

Full Paper

Investigation of Green Corrosion Inhibitor Based on *Aloe vera* (L.) Burm. F. for the Protection of Bronze B66 in 3% NaCl

Bouchra Benzidia,* Hind Hammouch, Ahmed Dermaj, Hayat Benassaoui, Said About and Najat Hajjaji

Laboratory of Materials, Electrochemistry and Environment (LMEE), Department of Chemistry, Faculty of Science, Ibn Tofail University, BP 133, 14000 Kenitra, Morocco

*Corresponding Author, Tel.: +212 6 03 27 09 30

E-Mail: benzidia1511@gmail.com

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Abstract- The objective of this work is the development of a new green inhibitor extracted from *Aloe vera* (L.) Burm. F. (syn. *Aloe barbadensis* Mill.) for the corrosion inhibition of bronze B66 in a neutral chloride environment (3%NaCl). The tannins extract was obtained from the green rind of *Aloe vera* by maceration process method. The major compound of the TAV is Linolenic acid (16.59%). The study of the tannins extract from *Aloe vera* (TAV) was carried out by coupling gravimetric and electrochemical (stationary and transitory) methods, namely the plot of the polarization curves and electrochemical impedance diagrams. Surface analysis of bronze samples was performed using an SEM (scanning electron microscope) coupled to EDS (energy dispersive X-ray spectroscopy), which helped to highlight the protective effect of the TAV studied. The experimental results obtained allowed to note that the inhibition efficiency reaches 89% at 150 ppm of TAV in 3%NaCl. This inhibitor acts by modifying the mechanism of the processes involved at the interface Bronze/3%NaCl.

Keywords- *Aloe vera*, Bronze B66, Corrosion inhibition, TAV, 3% NaCl

1. INTRODUCTION

During these recent years, the attention of researchers has focused on the anti-corrosive properties of natural plant products. Indeed, given the increasing use of metals and alloys in

modern life. Corrosion is a huge problem whose economic consequences are disastrous and invaluable. The use of corrosion inhibitors is one of the most convenient methods for the protection against corrosion in aggressive environments [1-4]. However, synthetic compounds used as inhibitors are expensive and for the most part, they are very dangerous for environment. The non-toxic and biodegradable nature has paved the way for the use of natural products as green inhibitors [5-10].

This is an ideal ecological alternative to replace the traditional corrosion inhibitors despite their efficiencies they represent a great danger and risk for the environment.

The *Aloe vera* (L.) Burm. F. (syn. *Aloe barbadensis* Mill.) is a plant widely known and used in several areas such as cosmetics and medicine, belongs to the family Xanthorrhoeaceae [11]. This plant has caught our attention because its medicinal use found no complications and did not raise any claims of side effects [12,13]. On our part, we have tried to apply *Aloe vera* in the field of the corrosion inhibition of bronze B66 in a neutral chloride environment equivalent by its ionic strength at the seawater.

The purpose of this document is to develop a new corrosion inhibitor for the protection of bronze B66 in a chloride-neutral medium, the corrosion inhibition efficiency of the tested TAV inhibitor was achieved by gravimetric measurements and supplemented by stationary and transitory electrochemical methods. To understand the phenomena that governing the bronze B66 interface in 3% NaCl in absence and presence of TAV as well to identify the nature of the products formed on the metal surface, we appealed to the surface analysis namely SEM coupled an EDX elemental analysis.

2. MATERIAL AND METHODS

2.1. Material used

The material used as the working electrode is bronze B66, the composition of which is given in the table below. The choice of bronze B66 is based on its composition, which is close to an archaeological bronze.

Table 1. Composition of bronze B66

	Sn	Pb	Ni	Zn	Cu
Phase I (wt. %)	5.12	0.59	0.39	0.79	93.11
Phase II (wt. %)	21.29	1.69	0.38	0.29	76.35

2.2. Electrolytic medium

The corrosive solution consists of an aerated solution of sodium chloride (30 g/l) prepared by dissolution of Merck NaCl in distilled water.

2.3. The inhibitor used

The inhibitory power against corrosion bronze was conducted with the tannins extract of *Aloe vera* (TAV). The extraction procedure was performed by the method of Benzidia et al [14].

2.4. Experimental procedure

2.4.1. Gravimetric Study

The gravimetric study is used because it has the advantage of being simple and does not require a large equipment. In this study, two types of gravimetric tests were performed, namely the loss of mass measurement and dosing of metal passed into solution by Flame atomic absorption spectroscopy.

