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Use of electrochemical measurements and surface analysis for the evaluation of the protective properties of 3-phenyl-1,2,4-tiazole-5-thione formulation of metallic cultural heritage

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ABSTRACT

In this work a formulation of a new organic compound, namely 3-phenyl-1,2,4-triazole-5-thione, was tested as a bronze corrosion inhibitor. This formulation (FPTS) has proven to be environmentally friendly, cheap and easy to use. The inhibitory effect of this formulation has been studied on commercial bronze (B66) with chemical composition, metallurgical features and micro-chemical structure similar to that of the ancient alloys installed in museum of Rabat (capital of Morocco) near the atlantic ocean, in order to be successfully employed and used for testing corrosion inhibitor validating cleaning and conservation techniques. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, Scanning Electron Microscopy coupled with chemical analysis (SEM and EDAX) and X-ray photoelectron Spectroscopy were used to study the inhibition action of FPTS in 3% NaCl. The obtained results show that the FPTS formulation has a significant effect against corrosion of B66 bronze in 3% NaCl solution, reaching an efficiency of 99% at 5.10^{-3} M. This result encouraged us to test this formulation on real archaeological objects. The evaluation of the protective effect of FPTS on archaeological bronzes shows that it provides good protection of the Bronze artefacts against atmospheric corrosion for a long duration of exposure.

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KEYWORDS

Bronze B66;
3% NaCl;
Corrosion;
Inhibition;
FPTS.

INTRODUCTION

Bronzes are subject to aggressive corrosion during their use especially when in contact with aggressive media such as air, sea or city with a high level of pollution. In general, it appears that for applications in harsh

environments, the use of protection methods is always tricky. Several methods used currently to prevent corrosion of Bronze. One of such methods is the use of organic inhibitors^[1-3]. Effective inhibitors are heterocyclic compounds that have π bonds, heteroatoms such as sulphur, oxygen and nitrogen^[4-6]. Heterocyclic com-

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pounds such as triazole-thione can provide excellent inhibition effect.

Regarding the adsorption of the inhibitor on the metal surface, two types of interactions are responsible. One is physical adsorption which involves electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge at metal/solution interface. The other is chemical adsorption, which involves charge sharing or charge transfer from inhibitor molecules to the metal surface to form coordinated types of bonds^[7,9].

In the present work, the inhibition characteristics of FPTS for bronze B66 in 3% NaCl was investigated using electrochemical techniques and surface analysis methods both in presence and absence of the inhibitor. From polarization curves and electrochemical impedance spectroscopy, the inhibition efficiency of FPTS was found to be around 99 % at 5 mM of inhibitor concentration. The obtained results show that FPTS reduce both the anodic and cathodic reaction rates. The surface analysis methods confirmed the good protective effect of the FPTS formulation.

EXPERIMENTAL

Inhibitor

The FPTS formulation is prepared in our Laboratory from 3-phenyl-1,2,4-triazole-5-thione and triethanolamine as described before^[9].

Electrolyte solution

The corrosive media is 3% NaCl solution similar by its ionic force to sea water, was prepared by dissolving NaCl (Fluka) in bidistilled water.

Bronze samples

The sample is a commercial biphasic Bronze B66 which composition was determined by EDX analysis, TABLE 1^[10].

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

Electrochemical techniques

Polarization measurements

Electrochemical measurements were conducted in

a conventional three electrodes cell, a platinum foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The working electrode was a Bronze B66. The specimens were cut in the shape of a disc, laterally isolated by a cathodic paint and an epoxy resin and screwed to a rotation axis. Was mechanically abrading with different grades of emery paper, degreased with acetone, rinsed with bidistilled water and dried between filter papers. All experiments were carried out at ambient temperature. The electrode area in contact with the corrosive solution was 0.78cm². The potentiodynamic polarization curves were recorded using an CHI 604 potentiostat and were recorded at a scan rate 1 mV S⁻¹ after the steady state is reached (1h) and the open circuit potential (OCP) was noted. The inhibition efficiency was calculated from equation (1):

$$E\% = \frac{I_{\text{corr}}^0 - I_{\text{corr}}}{I_{\text{corr}}^0} \times 100 \quad (1)$$

where i_{corr}^0 and i_{corr} are the corrosion current densities of uninhibited and inhibited solution, respectively.

