ELECTROLYTIC PREPARATION OF COPPER POWDER WITH PARTICLE SIZE LESS THAN 63µm

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Abstract

An electrochemical cell consisting of two electrodes (Lead-6%antimony alloy cathode and copper anode, (99.9%)) was used to study the electrolytic preparation of copper powder with particle size less than (63µm) directly as powdery form. Copper sulphate dissolved in sulfuric acid solution was used as electrolyte. The produced powder was thoroughly washed with an acidified distilled water and absolute ethanol, then dried under an inert atmosphere at $80^{o}C$, and classified by screening. Samples of prepared powder were taken to determine their purity by atomic absorption. The effects of current density, metal ion concentration, sulfuric acid concentration, and electrolysis time on the weight percent of copper powder less than (63µm), yield and current efficiency were studied.

It was found that copper powder with particle size less than (63µm) can be prepared at a weight percent (79.7%) and current efficiency(75%) using cathode current density (0.16 A/cm^2),copper ion concentration(5gm/l),sulfuric acid concentration(100gm/l)temperature($25-30^{o}C$)and electrolysis time equal to(2hr). The prepared powder having an apparent density (2.24 gm/cm^3) and specific surface area ($421 \text{ X } 10^3$ cm^2/gm). Its average particle size was (42 µm) and its purity was (99.7%)
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Keywords: Copper powder, electrolytic Copper, Electrodeposition of copper, electrolytic preparation

التحضير الكهروكيميائي لمسحوق النحاس بحجم حبيببي اقل من(63µm)

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الخلاصه

تم استخدام خليه كهروكيميائيه مؤلفه من قطبين احداهما كاثودي مصنوع من سبيكه رصاص-6%انتيمون والأخر انودي مصنوع من النحاس ذو نقاوة (99.9%). تم استخدام الكتروليت من كبريتات النحاس مذابه في حامض الكبريتيك.المسحوق الناتج تم غسله جيدا بماء محمض ومقطر ومن ثم بالأيثانول ثم تجفيفه تحت جو خامل بدرجة حراره ($80^{o}C$)تبع ذلك تصنيفه حسب الحجم الحبيبي. تم اخذ نماذج من المسحوق المحضر وحددت نقاوته باستخدام تقنية الأمتصاص الذري. تم دراسة تاثير كل من كثافة التيار,تركيز ايون النحاس ,تركيز حامض الكبريتيك وزمن التحلل الكهربائي على النسبه الوزنيه للمسحوق الناتج ذو الحجم الحبيبي الأقل من (63µm),الأنتاجيه,وكفائة التيار وجد انه بالأمكان تحضير مسحوق النحاس ذو الحجم الحبيبي الأقل من(63µm) بنسبه وزنيه لاتقل عن(79.7%) وكفائة تيار (75%)عند استخدام كثافة تيار (0.16 A/cm^2)وتركيز ايونات النحاس(5 gm/l) مذابه في حامض الكبريتيك ذو تركيز (100gm/ l) وإجراء عملية التحلل اكهربائي بدرجة حراره($25-30^{o}C$) بزمن تحلل (2hr.).المسحوق المحضر عند هذه الظروف كانت كثافته الظاهريه (2.24 gm/cm^3) و ذو مساحه سطحيه نوعيه ($421 \text{ X } 10^3$ cm^2/gm) ومعدل حجم حبيبي (42 µm)ونقاوه (99.7%) .

