

Anticorrosive Coating of Propolis Extract for CA-50 Carbon Steel Reinforcement

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This study investigated the efficiency of the natural anticorrosive coating of propolis extract (PE) on CA-50 carbon steel in a solution that simulates the liquid phase of the concrete pore condition, called cement extract (CE). Fourier transform infrared (FTIR) and high-performance liquid chromatography (HPLC) analyses of the propolis extract identified inhibitory functional groups, with Artepillin C (3,5-diprenyl-4-hydroxycinnamic acid) being the predominant component present in the propolis extract (PE). To examine the inhibition capacity of propolis extract on reinforcement, an aqueous solution of 3.5 wt.% NaCl solution was added to the cement extract in the presence and absence of PE. Electrochemical techniques such as open circuit potential, polarization curves and electrochemical impedance spectroscopy were carried out to study corrosion efficiency. Scanning electron microscopy (SEM) was performed to characterize the sample surface. The results show that PE was effective as an anti-corrosion coating for carbon steel in the environment studied, indicating the formation of a protective film with higher stability.

Keywords: Carbon steel, corrosion, natural coating propolis extract.

1. Introduction

Corrosion is the pathology that most affects reinforced concrete, causing problems in both the aesthetics and safety of the structures¹⁻⁴. One of the biggest problems in the application of the carbon steel as a reinforcement is its low corrosion resistance, especially when exposed to severe conditions, such as marine environments^{5,6}.

Usually, this phenomenon causes the cross-section to decrease, which directly affects the durability, performance, and ability of carbon steel to withstand the stresses asked; in addition to the high costs of corrective maintenance⁷.

Therefore, it is necessary to use methods to improve corrosion resistance, such as the use of inhibitors⁸. Inhibitors reduce and even prevent the reaction of exposed metal in harsh environments. These substances adsorb on the metal substrate through the adhesion of ions and molecules to the metal surface, generating a reduction in reactions between the corrosive medium and the material to be protected by blocking anodic reactions, reducing oxidizing species or blocking cathodic reactions⁹.

However, most of these inhibitors, although effective, are synthetic and toxic to the environment¹⁰. Currently, a study that has been attracting technological interest to delay/prevent corrosive processes is the use of coatings derived from natural products based on scientific sustainability, mainly because they have low toxicity and are renewable sources of materials¹¹.

Propolis is a resinous substance, originating from bees and is mostly made up of 50% resins, 30% waxes, 10% essential and aromatic oils, 5% pollen and 5% other organic substances and its color and flavor vary according to its botanical origin¹².

The chemical composition of propolis has a wide variety of components, as it depends on the geographical location, the local flora, and the climate, but some compounds are always present such as aromatic acids, fatty acids, flavonoids, esters, aldehydes, and others⁹. Propolis, even in the form of ethanolic extract, is widely marketed and due to its anti-inflammatory, antibacterial and antiviral characteristics can be used in various areas.

According to the literature, flavonoids are one of the most common groups found in propolis and have an anticorrosive activity. These phenolic compounds are naturally occurring pigments present in most plants and act as primary antioxidants where oxidation chain reactions are paused by flavonoids with the transfer of electrons or hydrogens to free radicals¹³.

It has been proven by studies that propolis extract can prevent the corrosion process of steels and bronze in aqueous solutions¹⁴⁻¹⁶.

To improve the performance of CA-50 carbon steel, the applicability of a sustainable material such as propolis extract forming a protective film on the metal substrate in a cement extract solution with and without the addition of chloride ions may increase the useful life and efficiency of this steel and increase the corrosion resistance of concrete reinforcement.

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2. Methodology

2.1. Sample preparation

The carbon steel bars, 10 cm long, were first polished with sandpaper of different grain sizes (220, 400 and 600 mesh) and washed with distilled water, ethyl alcohol and acetone. To delimit the coating studied, the lower end of the sample was filled with epoxy resin, leaving an exposed area of 0.5 cm², and the rest of the substrate was covered with insulating tape, leaving an area at the upper end to place the copper wire which is the electric contact with the potentiostat as shown in the Figure 1.

2.1.1. Obtaining the cement extract solution

With a mixture of cement and water (cement paste) in a ratio of 1:5, a solution was prepared that simulates the liquid phase of the concrete pore condition called cement extract (CE)¹⁷. To evaluate the concrete's exposure to the region's marine environment, 3.5 wt. % NaCl was added to the electrolyte (CE).

2.1.2. Coating preparation

To analyze the anticorrosive properties of the propolis extract (PE) on a metallic substrate, the steel was coated with green ethanolic propolis extract, with a minimum of 11% w/v. The steel bar samples were immersed in a beaker containing 2 ml of PE four times for 60 seconds and then slowly removed. The pH of the propolis extract used is 5.4. The steel bar samples are dried at room temperature for 1 hour and kept in desiccation.