2.4.1.1. Mass Loss measurement

The equipment necessary to perform the weight loss measures are:

- Analytical Balance Precision.
- 30 ml flasks for immersing the bronze substrates without and with inhibitor.

After preparing the substrates for performing the measurement of the initial mass m_1 (polishing, rinsing with distilled water, degreasing with acetone, drying, determining the diameter and thickness of each substrates, is carried out subsequently to the weighing m_1 noted the initial weight and the substrates are then immersed in the solutions.

After 24 h the coupons were removed; is performed rinsing with distilled water, dried, chemical stripping by aqua regia and then we proceed to the weighing of the coupons, Let m_2 is the mass after test. The corrosion rate W ($\text{g}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) can be calculated by the following equation (1):

$$W = \frac{m_1 - m_2}{(S \times T)} \quad (1)$$

The inhibitory efficiency (IE_w) is calculated by the following equation (2):

$$IE_w (\%) = \left[\frac{W - W_{inh}}{W} \right] \times 100 \quad (2)$$

Where S: surface of area of specimen (cm^2)
T: time (h)

W and W_{inh} are the rate of corrosion in the absence and in the presence of the inhibitor, respectively.

2.4.1.2. Quantification of copper ions contents in corrosive solutions

Dosage of the metal passed into solution has been performed by using Varian Spectra AA 220 Atomic Absorption Spectroscopy and in order to determine the concentrations of copper ions within corrosive solution in the absence and in the presence of the inhibitor, the corrosive medium dissolving in acid (aqua regia).

2.4.2. Electrochemical study

The electrochemical measurements were obtained using a three-electrode assembly; a platinum electrode as counter-electrode, an XR300/XR310 reference electrode Ag/AgCl, and the copper-working electrode of cylindrical shape (1 cm²). Before each test, the electrode was mechanically abraded by 600, 1000, 1200, 1500 and 2000 grades emery papers.

The stationary measurements were carried out in potentiodynamic mode using an SP-200 potentiostat/galvanostat of the "Bio-logic Science instruments" type. The working electrode is previously immersed in the free corrosion potential for one hour. The scanning speed chosen is 1 mV/s.

The determination of the electrochemical parameters (i_{corr} , E_{corr} , β_a and β_c) was established from the polarization curves, using the EC-Lab software. Thus, the inhibitory efficiency is calculated from the following formula (3):

$$IE (\%) = \left[\frac{i_{Corr}^{\circ} - i_{Corr}}{i_{Corr}} \right] \times 100 \quad (3)$$

Where i_{Corr}° and i_{Corr} are corrosion current densities values in the absence and in the presence of the inhibitor, respectively.

The plot of the electrochemical impedance diagrams was performed using the same device SP-200 with a signal amplitude of 10 mV. The frequency domain explored ranges from 100 kHz to 10 mHz, the inhibitory efficacy is calculated from the following formula (4):

$$IE (\%) = \left[\frac{R_p^{\circ} - R_p}{R_p} \right] \times 100 \quad (4)$$

Where the R_p° and R_p represent the polarization resistance in the absence and in the presence of inhibitor, respectively.

2.4.3. Surface analysis by SEM/EDX

The morphological characterization of the Bronze coupon surface was carried out by electron microscopy field emission scanning (SEM) and energy dispersion. The X-ray spectroscopy, EDX (model 6130 X flash the Bruker brand) is performed by FEI microscope (Quanta FEG model 450).

3. RESULTS AND DISCUSSION

3.1. Gravimetric study

The values of corrosion rate (W) and the percentage of inhibition efficiency (IE%) determined by the gravimetric method with different concentrations of the TAV extract after 24 hours of immersion are presented in Table 2, as well as the concentrations of copper ions (Cu^{2+}) determined by flame atomic absorption spectroscopy.

According to the table, it is found that the corrosion rate decreases with the increase of the concentration of the inhibitor in solution, it reaches a value of 7.5×10^{-7} (g/h.cm²) at a concentration of 150 ppm, corresponding to an efficiency of 97.9%. The flame atomic adsorption analyzes confirm the results obtained by gravimetric analysis, the concentration of Cu^{2+} decreases as a function of concentrations of the inhibitors, this allowed us to conclude that the TAV extract has good property of corrosion inhibition of the Bronze B66 in 3% NaCl for the immersion time studied.

