International Journal of Recent Development in Engineering and Technology
Website: www.ijrdet.com (2347 – 6435(Online), Volume 1, Issue 2, November 2013)

Inhibition of Copper Corrosion in The Presence of Synthesized (*E*)-2-(4-Bromophenoxy)-*N′*-(2,4-Dihydroxybenzylidene) Acetohydrazide in Polluted and Unpolluted Salt Water

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Abstract**-- (*E*)-2-(4-Bromophenoxy)-*N′*-(2,4-dihydroxybenzylidene) acetohydrazide (BDA) was synthesized in the laboratory and characterized by spectroscopic tools and evaluated as a corrosion inhibitor for copper in 3.5% NaCl by electrochemical studies. Results obtained revealed that BDA was a very good inhibitor with efficiency of about 82%, 57% in unpolluted polluted media respectively. Potentiodynamic polarization curves showed that BDA is a cathodic inhibitor. The ability of the studied inhibitor to inhibit the corrosion of copper was due to the presence of two nitrogen atoms and four oxygen atoms on its structure. Surface analyses were also carried out, to establish the mechanism of the corrosion inhibition of copper polluted and unpolluted salt water. The promising results were achieved in polluted sulfide media with good inhibition efficiency with regards to the film stability.**

Keywords**— Corrosion inhibitors, Copper Corrosion, (*E*)-2-(4-Bromophenoxy)-*N′*-(2,4-dihydroxybenzylidene) acetohydrazide Inhibition efficiency, Polarization curves, Surface analysis**

I. INTRODUCTION

Copper and its alloys are largely used in industrial applications because of their relatively good resistance against the corrosion and also because of its ionization potential is more anodic than the hydrogen evolution process. The presence of oxygen and in neutral medium, a stable oxide will cover the copper surface. However, in presence of some pollutants such as chlorine, sulfide or ammoniac in chloride medium, copper and its alloys may suffer a severe corrosion. An important position among inhibitors belongs to organic compounds that can form compounds hardly soluble in water with cations of the metal being protected [1-4]. Organic inhibitors are largely used, with success, to protect copper and copper alloys from the corrosion. Many papers reported that nitrogen containing organic compounds, such as azoles, reveal a marked inhibiting efficiency [5-16].

Generally, the organic molecules inhibit corrosion by creation of a physical barrier via adsorption at the metal-solution interface - typically by electrostatic adsorption, although other modes of adsorption are also possible. Equation (1) shows the adsorption of an organic inhibitor molecule at an electrolyte/metal interface is often considered as the displacement of adsorbed water at the inner Helmholtz plane of the surface [17].

$$Org_{(aq)}+nH_2O_{(ads)} = Org_{(ads)}+nH_2O_{(aq)} \qquad (1)$$

It is well known that organic compounds which can donate electron pair are potential corrosion inhibitors. Azoles, triazoles and sulfoxides are considered as potential inhibitors which are effective in neutral and basic solutions [18-21]. The inhibition of corrosion efficiency of these materials is depending upon their ability of bonding to copper metal with nitrogen or sulfur atoms. The mechanism of sulfide attack on the copper surface will be presented by the following equations [22]:

The first step is the hydrogen evolution:

$$2H_2O+2e^- = 2OH^-+H_2 \qquad (2)$$

Reduction of dissolved oxygen:

$$O_2+2H_2O+4e^- = 4OH^- \qquad (3)$$

Sulfide ion may hydrogenate:

$$S^{2-}+H_2O = HS^-+OH^- \ pK = 14.9 \qquad (4)$$

Sulfide ions combine with metallic copper:

$$Cu+HS^- = Cu(HS^-)_{ads} \qquad (5)$$

The anodic dissolution of copper may take place:

$$Cu(HS^-) = Cu(HS)+e^- \qquad (6)$$

Dissociation:

$$Cu(HS) = Cu^++HS^- \qquad (7)$$

Recombination:

$$2Cu^{+}+HS^{-}+OH^{-} = Cu_2S+H_2O \qquad (8)$$

Overall reaction:

$$4Cu+2S^{2-}+O_2+2H_2O = 2Cu_2S+4OH^{-} \qquad (9)$$

Formation of the cuprous oxide:

$$4Cu+O_2 = 2Cu_2O \qquad (10)$$

However, the presence of Cu_2S prevents the protective effectiveness of Cu_2O film. The adsorption of sulfide ions induces a negative charge at the copper surface, which catalyses the hydrogen evolution reaction [23]:

$$HS^{-}+e^{-} = H_{ads}+S^{2-} \qquad (11)$$

$$H_{ads}+H_{ads} = H_2 \qquad (12)$$

The formation of $Cu(H_2S)_{ads}$ complex or an establishment of sulfur and Cu linking weakens Cu and O or (OH) bonding, leading to the acceleration of corrosion rate. The aim of this paper is to study the corrosion behavior of copper in presence of the (*E*)-2-(4-Bromophenoxy)-*N'*-(2,4-dihydroxybenzylidene) acetohydrazide in a medium of 3.5% NaCl and/or polluted by the sulfide and the formula of this inhibitor is mentioned in figure (1).

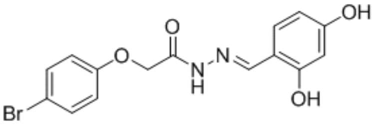


Figure (1) Molecular structure of (*E*)-2-(4-bromophenoxy)-*N'*-(2,4-dihydroxybenzylidene) acetohydrazide (BDA).

II. Materials And Methods

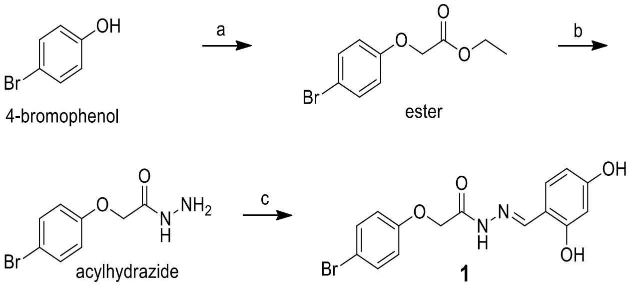
All chemicals were purchased from common commercial suppliers and used without further purification unless otherwise stated. Melting points were determined on a Gallenkamp melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Brucker Spectrometer, respectively, at 600 and 150.94 MHz using DMSO-d_6 as solvent and as a self-reference at (δ) 2.50 ppm. Mass spectra were recorded on a Finnigan mat. SSQ-7000 GC-MS spectrometer. Microanalyses were performed at the Microanalytical Center at Cairo University and their results were found to be in good agreement with calculated values (±0.2%). Analytical thin-layer chromatography (TLC) was carried out using Merck 60 F_{254} aluminum sheets and visualized by UV light (254 nm).

1- Synthesis of (E)-2-(4-bromophenoxy)-N'-(2,4-dihydroxybenzylidene) acetohydrazide (BDA).

In the present work, the (*E*)-2-(4-bromophenoxy)-*N'*-(2,4-dihydroxybenzylidene) acetohydrazide was synthesized in the laboratory following these procedures:

A solution of 2-(4-bromophenoxy) acetohydrazide (245mg, 1mmol) and 2,4-dihydroxybenzaldehyde (173mg, 1mmol) in absolute ethanol (15mL) was refluxed for 6h. The reaction mixtre was cooled to room temperature. The white craystalline product was filtered, dried, and recrystallized from absolute ethanol to afford the desired product BDA. To synthesize compound BDA, first, commercially available 4-bromophenol was treated with ethyl bromoacetate in boiling acetone in presence of anhydrous potassium carbonate as a heterogeneous base to afford the corresponding ester [24]. Next, the ester was converted to the acylhydrazide after the hydrazinolysis of the ester in refluxing absolute ethanol for 8h [25].