Introduction

Copper powders have been used in industrial applications for many years. Probably the best known is the self-lubricating bearing which was the first major application and still accounts for about 70% of the copper powder used (Dunkely,2002). This application takes advantage of the ability to produce a component with controlled interconnected and surface-connected porosity. The production of metallic filters also takes advantage of this ability. Pure copper powder is used in the electrical and the electronics industries because of its excellent electrical and thermal conductivities. Copper in powder form is used in structural parts and friction materials. Brasses, bronzes and other copper alloys produced by powder metallurgy methods have the physical and mechanical properties of their cast or wrought counterparts. Copper is used also as an alloying element in iron powder components to enhance the mechanical properties and control dimensional changes during sintering, the addition being made either by mixing or by infiltration. In addition to the above applications of copper powder, a large quantity of copper and copper alloy powder is used in flake form, *i.e.*, as a powder whose thickness is small in relation to its other dimensions. Such powders are used, for example, in antifouling paints, decorative and protective coatings, and printing inks. Copper powders are also used in such nonstructural applications as brazing, cold soldering, and mechanical plating, as well as for medals and medallions, metal-plastic decorative products and a variety of chemical and medical purposes (German.,1994)**.**

Copper powder can be produced by a number of methods, the most important being atomization, electrolysis, hydrometallurgy and solid state reduction. Each method yields a powder having certain inherent characteristics (Kirk-Othmer,1991).In atomization process, copper is melted and the liquid metal flows through an orifice where it is struck by a high velocity stream of gas or liquid, usually water, thus breaking the molten metal into particles which solidify rapidly. Particle size and shape are influenced particularly by the atomizing medium, pressure and the flow rate. Controlled small additions of deoxidizing elements, such as phosphorus, also influence the particle size and shape (4). The hydrometallurgy process can be used to produce copper powder from cement copper, concentrates or scrap copper. The copper is leached from these materials with sulfuric acid or ammoniacal solutions and the pregnant solution is separated from the residue by filtration. The copper is precipitated from solution by reduction with hydrogen under pressure. In one process, for example, reduction is accomplished in an autoclave at 225-280°F (107-138°C) in one hour under a partial pressure of hydrogen of 400 psig (total pressure 425 psig) with a thickening agent added to minimize plating and control the particle size. During reduction, 90-95% of the copper is precipitated as powder. The powder is pumped as slurry to a centrifuge where the powder is separated from the liquid and washed. The wet copper powder is dried in a reducing atmosphere, milled, classified and blended to achieve the desired particle size distribution. The physical characteristics of the powder can be varied over a considerable range. Temperature, time of reduction and the quantity of acrysol addition have a marked influence on the powder properties (5).

In solid state reduction method, oxides including mill scale are first ground to control particle size and then reduced by a gas, usually carbon monoxide, and hydrogen or cracked natural gas at temperatures below the melting point of copper. Particle size and shape can be controlled within rather wide limits by varying the particle size, shape of the oxides, reducing temperature, pressure and flow of the gas (Rutledge,1975).

The electrolytic method is probably the most economical method for producing cooper powder; moreover the copper powder obtained is the highest quality .The electrolytic powder consists of particles whose dimensions and form (dendritic shape) which can be well pressed and sintered. Besides, in recent years it has been shown that by different electrolysis regimes it is possible not only to obtain powders with a wide range of properties, but to predict the decisive characteristics of powders that are of vital importance for powder quality and for the final application. The major advantage of electrolytic method over the other methods lies in the possibility of conducting the process under conditions such that powders of a wide range of volumetric mass are obtained (0.4 - 4.0 gm/cm^3).Electrolytic copper powder is produced by following principles used in electroplating with the conditions changed to produce a loose powdery deposit rather than a smooth adherently solid layer. The techniques for electrodepositing of copper powder have advanced in two directions: electrodeposition of fragile deposits, which by grinding yield powders and electrodeposition of powder directly. Several parameters influence the characteristic and structure of copper powder produced as well as the yield and current efficiency which play an important role on the economy of the process .These are :metal ion concentration ,current density ,agitation ,temperature, conductivity of electrolyte and added colloids to solution. Current density and metal ion concentration are more pronounced on the yield and current efficiency (Calusaru,1979). **Table (1)** shows the typical properties of copper powder produced by various methods