Table 2. The corrosion rate, inhibitory efficiency and the copper ions (Cu^{2+}) concentrations as a function of different concentrations of the inhibitors

	W (g/h.cm ²)	IE_w (%)	Concentration of Cu^{2+} (ppm)	IE (%)
3%NaCl	$3,584 \times 10^{-5}$	-	11.6	-
50 ppm	2.99×10^{-6}	91.65%	5	56.9
100 ppm	1.49×10^{-6}	95.84%	2.4	79.31
150 ppm	7.5×10^{-7}	97.90%	1.6	86.20

3.2. Electrochemical study

3.2.1. Open circuit potential

Figure 1 represents the variation of the open circuit potential (OCP) based on the time of bronze B66 in 3% NaCl at different concentrations of the TAV extract.

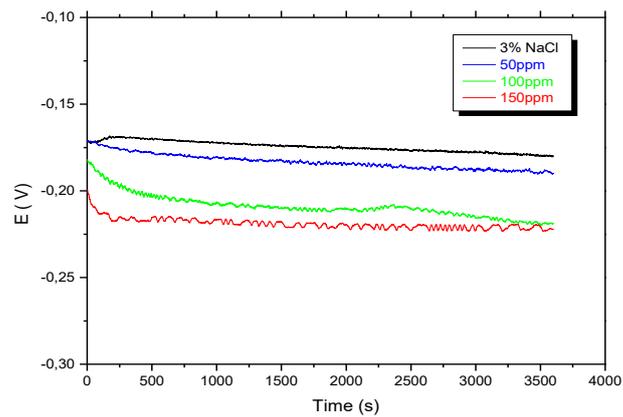


Fig. 1. Variation of the open circuit potential of bronze B66 in 3% NaCl as a function of time at different concentrations of the TAV

In the absence of the inhibitor, the corrosion potential of bronze B66 in a 3% NaCl solution undergoes a variation in the first few minutes, can be explained by the aggressive attack of the electrode by the chloride ions causing the destruction of the layer formed on the electrode and after 2500 s it stabilizes to -0.165 V. This stability can be attributed to the formation of corrosion product layer on the metal surface.

In the presence of TAV, there is a displacement of corrosion potential with a well noticeable stability from 3000 s. This movement becomes more important when the inhibitor concentration increases. This can be explained by the adsorption of TAV on the metal surface and the formation of an inhibitor film to a barrier effect against chloride ions [1].

3.2.2. Stationary electrochemical measurements

The cathodic and anodic polarization curves of the bronze B66 in 3% NaCl, in the absence and in the presence of the TAV extract at different concentrations are presented in Figure 2.

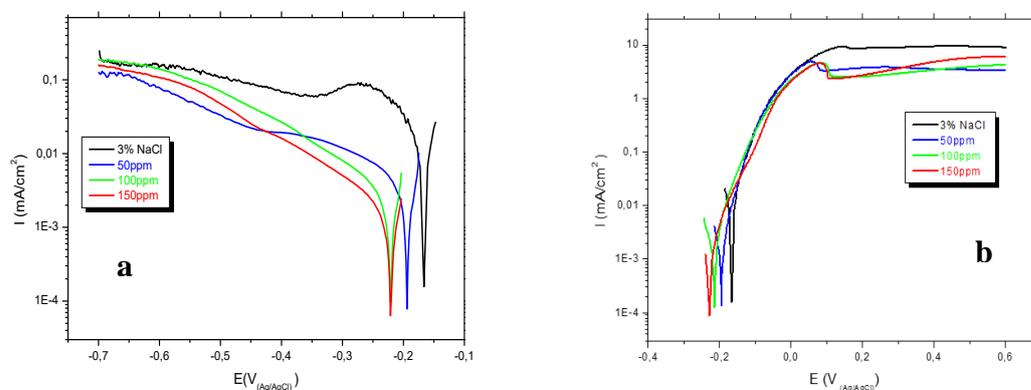


Fig. 2. Cathodic (a) and anodic (b) polarization curves of bronze B66 in the absence and in the presence of the inhibitor

The observation of Figure 2 shows that in the cathodic domain, in the absence of the inhibitor there are a rapid increase of the current density in the vicinity from the corrosion potential and then tend to stabilize towards a value of the order of 0.1 mA/cm^2 , corresponds to the limiting diffusion current of oxygen.