Impedance measurements

Electrochemical impedance spectroscopy (EIS) was carried out using Gamry Potentiostat/Galvanostat (model FAS-1). A computer was used for collecting data. EIS measurements were carried out in a frequency range of 100 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential. All measures were operated in Faraday cage to minimize ambient electrical noises. The working electrode was rotating disk at 1000 rpm (Tacusel-Radiometer, ED1).

Analytical study

SEM and EDS analyses

Scanning electron microscopy (SEM) studies were performed with Leica Stereoscan 440 coupled with EDS elemental semi-quantitative analyses (Princeton Gamma-Tech).

X-ray photoelectron spectroscopy

The chemical composition of the surface was determined by X-ray photoelectron

Spectroscopy (DRX) using a non-monochromated Mg (K α) photon source. The experiments were performed using a Philips apparatus equipped with cobalt as anticathode.

RESULTS AND DISCUSSION

Measurements of corrosion potential

Figure 1 shows the evolution of the corrosion potential (E_{corr}) as a function of immersion time of B66 bronze in a 3% NaCl solution at open circuit in the

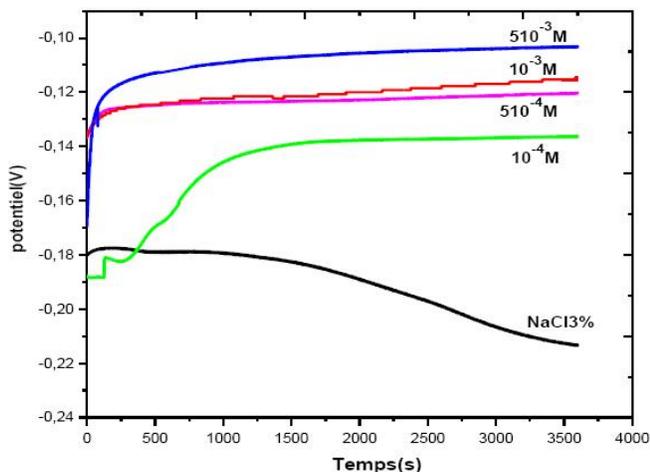


Figure 1 : Variation of the corrosion potential with Time for Bronze B66 in 3% NaCl solution containing different concentrations of FPTs

absence and presence of the studied inhibitor.

It can be observed from Figure 1 that the corrosion potential in the absence of inhibitor, tends to decrease with time. The decrease in corrosion potential has been attributed to the formation of the corrosion product on the Bronze surface. Therefore, there is a preferential dissolution of bronze in 3% NaCl.

Variation of the corrosion potential for FPTs at different concentrations shows in the few first minutes, a rapid increase in corrosion potential value with increasing FPTs concentrations. This trend may result from the fact that adsorption and surface coverage increase with the increasing inhibitor concentration. That is characteristic of anodic and cathodic inhibitor effect^[11]. It was explained that this shift in E_{corr} is due to active sites blocking effect that occurs when an inhibitor is added^[12]. Then, it changed towards more positive values and reached the steady-state value, thus the surface is effectively separated from the medium.

Polarization curves

The cathodic and anodic polarization curves were

plotted separately from a potential close to E_{corr} of Bronze in 3% NaCl solution in absence and presence of various concentrations of FPTs. Figures 2 and 3

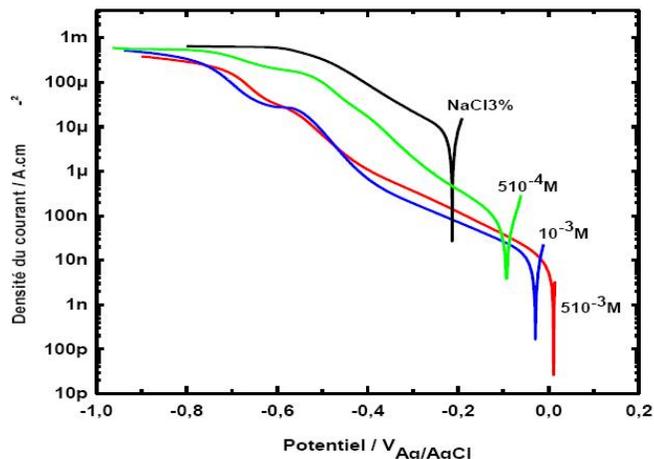


Figure 2 : polarization cathodic plots of Bronze B66 in 3% NaCl containing different concentrations of FPT obtained after one hour of immersion time at 1000 rpm and rate of 1 mV/s.

