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Article

Natural Tannin Layers for the Corrosion Protection of Steel in Contact with Water-Based Media

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Abstract: Numerous strategies have been developed for the corrosion protection of steel; however, most of them have a significant environmental impact and employ toxic compounds. Tannins are a green and promising solution for sustainable corrosion protection strategies. In this context, this work was focused on natural (condensed and hydrolysable) tannin layers as a possible corrosion protection strategy for carbon steel. The impact of the tannins' dissolution medium (ultrapure water or Phosphate-Buffered Saline), surface pre-treatment (acid pickling or plasma), and deposition technology (dipping or spin coating) on layer homogeneity and adhesion has been evaluated. The effects of these parameters on coating formation, homogeneity, and adhesion have been investigated by means of visual inspections, swabbing, Fourier Transformed Infrared spectroscopy (FTIR), Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM-EDS) and tape adhesion tests. Preliminary electrochemical corrosion tests have been performed on the most promising material (carbon steel acid pickled and coated with a hydrolysable tannin solved in water by spin coating) to estimate the protective ability of the developed layers and highlight the main criticisms to be overcome.

Keywords: steel; corrosion protection; tannins; sustainability; coating



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1. Introduction

Low-alloy steel is widely used in transportation, construction, industrial pipelines, and plants for its good mechanical properties and low cost [1], but, unfortunately, it is extremely sensitive to corrosion, which is critical in working conditions. Consequently, steel corrosion is a serious problem [2–7] leading to material loss, cost of substitution, traffic/production stops, and safety concerns. The estimated cost of steel corrosion is around 1\$ trillion annually, with an estimated twofold increase in 2050 [8], considering only direct expenses. Moreover, CO₂ emissions related to steel production replacing corroded material should also be considered [9]. Steel corrosion can derive from harsh environments, carbon dioxide, hydrogen sulfide, and chlorides [2–7] and can be aggravated by the action of microbes [10] present in different application fields. This scenario makes the corrosion protection of steel a significant need in numerous sectors, as well as a big challenge for research and industry.

Several strategies have been explored to limit steel corrosion in working environments, from the employment of corrosion inhibitors to the deposition of organic or inorganic coatings [1,11–14].

Incentivized by the increasing awareness of sustainability and environmental impact, corrosion protection is also moving through green approaches [15,16]. In this field, polyphenols are gaining increasing interest due to their strong affinity for metals, corrosion

protection ability, and sustainability [17–19]. Indeed, an increasing number of research papers report their application as green corrosion inhibitors or as part of protective coatings on steel substrates [20–24].

The present research aims to obtain tannin-based protective layers on carbon steel to be exploited as protective coatings or primers for natural polymeric top-layers. Hydrolysable and condensed tannins have been compared for their ability to react with steel substrates to obtain homogeneous coating films. In particular, Chestnut tannin (hydrolysable tannin) has been considered because it is obtained from local resources and for its proven corrosion inhibition properties [25]. Quebracho tannin was used as an example of a condensed one because it is widely studied for its corrosion inhibition properties [26]. Acid pickling and plasma surface pre-treatments have been investigated to improve tannin adhesion as examples of a conventional strategy and of a green innovative one. Plasma irradiation is a green (no requirement of toxic chemicals) and fast technique, but it requires specific equipment and is innovative in the field of surface preparation of steels. On the other hand, acid pickling does not require specific equipment; it is widely diffused for steel surface preparation but requires the use and disposal of large amounts of acid-producing waste.

Moreover, alternative strategies for coating deposition (spin coating or dipping in a tannin solution) have been explored to consider the requirements of different applications (e.g., plane steel plates or complex geometries).

The impact of the different process parameters on coating formation ability, homogeneity, and adhesion has been evaluated by means of visual inspections, swabbing, Fourier Transformed Infrared spectroscopy (FTIR), Scanning Electron microscopy equipped with energy Dispersive Spectroscopy (SEM-EDS), and tape adhesion tests. Layers produced in optimized conditions (tannin type and dissolution medium, pre-treatment, and coating strategy) were subjected to preliminary electrochemical tests to evaluate their effective corrosion protection ability.

A scheme of the rationale of the work and of the main parameters explored in the present research is reported in Figure 1.

