Enhancing Corrosion Resistance of Copper By Electrodeposition

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Abstract

Enhancing corrosion resistance of copper is often associated with the presence of cuprous oxide (Cu_2O) films on the substrate. The electrodeposition method is considered cost-effective due to its simple operation, high production rate and capability to handle complex geometry.

The present paper describes electrodeposition process of pure copper using 10%H_2SO_4 as an electrolyte solution and the voltage was 5 V for different times in an electrochemical cell.

Gelatin or Dimethoxymethane additives were applied to enhance the surface adhesion of the electrodeposited layer.

In addition, a calcination process (heating at 250 ˚C for 30 min) was performed to impart advanced surface properties.

The surface of electrodeposited samples in different conditions was investigated by means of X-ray diffraction.

Contact angle measurements were carried out at ambient temperature utilizing 5 µ-liter double distilled water droplets. Moreover, the electrochemical corrosion behavior was studied in 3% NaCl solution.

Good adhesion property and the lowest corrosion rate were observed at 10% wt. H_2SO_4 with 10 ppm Gelatin followed by calcination. The results showed that a super hydrophobic film (Cu_2O) with a high contact angle of about 162° and the lowest corrosion rate was 0.7 mpy, obtained after electrodeposited 10 min. The XRD analysis showed that the crystalline size of Cu_2O was about 80 nm.

Keywords: *Copper, Surface modification, Super-hydrophobic films, Nanotechnology, Electro-deposition, Surface properties, Cuprous oxides and Contact angle.*

1.Introduction

Copper has a good electrical and thermal conductivity, which makes it useful for engineering and thermal applications [1-4].

The main disadvantage of copper is its corrosion in natural water and corrosive media such as acidic or alkaline solution, or in the presence of a strong oxidizing [3,11-13].

Many surface modification techniques such as chemical etching [14], oxidation [15], inhibitors [16], sol-gel [17-18], and electrodeposition [19-20] could be used to improve the corrosion resistance of copper.

Liu et. al. [5] prepared a super-hydrophobic surface on copper with a contact angle of 161° by electrodeposition in an electrolyte solution of 0.038 M cerium chloride and 0.1 M meristic acid immersed in ethanol.

Abbas et. al. [6] improved the corrosion resistance of copper by forming a super-hydrophobic layer using chemical etching and immersion into stearic acid. They obtained a contact angle of about 160°.

In a further study, Abbas et. al. [7] carried out a surface modification of tin-bronze after immersion in a solution of distilled water with 10ml/l Capsaicin acid (8-Methyl-N-vanillyl-6-nonenamide) for 1 hr. They obtained a hydrophobic surface with a contact angle of about 134°.

The present study aims at development of a fast, facile, and low-cost electrodeposition process to construct a controlled Hydrophobic / super hydrophobic layer on the cathodic copper substrate with electrolyte solution of 10% H_2SO_4. The surface adhesion can be increased by adding some organic additives such as 10ppm Gelatin/ 10 ppm Dimethoxymethane. Electrochemical measurements, Contact Angle measurements, Adhesion Tape test, X-ray diffraction (XRD) and Salt Spray test will be used.

2. Experimental Work

2.1 Materials

The chemical analysis of the used copper was conducted by X-ray fluorescence (XRF) Spectrometer Model NITON XL3 T980 GOLD, as shown in Table 1, and it was received in the form of copper rods of 11.5 mm diameter. The rod was cut into specimens with a cross section area of 1 cm^2 and a height of 1 cm for experiments.

Table 1- Chemical composition of pure copper samples

Element	**Cu**	**Fe**	**In**	**Sn**	**Pb**
Composition (wt.%)	**99.99**	**0.014**	**0.012**	**0.031**	**0.023**

2.2 Specimen preparation

Specimens were ground progressively using wet silicon carbide (SiC) emery papers with grit number starting with 600-grit and proceeding to 2000-grit papers. Water is used to keep specimens cool and to flush away loose particles of metal and abrasive. Final polishing is performed on a low speed wheel covered with micro-cloth using 0.05 µm Alumina suspension (Al_2O_3), then samples were rinsed using distilled water and acetone, and air dried.

2.3 Applied surface modification techniques

2.3.1 Electrodeposition

Two copper plates were taken as cathode and anode in an electrolytic cell with a direct current (DC) at an operating voltage of 5V applied to the electrodes with a distance of 2 cm. For electrodeposited in 10 %H_2SO_4 for different times, as shown in Figure 1.

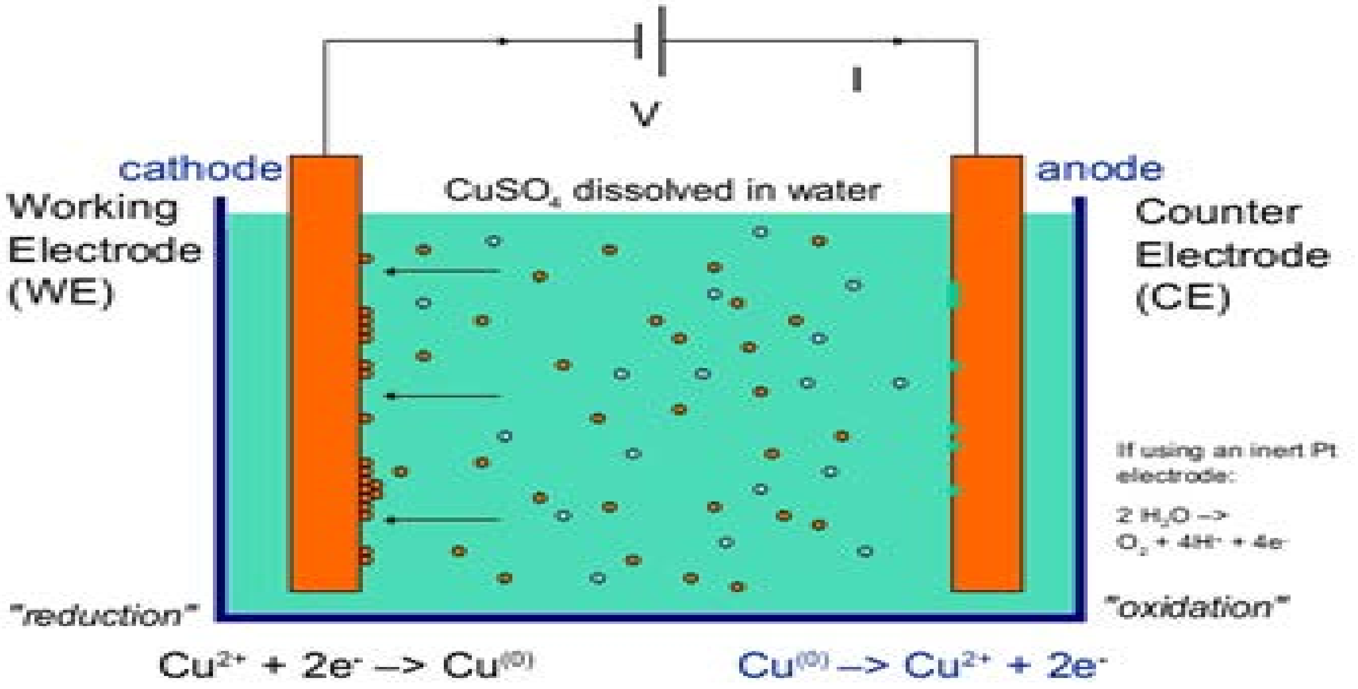


Fig1: Electrochemical cell of electrodeposited copper

In some cases, 10ppm Gelatin / 10ppm Dimethoxymethane were added to the 10% H_2SO_4 solution. After electrolysis at different time intervals from 2 up to 15 min, the working electrode was rinsed thoroughly several times with water, and then dried in atmosphere condition.

X-ray diffraction (XRD) was used to determine phases formed on Cu substrate surface. Water contact angle, metallography and adhesion tests were conducted. Then corrosion behavior was studied by potentiodynamic polarization technique.

2.3.2 Calcination

Some samples were calcined in the air using an electric resistant furnace of type (Nabertherm) at 250 ˚C for half an hour.

2.4 Characterization

The constituting phases of the electrodeposited samples was investigated using Panalytical XRD diffractometers. The contact angle was measured by the Attention Biolin device. Electrochemical corrosion behavior was studied in 3% NaCl aqueous solution at room temperature via a versa stat device. The adhesion was carried out using Adhesion Tape test (X-Cut) ASTM D3359 [22]. The salt spray test was carried on sample according to ASTM B117.

3. Results and discussion

3.1 contact Angle Measurement

The contact angle was determined at different periods of treatment conditions, namely, 10% H_2SO_4, 10% H_2SO_4 followed by calcination, 10% H_2SO_4 with 10ppm Dimethoxymethane ,10% H_2SO_4 with10ppm Dimethoxymethane followed by calcination, 10% H_2SO_4 with 10ppm Gelatin and 10% H_2SO_4 with 10ppm Gelatin followed by calcination.

Results revealed that using only10% H_2SO_4, the contact angle increases to reach the maximum value of about 92° at 10 min. as shown in Figure 2.

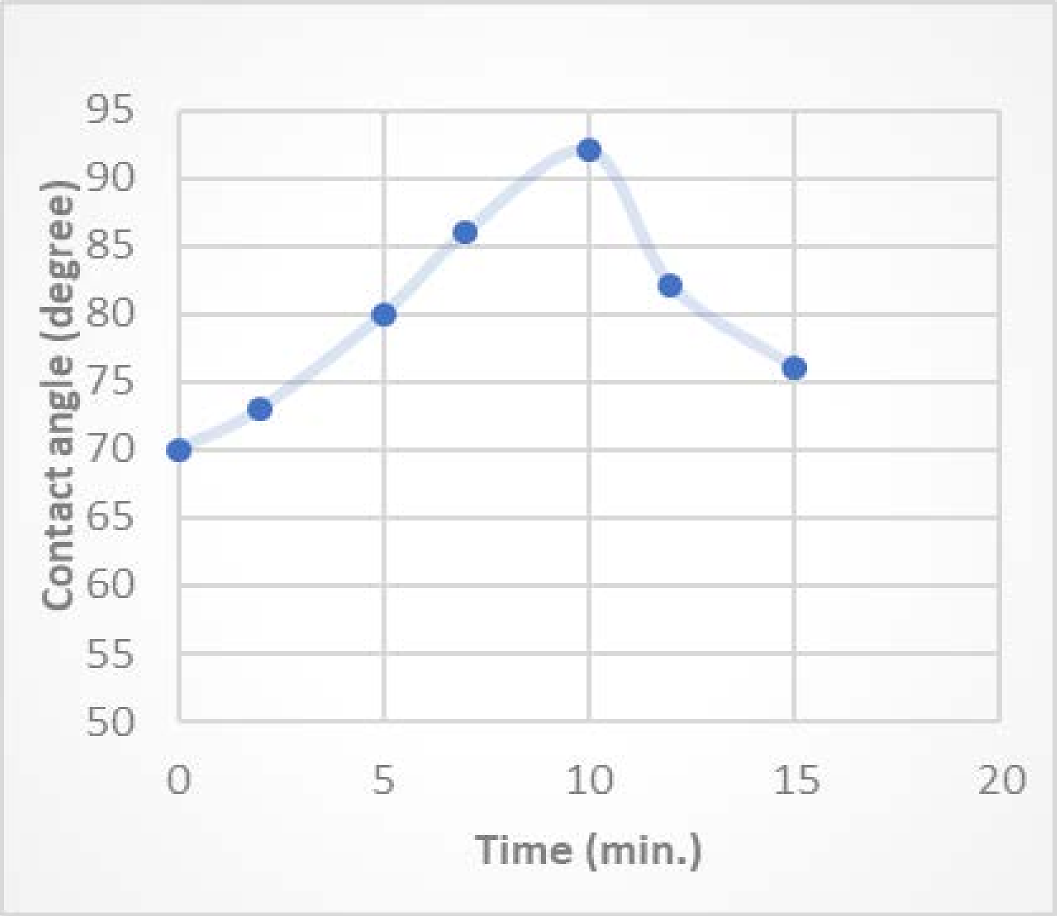


Fig 2: shows the effect of electrodeposition on contact angle at different times in 10%H_2SO_4

When electrodeposited samples were calcined at 250˚C for 30 min, the contact angle increased to reach the maximum value of 112˚ at 10 min. as shown in Figure 3.