Fourier Transform Infrared Spectroscopy (FTIR) and High-Performance Liquid Chromatography (HPLC) were used to characterize the inhibitor chemically. The functional groups of chemical compounds present in a sample of propolis extract dried at 105°C were identified using a Perkin Elmer BX FTIR equipment, where the sample was pressed into a KBr pellet.



Figure 1. Steel bar after pre-treatment and preparation with epoxy resin.

To separate the compounds in the PE, the SHIMADZU 20A HPLC modular series was manipulated at 25°C with a Nucleodur 100-5 C18 column with a dimension of 250 x 3.0 mm (Macherey Nagel).

The spectrum was progressed with a resolution of 4 cm⁻¹, with 2 cm⁻¹ wavenumber interruptions and taking an average of 128 scans.

In HPLC separation, 20 microliters of the sample were separated by a mixture where the mobile phase consisted of acetonitrile (eluent A) and 0.1% phosphoric acid in Milli-Q water (eluent B). The monitoring of the separated constituents was performed at 280 nm, and this peak was one of the maximum absorption of the phenolic substance.

To observe the surface of the coated and uncoated carbon steel samples after corrosion tests and their chemical composition, characterization tests were carried out using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). For the morphological analysis of the coatings, a Scanning Electron Microscope with field effect emission gun (FEG) Quanta 200 FEI with EDS from the Electron Microscopy Center of the Federal University of Minas Gerais was used.

2.2. Electrochemical techniques

Electrochemical tests were performed on an Autolab Potentiostat/Galvanostat model PGSTAT302N with computer-controlled NOVA 1.11 software. An electrochemical cell with three electrodes was used, with a reference electrode of Ag|AgCl|KCl_{sat} (silver-silver chloride in a saturated solution of potassium chloride), a titanium wire coated with rhodium as a counter electrode and the bar sample carbon steel with an exposed area of 0.5 cm² as the working electrode. Tests were performed in triplicate.

Initially, the open circuit potential (OCP) was measured, lasting 5400 seconds to stabilize the potential. Subsequently, electrochemical impedance spectroscopy (EIS) measurements were carried out at the OCP using a frequency range of 100 kHz to 0.01 Hz with 10 collection points per decade and a disturbance of 10 mV.

The polarization curves were also performed after potential stabilization, collected from the cathodic to the anodic region from -0.25 V to +0.75 V vs OCP with a scan rate of 0.5 mV.s⁻¹.

The tests used a cement extract solution as a medium with and without the addition of NaCl at 3.5% by weight to the electrolyte (CE) to represent exposure to the region's marine environment.

3. Results and Discussion

3.1. Fourier transform infrared spectroscopy (FTIR) and HPLC

Based on absorption peaks by FTIR, the sample contains conjugated rings, carboxylic acids and phenolic compounds confirming the presence of flavonoids and probably Artepillin C (DHCA).

Table 1 shows the possible bands and functional groups that play a predominant role in the propolis extract (PE) absorption spectra.

Table 1. Functional groups present in propolis extract responsible for absorption peaks in the infrared region.

Band wave number (cm ⁻¹)	Functional group	Probable Compounds
3700 - 3500	Carboxylic acid	Coumaric acid; Caffeic acid; Kaempferol; Quercertine; Ferulic acid; Artepilin;
2928	CH ₃ e CH ₂	Ferulic acid; Artepilin
2856	C-H aromatic	Coumaric acid; Caffeic acid; Kaempferol; Quercertine; Ferulic acid; Artepilin; Pinocebrina
1694 forte	(Ar-COOH) Dímero	Cumaric acid; Caffeic; Ferulic acid; Artepilin;
1634	C=C	Cumaric acid; Caffeic acid; Kaempferol; Quercertine; Ferulic acid; Artepilin; Pinocebrina
1516	C=C Aromatic Ring	Flavonoids Coumaric acid; Caffeic acid; Kaempferol; Quercertine; Ferulic acid; Artepilin;
1456	O-H	Phenols and polyphenols
1438	C=C Conjugated aromatic ring	Kaempferol; Quercertine Flavone; flavonol
1420	CH ₂ adjacent to C=O	Cumaric acid; Caffeic acid; Ferulic acid; Artepilin;
1378	CH ₃	Artepilin
1258	C-O phenol	Ferulic acid
1180	C-OH	Cumaric acid; Caffeic acid; Kaempferol; Quercertine; Ferulic acid; Artepilin; Pinocebrina
1038 media	Éter aril alquila	Kaempferol; Quercertin; Pinocebrina
982	Dissubstituted alkene (trans)	Artepilin

The band in the 3290 cm⁻¹ and 1456 cm⁻¹ regions may be related to axial O-H deformation. This functional group facilitates the adsorption of substances on the metal substrate and has strong bonds with the hydrogen present on the surface of the metal blocking the anodes formed on the metal surface that are close to the electrolytes, minimizing interfacial reactions and dissolution of the metal^{12,18,19}.

The bands in the region of 2928 cm⁻¹, 2856 cm⁻¹, 1420 cm⁻¹ and 1378 cm⁻¹ are associated with aliphatic carbon bonds (C-H), especially CH₂ and CH₃, characteristic of organic compounds²⁰. The band in the region of 1694 cm⁻¹ comes from the carbonyl group (C=O).