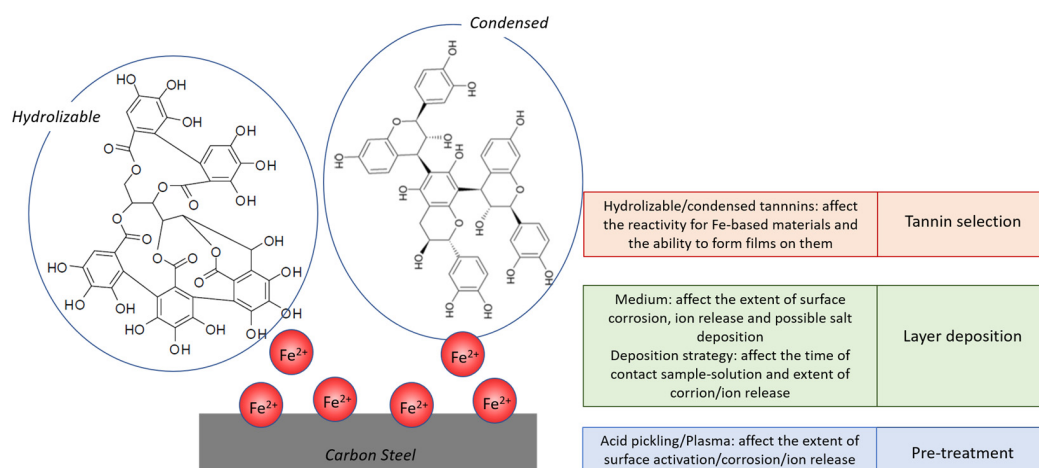


Figure 1. Rationale of the work.

Differently from what has been reported in the literature, the proposed solution involves only tannins in the coating formation. On the other hand, published works consider the combination of polyphenols with, for example, Polypyrrole (PPy) [27,28], polyethylenimine (PEI) [29], silanes [30,31], graphene oxide [32], or epoxy [33] for coating obtainment. Moreover, for the first time, this work deeply investigated the effect of surface pre-treatments on coating deposition, which was poorly considered in published papers [23].

2. Materials and Methods

2.1. Sample Preparation

Carbon steel sheets (Q-panel type R (0.15 wt% C-Fe bal.)—40 mm × 70 mm × 2 mm dimensions) were provided by Q-lab (Westlake, OH, USA), cut in 2 cm × 2 cm square samples, and used as substrates.

All the samples were degreased in acetone for 5 min in an ultrasonic bath and dried with compressed air.

Two different pre-treatments were studied before tannin coating: plasma treatment and acid pickling.

Plasma treatment was performed in a vacuum plasma device (Tucano table-top plasma system, Gambetti Kenologia, Binasco, Italy) for 10 min at 100 W using air as the treating gas. Acid pickling was performed in 2M HCl; two different pickling times were compared (20 min or 5 min), followed by washing in distilled water and compressed air drying.

Two different tannins were used for surface coating in order to investigate the performances of the condensed and hydrolysable ones in film formation and corrosion protection. Silvafeed, ENC (hydrolysable tannin from Chestnut, Silvateam SpA, San Michele Mondovì, Italy) was selected as a hydrolysable tannin and Fintan QSF (condensed tannin from Quebracho, Silvateam SpA, San Michele Mondovì, Italy) as a condensed one.

Different media and deposition techniques were investigated, and for each of them, the most suitable compositional range was selected. In particular, solutions of tannins were prepared in Phosphate-Buffered Saline (PBS, Phosphate-Buffered Saline 79382-50TAB Sigma Aldrich, St. Louis, MO, USA) at 2 and 4 mg/mL or in ultrapure water, 50, 100, or 150 mg/mL.

PBS was selected to work at a neutral pH, avoiding steel corrosion during coating deposition, while water was used to avoid of salt inclusion in the polyphenolic coating.

The deposition strategy was selected in order to maximize polyphenol deposition and avoid substrate corrosion as well as the formation of insoluble and poorly adhered iron-tannates. Dipping of pre-treated samples in a polyphenolic solution was carried out for PBS-based solutions; two different soaking times were considered; 10 min or 20 min. While for spin-coating, speed of 400 or 800 rpm, time of 30 or 60 s, and volume of liquid of 200 µL (spin coater WS-650MZ-23NPP/LITE, Laurell Technologies Corporation, Lansdale, PA, USA), were considered for the deposition of polyphenols from water-based solutions.