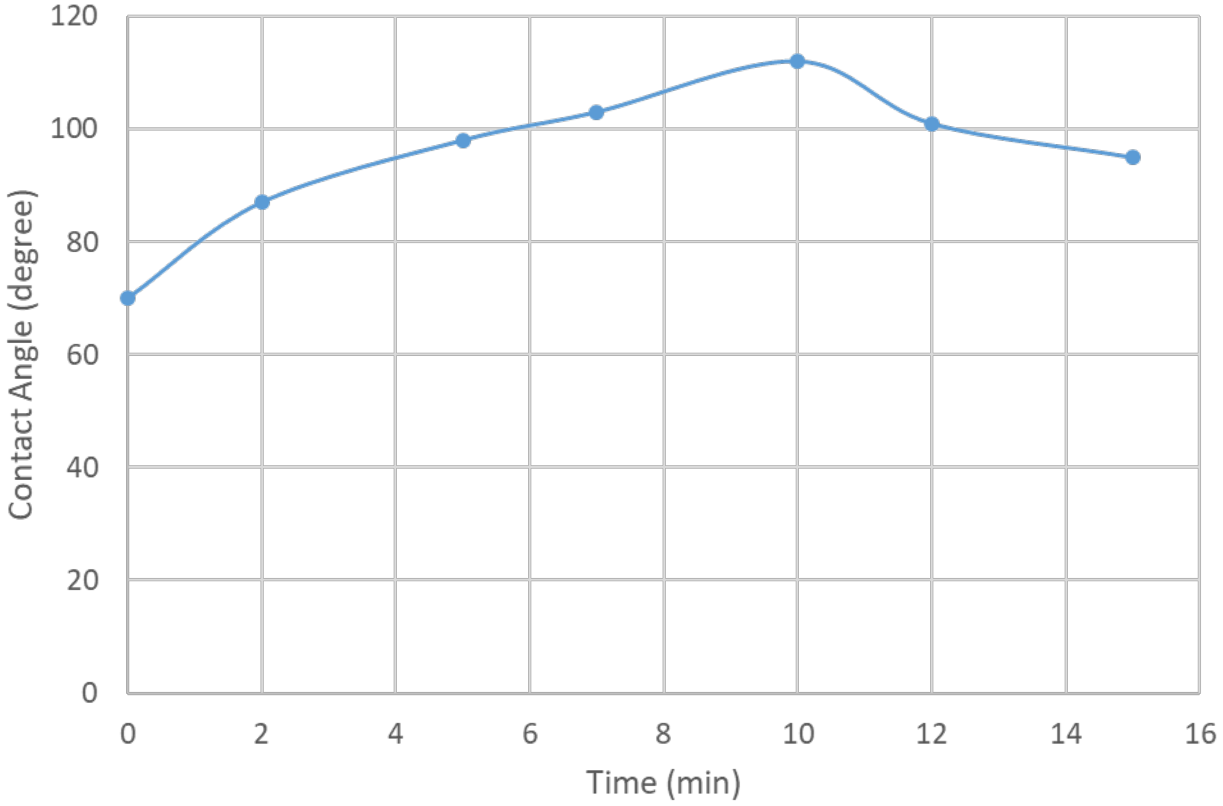


Fig 3: shows the effect of time on the contact angle of electrodeposited samples in 10% H_2SO_4 at different times followed by calcination

When using 10ppm Gelatin with an 10% H_2SO_4, the contact angle increased to reach the maximum value of 134˚ at 10 min deposition, as shown in Figure 4.

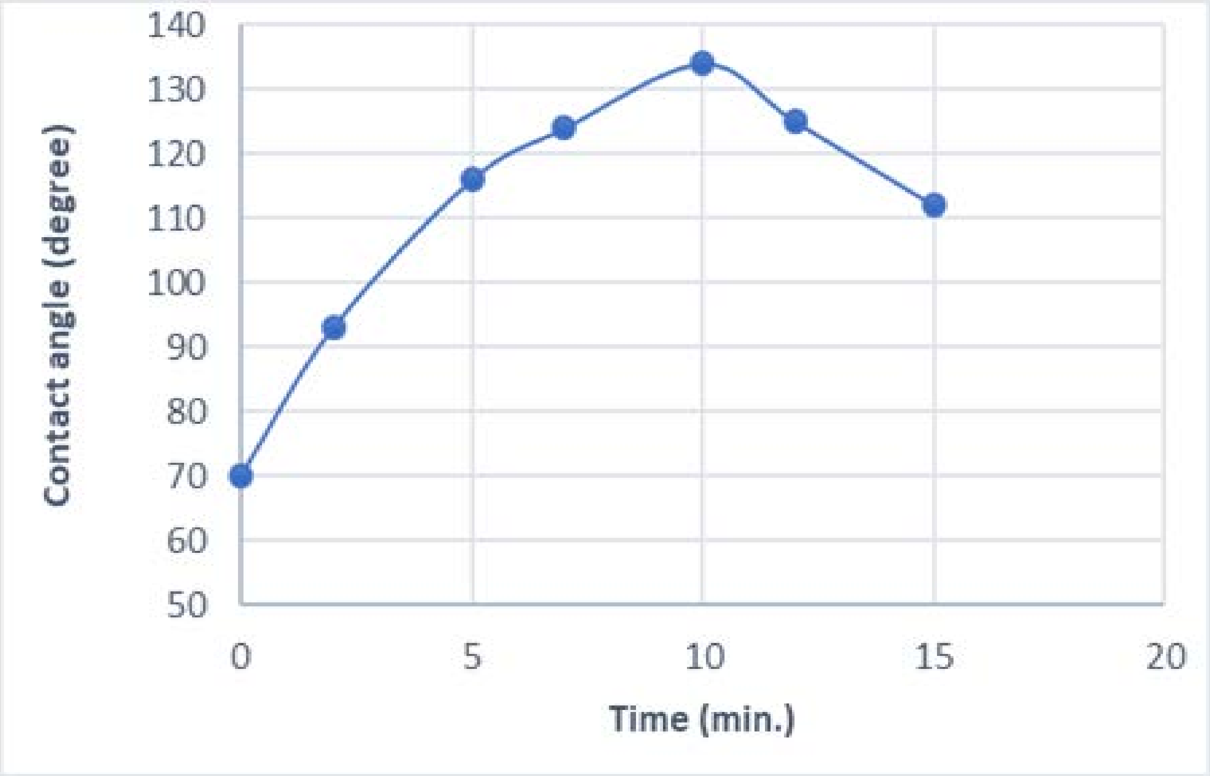


Fig 4: shows the effect of adding10ppm Gelatin with 10%H_2SO_4 on contact angle at different times.

When using 10 ppm Gelatin in 10 %H_2SO_4, then calcined at 250˚C for 30 min. the contact angle increases to reach the maximum at10 min. to be about162˚, i.e. a super hydrophobic surface has been formed, as shown in Figure 5.

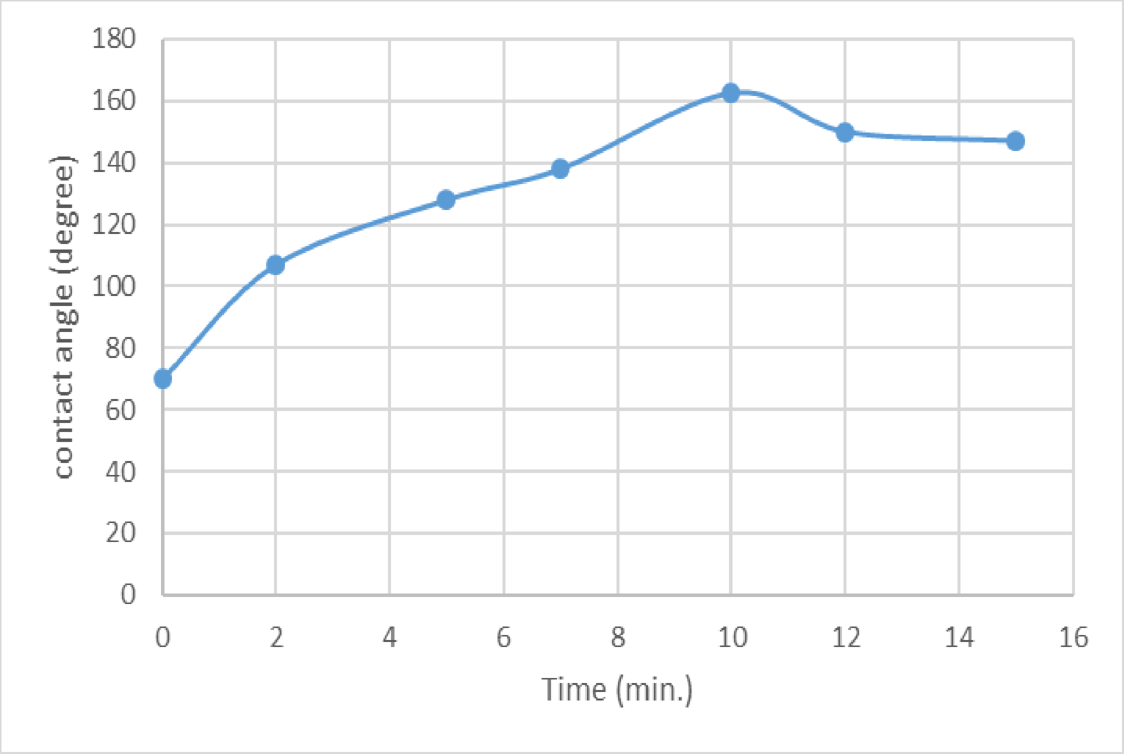


Fig 5: Shows the effect of adding10ppmGelatin with 10% H_2SO_4 followed by calcination on contact angle at different times.

When using 10 ppm Dimethoxymethane with 10% H_2SO_4, the contact angle increases to reach the maximum value of 130˚ at 7 min., as shown in Figure 6.

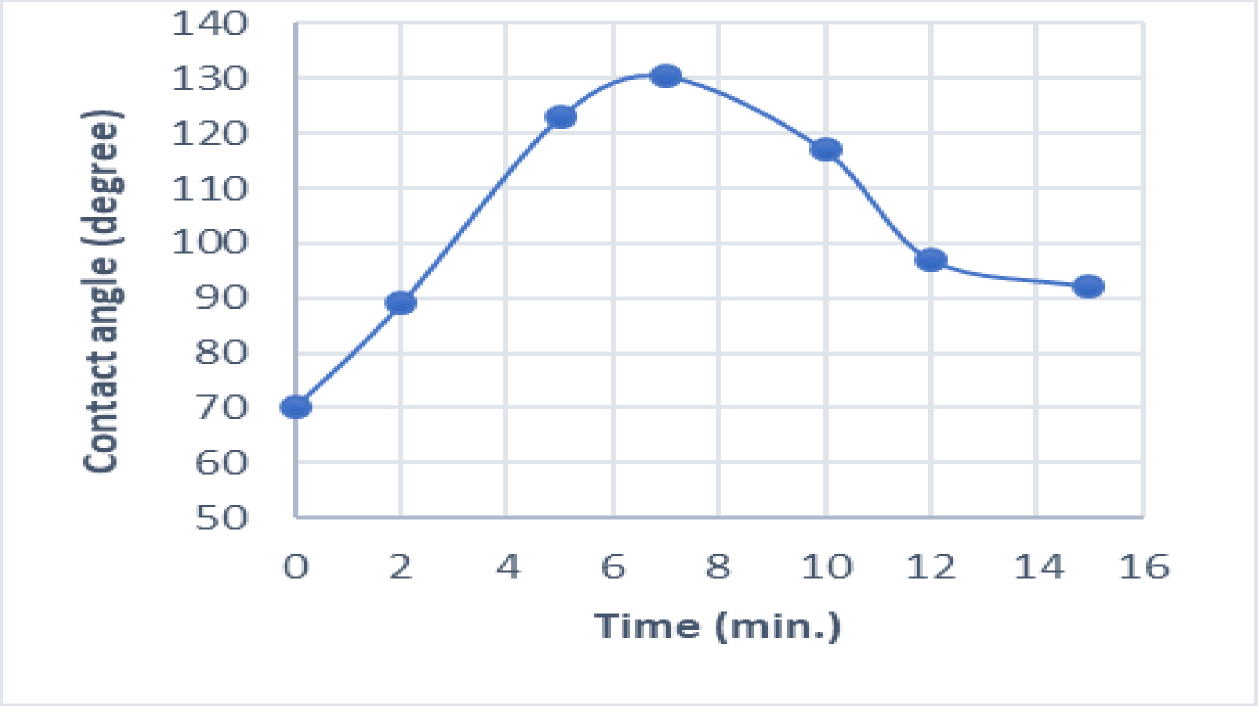


Fig 6: Shows the effect of adding 10ppm Dimethoxymethane with 10%H_2SO_4 on contact angle at different times.