In addition, in propolis extract, bands in the regions of 1516 cm⁻¹ and 1438 cm⁻¹ may be associated with the elongation vibration of the C=C bonds. This group is attributed to the aromatic compounds in flavonoids and is also found in natural inhibitors such as cocoa husks²¹.

Both cocoa husks, garlic and *Brugmansia arborea* have several antioxidant agents, such as phenolic compounds and flavonoids.

The existence of functional groups containing oxygen atoms and double bonds (C-O, O-H, C=O and C=C), analyzed in the FTIR spectrum, can facilitate the adsorption of the material on the metallic substrate, forming a protective barrier on the metallic surface separating the metal material of the electrolyte and reduction of the corrosive process²².

The mobile phase and gradient used in HPLC separation was effective, however the definition of all constituents was not possible due to the lack of standards. The Table 2 shows the presence of trans-cinnamic presence, caffeic, ferulic, p-coumaric acids, pinocebrin and 3,5-diprenyl-4-hydroxycinnamic acid (DHCA) were identified. According to Dolabella et al.¹³ the DHCA was present in the highest concentration, and it is the main constituent of the studied propolis extract.

The existence of the aforementioned compounds agrees with the FTIR spectra obtained, concluding that most of the main constituents are members of the flavonoid or phenolic classes.

Table 2. Chemical composition obtained by HPLC with 280nm detection for the propolis extract and models of phenolic compounds and hydroxycinnamic acids.

Constituent Name	Wavelength
Artepillin C	λ max= 302nm
Ferulic Acid	λ max= 321nm
Caffeic Acid	λ max= 327nm
Trans cinnamic acid	λ max= 277nm

3.2. SEM and EDS

SEM images and EDS analyzes were obtained for the coated and uncoated samples after 24 hours of immersion in a cement extract solution with and without chloride ions to analyze the steel surface under different conditions. Figures 2A and B and 3A and B show SEM and EDS images of the uncoated sample in the cement extract and in the cement extract solution with chloride ions, respectively. A passive layer containing iron and oxygen about 18 μm thick is identified in Figure 2. In Figure 3, in the cement extract medium with chlorides, the thickness of the oxide layer reached 100 μm, and carbon contamination was observed in the EDS analysis.

Figures 4A and B and 5A and B show SEM and EDS images of the coated sample in the cement extract solution and in the cement extract with chloride ions, respectively. A coating was formed on the steel after immersion in the propolis layer.

A chemical map was made using EDS analysis and it was possible to observe the presence of the elements Fe, C, O. Carbon is originated from the propolis extract. Oxygen is due to the passive layer of steel and propolis extract. In the presence of NaCl solution at 3.5% w/v, the Cl was observed. In Figure 4B, carbon is concentrated in the innermost layer and oxygen in the outermost layer of the coating. The average film thickness was 89 μm (Figure 5).

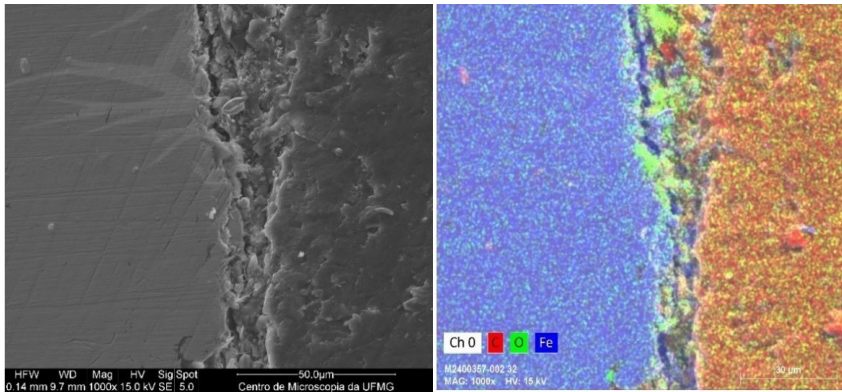


Figure 2. SEM image (a) and EDS map (b) of uncoated carbon steel after 24 hours of immersion in the cement extract.

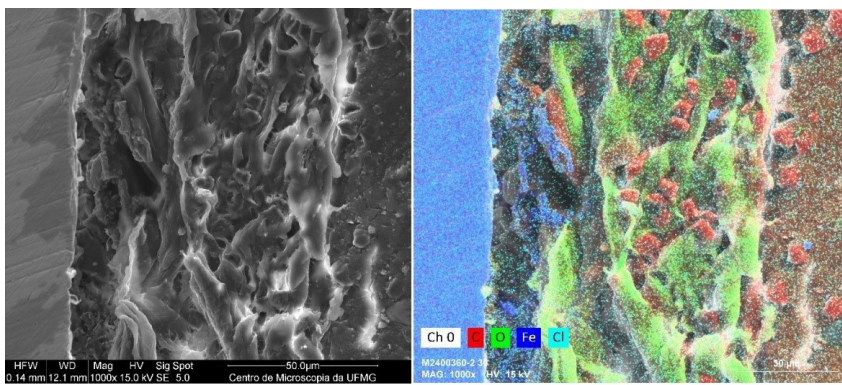


Figure 3. SEM image (a) and EDS map (b) of uncoated carbon steel after 24 hours of immersion in the cement extract containing chloride.