The complete list of samples and their acronyms is reported in Table 1.

Table 1. Sample acronyms and preparation strategies.

Acronym	Substrate	Pre-Treatment	Tannin (Type, Solution, Concentration)	Deposition Strategy and Parameters
CS	Carbon Steel	-	-	-
CS_PL_QSF_dip4_20	Carbon Steel	Plasma, air 10 min@100 W	QSF 4 mg/mL in PBS	Soaking 20 min
CS_PL_ENC_dip4_20	Carbon Steel	Plasma, air 10 min@100 W	ENC 4 mg/mL in PBS	Soaking 20 min
CS_PL_ENC_dip2_20	Carbon Steel	Plasma, air 10 min@100 W	ENC 2 mg/mL in PBS	Soaking 20 min
CS_PL_ENC_dip2_20	Carbon Steel	Plasma, air 10 min@100 W	ENC 2 mg/mL in PBS	Soaking 10 min
CS_pick20_ENC100_spin400_30	Carbon Steel	HCl 2M pickling 20 min	ENC 100 mg/mL in water	Spin coating 400 rpm 30 s
CS_pick5_ENC100_spin800_60	Carbon Steel	HCl 2M pickling 5 min	ENC 100 mg/mL in water	Spin coating 800 rpm 60 s

2.2. Surface Characterization

Visual inspection and swabbing (finger and glove) of treated surfaces were carried out for a first estimation of the homogeneity of the coating and its mechanical stability.

The presence of the coating was verified by means of Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR-ATR, Nicolet iS50 FTIR Spectrometer, Thermo Scientific, Waltham, MA, USA) for the investigation of surface chemical groups and of Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM, JEOL, JCM 6000 plus, and EDS, JEOL, JED 2300, Tokyo, Japan) for the investigation of surface morphology and semi-quantitative elemental chemical composition.

The tape adhesion test, according to the ASTM D 3359 standard [34], was performed to evaluate the tannin layer adhesion to the steel substrate.

The ability of the tannin layer to effectively protect steel from corrosion was evaluated by means of Electrochemical Impedance Spectroscopy (EIS) measurements. Measurements were conducted using a Parstat 2273 potentiostat (Princeton Applied Research by AMETEK, Oak Ridge, TN, USA) in conjunction with PowerSuit ZSimpWin software (version 2.40), employing a signal with approximately 15 mV (peak-to-peak) amplitude within the 10^5 to 10^{-2} Hz frequency range. The experimental setup included an Ag/AgCl reference electrode (+207 mV SHE) and a platinum counter electrode, both immersed in a 3.5 wt% sodium chloride aqueous solution. CS_pick5_ENC100_spin800_60 sample was selected for these measurements, which were conducted as a preliminary assessment of tannin-based coatings' effectiveness. The sample was immersed in the test solution (3.5% NaCl) for a total of 24 h, and measurements were taken over an area of 1.0 cm². After the test, the sample surface was examined using a Nikon SMZ25 optical stereomicroscope (Nikon Instruments Europe, Amstelveen, The Netherlands) to identify defects induced in the layer by accelerated corrosion measurements.

3. Results

The visual appearance of the bare and coated steel samples is shown in Figure 2a.

From a qualitative standpoint, it can be observed that homogeneous surface coverage was obtained with ENC tannin, while QSF did not produce uniform coatings. To confirm the presence of tannin functional groups and the formation of tannates on the surface, FTIR-ATR analyses were performed. FTIR-ATR spectra (Figure 2c,d) confirmed that signals characteristic of tannins (Figure 2b) were clearly detected on ENC-coated samples but not on the QSF-coated ones. In particular, a band between 3000 and 3600 cm⁻¹ attributable to OH groups, a peak at about 1700 cm⁻¹ associated with the C=O bond, and a peak around 1176 cm⁻¹ attributable to the C–O ester bond [35–38] can be highlighted on the spectra of ENC-coated samples (Figure 2c,d) as well as on the ENC spectrum (Figure 2b). These results can be explained by considering the higher reactivity of hydrolysable tannins on iron-based surfaces [39,40]. No particular differences can be noticed for different tannin concentrations in PBS, for the samples pre-treated by plasma and coated by dipping, or for different spin coating conditions, for the samples pre-treated by pickling and coated by spin coating, considering FTIR-ATR spectra.