Finally, the acyl hydrazide was reacted with 2,4-dihydroxybenzaldehyde in boiling absolute ethanol for 6h to afford the target product. The structure of the desired product was identified by using ^{1}H NMR, ^{13}C NMR, and other spectroscopies as stated in the experimental section. However, the ^{1}H NMR spectrum of hydrazone BDA revealed a characteristic singlet at δ = 4.66 due to $-O\underline{CH_2}CO$ protons, which was confirmed by its ^{13}C NMR signals at δ = 66.51. The signals at 8.40 were due to the vinyl proton whereas the D_2O exchangeable broad singlet peaks at δ = 9.95, 11.18, and 11.59, were assigned to one NH proton and two aromatic hydroxyl protons, respectively.



Scheme 1: Synthetic route of BDA (*E*)-2-(4-bromophenoxy)-*N'*-(2,4-dihydroxybenzylidene) acetohydrazide. (a) ethyl bromoacetate, K_2CO_3, acetone, reflux, 8-10 h. (b) hydrazine hydrate, ethanol, reflux, 8 h. (c) 2,4-dihydroxybenzaldehyde, ethanol, reflux, 6h.

2- Identification of BDA

Yield: 335 mg (92%) of white crystals; mp 234-6 °C. ^{1}H NMR, δ (ppm): 4.66 (s, 2H, linker), 6.32 (m, 2H, Ar), 6.94 (m, 2H, Ar), 7.29 (d, *J* = 8.6 Hz, 1H, Ar), 7.46 (m, 2H, Ar), 8.40 (s, 1H, vinyl, 9.95 ((s, 1H, br, NH, D_2O exchangeable), 11.18 (s, 1H, br, OH, D_2O exchangeable), 11.59 (s, 1H, br, OH, D_2O exchangeable); ^{13}C NMR, (ppm): 66.51, 102.55, 107.68, 110.31, 116.79, 116.95, 117.02, 131.92, 132.01, 132.12, 149.23, 157.01, 159.31, 160.77, 163.32. Anal. Calcd. for $C_{15}H_{13}BrN_2O_4$ (365): C, 49.33; H, 3.59; Br, 21.88; N, 7.67, O, 17.53. Found: C, 49.38; H, 3.54; Br, 21.81; N, 7.71; O, 14.72.

3- Electrochemical Measurements

The experiments were performed in a classical three-electrode electrochemical cell. Copper (99.9%) rods having 0.96 cm diameter was used as the working electrode, platinum electrode as a counter electrode and saturated Ag/AgCl electrode as a reference electrode, E = 0.197 V SHE. The working electrode was coated with protective adhesive except the cross sectional area is 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. Solutions were prepared using deionized water, Na_2S from Merck and NaCl from BDH. Potentiodynamic polarization curves were measured on the Cu electrodes at a voltage scan rate of $1mVs^{-1}$ in 3.5% NaCl solution containing 0.01M of sodium sulfide and laboratory synthesized BDA. Potential scanning started from the less to the more anodic potentials. The potential was controlled using a Gamry potentiostat. Measurements were performed at 25±1°C while the electrolyte was stirred using a magnetic stirrer. Scanning electron microscope was used to study the morphology of the copper surface and XPS, VG SCIENTIFIC 200 Spectrometer (UK), using MgK_α radiation (1253.6 eV) operating at 300 W, 13 kV and 23 mA.

III. RESULTS AND DISCUSSION

1- Polarization curves

Each experiment was carried out with a freshly abraded electrode. The electrode was first left at the open-circuit conditions during 30 min. Then, the polarization curves were recorded.

The polarization curves were carried out for serial concentrations from BDA 5, 10, 15, 25 and 50ppm and it is found that the minimum concentration with higher efficiency is 25ppm, so it is recommended for all next experiments. The polarization curves of copper in 3.5% NaCl and in presence of 25ppm BDA is expressed in Figure (2). The obtained results show that the presence of BDA decreases the rate of anodic dissolution of copper. The BDA shows inhibition efficiency with about 82%, which is clearly noticed from the limiting currents. The magnitudes of limiting currents of 3.5%NaCl only and in presence of 25ppm BDA are -1.34 mA and -2,4 mA respectively. The open circuit potential becomes more anodic in presence of BDA and shifted from -287.4 mV in case of NaCl only to -163.8 mV in the inhibited one. It is also noticed that in case on absence of inhibitor the current density showed higher magnitude due to the dissolution copper [26,27].

