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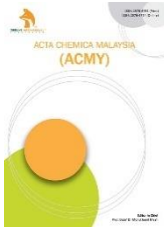

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RESEARCH ARTICLE

COMPARISON OF THE CORROSION INHIBITION PERFORMANCE OF TANNINS EXTRACTED FROM *STRYPHNODENDRON ADSTRINGENS* WITH THAT OF COMMERCIAL TANNINS EXTRACTED FROM BLACK WATTLE *(ACACIA MEARNSII)*

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ABSTRACT

Large amounts of low-carbon steel are used globally in many industrial sectors, as this material is very versatile, economical, and effective. The major problem with this type of steel is its susceptibility to corrosion, especially if used in acidic media, which is quite common in industry. Therefore, several anticorrosion methods are used for protecting structures and equipment, and an economical and effective method for protection is the use of inhibitors. The current ecological awareness, together with more rigid sustainability legislation, has created opportunities for research on the use of organic, nontoxic inhibitors from renewable sources. Tannins have been studied as likely inhibitors of the corrosive process due to their ability to form stable tannin complexes with corrosion products on the metal surface. These compounds are composed of flavonoid units and are considered an innovative line of anticorrosion products. This study evaluated the corrosion inhibition performance of tannins extracted from *Stryphnodendron adstringens* (Mart. Coville.) (barbatimão), a tree species characteristic of the Brazilian Cerrado biome, compared with the corrosion inhibition performance of commercial tannins extracted from *Acacia mearnsii* (De Wild) (black wattle) and cationically modified in terms of the protection of (Society of Automotive Engineers International) SAE 1020 carbon steel in a medium of 0.1 molar hydrochloric acid. The electrochemical methods of potentiodynamic polarization, electrochemical impedance spectroscopy, and gravimetry were used to characterize the inhibitory effects of the tannins, together with Fourier transform infrared spectroscopy for analysis of the reaction product between the iron and tannins. The results obtained showed the mixed inhibitor character of the tannins from barbatimão, which achieved good results, with an inhibition efficiency of up to 79%, compared with 95% for the modified tannins from black wattle.

KEYWORDS

Tannin, inhibitor, corrosion, carbon steel, barbatimão, black wattle

1. INTRODUCTION

Low-carbon steel is widely used as a building material in many industries due to its excellent mechanical properties and low-cost maintenance. The most diverse industrial segments use this type of steel, such as petroleum production, chemical manufacturing, civil construction, automotive production, and agricultural production. Acidic substances are also used in all of these segments for various purposes, such as oil well acidification, heat exchangers, and a multitude of other processes. Thus, an important measure in the industry is the prevention of corrosion, especially in acidic environments, where corrosive attack is greater (Zhao, 2018).

Corrosion of metals is one of the main causes of the wear and breakage of equipment and structures, which can cause contamination and alter the chemical structure where it occurs. The use of inhibitors as a method of protection and corrosion prevention is common; however, some of these inhibitors contain heavy metals in their formulation, which causes environmental contamination and harmful effects to human health. Given this scenario, a search for corrosion inhibitors for metals that are environmentally friendly was initiated, seeking to minimize the damage to the environment where the metal structures are located or disposed of (Rahim, 2007).

Due to growing ecological awareness, new environmental regulations and sustainability concerns, a new trend has emerged for the development of nontoxic alternatives for inorganic inhibitors. Tannins are a class of natural, nontoxic and biodegradable polyphenolic compounds extracted from plant sources that are already used as corrosion inhibitors in aqueous media, rust converter components, paint coating pigments, corrosion inhibitors of steel reinforcement in concrete, chemical cleaning agents for the removal of iron-based deposits, and oxygen scavengers for boiler water treatment systems, among other numerous uses, as reported in the scientific literature (Zhao, 2018; Rahim, 2007; Abiola, 2009; Agi, 2018b; De Hoyos-Martínez, 2019; Frangoza-Mar, 2012; Khan, 2015; Kodama and Hotsumi, 2011; Bastos, 2015; Obot and Madhankumar, 2015; Oguzie, 2008; Rani and Basu, 2012; Teixeira, 2015).

