

## Comparative Effects of Tolytriazole and Benzotriazole Against Sulfide Attack on Copper

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Corrosion inhibition of copper by tolytriazole (TTAH) in comparison with benzotriazole (BTAH) was investigated in unpolluted and sulfide polluted 3.5 % NaCl. Both TTAH and BTAH give approximately similar results in unpolluted salt water. Electrochemical techniques illustrate that TTAH gives about (40%) higher efficiency than BTA in case of sulfide polluted media. Surface analysis by X-ray photoelectron spectroscopy reveals the presence of both sulfide and TTAH on the corroded surface. In sulfide polluted salt water TTAH shows better performance than BTAH. The mechanism of protection is attributed to the formation of protective film of TTAH or BTAH. The rate of destruction of the protective film in TTAH is lower than that of BTAH in the presence of sulfide ions. This result is established at sulfide concentration as low as  $10^{-3}$  M in the presence of  $10^{-2}$  M TTAH. The gained results prove that TTAH gives better resistance against sulfide attack.

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**Keywords:** Corrosion inhibition, copper, tolytriazole, benzotriazole, sulfide attack

### 1. INTRODUCTION

Corrosive attack on copper by polluted salt water is well known in the water treatment industry. The surface activity of copper is controlled by use of azoles inhibitors such as benzotriazole (BTAH), as follows: Cuprous oxide is normally a protective film for copper, but is readily attacked by  $\text{Cl}^-$ ,  $\text{SH}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_4^+$  and to a lesser extent  $\text{CO}_2$  [1]. Nitrogen-containing compounds, such as benzotriazole (BTAH), are commonly used as corrosion inhibitors for copper and copper alloys [2-6] in many environments. The lone electron pairs on the nitrogen atom coordinate with the metal substrate by physical absorption. Such nitrogen containing inhibitors are referred to as azoles in the water treatment industry. They include the commonly applied tolytriazole (TTAH), BTAH, and variations of chemical structure that produce comparable inhibiting films on metal surfaces. Heterocyclic compounds

containing nitrogen atoms are known as good corrosion inhibitors for many metals and alloys in various aggressive media [7-17]. The inhibition effect of a benzotriazole derivative such as tolytriazole (5-methyl benzotriazole, TTAH) on the corrosion of Fe-Cr alloys [18], copper [19-23] and brass [24] has been investigated.

Copper is widely used in many industries in polluted and unpolluted environments. The mechanisms in unpolluted media are well known [25-35]. The mechanism of sulfide attack on copper surface is attributed to the formation of complex with copper ion and followed by the oxidation of this complex gives copper sulfide. Hence copper faces a corrosion problem in the environments containing sulfide ions. In the presence of inhibitors, the protection is depends on the efficiency of the inhibitor to compete the sulfide ion to reach copper surface. The azoles and azole derivatives have a good inhibiting efficiency against corrosion of copper in unpolluted medium. However, their inhibiting efficiency in sulfide polluted media is questioned, and the challenge now is how to deal with sulfide attack in polluted media. The objective of this paper is to study the comparative inhibition efficiency and interaction of tolytriazole and benzotriazole and sulfide ions on the copper surface in sulfide polluted salt solution.

## 2. EXPERIMENTAL PART

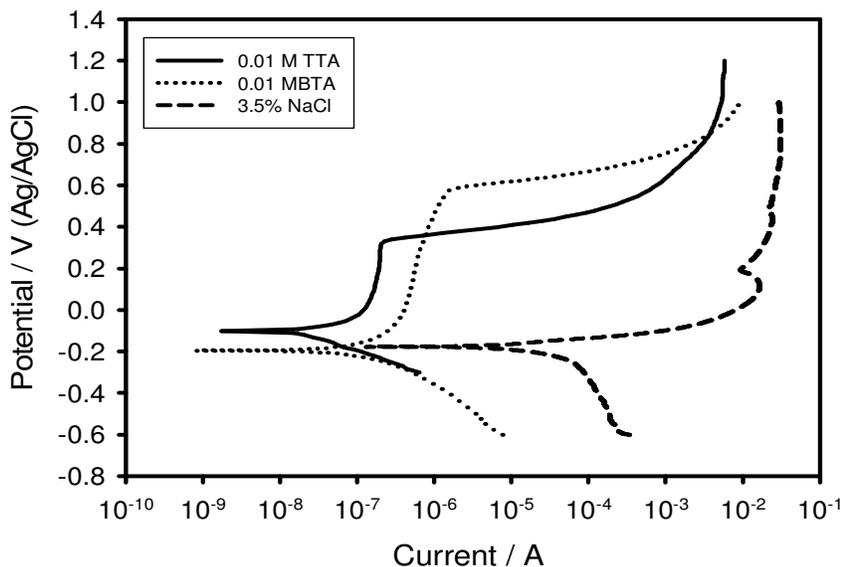
Electrolytic copper (99.9 %) was used as working electrode. The electrodes were in the form of rods having 0.96 cm. The working electrode was coated with protective adhesive except the cross sectional area, which exposed to the solution. The working electrodes were polished using SiC papers successively down to 2400 grits, followed by 0.3 micron alumina to acquire a mirror-like finish. Electrical contact to the external circuit was made through the rod. A conventional three-electrode cell was used with an Ag/AgCl reference electrode,  $E = 0.197$  V SHE, and a Pt sheet counter electrode. Solutions were prepared using deionized water, TTAH and BTAH from Aldrich, Analar Na<sub>2</sub>S from Merck and NaCl from BDH.

