Tanino da Acacia *mearnsii* De Wild como inibidor de corrosão para alumínio

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Abstract

Taking in consideration the large Brazilian marine coast as well as its number of rivers, one of the corrosion problems observed in Brazil is related to watercraft produced in aluminum. Even considering the necessity to replace toxic for natural or environmentally-friendly inhibitor and that Brazil is among the highest Acacia tree (Acacia *mearnsii* De Wild) producers, this work has been developed in order to evaluate the performance of tannin from Acacia as a corrosion inhibitor for aluminum. It was analyzed in the following concentrations of tannin: 0.5 $g.L^{-1}$; 2.0 $g.L^{-1}$; 3.0 $g.L^{-1}$; 4.0 $g.L^{-1}$; 5.0 $g.L^{-1}$, and 6.0 $g.L^{-1}$ along 1 h. The higher concentrations - 4.0 $g.L^{-1}$, 5.0 $g.L^{-1}$, and 6.0 $g.L^{-1}$ - presented the best results.

Keywords: corrosion, inhibitor, tannin, acacia.

Introduction

It is known that aluminum suffers differential aeration corrosion as water works like an aerobic electrolyte, resulting in localized corrosion such as pitting or honeycomb corrosion (1). Inorganic (2) and organic synthetic inhibitors have been used to minimize metallic corrosion. In general, those inhibitors are part of primers and anticorrosive coating, and can act as passivators avoiding physic/chemical interaction between corrosive species and the metal. However, the problem of those inhibitors is the toxicity and damaging effects for the environment. Moreover there is a world claim in order to develop urgently cheap, safe, non toxic inhibitor that can present good performance (2-5).

Nowadays the REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) regulation prohibits the use of toxic inhibitors - except for aerospace industry (6). That is a signal for other countries out of the European Union which will also ban those kinds of inhibitors very soon. So, it is mandatory to research non toxic and safe, environmentally friendly corrosion inhibitors. An alternative is to develop a natural or green inhibitor (7-10) which is biodegradable and with no heavy metals or any toxic substances.

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Considering the importance of Brazil as a tannin producer, this paper evaluates through electrochemical techniques the tannin from Acacia *mearnsii* De Wild, as a corrosion inhibitor for aluminum.

Methodology

The tannin sample – from black wattle tree bark extracted from Acacia *mearnsii* De Wild - was supplied by TANAC (Montenegro, Brazil). The metal used was aluminum 99.9%. Sodium chloride (REAGEN, Brazil) was used to prepare the electrolyte solutions. The surface of working electrodes was prepared by grinding it with silicon carbide paper up to grade number 600 followed by washing it with distilled water and drying it under a hot air stream.

The tests in triplicate were performed in aerated solution of NaCl 0.05 mol.L^{-1} at room temperature and on pH 6.5. A three-electrode system was used: working electrode with 1 cm^2 of expose area (aluminum 99.9%); a reference electrode (Saturated Calomel Electrode - SCE) and, a platinum counter electrode. The electrochemical measurements were performed using a potentiostat (Autolab PGSTAT 30, Echo Chemie, The Netherlands) coupled to a frequency response analyzer (FRA 2). The potentiodynamic polarization curves were recorded at a scan rate of 2 mVs^{-1}. The Electrochemical Impedance Spectroscopy (EIS) measurements were performed in potentiostatic mode at the open circuit potential, OCP. The amplitude of the EIS perturbation signal was 10 mV, and the frequency range studied was from 10^5 Hz to 10^{-2} Hz.

Results and Discussion

In this study we evaluated the tannin from black wattle tree bark as a corrosion inhibitor using Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization. The analyses were performed in order to assess the effect of the tannin concentration as a natural inhibitor of aluminum corrosion. Measurements were made after immersion the metal for 1 h in tannin solutions prepared in NaCl 0.05 mol. L^{-1} whereas a blank sample (Pb) was carried out in the absence of tannin.