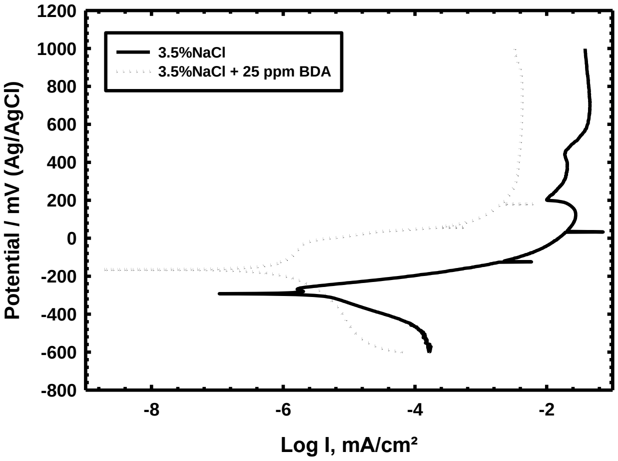


Figure (2) Effect of BDA on the polarization curves of copper in 3.5% NaCl

Figure (3) presents the effect of sulfide ions on the polarization curve of copper in the absence and presence of the recommended dose of BDA. The gained results illustrate that inhibition of copper corrosion with about 28% in the presence of BDA which is could be noticed from decreasing the limiting current from -3.28mA to -4.2mA in absence and presence of sulfide ions.

The sulfide ions have strong detrimental effect on copper surface and it is also noticed in presence of BDA which is related to its destructive effect on the protective film of organic inhibitor. The open circuit potential is affected by sulfide ions and it shifted to the cathodic regions with magnitude of -0.483 mV.

In the presence of inhibitor the open circuit potential was shifted to anodic direction with magnitude of -0.337 mV, which is proof that the BDA is showed slightly resistance of sulfide attack. On the other hand the sulfide ions have another effect on the polarization curves of copper, it decreasing the breakdown potential and increasing the current in the passive area and the rate of anodic dissolution is increased due to increasing current in the passive region.

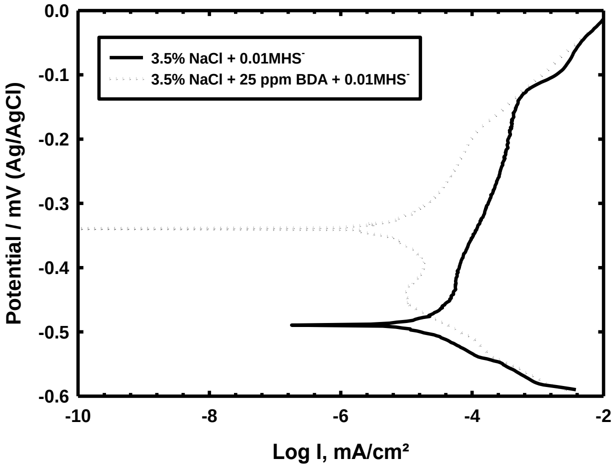


Figure (3): Effect of sulfide ions on the polarization curves of copper in absence and presence of BDA

2- Current transients

Figure (4) show the effect of BDA on the current transients measured on the copper electrode at a potential of 0.0 V vs Ag/AgCl (within the passive region). The results proved that the inhibition efficiency of BDA is about of 75% at the recommended concentration. It is clearly noticed that the initial rapid decrease of current with time before the steady value.

