitors, e.g., stainless steel, aluminum, aluminum alloys, copper, and copper alloys, which had reported low corrosion rates in different corrosion media (alkaline, acid, and neutral) [7]. One

mechanism action reported that explains the low corrosion rate observed in the presence of natural products is their adsorption on the metal surface, which could be affected by the inhibitor concentration since a concentration above or below the optimal can lead to desorb it [8]. Other factors that could affect the inhibition efficiency of the natural products are the chemical compound extracted, the type of metal, temperature, the extraction method, and even the solvent used to extract the active compounds.

Although the studies using natural products are extensive, some fruits have yet to be explored, such as *Persea schiedeana* Nees, a fruit tree endemic to Mesoamerica. In México, it is typically known as chinin or pagua in the Veracruz and Chiapas regions. It belongs to the Lauraceae family, such as avocado (*Persea americana* Mill), which had been analyzed as a corrosion inhibitor by other authors [9-11]. *Persea schiedeana* Nees's case has not been analyzed still as a corrosion inhibitor alternative. Even so, a few analyses were done by some authors, reporting that its chemical compositions found the presence of Fatty acids such as Oleic acid and Palmitic acid, also phenolic and antioxidant activities had been reported[12-14].

Based on the content reported for the *Persea schiedeana* Nees, which could contain OH groups and aromatic rings, this could be an excellent alternative to inhibit the negative effect of some corrosive environments on metal surfaces such as brass, which generally has been tested using organic and inorganic synthetic compounds which act forming complexes in active sites of the brass surface [15]. With the latter, the present research was focused on analyzing the inhibition activity of the hexane extract of *Persea schiedeana* Nees on the brass surface immersed in 0.5 M HCl, carrying out electrochemical analyses to estimate the corrosion rate. Also, a Fourier Transform Infrared spectrophotometry (FT-IR) was done to identify the functional groups in the extract, such as alcohol groups, carbonyls, alkanes, and aromatics, which could be adsorbed on the surface brass, preventing the corrosion increases. Gas chromatography-mass spectrometry (GC/MS) was used to identify primary and secondary components in the hexane extract of *Persea schiedeana* Nees.

2. Experimental procedure.

2.1 Materials.

Preparation of the extract as corrosion inhibitor

To prepare The *Persea schiedeana* Nees extract, the natural raw material was collected from a local market in Papantla, Veracruz México, during July and August. The part of the fruit used to prepare the extract was the seeds, which were cleaned with water. The excess water was dried with a wipe and left in the shade for one week to dry completely. Once the seeds were dried completely, they were ground up using a blender first, and a ceramic mortar was used to end the ground-up process to obtain a finer size of the seeds. The powdered seed of *Persea schiedeana* Nees was previously weighted for use in a Soxhlet extractor with a capacity of 500 ml; the quantity of powdered seed employed in each extraction cycle was 50 mg, and it was placed into a thimble in the extraction chamber. After that, the hexane was poured into a distillation flask, and the reflux condenser was coupled to the chamber extract. The hexane in the distillation flask was heated to evaporate at 60°C in a heating mantle. A refrigerant circulator system was used to ensure the condensation of the hexane and its drip down in the thimble; the extraction process was repeated several times (5 x 300 ml). The extract obtained (200 mg) was diluted in 10 ml of ethanol gauged with distiller water at 100 ml to prepare the inhibitor. After that, aliquots were prepared based on the test concentrations (100,200, 300, 400, and 500 ppm) diluted in a solution of 0.5 M HCl as the corrosive medium.

Metal surface preparation

A brass rod was used as a specimen for the test (Table 1), and from it, several samples were cut with an exposed area of 1 cm² at 1 cm length. The samples were ground using emery paper grade 150, 300, 500, 600, 800, and 1000 to obtain a flatter surface free of oxide products based on ASTM-G1-03. After this, the samples were rinsed with acetone and dried with hot air. A copper wire was welded to each sample to make the measurements and ensure an electric path between the samples and the equipment. Then, the samples were encapsulated with

epoxy resin to warrant an exposed area of 1 cm². To remove the excess resin from the exposed surface, they were again ground and cleaned following the procedure previously described.

Table 1. Chemical composition of the Brass.

Element	Cu	Pb	Al	Fe	Ni	Sn	Mn	Zn
% wt.	63	2.8	0.05	0.1	0.3	0.1	0.1	Balance

Electrochemical Test

To determine the effect of the hexane extract of *Persea schiedeana* Nees on mitigating the corrosion rate in the brass surface, electrochemical tests such as Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Polarization curves (PC), and Electrochemical Noise Analyses (ENA) were carried out. Before that, the Open Circuit Potential (OCP) was measured.

The OCP was measured by 3700 s to observe the E_{corr} behavior without and with the inhibitor addition. The EIS analyses were done following the procedure described on ASTM G 106, applying a sinusoidal amplitude of 10 mV in a frequency range from 10⁴ to 10⁻² Hz concerning OCP. The polarization curves were done by applying a start potential scan from -1000 to 1000 mV with a sweep rate of 60 mV/min vs. OCP. The ENA analyses were conducted according to the ASTM G 102, recording the current and potential taking 1023 points each second.

The electrochemical cell to carried out electrochemical analyses were conducted in a conventional cell of three electrodes using as working electrode (WE) the brass samples embedded in epoxy resin, a silver/chloride-silver electrode (Ag/AgCl) as reference electrode (RE), and a platinum wire was used as auxiliary electrode (AU). In the case of the ENA, two identical brass samples were used as working electrode pairs (WE1 and WE2), and a platinum wire was used as RE.

All measurements were done at least three times to ensure reproducibility in a Gamry Interface 1010E Potentiostat, previously calibrated using a 2k Ω calibration cell. Zview software was used to find the electrical circuit more appropriate based on the corrosion phenomena observed in the plots to fit the EIS results.

Chemical characterization

A Fourier-transform infrared spectroscopy (FT-IR) was used to identify the functional groups contained in the hexane extract of *Persea schiedeana* Nees (PSN) with a thermos scientific Nicole 6700 in a region of 500-4000 cm⁻¹, the sample used to carry out the analyses was placed in a sample holder for liquids. Also, a gas chromatographic (GC) 6890N (Agilent Technologies, San Francisco, CA, USA) and mass spectrometric (MS) 5975 (Agilent Technologies) were used to analyze the extract. The procedure used to carry out the GC-MS analyses was as follows: the samples were injected (2 μ l) automatically at 250 °C and separated through an HP5-MS: 5%Phenyl-95%methylpolisiloxane (30 m x 0.25 μ m). The carrier gas was helium (purity 99.99%), and the flow rate was maintained constant at 1 ml min⁻¹. The oven temperature started at 40°C and was gradually increased to 250°C for 5 min at a rate of 10°C/min-1 after it was raised to 285°C for 20 min at a rate of 10°C min-1. The mass spectrums were obtained by electronic impact (70 eV) and quadrupole mass analyzer. The scan mode (40–500 uma) was used to obtain the m/z, which was used to identify each compound.