The corrosion potential (Ecorr) was measured in order to determine the time to reach the stability in the Ecorr values which is necessary to perform the EIS analyses. The Ecorr was determined for the working electrode in relation to SCE (the reference electrode) in 4.0 g.L^{-1}, 5.0 g.L^{-1} and 6.0 g.L^{-1} of tannin solution. As it may be verified in Figure 4, the Ecorr changed for more negative values in the presence of tannin, comparing it to the sample in absence of tannin that was -0.65 V, using NaCl 0.05 mol.L^{-1} as electrolyte solution.

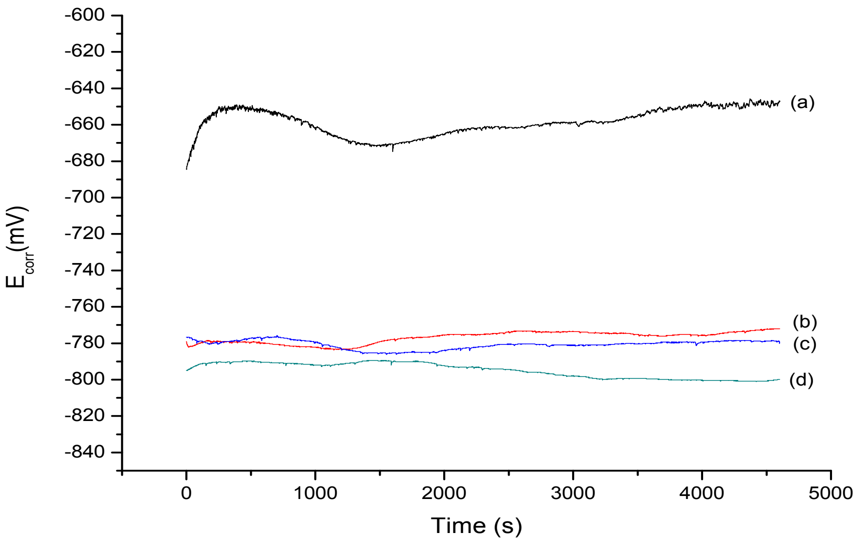

Figure 1 - Corrosion potential (E_{corr}) concerning the reference electrode (SCE) curves of aluminum immersed along the time in presence of tannin - 4.0 g.L^{-1} (b), 5.0 g.L^{-1} (c) and 6.0 g.L^{-1} (d) - and in absence of tannin (a).

After approximately 60 min it was observed a slight decrease of Ecorr, while the tannin concentration increased (-0.77 V, -0.78 V and -0.80 V in 4.0 g.L^{-1}, 5.0 g.L^{-1}, and 6.0 g.L^{-1} of tannin, respectively). On this immersion time, all samples reached stable Ecorr values indicating that it is the enough time to be applied in electrochemical studies for the system in use.

The Nyquist and Bode plots for different tannin concentrations are presented in Figure 2 and Figure 3, respectively.

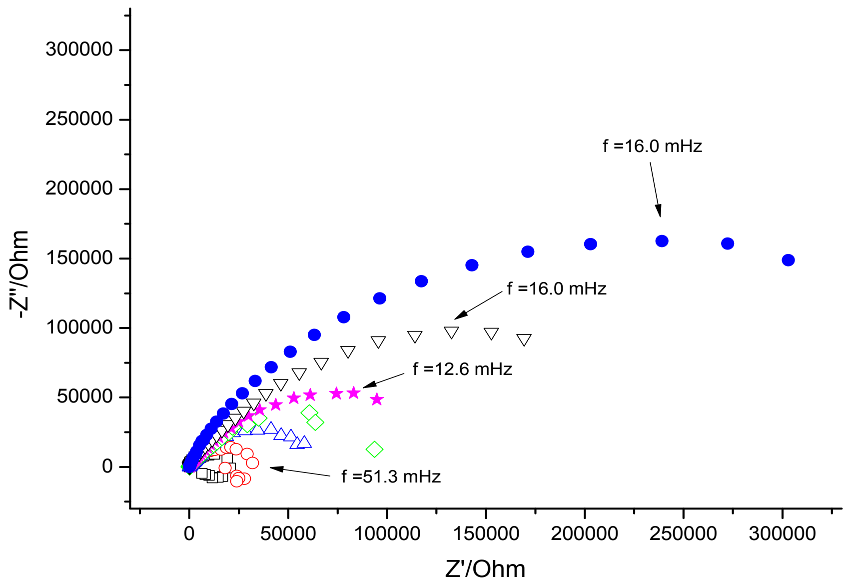

Figure 2 - Nyquist plots for aluminum immersed along 1 h in the following concentrations of tannin: 6.0 gL^{-1} (●); 5.0 gL^{-1}(▽); 4.0 gL^{-1}(★); 3.0 gL^{-1}(◇); 2.0 gL^{-1}(△); 0.5 gL^{-1}(○) and the blank sample (□).