Moreover, the visual observation after swabbing evidenced that mechanically more stable coatings were obtained with a low concentration and soaking time for the samples pre-treated by plasma and coated by dipping in PBS-based tannin solutions (CS_PL_ENC_dip2_10) and for low etching time and high speed/time coating parameters for the samples pre-treated by pickling and coated by spin coating (CS_pick5_ENC100_spin800_60). The lower mechanical stability of some samples, evidenced by the detachment of dark powders, can be associated with an excessive formation of iron tannates.

SEM observations and EDS analyses of bare and coated samples are reported in Figure 3 for the samples pre-treated by plasma and coated by dipping and in Figure 4 for the samples pre-treated by pickling and coated by spin-coating.

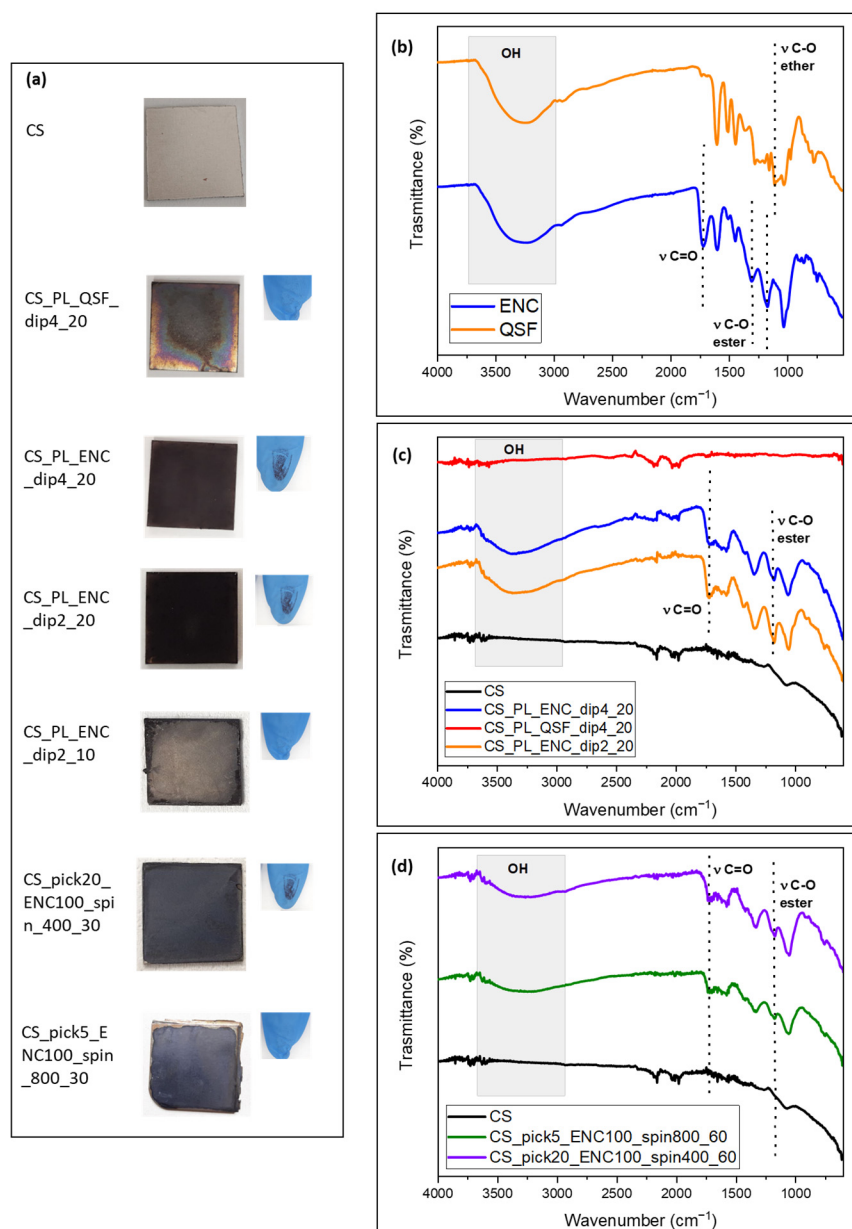


Figure 2. (a) Visual appearance of the sample surfaces and glove swabbing, (b) FTIR-ATR spectra of QSF and ENC tannins, (c) FTIR-ATR spectra of bare steel and samples plasma treated and coated by dipping in PBS solutions, (d) FTIR-ATR spectra of bare steel and samples pickled in acid and coated by spin coating from ENC water solutions.