Potentiodynamic polarization curves were measured on the Cu electrodes at a voltage scan rate of  $1 \text{ mV s}^{-1}$  in 3.5% NaCl solution in the absence and in the presence of 0.001 M of sodium sulfide and 0.01 M of TTA and/or 0.01 M BTAH. Potential scanning started from the less to the more anodic potentials. The potential was controlled using a Gamry potentiostat. Polarization resistance ( $R_p$ ) of the electrodes was measured using electrochemical impedance spectroscopy (EIS) under different conditions of TTAH and/or BTAH and 0.001 M sulfide concentration. EIS experiments were also performed using the Gamry potentiostat. The values of  $R_p$  were calculated from the EIS spectra using the Gamry software. Measurements were performed at  $25 \pm 1^\circ\text{C}$  while the electrolyte was stirred using a magnetic stirrer. The surfaces of the electrodes were examined using XPS, VG SCIENTIFIC 200 Spectrometer (UK), using MgK $\alpha$  radiation (1253.6 eV) operating at 300W, 13 kV and 23 mA.

### 3. RESULTS AND DISCUSSION

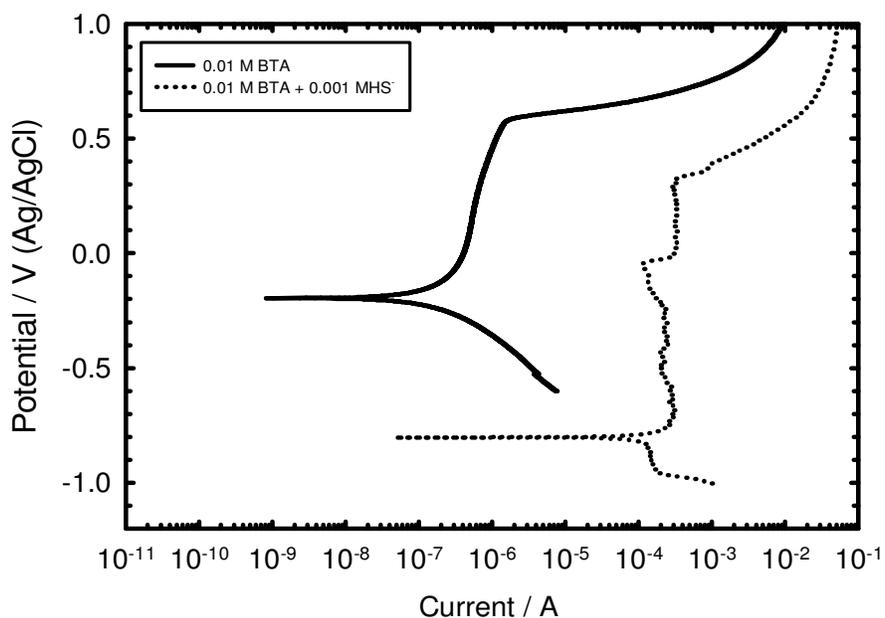
#### 3.1. Polarization curves

Figure 1 shows the effect of TTAH and BTAH on the polarization behavior of copper in 3.5 % NaCl. The obtained data refers to the TTAH shows higher effect of inhibition for the copper surface in saline media and this is very clear from the magnitude of the limiting currents. The protective film of TTAH copper complex which appeared in the anodic region gives better effect than the BTAH copper complex. These results were accepted because of the presence of methyl group in TTAH which have positive inductive effect (+I) makes the lone electron all the time on nitrogen atom and providing a good chance for coordination bond with copper surface. The passive regions in TTAH and BTAH ends at the break down potential,  $E_b$ , 0.56 and 0.58 V respectively, beyond which the current increases rapidly as the potential becomes more anodic. The rapid increase in current above  $E_b$  is caused by localized corrosion as a result of the breakdown of the protective film of TTAH and BTAH [36].