When using10 ppm Dimethoxymethane with 10% H_2SO_4 followed by calcination at 250˚C for 30 min, the contact angle increases to a maximum at 7 min. to be about 142˚, as shown in Figure 7.

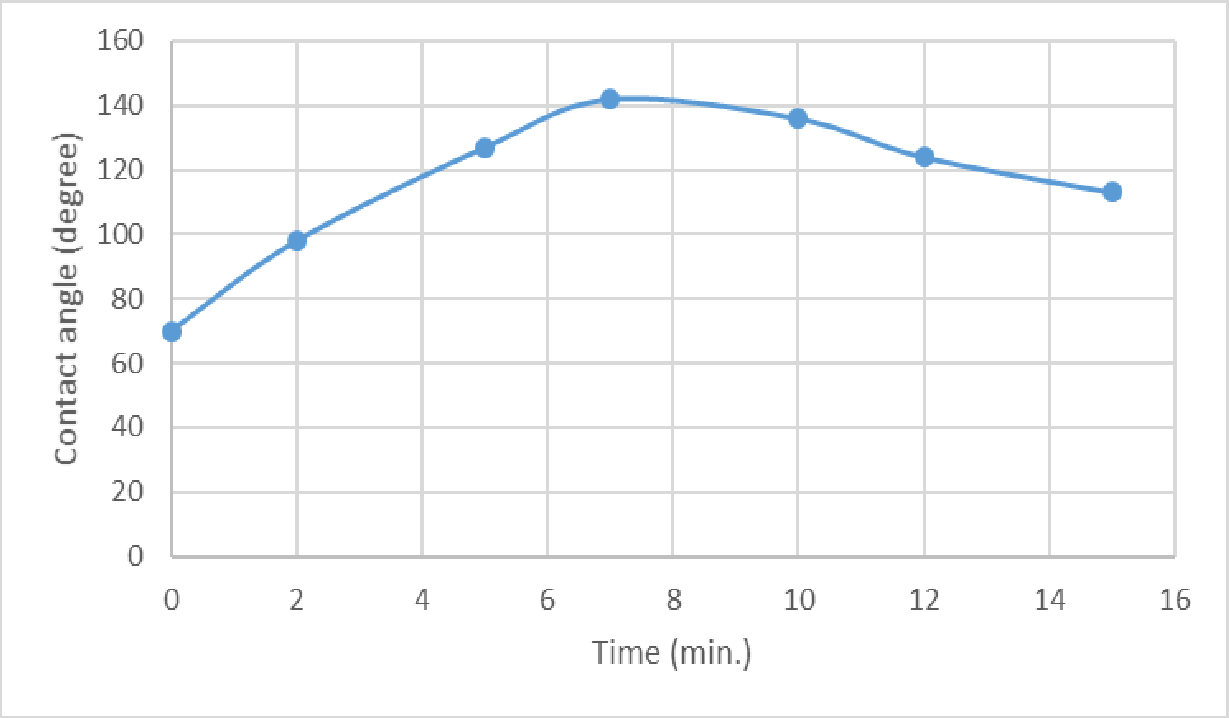
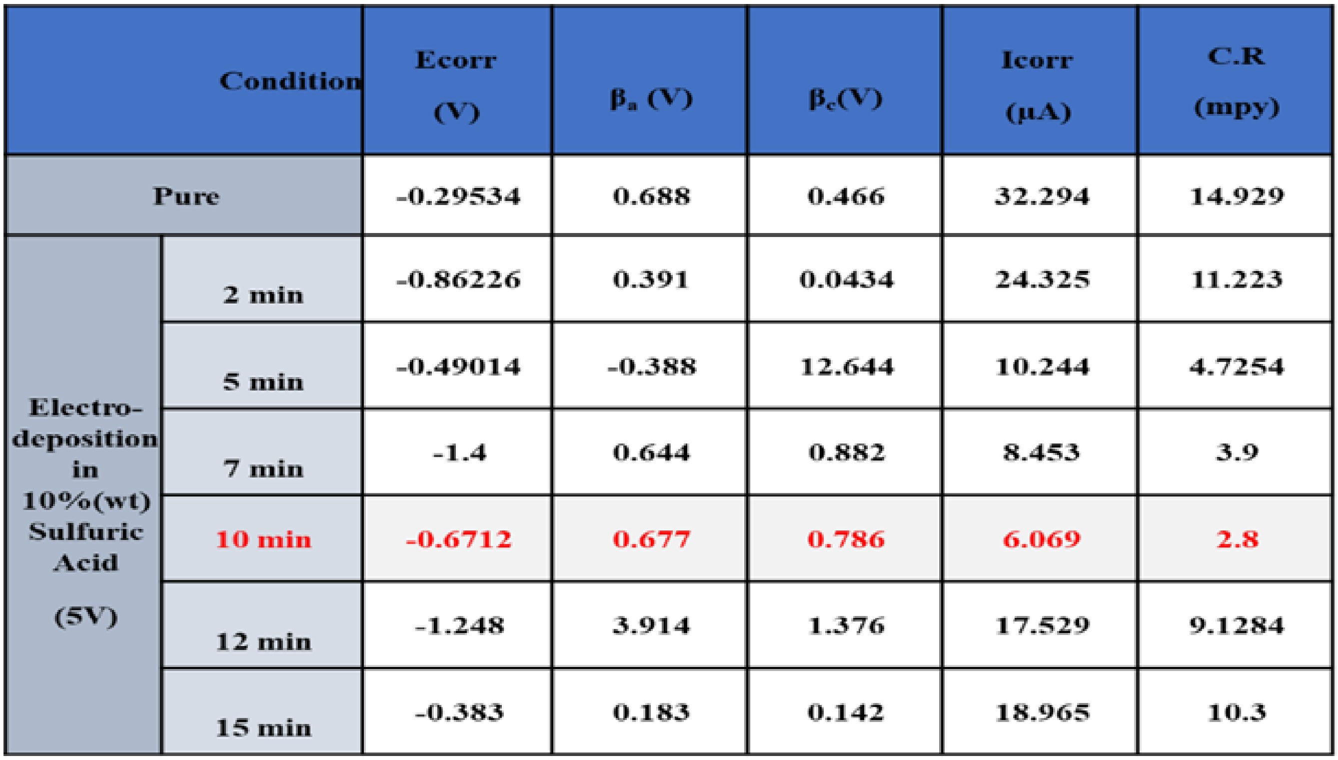


Fig7: Shows the effect of adding10ppm Dimethoxymethane with 10%H_2SO_4 followed by calcination on contact angle at different times.

3.2Corrosion test

Results of the potentiodynamic polarization tests of all electrodeposited specimens (electrodeposition in 10 %H_2SO_4at 5 V) are given in Table 2. It could be observed that treating for 10 min resulted in the lowest corrosion rate of 2.8 mpy, which confirms the results of contact angle measurements.

Table 2- Corrosion parameters of electrodeposited samples at different times.



Condition		Ecorr (V)	β_a (V)	β_c(V)	Icorr (μA)	C.R (mpy)
Pure		-0.29534	0.688	0.466	32.294	14.929
Electro-deposition in 10%(wt) Sulfuric Acid (5V)	2 min	-0.86226	0.391	0.0434	24.325	11.223
	5 min	-0.49014	-0.388	12.644	10.244	4.7254
	7 min	-1.4	0.644	0.882	8.453	3.9
	10 min	-0.6712	0.677	0.786	6.069	2.8
	12 min	-1.248	3.914	1.376	17.529	9.1284
	15 min	-0.383	0.183	0.142	18.965	10.3

Where,

Ecorr =corrosion potential,

Icorr =corrosion current density

βa =Anodic TAFEL slope,

βc = Cathodic TAFEL slope,

and C.R =corrosion rate

Figure 8 showed that as treating time increased to 10 min the polarization curves shifted to left i.e. less dissolution of material in solution and then polarization curves shifted to the right indicating more dissolution of materials i.e. less corrosion resistance. Figure 9 illustrates the variation in the corrosion rate of copper after electrodeposition in 10% H_2SO_4 at different times after surface treatment in 10 ml/L HMMT/distilled water solution.

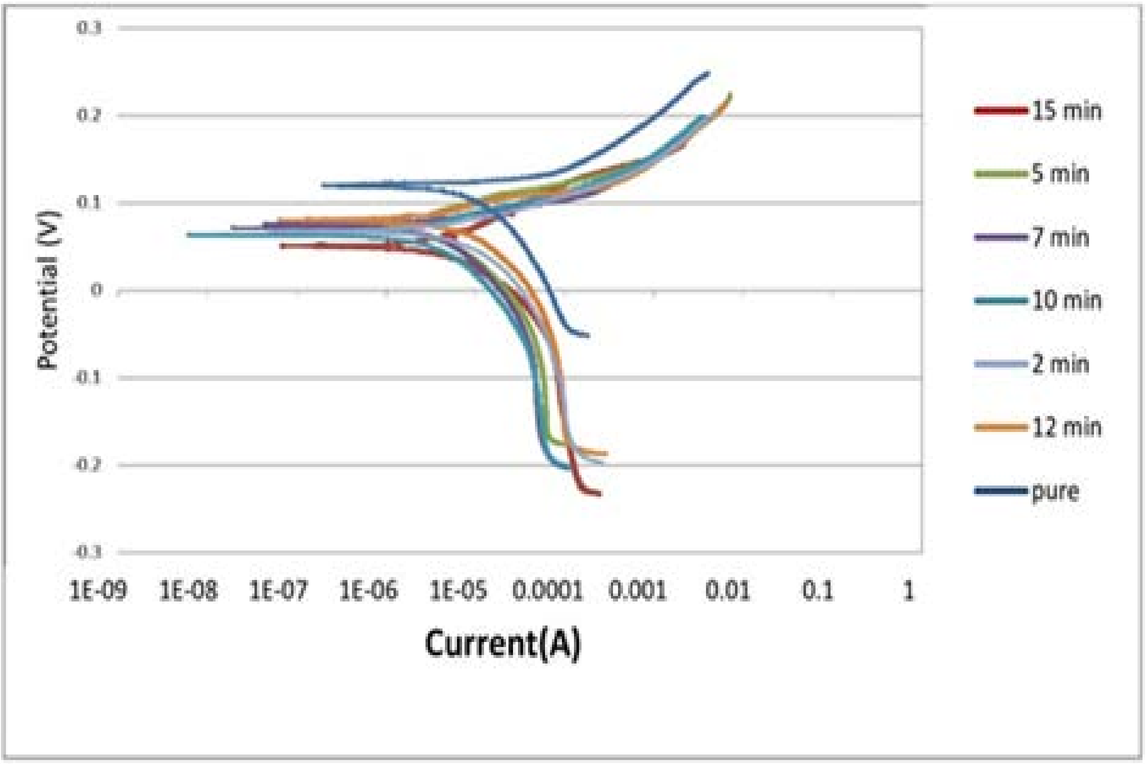


Fig 8: Polarization curves of electrodeposited samples at different times.