The use of plant extracts has been found to be a viable and environmentally friendly alternative to corrosion inhibitors for metals (Agi, 2018; Abdulmajid, 2019; Bacca, 2019; Obot, 2015; Raja, 2008). Tannins are flavonoid plant extracts derived from plant defence systems and are found mainly in the bark and leaves of tree species. Tannins are

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divided into two groups, condensed and hydrolysable, and condensed tannins have greater importance for use in industrial environments due to their stability and chemical structure.

Tannins are most efficient in inhibiting the corrosion of carbon steel when in acidic environments because of the reaction of iron with insoluble ferric tannate compounds, forming a protective violet film on the metal (Oguzie, 2008). The species *Stryphnodendron adstringens* (Mart. Coville.), popularly known as barbatimão, is characteristic of the Brazilian Cerrado biome. The extraction of tannins from its leaves and bark, the latter containing the highest tannin concentrations, has great economic importance for use in various sectors, such as in tanneries for leather tanning, in the pharmaceutical industry for drug production, and in the oil industry as a dispersing agent to control the viscosity of clays in well drilling (De Macedo, 2007).

Conversely, *Acacia mearnsii* (De Wild), known as black wattle, is a legume tree originally from Australia that has been cultivated in several countries due to its rapid growth. In Brazil, Rio Grande do Sul is the state with the most commercial plantations of the species. Black wattle bark is approximately 20% tannins, and its wood has been used for energy, cellulose, and fibreboard production (Santos and Ferreira, 2002).

In this study, was evaluated the performance of tannins extracted in the laboratory from the bark of barbatimão (*S. adstringens*) compared with the performance of commercially modified tannins cationically extracted from black wattle (*A. mearnsii*) in terms of the protection of SAE 1020 carbon steel in an acidic medium, with electrochemical measurements and analysis of the product formed on the metal surface to assess the efficiency of the tannins and consequently to make their applications as corrosion inhibitors viable in the most diverse industrial segments.

2. Materials and Methods

2.1 Sampling

Was collected bark of *S. adstringens* (barbatimão) from the Cerrado biome from the municipality of Ouro Branco, located in the central region of the state of Minas Gerais, Brazil (20°31"9.1'S and 43°42"47.5'E). Was removed trunk bark from three individuals with a mean diameter at breast height (DBH) of 31.06 cm and a height of 4-5 m.

Was purchased cationically modified commercial tannins from *A. mearnsii* (black wattle) from the local market.

2.2 Determination of the Condensed Tannin Content by the Stiasny Index

Was weighed the tannins (0.25 g, dry basis) in a 250-mL flat-bottomed volumetric flask. Then, was added 50 mL deionized water, 5 mL concentrated hydrochloric acid (HCl), and 10 mL formaldehyde (37%). Was heated the sample in a heating mantle under reflux for 30 min. After this period, was filtered the sample into a #2 crucible under vacuum. Was placed the crucible in a forced air oven at 105 °C ± 3 °C for 24 h and then removed it and allowed it to cool in a desiccator for at least 30 min. Was weighed the crucible and obtained the dry weight of the precipitate by subtracting the crucible weight. Was calculated the Stiasny index according to Equation 1:

$$Stiasny\ index = \frac{Dry\ weight\ of\ the\ precipitate}{(0.25\ g\ of\ tannins\ (dry\ basis))}\ x\ 100\% \qquad (1)$$

Was calculated the content of condensed tannins according to Equation 2:

$$\%\ condensed\ tannins = \frac{\%\ Stiasny\ index\ x\ \%\ solids\ content\ of\ powder}{100} \qquad (2)$$

2.3 Extraction of tannins from barbatimão

Was extracted the tannins using the method proposed for barbatimão (*S. adstringens*) by (Mori et al., 2003). Was performed the extraction using 100 g of ground barbatimão bark and 1500 mL of water at 70 °C for 3 h with a concentration of 3% sodium sulfite (Na_2SO_3) relative to the dry weight of the ground material. At the end of the extraction, was first filtered the material using a 1 mm² mesh sieve, and was discarded the part retained in the filter.