As for the plasma-pretreated samples, a significant increase in carbon content (and consequent reduction in iron content) can be observed after the coating. The increase in carbon content was around 20 wt% (more than 200% compared to the starting value); this means that, even if EDS is a semi-quantitative technique; not specific for low-atomic-weight elements such as carbon, it allowed a clear detection of the organic coating and a significant comparison among the samples. However, if samples were not washed at the end of soaking, a significant amount of salt (from PBS) was formed on the surface, as evidenced by deposits on SEM images and the presence of not negligible amounts of phosphorous, chlorine, and sodium from EDS analyses. After washing, the appearance of the surface was more homogeneous, the amount of salts was reduced, and the difference between samples coated with ENC and QSF was more evident with functionalization, with ENC being more

effective and stable to washing. However, there is a high corrosion risk in using a washing step in coating carbon steel, and a procedure without it must be preferred.

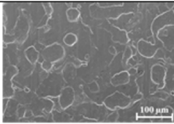
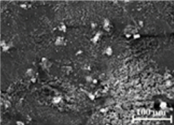
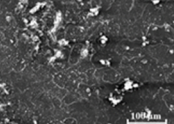
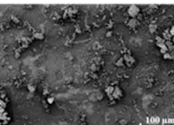
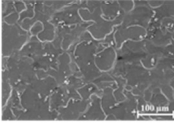
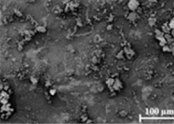
Sample	C	O	Na	P	Al	Cl	K	Ca	Fe	SEM image
CS	7.10 ± 0.72	3.80 ± 0.37	-	-	0.50 ± 0.03	-	-	-	88.60 ± 1.12	
CS_PL_ENC_dip4_20	26.10 ± 2.08	35.60 ± 1.24	15.70 ± 1.53	0.60 ± 0.09	-	4.40 ± 0.61	0.30 ± 0.03	0.10 ± 0.03	18.20 ± 1.41	
CS_PL_QSF_dip4_20	20.10 ± 3.19	23.90 ± 1.93	15.20 ± 2.45	0.50 ± 0.16	-	3.50 ± 0.54	0.20 ± 0.06	-	36.70 ± 2.74	
CS_PL_ENC_dip4_20_wash	18.50 ± 2.02	33.30 ± 3.04	8.00 ± 2.27	-	-	1.60 ± 1.46	0.10 ± 0.10	-	38.50 ± 7.06	
CS_PL_QSF_dip4_20_wash	10.70 ±1.40	15.00 ± 1.89	0.70 ± 0.48	-	-	0.10 ± 0.05	0.10 ± 0.07	-	73.50 ± 2.22	
CS_PL_ENC_dip2_20_wash	22.70 ± 2.74	29.43 ± 6.04	8.61 ± 2.32	-	-	1.57 ± 1.01	-	-	37.70 ± 1.16	

Figure 3. SEM images and EDS analyses of plasma pre-treated samples after coating by dipping in different tannins solutions.

Looking at samples pre-treated by pickling, no significant differences were evident between samples pickled for 5 min or 20 min. Both strategies were effective in terms of ENC coating on the carbon steel surface.

Samples coated with ENC tannin (the most promising ones) in the best conditions of pre-treatment were subjected to the tape adhesion test to evaluate the coating adhesion in a semi-quantitative way. Results are reported in Figure 5.

A homogeneous, thin layer of the coating was removed by the tape for CS_PL_ENC_dip2_10 and CS_pick20_ENC100_spin400_30. The removed layer is observable on the adhesive. However, part of the coating remained on the surface, suggesting a cohesion problem within the coating, probably due to the formation of a too-thick coating and an excess of poorly adhered iron tannates. The adhesion of these coatings was difficult to quantify because it was affected by the thickness and cohesion of the layer, but was estimated to be be-

tween 1B and 2B according to the standard. On the other hand, an almost optimal adhesion (classified as 4-5B, 0%–5% detachment) was obtained for CS_pick5_ENC100_spin800_60. The tape was almost clean after the test on this sample, and the coating had no evident sign of detachment.

