

Tannin of *Acacia mearnsii* as green corrosion inhibitor for AA7075-T6 aluminum alloy in acidic medium

Letícia A. L. Guedes | Katryanne G. Bacca | Natália F. Lopes |

Eleani M. da Costa 

School of Technology, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, RS, Brazil

Correspondence

Eleani M. da Costa, School of Technology, Pontifical Catholic University of Rio Grande do Sul, 6681 Ipiranga Avenue, Building 30, Room 111/F, 90619-900 Porto Alegre, RS, Brazil.
Email: eleani@pucrs.br

Funding information

Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES)

The inhibition performance of *Acacia mearnsii* bark tannin was investigated as eco-friendly green inhibitor on the corrosion of AA7075-T6 aluminum alloy in 0.1 M HCl solution by potentiodynamic polarization technique, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). Polarization curves showed that this tannin acts predominantly as a cathodic inhibitor. High corrosion inhibition performance was achieved with inhibition efficiencies of 95% and 97% at 14 g L^{-1} as obtained by polarization and EIS electrochemical techniques, respectively. The SEM images revealed that localized attack initiated at intermetallic particles causing local dissolution of the matrix due to potential differences between them. EIS results and SEM images confirmed the protection of AA7075-T6 aluminum alloy by *A. mearnsii* bark tannin, evidencing the formation of an adsorbed film on the metal surface that attenuate the aluminum dissolution reaction.

KEYWORDS

Acacia mearnsii tannin, aluminum alloy, green corrosion inhibitor

1 | INTRODUCTION

Aluminum and aluminum alloys are used in an extensive variety of applications due to their distinguished properties including low density, high strength good ductility, high thermal and electrical conductivity. In addition, aluminum and its alloys are highly recyclable. Commercial aluminum alloys can be classified into two groups depending on hardening mechanism, which are heat-treatable and non-heat treatable alloys. AA7075 aluminum alloy makes part of the 7XXX series alloys containing Zn, Mg, and Cu as alloying elements and the mechanical resistance of this alloy can be improved by heat treatment. AA7075 alloy is mostly used in components for the aviation and automotive industries.^[1–3] Many components for sporting equipment are also manufactured with this alloy, such as bicycle parts, climbing equipment, skid frames, and hang glider holders.^[4–11] The

heat treatable alloys, as aluminum alloy AA7075, usually have a lower corrosion resistance when compared to the alloys non-heat treatable. The microstructure of these alloys is complex, and the precipitates and intermetallic compounds have electrochemical potentials different from Al matrix, that can cause localized corrosion. In addition, the susceptibility to pitting corrosion increases when the alloys have more than 0.15 wt% of Cu, particularly in environments with the presence of chlorides.^[9,12] The high corrosion resistance of aluminum and its alloys is credited to the formation of a passive oxide film (Al_2O_3) on the surface, which is thin, compact, and adherent. This film is amphoteric and can suffer localized attack when the aluminum is exposed to acid or alkaline solutions and as well as in solutions with the presence of chlorides.^[2,12–17] Hydrochloride acid is very often used to clean the aluminum surface before some industrial processes, such as hot-dip coating or electroplating, in order to remove

scales and dust, but it can cause severe corrosion.^[10,17] Thus, the corrosion control in aluminum and aluminum alloys is very important for some practical applications in the industry.^[3,10,17] Many methods have been proposed for the aluminum corrosion control in different environments, such as anodizing, coatings, and the use of inhibitors. The inhibitors are substances from inorganic or organic nature that when added in small amounts can significantly retard the corrosion. This form of corrosion control has been frequently applied in the industry because the addition of the inhibitor can be done without interruption of the process, which makes this practice particularly advantageous.^[17–19,20]

Corrosion inhibitors based on organic compounds are often applied for aluminum and its alloys to corrosion control and are known as adsorption inhibitors because they have heteroatoms (N, S, O, and P) in the structure that can act as adsorption centers since they have high electron density acting as electron donors, while the metal is the receptor.^[17] However, many commercial corrosion inhibitors cause some concerns related to human health and environment impacts. Thus, the development of nontoxic and environmentally friendly inhibitors is of great importance principally considering the restrictions imposed by recent environmental regulations. The use of different green organic compounds as corrosion inhibitors is very promising because they are renewable, accessible, inexpensive, and non-toxic.^[10,19] The corrosion inhibition action of majority of plant extracts is due to the presence of alkaloids and flavonoids and/or other heterocyclic components.^[19,20–32]

Different extracts have been tested as inhibitor for aluminum alloys in both acid and alkaline mediums. Khadraoui et al.^[23] evaluated the use of the *Thymus algeriensis* plant extract as corrosion inhibitor for the AA2024 aluminum alloy in acid medium (1 M HCl) and at different temperatures. The inhibition efficiency increased with increasing extract concentration reaching 79% of efficiency when 0.75 g L⁻¹ of extract was added in solution. Chaubey et al.^[16] used papaya peel extract as a corrosion inhibitor for aluminum in 1 M HCl. In their studies, inhibition efficiencies of 95% and 98% were found for 2.0 g L⁻¹ of inhibitor by potentiodynamic polarization and by electrochemical impedance, respectively. The papaya extract acted as a cathodic inhibitor, according to the results presented by the authors. Gerengi^[4] investigated the effect of *Phoenix dactylifera* L.-PDL fruit juice on AA7075 aluminum alloy in 3.5% NaCl. The PDL fruit juice behaved as a cathodic inhibitor and the inhibition efficiencies were higher when concentration of PDL fruit juice was increased. Inhibition efficiency of 63% was found for the concentration of 2000 ppm of inhibitor present in solution. In another study, Singh et al.^[10] investigate the efficiency of berberine, an alkaloid found in different plants, in the aluminum alloy AA7075 in 3.5% NaCl solution. This study confirmed that the

effectiveness of the inhibitor decreases with increasing temperature, and increases with the concentration of berberine. Polarization curves showed that both anodic and cathodic branches were changed due to addition of this compound, indicating that berberine performed as mixed type inhibitor. However, many of tested extracts have limited potential when considering the need for large-scale production for industrial application.

