

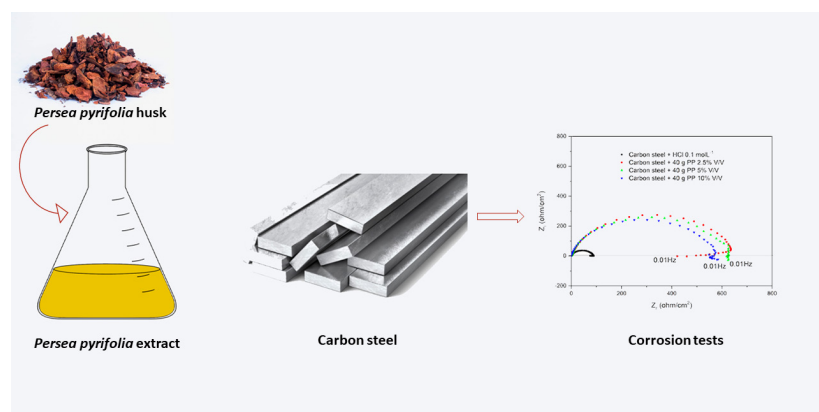
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Persea pyrifolia Peel Extract as a Carbon Steel Corrosion Inhibitor

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Carbon steel is one of the most widely used alloys in industrial applications. However, the use of this metal may be limited because of corrosion tendency. Thus, it is necessary to develop methods that inhibit its degradation. One way to inhibit corrosion is to use organic inhibitors. Some organic compounds with heteroatoms inhibit corrosion by forming a protective film. In this study, the corrosion inhibition of carbon steel 1020 in 0.1 mol L⁻¹ hydrochloric acid medium was evaluated. The natural inhibitor used was an aqueous extract of the bark of *Persea pyrifolia* (PP) plant at concentrations of 2.5, 5 and 10% V / V. The electrochemical response was determined by open circuit potential measurements, electrochemical impedance spectroscopy, and anodic potentiodynamic polarization. Therefore, mass loss was measured, and inhibitory efficiency was evaluated. The best results were observed for the concentration of 2.5% V / V of *Persea pyrifolia* extract, presenting an inhibition efficiency of 82.5% on the 1020 carbon steel. The electrochemical results indicate that PP extract can be used as a green corrosion inhibitor in acidic medium.

Graphical abstract



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1. Introduction

Carbon steel is one of the most widely used metal alloys in industrial systems because of its excellent molding, machining, and weldability characteristics as well as low cost [1-4]. However, the use of this alloy may be limited because of its corrosive nature [5].

One of the most interesting methods to combat corrosion is the use of organic inhibitors, which are generally organic compounds, as protective films. Their corrosion inhibition property can be attributed to the presence of functional groups containing heteroatoms such as phosphorus, selenium, sulfur, nitrogen and oxygen, which interact with the

metal surface [6-8].

This interaction occurs between the electron pair of the donor atoms (heteroatoms) and the metal surface, thereby promoting adsorption. The intensity of this interaction depends on the electron density of the donor atom and the polarization of the group, thus reducing corrosion [9].

The use of some inhibitors is limited because of environmental concerns and synthesis cost [10, 11].

Therefore, the search for environmentally friendly corrosion inhibitors has increased significantly in recent years [12]. The use of natural products as corrosion inhibitors is justified owing to the presence of phytochemical compounds and the similarities in the molecular and electronic structures between these products and conventional organic inhibitors [13-15].

In this regard, following natural products have been used as corrosion inhibitors: bamboo extract [16], garlic peel extract [8], guinea pepper leaves [17], lemon leaves [18], winter jasmine leaves [19], cassava starch [20], henna leaves [21], watermelon rind extract [22], and castor leaves [23].

In this study, the ecologically friendly bark extract of *Persea pyrifolia* (PP) was first used as a corrosion inhibitor in a HCl medium, which is a strong corrosive solution for carbon steels [24].