Subsequently, was filtered the liquid containing the tannins using a vacuum pump and glass crucibles lined with glass wool with porosity = 2. Was then dried the filtered material by evaporation in a forced air oven and macerated it until it became a powder.

2.4 Solution preparation

Was prepared the base solution using a concentration of 0.1 M HCl in distilled water, followed by dilution, to the desired concentration of tannins. Was used concentrations of 0, 1, 3 and 6 g/L tannins relative to the total solution for the tests.

2.5 Specimen preparation

Was used specimens of SAE 1020 steel. SAE 1020 steel consists primarily of carbon (0.17% – 0.23%), small amounts of manganese (0.3 - 0.6%) , and possible traces of phosphorus (≤ 0.04 %) and sulfur (≤ 0.05 %). The exact composition varies from manufacturer to manufacturer.

First, was cut the steel into small plates, and then, was welded a conductive wire and embedded it in epoxy resin for better delimitation of the area of contact with the solution. Subsequently, was sanded the plates with a sander using water and sandpaper with grit decreasing from 180 to 600, washed them with acetone, and dried them with a hot air jet. Then, was marked a 1 cm² area with liquid electrical tape that would come into contact with the solution.

2.6 Electrochemical measurements

Was immersed the specimens in the solution for 1 h for stabilization of corrosion potential before starting the tests. Was used an conventional electrochemical cell of 3 electrodes, with as the reference electrode, the calomel saturated, platinum as the counter electrode and as a working electrode, the 1020 steel specimen. Was performed the electrochemical measurements in an Autolab Type III potentiostat/galvanostat coupled to a microcomputer with NOVA 1.11 software.

Was performed electrochemical impedance spectroscopy (EIS) measurements with an open-circuit potential over a frequency range of 50 kHz to 20 mHz with a peak-to-peak amplitude of 10 mV and 10 readings per decade of frequency.

Was carried out potentiodynamic polarization electrochemical tests on the specimens following the EIS. Was performed scans between ± 500 mV relative to the corrosion potential at a speed of 1 $mV.s^{-1}$.

Was analysed all data using NOVA 2.1 software and plotted the graphs using Origin 2016 software.

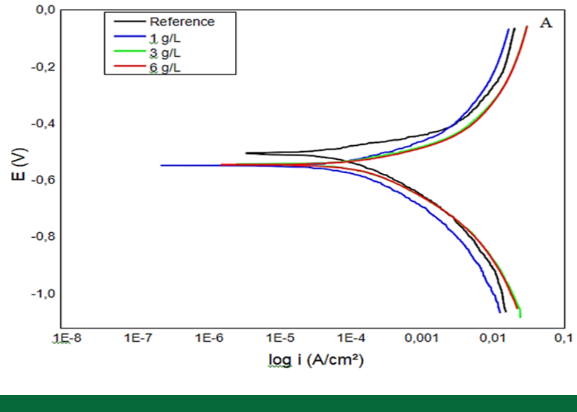
2.7 Fourier transform infrared spectroscopy

Was performed Fourier transform infrared spectroscopy (FTIR) in direct transmission mode in the 400–4000 cm^{-1} region with a resolution of 2 cm^{-1}. Was collected these data from 32 scans. Was analysed the samples using the attenuated total reflectance (ATR) technique on a Varian 600-IR Series Spectrometers, with the Pike Technologies GladiATR accessory attached for ATR measurements.