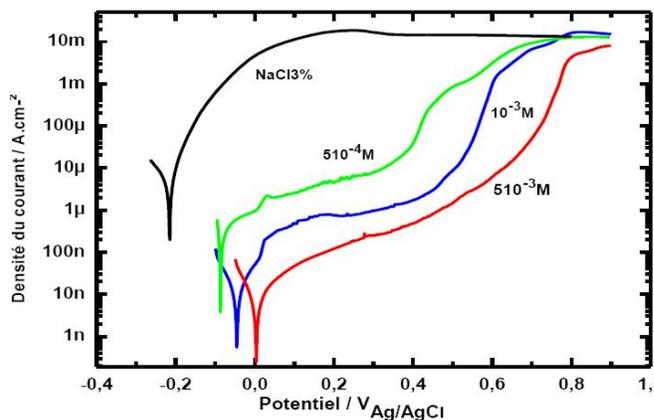


Figure 3 : polarization anodic plots of Bronze in 3% NaCl containing different concentrations of FPTs at 1000 rpm and of 1mV/s

present the obtained results.

Cathodic polarization

Figure 2 shows that the addition of the inhibitor results in a significant decrease in the corrosion current density. This later spends from $8.78 \mu\text{A} \cdot \text{cm}^{-2}$ in the absence of inhibitor to $12 \text{ nA} \cdot \text{cm}^{-2}$ in the presence of $5, 10^{-3} \text{ M}$ of FPTs. For higher potential $-0.45 \text{ V}_{\text{Ag}/\text{AgCl}}$, the variation of the current density in the semi-logarithmic scale is linear for all concentrations, the Tafel slope was not the same in the whole concentration range examined. Beyond this potential value, the current density

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increases in the cathodic direction to the value $-0.75 V_{Ag/AgCl}$, and then stabilizes the plateau current density is around (1mA). The latter is attributed to the diffusion limited reduction current of dissolved oxygen^[13] that persists in all concentrations of the inhibitor.

Anodic polarization

Figure 3 shows that in the absence of inhibitor, the current density increases rapidly in the vicinity of the corrosion potential, and then stabilizes at the higher anodic overvoltage.

In the presence of inhibitor, it can be clearly seen that the addition of FPTs to the corrosive solution reduces anodic dissolution of Bronze. The corrosion potential values shifts to more positive values. For potential lower than $0.5 V_{Ag/AgCl}$, the variation of the current density showing a pseudo current plateau whose density is less than $5 \mu A \cdot cm^{-2}$. This bearing becomes larger when the FPTs concentration increases. These results indicate the adsorption of inhibitor molecules on the Bronze surface. For more positive potential, the current density reaches a value of 10 mA. This is due to the inhibitor desorption from the metal surface. It also

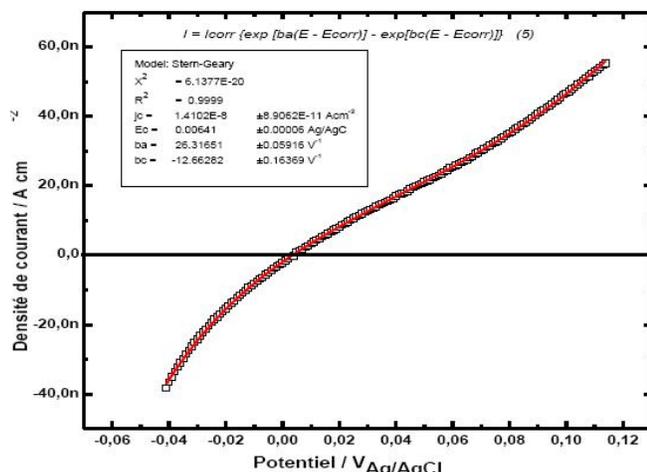


Figure 4 : Evaluation of corrosion current densities with Stern- Geary equation: B66 electrode in 3% NaCl + $5.10^{-3}M$ en FPTs for the anodic branches

TABLE 2 : Corrosion parameters of Bronze B66 in 3% NaCl with and without FPTs determined with Stern-Geary equation