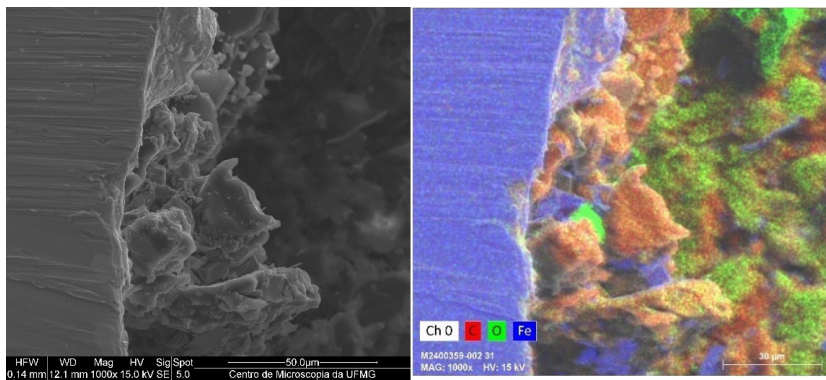


Figure 4. SEM image (a) and EDS map (b) of coated carbon steel after 24 hours of immersion in the cement extract.

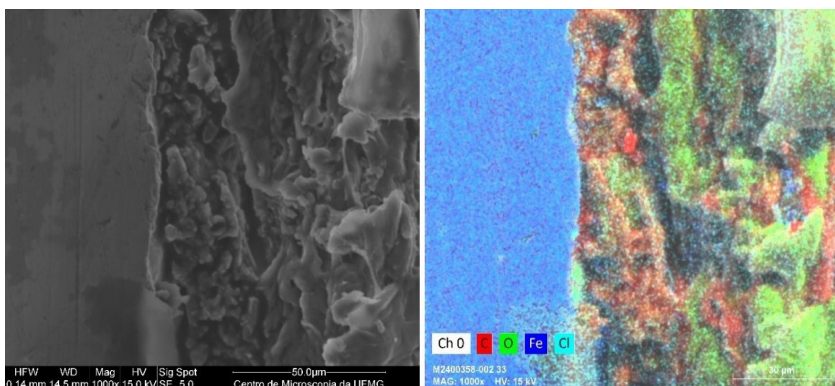


Figure 5. SEM image (a) and EDS map (b) of coated carbon steel after 24 hours of immersion in the cement extract containing chloride.

3.3. Electrochemical techniques

3.3.1. Open circuit potential (OCP)

The open circuit potential was measured for 5400 seconds for coated and uncoated carbon steel reinforcement in cement extract solution with and without chloride ions (Figure 6).

The steel coated with the propolis extract showed the highest open circuit potential in the cement extract, suggesting a corrosion protection. The presence of chlorides decreased the corrosion potential of the coated sample. The samples showed a decrease in OCP values with the time of immersion in the cement extract with and without chlorides, indicating a process of dissolution of the passive layer²³.

3.3.2. Electrochemical impedance spectroscopy (EIS)

The EIS analysis indicated that the coated reinforcements (Figure 7), in both environments, showed the largest diameters of the capacitive arcs and, consequently, the greatest corrosion resistance²⁴.

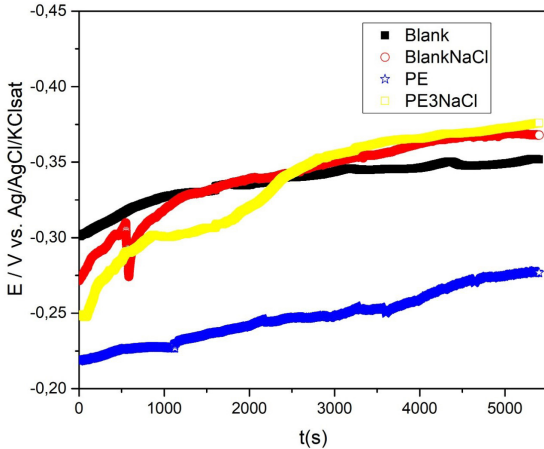


Figure 6. Measurement of the open circuit potential of coated and uncoated carbon steel in the cement extract with and without chloride ions for 5400 seconds.