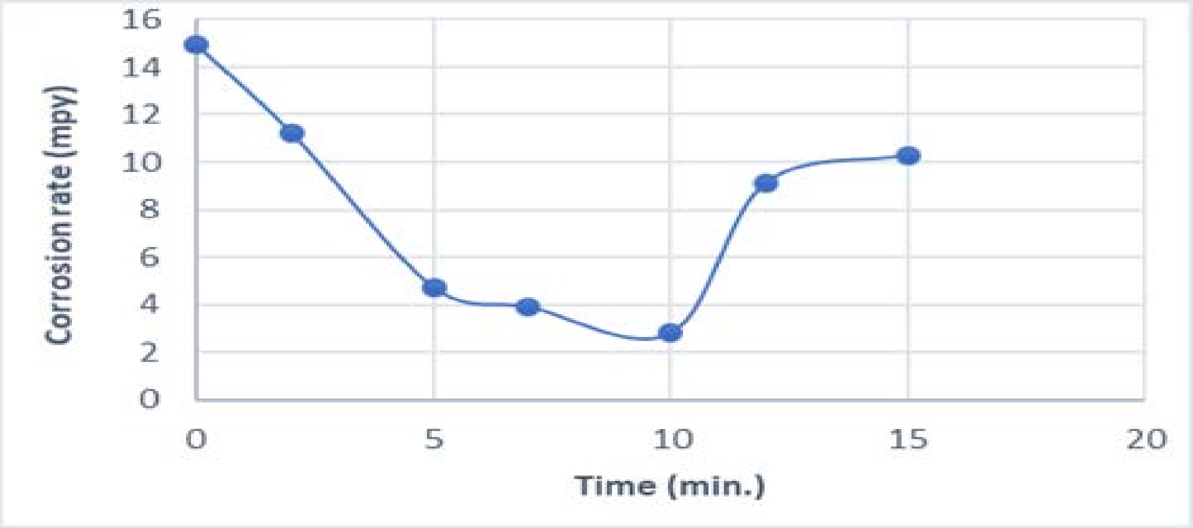
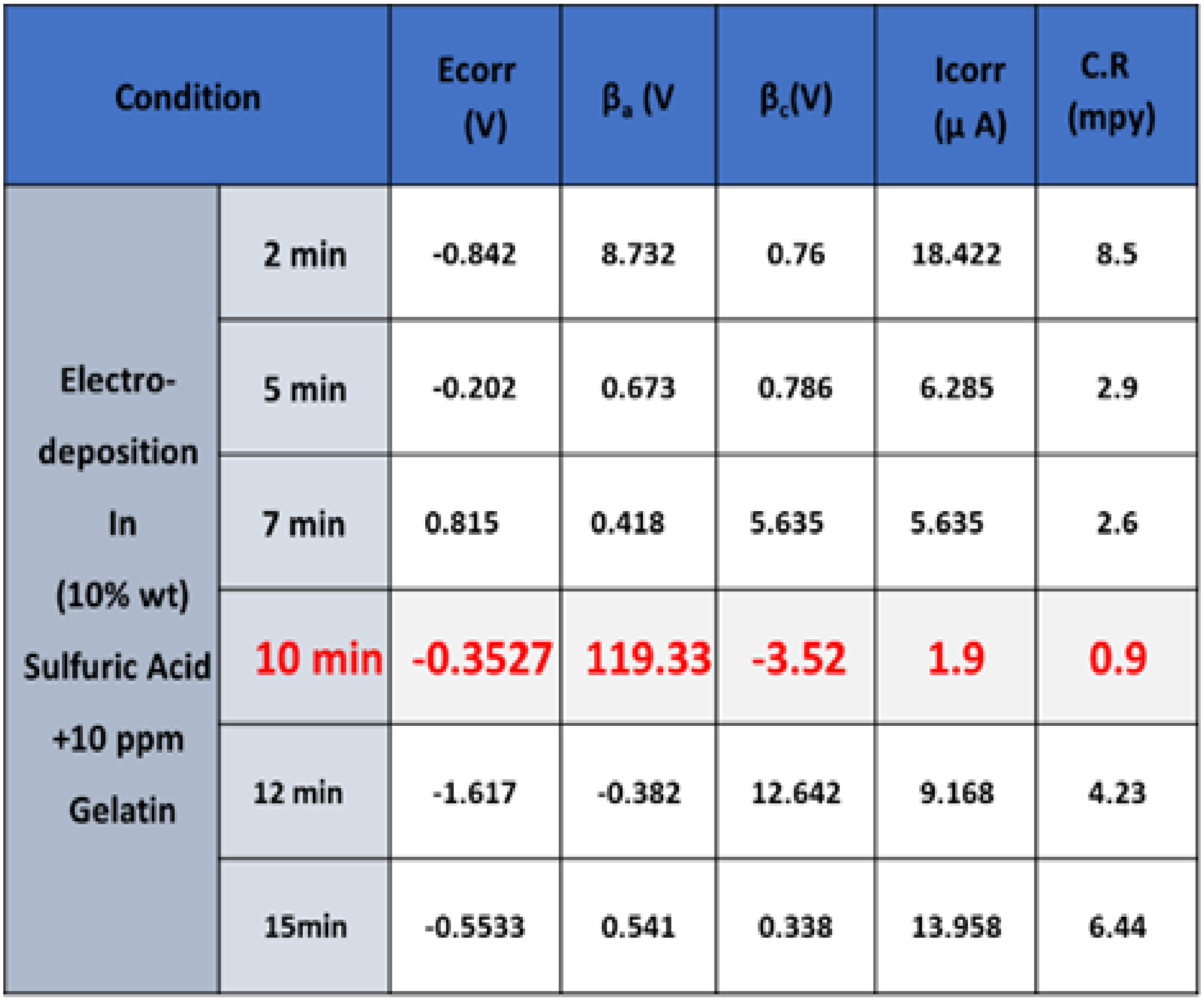


Fig 9: Variation of corrosion rate of copper after electrodeposition in 10 % H_2SO_4 at different times

Table 3, figure 10 and figure 11 show corrosion parameters, polarization curves and variation of corrosion rate of electrodeposited samples at different times after adding 10ppm Gelatin with 10%H_2SO_4, respectively.

Table 3- Corrosion parameters after adding 10 ppm Gelatin with 10% H_2SO_4



Condition		Ecorr (V)	β_a (V	β_c(V)	Icorr (µ A)	C.R (mpy)
Electro-deposition In (10% wt) Sulfuric Acid +10 ppm Gelatin	2 min	-0.842	8.732	0.76	18.422	8.5
	5 min	-0.202	0.673	0.786	6.285	2.9
	7 min	0.815	0.418	5.635	5.635	2.6
	10 min	-0.3527	119.33	-3.52	1.9	0.9
	12 min	-1.617	-0.382	12.642	9.168	4.23
	15min	-0.5533	0.541	0.338	13.958	6.44

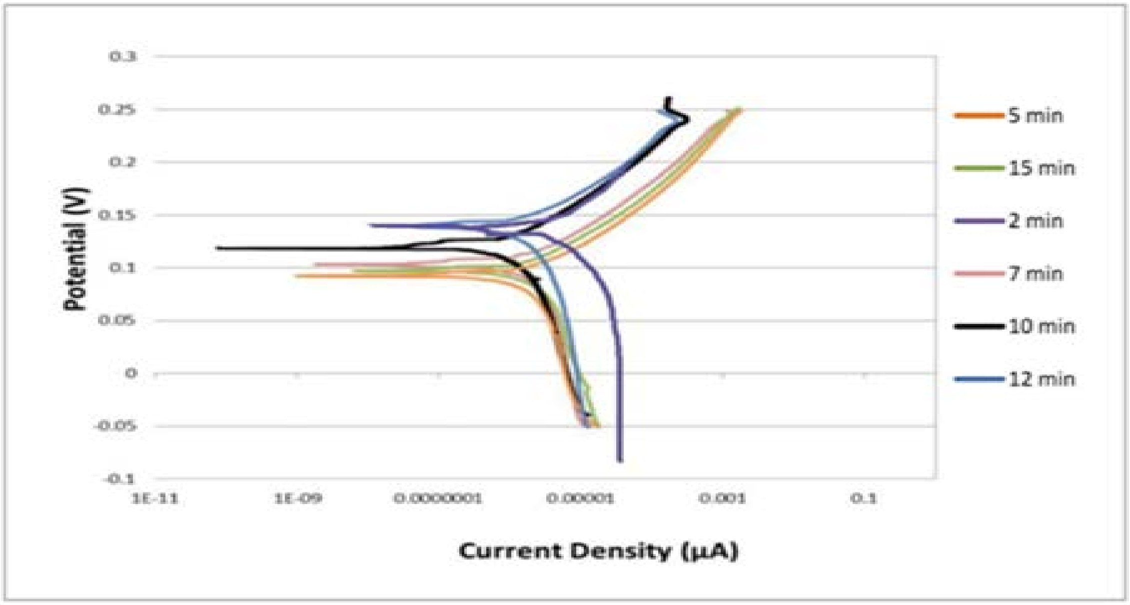


Fig 10: Polarization curves of electrodeposited samples at different times after adding 10 ppm Gelatin

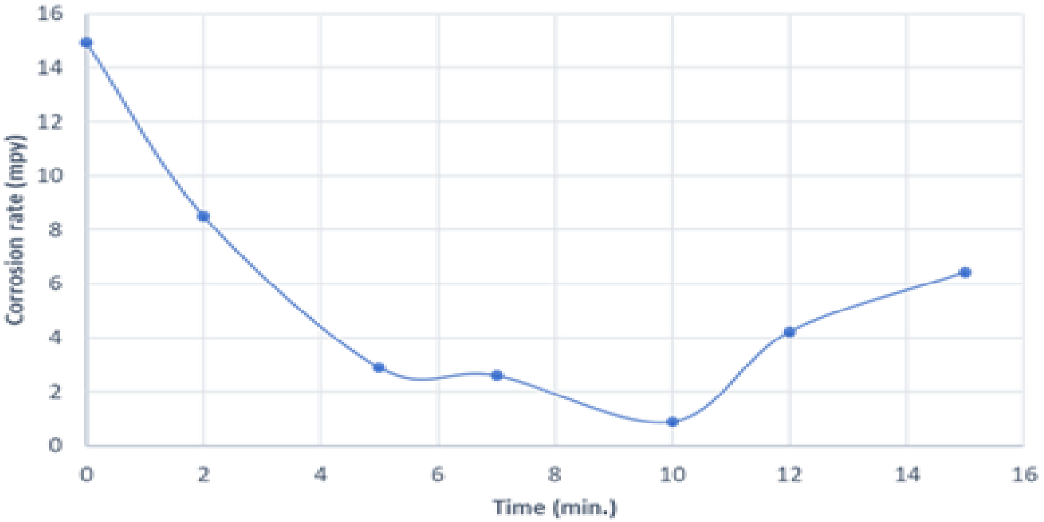
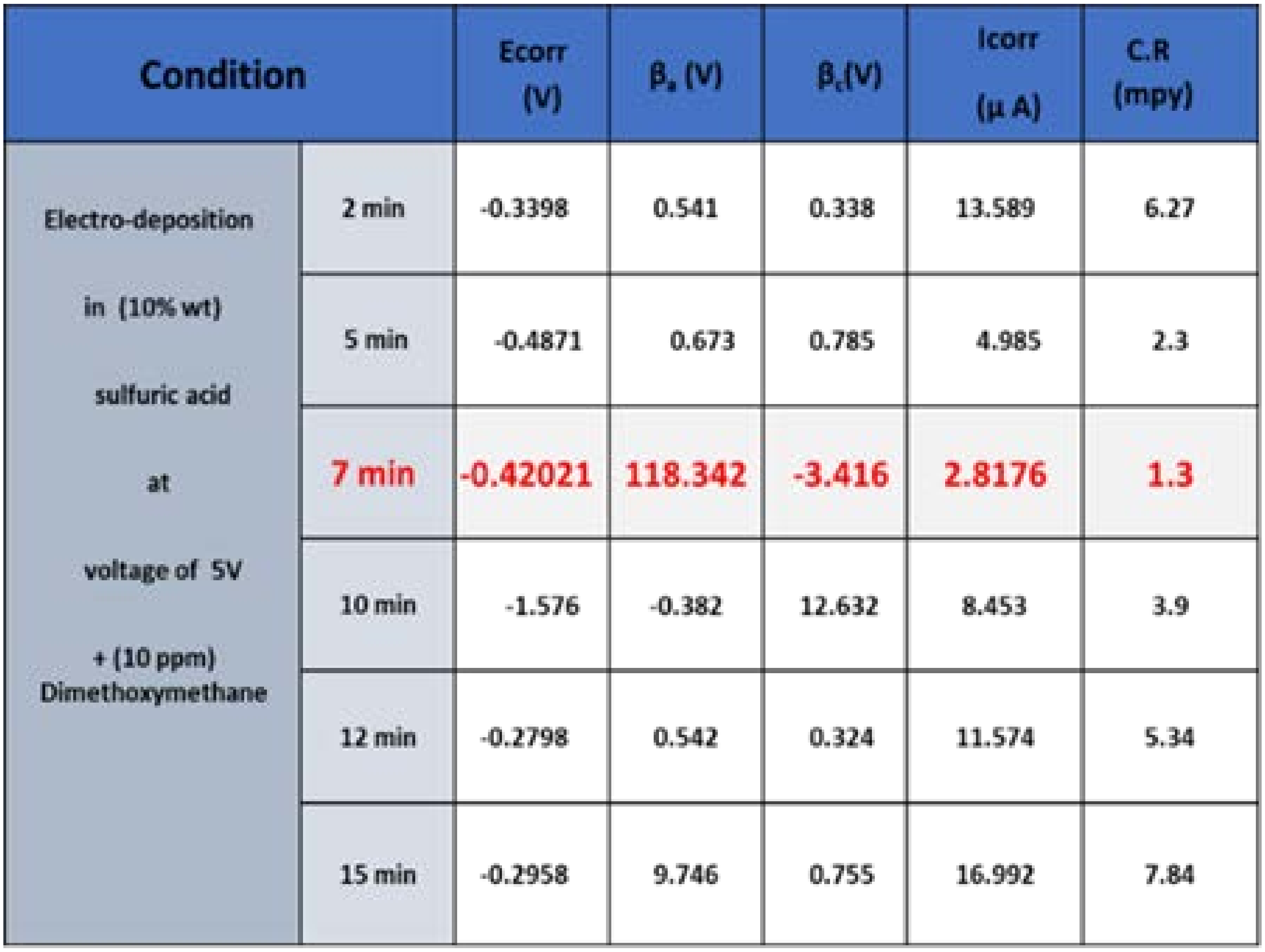


Fig 11: Variation of corrosion rate of copper after adding 10ppm Gelatin at different times.