The addition of the inhibitor at different concentrations leads to a decrease in the values of the cathodic current density in the vicinity of E_{cor} . This decrease appears in a broad area of potential. Then a displacement of corrosion potential towards the cathodic direction. This can be explained by the formation of an inhibitor film causing a barrier effect to the oxygen reduction reaction according to Figure 2(a) [15].

In the anode domain, the current density increases rapidly in the absence of the inhibitor in the vicinity of the corrosion potential, reflecting the oxidation of the material, then tends to stabilize towards at a value of 10 mA/cm^2 , which is too high to signify the metal passivation. On the other hand, there is a decrease in the values of the density from the anode current in the presence of the inhibitor, which is less pronounced with respect to the cathodic domain, so from these results it can be seen that the test compound is a cathodic inhibitor. For more cathodic potentials note the destruction of the film formed because of the diffusion from the oxygen towards the interface metal/solution. This is justified by the high value of the currents which is of the order of 0.1 mA . The electrochemical parameters derived from the polarization curves are shown in Table 3.

Table 3. Electrochemical parameters derived from polarization curves of Bronze B66 in 3% NaCl in the absence and in the presence of TAV

Concentration of inhibition (ppm)	$-\beta_c$ (mV)	E_{corr} (mV _{Ag/AgCl})	I_{corr} ($\mu\text{A/cm}^2$)	IE (%)
3% NaCl	63.4	-165.86	9.48	----
50 ppm	19.1	-193.51	0.73	92.27
100 ppm	30.3	-220.56	0.65	93.08
150 ppm	30.4	-220.78	0.42	95.56

Examination of this table shows a displacement of the corrosion potential towards the cathode direction, with a decrease in the values of the current density in the vicinity of the corrosion potential, this decrease becomes more and more important when the concentration of inhibitor increases. At high cathodic overvoltages the inhibitor does not seem to affect the behavior of bronze. The inhibitory efficiency is of the order of 95% for a concentration of 150 ppm.

The results obtained show that the product added as inhibitor for bronze B66 in a simulated seawater solution, is a cathodic type inhibitor. It acts in low concentration, its protective effect

results in the formation of an inhibitor film on the metal surface causing a decrease in the value of the corrosion current density.

3.2.3. Transient electrochemical measurements

To really understand, the phenomena that react at the metal/solution interface and to determine the mechanism of action of our TAV extract, we plotted the electrochemical impedance diagrams at different concentrations, as well as the plot at 150 ppm; better inhibitor concentration more effective for different immersion times.

3.2.3.1. The concentration effect of TAV extract

The impedance diagrams plotted in the Nyquist plane after one hour of immersion in the corrosive solution without and with inhibitor are shown in Figure 3.

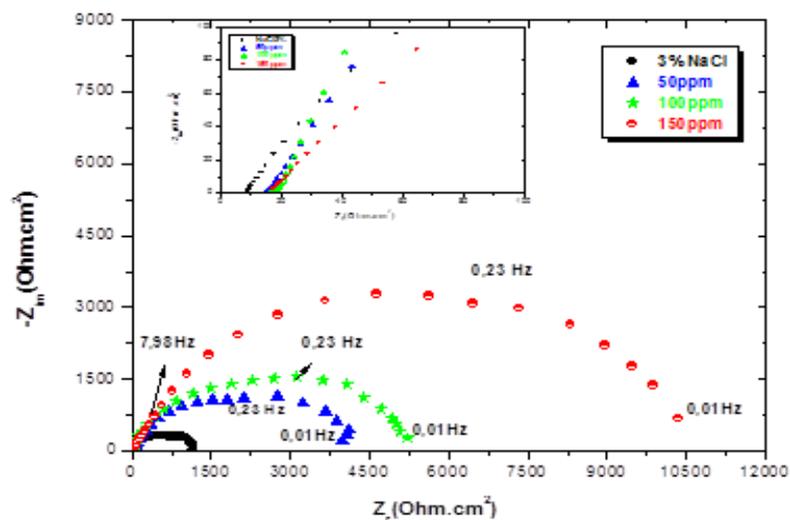


Fig. 3. Electrochemical impedance diagrams of bronze B66 in 3% NaCl at different concentrations of corrosion inhibitor after 1 h of immersion

In the absence of the inhibitor, it is observed that the impedance diagram represented in the Nyquist plane is an arc of a circle with weak flattening at high frequencies.