[FPTS] (M)	Domaine cathodique			Domaine anodique			E (%)
	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	B_c (V^{-1})	E_{corr} ($V_{Ag/AgCl}$)	I_{corr} (μAcm^{-2})	B_a (V^{-1})	
0	-0.215	8.861	-9.511	-0.218	9.859	24.442	-
$5 \cdot 10^{-4}$	-0.092	0.095	-13.531	-0.091	0.251	29.156	97.5
10^{-3}	-0.029	0.011	-10.083	-0.045	0.015	28.967	99.8
$5 \cdot 10^{-3}$	0.008	0.010	-12.662	0.006	0.014	26.312	99.8

may due to pitting corrosion which comes under inhibitor film. As we have shown above, in the vicinity of corrosion potential, linear behavior is expected. The E_{corr} and the corrosion current density i_{corr} were evaluated from non-linear regression calculation near zero overall current. The result of regression calculation according to Stern-Geary equation^[14] is presented in Figure 4. The comparison of experimental and calculated data indicates that the regression procedure is very satisfactory.

E_{corr} and i_{corr} calculated from cathodic and anodic polarization curves are presented in TABLE 2.

E_{corr} shifted towards more positive value with increasing inhibitor concentrations, whereas i_{corr} decreased with addition of inhibitor, from 8.861 without inhibitor to $0.010 \mu A \cdot cm^{-2}$ at $5 \cdot 10^{-3}M$ of FPTs. This good inhibiting effect may be attributed to inhibitor film formation at the electrode surface, which seems to slow down the corrosion rate of Bronze B66 in 3% NaCl solution. The inhibition efficiency was around 99%. This confirms the protective effect of the FPTs.

Electrochemical impedance spectroscopic studies

The corrosion behaviour of Bronze B66 in 3% NaCl solution with and without various concentrations of FPTs was investigated by the impedance method at room temperature after 1h of immersion time. The effect of immersion period was also examined for FPTs at $5 \cdot 10^{-3}M$.

The Nyquist plots of bronze B66 at different concentrations of FPTs in corrosive solution are shown in Figure 5. The inhibition efficiency was calculated using charge transfer resistance from equation 2:

$$E \% = \frac{R_t^{-1} - R_{t(inh)}^{-1}}{R_t^{-1}} \times 100 \quad (2)$$

Where $R_{t(inh)}$ and R_t are the charge transfer resistance in the presence and absence of FPTs, respectively.

An examination of Figure 5 shows that in the ab-

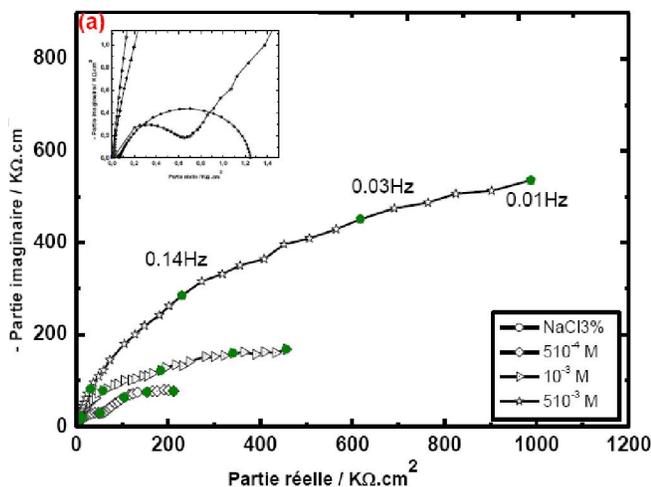


Figure 5 : Impedance diagrams of Bronze B66 in 3% NaCl at different concentrations of FPTs obtained at free corrosion potential at $\omega = 1000 \text{ tr min}^{-1}$

sence of inhibitor, the impedance diagram in the Nyquist plot is an arc with a small flattening at high frequencies. The polarization resistance determined from the extrapolation of the impedance spectra is about $1290 \Omega\text{cm}^2$. Although this diagram does not appear to represent a single capacitive loop, introducing a second time constant is needed to adequately model of the impedance diagrams. The corresponding electrical equivalent circuit consists of two parallel R and C, whose components are attributed to: R_e : electrolyte resistance, R_t : charge transfer resistance, C_d : double layer capacity, (R_F , C_F): Faradic impedance which appears as capacitive one, whereas the low frequency elements are related to the probable oxidation–reduction contribution of the corrosion products (R_F – C_F) as indicated in previous papers^[15].