Table 4, Figure 12 and Figure 13 show corrosion parameters, polarization curves and variation of corrosion rate of electrodeposited samples at different times after adding 10ppm Dimethoxymethane with 10%H_2SO_4, respectively.

Table 4- Corrosion parameter of electrodeposited samples after adding 10 ppm Dimethoxymethane at different times



Condition		Ecorr (V)	β_a (V)	β_c(V)	Icorr (µ A)	C.R (mpy)
Electro-deposition in (10% wt) sulfuric acid at voltage of 5V + (10 ppm) Dimethoxymethane	2 min	-0.3398	0.541	0.338	13.589	6.27
	5 min	-0.4871	0.673	0.785	4.985	2.3
	7 min	-0.42021	118.342	-3.416	2.8176	1.3
	10 min	-1.576	-0.382	12.632	8.453	3.9
	12 min	-0.2798	0.542	0.324	11.574	5.34
	15 min	-0.2958	9.746	0.755	16.992	7.84

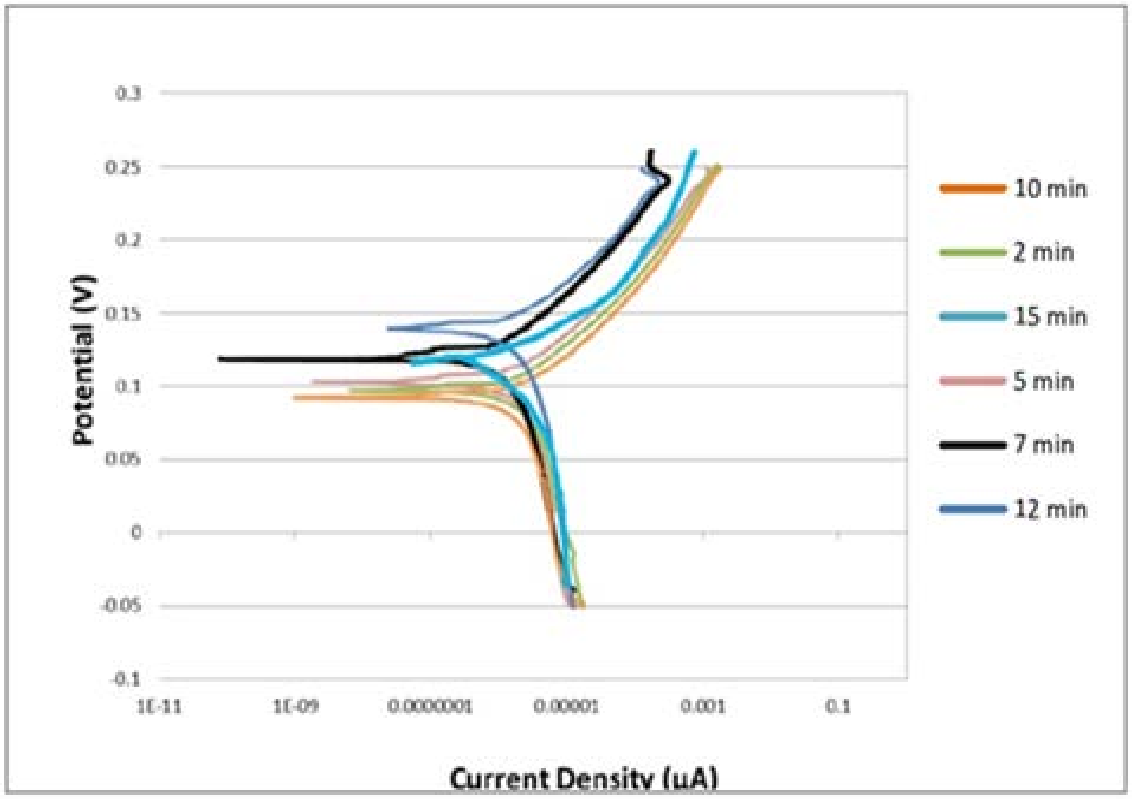


Fig 12: Polarization curves of electrodeposited samples after adding 10ppm Dimethoxymethane at different times

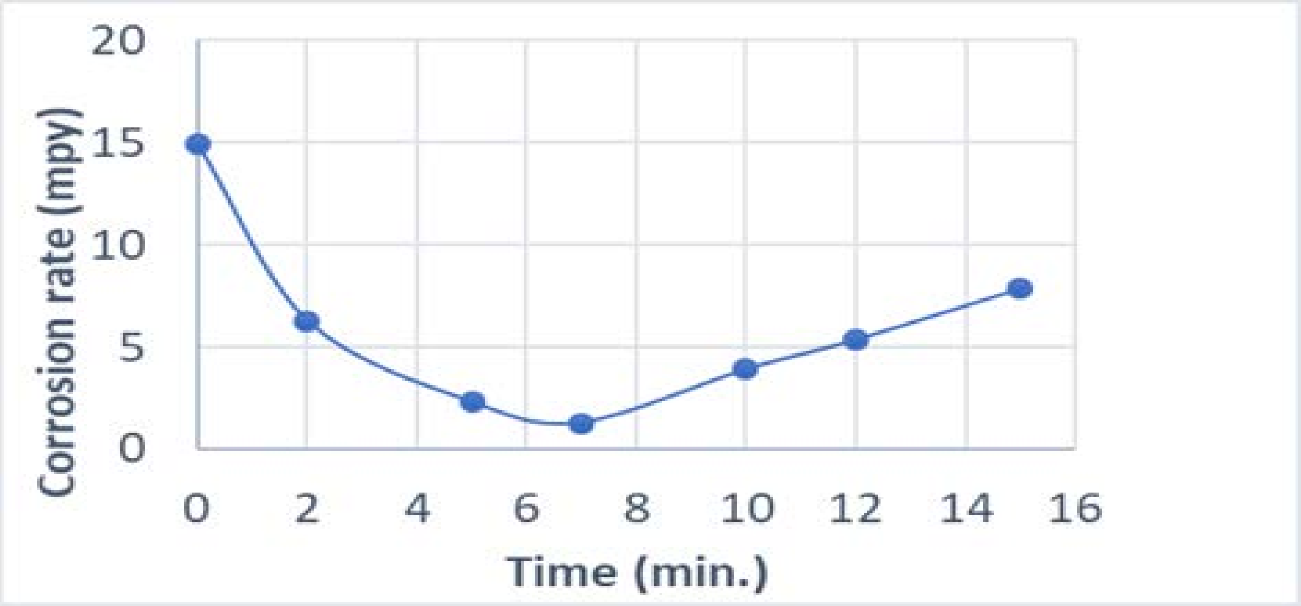


Fig13: Variation of corrosion rate of copper after adding 10 ppm Dimethoxymethane at different time

2.3 X-Ray Diffraction

X-ray diffraction patterns for the samples of conditions; 10% H_2SO_4, 10% H_2SO_4followed by calcination, 10% H_2SO_4 with10ppm Gelatin and 10% $H_2SO_4$with 10ppm Gelatin followed by calcination as shown in Figures 14, 15, 16 and 17 respectively while Figure 18 show XRD for all results.