Research shows that some chemical compounds belonging to the polyphenol group, such as condensed tannins and flavonoid glycosides, are present in the bark of this plant and have potential for corrosion inhibition [25, 26]. The presence of oxygen heteroatoms and aromatic compounds can facilitate the use of such compounds as an inhibitor in acidic media [25, 26].

In this context, the relevance of this work is based on the replacement of a toxic synthetic corrosion inhibitor with a naturally occurring corrosion inhibitor, aiming at reducing undesirable effects on the environment.

2. Material and Methods

2.1 Metallic Substrate Preparation

Square carbon steel plates 1020 (2 × 2 cm) were used. The samples were previously sanded with silicon carbide (SiC) sandpapers having grit sizes of 400, 600 and 1200 mesh.

2.2 Electrolyte

A 0.1 mol L⁻¹ HCl solution was used as the electrolyte for corrosion testing and determination of the electrochemical behavior of the base metal without and with the presence of the inhibitor. For the evaluation of the inhibition promoted by PP extract, 0.1 mol L⁻¹ HCl solution was used as a solvent for the preparation of inhibitor solutions at 2.5, 5 and 10% V / V concentrations based in preliminary tests.

2.3 Inhibitor Extraction

The inhibitor used was purchased from natural product stores of the local trade of Guarapuava / PR. The shells were macerated using mortar and pistil to a powder form. Extraction was performed by adding 40 g of plant shell to 1 L of H₂O. The mixture was boiled for 15 min and filtered with filter paper just before application.

2.4 Corrosion Tests

All electrochemical assays were conducted at 22 °C and were performed in triplicate. A cylindrical electrochemical cell made of PVC containing three electrodes a 1020 carbon steel working electrode, an Ag / AgCl reference electrode and a platinum counter electrode was used. The electrolytes used were the solutions described in section 2.2. The electrochemical assays performed were: Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS) and Anodic Potentiodynamic Polarization (APP). The samples were immersed in the electrolyte for 1 h prior to the electrochemical tests. The EIS tests were performed at the open circuit potential, with a ± 10 mV potential disturbance at frequencies from 10⁴ Hz to 10⁻² Hz from the open circuit potential with a sweep speed of 1 mVs⁻¹.

2.5 Mass Loss Tests: Corrosion Penetration Rate (CPR)

Mass loss tests were performed according to ASTM G31-72 (2004) [27], from which the masses of each sample were determined before and after immersion to calculate the mass difference due to corrosion. promoted by the middle. After immersion, the samples were washed with distilled water and hot air blasted before the final weighing. Mass loss was determined according to equation (1):

$$W = m1 - m2 \quad (\text{Equation 1})$$

Where m1 is the mass before immersion (g), m2 is the mass after immersion (g); The velocity of corrosion was expressed by calculating the corrosion penetration rate (CPR) in millimeters per year (mm / year) using equation (2):

$$CPR = \frac{K.W}{A.t.\rho} \quad (\text{Equation 2})$$

Where K represents a constant (87.6), W is the mass loss in mg, A is the exposed area in cm², t is the time in h and ρ is the specific mass of the material in g / cm³, for carbon steel this value is 7.86 g / cm³. From these results, inhibition efficiencies (IE%) were calculated by mass loss assays using equation (3).

$$IE\% = \left(\frac{CPR_{blank} - CPR_{with\ extract}}{CPR_{blank}} \right) \times 100 \quad (\text{Equation 3})$$

IE% is the inhibition efficiency from the mass loss results and it is the ratio of the corrosion rate of the medium without inhibitor and the corrosion rate of the medium with the inhibitor extract.

2.6 Inhibition efficiency

The inhibition efficiency promoted by the inhibitors was obtained from equation (4) shown below. These values were obtained from the potentiodynamic polarization (PPA) curves.

$$\theta = \left(\frac{j^{\circ}corr - j_{corr}}{j^{\circ}corr} \right) \times 100 \quad (\text{Equation 4})$$

Thus, the corrosion rate of carbon steel with and without the inhibitor were determined.

3. Results and Discussion

3.1 Open Circuit Potential (OCP)

Figure 1 shows the OCP results.