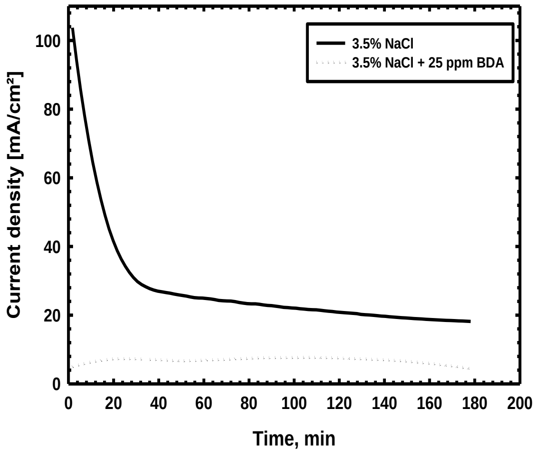


Figure (4) Effect of BDA on the potentiostatic current transients produced by the copper electrode in the presence of 3.5% NaCl only and in the presence of 25ppm BDA

After 3h the currents were 18.53 mA cm^{-2} and 4.62 mA cm^{-2} in the absence and presence of BDA respectively. The decreasing of current in the presence of BDA is dealing with the formation of protective film of copper inhibitor complex.

The adsorption of inhibitor on the copper surface is attributed with presence of copper oxide, which constitutes the main role of formation of copper inhibitor complex eq. (10). It is well known that in the presence of chloride ion CuCl is produced and it attract another chloride ion and form $CuCl_2^-$ see eq. (13,14)

$$Cu+Cl^- = CuCl+e^- \quad (13)$$

$$CuCl+Cl^- = CuCl_2^- \quad (14)$$

To perform the protective film on the copper surface the interaction between copper (II) chloride and BDA should be occurring see Eq. (20). Equation (15) will constitute the first step for preparation of the protective film by producing the positive copper ion.

$$CuCl_2^-+e^- = Cu^{2+}+2Cl^-+e^- \quad (15)$$

The postulated mechanism for the formation of the protective film on the copper surface is could be proved through the following equations:

$$\mathrm{Cu^{+}_{(aq)}+BDAH_{(aq)}= Cu(I)BDA_{(s)}+H^{+}_{(aq)}} \qquad (16)$$

$$\mathrm{Cu+2Cl^{-} = CuCl_2^{-}+e^{-}} \qquad (17)$$

$$\mathrm{CuCl_2^{-}+BDAH_2^{+} = Cu(I)BDA+2H^{+}+2Cl^{-}} \qquad (18)$$

The other mechanism postulates an adsorbed layer of BDA i.e.

$$\mathrm{Cu_{(s)}+BDAH = Cu{:}BDAH_{(ads)}+H^{+}_{(aq)}} \qquad (19)$$

$$\mathrm{CuCl_2^{-}+BDAH = Cu(I)BDA+H^{+}+2Cl^{-}} \qquad (20)$$

Equation (20) shows the formation of a expected polymeric Cu(I)-BDA film by the interaction between $\mathrm{CuCl_2}$ and BDA and Figure (5) explain the probable adsorption form of inhibitor on the copper surface.

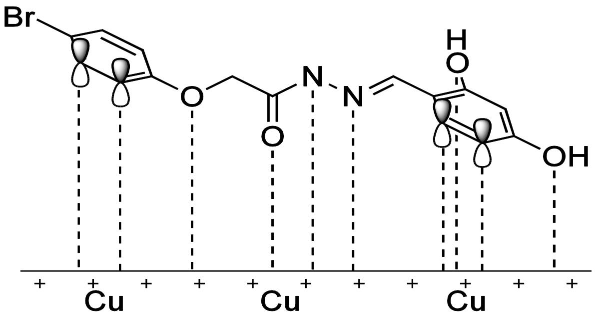


Figure (5) Mechanism of Adsorption of BDA on copper

Figure (6) presents the effect of sulfide ions on the current transients measured on the copper electrode at a potential of 0.0 V vs Ag/AgCl (within the passive region) in absence and presence of BDA. The obtained results proved that the inhibition efficiency of BDA in presence of sulfide ions is about of 57%, which is considered as a good efficiency if it compared with the best inhibitor for copper benzotriazole. The protected film of benzotriazole is completely destroyed in presence of sulfide ions. The results also show that after 3h the currents were 19.58 mA $\mathrm{cm^{-2}}$ and 8.43 mA $\mathrm{cm^{-2}}$ in the absence and presence of BDA respectively. The decreasing of current in the presence of BDA is dealing with the stability of protective film of copper inhibitor complex against sulfide ions.