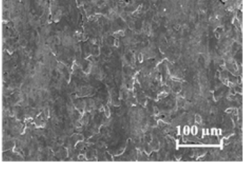
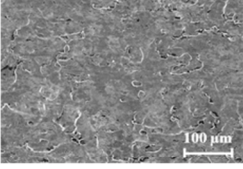
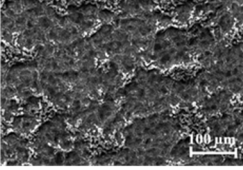
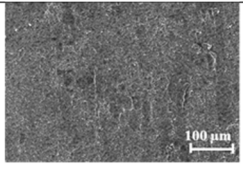
Sample	C	O	Fe	SEM image
CS_pick20	6.85±1.97	0.795±0.742	93.8±2.83	
CS_pick5	3.47±2.74	0.680±0.597	98.2±2.71	
CS_pick20_ENC100_spin400_30	25.9±1.68	26.5±2.33	46.9±2.32	
CS_pick5_ENC100_spin800_60	25.5±1.76	24.5±2.69	50.0±2.83	

Figure 4. SEM images and EDS analyses of samples pre-treated by pickling and coated by spin coating in different ENC water solutions.

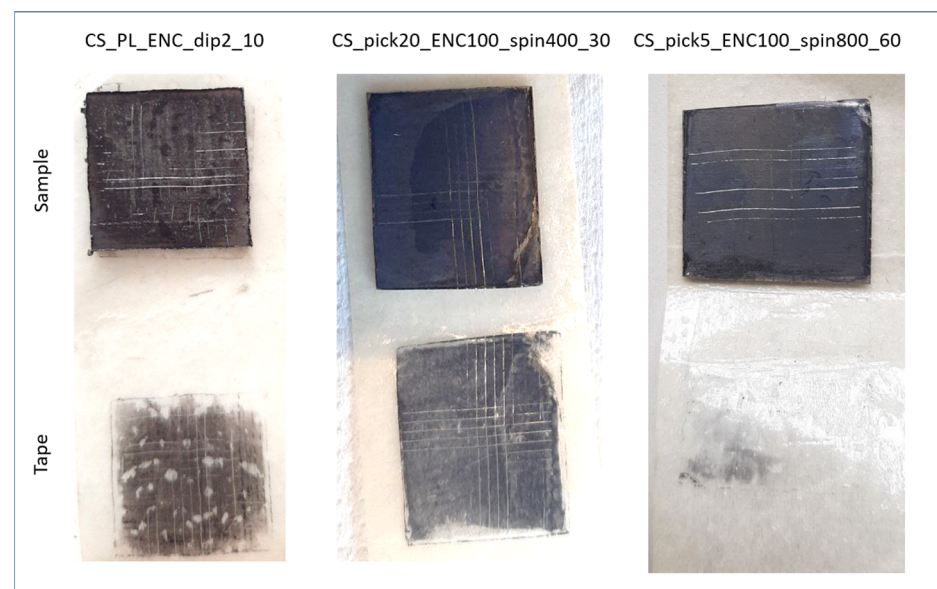


Figure 5. Images of the samples (in the first row) and of the tapes (in the second row) after the tape test.

Since this sample appeared to be the most promising in terms of protective performance for the metal substrate, it was subjected to EIS measurements as a preliminary test to

evaluate the potential of tannin-based layers. Figure 6 presents the results of these analyses. Figure 6a illustrates the trend in the Bode impedance modulus measured at low frequencies (10^{-2} Hz), denoted as $|Z|_{(0.01)}$. This parameter offers a preliminary quantitative estimation of the coating's protective effectiveness. The $|Z|_{(0.01)}$ value is initially very low and continues to decrease over time. In contrast, Figure 6b shows the appearance of the sample surface at the conclusion of the measurements. The top-view image highlights various corrosion products and a significant defect, characterized by the partial detachment of the protective layer.