The *Acacia mearnsii* (De Wild) is a plant that belongs to the family Fabaceae and subfamily Mimosoideae originated from Australia and is a very common hardwood species being cultivated in several countries. The bark of *A. mearnsii* contains large amounts of tannins, and can reach 30% of the dry weight depending on the process used to extract the tannin. Among other applications, tannin extracted from the bark of *A. mearnsii* (known as black wattle) is currently used industrially to produce vegetable tanned leather, adhesives, and for additives in drilling in the petroleum sector, etc. *A. mearnsii* bark tannin has a great potential to be used as a green inhibitor not only due its antioxidant properties but also because it comes from a renewable source and is already industrially produced in large scale. This tannin is condensed tannin and this group of compounds has a diversity of structures, being formed by flavonoid units.^[26,27,33–37] Peres et al.^[34] applied *A. mearnsii* tannin as a corrosion inhibitor for carbon steel reaching efficiencies up to 97%, and they observed that its efficiency depends on tannin concentration and that it was more effective as inhibitor in acidic medium. In aqueous solutions, tannins form complexes that polymerize on the metal surface forming a protective monolayer that can act as a barrier for the corrosion process. This layer is composed by tannates that are of amorphous nature and are usually insoluble in aqueous solutions. Tannates are organo-metallic compounds resultant from the chemical interaction between tannins and metallic ions.^[37] we did not found in the literature studies about the performance of *A. mearnsii* as inhibitor for aluminum and aluminum alloys. In this context, the objective of this work is to evaluate the potential of the tannin of the *A. mearnsii* as a green inhibitor of the corrosion process on aluminum alloy AA7075-T6 in acidic medium.

2 | MATERIALS AND METHODS

The specimens 2 × 2 mm and 3.2 mm thick used in corrosion tests were obtained from AA7075 aluminum alloy cold-rolled, followed by precipitation hardening heat treatment (T6 temper, solution heat treated and then artificially aged). The alloy chemical composition is shown in Table 1.

The electrochemical study was done using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The electrochemical measurements were carried out with an Autolab potentiostat/galvanostat

TABLE 1 Chemical composition of the AA7075 aluminum alloy obtained by optical emission spectroscopy

Element	Al	Zn	Mg	Cu	Fe	Cr	Si	Mn	Ti	V
% in weight	89.43	5.88	2.47	1.70	0.19	0.173	0.08	0.03	0.02	0.014

(PGSTAT302 N) by using a three-electrode cell. Saturated calomel electrode (SCE) was used as reference electrode and platinum as auxiliary electrode. The working electrode was maintained immersed in the solution for 1 h to reach a steady-state open-circuit potential (OCP) before each electrochemical measurement. For the assembly of the working electrode for electrochemical measurements, the specimens of AA7075-T6 alloy were embedded with epoxy resin using copper wires as contact, and were ground with silicon carbide paper (from # 200 to # 1200), polished with alumina of 1 μm , washed in distilled water and dried with hot air. The exposed area of specimens to the corrosion solution was approximately 2 cm^2 . The EIS was measured at OCP using a sinusoidal potential excitation of 10 mV of amplitude in the frequency range from 10 000 to 0.1 Hz. The impedance data with the equivalent electrical circuits were fitted with Autolab NOVA software. The polarization curves were obtained in a potential range from ± 300 mV in relation to the OCP, with a scanning speed of 1.0 mV s^{-1} . The electrochemical parameters were taken by the Tafel extrapolation method.

The inhibition efficiency E (%) obtained by potentiodynamic polarization technique was calculated as follows:

$$E(\%) = \frac{(CR_0 - CR_{\text{inh}})}{CR_0} \times 100 \quad (1)$$

where CR_0 and CR_{inh} are the corrosion rate of aluminum in 0.1 M HCl without and with inhibitor, respectively.

The degree of surface coverage θ is given by Equation (2):

$$\theta = 1 - \frac{W'_{\text{corr}}}{W_{\text{corr}}} \quad (2)$$

The inhibition efficiency ($\eta\%$) was also obtained by EIS technique using the Equation (3):

$$\eta(\%) = \frac{(R_{\text{po}} - R_{\text{pinh}})}{R_{\text{pinh}}} \times 100 \quad (3)$$

where R_{pinh} and R_{po} are the polarization resistance of aluminum in 0.1 M HCl with without inhibitor, respectively.

Commercial tannin from bark of *A. mearnsii* (Weibull AQ, TANAC, Brazil) in different concentrations (0, 2, 6, 10, 12, and 14 g L^{-1}) was used in corrosion tests. This tannin is extracted with hot water, and afterwards spray drying is used to produce the extract in the form of powder. The tannin was weighted in 0.0001 g precision balance and then diluted in

0.1 M HCl solution to obtain inhibitor test solutions. The homogenization of the solution was carried out in ultrasonic bath during 10 min.

After corrosion tests, the specimens were washed, dried, and kept in desiccator for analysis of corroded surface by scanning electron microscopy with field emission gun (SEM/FEG).

3 | RESULTS AND DISCUSSION

The potentiodynamic polarization curves for the AA7075-T6 aluminum alloy in 0.1 M HCl solution with different concentrations of tannin from the bark of *A. mearnsii* are shown in Figure 1. Table 2 shows the potentiodynamic polarization parameters obtained by the Tafel extrapolation method on the linear part of the cathodic polarization curves, as well the inhibition efficiency (E) and the degree of surface coverage (θ).