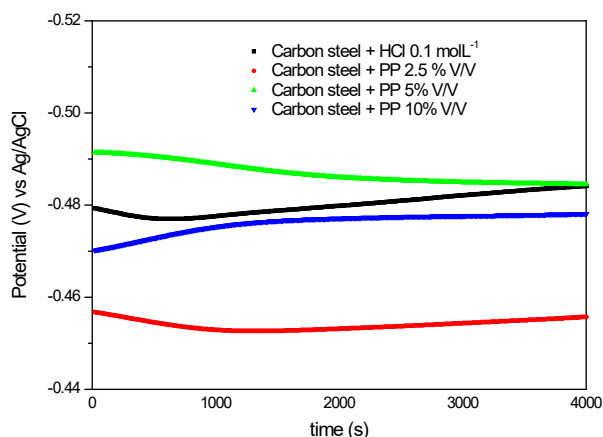


Fig. 1. Open Circuit Potential for the mean values, in 0.1 mol L^{-1} HCl solution and in the presence and absence of inhibitor extracts.

Previous tests showed that in 4000 s the OCP did not vary by more than 5 mV, which show the potential stabilization. Potential time-response responses show a shift to more positive values for samples with inhibitors at 2.5 and 10% concentration. Such a result suggests a higher corrosion resistance for these samples as they make the surface of the nobler metal.

3.2 Electrochemical Impedance Spectroscopy (EIS)

The results of Electrochemical Impedance Spectroscopy in the form of Nyquist diagrams are presented in Figure 2.

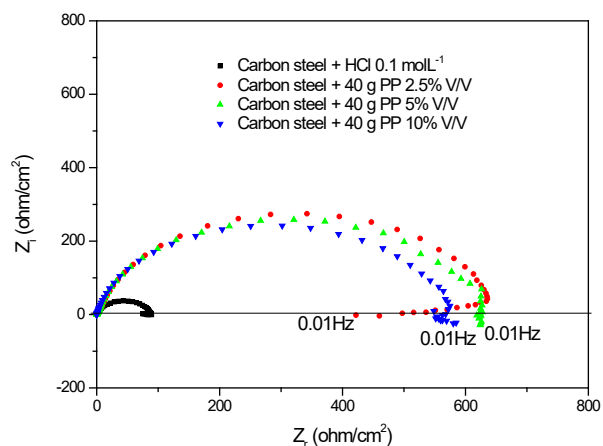


Fig. 2. Nyquist EIS diagrams for the mean values obtained in 0.1 mol L^{-1} HCl in the presence and absence of extracts.

The diagrams have only one capacitive arc for all samples and indicate that the occurrence of only one process. Higher impedance values were measured for the

samples in the presence of the inhibitor, suggesting higher resistance, which is promoted by the presence of inhibitor compounds. In the curves of inhibitory solutions inductive arcs are observed at low frequencies.

This observed result is related to the inhibitor adsorption process on the electrode surface. Da Rocha [28] obtained a similar response when studying papaya seed extract in neutral medium at concentrations of 200, 400 and 1000 ppm. The presence of this extract increases the corrosion resistance at the studied concentrations, and at higher concentrations this effect decreases. Therefore, with increasing concentration, a less protective film is likely to form on the metal surface. Bode phase angle impedance diagrams are shown in Figure 3.

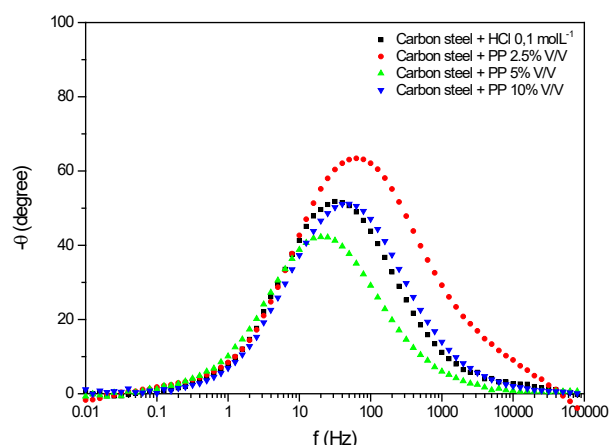


Fig. 3. Bode phase angle EIS diagrams for the mean values obtained in 0.1 mol L^{-1} HCl in the absence of extracts.