3. Results and discussions.

3.1 Identification of chemical compounds in PSN by FT-IR and GC/MS

The FTIR analysis carried out on the *Persea schiedeana* Nees (PSN) is shown in Figure 1. The highest intensity absorbance peaks for the PSN extract are localized at 2921, 2852, 1709, 1464, 1411, 1376, 1281, 1242, 1115,

1088, 938 and 722 cm^{-1} . The absorbance peak between at 2921 and 2852 cm^{-1} corresponds with the C-H stretching vibration of the CH_3 and CH_2 functional alkyl groups [16]. The strong peak at 1709.613 cm^{-1} is assigned to the C=O stretching vibration of aldehydes, ketones, and carbonyl groups found in flavonoids and fatty acids[17]. The weak peaks between 1464 and 1376 cm^{-1} correspond with the C-H bending vibration of the aldehyde group[18]. Meanwhile, the weak peaks between 1115 and 1088 cm^{-1} correspond with the C-O stretching vibration of the ether and ester group. The small peak at 722 cm^{-1} corresponds to the CH out-of-plane bending vibrations in the PSN constituents [19].

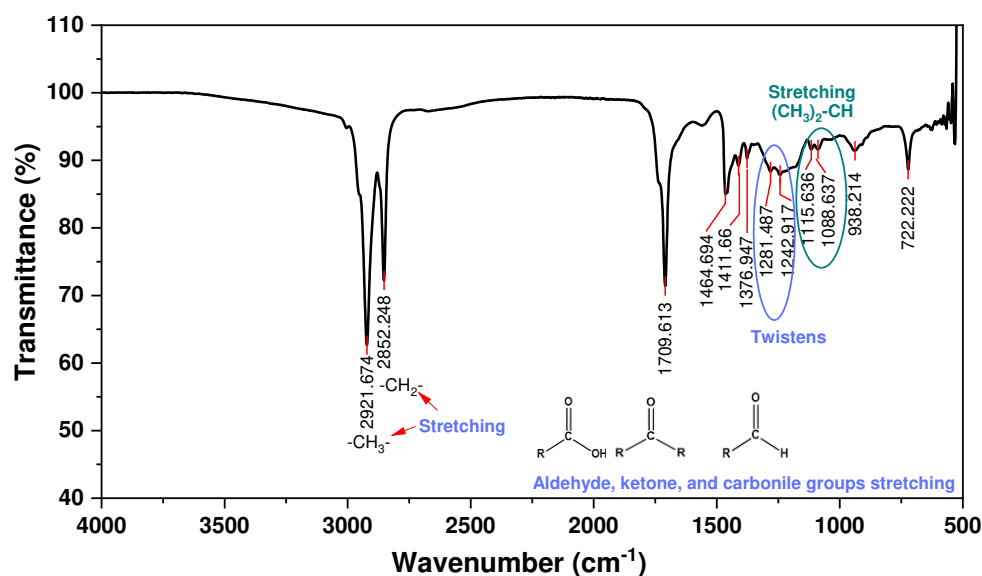


Figure 1. FT-IR for the hexane extract of *Persea schiedeana* Nees (PSN)

3.2 Chemical constituents of PSN via GC-MS.

Figure 2 shows the GC-MS chromatogram of the hexane extract of PSN constituents, which was carried out by comparing their spectral fragments with available database libraries Wiley and NIST. Table 2 lists essential oils and fatty acid constituents identified in the hexane extract. The primary constituents of them correspond with Oleic Acid (25.13 %), Humulane-1,6-dien-3-ol (25.39 %), Undecanoic acid, ethyl ester (27.85 %), n-Hexadecanoic acid (62.25 %), and Ethyl Oleate (64.32%). The last two compounds represent the main constituent in the PSN extract. Based on this, the fatty acids have been identified in other extracts as responsible for the corrosion mitigation on metal surfaces. Its formula chemical is R-COOH , where R represents the alkyl chain. Its long carbon chain and its feature of having a hydrophilic head (polar) and a hydrophobic tail (nonpolar) are the main features that confer good anticorrosion properties (Figure 2), i.e., the Hexadecanoic acid known as palmitic acid has a carboxylic group (COOH), which represents the hydrophilic part in the molecule, which can be adsorbed via Cu^+ and Cu^{2+} oxide states to form copper carboxyl on the metal surface. Meanwhile, the alkyl chain's methyl group (CH_3) represents the hydrophobic part that repels the H_2O molecules from the metal surface. The compounds found in the GC-MS chromatogram confirm the observed on the FT-IR analysis since functional groups such as CH_3 and COOH were detected.

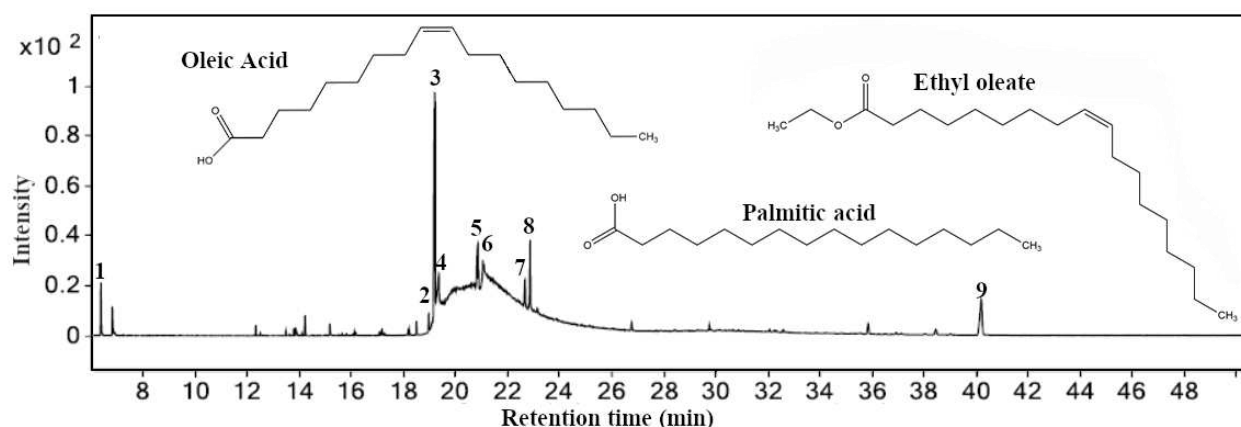


Figure 2. GC-MS chromatogram of hexane extract of PSN.