As can be seen in Figure 1, the presence of the *A. mearnsii* tannin in 0.1 M HCl solution did not result in a remarkable alteration in the corrosion potential (E_{corr}) value. However, it shifts the cathodic part of the polarization for lower currents densities indicating that the tannin of bark of *A. mearnsii* acts mainly as a cathodic inhibitor for the aluminum alloy AA7075-T6. This behavior was similar to that observed by Gerengi^[4] using fruit juice of the *Phoenix dactylifera L.* palm as a corrosion inhibitor for the same alloy. The fact that the cathodic part of the polarization curves is parallel regardless

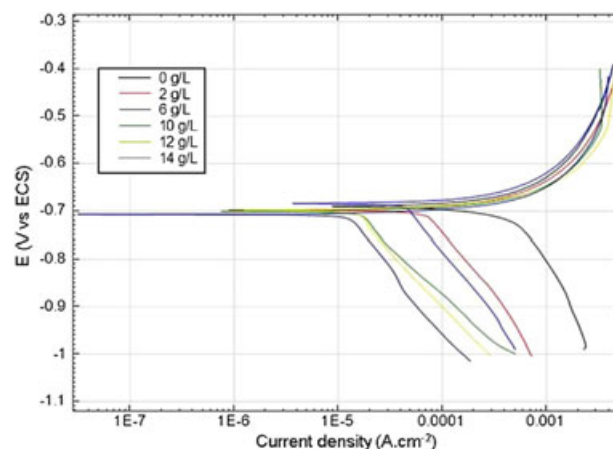


FIGURE 1 Polarization curves for the AA7075-T6 aluminum alloy in 0.1 M HCl with different concentrations of tannin from bark of *A. mearnsii* [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Potentiodynamic polarization parameters obtained for the aluminum alloy AA7075-T6 in 0.1 M HCl with different concentrations of tannin from bark of *A. mearnsii*

C_{inh} [g L ⁻¹]	E_{corr} [mV]	i_{corr} [mA]	Polarization resistance (R_p) [Ω cm ⁻²]	Corrosion rate [mm/year]	Inhibition efficiency (E) %	Degree of surface coverage (θ)
0	-693	0.52	46.80	3.03	0	0
2	-717	0.17	97.71	0.97	67.89	0.68
6	-684	0.11	121.42	0.64	78.88	0.79
10	-737	0.10	134.47	0.53	82.67	0.83
12	-734	0.06	246.42	0.35	88.31	0.88
14	-717	0.03	191.90	0.16	94.67	0.95

of tannin concentrations is an indication that the presence of inhibitor does not alter the hydrogen evolution mechanism (cathodic reaction). The decrease in the rate of cathodic reaction may be related to the fact that with increasing tannin concentration in solution a greater number of tannin molecules are adsorbed on the surface of the alloy, improving the surface coating.^[26]

In the same way, as the tannin behaves as an adsorption inhibitor, the inhibition efficiency (Table 2) increases with the increase of inhibitor concentration providing larger surface coverage because more inhibitor molecules are adsorbed on the metal surface. The inhibition efficiencies calculated are relatively high when compared to the efficiencies reported in literature with the use of green organic inhibitors for aluminum and aluminum alloys in acid medium.^[16,23–25]

It is well known that the inhibitor molecules can be adsorbed on a metal surface by means of forces of physical or chemical nature. In case of physical adsorption, the electrostatic forces are responsible for adhesion of charged inhibitor molecules on the metal surface, while the chemisorption involves the establishment of covalent or coordinate bonds between inhibitor molecules and the metal.^[5] Therefore, adsorption isotherms are frequently used to obtain information about the predominant manner of adsorption of inhibitor molecules on the metal surface. Among other adsorption models, the Langmuir model is often applied. This model assumes that the adsorbed inhibitor molecules do not interact with each other and that a monolayer of adsorbed inhibitor molecules is formed. The general form of Langmuir isotherm model is shown in Equation (4).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

We used Langmuir isotherm model to obtain information about the mode of adsorption of tannin molecules of bark of *A. mearnsii* on the surface of AA7075-T6 alloy. Figure 2 illustrates the relation of the portion of the surface protected

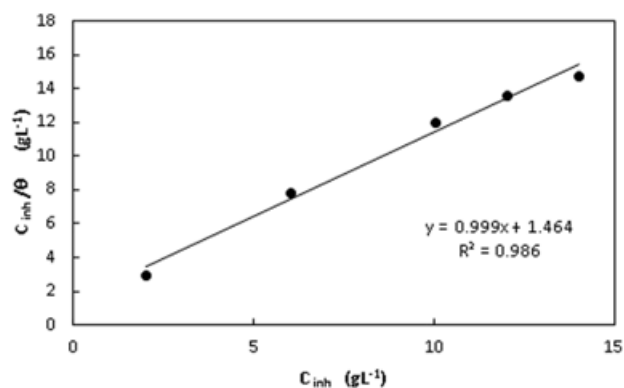
by the adsorbed molecules with the inhibitor concentration (C_{inh}). As can be seen, a straight line with 0.986 of linear regression coefficient (R^2) and a slope very close to unit (0.999) was obtained when C_{inh}/θ versus C_{inh} is plotted, suggesting that the adsorption of inhibitor molecules on the AA7075-T6 aluminum alloy surface obey Langmuir isotherm. This means that the adsorbed molecules of inhibitor do not interact with each other or that there are no repulsion forces involved between them.

Equation (5) shows the relation between K_{ads} and standard Gibbs free energy of adsorption (ΔG_{ads}°):

$$K_{ads} = \frac{1}{C_{(sol)}} e^{\left(\frac{-\Delta G_{ads}^\circ}{RT}\right)} \quad (5)$$

where $C_{(sol)}$ is the concentration of water in solution, R is universal gas constant, and T is the absolute temperature (298 K), and K_{ads} can be obtained from the intercept of Figure 2.

If values of standard Gibbs free energy of adsorption (ΔG_{ads}°) are less than 20 kJ mol⁻¹ (in module) the interaction between the adsorbent and adsorbate is

**FIGURE 2** Adsorption Langmuir's isotherm for tannin molecules from bark of *A. mearnsii* on AA7075-T6 aluminum alloy in 0.1 M HCl.