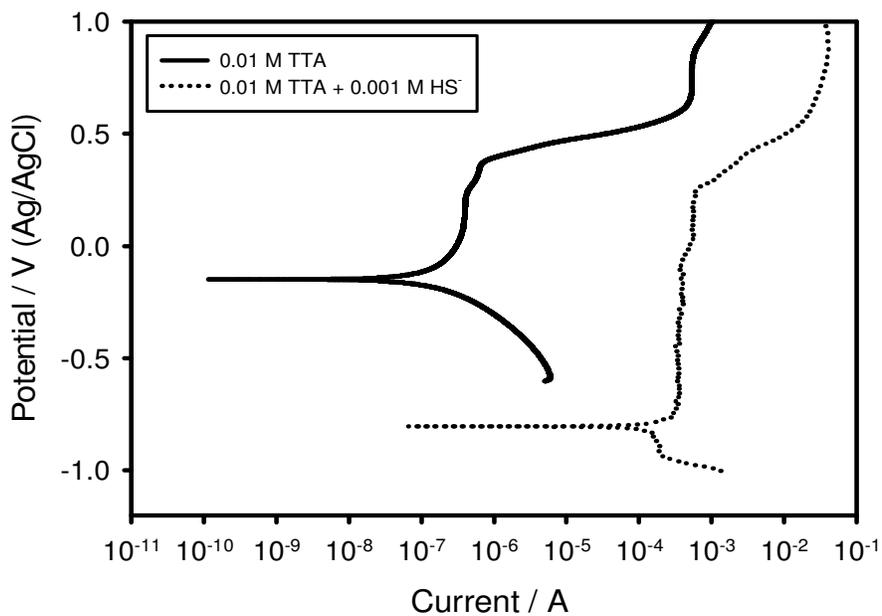


**Figure 1.** Comparison of the effects of BTA and of TTA on the polarization curves of copper in 3.5% NaCl.

Figures 2a and 2b show the effects of sulfide ions on the polarization curves of copper in the BTAH and TTAH solutions respectively. The sulfide ions have strong detrimental effect on the passivity caused by BTAH and TTAH. The obtained data shows the highly effect of sulfide ions on the decrease of the breakdown potential and increase of the current in the passive area. The current in the passive region is increased and similar rate of anodic dissolution is obtained. It is also noticed the shift of free corrosion potential in the cathodic direction.



**Figure 2a.** Effect of sulfide ions on the polarization curve of copper in the presence of  $10^{-2}$  M BTAH at  $1\text{mV s}^{-1}$ .



**Figure 2b.** Effect of sulfide ions on the polarization curves of copper in the presence of  $10^{-2}$  M TTA.

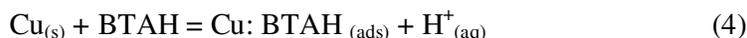
### 3.2. Current transients

Fig.3 illustrates the current transients measured in the presence of  $10^{-2}$  M of BTAH and TTA at a potential of 0.0 V vs Ag/AgCl (within the passive region). It is clearly noticed that the initial rapid

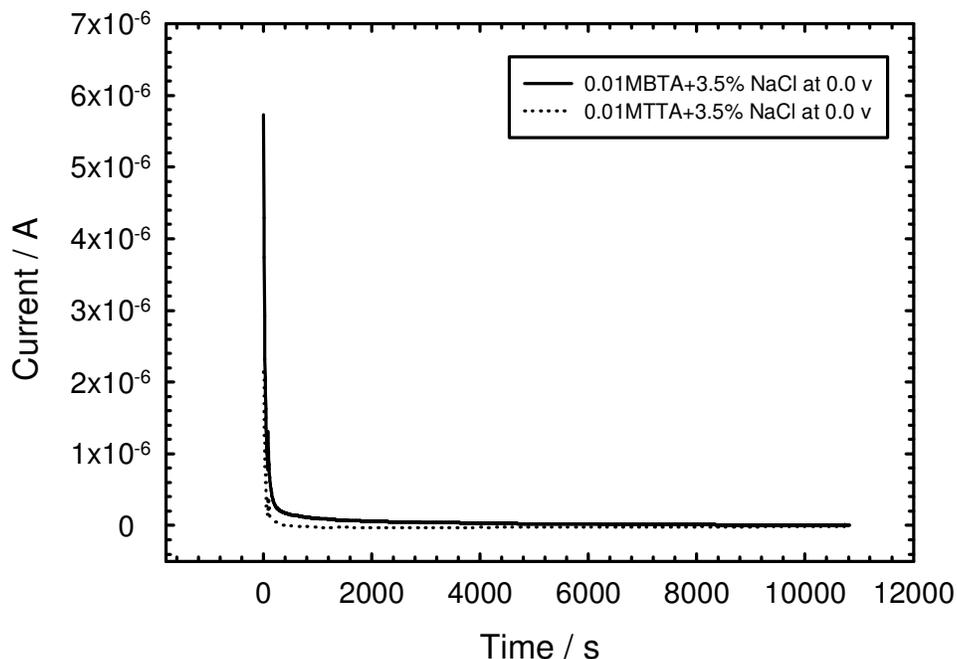
decrease of current with time before it reaches a steady value. After 1 h the currents were  $790 \text{ nA cm}^{-2}$ . The obtained data is illustrating the higher efficiency of BTAH and TTA against copper dissolution in the passive region. The passive region potential shows corrosion protection which is related to the formation of protective film of copper inhibitor complex according to the following equations [37-39].



The other mechanism postulates an adsorbed layer of BTAH or TTA i.e.



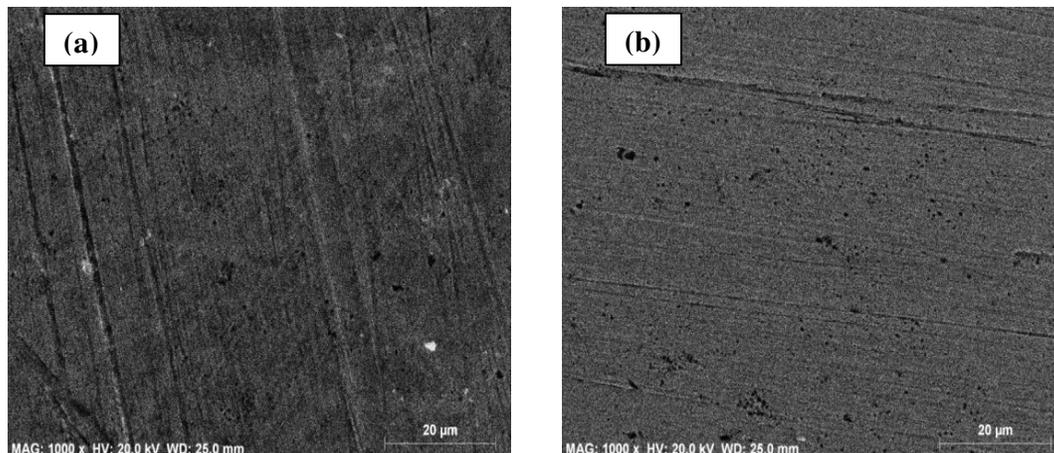
The formation of Cu (I)-TTA film [40-42] is attributed to the presence of  $\text{Cu}_2\text{O}$  which play an important role in the TTA adsorption. Positively charged surface will attract  $\text{Cl}^{-}$  ions and form  $\text{CuCl}_2^{-}$  complex with Cu. Equation (5) shows the formation of a polymeric Cu (I)-TTA film by the interaction between  $\text{CuCl}_2$  and TTAH.