Table 2. GC-MS data of the hexane extract of PSN.

Peak	RT	Molecular Formula	Compound	Area (%)
1	6.374	C ₁₀ H ₁₆	Bicyclo[3.1.0]hexane, 4-methylene-1-(1-methylethyl)	6.7
2	18.973	C ₁₈ H ₃₄ O ₂	Ethyl 9-hexadecenoate	6.64
3	19.216	C ₁₈ H ₃₆ O ₂	Hexadecanoic acid, ethyl ester	100
4	19.36	C ₁₆ H ₃₂ O ₂	n-Hexadecanoic acid	62.25
5	20.773	C ₂₀ H ₃₆ O ₂	Linoleic acid ethyl ester	7.78
6	20.85	C ₂₀ H ₃₈ O ₂	Ethyl Oleate	64.32
7	22.671	C ₁₈ H ₃₄ O ₂	Oleic Acid	25.13
8	22.868	C ₁₃ H ₂₆ O ₂	Undecanoic acid, ethyl ester	27.85
9	40.196	C ₁₅ H ₂₆ O	Humulane-1,6-dien-3-ol	25.39

3.3 Open circuit potential analyses.

The behavior of the corrosion potential (E_{corr}) for the brass immersed in 0.5 M HCl without and with hexane extract of PSN is shown in Figure 3. Without PSN (0 ppm), The E_{corr} for the brass held a stable behavior of -0.385 ± 0.059 mV until the end of the test. With the inhibitor addition at 100 ppm, the E_{corr} of the brass shifted to more active potentials, meaning an increase in the corrosion process with a stable behavior in its E_{corr} of -0.402 ± 0.063 mV. With the concentration increased at 200 ppm, the E_{corr} observed a slight change toward a nobler direction with a value of -0.376 ± 0.073 mV. The most active behavior was registered at 300 ppm, where the PSN helped to shift the E_{corr} values toward more active values with -0.533 ± 0.053 mV, suggesting an increase in the corrosion rate where the compounds contained in the PSN could interact with the active sites on the brass, increasing the corrosion in the areas susceptible to Cl⁻ diffusion, avoiding the adsorption of the inhibitor over the brass surface. At 400 and 500 ppm of PSN, the E_{corr} was displaced again in the noble direction (407 ± 0.029 and 321 ± 0.068 mV, respectively). Based on the behavior observed with the inhibitor addition, the PSN suppresses both anodic and cathodic reactions, suggesting it acts as a mixed corrosion inhibitor.

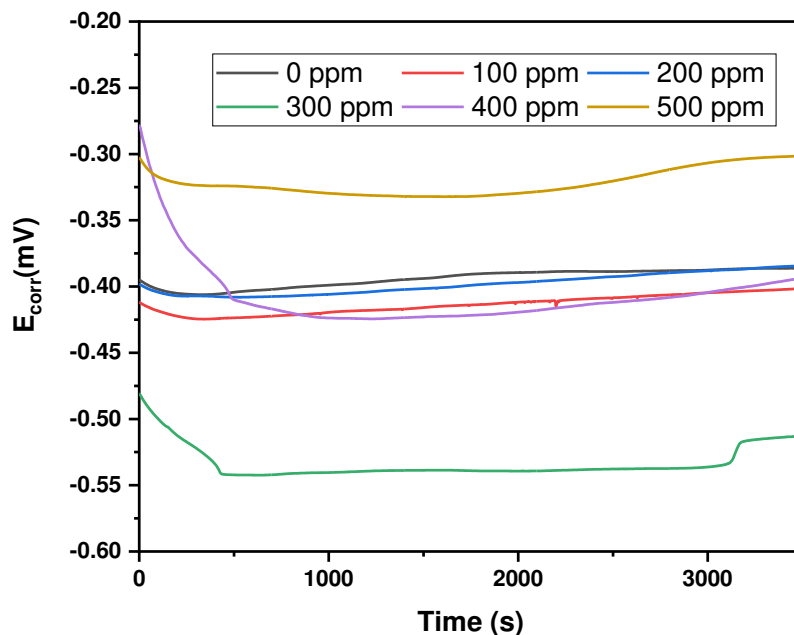


Figure 3. OCP behavior for brass immersed in 0.5 M HCl, without and with hexane extract of PSN as corrosion inhibitor at different concentrations.

3.4 Electrochemical Impedance Spectroscopy (EIS)

Figure 4 shows the EIS plots for the brass without and with PSN immersed in 0.5 HCl. With the addition of PSN, the semicircle diameter increased from high to middle frequencies with a displacement of the constant phase element toward high frequencies, which can be appreciated in Figure 5. Also, an elongation for the time constant at this frequency range was appreciated for all PSN concentrations. The depression observed in the Nyquist plots can depart from different reasons, such as roughness, impurities, and adsorption of corrosion products, suggesting a non-ideal capacitive behavior. Based on the latter, the test without inhibitor showed a depressive semicircle from high to middle frequencies due to charge transfer resistance from the electrolyte to the metal surface with a phase angle of -52° at 2 Hz (middle frequencies). At 100 ppm, an increase in the depressive semicircle was observed with a diffusion attempt at low frequencies, observing a displacement in its phase angle toward high frequencies (>100 Hz) with a value of -60° (Figure 5). This suggested that the PSN was adsorbed on the metal surface, avoiding oxygen and chloride diffusion on active brass sites, leaving it clear that the charge transfer resistance controls the corrosion process. At 200 ppm, a reduction in the semicircle diameter was observed, with a diffusion attempt of Cl^- and O atoms into the metal surface. Its phase angle decreased from -60° to -53° , displacing to higher frequencies with the inhibitor concentration increases, suggesting a decrease in the covered degree (θ) of the PSN on the brass surface. This is because, with the concentration, occur a change in the way that the inhibitor is adsorbed on the brass surface, which could change from horizontal to vertical, taking place a not homogenous cover of the surface [20]. At 300 ppm, the semicircle diameter increased from high to middle frequencies, increasing the impedance magnitude and decreasing the phase angle (-56°) with a displacement of the time constant from high to middle frequencies. However, a diffusion intent was observed at low frequencies. However, the predominant mechanism continues to be the charge transfer resistance. At 400 ppm, the semicircle diameter increased, reaching its maximum, with an increase in the phase angle of (-64°), keeping without displacement concerning the behavior at 300 ppm. Its impedance magnitude reaches a value of $10^4 \Omega\text{cm}^2$, one order more, concerning the test without PSN, which was $10^2 \Omega\text{cm}^2$. However, at the highest concentrations (500 ppm), the semicircle diameter decreased again,

keeping the total impedance of the brass in the order of $10^3 \Omega\text{cm}^2$, suggesting a non-linear behavior of the resistance with the inhibitor concentration.