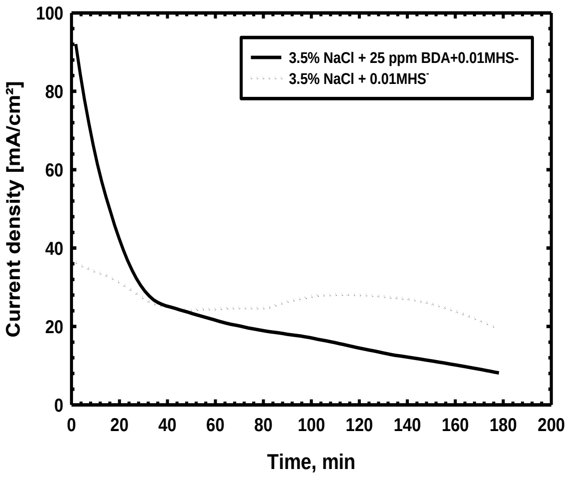


Figure (6) Effect of sulfide ions on the potentiostatic current transients produced by the copper electrode in the presence of 25 ppm BDA

2- Surface characterization

The surface of copper electrode after the potentiostatic polarization at 0.0 V was subjected to surface analysis by SEM. The obtained first image illustrate that the copper surface was covered with corrosion products due to the reaction between copper and chloride ions. The scanning electron microscope images of copper surface in the presence and absence of BDA is showed in Figure (7) images A and B. The obtained image showed corrosion products in absence of BDA but in case of presence of BDA no observed corrosion product on copper surface, which is means that the BDA gives good corrosion resistance in salt water, which is strictly closed with the current transient's curves Figure (4), which are very clearly noticed from the low magnitude of current in presence of BDA. These results are related to the formation of Cu (II)-BDA complex, which constitute the protective film. The images C and D are represents the effect of sulfide in absence and presence of BDA respectively. The obtained images show presence of corrosion products in the two images but in case of presence of BDA the corrosion products is slightly less that the image C, which is strictly closed with the current transient's curves Figure (6).

These obtained results explain that the partially destroy of protective film due to the priority of attack of sulfide ion with copper surface to form CuS which is noticed obviously from the black precipitate in the experiment solution, which is related to the partial dissolution of copper.

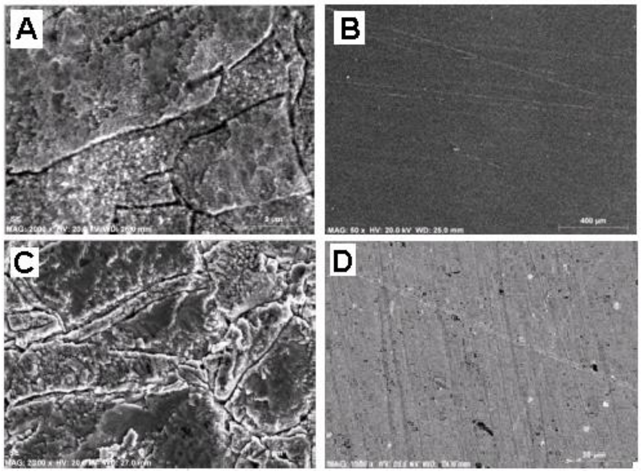


Figure (7) SEM images of Cu electrode surface at open circuit potential in (a) 3.5% NaCl; (b) 3.5% NaCl+25 ppm BDA; (c) 3.5% NaCl+0.01MHS^- and (D) 3.5% NaCl+25 ppm BDA+0.01MHS^-

The surface of copper electrode was subjected for more investigation by using EDS and XPS. The energy dispersive X-ray spectroscopy (EDS) was used to characterize the corrosion products, the results were mentioned in Figures 7,8 and 9. The measurements were performed on selected regions of the corroded surface. On the other hand the scale of micrometers it requires a fairly thick layer of the order of micrometers to be able to detect the presence of a certain element, with no indication of its oxidation state.