In the Nyquist diagram (Figure 2) it is possible to observe that the resistance values increased with the tannin concentration. For concentrations higher than 0.5 g.L^{-1} inductance was not observed as verified in the blank and 0.5 g.L^{-1} tannin solution. Tannin concentrations up to 4.0 g.L^{-1} showed no significant differences as observed in 5.0 and 6.0 g.L^{-1} which resistance values were significantly higher than the previous tannin concentrations.

The resistance of the metal in absence of tannin was 7.3 kΩcm², meanwhile the polarization resistance (Rp) was 20.9 kΩcm², 79.1 kΩcm², 103.7 kΩcm², 176.0 kΩcm², 282.8 kΩcm², and 461.3 kΩcm² for 0.5 g.L^{-1}, 2.0 g.L^{-1}, 3.0 g.L^{-1}, 4.0 g.L^{-1}, 5.0 g.L^{-1}, and 6.0 g.L^{-1}, respectively for the metal immersed in tannin solution. Thereby those results show that the tannin should be used as an environmentally compliant inhibitor for aluminum.

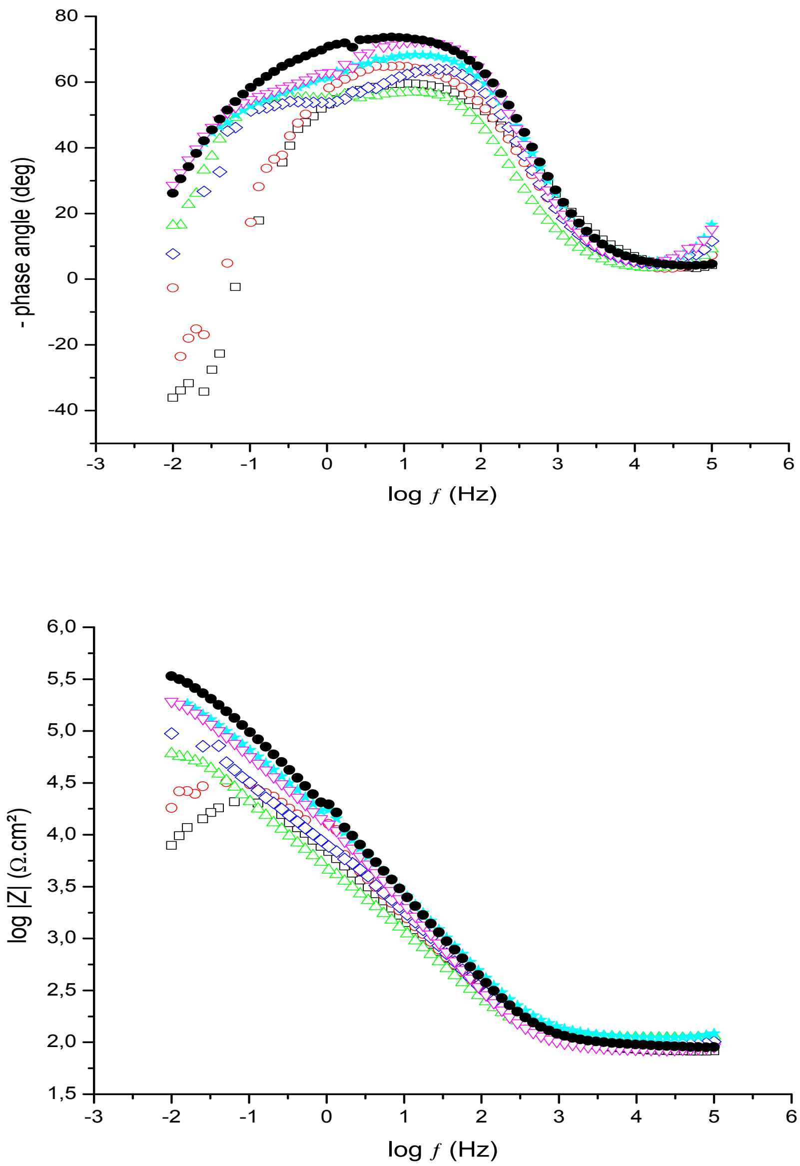

Figure 3 - Bode plots for aluminum immersed along 1 h in the following concentrations of tannin solution: 6.0 gL^{-1}(●; 5.0 gL^{-1}(▽); 4.0 gL^{-1}(★); 3.0 gL^{-1} (◇); 2.0 gL^{-1}(△); 0.5 gL^{-1}(○) and the blank sample (□).

According to Figure 3, the plot results obtained when the metal was immersed in the 0.5 $g.L^{-1}$ tannin solution and the one obtained in the absence of tannin were very similar. The tannin concentration in the 0.5 $g.L^{-1}$ tannin solution may not have been sufficient to work as an inhibitor and, probably, it was not enough to be adsorbed on the aluminum surface. On the other hand, all the samples plot, except 0.5 $g.L^{-1}$, presented overlapped two time constants, one at medium frequency and one at low frequency, which can be observed in the Bode plot. The maximum phase angles were around -70º and -50º, respectively. The EIS spectra can be explained by the inhibitor adsorption on the metal surface which resulted in an increase polarization resistance of metal.