**Figure 3.** Potentiostatic current transients produced by the copper electrode in the presence of  $10^{-2}$  M BTAH and TTA at 0.0 V.

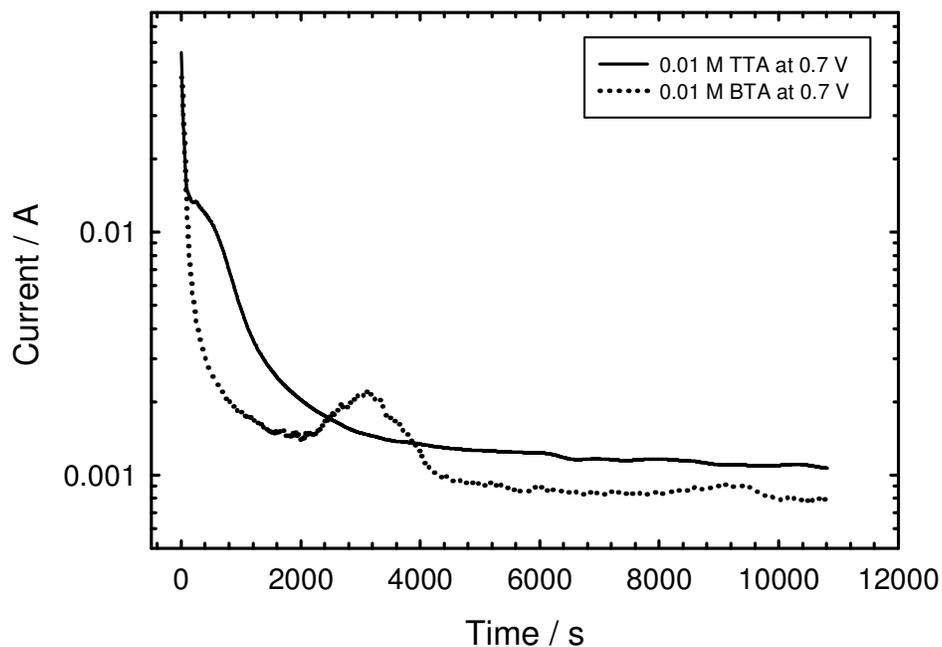
Figure 4 illustrates the scanning electron microscope images of the treated copper surface in the presence of TTAH and BTAH at 0.0 potential (passive region). The surface of copper after treatment

of inhibitors shows no corrosion products and the surface is very clear and shiny with no evidence of attack with chloride ions. These results agree with the current transients curves which give very low current approach zero ampere and it is prove that the two inhibitors shows higher efficiency in the unpolluted sulfide media.



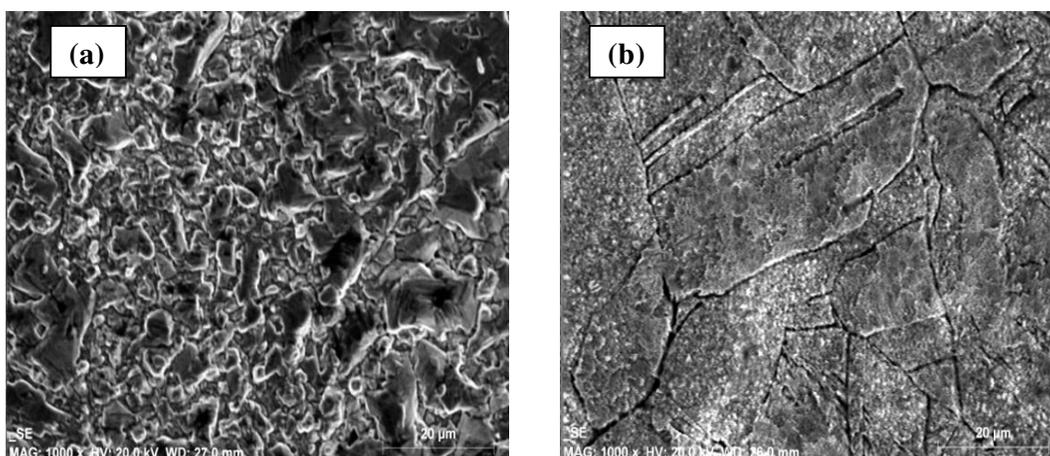
**Figure 4.** SEM images of Cu electrode surface at 0.0 V in 3.5 %NaCl in the presence of (a)  $10^{-2}$  M TTA (b)  $10^{-2}$  M BTAH.