Electrodeposition of copper powder dates back to 1920 when Leach and Henry used a bath of copper sulphate and sulfuric acid without additives (B.Leach and Henry,French,1920).Formation of copper powder by electrodeposition has been examined on a laboratory scale by Drumill where high apparent density (2.7gm/cm ^{3}) obtained using acid sulphate bathes(Drumiller ,Moulton,1920) .the first serious attempt to produce electrolytic copper in quantities was in 1959, when the metal was deposited at a current density of (0.05-0.5 A/cm^2) at 30°C and an average voltage of the cell(2.3volt)(Mantell,1959) .Enchevl used reversing current for copper powder preparation by electrolytic extraction where high purity of powder was obtained(99.99%), (Enchevl, Kharizanov, 1974).Ralph used Electrolytic method for making high density copper powder starting with copper powder of lower apparent density in this method, an integral two-phase process is provided in which copper powder of relatively lower apparent density is formed by electrodeposition, and the powder so-formed is then used in a second phase electrodeposition process as a cathode on which copper powder of the desired relatively high apparent density is formed (Rippere, 1976).later on a method of producing copper powder is provided that uses electrolytic cuprous oxides as the starting material for production copper powder suitable for a conductive filler. This method is developed instead of the well known methods that used electrolytic copper powder obtained as compact deposits (Yamada, Hirata,2006).

The aim of the present research is to prepare an electrolytic copper powder directly in powdery form rather than compact deposits to be suitable for conductive filler.

Experimental Work

The copper powder electrodeposition was carried out at constant current operation during the electrolysis (galvanostatically) using a 3.5-liter capacity electrolytic cell (made of Perspex) having provision for electrode adjustment in all required directions as shown in **Fig. (1)**.

The dimensions of the cell were (18x32x6 cm) having a top coversheet. the cell consisting of two electrodes: cathode plate made of (lead-6%antimony alloy)with dimensions(30x16cm),and anode made of copper plate with dimensions(30x16cm),having a purity not less than (99.9%).An enter electrode distance of (3cm) was maintained to minimize the current losses due to solution resistance .The effective surface area of cathode (immersed area)suitable for applying the limited current density was determined by moving vertically the cathode up or down the level of the electrolyte The two electrodes were first subjected to mechanical treatment with first rough and fine emery paper, kept in dichloroethane in order to remove any grease from the electrode surface, shaken in distilled water for a few minutes and wiped with drying paper before being placed in the cell. A power supply (20 Ampere, 30 volt) was used to driven the circuit, currents (8-30 amperes) were applied through the experiments and the electrolysis was proceded at room temperature. All the reagents used for preparing the electrolyte were of analytically grade (Merck) and did not undergo further purification .distilled and deionized water was used in preparing the solutions. A 2.5-liter electrolyte was prepared for each run by dissolving copper sulphate(99.9%) in sulfuric acid solutions(25-150gm/l). The amount of copper ion in the electrolyte at the starting and during the electrolysis was determined by using atomic absorption technique (SHEMADZO-2100 at the laboratories of IBNSINA STATE Company /Ministry of industry/Iraq). At the end of each run , copper powder was scraped out the cathode , washed with distilled water (Luke-warm and acidified , PH=2) and absolute ethanol , dried under nitrogen atmosphere at 80^{o}C, screened using (63 µm) sieve and weighted the two cuts (upper and lower than 63µm) . Samples of the prepared powder were taken to determine their purity by atomic absorption. The cathode in turn was rinsed in dilute sulfuric acid and made ready for subsequent use. Factorial experimental design was used to study the effect of the main parameters on the percent of powder having particle size less than (63µm), current efficiency and yield.

Results and Discussion

The effects of the main parameters were studied in order to determine the preferred conditions for obtaining copper powder directly in powdery form at higher percent of particle size less than (63µm) with a suitable current efficiency.

1-Current density: **Figures (2, 3, and 4)** show the effect of current density (0.06-0.25A/cm^2) on the percent of copper powder less than (63µm), current efficiency and yield respectively.