From the Nyquist plot it was possible to calculate the inhibition efficiency (EI) as it is shown in Table 1.

Table 1 - Tannin inhibition efficiency obtained from electrochemical impedance spectroscopy (EIS)

Tannin concentration ($g.L^{-1}$)	**Inhibition efficiency (%)**
0.5	43.24
2.0	74.26
3.0	80.36
4.0	88.42
5.0	92.80
6.0	95.58

The inhibition efficiencies IE (%) values were calculated from the polarization resistance by the ratio between the difference of polarization resistance of the metal in the electrolyte solution when in presence and absence of tannin and the polarization resistance with tannin for each concentration of tannin solution (11). This polarization resistance corresponds to the overall resistance encompassing the charge transfer resistance and the process of substrate dissolution resistance. According to the values obtained, the IE increased with the concentration of tannin in the solution. The tannin concentrations of 4.0 $g.L^{-1}$, 5.0 $g.L^{-1}$, and 6.0 $g.L^{-1}$ showed high inhibition efficiency, as it can be verified in Table 1. Besides, it is possible to realize that the tannin solutions content 5.0 $g.L^{-1}$ and 6.0 $g.L^{-1}$ presented very close IE, which was 92.80 % and 95.58 %, respectively. These findings suggest the good action of tannin in corrosion protection of aluminum samples.

Taking into account the good results of IE presented by solutions with 5.0 $g.L^{-1}$ and 6.0 $g.L^{-1}$ of tannin, the polarization curves were plotted as showed in Figure 3.

