

Research Article

Black Wattle Tannin As Steel Corrosion Inhibitor

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In order to reduce the environmental impacts caused by chemical substances harmful to the environment and human health, the black wattle tannin can be used as an environmentally friendly corrosion inhibitor in acid and near neutral media. This paper provides information on the application of black wattle tannin as an inhibitor against the corrosion of carbon steel. The inhibition was evaluated using potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS) at room temperature in aerated 0.1 mol L⁻¹ Na₂SO₄ (pH 6.0 and 2.5). The black wattle tannin when used as a corrosion inhibitor is more effective at acidic pH, its efficiency being dependent on its concentration. At the higher pH value (pH 6.0), a blue-black film (ferric tannate) with a short-term protection against corrosion was formed in aerated aqueous solution. At pH 2.5, this blue-black film was not observed.

1. Introduction

Tannins comprise two different classes of polyphenolic compounds; hydrolysable and condensed tannins. The condensed tannins are found in substantial concentration in the wood and bark of several trees, for instance, black wattle [1]. The tannin extracted from the bark of the black wattle tree contains flavonoid units such as (-)-robinetinidol, (+)-catechin, and (+)-gallocatechin [2]. The flavonoid units are tree-ring flavonols with fifteen carbons. The molecular weight of condensed tannins ranges from around 500 to over 20,000 [1–3].

The hydrolysable tannins are obtained from the fruit, pod, and wood of several trees (fruit of *Terminalia chebula*, pod of *Caesalpinia coriaria*, and wood of *Castanea valonea*) [1–4]. This class of tannin is made up mainly of gallic and digallic acids, which are often esterified to polyols [3], and have molecular weights of up to 3000 [1].

Due to the OH⁻ groups in the ortho position on the aromatic rings, tannins are able to form chelates with iron and other metallic cations (e.g., copper) [5]. Yahya et al. reported the formation of ferric tannate with both condensed and hydrolysable tannins [6]. When Fe³⁺ ions react with OH⁻

groups in the orthoposition in aerated aqueous solution, a highly insoluble and blue-black complex (ferric tannate) is formed [7].

The application of tannins in corrosion studies has been investigated by several authors and their efficiency is controversial. According to Favre et al. the presence of hydrolysable tannin (gallic acid) inhibits the formation of magnetite when lepidocrocite is reduced [8, 9]. Electrochemical impedance spectroscopy (EIS) experiments performed by Galvan et al. showed no substantial increase in the polarization resistance (R_p) of steel due to treatment of a rusted surface with tannins [10]. On the other hand, some authors have developed a tannin primer that exhibited excellent anticorrosive properties [11–14]. Rahim et al. found that the mangrove tannin and its flavonoid monomers are potential corrosion inhibitors for steel in acidic medium [15]. According to Ross and Francis, some of the rust is converted to more stable, inert, and adherent products [16]. These contradictory results may be due to the diversity of material used in the different studies [17, 18].

Martinez investigated the mechanism of the adsorption of mimosa tannin onto low-carbon steel in sulphuric acidic solutions. At pH 1 and 2, the value of the free energy of adsorption suggests a chemisorption mechanism. This mechanism

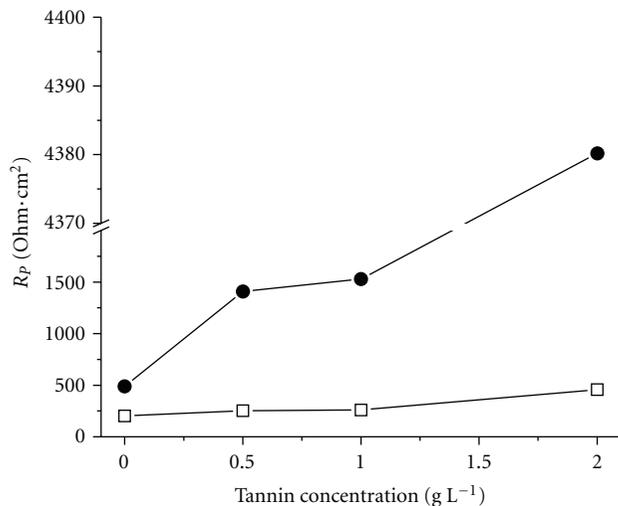


FIGURE 1: Influence of tannin concentration in the polarization resistance (R_p) for carbon steel samples immersed 1 day in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solutions: (□) pH 2.5 medium and (●) pH 6 medium.

occurs due to the formation of an adsorption bond between the oxygen lone-pair electrons of the tannin ^-OH group and the metal surface. At $\text{pH} \geq 3$, ferric tannate is formed and the value of the free energy of adsorption suggests a physisorption mechanism of ferric tannate adsorption onto the steel surface [19].

The aim of this study was to evaluate the anticorrosive properties of tannin extracted from the bark of the black wattle tree (*Acacia mearnsii* De Wild.) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at pH 6.0 and 2.5 for application on carbon steel. The corrosion tests were carried out in aerated sulphate solution at room temperature, using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP).