The bias resistance is of the order of $1143 \Omega \cdot \text{cm}^2$. The introduction of a second time constant becomes necessary to properly model, this spectrum. As can be seen in Figure 3, in the presence of inhibitor on the metal surface, one notes that the impedance changes in shape and size.

The equivalent electrical circuit (Figure 4) consists of three parallel RC circuits, the components of which are ascribed to R_e : Electrolyte resistance, R_t : Load transfer resistance, C_d : Double layer capacitance, (R_F-C_F) : Faradic impedance which occurs in capacitive form.

The value of the bias resistor (R_p) is determined by the sum of values of R_t and R_F . The value of R_p corresponds to the slope of the polarization curves at the point of operation (E_{corr} , I_{corr}).

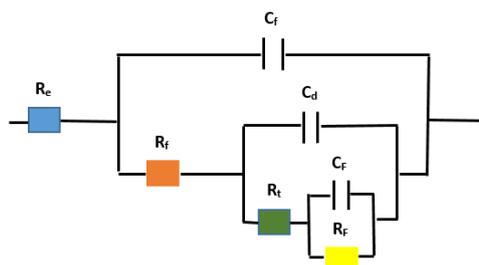


Fig. 4. Equivalent electrical circuit

In the presence of inhibitor, the impedance diagrams show a capacitive behavior different from that of bronze B66 immersed in a 3% NaCl solution.

These diagrams show a significant increase in polarization resistance as a function of inhibitor concentration. Indeed, these curves cannot be modeled by a 2 RC circuit, but can be interpreted by a circuit equivalent to 3 RC in parallel.

A contribution to the high frequencies ($R_f - C_f$) whose capacitive loops diameter is of the order of $2.13 \Omega\text{cm}^2$, $2.26 \Omega\text{cm}^2$ and $3.55 \Omega\text{cm}^2$ respectively for the concentrations of 50 ppm, 100 ppm and 150 ppm in TAV. These values are lower than that of 3% NaCl alone (Table 4). This can only be attributed to a protective film effect that blocks the cathodic reaction. The capacity values associated with these loops are less than $1 \mu\text{F}/\text{cm}^2$ for all concentrations.

These values are too low compared to that usually attributed to the double layer (of the order of $20 \mu\text{F}/\text{cm}^2$), which supports the hypothesis of the presence of a relatively thick and compact inhibitor film. At low frequencies, a redox contribution of corrosion products ($R_F - C_F$). The polarization resistance increases significantly with the concentration, this resistance increases in relation to 15 in the presence of 150 ppm in TAV, which shows that this inhibitor has a significant effect on the reduction of charge transfer to the interface.

The inhibitory efficacy of TAV increases with the concentration of inhibitor, it reaches a maximum of 89% for the concentration of 150 ppm in TAV. The electrochemical parameters derived from these curves are shown in Table 4.

Table 4. Electrochemical parameters derived from impedance diagrams

	R_e ($\Omega\cdot\text{cm}^2$)	R_f ($\Omega\cdot\text{cm}^2$)	C_f ($\mu\text{F}/\text{cm}^2$)	R_t ($\Omega\cdot\text{cm}^2$)	C_d ($\mu\text{F}/\text{cm}^2$)	R_F ($\Omega\cdot\text{cm}^2$)	C_F ($\mu\text{F}/\text{cm}^2$)	R_p ($\Omega\cdot\text{cm}^2$)	IE(%)
3%NaCl	8.91	-----	-----	703	147.9	440	860	1143	----
50 ppm	15.02	2.13	0.90	1372	79.81	2687	587.71	4059	71.84
100 ppm	15.07	2.26	0.50	1906	58.87	3229	435.20	5137	77.75
150 ppm	14.05	3.55	0.17	3681	50.02	7065	197.01	10750	89.36

The observation of this table shows that the addition of the inhibitor leads to an increase in the values of R_f , thus reducing of the values from the associated capacities. This can be explained by the formation of a thin film of inhibitor [16].

There is also a decrease in the double layer capacity (C_d), which can testify to a more homogeneous surface in the presence of inhibitor at the interface metal/solution. The increase of the R_t values in the presence of the inhibitor is also noted, The charge transfer resistance, $703 \Omega \cdot \text{cm}^2$ in absence of inhibitor, increased significantly by addition of TAV, and reached $3681 \Omega \cdot \text{cm}^2$ testifying to a protection of the metal.

The results obtained show that the best efficiency obtained is 89% for a concentration of 150 ppm. That is why we studied the effect of immersion time on the efficiency obtained at 150 ppm.