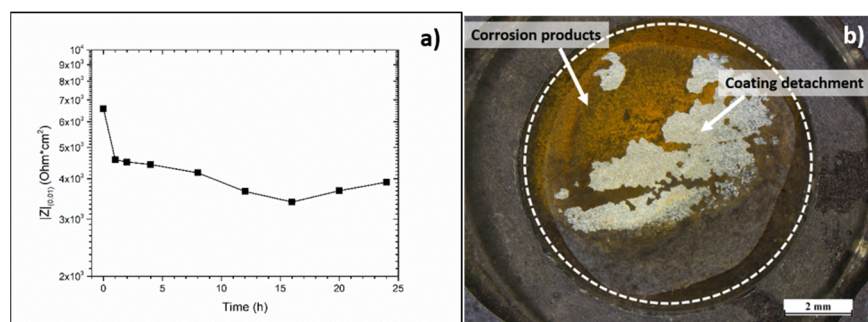


Figure 6. (a) Evolution over time of $|Z|_{(0.01)}$ (the Bode impedance modulus measured at low frequencies) and (b) aspect of the sample at the end of the test (24 h of immersion).

4. Discussion

Hydrolysable tannin from chestnut (ENC) and condensed tannin from quebracho (QSF) were considered protective layers on carbon steel. The capability of tannins to act as polydentate ligands for metal ions has been well known [23,41–43]. Phenolic moieties of tannin can interact with iron by means of coordination bonds. As a result, the formation of complexes, called iron tannates, leads to an amorphous blue/black layer on the steel surface [44–46]. Tannates' ability to prevent corrosion can be explained by their high crosslinked network and high insolubility [47,48]. As evidenced in Figure 1, the type of tannin affected the reactivity with Fe-based materials and the ability to form films on them.

Visual inspection (Figure 2a), FTIR-ATR spectroscopy (Figure 2b,c), and SEM-EDS analyses (Figure 3) evidenced that hydrolysable tannins (ENC) were able to effectively form a homogeneous film on the steel surface after plasma pre-treatment (air, 10 min@100 W). On the other hand, the coating formation was less effective when QSF condensed tannin was used. The higher reactivity of hydrolysable tannins for iron-based surfaces has been previously reported in the literature [29,30] and can explain this behavior. Indeed, the tannin's capability to chelate metals increases as tannin molecular weight increases, as does the number of hydroxyl groups [30,49]. Considering these results, only hydrolysable tannin (ENC) was employed for coating pickled substrates.

As previously reported by the authors [23], the surface pre-treatment of steel before the application of primers and coatings is still poorly discussed in the literature, even if it has a significant role in coating development and adhesion. The pre-treatment allowed surface activation and involved the exposition/release of metallic ions able to form complexes with tannin molecules. A proper balance in this step is useful to obtain an effective deposition of tannin molecules, avoiding the formation of excess iron tannates, which can easily detach from the surface [40]. Plasma pre-treatment has been considered in this research as an innovative strategy because it is a green technique, as solvents and acids are not necessary, and it is a quick technology that is easy to industrialize. Moreover, the plasma treatment does not induce any kind of surface corrosion, leaving the material clean and prone to the chemical bonding of coating molecules. Actually, it is not yet applied for steel pre-treatment before coating deposition, but it is already industrially diffused in the field of joining [50–55]. Vacuum plasma 10 min@100 W with air as gas was used for the steel pre-treatment on the basis of previous experience of the authors in the activation of metallic surfaces for coating deposition [56].

The selected solvent medium for tannin dissolution and technique for coating deposition affected the extent of surface corrosion and ion release and avoided eventual salt deposition (Figure 1). At first, the coating preparation by dipping steel substrates in tannin solutions was considered with the aim of promoting iron release and complexation with tannins for the obtainment of a chemically bonded protective layer, as previously carried out by the authors on magnesium substrates [57]. Due to the rapid oxidation of carbon steel in acidic solutions (the pH of tannins in water is about 3.7 for the ENC solution and 4.5 for the QSF solution), the dissolution of tannins in a buffer (PBS) was explored to work in an almost neutral condition. In these conditions, a final water wash is unavoidable for the elimination of excessive salts but potentially dangerous for steel corrosion. The reduction in the soaking time (from 20 to 10 min) and the solution concentration (from 4 to 2 mg/mL) allowed the obtainment of a homogeneous coating mechanically stable to surface swabbing (Figure 2a). These results can be explained by considering the reduction in the amount of iron tannates formed in a solution with a lower concentration. A reduction in the coating thickness, with consequent improvement of the coating stability, can also be hypothesized in these conditions.