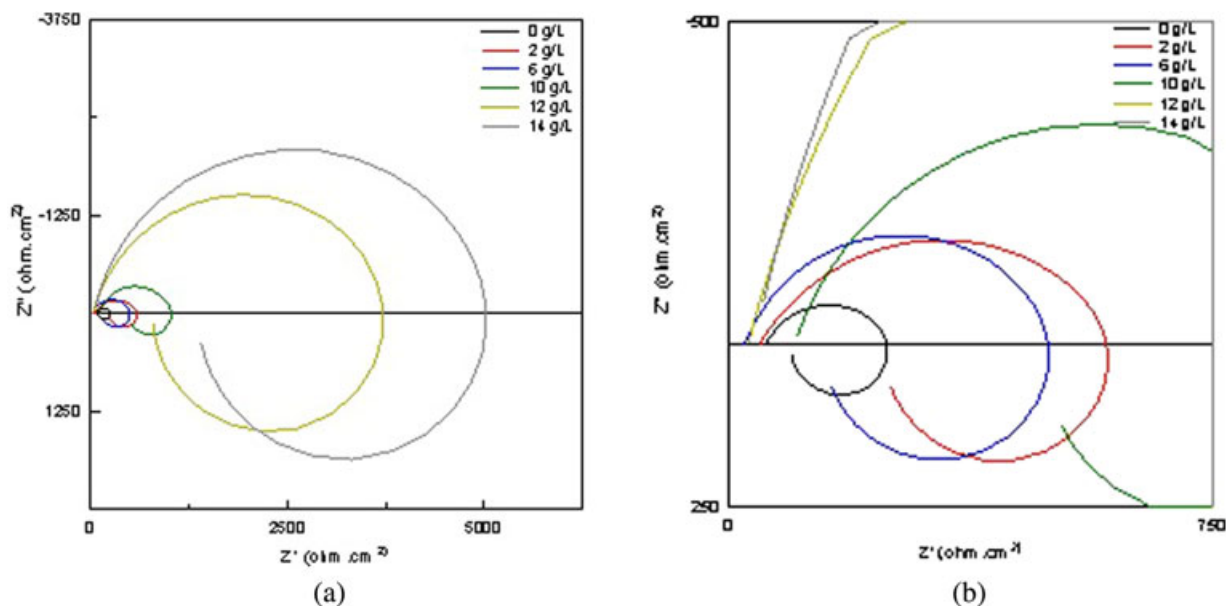


FIGURE 3 (a) Nyquist plot of aluminum alloy AA7075-T6 for different concentrations of tannin from bark of *A. mearnsii* in 0.1 M HCl. (b) Zoom in high frequency zone [Color figure can be viewed at wileyonlinelibrary.com]

electrostatic (physisorption occurs). On the other side, when $\Delta G^{\circ}_{\text{ads}}$ is higher than 40 kJ mol^{-1} (in module) there is sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond (chemisorption).^[30] The calculated value of $\Delta G^{\circ}_{\text{ads}}$ using Equation (4) was -26 kJ mol^{-1} indicating that adsorption of compound molecules of tannin from bark of *A. mearnsii* occurs by both chemisorption and physisorption. The negative value of $\Delta G^{\circ}_{\text{ads}}$ indicates that the *A. mearnsii* inhibitor molecules are adsorbed on the surface of the aluminum alloy spontaneously.

EIS measurements were carried out to investigate the surface properties of the specimens with and without inhibitor. Nyquist diagrams and Bode modulus and frequency phase-angle plots of AA7075-T6 aluminum alloy in HCl solution in absence and presence of tannin from bark of *A. mearnsii* are shown in Figures 3 and 4.

It can be seen in Nyquist diagrams (Figure 3) that a single capacitive arc and an inductive loop appeared for all systems, with and without inhibitor. The fact that the shape of Nyquist plots do not change with addition of inhibitor suggests that the tannin from bark of *A. mearnsii* inhibit the aluminum corrosion in 0.1 M HCl without altering the aluminum dissolution mechanism, with is in a good agreement with potentiodynamic polarization results (Figure 1). Other studies about aluminum corrosion in acid medium have obtained similar results.^[16,21,24] A capacitive arc of small diameter was observed for uninhibited system but due to increase on resistance, the diameter of capacitive arc rises as the concentration of tannin increases. The larger the diameter of capacitive arc, the higher the

polarization resistance and consequently the lower the corrosion rate is.

Two time constants are present in all cases: a capacitive time constant at high frequencies above the real axis and an inductive time constant at low frequencies below the real axis. The high frequency loops are usually credited to the phenomenon related with the double electric layer due to the presence of oxide film on the aluminum surface. Thus, the

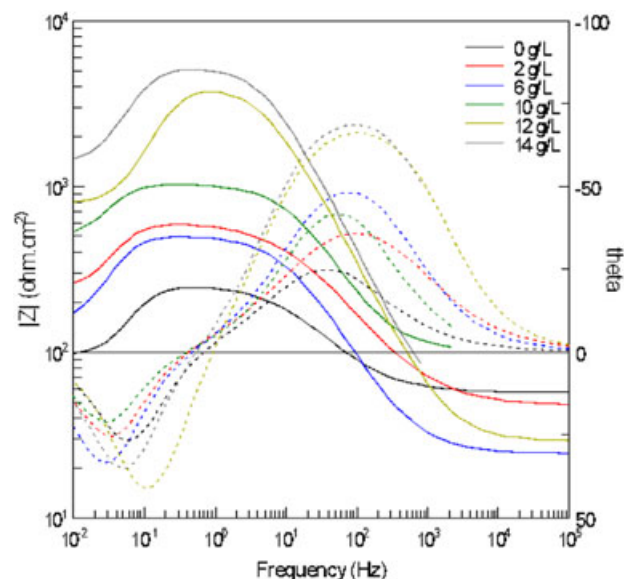


FIGURE 4 Bode modulus and frequency phase-angle plots of AA7075-T6 aluminum alloy for different concentrations of tannin from bark of *A. mearnsii* in 0.1 M HCl [Color figure can be viewed at wileyonlinelibrary.com]