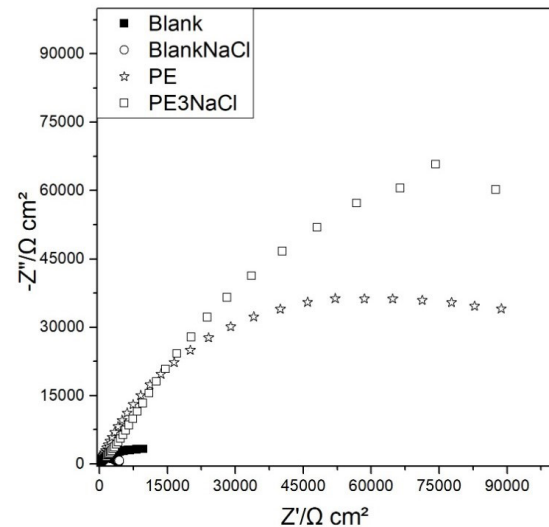


Figure 7. Nyquist diagram of coated and uncoated carbon steel in cement extract solution with and without chloride ions.

The Bode diagram of the impedance modulus (Figure 8A) indicates that chlorides decreased the impedance modulus for the uncoated armature and did not decrease the impedance modulus for the coated armature. Chloride was unable to have a harmful effect on the impedance of the coated armature. In the Bode diagram of the phase angle (Figure 8B), specifically in the coated reinforcement in the cement extract with chlorides (PENaCl), apparently there is two-time constants, one at high frequencies which is related to the interfacial reactions of the coating and the electrolyte and another at low frequencies related to the interfacial reactions between the substrate and the coating²⁵. The uncoated steel in the cement extract with chlorides showed a lower phase angle at low frequencies than the uncoated steel in the cement extract, indicating the deleterious effect of chlorides on corrosion resistance of the uncoated steel (Figure 8B). At low frequencies, the coated steel in the medium with chlorides presented a higher phase angle in relation to the other samples, especially in relation to the uncoated samples (Figure 8B).

Figure 9 shows the equivalent circuit adjusted to the EIS data. The steel in the cement extract and the coated steel in the cement extract with chlorides showed two-time constants (Figure 9B). The other samples present one time-constant (Figure 9A). The equivalent circuit models used in this research are frequently applied in the literature, both for the circuit with one constant and for the model with two-time constants²⁶⁻²⁸.

In the equivalent circuit with one time constant, R1 is the solution resistance, R2 and CPE1 are the charge transfer resistance and the constant phase element of the double layer. For the electric circuit with two time-constants, R1 is the solution resistance, R2 is the coating resistance, R3 is the charge transfer resistance, CPE 1 is the constant phase element of the coating, and CPE2 is the constant phase element associated with the double layer. Due to the roughness and heterogeneity of the working electrode, the constant phase element (CPE) is used to replace the ideal capacitor¹.

Table 3 shows the values of the electrical circuits obtained from the impedance diagrams. The effective capacitance (C_{eff}) associated with the phase constant element was calculated according to the literature^{29,30} using Equation 1, and the C_{eff} values are shown in Table 4.

$$C_{eff} = Q^{1/\alpha} R_e^{(1-\alpha)/\alpha} \quad (1)$$

Where R_e is the global ohmic resistance and Q and α represent global properties, the constant phase element and the dimensionless parameter which has a value between zero (the system behaves as a pure resistor) and the unity (the system behaves as a pure capacitor)^{29,30}.

The chi square values (χ^2) determine the quality of adjustment to the applied equivalent circuit. The chi square values are in the range of $1.05 \cdot 10^{-3}$ to $5.36 \cdot 10^{-3}$. Some studies in the literature showed values lower than 10^{-2} , which were considered an indication of a good fit of the data³¹.

Comparatively, higher polarization resistance values and lower CPE and capacitance values indicate greater corrosion resistance of the steel in the studied environment. The CPE1 values were $10^{-5} \text{ F} \cdot \text{cm}^{-2} \cdot \text{s}^{\alpha-1}$ and the CPE2 values were greater than $10^{-5} \text{ F} \cdot \text{cm}^{-2} \cdot \text{s}^{\alpha-1}$ for the steel in the cement extract medium and lower by an order of magnitude for the steel coated in