The results show that there is only one time constant, indicating the occurrence of a single process. This process is associated with charge transfer at the metal / solution interface. A larger displacement of this constant can be observed for the sample in the presence of the 2.5% V / V inhibitor extract, indicating an increase in the corrosion resistance.

3.3 Anodic Potentiodynamic Polarization (APP)

Potentiodynamic polarization results are presented in Figure 4.

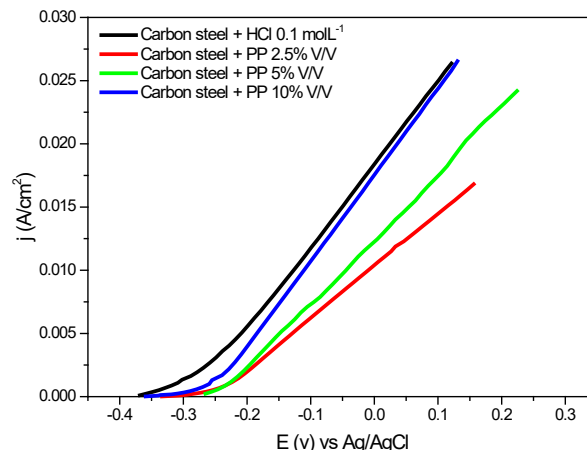


Fig. 4. APP curves for the mean values in 0.1 mol L^{-1} HCl medium in the presence and absence of inhibitory extract.

The polarization behavior presents lower current density for samples with 2.5 and 5% inhibitor concentrations, thus demonstrating greater corrosion resistance, which is in agreement with the impedance results. However, for the 10% sample there was a shift of the current density elevation potential to more negative values, indicating a depolarization of the anodic reaction when compared to the 2.5 and 5% samples suggesting a lower corrosion resistance between the two extracts tested. Additionally, typically passive behavior is observed for samples in the presence of inhibitor at potentials close to corrosion up to -0.250 V.

3.4 Mass Loss Tests: Corrosion Penetration Rate (CPR)

Table 1 shows the corrosion rate values, as well as the mass loss and its efficiencies, obtained in the absence and presence of the 2.5% V / V PP inhibitor extract.

Note that the CPR value decreased in the presence of inhibitory extract as compared to non-inhibitory medium for all immersion times. It can be verified that the EI% value was higher for the 24 h immersion time. SOUZA et al. [29] obtained similar results when evaluating the behavior of carbon steel 1020 in 1 mol L⁻¹ HCl in the presence of 400 mg L⁻¹ of the mate herb aqueous extract and resulted in 89% efficiency after 24 h soaking.

Table 1. Mass loss for carbon steel in the presence and absence of inhibitory extract after 24, 48 and 72 h of immersion.

Sample	Immersion Time (h)	Average Mass Loss (gcm ⁻²)	CPR (mm/year)	Inhibition efficiency (%)
Carbon Steel 1020	24	0.1274	6.7229	-
	48	0.1323	3.4907	-
	72	0.0233	2.3659	-
2.5 % V/V PP	24	0.0103	0.7247	89
	48	0.0233	0.8197	77
	72	0.0310	0.7271	69

3.5 Inhibition efficiency

Inhibitory efficiency was determined for the 2.5, 5 and 10% inhibitory extract concentrations and the result is presented in Table 2.

Table 2. Inhibitory efficiency determined for 2.5 and 5% PP extract at -0.27 V potential.

Sample	j _{CORR} (A/cm ²)	θ (%)
Carbon Steel 1020	1.72x10 ⁻³	-
Carbon Steel + 2.5 % PP	3.05x10 ⁻⁴	82.5 %
Carbon Steel + 5% PP	3.51x10 ⁻⁴	79.5 %
Carbon Steel + 10% PP	4.80x10 ⁻⁴	72%

The 2.5% PP extract showed 82.5% inhibitory efficiency, a relatively higher value than the 5 and 10% PP extracts, which presented values of 79.5 and 72% respectively, proving the higher inhibition of carbon steel corrosion at a concentration of 2.5%. Similar results were found by Vasconcelos [30] for the coffee extract in 1 mol L⁻¹ HCl which showed 88% inhibition efficiency.