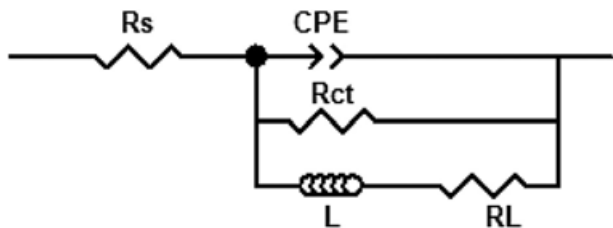


FIGURE 5 Equivalent circuit used to simulate the EIS diagram.

capacitive comportment at high frequencies indicates that the corrosion of AA7075-T6 aluminum is principally controlled by charge transfer process and adsorption of layer that protects the metallic surface. The inhibitor molecules adsorbed on the metallic surface dislocate water molecules and adsorbed ions from the surface, decreasing its electrical capacity. The inductive behavior at low frequency is probably related to relaxation of the adsorption of intermediate species due to corrosion or the adsorption of inhibitor molecules on the surface. The relaxation phenomenon has been associated with distinct adsorbed species like H^+ , Cl^- , O^{2-} or inhibitor species on the metal surface.^[14,16,38]

The two time constants are also evident in the Bode diagrams (Figure 4) and it is observed that the total impedance increases with increasing inhibitor concentration due to a decrease in active sites on the aluminum surface. Additionally, Bode diagrams also show that the impedance modulus $|Z|$ and the phase angle increase with inhibitor concentration, because of intensification of inhibitor adsorption on the aluminum surface.

The EIS results were analyzed by testing the fitting of the experimental data to a suitable equivalent circuit in order to determine the electrochemical parameters. The best fit was found to an electrical circuit proposed by Chaubey et al.^[16] and is shown in Figure 5. The elements specified in the electrical circuit are the solution resistance (R_s), the charge transfer resistance (R_{ct}), the constant phase element (CPE), and R_L and L are the inductive elements.

The polarization resistance (R_p) was calculated using the following equation:

$$R_p = \frac{R_{ct} \cdot R_L}{R_{ct} + R_L} \quad (6)$$

The following equation was used to obtain the double layer capacitance (C_{dl}) values:

$$C_{dl} = Q(\omega_{max})^{n-1} \quad (7)$$

where ω_{max} is the angular frequency at which the imaginary part of the impedance assumes maximum value.

The impedance parameters obtained for corrosion of aluminum alloy in 0.1 M HCl tannin and with different concentrations of tannin from bark of *A. mearnsii* are shown in Table 3.

The capacitive behavior of the impedance indicates that the dissolution process of the AA7075 alloy is controlled by the charge transfer process from the aluminum matrix anodic sites to cathodic sites (intermetallic particles), as also observed by Fetouh et al.^[14] It can be seen that R_{ct} and C_{dl} are higher in the presence of inhibitor, probably due to a decrease in local dielectric constant and/or an increase in the electrical double layer thickness due to the adsorbed inhibitor molecules at the metal/solution interface.

For comparison, Figure 6 shows the microstructure of AA7075-T6 before corrosion and EDS. The microstructure of this alloy is composed of an aluminum matrix (Al) with intermetallic particles and strengthening precipitates. The strengthening precipitates have composition $MgZn_2$ and size in the nanometer range, and are formed during aging and provide strength to the alloy. The solution heat treatment and the aging change the size, the composition, and the distribution of the strengthening precipitates in the microstructure of AA7075 alloy. The strengthening particles precipitate at the grain boundaries affecting the resistance to intergranular corrosion of the alloy.^[9,12] The intermetallics

TABLE 3 Impedance parameters and R_p , and η calculated for corrosion of AA7075-T6 aluminum alloy in 0.1 M HCl in the absence and presence of different concentrations of tannin from bark of *A. mearnsii*

C_{inh} ($g L^{-1}$)	R_s (Ω)	R_{ct} (Ωcm^{-2})	n	L ($H cm^{-2}$)	R_L (Ωcm^{-2})	CPE (Q) ($F cm^{-2}$)	ω_{max} (Hz)	C_{dl} ($F cm^{-2}$)	R_p (Ωcm^{-2})	η (%)
0	56.79	199.1	0.70	386.8	46.9	2.29×10^{-4}	12.92	1.06×10^{-4}	37.93	–
2	47.31	566.5	0.66	2451.0	288.0	9.17×10^{-5}	12.92	3.84×10^{-6}	190.93	80
6	24.35	485.3	0.78	1904.0	162.8	7.74×10^{-5}	10.00	4.61×10^{-5}	121.91	69
10	101.2	940.9	0.80	5920.0	645.6	3.22×10^{-5}	12.91	1.92×10^{-5}	382.88	90
12	28.98	3952.0	0.84	3013.0	935.3	1.32×10^{-5}	5.99	9.86×10^{-6}	756.31	95
14	38.44	5170.0	0.87	10 935.0	1790.0	9.21×10^{-6}	5.99	7.26×10^{-5}	1329.64	97