2. Experimental Procedure

2.1. Material. The tannin sample used in this work was supplied by TANAC (Montenegro, Brazil). The chemical composition of the carbon steel samples is given in Table 1. All solutions and samples were prepared with analytical grade reagent. Sulphuric acid (Synth, Brazil) was used to adjust the pH value. Sodium sulphate (VETEC, Brazil) was employed in the preparation of the electrolyte solutions.

2.2. Sample Preparation and Experimental Setup. Disc-working electrodes with an area of approximately 1.0 cm^2 were prepared from the steel samples by cold resin (epoxy) embedding. The surface was prepared by grinding with silicon carbide paper up to grade number 1200 followed by degreasing with an acetone/chloroform mixture (1 : 1) and drying under a hot air stream.

A saturated calomel electrode ($E = 0.241 \text{ V/NHE}$) was used as the reference electrode, and all potentials are referred to it. The auxiliary electrode was a Pt wire. The experiments were carried out under naturally aerated conditions at 25°C .

TABLE 1: Chemical composition of carbon steel sample.

Element	Chemical composition					
	C	Mn	P	S	Cu	Cr
wt.%	0.103	0.46	0.013	0.096	0.01	0.18

The electrochemical measurements were performed using a potentiostat (AUTOLAB PGSTAT 30, (Echo Chemie, The Netherlands)) coupled to a frequency response analyser (FRA 2). The software used for analysis of impedance spectra was FRA 4.9 (Echo Chemie, The Netherlands). The potentiodynamic polarization curves were recording at a scan rate of 1 mVs^{-1} . The corrosion potentials (E_{corr}) and the polarization resistances (R_p) were calculated at a scan rate of 0.1 mVs^{-1} with potential range of $E_{\text{corr}} \pm 20 \text{ mV}$. This method was based on ASTM G59 [20] and ASTM G102 [21] standards.

The EIS measurements were performed in potentiostatic mode at the open circuit potential, OCP. The OCP after potential stabilization is referred to in this study as the corrosion potential, E_{corr} . The amplitude of the EIS perturbation signal was 10 mV , and the frequency range studied was from 10^5 to 10^{-2} Hz .

Fourier transform infrared (FTIR) analysis was performed with a Perkin Elmer Spectrum 1000 spectrometer.

3. Results and Discussion

3.1. Influence of Black Wattle Tannin Concentration. Figure 1 shows the polarization resistance (R_p) for carbon steel samples immersed for 1 day in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solutions (pH 2.5 and 6) with different concentrations of black wattle tannin. The R_p values were obtained from stepwise potentiostatic polarization using a single small potential step (ΔE) of $\pm 20 \text{ mV}$.

At concentrations of up to 2 g L^{-1} of tannin, the R_p values of the steel samples increase for both mediums (pH 2.5 and pH 6). Concentrations above 2 g L^{-1} were not tested due to the presence of nondissolved black wattle tannin particles in Na_2SO_4 solutions at room temperature. Thus, in this study, the concentration of tannin used as an inhibitor was 2 g L^{-1} in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution. This concentration is not very different from that reported by Rahim et al. who tested the efficiency of mangrove tannin [15, 22].

3.2. Study at pH 6.0. After one hour of immersion in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0), a nonadherent blue-black film on the steel surface and a blue-black precipitate on the bulk of the electrolyte were observed. Some authors have attributed the formation of these blue-black products to ferric-tannate formation [23]. Fourier transform infrared (FTIR) analysis was performed in order to verify whether these blue-black products were ferric tannate.

3.2.1. Results of Fourier Transform Infrared (FTIR) Analysis. The FTIR spectrum of the black wattle tannin (Figure 2(a)) shows a broad absorption band with a maximum absorbance

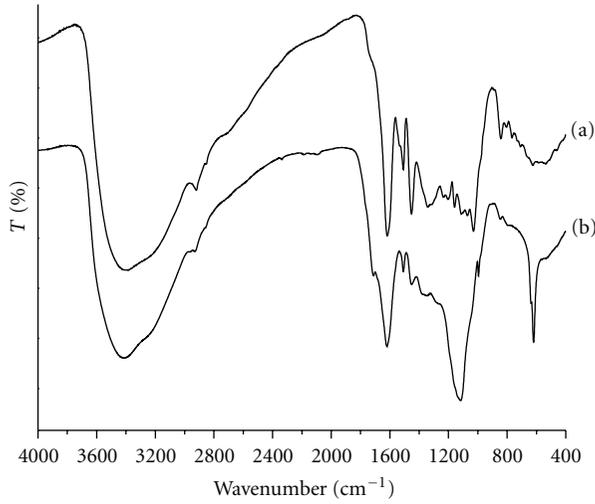


FIGURE 2: (a) FTIR spectrum of the black wattle tannin and (b) FTIR spectrum of the blue-black precipitate formed in the bulk of the electrolyte after one hour of immersion of steel in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0) in the presence of acacia tannin.

at 3413 cm^{-1} which is due to the presence of hydroxyl groups [15]. Peaks occurring between 1600 and 1450 cm^{-1} are characteristic of aromatic compounds [15]. Various peaks in the 600 – 1300 cm^{-1} correspond to substituted benzene rings [15].