Figures 5a and b shows the effect of polarization of copper at potential higher than the breakdown potential on the current transients of TTAH and BTAH. The obtained current for both inhibitors was 1 mA.



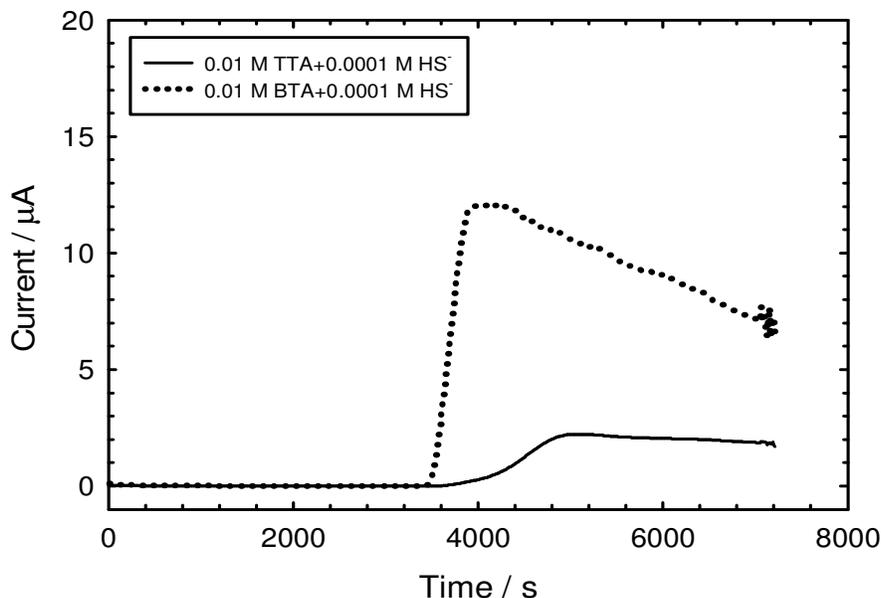
**Figure 5.** Potentiostatic current transients produced by the copper electrode in the presence of  $10^{-2}$  M BTAH and TTA at 0.7 V.

Figure 6 shows the SEM images under these conditions which, illustrated that copper surface in case of TTAH shows general corrosion but in case of BTAH shows inter-granular corrosion. The protective film of TTAH is completely destroyed at the breakdown potential and so the general corrosion is clearly noticed on the copper surface. The obtained results explained that the protective film of benzotriazole is still occupy some of copper surface and the inter-granular corrosion is occurred only in the weak points of protective film and as we know the localized corrosion is very dangerous more than the general corrosion.

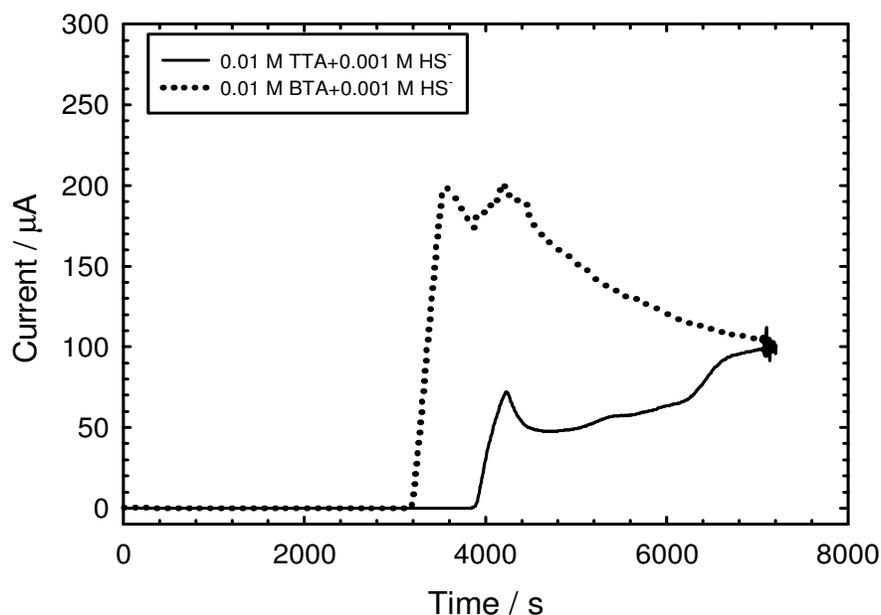


**Figure 6.** SEM images of Cu electrode surface at 0.7 V in 3.5 %NaCl in the presence of (a)  $10^{-2}$  M TTA (b)  $10^{-2}$  M BTAH.

Figure 7 a and b illustrate the effect of sulfide injection on the current transients of copper electrodes which pretreated for 1 hr at the passive potential 0.0 V in  $10^{-2}$  M TTAH and BTAH salt solution before injection. The injected sulfide concentrations were  $10^{-4}$  M and  $10^{-3}$  M respectively. The obtained results showed rapid increase in current upon injection of sulfide ions that appears in all concentrations of sulfide ions. The results indicate that destroying of the protective film of TTAH and BTAH but with difference of resistance of sulfide attack with copper surface. The magnitude of this sudden increase in current upon injection of sulfide ions is taken as a measure of the intensity of sulfide attack. The sulfide concentration of  $10^{-3}$  M makes rapid increase in current of about 200  $\mu$ A in case of BTAH and 78  $\mu$ A in case of TTAH. This indicates that the resistance of sulfide attack of TTAH is greater than BTAH by about 40 %. In case of sulfide concentration of  $10^{-4}$  M the increase of current 12  $\mu$ A in case of BTAH and 2  $\mu$ A in case of TTAH. In general the two inhibitors does not prevent the sulfide attack, however the TTAH lower its intensity against copper surface. The reasons of current jump upon sulfide ions injection is related to the oxidation of sulfide ions to CuS and the increase of corrosion rate of copper. Some reviews proved that the oxidation of the sulfide ions contributes only 8% of the charge passed upon injection of the sulfide ions while the rest of the charge is due to enhanced corrosion of copper [43, 44].