3. Results and Discussion

The barbatimão tannins show a Stiasny index of 88.52%, which represents the amount of substances in the total extract that react with formaldehyde in the acidic medium, and a condensed tannin content of 81%, which indicates the proportion of tannins present in the analysed materials (Sartori, 2014). The black wattle tannins have a Stiasny index of 84.15% and condensed tannin content of 75%.

Figure 1A shows the polarization curves for different concentrations of barbatimão extract in a 0.1 M HCl solution with SAE 1020 steel. Figure 1B shows the polarization curves for different concentrations of commercial black wattle tannins in a 0.1 M HCl solution with SAE 1020 steel. Table 1 shows the electrochemical parameters obtained from the polarization curves by the Tafel extrapolation method.



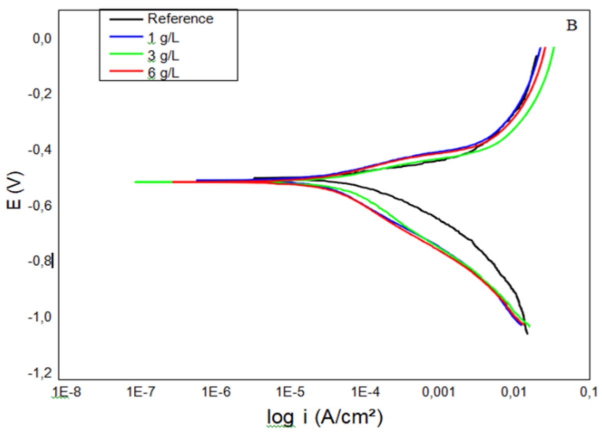


Figure 1: A-Polarization curves for different concentrations of barbatimão extract with SAE 1020 steel in 0.1 M HCl solution; B-Polarization curves for different

Was observe a reduction in the corrosion potential according to the barbatimão addition. The the polarization parameters (Table 1) and the polarization curves (Figure 1A) show that the presence of barbatimão leads to a reduction in the corrosion current density of the anodic and cathodic branches, with a change to a more active corrosion potential, behaving as a mixed inhibitor of the corrosion of SAE 1020 steel in 0.1 MHCl (Negm, 2010; Tan and Kassim, 2011). Table 1 shows that the polarization resistance increases and the current density decreases in the absence of barbatimão and that was obtain the best results at 1 g/L, indicating that this is the optimal concentration for the use of barbatimão extract. The presented similar results (Bacca et al., 2020). In the polarization results of black wattle tannins, the cathodic region is more affected by the addition of tannins (Figure 1B), exhibiting more activity in terms of hydrogen reduction (Sorkhabi, 2004). However, a chemical compound can be recognized as a mixed-type inhibitor if the variation in the corrosion potential is less than 85 mV; otherwise, the inhibitor is classified as anodic or cathodic (Amin, 2007). The change in the corrosion potential exhibits a maximum variation of 12 mV (in Table 1), classifying the commercial tannin as a mixed-type inhibitor; the tannins delay the hydrogen reduction reaction and reduce the dissolution of the metal by forming a protective layer through adsorption onto the steel surface (Rahim, 2007).

Table 1: Potentiodynamic polarization parameters with SAE 1020 steel in 0.1 M HCl.concentrations of modified commercial black wattle tannins with SAE 1020 steel in 0.1 M HCl solution.

Concentration	Barbatimão			Black wattle		
	Ecorr	Icorr	Polarization resistance	Ecorr	Icorr	Polarization resistance
(g/L)	(V)	(A/cm^2)	(Ω)	(V)	(A/cm^2)	(Ω)
0	-0.510	2.14 x 10^{-4}	102.81	-0.510	2.14 x 10^{-4}	102.81
1	-0.545	9.24 x 10^{-5}	242.10	-0.511	4.15 x 10^{-5}	559.19
3	-0.533	1.19 x 10^{-4}	196.13	-0.522	2.95 x 10^{-5}	779.84
6	-0.539	1.44 x 10^{-4}	142.00	-0.517	3.03 x 10^{-5}	779.18

The corrosion current density decreases in the presence of tannins, and for the sample with black wattle tannins, the greatest reduction occurs at the highest concentrations, with very similar results for 3 g/L and 6 g/L. Was observe the same pattern for the increase in polarization resistance, which indicates that corrosion is inhibited with the addition of the tannins.