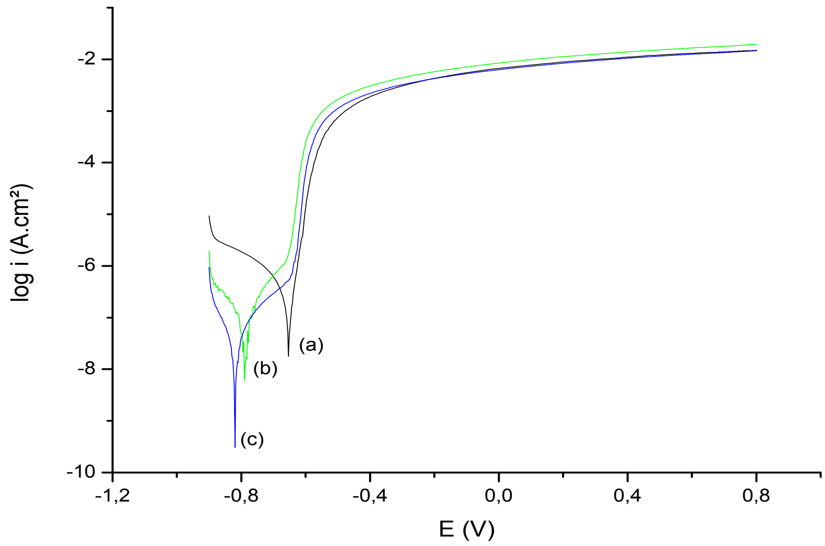

Figure 4 - Potentiodynamic polarization curves of aluminum immersed along 1 h in the following concentrations of tannin solution: 6.0 gL^{-1} (c); 5.0 gL^{-1} (b), and the blank sample (a).

The Figure 4 shows the potentiodynamic polarization comparison among the samples in absence of tannin (a) and in 5.0 $g.L^{-1}$ (b) and 6.0 $g.L^{-1}$ (c) of tannin solution. It is verified that the cathodic current densities prominently decreased in the presence of tannin. Meanwhile the anodic current densities showed no significant alteration. As it can be seen the corrosion rate decreased by shifting the cathodic curves, indicating that the black wattle tree bark tannin in 0.05 $mol.L^{-1}$ NaCl solution acts as cathodic inhibitor for aluminum.

In order to verify the electrochemical performance, the resistances were analyzed for a longer period above 1 h. In the Figure 5 are depicts the EIS diagrams obtained to aluminum panels after 72 h of immersion in 4.0 $g.L^{-1}$ and 6.0 $g.L^{-1}$ of tannin solution and in absence of tannin.

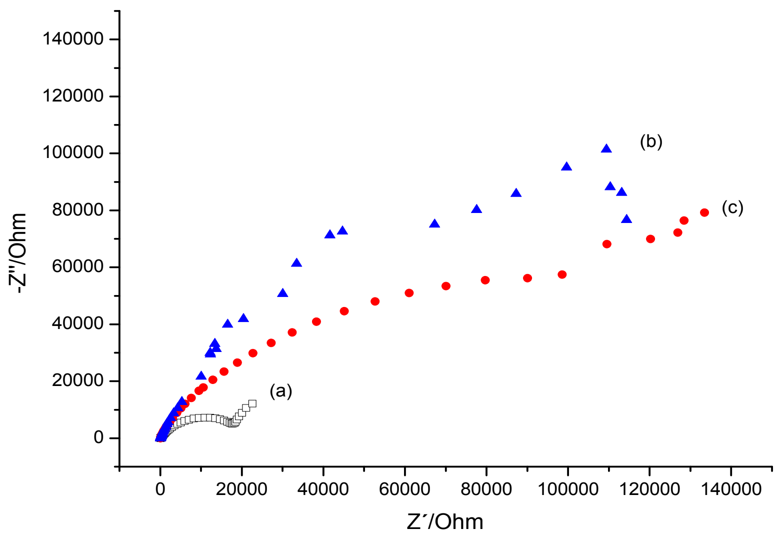

Figure 5 - Nyquist plots for aluminum immersed along 72 h in 4.0 $g.L^{-1}$ (b) and 6.0 $g.L^{-1}$ (c) of tannin and in absence of tannin (a).

Even within 72 h aluminum immersion in 4.0 g.L^{-1} (Figure 5b) and 6.0 g.L^{-1} (Figure 5c) tannin solution, it was observed in the Nyquist plots (Figure 5) that the system still maintained good inhibitor properties which can be compared to the solution in absence of tannin (Figure 5a).