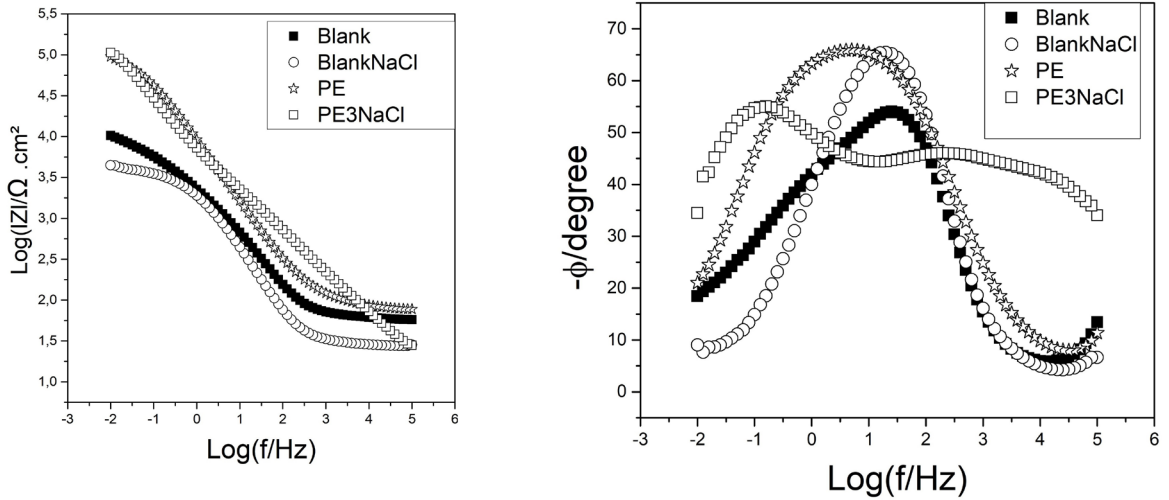


Figure 8. Bode diagrams of coated and uncoated carbon steel in the cement extract with and without chloride ions. Impedance modulus (A) and phase angle (B).

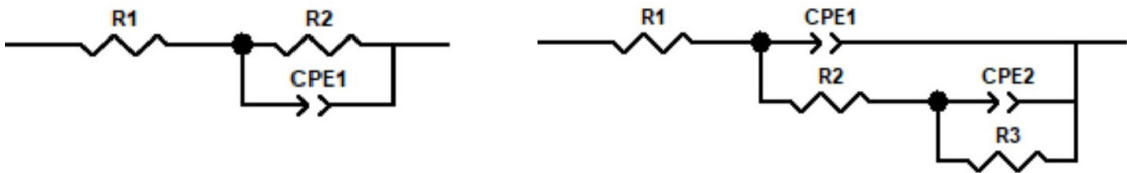


Figure 9. Equivalent circuit simulated from EIS data with one time-constant (A) and two time-constants (B).

Table 3. EIS data for coated and uncoated carbon steel bars in the cement extract with and without chloride ions.

Sample	R1 ($\Omega.cm^2$)	R2 ($\Omega.cm^2$)	CPE1 ($F.cm^{-2}.s^{\alpha-1}$)	α	R3 ($\Omega.cm^2$)	CPE2 ($F.cm^{-2}.s^{\alpha-1}$)	α	χ^2
Steel in CE	61.15	1617	$4.87.10^{-5}$	0.78	10828	$1.56.10^{-4}$	0.62	$1.05.10^{-3}$
Steel in CE with Cl ⁻	28.27	3665	$8.12.10^{-5}$	-	-	-	0.81	$5.36.10^{-3}$
Coated steel in CE	85.97	107840	$2.70.10^{-5}$	-	-	-	0.75	$3.13.10^{-3}$
Coated steel in CE with Cl ⁻	13.92	11086	$3.91.10^{-5}$	0.64	180000	$9.87.10^{-6}$	0.85	$3.5.10^{-3}$
Coated steel immersed in CE for 72h	80.50	94633	$3.44.10^{-5}$	-	-	-	0.76	$4.4.10^{-3}$
Coated steel immersed in CE with Cl ⁻ for 72h	12.46	11223	$9.12.10^{-5}$	-	-	-	0.55	$4.07.10^{-4}$

Table 4. The effective capacitance associated with the CPE.

Sample	C_{eff1}	C_{eff2}
	(F/cm^2)	(F/cm^2)
Steel in CE	$9.38.10^{-6}$	$6.62.10^{-7}$
Steel in CE with Cl ⁻	-	$2.08.10^{-5}$
Coated steel in CE	-	$3.29.10^{-6}$
Coated steel in CE with Cl ⁻	$4.28.10^{-8}$	$2.25.10^{-6}$
Coated steel immersed in CE for 72h	-	$5.05.10^{-6}$
Coated steel immersed in CE with Cl ⁻ for 72h	-	$2.55.10^{-7}$

the cement extract medium with chlorides. The capacitance associated with the coating is lower for the coated steel in medium of CE with chlorides than for the uncoated steel in CE without chlorides (Table 4). This result again indicates a more protective effect of the coating on the electrolyte medium containing chlorides. The polarization resistance

of the coated steel in the cement extract is $107840 \Omega.cm^2$, and the polarization resistance of the uncoated steel is $10828 \Omega.cm^2$, exhibiting an inhibition efficiency of 89.96%. In the cement extract with chlorides, the inhibition efficiency is higher (98.08%); the polarization resistance of the coated steel increased to $191086 \Omega.cm^2$ (R2 + R3), and the Rp of

the uncoated steel decreased to $3665 \Omega \cdot \text{cm}^2$. In the medium containing chlorides, the action of the propolis extract coating is enhanced, and the inhibition efficiency is greater. The inhibition efficiency (η) was calculated using Equation 2. R_p is the coating polarization resistance and R_{p_0} is the polarization resistance of the uncoated steel.

$$\eta(\%) = (R_p - R_{p_0}) / R_p \times 100 \quad (2)$$

Aiming to verify the degradation of the coating in the medium, impedance tests were carried out after 2, 6, 12, 24, 48 and 72 hours of coated steel immersion in the cement extract solution with and without chlorides.