Figure 2(b) shows the FTIR spectrum of the blue-black precipitate. The reduced intensity (11.90% to 20.02% of transmittance) of the broad peak at around 3413 cm^{-1} shows the reduction of free OH groups [24]. These hydroxyl groups in aromatic rings enable the tannins to form ferric-tannate complexes. In this way, the formation of ferric tannate was detected. The peaks occurring at 1110 cm^{-1} and 619 cm^{-1} are characteristic of sulphate groups (electrolyte solution) [25, 26].

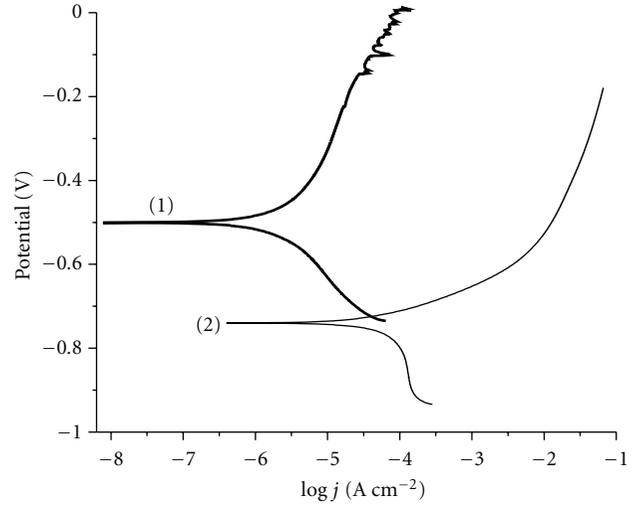
3.2.2. Potentiodynamic Polarization. The potentiodynamic polarization curves of steel immersed in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0), in the presence and absence of tannin, were obtained from 600 mV up to E_{corr} and 300 mV down to E_{corr} after different periods of immersion (Figure 3).

According to Figure 3, the anodic current densities decrease in the presence of tannin in all immersion times, while the cathodic current densities show no significant modification. The presence of the black wattle tannin shifts the E_{corr} to more positive values in all immersion times.

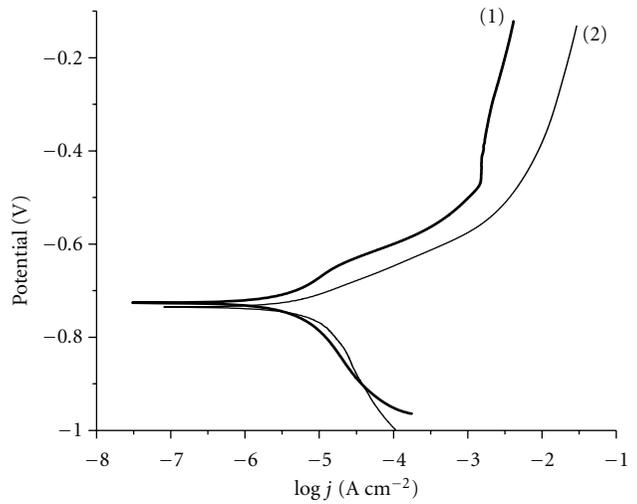
The corrosion current densities (j_{corr}) in Table 2 were calculated from the extrapolation of the anodic and cathodic Tafel lines (Figure 3). The inhibition efficiencies IE (%) were calculated by the polarization resistance according to (1) [15]:

$$\text{IE (\%)} = \frac{R_{p_{\text{tannin}}} - R_p}{R_{p_{\text{tannin}}}} \times 100, \quad (1)$$

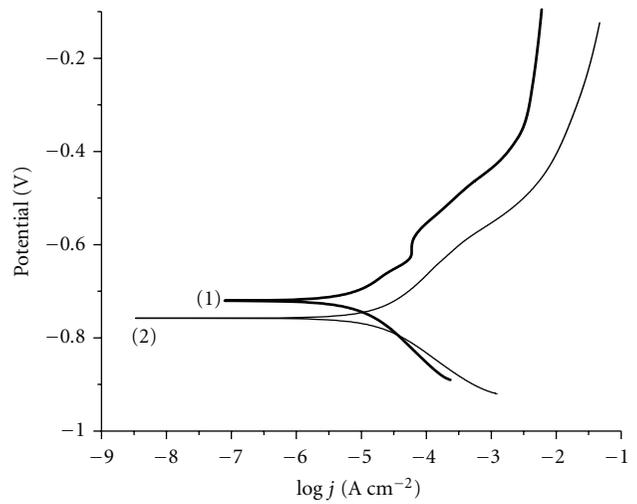
where $R_{p_{\text{tannin}}}$ and R_p are the polarization resistance value with the presence and absence of black wattle tannin, respectively.



(a)



(b)



(c)

FIGURE 3: Potentiodynamic polarization curves of steel immersed in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0) in the presence of tannin (1) and absence of tannin (2) for (a) 1 day, (b) 3 days, and (c) 7 days.