Besides, it is possible to compare the Nyquist plot presented in Figure 5 (72 h immersion) to that one presented in Figure 1 (1 h immersion). The inductance noticed in the 1 hour immersion blank sample was not observed in the 72 h immersion sample. That behavior can be associated to formation of corrosion products on the metallic surface. In relation to 4.0 g.L^{-1} tannin solution, the working electrode showed higher resistance when it was immersed along 72 h than the one was immersed along 1 h. However, for the highest concentration - 6.0 g.L^{-1} tannin solution - when the working electrode was immersed along 72 h, the resistance was lower than the one immersed along 1 h. That can be noticed by the Rp shifted from 94.9 kΩcm² and 303.0 kΩcm² to 181.2 kΩcm² and 200.0 kΩcm² in 1 h and 72 h for 4.0 g.L^{-1} and 6.0 g.L^{-1}, respectively, and from 7.3 kΩcm² at 1 h to 21.8 kΩcm² at 72 h in the absence of tannin. That behavior can be associated to deposition of corrosion products on the aluminum surface.

In Figure 6 are presented the Bode plots related to 72 h aluminum immersion in 4.0 g.L^{-1} and 6.0 g.L^{-1} tannin solution. Both plots showed better results in relation to the one in absence of tannin. In comparison with Figure 3 it is possible to compare the maximum phase angles between 1 h and 72 h of aluminum immersion in tannin solution that were around -70º and -50º at 1 h and -70º and -75º at 72 h for 4.0 g.L^{-1} and 6.0 g.L^{-1}, respectively.

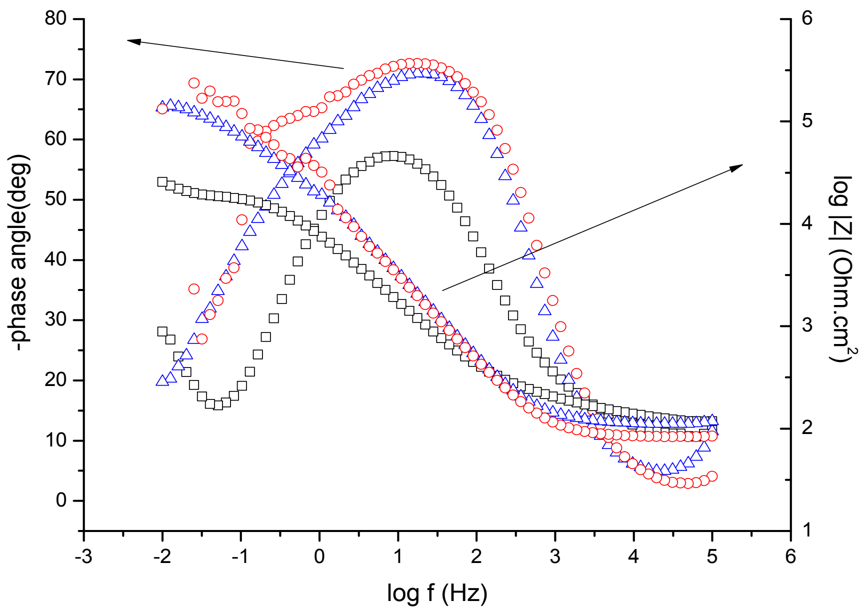

Figure 6 - Bode plots for aluminum immersed along 72 h in 4.0 g.L^{-1} (Δ) and 6.0 g.L^{-1} (○) of tannin and in absence of tannin (□).

Conclusion

In this study it was observed that the tannin inhibition action increases with the tannin concentration in a 0.05 mol.L^{-1} NaCl solution along 1 h of aluminum immersion.

The EIS spectra demonstrated that inhibitor adsorption occurs on the metal surface, resulting in a metal resistance increase for polarization. The inhibition efficiency was calculated for samples over 2.0 g.L^{-1} tannin solution, which were higher than 50 % whereas 5.0 g.L^{-1} and 6.0 g.L^{-1} of tannin solution achieved higher than 95 % of inhibition efficiency. The satisfactory inhibition efficiency can be related to the inhibitor adsorption on the metal surface which was observed by the overlapping two times constant that appeared for samples immersed in tannin solutions over 2.0 g.L^{-1}. According to the dynamic polarization, in presence of tannin solution there was diminishing of cathodic current densities.

It was also verified that in 72 h the tannin still presented a good inhibition action.

The results obtained in this work revealed that tannin from black wattle tree bark extracted from the Acacia *mearnsii* De Wild presents good electrochemical properties, suggesting that tannin should be used as an environmentally compliant inhibitor with good action in corrosion protection of aluminum.

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