In the cement extract medium, the steel coated with propolis maintained superior corrosion resistance for immersion times up to 24 hours (Figure 10A). After 48 h and 72 h, the coating still showed an important protection against corrosion. Carbon steel coated with propolis in the cement extract medium showed a higher impedance modulus value than the uncoated steel for immersion times up to 72 hours (Figure 10B). This result is confirmed by the lowest phase angle values presented by the uncoated steel at low frequencies and at the maximum peak in Bode diagrams (Figure 10C). After 2 hours of immersion, the impedance values decrease and are lower than the impedance value after 48 hours of immersion. But after 2 h, the impedance of the coated steel regains its protection, and one hypothesis for this behavior is the filling of pores with steel corrosion products. In the cement extract medium (CE), even after 72 h of immersion, the coated steel showed a higher phase angle at low frequencies than the uncoated steel recently immersed

in the solution. The coated steels immersed in CE after 24 h, 48 h and 72 h showed a maximum close to 1 Hz with the largest phase angles, of 65 degrees (Figure 10C). A larger maximum phase amplitude represents a more capacitive behavior and a lower tendency for corrosion in the medium.

In the medium of propolis extract with chlorides (Figure 11A), the coated steel proved to be resistant to corrosion for up to 48 hours of immersion. For 72 hours of immersion, the corrosion resistance of the steel coated with propolis in the chloride medium deteriorated, becoming close to that of uncoated carbon steel (Figure 10 and 11). Again, after 2 h of immersion, the impedance values decrease and are lower than the impedance value after 24 h of immersion (Figure 11A and 11B).

The highest impedance modulus was obtained for the coated steel after 12 h of immersion, a result similar to that of the medium without chlorides (Figure 10 and 11). The impedance modulus values remained at approximately $10^5 \Omega \cdot \text{cm}^2$ for up to 48 hours of immersion (Figure 11B). After 72 hours of immersion, the impedance modulus decreased by an order of magnitude, but remained higher than that of uncoated steel (Figure 11B). The highest phase angle was obtained for the coated steel after 12 hours of immersion at a maximum near 1 Hz (Figure 11C). The coated steels showed higher phase angle values than the uncoated steel at lower frequencies, indicating a higher corrosion resistance in the cement extract with chlorides than the uncoated steel (Figure 11C). In the cement extract medium with chlorides, the protective capacity of the propolis coating degraded after 72 h of immersion.

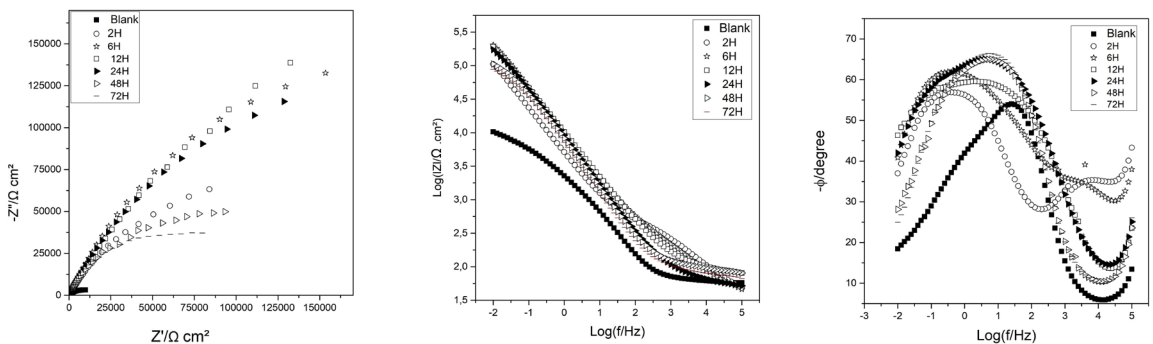


Figure 10. Nyquist diagram (A), Bode impedance modulus (B) and Bode phase angle (C) of PE coated carbon steel for different immersion times in the cement extract solution.

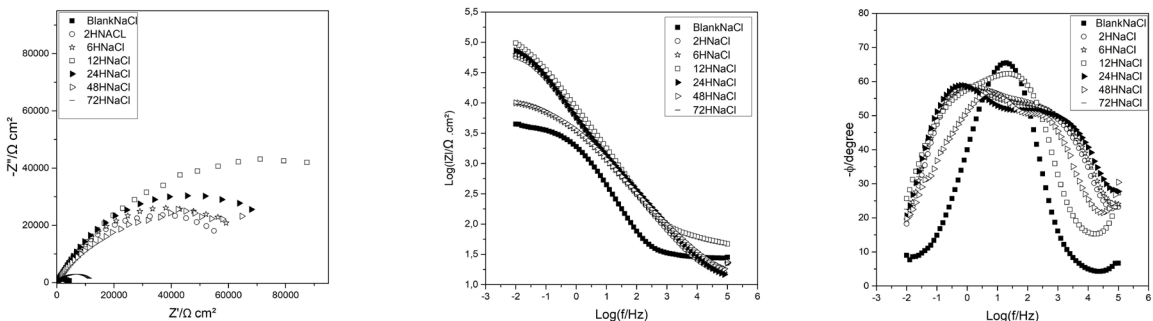


Figure 11. Nyquist diagram (A), Bode impedance modulus (B) and Bode phase angle (C) of PE coated carbon steel for different immersion times in cement extract solution with chloride ions.