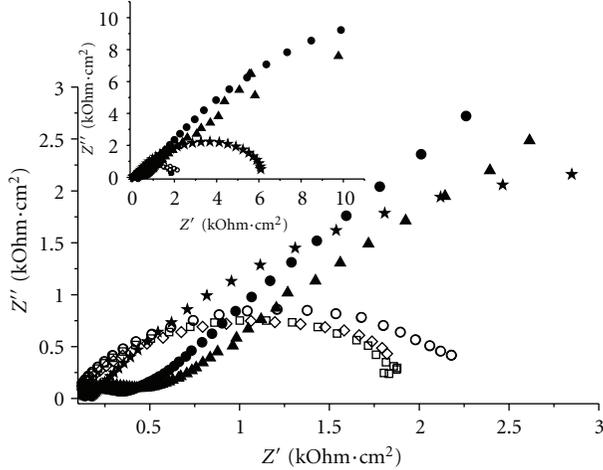


FIGURE 4: Nyquist plots for steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0) for 1 day (closed triangle), 3 days (closed circle), and 7 days (closed star) in the presence of tannin; and for 1 day (open square), 3 days (open lozenge), and 7 days (open circle) in the absence of tannin.

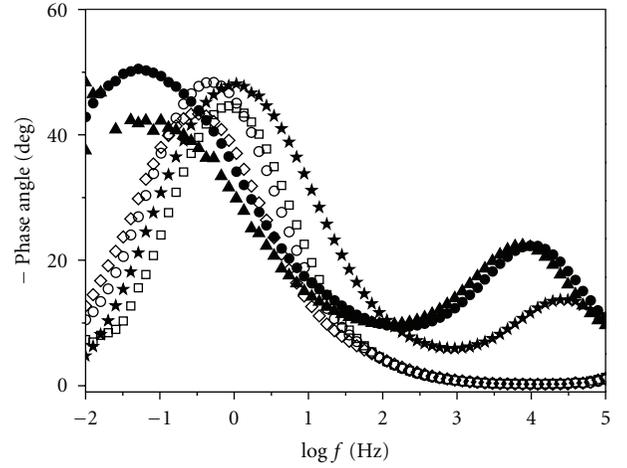
TABLE 2: Polarization parameters for the corrosion of carbon steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0), in the presence and absence of tannin, for different periods.

	j_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (V)	R_p ($\Omega \text{ cm}^2$)	IE (%)
1 day	39.66	-0.73	486.46	91.06
1 day with tannin	0.883	-0.50	5446.0	
3 days	20.52	-0.73	461.37	93.03
3 days with tannin	1.512	-0.72	6622.2	
7 days	13.58	-0.75	481.21	75.74
7 days with tannin	3.241	-0.72	1984.3	

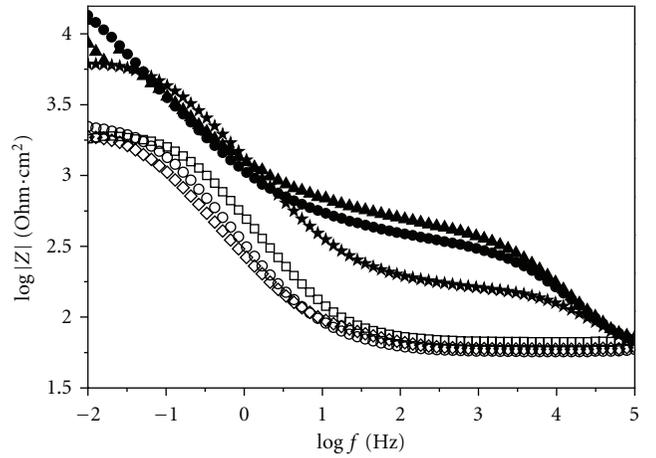
The j_{corr} value decreases significantly in the presence of tannin during the first three days of immersion. In the seventh day, the difference between the blank j_{corr} and the inhibitor j_{corr} decreases. The inhibition efficiency remains almost constant for the first and third days, though decreased on the seventh day of immersion.

3.2.3. Electrochemical Impedance Spectroscopy (EIS). The EIS spectra for the steel in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0), in the presence and absence of tannin, for different periods are shown in Figures 4 and 5.

After 1, 3, and 7 days of immersion in the presence of tannin the plots show two time constants, one at high frequency and one at low frequency with maximum phase angles of around -20° and -45° , respectively. The evolution of the EIS spectra may be related to the adsorption of the inhibitor on the metal surface resulting in an increase in the resistance of the steel to polarization. The experimental data shown in Figures 4 and 5 were fitted using two different equivalent circuits (EC) depending on the immersion time as shown in Figure 6. The fitting quality was evaluated based on



(a)



(b)

FIGURE 5: Bode plots for steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0) for 1 day (closed triangle), 3 days (closed circle), and 7 days (closed star) in the presence of tannin; for 1 day (open square), 3 days (open lozenge), and 7 days (open circle) in the absence of tannin.

the error percentage associated with each component, showing errors smaller than 5%. The software used to simulate the EIS data was NOVA 1.7 (Echo Chemie, The Netherlands). The simulated data obtained from the fittings are given in Table 3.