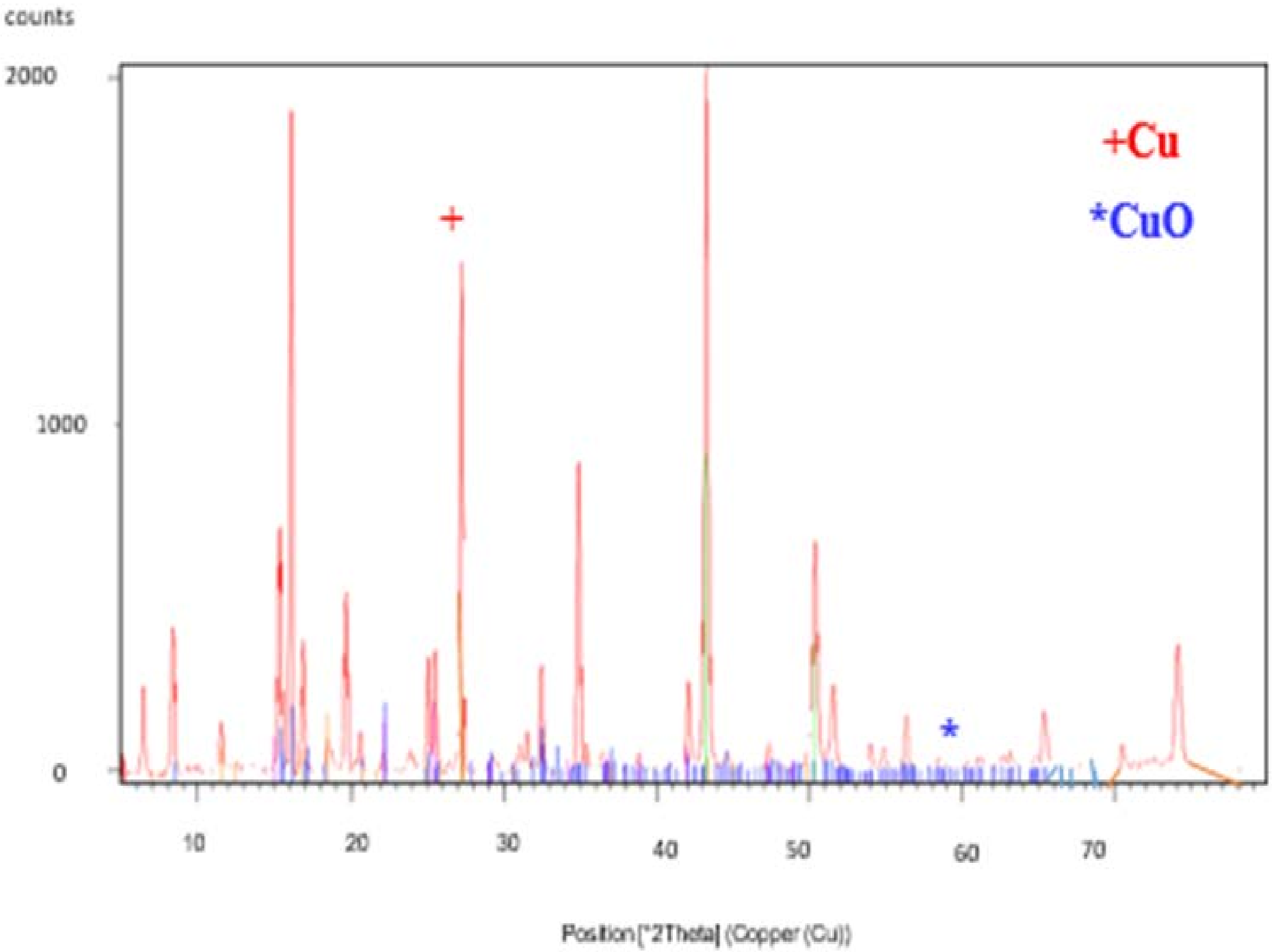


Fig. 14: XRD analysis of the sample electrodeposited with 10% wt. H_2SO_4

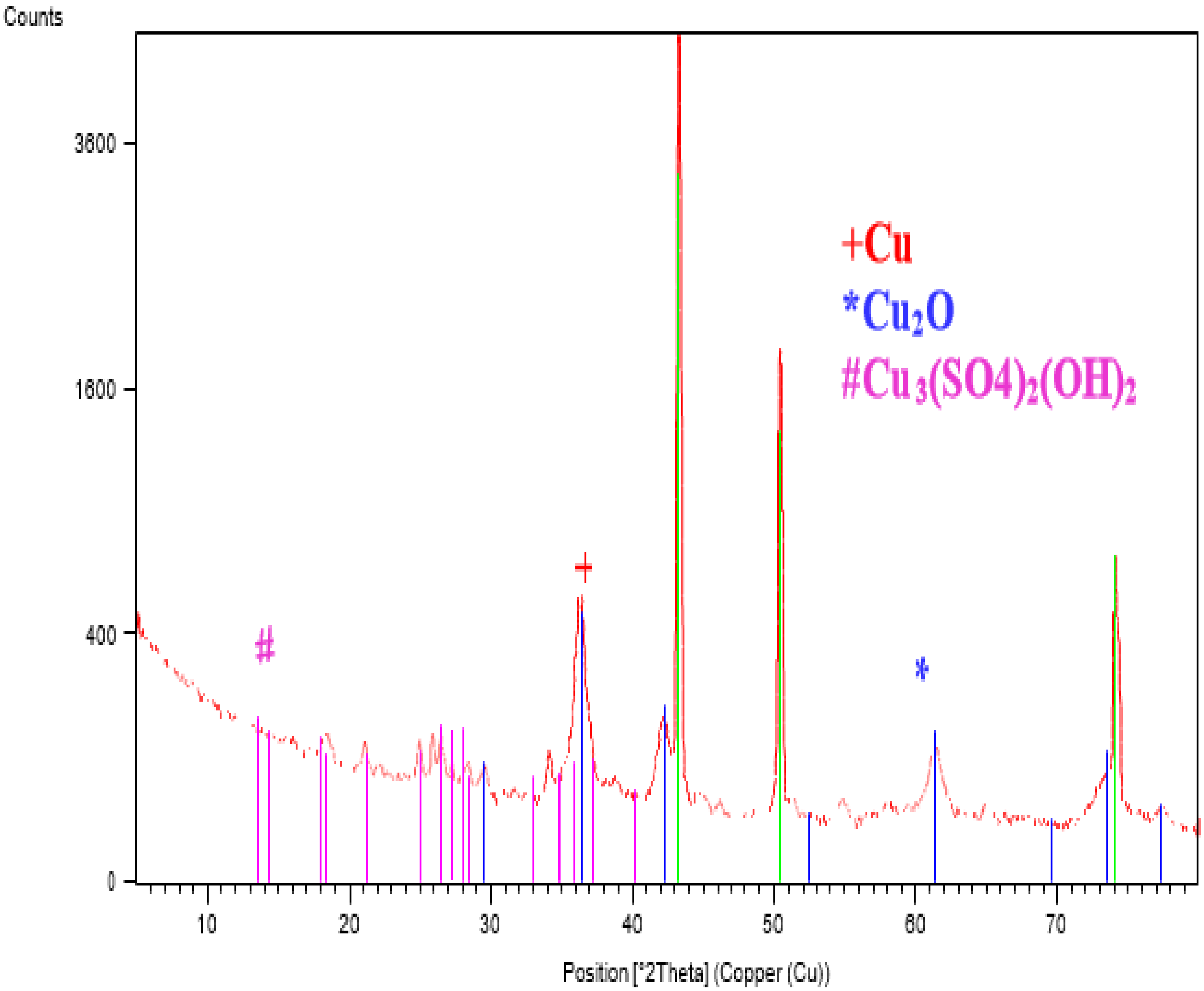


Fig.15: XRD analysis of the sample electrodeposited with 10% wt. H_2SO_4Followed by calcination

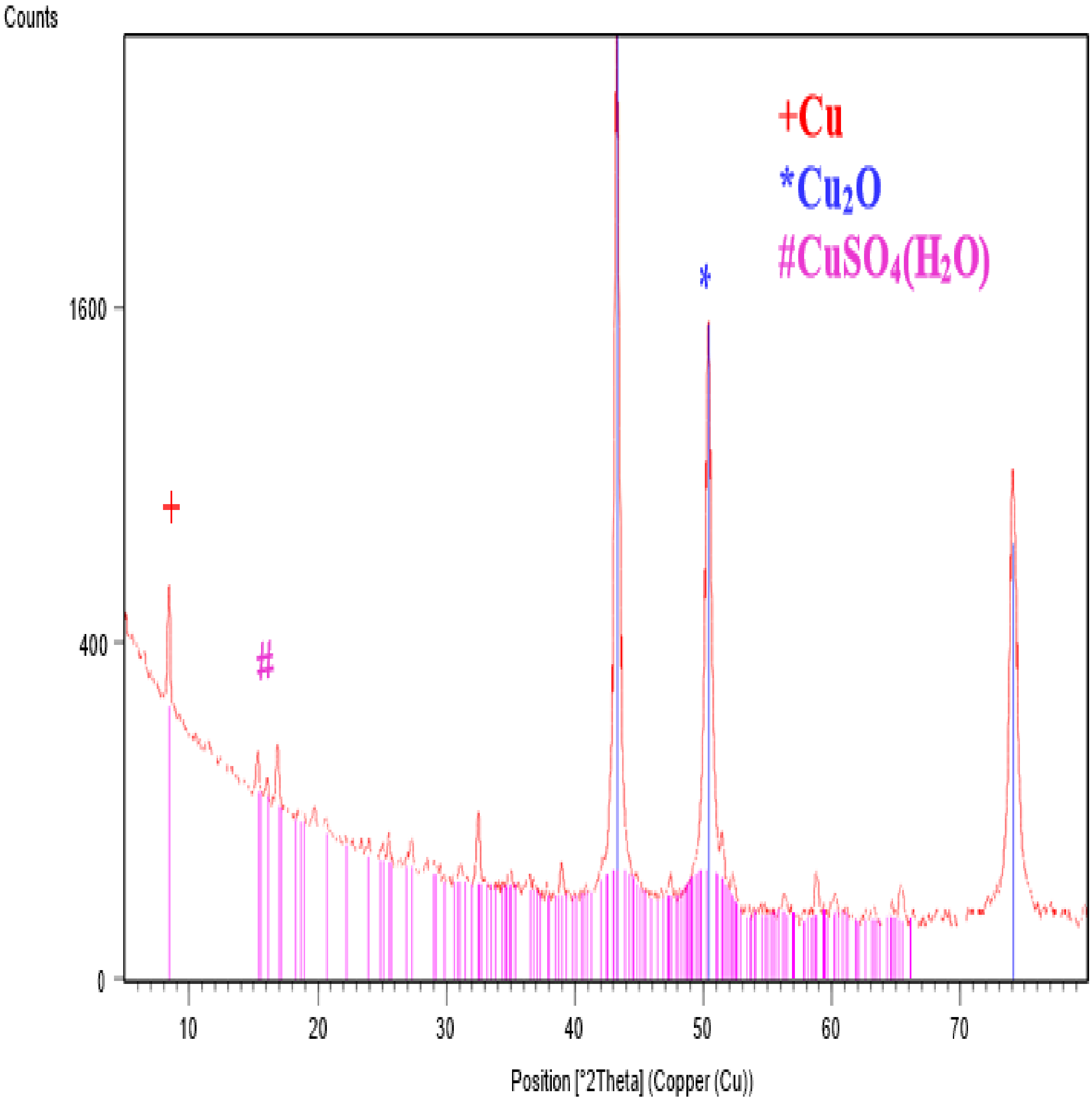


Fig.16: XRD analysis of the sample electrodeposited with 10% wt. H_2SO_4 with 10ppm Gelatin

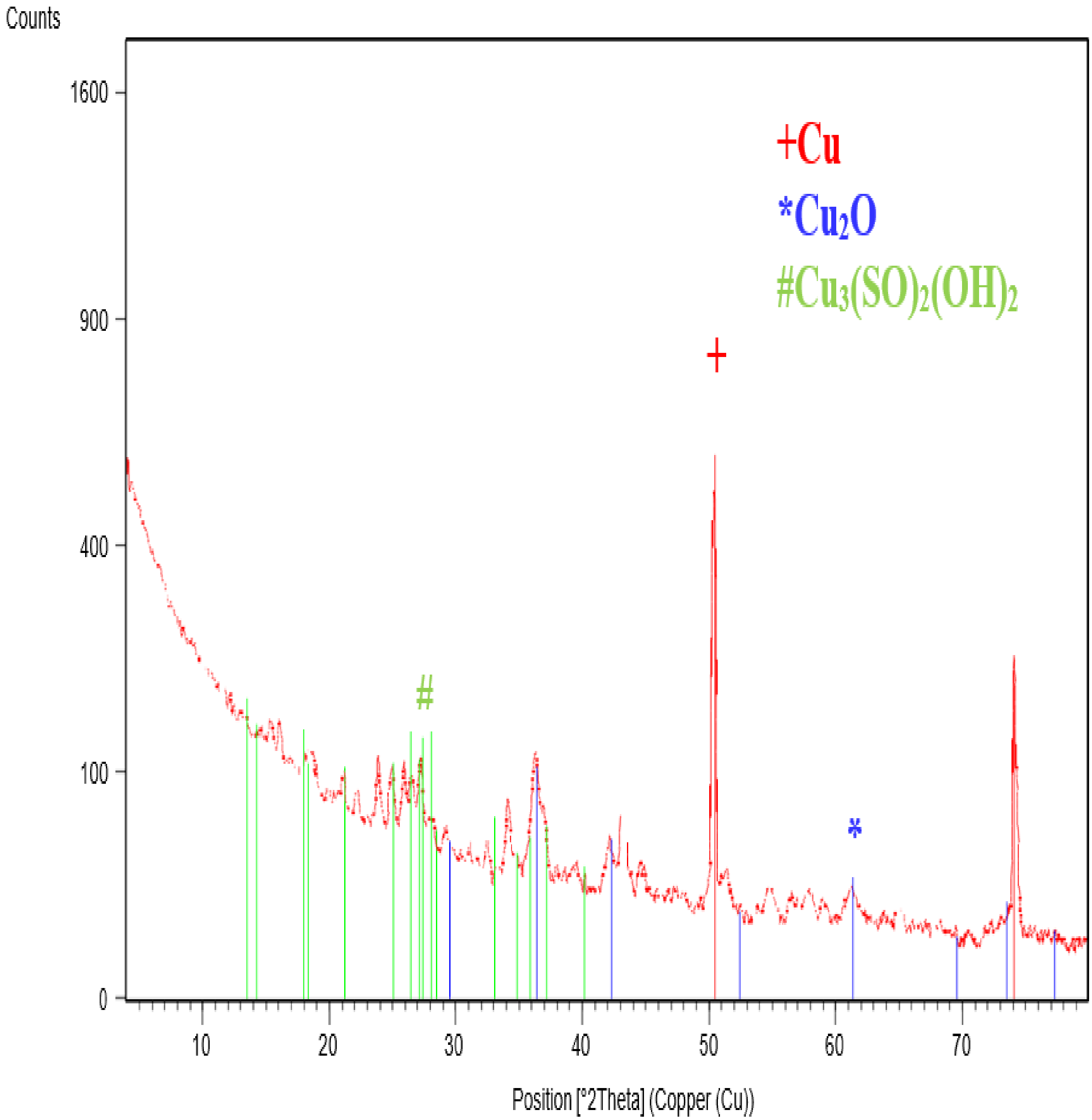


Fig.17: XRD analysis of the sample electrodeposited with 10% wt. H_2SO_4 with 10ppm Gelatin followed by calcination