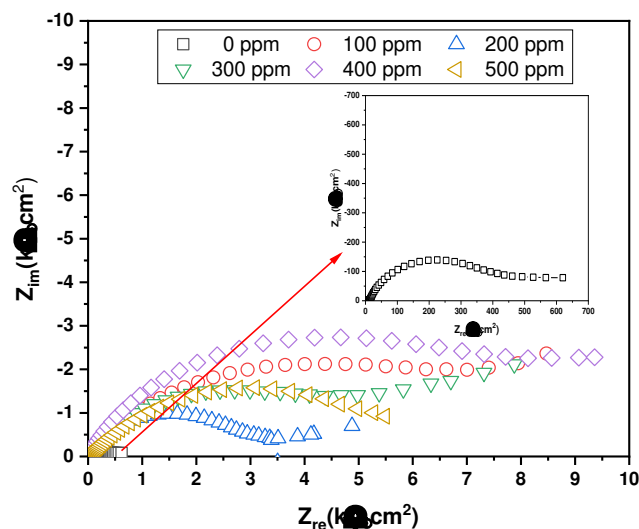


Figure 4. Nyquist plot for the brass immersed in 0.5 HCl, without and with hexane extract of PSN as corrosion inhibitor at different concentrations.

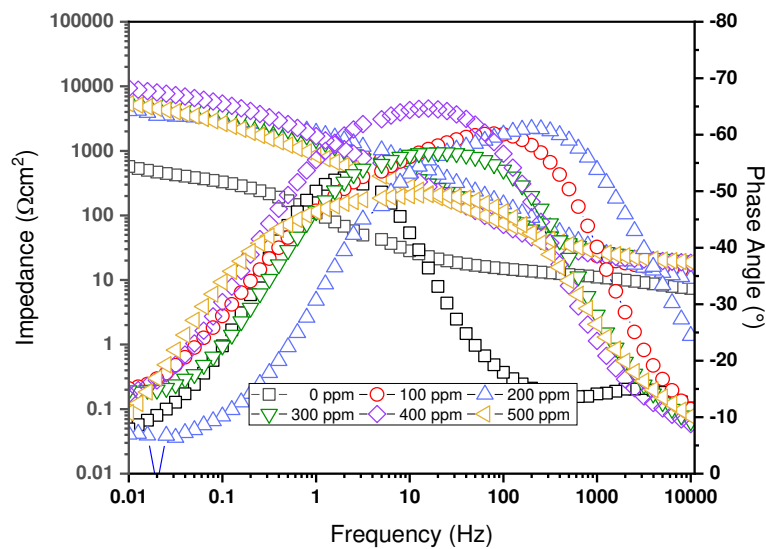


Figure 5. Bode plots for the brass immersed in 0.5 M HCl, without and with hexane extract of PSN as corrosion inhibitor at different concentrations.

To explain the impedance behaviors of the brass without and with PSN as corrosion inhibitors at different concentrations, the experimental data were fitted with the electrical equivalent circuits shown in Figure 6. The EEC of Figure 6 a was used to fit the experimental data from the test without inhibitor, where the first element consists of a constant phase element (CPE_{ox}) at high frequencies, which corresponds to the layer of corrosion products formed over the metal surface configured in parallel with an oxide resistance (R_{ox}). After, it was connected in series with a constant phase element corresponding to the double layer formed between the metal surface and the electrolyte (CPE_{dl}). This latter, in turn, was connected in parallel with a charge transfer resistance (R_{ct}). With the inhibitor addition, Figure 6 b, a CPE_{ox+inh} element is added in parallel with a R_{inh+ox} , and a CPE_{dl} was connected in parallel with an R_{ct} . Both, in turn, were in series with the R_{inh+ox} . The CPE parameters calculated with the EEC fit are the admittance (Y_0) and the n parameter. To give a better physical explanation of CPE, it can be converted to capacitance values (C_x) with equation 1 [21, 22]. In the case of n values, these are related to the surface roughness, where some authors suggested that values near 1 mean a more homogeneous surface. Meanwhile, values near 0 suggest a more heterogeneous surface [23]. Also, these values near 1 or near 0 mean an ideal (capacitor) and non-ideal (resistor) capacitive behavior, respectively. Meanwhile, values near 0.5 mean a finite or infinite Warburg diffusion[24]. The EIS efficiency was calculated with equation 2, where R_p^0 is the polarization resistance without PSN, and R_p is the polarization resistance at different PSN concentrations.

$$C_x = (Y_0 R_x^{1-n})^{1/n} \quad (1)$$

$$\%IE_{EIS} = 100 \left[1 - \frac{R_p^0}{R_p} \right] \quad (2)$$

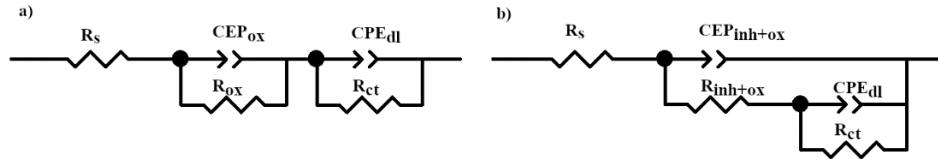


Figure 6. Equivalent circuits to fit the experimental data from the brass immersed in 0.5 M HCl without (a) and with (b) hexane extract of PSN as corrosion inhibitor.

Table 3 shows the parameters calculated with the EECs. The blank's total polarization resistance (R_p) was $554 \Omega\text{cm}^2$, and its R_{ox} got a value of $13 \Omega\text{cm}^2$. Meanwhile, its R_{ct} got a value of $536 \Omega\text{cm}^2$. It means that the surface protection was due to the charge transfer resistance. With the presence of PSN in the electrolyte at 100 ppm, the R_p increased at least one order with $9025 \Omega\text{cm}^2$, observing a synergistic effect via adsorption of the PSN with the oxide products formed on the brass. In this sense, as is known, copper is protected due to a film formed by Cu_2O and CuO , which could react via their dissolution due to the Cl^- with the OH^- and O contained in the hydrophilic part of the palmitic and oleic acids, forming a passive film via adsorption of both compounds, avoiding that the H_2O molecules are kept in touch with the metal surface due to the hydrophobic part in both compounds. At 200 ppm, the R_p got a value of $4492 \Omega\text{cm}^2$, observing that the R_{inh+ox} increased its value at $3040 \Omega\text{cm}^2$. At 300 and 400 ppm of PSN in the solution, the R_p values increased at 8680 and $9878 \Omega\text{cm}^2$, reaching inhibition efficiencies above 90%. As was discussed before, at 500 ppm, the R_p decreased at this concentration with an inhibition efficiency of 84%.