Due to the hydroxyl groups of tannins, they are able to react with iron (Fe^{2+} ion) or iron oxide, forming ferrous tannates, which when in contact with oxygen in air are easily oxidized, forming ferric tannate, a compact and strong insoluble compound (Gust, 1994). In addition to reacting with Fe^{2+} ions, tannins can react directly with Fe^{3+} ions to form ferric tannates. Finally, due to the reducing capacity of tannins, Fe^{3+} oxides can be reduced to Fe^{2+} ions, which can complex with tannins to form ferrous tannins. These ferrous tannins are then converted into ferric tannins when they come in contact with oxygen (Rahim, 2011). The formation of this ferric tannate film prevents sensitive iron layers from reacting with the environment for some time, which leads to corrosion (Mourey, 1997). According to the following reaction path, the relatively easy conversion of iron oxides into ferric tannate deposits is explained by this mechanism (Rahim, 2007):

$Fe_{(s)} \rightleftharpoons Fe^{2+} + 2e^-$

$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightleftharpoons Fe^{3+} + \frac{1}{2}H_2O$

$FeOOH + nH^+ \rightleftharpoons Fe^{3+} + nH_2O$

Followed by reduction of Fe^{3+} ions and reaction with tannins,

$nFe^{3+} + ne^- \rightarrow nFe^{2+}$

$\text{tannins} \rightarrow \text{tannates} + ne^- + nH^+$

$nFe^{3+} + \text{tannins} \rightarrow (Fe^{2+})_n\ \text{tannate} + nH^+$

Consequently,

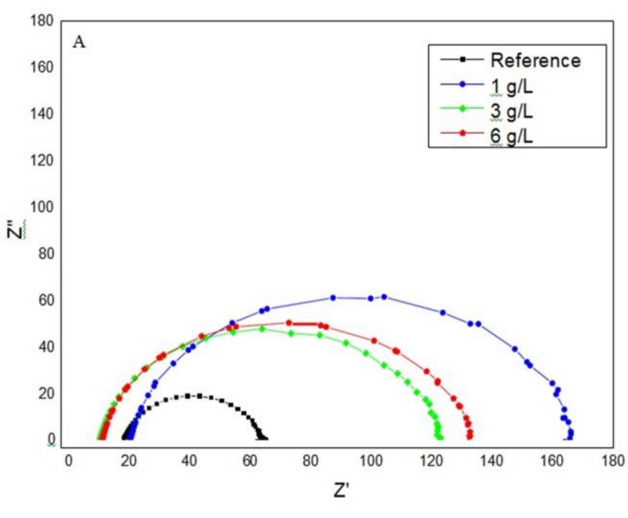
$(Fe^{2+})_n\ \text{tannate} \rightarrow (Fe^{3+})_n\ \text{tannate} + ne^-$

$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$(Fe^{2+})_n\ \text{tannate} + \frac{1}{4}nO_2 + nH^+ \rightarrow (Fe^{3+})_n\ \text{tannate} + \frac{1}{2}nH_2O$

Tannins contain polyphenolic portions that react with ferric ions, forming a reticulated network of ferric tannates that forms a physical barrier at the metal and electrolyte interface due to the insoluble ferric tannate complexes, which are products of the reaction between iron ions and tannins, explaining the greater polarization resistance and lower current density obtained with the addition of tannins (Rahim, 2007; Sezer and Ozturk, 2019).