The equivalent circuit (EC) proposed for fitting the EIS diagram after 1, 3, and 7 days of immersion in the presence of tannin is $R_s(Q_1[R_1(Q_2R_2)])$ where R_s represents the ohmic resistance between the reference and working electrodes, R_1 and R_2 represent the resistance or charge transfer in physical meaning [27]. The Q_1 and Q_2 parameters are the impedance related to a constant phase element (CPE) and can be attributed electrode surface or adsorbed species [27]. The CPE impedance takes into account the phenomena due to the surface heterogeneities. The CPE impedance is given by (2) [27]:

$$\frac{1}{Z_{\text{CPE}}} = Q(j\omega)^n, \quad (2)$$

TABLE 3: Fitting parameters used to simulate the EIS plots for steel immersed for 1, 3, and 7 days in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0) in the presence and absence of tannin.

Immersion time	Chi-square	Equivalent circuit	Fitting parameters									
			R_s ($\Omega \text{ cm}^2$)	R_1 ($\text{k}\Omega \text{ cm}^2$)	Q_1 (F cm^2)	n	R_s ($\Omega \text{ cm}^2$)	Q_1 (F cm^2)	n_1	R_1 ($\text{k}\Omega \text{ cm}^2$)	Q_2 (F cm^2)	n_2
1 day	1.3×10^{-3}		69.2	1.85	1.48×10^{-4}	0.80						
3 days	0.9×10^{-3}	$R_s(R_1Q_1)$	61.4	2.13	3.01×10^{-4}	0.73						
7 days	1.1×10^{-3}		58.6	2.30	2.24×10^{-4}	0.78						
1 day with tannin	3.1×10^{-3}		64.1	2.34×10^{-6}	0.64	0.369	1.84×10^{-4}	0.57	53.7			
3 days with tannin	2.6×10^{-3}	$R_s(Q_1[R_1(Q_2R_2)])$	62.3	3.10×10^{-6}	0.60	0.378	1.57×10^{-4}	0.63	66.5			
7 days with tannin	3.4×10^{-3}		65.6	2.68×10^{-6}	0.60	0.112	7.83×10^{-5}	0.73	6.56			

R_s represents the ohmic resistance between the reference and working electrodes; R_1 and R_2 represent the resistance or charge transfer; Q_1 and Q_2 are the impedance related to a constant phase element (CPE) and can be attributed to electrode surface or adsorbed species; n , n_1 , and n_2 represent a CPE exponent. Capacitor for $n = 1$, a resistor for $n = 0$, and a diffusion process for $n = 0.5$.

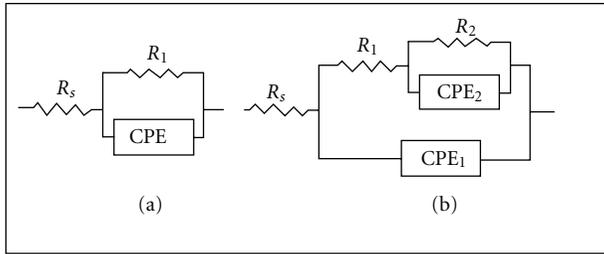


FIGURE 6: Equivalent electric circuits proposed to simulate the experimental data of steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ (pH 6.0) for (a) 1, 3, and 7 days in the absence of tannin; for (b) 1, 3, and 7 days in the presence of tannin.

TABLE 4: Black wattle tannin inhibition efficiencies obtained from electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 6.0).

	Potentiodynamic polarization (PP)	Electrochemical impedance spectroscopy (EIS)
	IE (%)	IE (%)
1 day	91.06	96.57
3 days	93.03	96.81
7 days	75.74	65.52

where Z_{CPE} is the impedance and ω is the angular frequency. The CPE represents a capacitor for $n = 1$, a resistor for $n = 0$, and a diffusion process for $n = 0.5$.

The EC proposed for 1, 3, and 7 days in the presence of tannin has two time constants. The first constant R_1Q_1 represents the time constant of high frequency which is relative to the charge transfer reactions and double layer. The second constant R_2Q_2 represents the time constant of low frequency which is relative to the adsorption processes. For all times of immersion in the absence of tannin, the EC proposed was $R_s(R_1Q_1)$, which contains one time constant which is related with charge transfer reactions and double layer.

The Nyquist diagram (Figure 4) shows a small variation in the polarization resistance during the first three days of immersion in the absence of tannin. On the seventh day,

TABLE 5: Polarization parameters for the corrosion of carbon steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5), in the presence and absence of tannin, for different periods.

	j_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (V)	R_p ($\Omega \text{ cm}^2$)	IE (%)
1 day	103.4	-0.65	202.76	55.7
1 day with tannin	25.90	-0.60	457.58	
3 days	123.73	-0.68	76.863	62.0
3 days with tannin	25.93	-0.63	202.23	
7 days	122.90	-0.68	68.152	68.7
7 days with tannin	29.20	-0.63	217.72	

there is a small increase in the resistance value which can be attributed to deposition of corrosion products on the metal surface. The R_p values were obtained from the simulated parameters considering that, in all cases, R_p represents the overall resistance. Thus, for the $R_s(Q_1[R_1(Q_2R_2)])$ circuit, this value was obtained from the sum of R_1 and R_2 . The highest values for polarization resistance were found on the first and third day of immersion in the presence of tannin. Table 4 shows the inhibition efficiencies (IE) obtained from electrochemical impedance spectroscopy (EIS) and Potentiodynamic Polarization (PP) by (1). The IE values obtained from both methods are in agreement and show a decrease in corrosion resistance with longer immersion times. This fact can be attributed due to the inhibition mechanism at this pH value which provides a formation of nonadherent and porous ferric tannate complex layer.