Figure (8) represents the EDS spectrum of measurements obtained from subjecting of the copper electrode to 0.0 V (Ag/AgCl) and potentiostated for 3 hours in 3.5% NaCl. The copper and chlorine signals were only detected which is agreeing with the gained results.

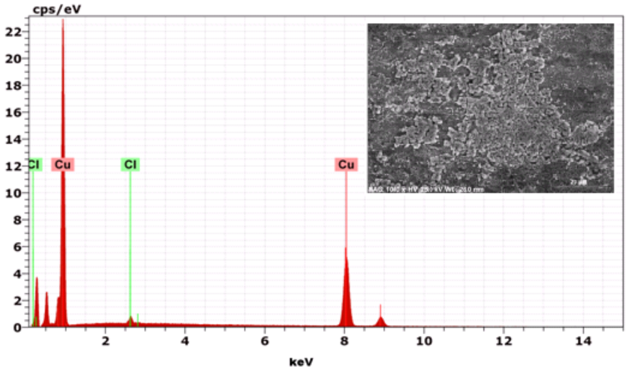


Figure (8) EDS spectrum of copper electrode potentiostated for 3hrs in 3.5% NaCl. The spectrum was taken from a random spot of surface.

Figure (9) represents the EDS spectrum of measurements obtained from subjecting of the copper electrode to 0.0 V (Ag/AgCl) and potentiostated for 3 hours in 3.5% NaCl+25 ppm BDA. The copper signals were only detected which is agreeing with the gained results.

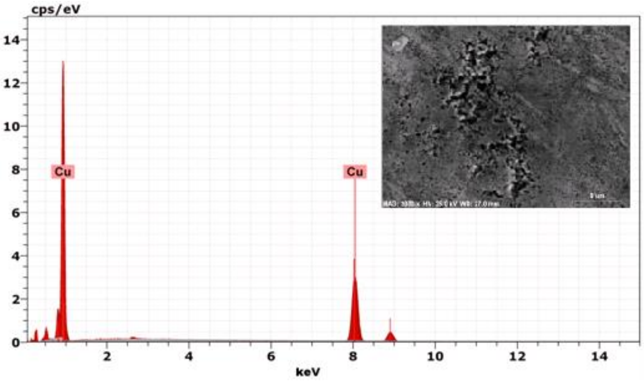


Figure (9) EDS spectrum of copper electrode potentiostated for 3hrs in 3.5% NaCl+25 ppm BDA. The spectrum was taken from a random spot of surface.

Figure (10) shows the EDS spectra of copper electrode in presence of 3.5% NaCl+25 ppm BDA+0.01M sulfide ions and it is very clearly notice a peak at 2.5 kev, which is attributed to sulfur this result is agreeing with the obtained result of XPS spectra.

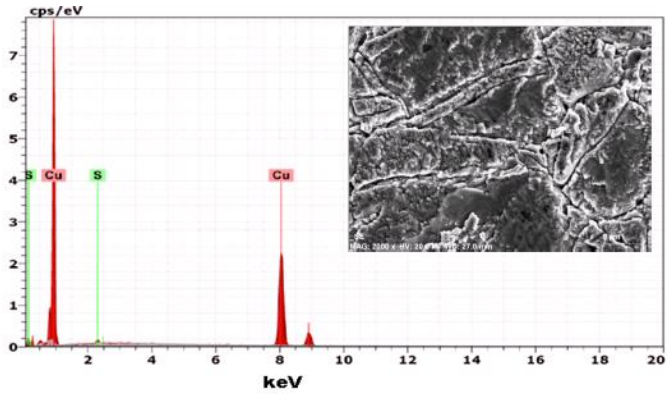


Figure (10) EDS spectrum of copper electrode potentiostated for 3hrs in 3.5% NaCl+25 ppm BDA and 0.01M HS$^-$. The spectrum was taken from a spot of white area inside the corroded grain boundary.