Table 3. Fitting results from EIS analyses for the brass immersed in 0.5 M HCl without and with hexane extract of PSN as corrosion inhibitor.

C_{inh}	Chi-Sqr	R_s	C_{ox}	n_{ox}	R_{ox}	C_{dl}	n_{dl}	R_{ct}	R_p	%IE
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(ppm)		(Ωcm^2)	(Fcm^{-2})		(Ωcm^2)	(Fcm^{-2})		(Ωcm^2)	(Ωcm^2)	
0	1.7×10^{-3}	5	2.0×10^{-5}	0.5	13	8.4×10^{-4}	0.9	536	554	
100	4.6×10^{-5}	9	5.7×10^{-7}	0.6	8	1.3×10^{-5}	0.9	9008	9025	90
200	1.0×10^{-3}	7	3.4×10^{-5}	0.7	3040	4.5×10^{-3}	0.7	1446	4493	80
300	1.4×10^{-3}	18	9.3×10^{-5}	0.7	4516	1.9×10^{-3}	0.6	4146	8680	90
400	3.6×10^{-4}	19	8.4×10^{-5}	0.8	5496	3.8×10^{-4}	0.5	4363	9878	91
500	2.7×10^{-4}	17	1.2×10^{-4}	0.7	1491	1.2×10^{-4}	0.7	4291	5799	84

3.5 Potentiodynamic Polarization curves.

The polarization curves (PC) done to the brass immersed in 0.5 M HCl without and with PSN are shown in Figure 7. The parameters calculated from PC via the Tafel extrapolation method are shown in Table 4. All plots present an active-passive behavior, with a decreased corrosion rate with the PSN concentrations. The higher corrosion current density (i_{corr}) was at 200 ppm PSN with $2.1 \times 10^{-3} \text{ mA/cm}^2$, followed by the concentration at 400 ppm with $2.4 \times 10^{-3} \text{ mA/cm}^2$. The remaining concentrations got values relatively higher in the same order. The PSN's inhibition efficiency (IE) at all concentrations was above 90% and was calculated with Equation 3. Also, with the PSN concentration, the critical current density (i_{cp}) was displacement toward lower values, and their passivation currents (i_p) observed the same behavior. The corrosion potential (E_{corr}) was more active for the studies done in the presence of PSN, increasing or decreasing based on its concentration, suggesting that the PSN blocks both anodic and cathodic processes on the brass surface. An active region followed by a passive zone confirms that a layer of corrosion products is formed on the metal surface. Although the latter is observed even without PSN, the inhibition effect at all concentrations is appreciated in both i_{cp} reduction and passive potential (E_{pp}) increases, which tend to shift in the active direction, suggesting that the PSN acts, increasing the active dissolution of Cu to Cu^{2+} , adsorbing on the corrosion products layer on the brass allowing get i_p values in the order of 10^{-3} mA/cm^2 .

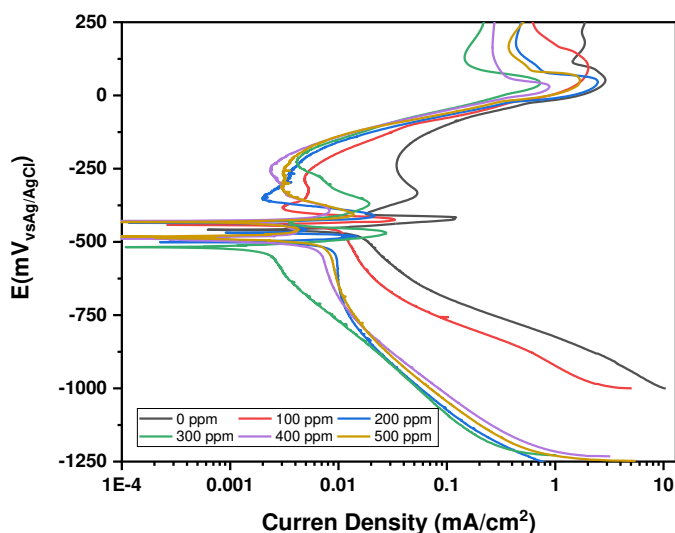


Figure 7. Polarization curves for the brass at different concentration of hexane extract of PSN as corrosion inhibitor immersed in 0.5 M HCl.

$$IE\% = \left(\frac{I_{corr}^{inh} - I_{corr}}{I_{corr}} \right) * 100 \dots\dots\dots(3)$$

Table 4. Polarization curves data determined by Tafel extrapolation for the brass at different concentrations of hexane extract of PSN as corrosion inhibitor immersed in 0.5 M HCl.

C_{inh} (ppm)	i_{corr} (mA/cm ²)	E_{corr} (mV)	i_{cp} (mA/cm ²)	E_{pp} (mV)	i_{pit} (mA/cm ²)	E_{pit} (mV)	i_p (mA/cm ²)	E_p (mV)	E_{tr} (mV)	EI%
0	3.4×10^{-2}	-463	1.1×10^{-1}	-416	1.9×10^{-2}	-403	5.1×10^{-2}	-330	-192	
100	3.1×10^{-3}	-441	3.2×10^{-2}	-427	3.1×10^{-3}	-379	3.1×10^{-3}	-379	-276	91
200	2.1×10^{-3}	-506	1.2×10^{-2}	-478	1.3×10^{-3}	-469	-----	-----	-345	94
300	3.5×10^{-3}	-518	2.7×10^{-2}	-466	3.7×10^{-3}	-431	4.2×10^{-3}	-239	-222	90
400	2.4×10^{-3}	-483	4.0×10^{-3}	-469	2.4×10^{-3}	-429	3.3×10^{-3}	-340	-244	93
500	3.0×10^{-3}	-488	4.1×10^{-3}	-456	1.4×10^{-3}	-429	3.1×10^{-3}	-330	-239	91