In the presence of inhibitor, the impedance diagrams show a capacitive behavior different from that of the witness. This difference can be attributed to changes in the mechanism of the processes involved in the interface Bronze / electrolyte, due to the effect of FPTs. These diagrams show the appearance of three capacitive loops. At high frequencies, the capacitive loop di-

ameter is of the order $657 \Omega\text{cm}^2$, $678 \Omega\text{cm}^2$ and $912 \Omega\text{cm}^2$ respectively for $5 \times 10^{-4} \text{ M}$, 10^{-3} M and $5 \times 10^{-3} \text{ M}$ FPTs concentrations.

The polarisation resistance increase with increasing concentrations of inhibitor. It shifts from $1,2 \text{ K}\Omega\text{cm}^2$ without inhibitor to 264 , 541 and $1360 \text{ K}\Omega\text{cm}^2$ at 5×10^{-4} , 10^{-3} and $5 \times 10^{-3} \text{ M}$ of FPTs respectively. This indicates that the effect of the FPTs against Bronze corrosion can be attributed to its adsorption on the metal surface and limits the dissolution of Bronze^[16].

It was found that the results cannot be represented suitably by only one time constant circuit (2RC), but two capacitive loops are necessary for computer fitting of experimental data with an electrical equivalent circuit (3RC). The electrochemical parameters, C_f , R_p , C_d , R_t , C_F and R_F obtained from the EIS measurements are listed in TABLE 3

The data exhibited that the capacitive value C_f in presence of inhibitor is lower than $1 \mu\text{Fcm}^2$. Which confirm that the FPTs act by establishment of a protective inhibitor film relatively thick and compact. At low frequencies, there is a significant increase in the polarization resistance. Reached a value around $1360 \text{ k}\Omega\text{cm}^2$ in the presence of $5 \times 10^{-3} \text{ M}$ of FPTs, which shows that the FPTs has a significant effect on reducing the charge transfer at the interface is substantially constant for all concentrations. The efficiency of inhibitor is about 99%, which justifies the protective nature of FPTs. The $5 \cdot 10^{-3}$ of FPTs is selected as the best concentration.

The inhibition efficiencies are in a good agreement with that calculated from potentiodynamic measurements.

Effect of immersion time

Figure 6 presents the evolution of impedance spectra in 3% NaCl containing $5 \cdot 10^{-3} \text{ M}$ of FPTs for different immersion times. These diagrams have the same shape. It can be seen that R_t increases with time. This increase appears to be linear at low frequencies after 8

TABLE 3: Fitting parameters for the three circuits R - C parallel Figure. 5 by the simplex.

[FPTS] (M)	C_f (μFcm^2)	R_t ($\Omega \text{ cm}^2$)	C_d ($\mu\text{F cm}^2$)	R_i ($\text{k} \Omega \text{ cm}^2$)	C_F (μFcm^2)	R_F ($\text{k} \Omega \text{ cm}^2$)	IE %
0	8.23	0.331	67.5	1.29	-	-	-
$5 \cdot 10^{-4}$	0.066	657	0.62	88	0.32	264	99.5
10^{-3}	0.077	677	0.61	290	0.46	541	99.7
$5 \cdot 10^{-3}$	0.035	912	0.41	680	0.83	1360	99.9

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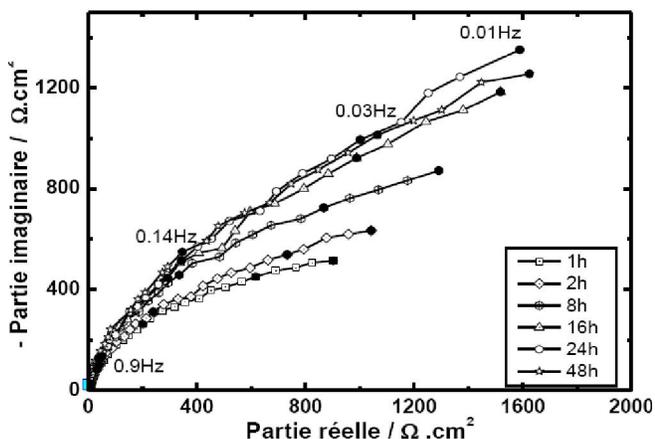


Figure 6 : Impedance data obtained from the Bronze B66 electrode exposed for different times to the 3% NaCl with $5.10^{-3}M$ of FPTs at 1000 tr min^{-1}

hours of immersion, reflecting diffusion through the inhibitor film.