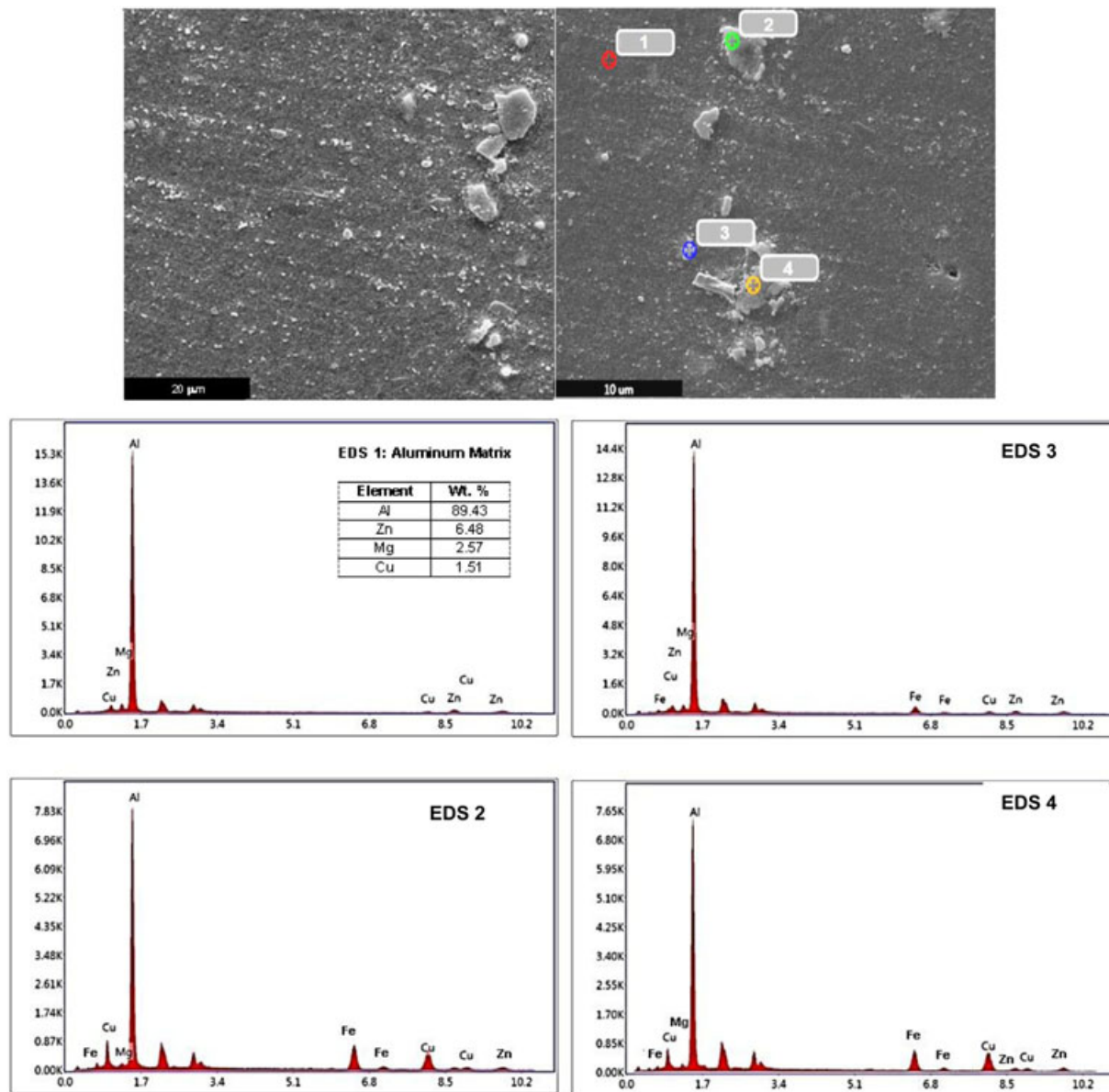


FIGURE 6 SEM images of AA7075-T6 aluminum alloy before corrosion and respective EDS spectra [Color figure can be viewed at wileyonlinelibrary.com]

are formed due to interaction between alloying elements and impurities present in the alloy. These EDS analyses, identified in the microstructure of Figure 6, indicate that the main intermetallic phases contain Fe. In AA7075 alloy, the $\text{Al}_7\text{Cu}_2\text{Fe}$ and $(\text{Al,Cu})_6(\text{Fe,Cu})$ are the most abundant intermetallics, while Mg_2Si and Al_2Cu phases are present in smaller quantities.^[7,9]

Figure 7 shows SEM images of the corroded surface of the AA7075-T6 aluminum alloy with different concentrations of tannin from the bark of *A. mearnsii*. The surface of the specimens exposed to the medium with tannin show comparatively less corrosion and a smooth surface when compared to the surface of the specimen

without tannin, indicating that a protective film has formed on the surface. In the images corresponding to the samples exposed to solutions with concentrations of 0, 2, 6, and 10 g L^{-1} of tannin it can be seen localized mass loss, which is probably associated to formation of galvanic couple due to chemical potential differences between intermetallic particles and matrix, as previously reported in other studies with the same material.^[7,17] It is observed that the corrosion occurs near the intermetallic precipitates, indicating that they are cathodic in relation to Al matrix. In the images of samples exposed to higher concentration of tannin (12 g L^{-1} and 14 g L^{-1}) it is evident that material adsorbed on the surface.