3.6 Electrochemical Noise Analyses (ENA).

ENA analyses done on the brass immersed in 0.5 M HCl in the absence and presence of PSN are shown in Figure 8. The electrochemical potential noise (EPN) without PSN (0 ppm) shows an increase in the corrosion potential from active to noble potential values, keeping stable throughout the time with some transients of high amplitude (± 0.6 mV) at 600s, suggesting an increase in the energy consumption in the mass transfer. In the case of the electrochemical current noise (ECN), the current remains stable with some transients of low amplitude around $\pm 2.0 \times 10^{-4}$ mA/cm². After 600 s, their amplitude increased above $\pm 4 \times 10^{-4}$ mA/cm², suggesting the formation of pits on the brass surface, indicating a localized corrosion type. With the PSN addition (200 ppm), an increase in EPN during the first 200 s is observed, which confirms that PSN increases the active dissolution of Cu to Cu² due to the high energy consumption in the mass transfer. However, the EPN transients decreased afterward, keeping stable with some low amplitude transients until the test's end. Its corresponding ECN analysis reveals that the current at the beginning of the test showed transients of high amplitude and low frequency decreasing after 200s from $\pm 4 \times 10^{-4}$ to $\pm 2 \times 10^{-4}$ mA/cm², with transients of low amplitude and low frequency, suggesting a generalized corrosion type due to the PSN adsorption in the metal surface helping to produce a more stable layer of corrosion products that avoid the H₂O interaction with the metal surface due to the hydrophobic part contain in the oleic and palmitic acids compounds found in the PSN extract. The same behavior was observed at 400 ppm of PSN, where a reduction in the corrosion current is appreciated again with few localized events with time. These results agree with the CP and EIS analyses, where low currents and high polarization resistances were observed at these PSN concentrations against the test without PSN.

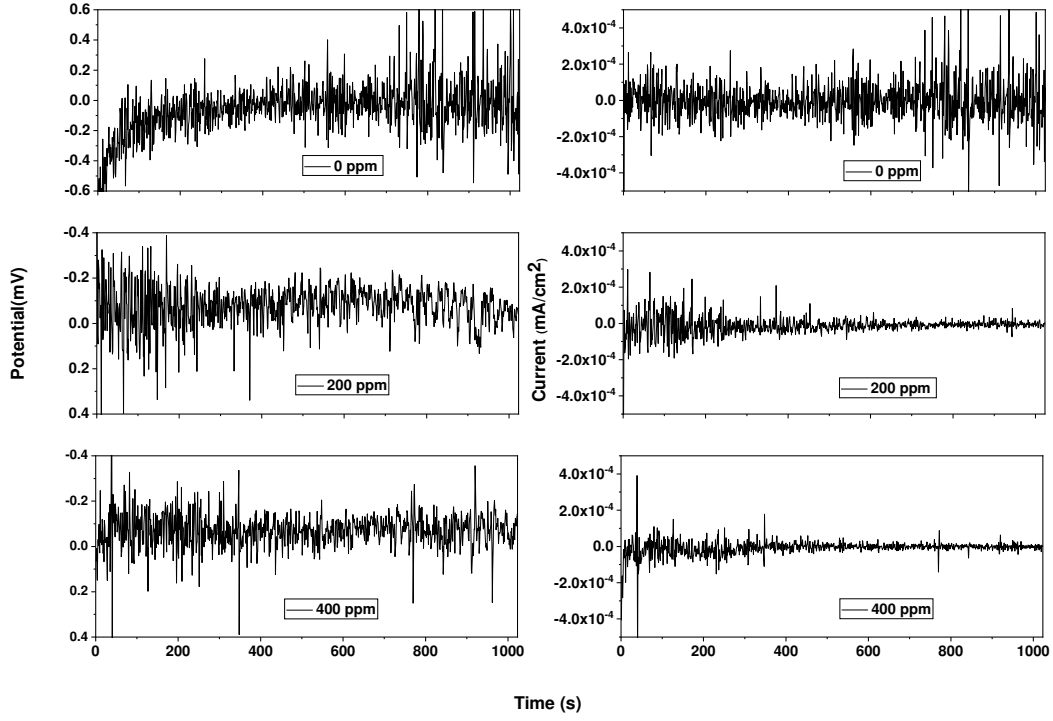


Figure 8. Time domains for the Potential and current of the brass without and with *Persea schiedeana* Nees (PSN) as corrosion inhibitor immersed in 0.5 M HCl.

Some statistical approaches were conducted to determine parameters such as noise resistance (R_n), limit index (LI), Skewness, and Kurtosis. To obtain these values, it is necessary to calculate firstly the standard deviation of the current and potential (σ_x) with equation 4.

$$\sigma_x = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N}} \quad (4)$$

With the standard deviation of the current (σ_i) and potential (σ_v), it is possible to obtain the noise resistance parameter (R_n) by applying equation 5.

$$R_n = \frac{\sigma_v}{\sigma_i} \quad (5)$$

To determine the corrosion type on the brass surface, Skewness and Kurtosis were calculated with equations 6 and 7, where the first refers to the skewed data and the second refers to the outliers found in the EN data measured. Some values of Skewness (I_{skew}) and Kurtosis (I_{kurt}) in the current have been proposed by Jázquez-Muñoz *et al.* as a reference to determine the type of corrosion present in a metal surface. These values are used here, and the results are shown in Table 5 [25].

$$skewness = \frac{1}{N} \sum_{i=1}^N \frac{(x_i - \bar{x})^3}{\sigma^3} \quad (6)$$

$$kurtosis = \frac{1}{N} \sum_{i=1}^N \frac{(x_i - \bar{x})^4}{\sigma^4} \quad (7)$$

Table 5. Time domain analyses for the current and voltage of the brass via statistical approaches.

C _{inh} (ppm)	R _n (Ωcm ²)	σ _i (mA/cm ²)	E _{kurt}		E _{skew}		i _{kurt}		i _{skew}	
0	103	1.72 x 10 ⁻³	7	pitting	2.0		2.0	uniform	0.8	uniform
100	7434	8.24 x 10 ⁻⁴	2	uniform	-0.2	uniform	1.8	uniform	-0.4	pitting
200	6590	3.70 x 10 ⁻³	2	uniform	-0.1	uniform	1.8	uniform	0.5	uniform
300	18018	8.26 x 10 ⁻⁴	2	uniform	-0.3	uniform	3.1	pitting	0.6	uniform
400	11826	1.75 x 10 ⁻³	2	uniform	-0.1	uniform	4.7	pitting	1.7	pitting
500	6526	3.27 x 10 ⁻³	3	pitting	1.2	uniform	3.0	pitting	1.1	pitting

The noise resistance (R_n) estimated denotes that the brass resistance tends to increase with the PSN addition into the solution. For the solution without PSN, an R_n of 103 Ωcm² was calculated. Meanwhile, at 100 ppm, the R_n increased to 7434 Ωcm². With the inhibitor increase at 200 ppm, a decrease in the R_n was recorded with 6590 Ωcm². This behavior was like that observed in the EIS test at this concentration. The R_n increased again at 300 and 400 ppm with 18018 and 11823 Ωcm², respectively. At 500 ppm, a drop in the R_n was observed, suggesting that the optimal PSN concentration is below this. Figure 9 describes better the R_n and R_p behavior, where both have similarities in trend and magnitude.