It can be seen that the percent of copper powder and yield increase with increasing the current density while the current efficiency decreases. This is because of the increasing in the rate of hydrogen evolution as current density increases leading to increase the penetration and distribution of hydrogen bubbles through the bed of copper powder formed on the cathode surface which make the particles of copper finer. It is to be noted that current efficiency drops down (60%) as the current density reaches (0.2 A/cm^2) .From practical view point, it is not recommended that the current efficiency reduces lower than 60% because of a high electrical energy will be lost and to avoid excessive heating of the electrolyte, formation of dendritic-tree growths on the cathode and to maintain a useful electrolytic deposition rate. In addition, the temperature of the electrolyte reached to (50 ^{o}C) at current density (0.2 A/cm^2) as observed in the experiments. the temperature increasing led to increasing the copper ion concentration in the electrolyte higher than 50%of the initial value (5gm/l) . Therefore current density (0.16A/cm^2) be suitable for copper powder preparation in powdery form in which current efficiency higher than 65%could be obtained and copper ion concentration increasing during the electrolysis not higher than 5%of the initial value.

2-Copper ion concentration

Figures (5, 6, and 7) show the effect of copper ion concentration (3-25gm/l) on the percent of copper powder less than (63µm), current efficiency and yield respectively.

In this case ,both the percent of copper powder less than (63µm) and yield increase with decreasing the copper ion concentration while the current efficiency decreases .this can be interpreted as that the mass transfer of copper ions decreases as the concentration decreases leading to increase the electrode potential where the rate of hydrogen evolution will be increased. Figure (6) shows that the current efficiency drops lower than (70%) as the copper ion concentration lowers than (5 gm /l). Therefore ,it is preferred to operate at concentration of copper ion close or equal to(5gm/l)to insure the current efficiency being higher than (70%)and maintaining the percent of copper iron powder less than (63µm) as high as possible with a reasonable yield.

3-Sulfuric acid concentration

Figures (8, 9, and 10) show the effect of sulfuric acid concentration (25-150gm/l) on the percent of copper powder less than (63μm), current efficiency and yield respectively. It is observed that any increasing in sulfuric acid concentration leads to increasing the percent of copper powder less than (63μm) and yield with decreasing the current efficiency, however the effect is not critical as those in the current density and copper ion concentration. it was observed that current efficiency drops lower than 68% when sulfuric acid concentration became higher than 100gm/l.therefore it is preferred to maintain the concentration of acid on or below this value.

4-Time of electrolysis:

The effect of electrolysis time (0.5-5hr.) on the percent of copper powder less than (63μm), current efficiency and yield are given in **Figures (11, 12, and 13).**

These figures show that each of weight percent of powder less than (63 μm), and yield decrease with increasing time of electrolysis while the current efficiency increased. This is because of the increasing in the effective surface area of the cathode as time increases, so that current density will be lowered. Accordingly, it is not preferred to operate at time higher than (2 hr.) since the percent of copper powder less than(63 μm) Lowered than (60%).from technical standpoint, the powder must be removed periodically after (2 hr) to insure high percent of powder less than 106μm at reasonable current efficiency.

The Preferred Conditions

The preferred conditions for preparing copper powder directly in powdery form are summarized in **Table (2)**.

A run was achieved under these conditions, the results indicate that a weight percent of copper powder less than (63 μm) equal to(80%) can be obtained with reasonable current efficiency (75%) ,the powder obtained having the analysis shown in **Table(3)**which is acceptable From industrial point view to be used as conductive filler(13).

Conclusion

1- The electrodeposition of copper powder with particle size less than (63 μm) directly in powdery form can be achieved by an electrochemical cell consisting of cathode made from lead-6%antimony and anode made from copper(99.9%)with applying the following operating conditions:-

- cathode current density	(0.16 A/cm^2)
- Copper ion concentration	(5 gm/l)
- Sulfuric acid concentration	(100gm/l)
- Time of electrolysis per batch	(2 hr.)
- Temperature	(25-30^{o}C)

2- It was found that the powder obtained according to above conditions has a weight percent of particle size less than (63μm) close to 80% and an average particle size (42 μm) .This result is a promoting step for the economy of the present work .