3.3. Study at pH 2.5. In the case of the immersion in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5), the formation of the blue-black ferric tannate on the steel surface and in the electrolyte was not observed. According to Martinez and Störn [23], the formation of ferric tannate is not detected at this pH.

3.3.1. Potentiodynamic Polarization. The potentiodynamic polarization curves of steel immersed in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5), in the presence and absence of

TABLE 6: Fitting parameters used to simulate the EIS plots for steel immersed for 1, 3, and 7 days in 0.1 mol L⁻¹ Na₂SO₄ solution (pH 2.5) in the presence and absence of tannin.

Immersion time	Chi-square	Equivalent circuit	Fitting parameters										
			R_s (Ω cm ²)	R_1 (k Ω cm ²)	Q_1 (F cm ²)	n	R_s (Ω cm ²)	Q_1 (F cm ²)	n_1	R_1 (Ω cm ²)	Q_2 (F cm ²)	n_2	R_2 (k Ω cm ²)
1 day with tannin	1.9×10^{-3}		48.1	1.76	4.73×10^{-6}	0.91							
3 days with tannin	2.1×10^{-3}		49.6	2.34	5.68×10^{-6}	0.91							
7 days with tannin	1.4×10^{-3}	$R_s(R_1Q_1)$	57.4	3.08	4.43×10^{-6}	0.89							
1 day without tannin	2.3×10^{-3}		63.6	0.71	2.80×10^{-5}	0.76							
3 days without tannin	2.1×10^{-3}		49.8	0.70	9.21×10^{-5}	0.66							
7 days without tannin	4.5×10^{-3}	$R_s(R_1Q_1)(R_2Q_2)$	47.2	1.53×10^{-5}	0.74	112	5.49×10^{-4}	0.8	0.68				

R_s represents the ohmic resistance between the reference and working electrodes; R_1 and R_2 represent the resistance or charge transfer; Q_1 and Q_2 are the impedance related to a constant phase element (CPE) and can be attributed to electrode surface or adsorbed species; n , n_1 , and n_2 represent a CPE exponent. Capacitor for $n = 1$, a resistor for $n = 0$, and a diffusion process for $n = 0.5$.

tannin, were obtained from 600 mV up to E_{corr} and 300 mV down to E_{corr} after different periods of immersion (Figure 7).

The anodic current density values decreased in the presence of tannin for all exposure periods tested. Accordingly, the corrosion potential (E_{corr}) of the metal was shifted to a more positive value and the polarization resistance (R_p) increased in the presence of tannin as observed in Table 5. The corrosion current densities (j_{corr}) in Table 5 were calculated from the extrapolation of the anodic and cathodic Tafel lines (Figure 7). The inhibition efficiencies IE (%) were calculated by the polarization resistance according to (1).

The j_{corr} value decreases significantly in the presence of tannin during all days of immersion. The inhibition efficiency increases with the increases of exposure days.

3.3.2. Electrochemical Impedance Spectroscopy (EIS). The EIS spectra for the steel immersed in aerated 0.1 mol L⁻¹ Na₂SO₄ solution (pH 2.5), in the presence and absence of tannin, at OCP, for different periods are shown in Figures 8 and 9.

The Nyquist plots (Figure 8) show a decrease in the R_p value for steel with and an increase in the time of immersion in the aerated 0.1 mol L⁻¹ Na₂SO₄ solution (pH 2.5). In the presence of tannin, the R_p shows the opposite behaviour (increase with increased time of immersion). This can be attributed to the kinetics mechanism of the adsorption of tannin onto the metal surface and/or the formation of corrosion products from the reaction of iron with tannin. The phase angles in the presence of tannin are higher than those in the absence of tannin, reaching a maximum value of -65° which indicates an increase in the capacitive character of the film formed.

The experimental data presented in Figures 8 and 9 were fitted using the two proposed equivalent circuits (EC) shown in Figure 10. The software used to simulate the EIS data was NOVA 1.7 (Echo Chemie, The Netherlands). The simulated data obtained from the fittings are given in Table 6.