3.2.3.2. Immersion time effect

The evolution of the electrochemical impedance diagrams, at different immersion times of B66 in 3% NaCl, in the presence of 150 ppm from the TAV extract, is shown in Figure 5.

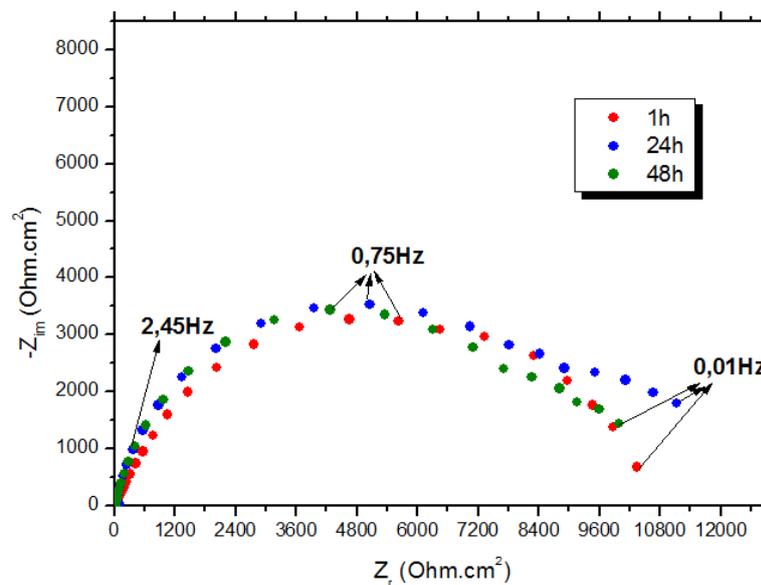


Fig. 5. Electrochemical impedance diagrams of B66 in 3% NaCl in the presence of 150 ppm from TAV, for different immersion times

In this figure, it is observed that the electrochemical impedance diagrams after 24 h and 48 h of immersion in presence of 150 ppm look the same in size and shape with a slight increase in polarization resistance. These results show that the TAV inhibitor does not degrade the protective film after 24 h and 48 h of immersion. To confirm these results, we completed this study with surface analyzes the SEM coupled with EDX.

3.4. Surface Analysis: Scanning electron microscope coupled to EDX

The surface condition of the bronze B66 shown in Figure 6 (Fig. 6A) was characterized, prior to the experiment and after polishing of the sample, by SEM coupled with EDX analysis. The results obtained show a surface heterogeneity of B66. This alloy is a bronze cast iron with a dendritic structure, characterized by a low percentage of tin.