Pickling is one of the most used techniques in the surface pre-treatment of steels [23,58–60] even if it requires the use and disposal of large amounts of acids with consequent possible environmental issues. This pre-treatment was considered for comparison with the innovative technique of plasma irradiation. In order to overcome problems related to salt deposition from PBS, tannin solutions in pure water were employed in this case. Moreover, in order to avoid excessive oxidation of carbon steel during coating formation and excessive production of iron tannates, spin coating was selected as a strategy for tannin deposition. Due to the reduced contact time and deposition mechanism involved in spin coating, solutions with higher tannin concentrations were explored in this case. Both the explored pickling times (20 and 5 min) were effective in obtaining ENC deposition on carbon steel (SEM-EDS and FTIR-ATR data, Figures 2d and 4). However, if longer pickling was used as a pre-treatment, part of the coating was removed by swabbing, evidencing a still excessive formation of iron tannates and the development of a too-thick coating. On the other hand, the reduction in the pickling time and the increase in the spin coating time and speed allowed the formation of a stable and thin coating that was not removed by swabbing. Tape adhesion tests (Figure 5) evidenced that plasma-pretreated samples, even in optimized conditions, still undergo the removal of a thin surface layer of the coating during the test. Similar behavior was evidenced for pickled samples with a longer pickling time. On the other hand, an almost optimal adhesion was observed for samples pickled for a shorter time. This result was due to both reduced coating thickness and iron tannate formation and to improved adhesion to pickled surfaces, as already evidenced by the authors for tannin-enriched epoxy coatings [61].

Despite the excellent adhesion exhibited by the CS_pick5_ENC100_spin800_60 sample layer, its protective properties were insufficient, as indicated by the EIS measurements. Various literature sources define a $|Z|_{(0.01)}$ value of $10^6 \Omega\text{cm}^2$ as the minimum threshold for a coating to be considered 'protective' [62,63]. In this case, the sample showed values below $10^4 \Omega\text{cm}^2$ from the outset, which further decreased over the 24 h of contact with the test solution (Figure 6a). These values suggested that the system immediately detected the exposition of the steel substrate, indicating an inadequate barrier effect. This implies that the layer was highly porous, allowing the test solution to penetrate easily. Supporting this assumption, the sample's appearance at the end of the test (Figure 6b) revealed the formation of extensive corrosion products due to the direct contact of the aggressive solution with the steel substrate. Therefore, despite the promising results demonstrated by the CS_pick5_ENC100_spin800_60 sample in terms of tannins promoting adhesion to the metal substrate, the porous and permeable nature of the layer indicated that further studies are needed to enhance its barrier properties. This result from electrochemical tests can be explained considering the porous nature of the coating, probably due to insufficient cohesion among tannin molecules. The strategies reported here (selection of surface pre-

treatment, solvent medium, and deposition strategy) worked on the adhesion of the coating to the metallic substrates. However, further improvements should be made to increase the bonding between phenolic moieties [64], especially tannin molecules [65,66].

5. Conclusions

Hydrolysable tannin from chestnut and condensed tannin from quebracho were compared for green protective layers on carbon steel. Hydrolysable tannins (solved in water) were more effective in film formation and adhesion to the ferrous substrate, due to a higher reactivity with Fe-based materials.

For the first time, a systematic comparison between different surface pre-treatments for corrosion protection layers on steel has been performed. In particular, plasma activation and acid pickling were investigated as possible pre-treatments to improve tannin adhesion. Even if plasma is a green solution with a low risk of corrosion during the pre-treatment steps, stronger adhesion (tape test) of the tannin layer was obtained on pickled samples (with a short pickling time). The combination of acid pickling and spin coating (with high rotation speed and deposition time) produced homogeneous layers of hydrolysable tannins that were stable for swabbing and tape tests. However, preliminary electrochemical corrosion tests evidenced that the coating was still porous and not able to effectively protect carbon steel from corrosion phenomena. These results suggest that the homogeneity and adhesion of the tannin layers were not sufficient for effective corrosion protection. From this research, the need to optimize the coating reduces its porosity, improving its barrier effect clearly emerges. Future works will be dedicated to solving these issues, for example, by investigating suitable top-coats or improving tannin polymerization ability.

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