The R_s represents the ohmic resistance between the reference and working electrodes, R_1 and R_2 represent the resist-

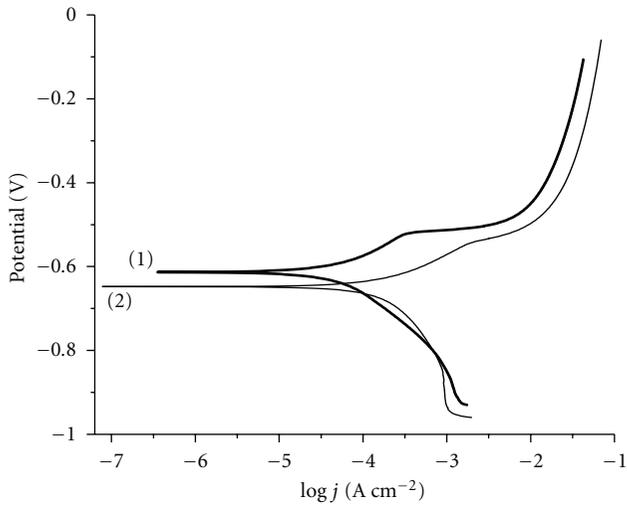
TABLE 7: Black wattle tannin inhibition efficiencies obtained from electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP) in 0.1 mol L⁻¹ Na₂SO₄ solution (pH 6.0).

	Potentiodynamic Polarization (PP)	Electrochemical impedance spectroscopy (EIS)
	IE (%)	IE (%)
1 day	55.7	59.6
3 days	62.0	70.1
7 days	68.7	74.3

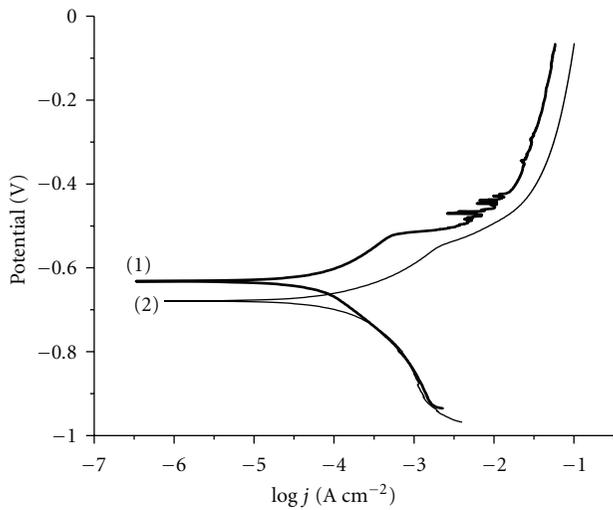
ance or charge transfer in physical meaning [27]. The Q_1 and Q_2 parameters are the impedance related to a constant phase element (CPE) and can be attributed to electrode surface or adsorbed species. The EC proposed for all immersion times in the presence of tannin, and for 1 and 3 days, and in the absence of tannin, was $R_s(Q_1R_1)$. The R_1Q_1 represents the time constant which is relative to the charge transfer reactions and double layer. For fitting, the EIS diagram for 1 day of immersion in the absence of tannin the EC used was $R_s(Q_1R_1)(Q_2R_2)$, which has two time constants. The first constant R_1Q_1 represents the time constant of high frequency which is relative to the charge transfer reactions and double layer. The second constant R_2Q_2 represents the time constant of low frequency which is relative to the adsorption processes.

A comparison between the capacitance values obtained after 1 and 3 days of immersion in solutions with and without tannin shows that this parameter decreased in the presence of tannin, which is probably due to the adsorption of inhibitor on the metal surface. Accordingly, higher values of R_p were found in the presence of tannin (EIS parameters in Table 6).

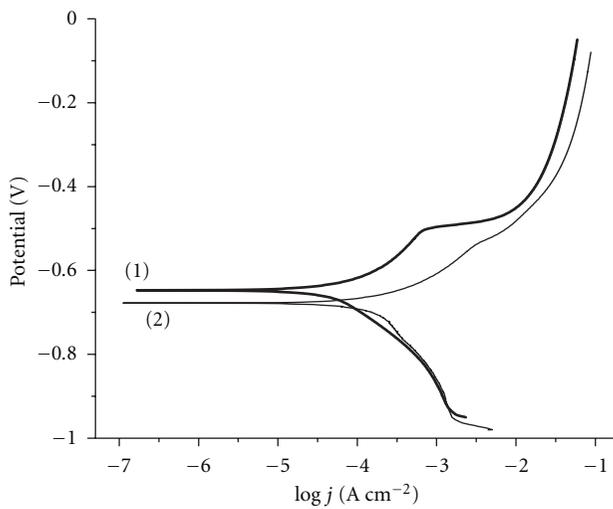
Table 7 shows the inhibition efficiencies (IE) obtained from electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP). The IE values obtained from both methods are in agreement and show an increase



(a)



(b)



(c)

FIGURE 7: Potentiodynamic polarization curves of steel immersed in aerated $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5) in the presence of tannin (1) and absence of tannin (2) for (a) 1 day, (b) 3 days, and (c) 7 days.