The X-ray photoelectron spectroscopy (XPS) have the ability to scan large area from the corroded surface so it can detect as little as several atom layers of a certain elements and can reveal its oxidation state. However, the XPS technique gives its data from a sample of the copper surface, and hence it cannot be performed on selected regions. These techniques were carried out on the treated copper surface in presence of sulfide at 0.0 V. Figure (11) shows the XPS spectra of copper electrode in presence of 3.5% NaCl+25 ppm BDA and 0.01M HS$^-$, the results two interesting signals (S2p) one of them at 163.0 eV compared to C1 at 248.6 eV and the other at 168.6, these signals are characteristic for copper sulfide and sulfate respectively. This indicates that the sulfide ions oxidized under the noble potential of 0.0 V (Ag/AgCl) in addition to the formation of copper sulfide.

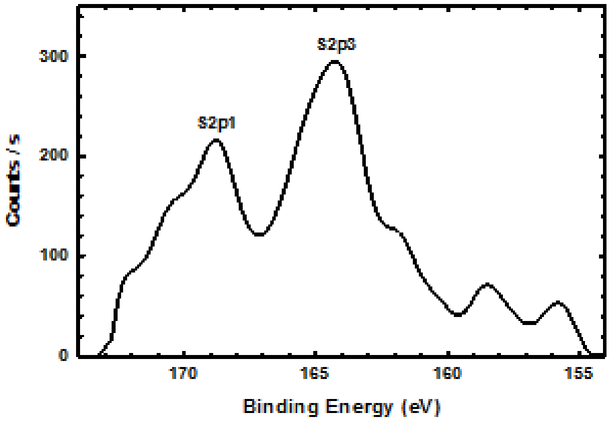


Figure (11) XPS spectrum of the S2p1 and S2p3 signals obtained from the copper electrode in a medium of 3.5% NaCl+25 ppm BDA+0.01M HS$^-$

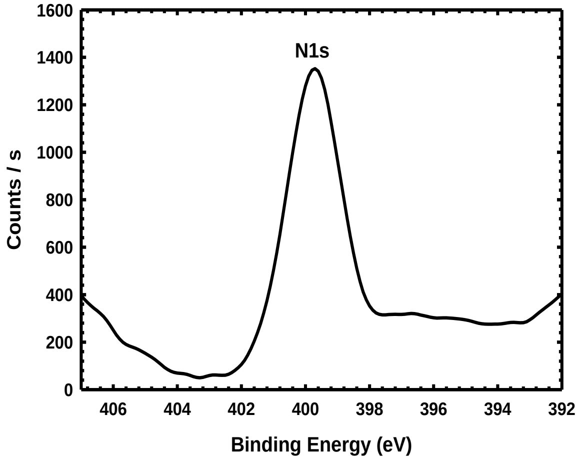


Figure (12) XPS spectrum of the N1s signal obtained from the copper electrode in a medium of 3.5% NaCl+25ppm BDA + 0.01M HS$^-$

Figure (12) shows the XPS charts of N1s in presence of 3.5% NaCl+25ppm BDA only. The results illustrate that the counts of nitrogen with about 1350. These results help to maintain the idea of the BDA is present with good coverage and high concentration on the metal surface, which make a good prevention of corrosion and the SEM images prove that.

IV. CONCLUSION

The BDA inhibit the corrosion of copper in unpolluted salt water and in case of polluted salt water it shows a slightly effect. The inhibition of corrosion of copper metal may be due to the formation of a thick adsorbed and impervious protective film, which has been confirmed by surface morphological studies. The presence of sulfide ions makes destruction of about 43% from the protective film of BDA and the corrosion is observed due to the copper dissolution. The BDA is a good inhibitor in unpolluted environments and give slightly stable film in polluted media.

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