Surface Analysis

a- Analyse EDS

Figures 7a and 7b show a micrographs and EDS spectras for the Bronze B66 in 3% NaCl without and with FPTs after 24h immersion time. The pictures of uninhibited B66 show that the surface is covered with corrosion products and appearing to be full of pits which are attributed to the presence of chloride ions. This effect is more pronounced in poor areas in tin (black spots). The presence of the $10^{-3}M$ of FPTs leads to the formation of protective layer adsorbed on the surface, which is responsible for the observed suppression of the rate of corrosion.

In the absence of inhibitor, Figure 7b exhibits the characteristics peaks which are related to Cu, Sn, Cl and Oxygen elements. This indicates that the corrosion product on Bronze surface being metal oxide. However, the data in Figure 7b in the presence of $10^{-3}M$ of inhibitor show additional peak characteristic of K and S elements, and the lower peaks height of oxygen and Cl that observed in the absence of inhibitor. These re-

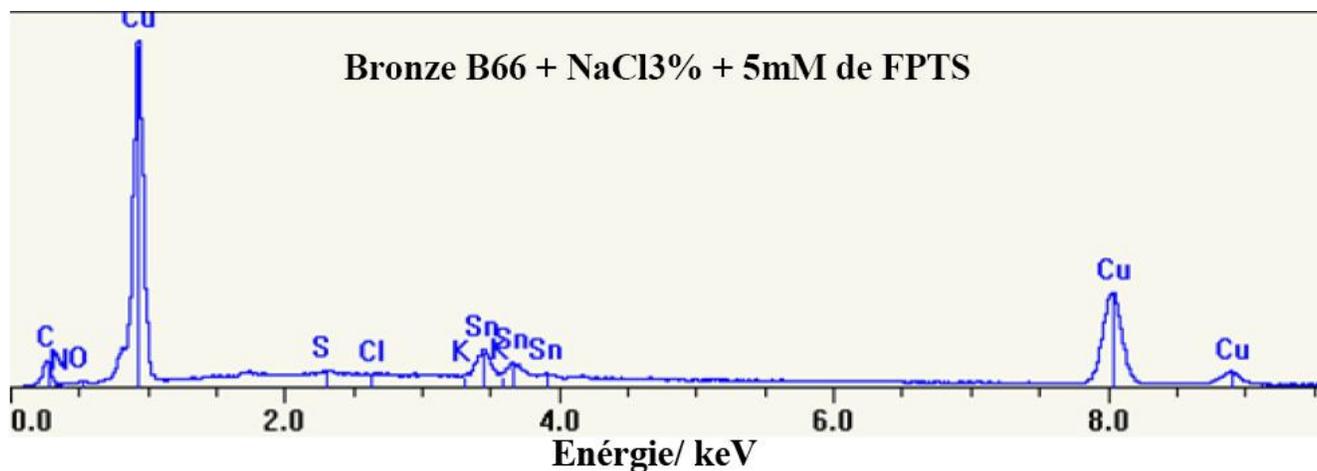
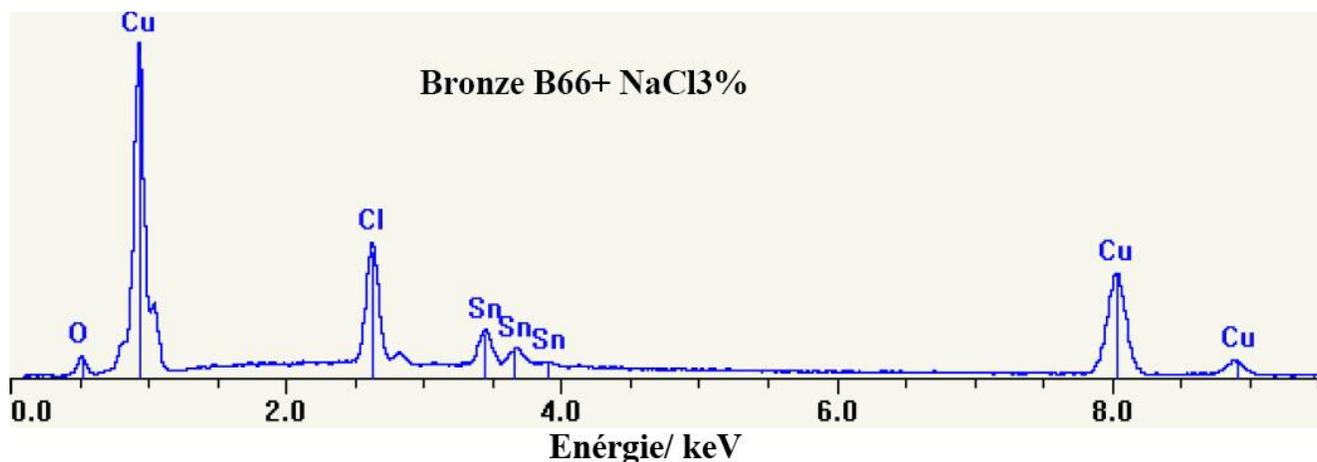