3.2.3. Polarization curves

The polarization curves of the samples (Figure 12) indicated the highest corrosion potential for the coated carbon steel in the cement extract (PE), displacing it to anodic regions. On the other hand, for the PENaCl sample, the potential is shifted to more negative, cathodic regions. The lowest anodic current densities were obtained for carbon steel coated with propolis extract in both media. The passive current density was lower for the coated steel in both media, indicating a reduction in the process of exchanging charges between the electrolyte and the metal surface, thereby reducing corrosion^{23,32}. The polarization curves of the samples indicated the coated and uncoated steel samples showed a passive behavior in the cement extract with and without chlorides. The pitting potential was only observed for media containing chlorides, with the uncoated sample showing the lowest pitting potential and the highest passive current density in the cement extract with chlorides.

With the values presented in Table 5, the inhibition efficiency (η) was calculated using Equation 3³³.

$$\eta(\%) = (i_{corr0} - i_{corr}) / i_{corr0} \times 100 \quad (3)$$

where i_{corr} and i_{corr0} represents the polarization resistance of the reinforcement with and without coating, respectively.

The inhibition efficiency of the coated steel in the cement extract with chloride ions is 96.11% and the inhibition of the

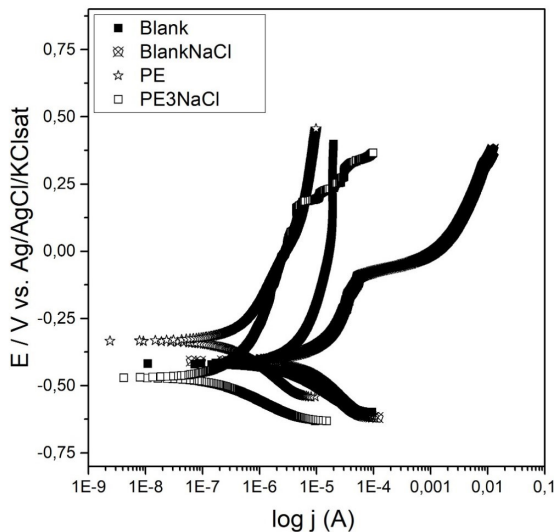


Figure 12. Polarization curves of coated and uncoated carbon steel in the cement extract with and without chloride ions.

Table 5. Polarization results for coated and uncoated steel in the cement extract with and without chloride ions.

Sample name	E_{corr}	I_{corr}	Corrosion Rate
	(V) _{Ag/AgCl}	(A/cm ²)	
Uncoated steel in CE	-0.4193	$1.90 \cdot 10^{-6}$	0.0221
Uncoated steel in CE with Cl ⁻	-0.4096	$4.09 \cdot 10^{-6}$	0.0475
Coated steel in CE	-0.3269	$1.54 \cdot 10^{-6}$	0.0179
Coated steel in CE with Cl ⁻	-0.4704	$1.59 \cdot 10^{-7}$	0.0018

PE coating in the cement extract is 18.95%, validating the effect of corrosion coating on reinforced concrete.

4. Conclusions

The chemical characterization of propolis extract confirmed the presence of functional groups, already recognized in the literature as corrosion inhibitors for carbon steel reinforcements, and the presence of multiple aromatic rings may explain the effectiveness of propolis extract as a corrosion inhibitor.

Adding chloride ions to the cement extract reduced the corrosion resistance of the carbon steel reinforcement, but it was not detrimental to the corrosion behavior of the coated reinforcement.

The inhibition efficiency of the PE coated steel in the solution without chloride ions is 18.95% and the corrosion inhibition of the PE coating in the cement extract with chloride ions is 96.11%, considering the corrosion current densities. The pitting potential was only observed for media containing chlorides, with the uncoated sample showing the lowest pitting potential and the highest passive current density in the cement extract with chlorides.

The polarization resistance of the coated steel in the cement extract is $107840 \Omega \cdot \text{cm}^2$, and the polarization resistance of the uncoated steel is $10828 \Omega \cdot \text{cm}^2$, exhibiting an inhibition efficiency of 89.96%. In the cement extract with chlorides, the inhibition efficiency is higher (98.08%); the polarization resistance of the coated steel increased to $191086 \Omega \cdot \text{cm}^2$ ($R_2 + R_3$), and the R_p of the uncoated steel decreased to $3665 \Omega \cdot \text{cm}^2$. In the medium containing chlorides, the action of the propolis extract coating is enhanced, and the inhibition efficiency is greater.

For immersion times of 72 h, chlorides deteriorate the corrosion resistance of the coating, reducing its polarization resistance to values similar to those of uncoated steel.

5. Acknowledgments

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