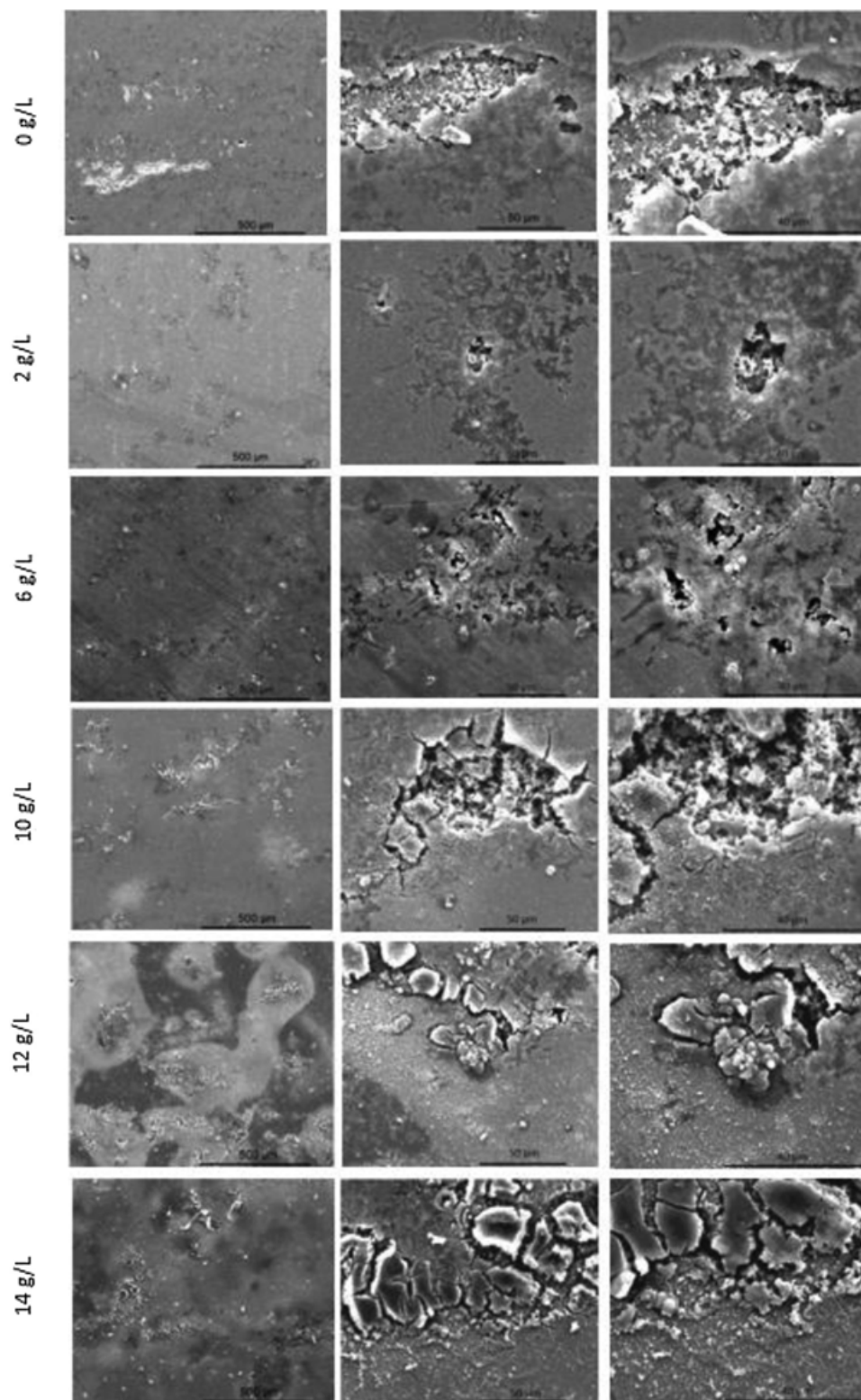


FIGURE 7 SEM images of corroded surface of aluminum alloy AA7075-T6 for different concentrations of tannin from bark of *A. mearnsii* in 0.1 M HCl.

The inhibition process of AA7075 aluminum alloy in the presence of tannin can be explained by the adsorption of the tannin components (tannates) on the metal surface. Tannin is constituted by nitrogen and

oxygen atoms in functional groups (N—H, O—H, C—H, C—O, and C=O), and the adsorption of these compounds on the alloy surface reduces the surface area that is available for the attack of the aggressive ions. It can be

seen on SEM images that as the tannin concentration increases more tannates are adsorbed on the surface, which is in good agreement with potentiodynamics polarization and EIS results. Although not covering the entire metal surface, adsorption inhibitors, as tannin from the bark of *A. mearnsii*, reduce the extent of anodic and cathodic reactions, since they occupy electrochemically active sites. Thus, the reduction in corrosion rates will be proportional to the coated surface that increases with tannin concentration. This type of inhibitor may also provide a physical barrier to the diffusion of ions or molecules and increase the electrical resistance of the metal surface.

4 | CONCLUSIONS

Considering the results obtained in this work, we can conclude that

- the tannin from bark of *A. mearnsii* acts as a suitable eco-friendly green inhibitor for controlling the corrosion process of AA7075-T6 aluminum alloy in 0.1 M HCl medium;
- the inhibition efficiency of the tannin from bark of *A. mearnsii* increased with the concentration and reached efficiencies of 95% and 97% as obtained by polarization and EIS techniques, respectively, at 14 g L^{-1} ;
- the results of potentiodynamic polarization curves reveal that the tannin from bark of *A. mearnsii* can be considered as a cathodic inhibitor AA7075-T6 aluminum alloy in 0.1 M HCl medium once a pronounced decrease of cathodic current densities were observed;
- adsorption of the bark of *A. mearnsii* tannin on the AA7075-T6 alloy surface in HCl follows the isotherm of Langmuir;
- the EIS results indicate that the aluminum dissolution process is controlled by charge transfer from anodic to cathodic sites;
- the SEM images corroborate the protection of AA7075-T6 aluminum alloy corrosion in 0.1 M HCl solution by the tannin from bark of *A. mearnsii*;
- the results indicate that inhibition process occurs by formation of a tannate compound adsorbed layer on the aluminum surface that reduces the metal dissolution reaction.