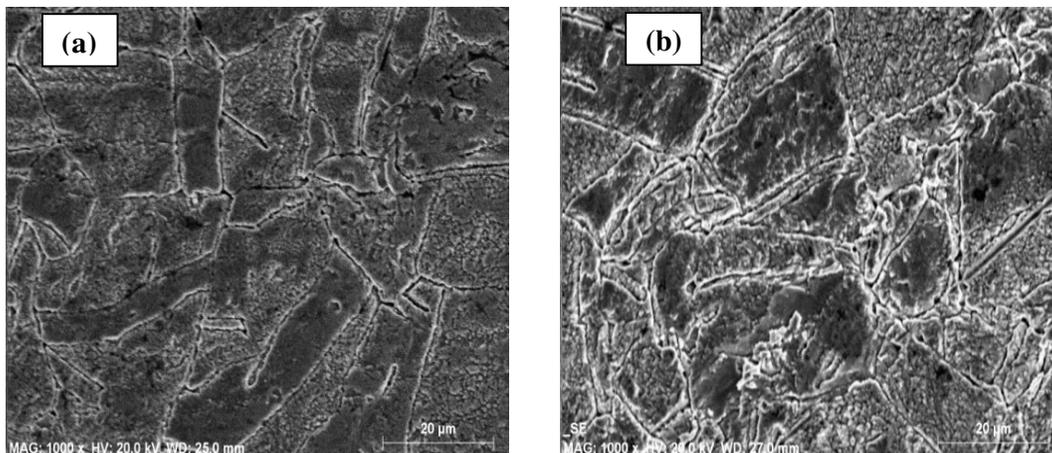
**Figure 7a.** Comparison of the current transients of copper electrodes polarized in the presence of  $10^{-2}$  M TTA and  $10^{-2}$  BTAH before and after injection of  $10^{-4}$  M sulfide ions. The electrode was polarized at 0.0 V vs Ag/Ag/Cl.



**Figure 7b.** Comparison of the current transients of copper electrodes polarized in the presence of  $10^{-2}$  M TTA and  $10^{-2}$  BTAH before and after injection of  $10^{-3}$  M sulfide ions. The electrode was polarized at 0.0 V vs Ag/Ag/Cl.

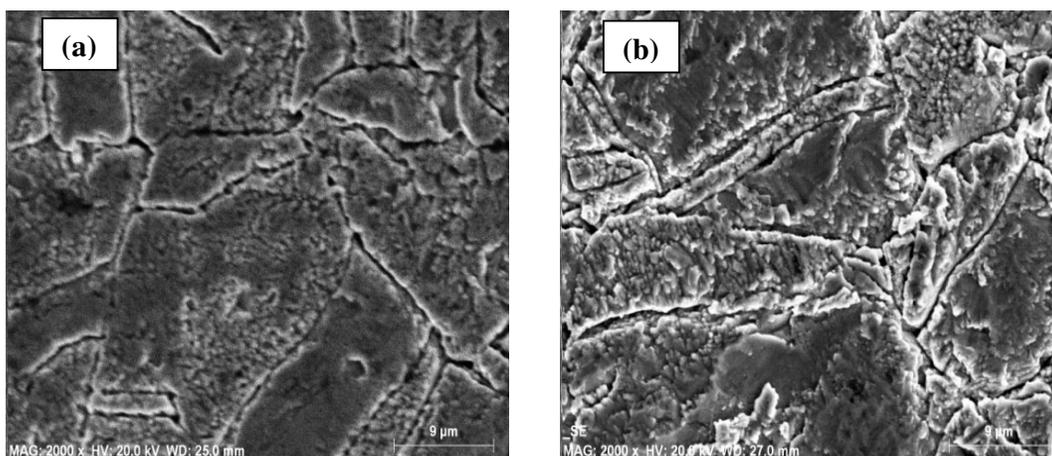
Figure 8 shows the difference between the surfaces of copper electrodes after the injection of sulfide ions to the  $10^{-2}$  M TTAH and  $10^{-2}$  M BTAH solutions at the passive potential (0.0V). The obtained images illustrate that the copper surface which treated with BTAH have localized (intergranular corrosion) and general corrosion and these results is attributed with the fully destruction of the

protective film due to the sulfide attack. In case of TTAH it is clearly noticed that the surface have only localized corrosion and this means that the film is not fully destroyed so the attack occur only in the weak points of the protective film and the current transient proved these results.