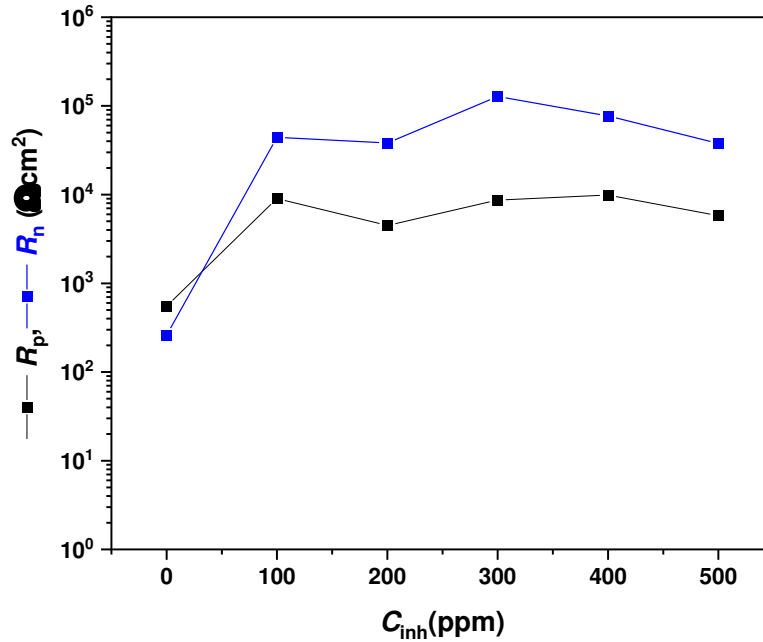


Figure 9. R_n and R_p behavior for the brass without and with *hexane extract of PSN* as corrosion inhibitor immersed in 0.5 M HCl.

3.7 Adsorption Isotherm for the hexane extract of PSN.

The coverage degree (θ) was calculated using the R_n values with equation 8.

$$\theta = \frac{R_n^0 - R_n^i}{R_n^0} \quad (8)$$

Where R_n^0 and R_n^i are the noise resistance without and with PSN as corrosion inhibitor, respectively.

Adsorption models were tested using the θ calculated with the R_n values (equation 8). Temkin, Flory Huggins, and Freundlich were some of them, where a correlation coefficient (R^2) lower than 0.5 was estimated. Also, the Langmuir isotherm model in its linear form (equation 9) was evaluated and got an R^2 of 0.999 with a slope near 1 (0.9984) estimated via plotting $\ln(C/\theta)$ vs. $\ln C$ (Figure 10). The parameters obtained mean that the inhibitor is adsorbed, obeying this model isotherm, which suggested that each molecule in the PSN occupies one active site, forming a layer on the metal surface without interaction between them. An equilibrium constant (K_{ads}) of 0.02 was calculated from the reciprocal of the intercept estimated in Figure 10. This value was used to determine the Gibbs Free Energy (ΔG_{ads}^0) behavior at 25°C for the PSN by using equation 10, got a ΔG_{ads}^0 of -51.98 kJ/mol which suggest chemisorption of the PSN compounds since based on the literature values above -40 kJ/mol means this, so its negative ΔG_{ads}^0 value suggests that PSN adsorption is spontaneous.

$$\ln\left(\frac{C}{\theta}\right) = \ln C - \ln k \quad (9)$$

$$\Delta G_{ads}^0 = -RT \ln 55.5(k) \quad (10)$$

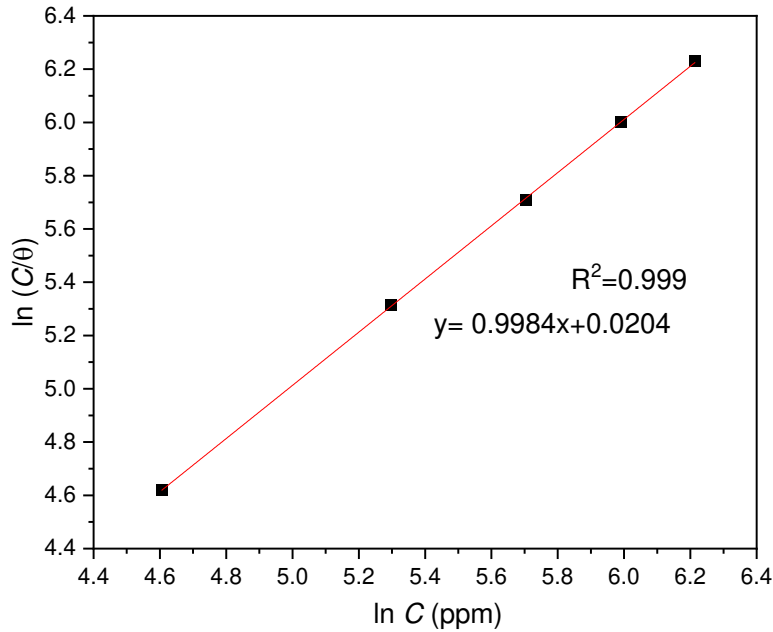
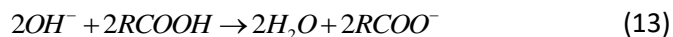


Figure 10. Langmuir adsorption isotherm for the hexane extract of PSN on brass surface immersed in 0.5 M HCl.

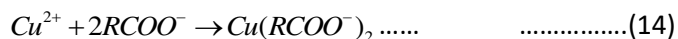
Considering the compounds found via GS-MS, where the main constituents were fatty acids. These can be reacted with the Cu^{2+} and OH^- ions produced on the anodic (equation 11) and cathodic (equation 12).



Then the 2OH^- react with the fatty acids to form carboxylate ions (RCOO^-) as is mentioned:

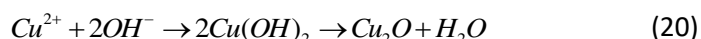


Now, The Cu^{2+} formed from the anodic reaction (equation 11) can react with the carboxylate ions to form copper carboxylate as follows:



The reaction from equation 14 leave clears the interaction between the metal surface and the PSN extract, which is added to the surface-formed complexes in the interface metal-PSN inhibitor via chemical adsorption, decreasing the metal dissolution and avoiding the H_2O -metal interaction due to the alkali chain in the fatty acid ligand which is hydrophobic part in the fatty acid.

Moreover, the Cl^- ions in the solution can react with the Cu to promote the formation of unstable compounds such as CuCl^- and CuCl_2^- (equation 15 and 16), which increase the metal dissolution due to Cl^- diffusion. However, it can also occur that Cu^{2+} could be produced via CuCl^- and CuCl_2^- dissolution (equations 17 and 18) and then Cu^{2+} react with the OH^- ions to form CuO or Cu_2O (equations 19 and 20), highly protective products, improving the corrosion resistance of the brass surface.