ACKNOWLEDGMENTS

The authors acknowledge the support provided by CNPq (The Brazilian Research Council) and TANAC A. S. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

ORCID

Eleani M. da Costa  <http://orcid.org/0000-0001-8733-3083>

REFERENCES

- [1] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, I. M. Didahmed, A. M. El-Zayady, M. Saadawy, *Mater. Chem. Phys.* **2006**, *98*, 291.
- [2] N. Chaubey, Savita, V. K. Singh, M. A. Quraishi, *J. Assoc. Arab Univ. Bas. App. Sci.* **2017**, *22*, 38.
- [3] R. Rosliza, H. B. Senin, W. B. Wan Nik, *Colloids Surf. A.* **2008**, *312*, 185.
- [4] H. Gerengi, *Ind. Eng. Chem. Res.* **2012**, *51*, 12835.
- [5] H. Gerengi, M. M. Solomona, E. Kayaa, F. E. Bagcia, E. J. Abai, *Meas.* **2018**, *116*, 264.
- [6] T. G. Harvey, S. G. Hardin, A. E. Hughes, T. H. Muster, P. A. White, T. A. Markley, P. A. Corrigan, J. Mardel, S. J. Garcia, J. M. C. Mol, A. M. Glenn, *Corros. Sci.* **2011**, *53*, 2184.
- [7] J. A. Hill, T. Markley, M. Forsyth, P. C. Howlett, B. R. W. Hinton, *J. Alloys Compd.* **2011**, *509*, 1683.
- [8] I. W. Huang, B. L. Hurley, F. Yang, R. G. Buchheit, *Electrochim. Acta* **2016**, *199*, 242.
- [9] Q. Meng, G. S. Frankel, *J. Electrochem. Soc.* **2004**, *151*, 1945.
- [10] A. Singh, Y. Lin, W. Liu, S. Yu, J. Pan, C. Ren, D. Kuanhai, *J. Ind. Eng. Chem.* **2014**, *9*, 1584.
- [11] H. Wang, C. Ning, Y. Huang, Z. Cao, Z. Chen, W. Zhang, *Opt. Lasers Eng.* **2017**, *90*, 179.
- [12] W. A. Badawy, F. M. Al-Kharafi, A. S. El-Azab, *Corros. Sci.* **1999**, *41*, 709.
- [13] G. O. Avwiri, F. O. Igho, *Mater. Lett.* **2003**, *57*, 3705.
- [14] H. A. Fetouh, T. M. Abdel-Fattah, M. S. El-Tantawy, *Int. J. Electrochem. Sci.* **2014**, *9*, 1565.
- [15] A. M. Abdel-Gaber, E. Khamis, H. Abo-ElDahab, S. Adeel, *Mater. Chem. Phys.* **2008**, *109*, 297.
- [16] N. Chaubey, V. K. Singh, M. A. Quraishi, *Ain Shams Eng. J.* **2018**, *9*, 1131.
- [17] K. Khanari, M. Finsgar, *Arab. J. Chem.* **2016**, In press <https://doi.org/10.1016/j.arabjc.2016.08.009>
- [18] E. McCafferty, *Mater. Lett.* **2008**, *62*, 113.
- [19] B. E. A. Rani, B. B. J. Basu, *Int. J. Corros.* **2012**, *2012*, 1.
- [20] Y. Du, H. Wang, Y. Chen, H. Qi, W. Jiang, *J. Environ. Chem. Eng.* **2017**, *5*, 5891.
- [21] J. Halambek, K. Berkovic, J. Vorkapic-Furac, *Mater. Chem. Phys.* **2013**, *137*, 788.
- [22] A. Khadraoui, A. Khelifa, K. Hachama, R. Mehdaoui, *J. Mol. Liq.* **2016**, *214*, 293.
- [23] K. Krishnaveni, J. Ravichandran, *Trans. Nonferrous Met. Soc. China.* **2014**, *24*, 2704.
- [24] E. E. Oguzie, *Corros. Sci.* **2007**, *49*, 1527.
- [25] A. A. Rahim, E. Rocca, J. Steinmetz, M. J. Kassim, R. Adnan, M. S. Ibrahim, *Corros. Sci.* **2007**, *49*, 402.
- [26] A. A. Rahim, E. Rocca, J. Steinmetz, M. J. Kassim, *Corros. Sci.* **2008**, *50*, 1546.
- [27] A. Singh, I. Ahamad, M. A. Quraishi, *Arab. J. Chem.* **2016**, *20*, 4276.
- [28] T. Rabizadeh, S. Khameneh Asl, *Mat. Corros.* **2018**, *11*, 1.

- [29] N. Abdel Ghany, M. Shehata, R. Saleh, A. El Hosary, *Mater. Corros.* **2017**, *68*, 355.
- [30] G. I. Ramírez-Peralta, U. León-Silva, M. E. Nicho Díaz, M. G. Valladares-Cisneros, *Mater. Corros.* **2018**, *69*, 1631.
- [31] A. Abdel-Gaber, E. Khamis, A. Hefnawy, *Mater. Corros.* **2011**, *62*, 1159.
- [32] O. R. Pardini, J. I. Amalvy, A. R. Di Sarli, R. Romagnoli, V. F. Vetere, *J. Coat. Technol.* **2001**, *73*, 99.
- [33] R. S. Peres, E. Armelin, C. Alemán, C. A. Ferreira, *Ind. Crops Prod.* **2015**, *65*, 506.
- [34] W. M. Chai, Y. Shi, H. L. Feng, L. Qiu, H. C. Zhou, Z. W. Deng, C. L. Yan, Q. X. Chen, *J. Agric. Food Chem.* **2012**, *60*, 5013.
- [35] R. S. Peres, E. Cassel, C. A. Ferreira, D. S. Azambuja, *Surf. Interface Anal.* **2014**, *46*, 1.
- [36] N. Slabbert, *Plant Polyphenols* (Eds.: R. Hemingway, P. Laks), Springer, New York USA **1992**.
- [37] H. J. W. Lenderink, M. V. D. Linden, J. H. W. Dewit, *Electrochim. Acta* **1993**, *38*, 1989.

How to cite this article: Guedes LAL, Bacca KG, Lopes NF, da Costa EM. Tannin of *Acacia mearnsii* as green corrosion inhibitor for AA7075-T6 alluminum alloy in acidic medium. *Materials and Corrosion*. 2019;70:1288–1297.
<https://doi.org/10.1002/maco.201810667>