**Figure 8.** SEM images of Cu electrode surface at 0.0 V in 3.5 %NaCl and  $10^{-3}$  M sulfide in the presence of (a)  $10^{-2}$  M TTA (b)  $10^{-2}$  M BTAH. 1000 X

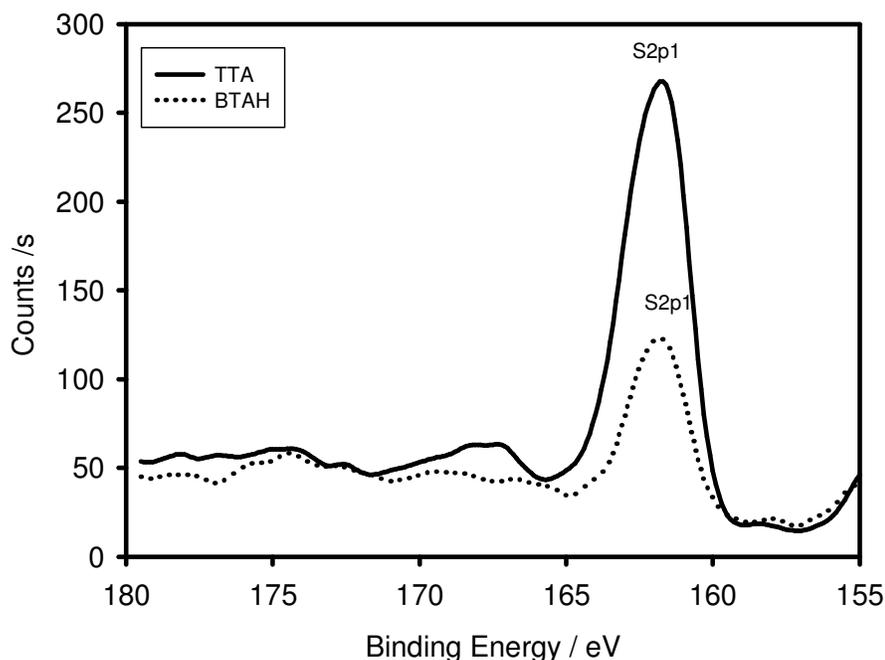
The high magnification images in Figure 9 shows the difference between TTAH and BTAH in the depth and width of the inter-granular corrosion. It is clearly noticed that the image of BTAH have more depth and width more than TTAH. The SEM images in figure give further prove for the good resistance of TTAH compared with BTAH in polluted media.



**Figure 9.** SEM images of Cu electrode surface at 0.0 V in 3.5 %NaCl and  $10^{-3}$  M sulfide in the presence of (a)  $10^{-2}$  M TTA (b)  $10^{-2}$  M BTAH. 2000 X

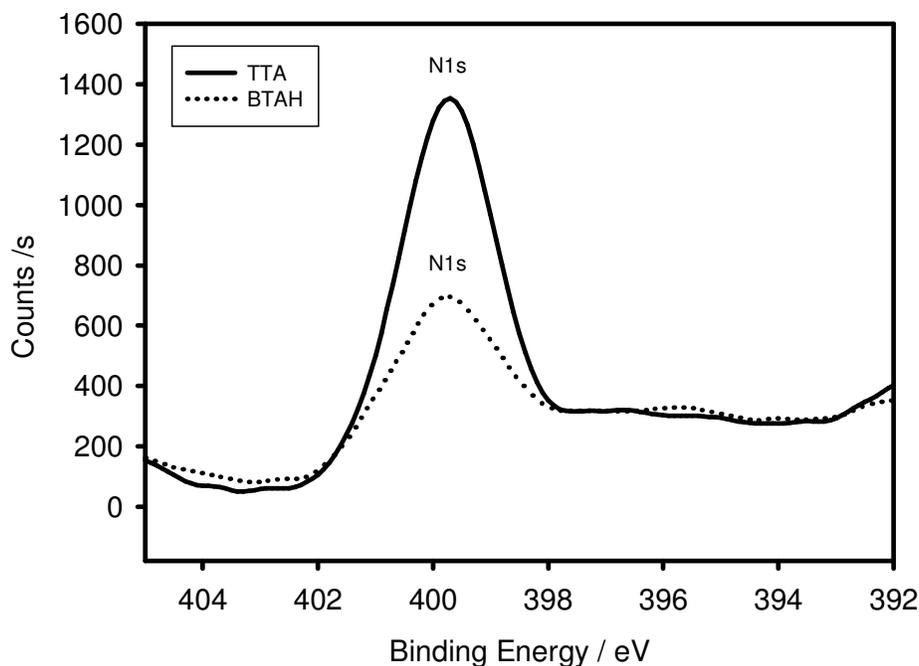
### 3.3. X-ray photoelectron spectroscopy (XPS)

Figures 10a explain the XPS spectrum obtained from the corroded copper surface in sulfide polluted salt water in the presence of 0.01 M TTAH and 0.01M BTAH. The electrode was subjected to 0.01M TTAH for 1 hr at 0.0V vs Ag/AgCl before injection of 0.001 M sulfide ions, which remained in contact with copper surface for another 1 hr. The XPS spectrum shows a peak of S2p at a binding energy of 162.0 eV reveals the presence of sulfide ions in the form of copper sulfide. The absence of an S2p at 164.0 eV reveals the absence of elemental sulfur on the corroded copper surface [43]. The XPS results of TTAH show a counts of sulfide ion of 260 and 120 in case of BTAH, which indicates that the amount of sulfide ions on the copper surface in case of TTAH are more than the case of BTAH and this proves that the TTAH is more resistant to the sulfide attack than BTAH. The dissolution of copper as copper sulfide in case of BTAH is more than in case of TTAH as shown by the low counts of sulfide ions on the copper surface in case of BTAH, furthermore the fully destruction of BTAH protective film. The high amount of sulfide ions reveals to low dissolution rate of copper as copper sulfide due to the presence of covered area with TTAH protective film.