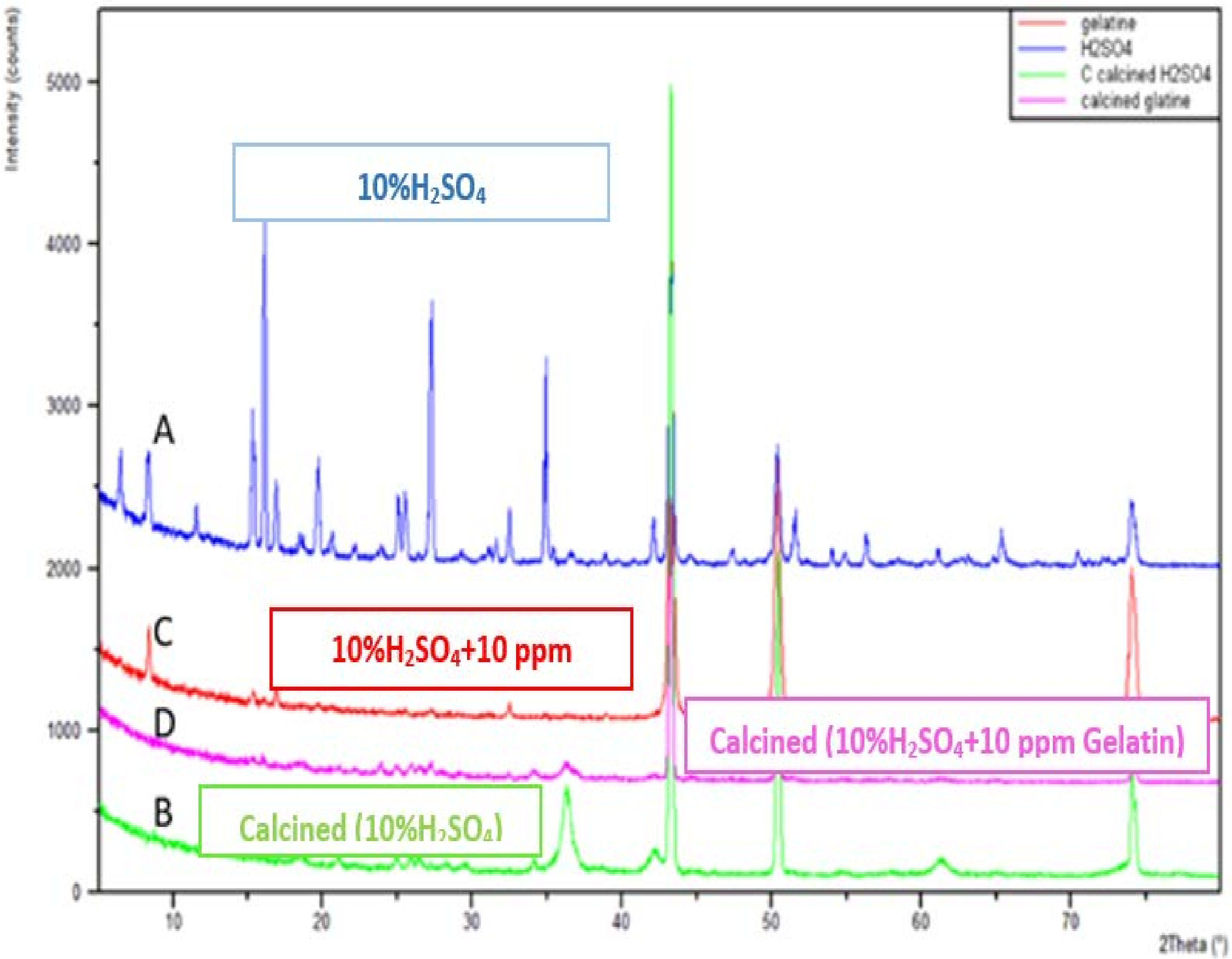


Fig.18: XRD analysis for all results

The results showed that the surface of the modified samples formed cupric oxide (CuO) and cuprous oxide (Cu_2O). By comparing the above results of the XRD pattern with the XRD pattern of NANOPARTICLES from the articles, we found that our surface is expected to be NANOPARTICLES.

By using EVA Topaz software, which can calculate Nano crystalline size according to the Scherrer Equation [22] to estimate more accurately Nano-crystalline size using XRD. The results are shown in the Tables 5,6,7and 8.

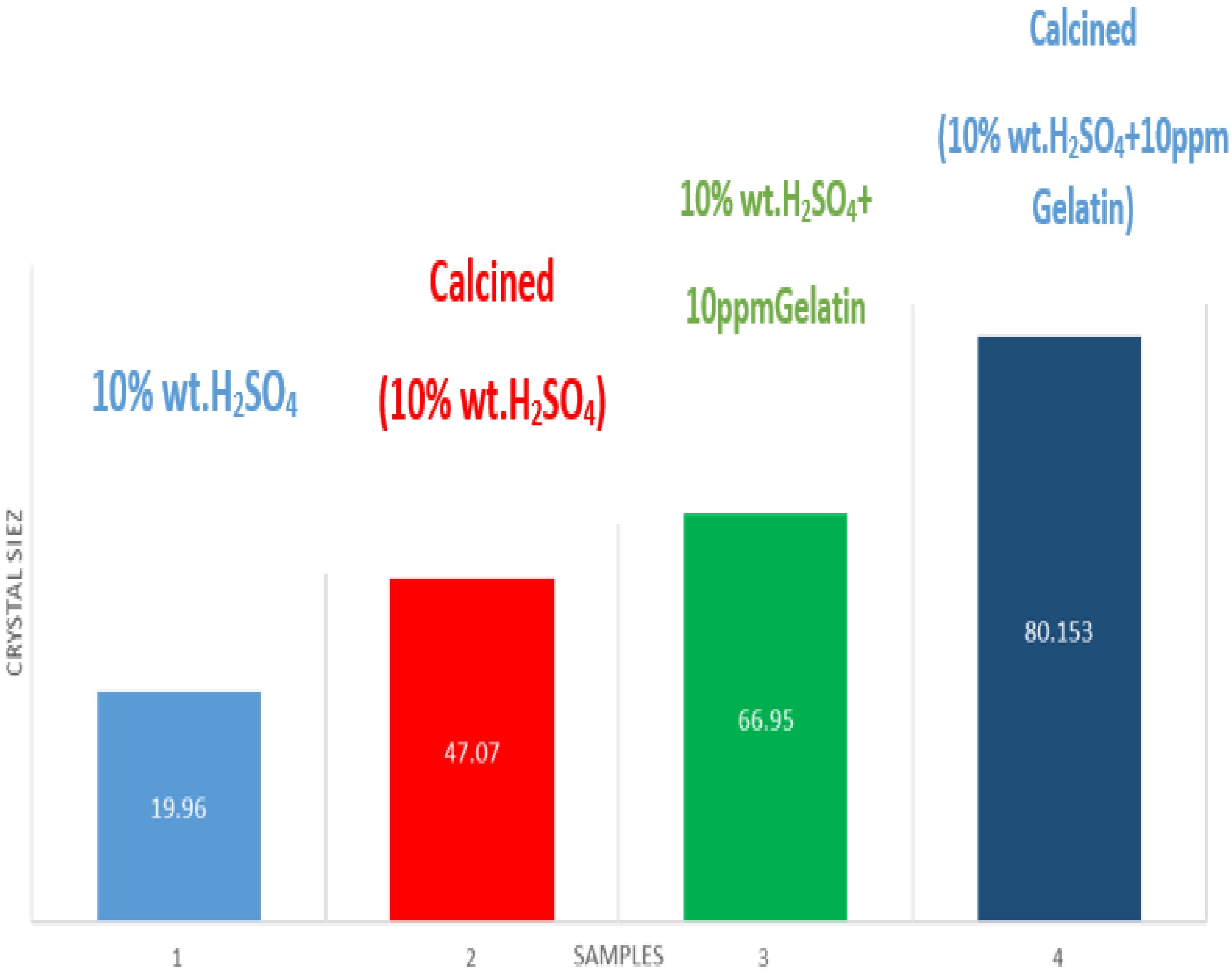


Fig.19: shows the average of crystal size of all points in all conditions.

From this results there are observation:

1. **The crystalline size plays an important role in the corrosion properties.**
2. **The corrosion rate was decreased as the size of Nano crystalline increased.**
3. **This was attributed to the increased number of active sites caused by Nano crystalline surface.**

This observation is in a good an agreement with VAHID AFSHARI International Journal of Modern Physics: Conference Series 2012[23].

2.4 Adhesion Test

The adhesion test was carried out using Tape Adhesion test (X-Cut) ASTM D3359[21] at Alfa Egypt Company on the three conditions:

A. Adhesion of Electrodeposited-Calcined Sample in 10 % H_2SO_4 :

the surface in this condition had a very good result on contact angle determination and corrosion rate test but it is loose, as shown in Figure 20.

Fig 20: Optical images of the electrodeposited-calcined sample after Tape Adhesion test

B. Adhesion of Electrodeposited-Calcined Sample in 10 % H_2SO_4 with adding 10ppm Dimethoxymethane:

The surface in this condition is better than the upper one, as shown in Figure 21.

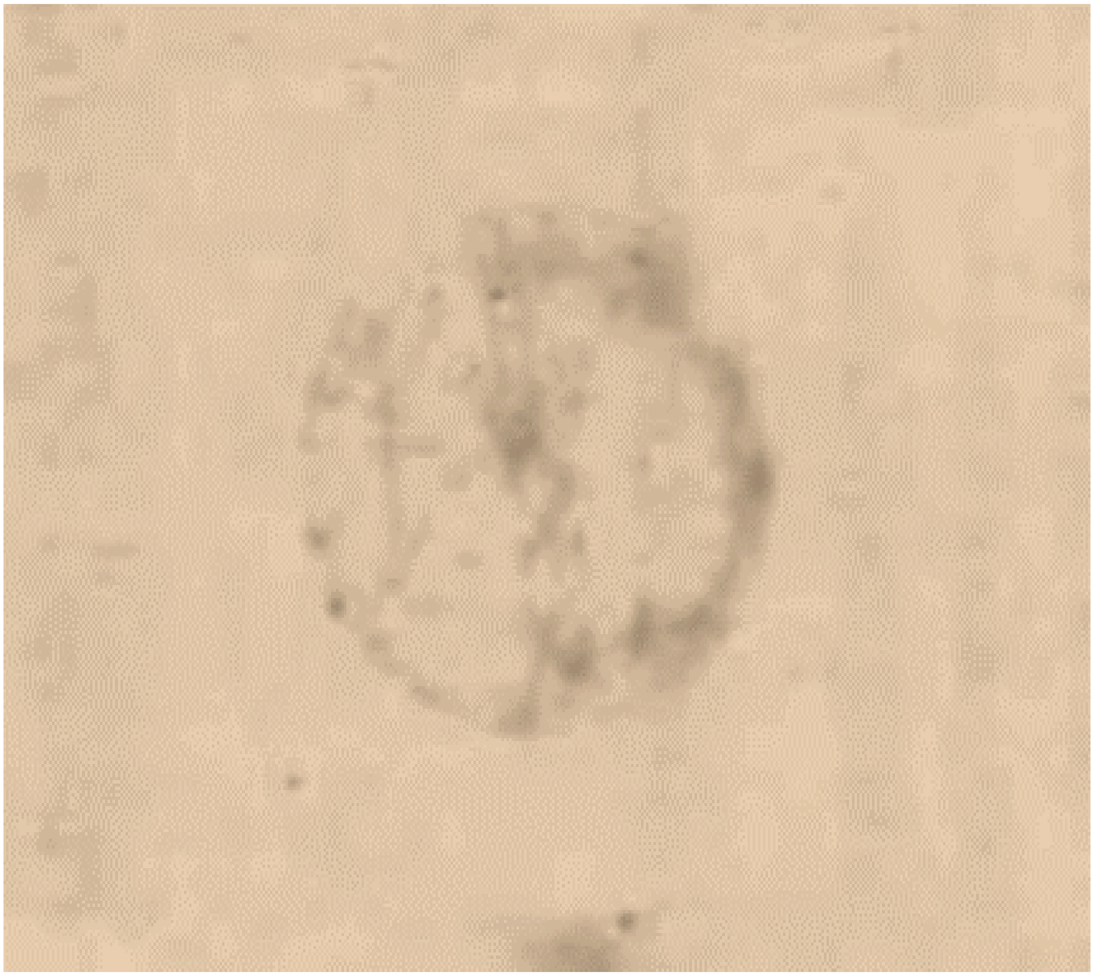


Fig .21: Optical images of electrodeposited with 10ppm Dimethoxymethane calcined sample after Tape Adhesion test