At this estate the cupric and cuprous oxide can react again with the carboxyl group found in the primary constituents from the hexane extract of PSN to form copper-inhibitor complexes, as was described in equation 14.

3.8 Corrosion product morphologies.

SEM micrographs are shown in Figure 11. Figures a and b represent the metal surface without PSN in the solution. The panoramic view (Figure a) shows pits with a diameter of $7 \pm 2 \mu\text{m}$. Also, a corrosion product scale with an irregular form is present along the metal surface. Figure 11 b shows a zoomed view of the corroded

surface where the presence of pits on the metal surface generated by the diffusion of Cl^- ions into the porous forming CuCl^- and CuCl_2^- increased the localized corrosion, generating a detachment on the scale formed by CuO and Cu_2O from the metal surface. Panoramic views of the brass surfaced exposed at 100 and 200 ppm of PSN concentrations are shown in Figure 11 c and e, respectively, where fewer porosities are observed on the brass surface with an average diameter of $5 \pm 2 \mu\text{m}$. The zoom views for the brass at 100 and 200 ppm of PSN (Figure 11 d and f, respectively) show the corrosion products layer with fewer zones susceptible to localized corrosion due to the presence of the copper carboxylates in the solution, which helps to avoid the Cl^- diffusion into the metal surface due to the barrier formed by the PSN.

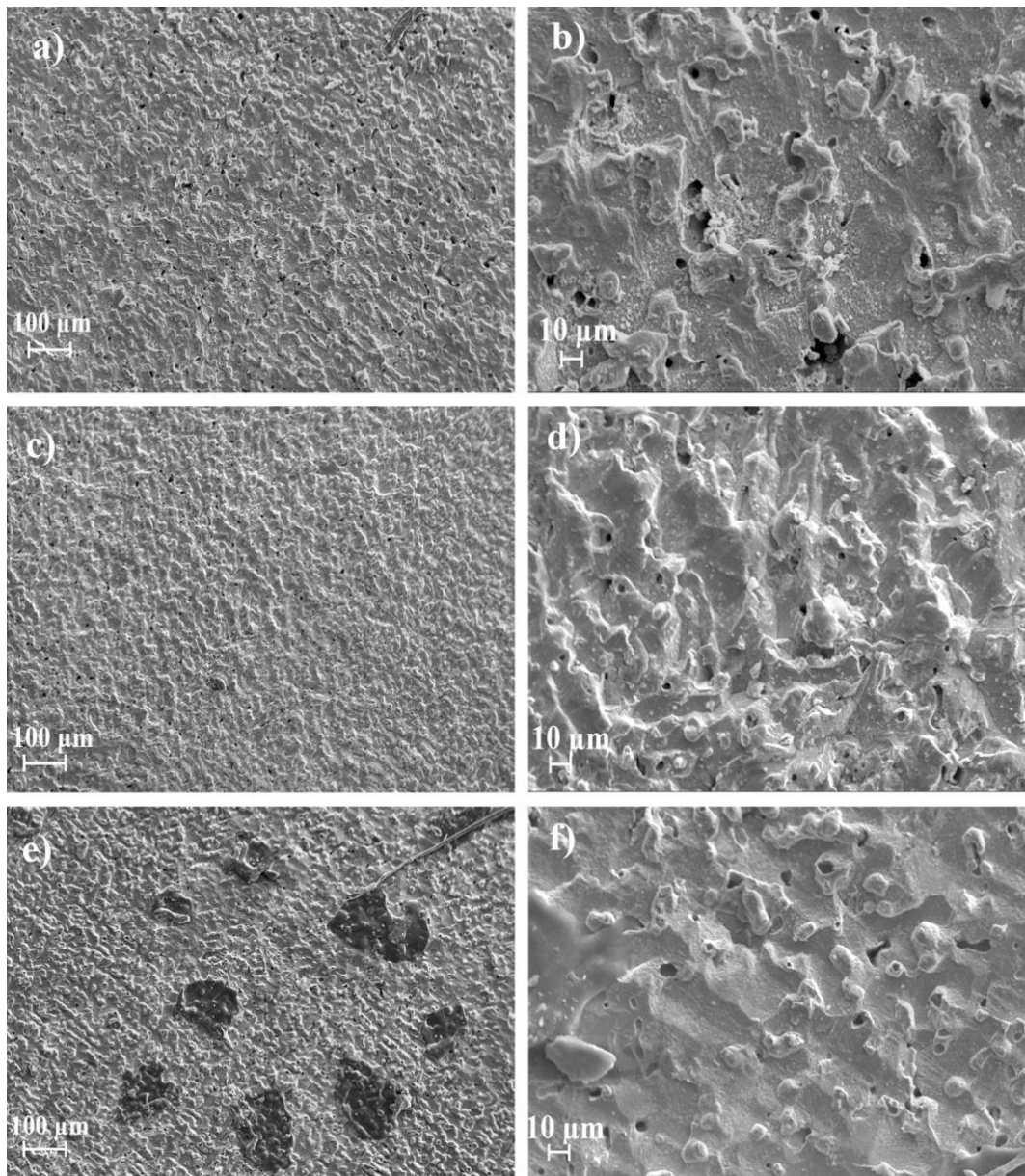


Figure 11. Corroded Surface for the brass without (a and b) and with hexane extract of PSN at 100 (c and d) and 200 ppm (e and f) immersed in 0.5 M HCl.

Conclusions.

Based on the results obtained from the electrochemical test, it was possible to determine that the PSN works as a suitable corrosion inhibitor with efficiencies above 90% in almost all concentrations. The efficiency calculated from EIS and CP confirms that the PSN reduces the corrosion rate on the brass in the presence of HCl. The ENA applied suggested a mixed corrosion phenomenon on the metal surface, which decreased with the inhibitor addition. Even the R_n calculated got the same trend as the R_p estimated from EIS. The MS-GS analyses to characterize the PSN hexane extract allowed the identification of the main compounds in the PSN, finding that fatty acids such as palmitic acid, oleic acid, and ethyl oleate were the primary constituents in the extract. As was explained, based on the chemical structure of the fatty acid identified, they have a carboxyl group joined to an alkyl chain where the first can form copper carboxylate with the brass surface, allowing the PSN molecule to keep adsorbed over it. Also, the alkyl chain has a methyl group that works as a repellent from the H_2O molecules, reducing their interaction with the metal surface. Also, the IR analysis confirmed the presence of the functional groups found in the chromatograms.

Declarations

Competing interest

The authors have no competing interests or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Ethical Approval

The declaration is not applicable.

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Availability of data and materials

The authors confirm that the data supporting the findings of this study are available within the article.

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