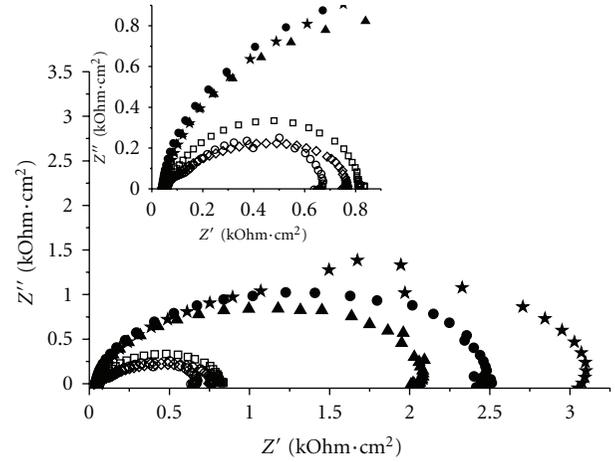
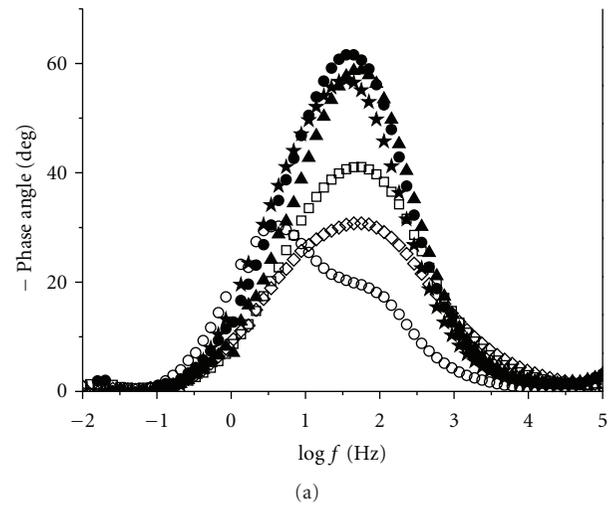
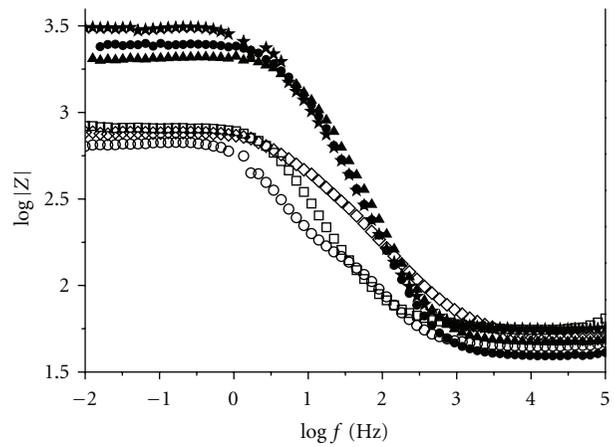


FIGURE 8: Nyquist plots for steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5) for 1 day (closed triangle), 3 days (closed circle), and 7 days (closed star) in the presence of tannin; for 1 day (open square), 3 days (open lozenge), and 7 days (open circle) in the absence of tannin.



(a)



(b)

FIGURE 9: Bode plots for steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5) for 1 day (closed triangle), 3 days (closed circle), and 7 days (closed star) in the presence of tannin; for 1 day (open square), 3 days (open lozenge), and 7 days (open circle) in the absence of tannin.

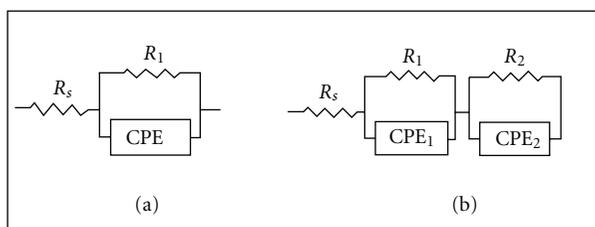


FIGURE 10: Equivalent electric circuits proposed to simulate the experimental data of steel immersed in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution (pH 2.5) for (a) 1, 3, and 7 days in the presence of tannin, 1 and 3 days in the absence of tannin; for (b) 7 days in the absence of tannin.

in corrosion resistance with longer immersion times.

The EIS data demonstrated that at pH 2.5 a distinct behaviour was detected in the presence of tannin, with the formation of a more protective film. The inhibition mechanism of tannin at this pH value should be initially adsorbed on metal surface by electron rich centers of molecule. With increase of immersion time, a layer with adherent nature was formed. That might be a reason of increasing of inhibition efficiency with the increase of immersion time at pH 2.

4. Conclusions

- (i) The inhibition action of black wattle tannin towards the corrosion of steel is dependent on the concentration of tannin added and the pH value of the electrolyte.
- (ii) A nonadherent ferric tannate complex was formed on the steel surface at pH 6 in the presence of black wattle tannin.
- (iii) Ferric tannate was not formed on the steel surface at pH 2.5 in the presence of black wattle tannin.
- (iv) The black acacia tannin showed the formation of a layer with a short-term protection against corrosion at pH 6.
- (v) The black acacia tannin showed the best performance as a corrosion inhibitor at pH 2.5. The inhibition efficiency increased in the presence of tannin.
- (vi) Through EIS, the characteristics and behaviour of the films formed on the steel surface can be identified more clearly. The porosity of the ferric-tannate film and the stronger capacitive character of the film formed in acid medium were identified.

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