**Figure 10a.** XPS spectrum of the S2p signal obtained from the copper electrode in a medium of 3.5% NaCl + 0.01 M TTA and/ or 0.01 M BTA after injection of 0.001 M sulfide ions at 0.0 V.

Figures 10b explain the XPS spectrum of N1s obtained from the corroded copper surface in polluted salt water in presence of 0.01 M TTAH and 0.01 M BTAH. The XPS spectrum reveals the presence of N1s peak at a binding energy of 400 eV referred to the peak of C1s at 284.6 eV [44]. The N1s peak of TTAH shows counts about 1380 and in case of BTAH shows counts about 700, these results reveals to the presence of the protective film of inhibitor but in case of TTAH more than BTAH by about 50 % and these results are clearly noticed in SEM Images and the difference of current increase after sulfide ions injection (Figures 7a and 7b).



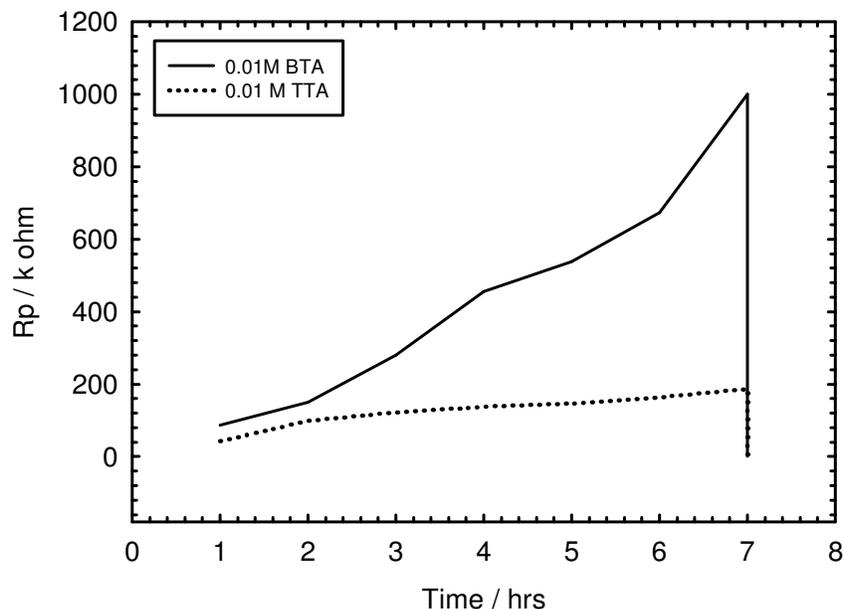
**Figure 10b.** XPS spectrum of the N1s signal obtained from the copper electrode in a medium of 3.5% NaCl + 0.01 M TTA and/or BTA 0.01 M after injection of 0.001 M sulfide ions at 0.0 V.

### 3.4. Polarization resistance

Figure 11 shows the electrochemical impedance spectra of immersed copper electrode in the inhibited unpolluted brine solution for 7 hours before injection of sulfide ions. The results show gradual increase of polarization resistance with time intervals which prove that the inversely proportional relation between polarization resistance and the corrosion rate. Equation (6) gives the relation between  $R_p$  and the  $i_{corr}$  which used as a function of corrosion rate [44-48]:

$$R_p = K/i_{corr} \quad (6)$$

where  $K$  is a constant for each system. Although the BTAH gives higher polarization resistance more than TTAH, the injection of sulfide ions gives suddenly decrease of polarization resistance in the two inhibitors, which indicates to the failure of protective film and increasing of corrosion rate. The BTAH shows decrease of  $R_p$  from 1000 to 0.3 Ohms but incase of TTAH the  $R_p$  decreases from 186 to 1.6 Ohms. The gained results prove that the resistance of TTAH for sulfide ion more than BTA and the results agree with the curves of current transients Figs 7a and 7b. The obtained data prove the rapid effect of sulfide ions, which is clearly noticed from the rapid decrease of polarization resistance.



**Figure 11.** Effect of immersion time and sulfide injection on the polarization resistance, determined by EIS technique, of copper electrode immersed in a solution of 3.5 % NaCl+ $10^{-2}$  M TTA. Note the sudden decrease of  $R_p$  upon injection of  $10^{-3}$  M sulfide ions.

#### 4. CONCLUSIONS

The current transients reveal interesting interaction between the injected sulfide ions and the TTAH on copper surface as well as the effect of the concentration of sulfide ions. BTAH gives lower efficiency against the injection of sulfide ions, which depends on the sulfide concentration. On the contrary, an order of magnitude the TTAH gives 40 % higher efficiency than BTAH in case of  $10^{-3}$  M sulfide ion concentration and gives about 16.6% higher that BTAH in case of  $10^{-4}$  M sulfide concentration. It is concluded that the TTAH gives higher effect more than BTAH against sulfide attack on the copper surface. Extended pre-passivation of the copper surface in the presence of TTAH improves its resistance to sulfide attack more than BTAH.

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