Figure 2A shows the Nyquist plots for different concentrations of barbatimão extract in 0.1 M HCl solution with SAE 1020 steel after immersion for 1 h. Figure 2B shows the Nyquist plots for different concentrations of black wattle tannins in 0.1 M HCl solution with SAE 1020 steel after 1 h of immersion. Both Nyquist plots show a single capacitive semicircle attributed to the electrical double-layer capacitance and the charge transfer resistance (Zhao, 2018). The addition of barbatimão extract leads to an increase in the diameter of the semicircle, which is attributed to a greater resistance to charge transfer and therefore to a higher inhibition efficiency. Thus, the Nyquist plot (Figure 2A) corroborates the polarization curves, i.e., greater resistance to charge transfer and consequently higher inhibition efficiency of the solution containing 1 g/L barbatimão extract.



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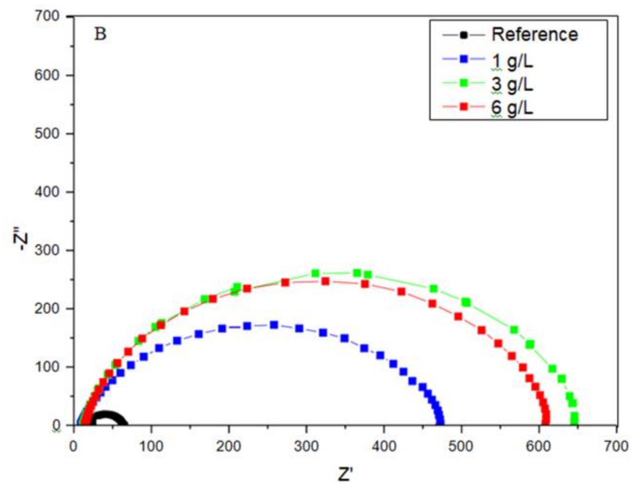
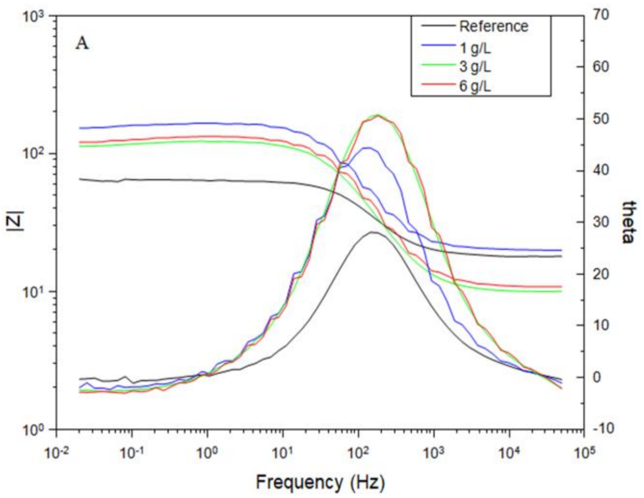


Figure 2: A-Nyquist plot of SAE 1020 steel and different concentrations of barbatimão extract in 0.1 M HCl solution. B Nyquist plot of SAE 1020 steel and different concentrations of modified commercial black wattle tannins in 0.1 M HCl solution.

In the higher frequency region, the impedance reaches a horizontal amplitude, while the phase angle tends to 0°, a result typical of a resistor. In the lower frequency region, the phase angle tends to 0° (Zhao, 2018).

In Figure 2B, the shape of the arcs does not change with the addition of the tannins, suggesting that the steel dissolution mechanism is not altered in the presence of the inhibitor, However, the diameter of the capacitive markedly increases with the addition of the tannins, with very similar results for the concentrations of 3 g/L and 6 g/L, indicating that there may be an optimal concentration for use of the inhibitor and that no significant improvement is obtained with an increase. The larger arc diameter in the Nyquist plot is indicative of higher charge transfer resistance and is thus attributed to greater corrosion inhibition efficiency (Bacca, 2020).

The Bode phase plots (Figure 3A and 3B) show only one capacitive time constant, and their parameters are essential for the calculations of the equivalent circuit.