Somensi and co-workers (2017) [25] identified in the plant shell some chemical components belonging to the

group of polyphenols, such as condensed tannins and flavonoid glycosides derived from quercetin and kaempferol. These compounds have in their structures hydroxyls, carbonyls and oxygen groups, which may be responsible for the adsorption on the metal surface, promoting corrosion protection.

Since quercetin and kaempferol are responsible for the antioxidant properties of the plant extract, it is possible to suggest that they can act as reducing agents or electron donors. Thus, it can form a protective layer on the metal surface by adsorption. The model depicted in Figure 5, represents a proposal for the process of *Persea pyrifolia* extract inhibition.

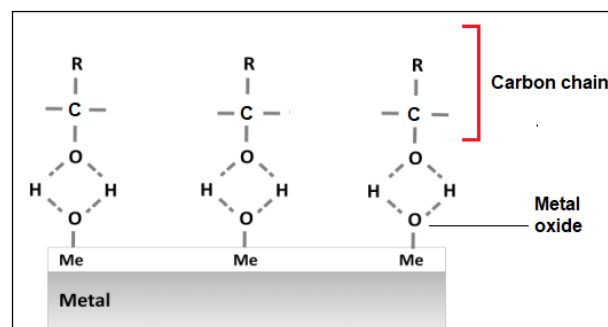


Fig. 5. Proposed model to protective layer to corrosion inhibition.

In the suggested model, the participation of the iron oxide layer spontaneously formed on the carbon steel surface can be observed, which promotes the interaction of H-bond with the hydroxyls from the phenolic compounds that constitute the *Persea pyrifolia* extract [31, 32]. The carbon chain structure of the inhibitor may lead to intermolecular interactions which can generate stability to the generated protective film, increasing the barrier against corrosion.

4. Conclusions

The results of electrochemical impedance spectroscopy demonstrated that there was an increase in the corrosion resistance of Carbon Steel 1020, as higher impedance values and phase angles were measured.

The results of anodic potentiodynamic polarization corroborate with the impedance results since lower values of current density were determined for the samples in the presence of inhibitory extract. The best response to corrosion inhibition was in the presence of the 2.5% V / V extract, as higher impedance values and lower current densities were measured for this sample. The inhibition efficiency at 2.5% V / V was 82.5%, which was considered to be the most effective.

The results of mass loss indicated that there is a dependence on the inhibition efficiency as a function of immersion time in the corrosive medium. An increase in the immersion time decreases the inhibition efficiency, however, even after 72 hours the efficiency remained at 69%.

The results of this study indicate that the tree shell extract of the PP plant can be used as a green corrosion inhibitor for 1020 grade carbon steel in 0.1 mol L⁻¹ HCl.

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Author Contributions

Conceptualization, Carine Vieira; Danielle Cristina Silva Oliszeski; Methodology, Carine Vieira; Gideã Taques Tractz; Felipe Staciaki da Luz Investigation, Carine Vieira; Bianca Vanjura Dias; Gideã Taques Tractz; Felipe Staciaki da Luz.; Resources, Everson do Prado Banczek; Paulo Rogério Pinto Rodrigues; Data curation, Gideã Taques Tractz; Bianca Vanjura Dias; Danielle da Silva Oliszeski; Writing—original draft preparation, Gideã Taques Tractz; Felipe Staciaki da Luz, Bianca Vanjura Dias; Writing—review and editing, Carine Vieira; Danielle da Silva Oliszeski; Bianca Vanjura Dias; Felipe Staciaki a Luz.; Supervision, Everson do Prado Banczek; Paulo Rogério Pinto Rodrigues.; Project administration, Everson do Prado Banczek; Paulo Rogério Pinto Rodrigues.; All authors have read and agreed to the published version of the manuscript.

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