C. Adhesion of Electrodeposited-Calcined Sample in 10 % H_2SO_4 with adding 10ppm Gelatin:

The surface in this condition is the best one, as shown in Figure 22

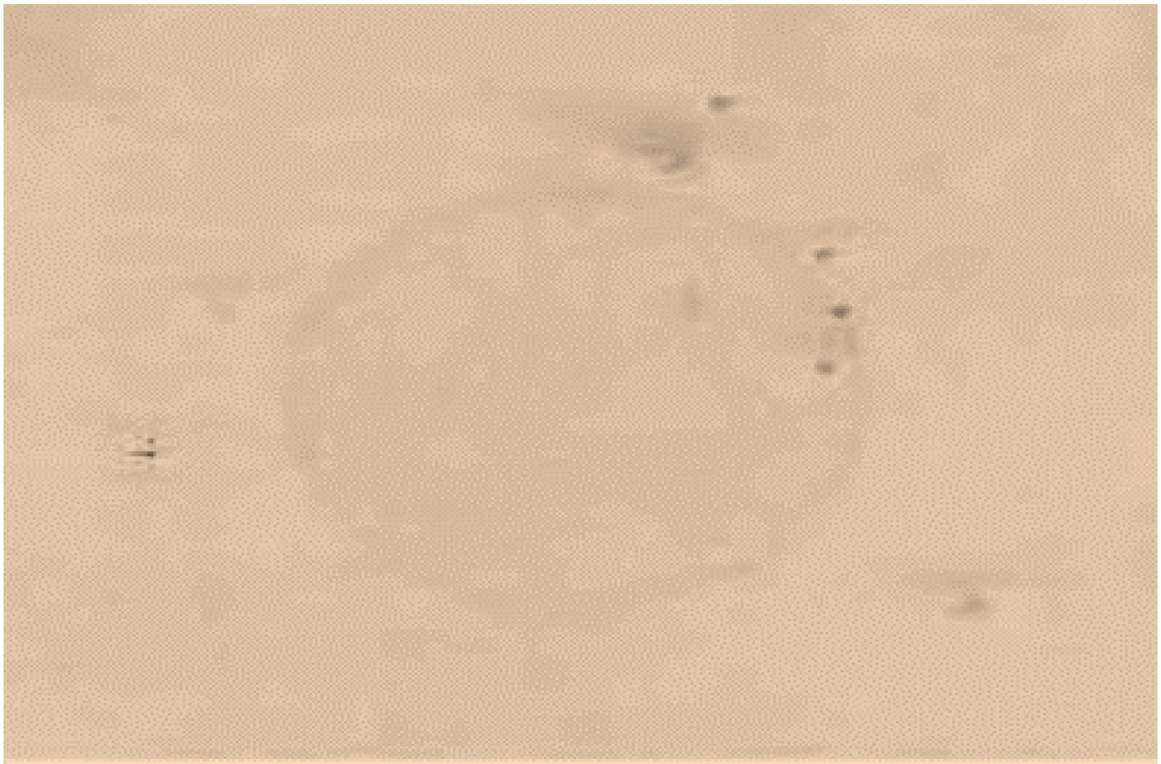


Fig22: Optical images of electrodeposited with 10ppm Gelatin-calcined sample after Tape Adhesion test.

2.5 Salt Spray Test Result

According to ASTM B117 edition 2011salt spray test was carried on sample (Half of it as received, and the other half had electrodeposited in 10% wt. H_2SO_4 with 10 ppm Gelatin followed by calcination (heated at 250°C for 30 min.) because of this, the pure side couldn't handle the conditions, and that it wasn't protected, so **corrosion** is always happening. On the other hand, the copper oxide film that was on the surface of the sample that had been treated on the outside kept it safe the whole time.as shown in Figure 23 This is macrograph of the sample before and after the Salt Spray test.

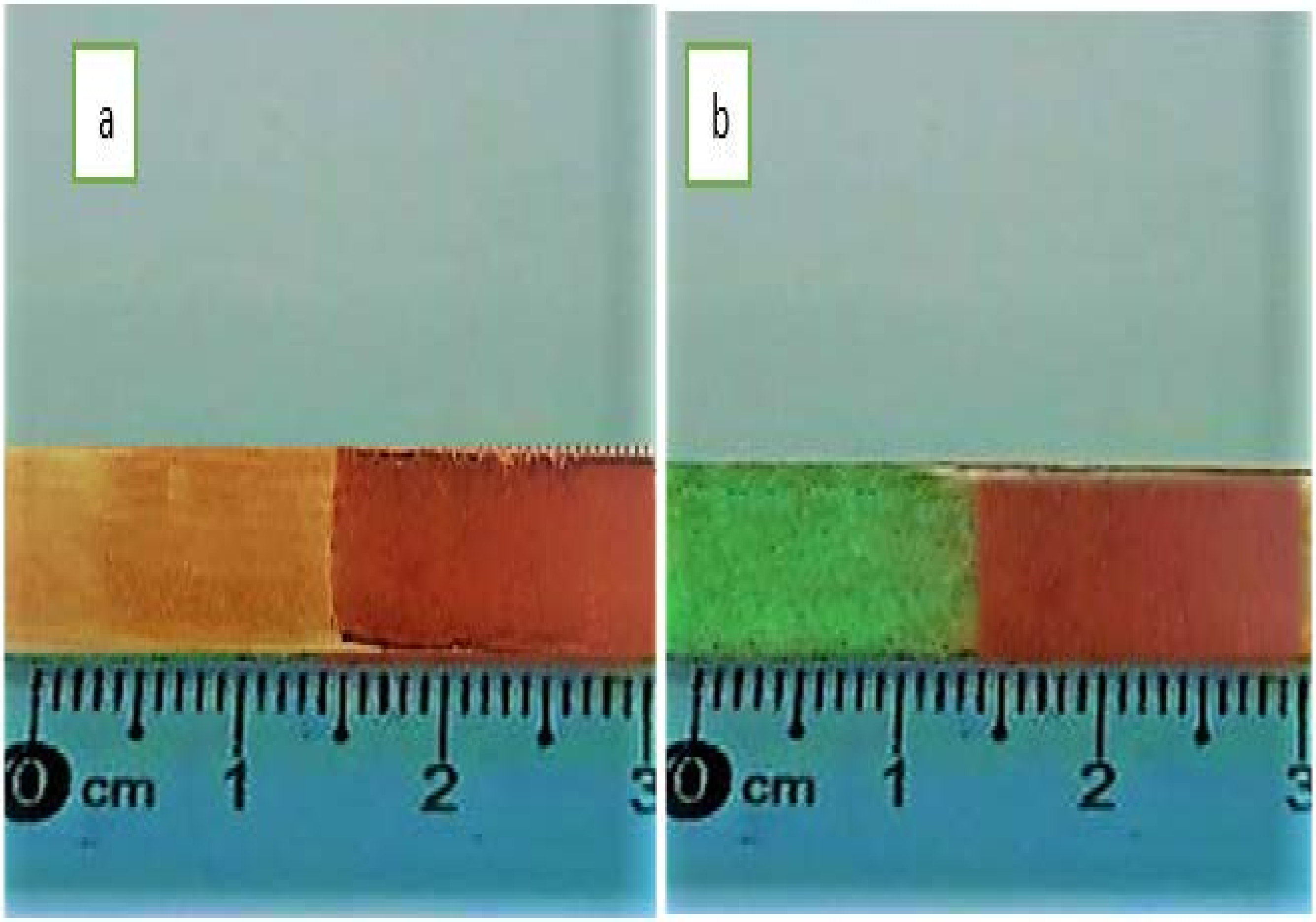


Fig.23: Micrograph of the sample before and after the salt spray test:

(a)Sample before Salt Spray test (b)Sample after Salt Spray test

Figure 24 is a macrograph of a sample after a 3-days in Salt Spray test with pure half copper side and half side electrodeposited in 10% wt. H_2SO_4 with 10 ppm Gelatin followed by calcination (heated at 250°C for 30 minutes) before the test for 50X.

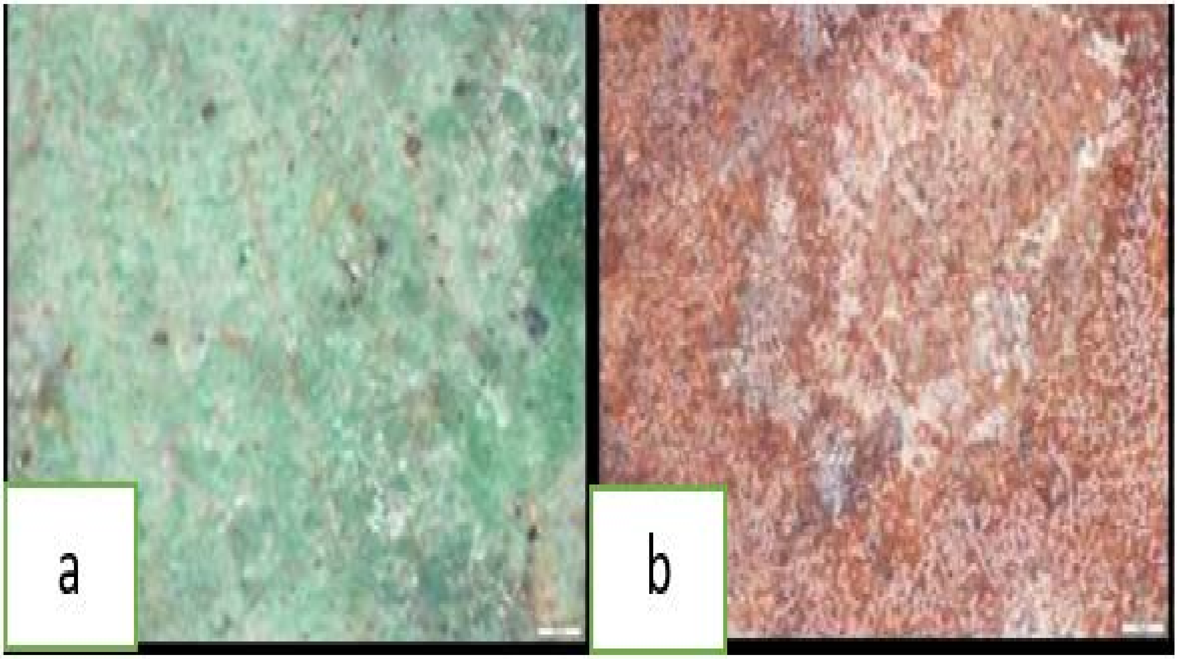


Fig. 24: Macrograph of pure copper sample after salt spray test lasted for 3 days (a) pure half copper side, (b) half side electrodeposited in (10% wt. H_2SO_4 with 10 ppm Gelatin, then calcination (heated at 250°C for 30 min.) before the test) for 50X.

Figure25 is a 50X macrograph of a cross-section of a protective Cu_2O film and the base metal after a salt spray test that lasted for 3 days.

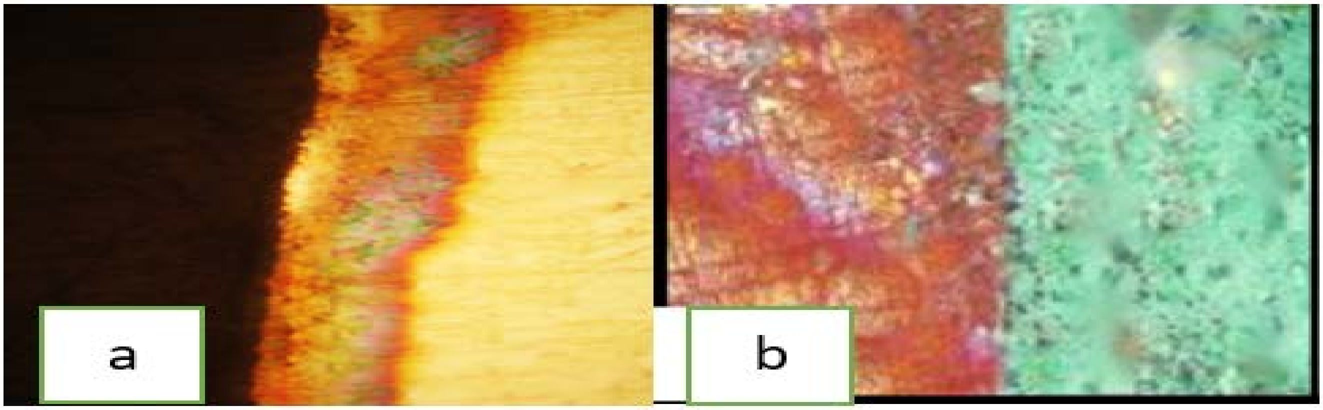


Fig.25: Macrograph of a cross-section of protective Cu_2O film and the base metal after Salt Spray test lasted for 3 days: (a) before test (b) after test

Conclusions

1. We have developed a fast, facile, and a very low-cost electrodeposition process to construct a controlled hydrophobic\ super- hydrophobic surface on the cathodic substrate with an electrolyte solution on the copper in different conditions.

2. **The surface adhesion can be simply controlled by changing the additives.**
3. **A maximum contact angle of 162 ° was achieved on the high-adhesion super hydrophobic surface by using10 ppm Gelatin as additives in electrolyte solution followed by calcination.**
4. **contact angle of pure Cu increased from 70 ° to 162 °.**
5. **Corrosion rate of Cu decreased from 15 to 0.7mpy.**
6. **The crystalline size plays an important role in the corrosion properties. This was attributed to the increased number of active sites caused by Nano crystalline surface**

4. References

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