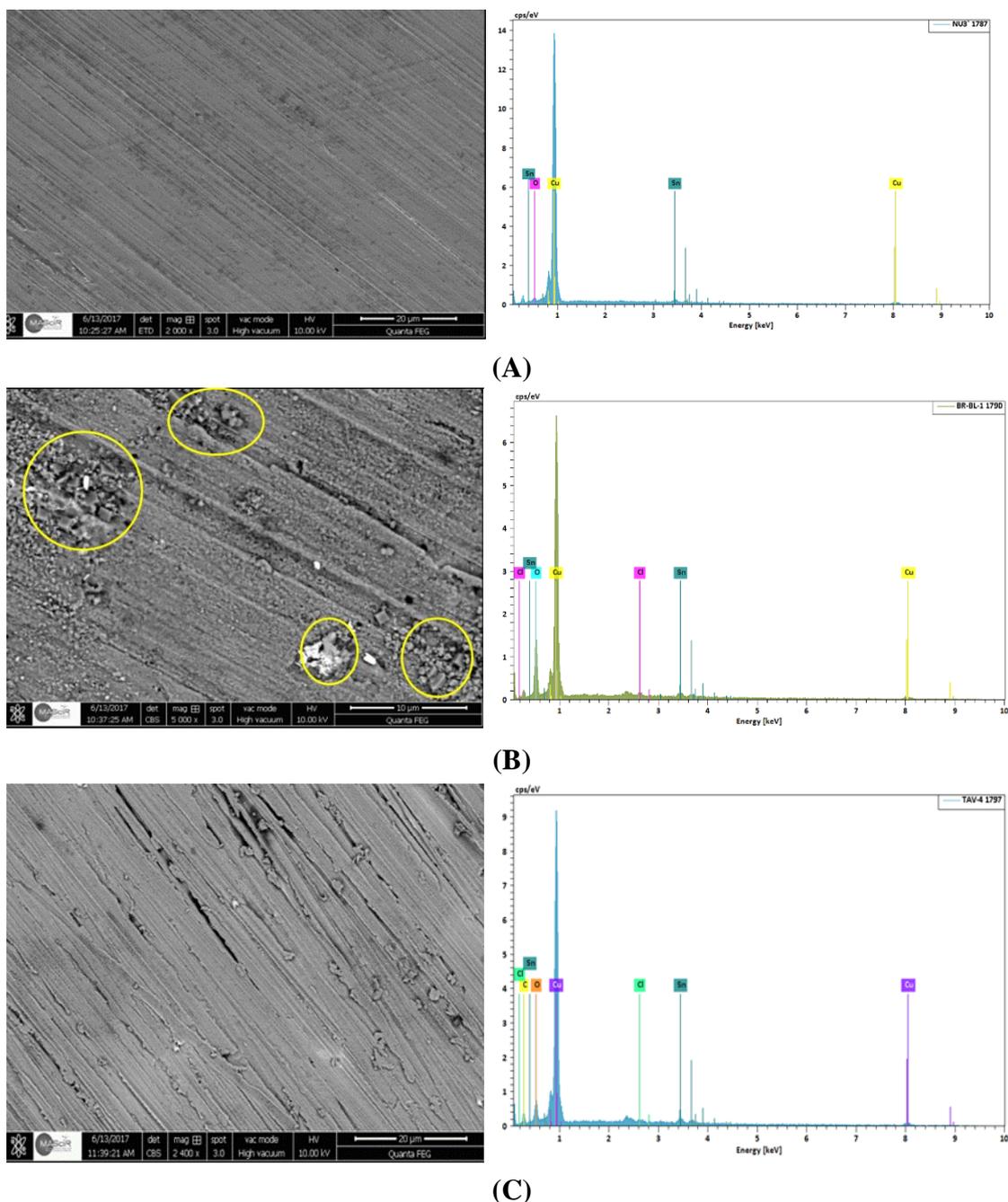


Fig. 6. (A) SEM images coupled with EDX analyzes of bronze B66 after polishing; (B) SEM images coupled with EDX analyzes of bronze B66 after 24 h of immersion in a solution of 3% NaCl; (C) SEM images coupled with EDX analyzes of bronze B66 after 24 h of immersion in a 3% NaCl solution in the presence of 150 ppm from TAV

After the experiment, the results obtained by the SEM and EDX analyzes in the absence and the presence of 150 ppm in TAV, after 24 h of immersion in a 3% NaCl solution are represented in Figure 6 (B and C).

Examination of Figure 6 shows that in the absence of the inhibitor (Fig. 6B), the appearance of a clear attack and development of several corrosion sites in the form of "bites". The EDX elemental analysis of this sample shows the presence of oxygen and chlorine in addition to the major elements (Cu, Sn and Pb), this favors the formation of corrosion products which would therefore be mainly in the form of oxides and copper chlorides. On the other hand, in the presence of the TAV inhibitor (Fig. 6C), the attack is markedly less marked, confirming the protective effect of the latter, which results in a low content of chlorine and oxygen and by the appearance of carbon. The main constituents of TAV were palmitic acid (11.91%), phytol (14.40%), linolenic acid (16.59%), diisooctylphthalate (11.84%) [14], may be responsible for this increase in carbon.

4. CONCLUSION

In this work we opted for the extraction of tannin from the green rind of *Aloe vera* noted TAV to be able to apply it in corrosion inhibition of Bronze B66 in a medium simulated with seawater. Inhibitory properties were achieved by gravimetric and electrochemical stationary (potentiodynamic polarizations) and transient (electrochemical impedance spectroscopy) methods.

The results obtained by gravimetric measurements and electrochemical methods, have shown that the extract TAV effectively inhibits the corrosion of Bronze B66 in 3% NaCl. Its inhibitory efficiency increases with the increase of inhibitor concentration.

We performed the analysis of the Bronze B66 surface by MEB/EDX after 24 h immersion in 3% NaCl, in the absence and in the presence of 150 ppm inhibitor, the surface analysis clearly shows the protection of the substrate in the presence of the inhibitor. These results contribute to the enhancement of natural products as green corrosion inhibitors. This is of significant economic interest at a time when synthesized organic inhibitors are toxic and expensive.

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