Figure 7b : EDS analysis of Bronze electrode surface in 3% NaCl for 20h immersion time with and without FPTs

sults proved that, the adsorption of inhibitor molecule on Bronze surface leads to high diminution of characteristic elements of metal oxides and chloride related to the blocking of active sites for the adsorbed inhibitor and isolate the metal surface from the corrosive environment, causing much reduced in the corrosion rates.

b- Analysis by X-ray diffraction

Figure 8 shows X-ray analysis of the B66 surface after 24 hours of immersion in a 3% NaCl solution without and with 1 mM of FPTs. In the absence of inhibitor, five bands were appeared around ($2\Theta=19.28, 22.32, 27.24, 31.77$) corresponding to the crystal structures ([1.1.1], [2.0.0], [2.1.0], [2.2.0]) of Bronze B66 and one band at ($2\Theta = 16.54$) characterizes the presence of copper oxide Cu_2O ^[17]. In the presence of FPTs, we note disappearance of the band corresponding to the copper oxide Cu_2O . It is attributed to the formation of a protective film on electrode surface. This

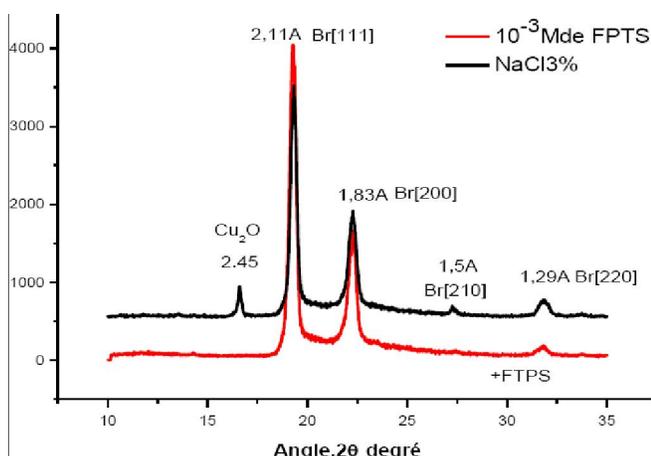


Figure 8 : X-ray spectra of Bronze B66 after 20 hours of immersion in 3% NaCl with and without FPTs

film acts as a barrier against aggressive ions and confirms the results obtained by EDS.

CONCLUSION

The study of the inhibition of Bronze corrosion in 3% NaCl using FPTs formulation as inhibitor, showed that this formulation inhibits both anodic and cathodic reactions by a decrease in current density and a shift of the corrosion potential to positive values. The FPTs may be considered a mixed corrosion inhibitor. In the anodic domain, we note a significant decrease in current density values in a large potential range. at high

concentration of inhibitor, It is important to note the existence a potential domain corresponding to an passive state. The inhibition efficiency reached a value of 99% at a concentration of 1 mM.

The electrochemical impedance spectra obtained at the corrosion potential confirm the protective effect of FPTs. This effect has been maintained during a long immersion time in the corrosive solution. It is attributed to establishment of thick and compact protective film on the metal surface, probably enhanced by the corrosion products. The dielectric properties of such a film can be deduced from the analysis of HF loops highlighted by these measures.

The EDX analysis and the X-ray spectra confirm the protective effect of FPTs formulation by the presence of chemical elements from the molecular structure of the inhibitor.

The FPTs represents an adequate solution for the protection of archaeological bronzes.

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