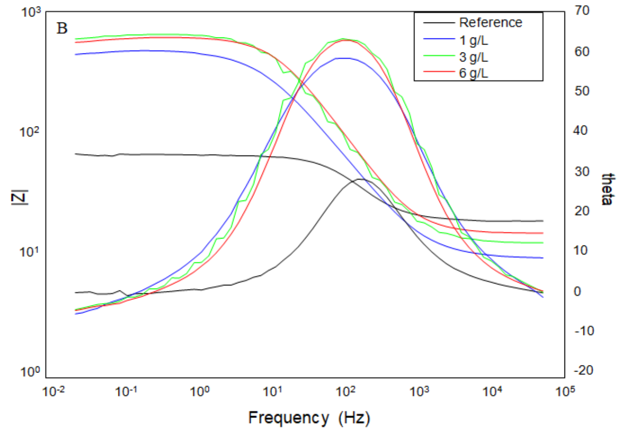


Figure 3: A- Bode module and frequency phase angle plot of SAE 1020 steel and different concentrations of barbatimão extract in 0.1 M HCl solution. B - Bode module and frequency phase angle plot of SAE 1020 steel and different concentrations of commercial modified black wattle tannins in 0.1 M HCl solution.

The Bode plot in Figure 3A shows that the sample with the highest impedance after 1 h of immersion in the electrolyte is that with 1 g/L, with the lowest impedance reduction at the end of the test. In turn, the Bode diagram in Figure 6, in which black wattle tannins are used, shows that the samples with the highest impedance after 1 h of immersion in the electrolyte are the samples with 3 g/L and 6 g/L, but the sample with 3 g/L shows a greater impedance reduction at the end of the than the 6 g/L sample.

Figure 3B shows that the impedance modules and the phase angle increase with the inhibitor addition as the adsorption of the inhibitor onto the steel surface is intensified.

Was introduce an equivalent circuit composed of a constant phase element (CPE), charge transfer resistance (Rp), and solution resistance (Rs) (Figure 4) to illustrate the information extracted from the EIS data (Tan and Kassim, 2011).

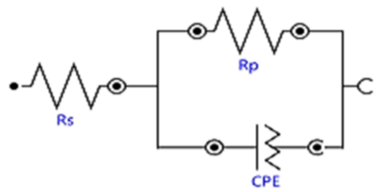


Figure 4: Electrical equivalent circuit for EIS data assembly.

The results obtained for each of the elements are shown in Table 2, together with the inhibition efficiency, which is calculated using Equation 3:

$$n_i = \frac{(R_p - R_{pi})}{R_p} \ x \ 100\% \quad (3)$$

where R_{pi} is the charge transfer resistance in the absence of tannins and R_p is the charge transfer resistance in the presence of tannins, i.e., polarization resistance.

Table 2: EIS parameters in 0.1 M HCl.

Concentration	Barbatimão				Black wattle			
	CPE	Rp	Rs	η	CPE	Rp	Rs	η
(g/L)	(F)	(Ω)	(Ω)	(%)	(F)	(Ω)	(Ω)	(%)
0	6.38 x 10-5	30.60	15.01	- -	6.38 x 10-5	30.60	15.01	- -
1	2.70 x 10-5	149.63	19.61	79.54	3.46 x 10-5	390.40	11.66	92.16
3	2.66 x 10-5	129.29	15.78	76.32	2.45 x 10-5	642.00	11.85	95.23
6	2.65 x 10-5	124.57	9.96	75.43	2.28 x 10-5	600.70	13.89	94.90

Based on the results in Table 2, was generally expect that the addition of inhibitors causes a significant increase in the Rp value, indicating the inhibition efficiency (Tan and Kassim, 2011). The fact that the highest inhibition efficiency is obtained with 1 g/L barbatimão can be explained by the formation of a porous layer and/or weak adsorption of the inhibitor, which causes secondary desorption of the metal surface with the increase in the concentration past a certain value, a phenomenon also described in other studies (Rahim, 2007; Bacca, 2020; Morales, 2004).

All plots converge very well for the proposed electrical equivalent circuit, confirming the aforementioned data of a higher efficiency for the solution containing 1 g/L barbatimão extract. Was observe a decrease in efficiency as the concentration increases, reaching 79.54% inhibition at the lowest concentration of 1 g/L barbatimão extract, as calculated by the polarization resistance; similar behaviour was observed by (Rahim et al., 2007).

The results with black wattle tannins are also consistent with the proposed electrical equivalent circuit, with very similar results for the concentrations of 3 and 6 g/L, where the results of 3 g/L are slightly better. This indicates that this is an optimal concentration for the tannins, with an inhibition efficiency of 95.23%.

The FTIR results for the samples with barbatimão are shown in Figure 5 (black), and those with black wattle tannins are shown in Figure 5 (red). The FTIR experiments show practically the same spectra for the violet deposits of ferric tannins, regardless of the origin of the tannins. The broad adsorption range between 3700 and 2600 cm^{-1}, with maximum absorbances at 3293 cm^{-1}, refers to the presence of hydroxyl groups. The peaks between 1800 cm^{-1} and 1300 cm^{-1} are characteristic of aromatic compounds (Nardella, 2019). Several smaller peaks between 1000 and 1400 cm^{-1} correspond to substituted benzene rings (Rahim, 2007; Agi, 2018). The 2600-1700 cm^{-1} band is due to the stretching vibration of CH.

The protection mechanism of the metal by the tannin extract is mainly due to hydroxyl groups in the vicinity of aromatic rings reacting with iron ions and forming ferric tannates that adsorb onto the surface of the specimens (Rahim, 2007; Gust, 1991). Thus, was confirm the formation of ferric tannate.

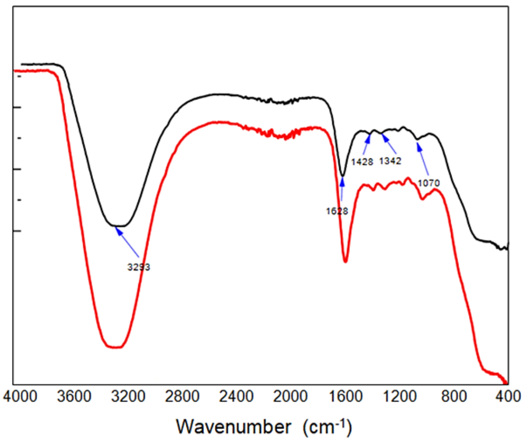


Figure 5: Fourier transform infrared spectroscopy (FTIR) of samples of barbatimão extract in black. Fourier transform infrared spectroscopy (FTIR) of samples of modified commercial black wattle tannins in red.

4. Conclusion

Tannins from barbatimão are organic compounds that are biodegradable, easy to obtain, and low cost. In this study, they were shown to be promising corrosion inhibitors for SAE 1020 carbon steel in electrochemical analyses, demonstrating characteristics of mixed inhibitors in acidic media, reaching an inhibition efficiency of approximately 79% with a barbatimão tannin concentration of 1 g/L. FTIR showed that the hydroxyl groups of the tannin reacted with the iron ions of the steel (Fe^{2+} and/or Fe^{3+}), forming ferric tannate. Thus, plant-derived tannins are a great alternative to the inhibitors currently available on the market. The electrochemical results obtained for the commercial black wattle tannins reached an optimal level, showing mixed-type inhibition, with greater action on the cathodic branch of the reaction of SAE 1020 steel in an acidic medium of up to 95.23%, reducing the current density and increasing its charge transfer resistance. These results, in addition to the economic and sustainable nature of tannins from black wattle – since it is a product extracted from a renewable and natural source – show these tannins are viable for industrial use in various segments, such as the oil, food and chemical industry. The fact that tannins is already a commercial source further facilitates its use because it is already available on the market.

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