3- If we considered the additional step of milling required in the production of copper powder as a compact deposit, and the cheap of electrical energy in the case of the energy producing countries(petroleum countries).the prepared powder could be used as a conductive fillers since the level impurities lower than the standard level.

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Table 1:Typical Properties of Copper Powder Produced by Various Methods

Properties	**Atomized**	**Electrolytic**	**Hydro-metallurgy**	**Solid State Reduction**
Copper, %	99-99.5	99-99.5	99-99.5	98-99
Weight Loss in H_2, %	0.1-0.75	0.1-0.75	0.1-0.75	0.1-0.75
Acid Insoluble, %	0.5-0.1 max	0.03 max	0.03 max	0.3 max
Apparent Density, g/cm^3	2-4	1.5-4	1.5-2.5	2-4
Flow, sec/50 gm	20-35	30-40	none	20-35
Green Strength, psi	nil-2500	400-6000	nil-10,000	nil-2500
MPa	nil-17.2	2.8-41.3	nil-68.9	nil-17.2
-325 mesh, %	25-80	5-90	60-95	25-50

Table (2): The Preferred conditions of the present work

Conditions	**The present work (powdery deposits)**
Cathode:	
Material	Lead-6%antimony
Current density(A/cm^2)	0.16
Anode:	
Material	Copper (99.9%)
Current density(A/cm^2)	0.16
copper ion concentration (gm/l)	5
Sulfuric acid concentration(gm/l)	100
Temperature(^oC)	25-30
Cell voltage(volt)	2.5
Current efficiency (%)	75
Weight percent of particle size less than (63μm) (%)	79.7
Average particle size(μm)	42
Yield ($gm/cm^2.hr.$)	0.09
Specific surface area(cm^2/gm)	421×10^3
Apparent density(gm/cm^3)	2.24

Table (3): the purity of the prepared copper powder

analysis chemical	Cu	As	Fe	Bi	Ni	Cd	Si	Sn	Al
measured values	99.7%	<2ppm	<2ppm	<2ppm	<10ppm	<1ppm	<1ppm	<10ppm	<1ppm

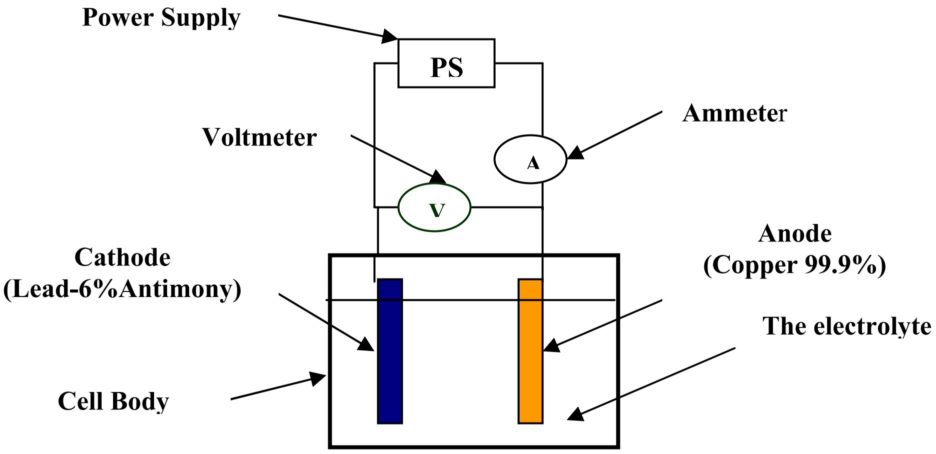

Figure (1): The Electrolytic cell

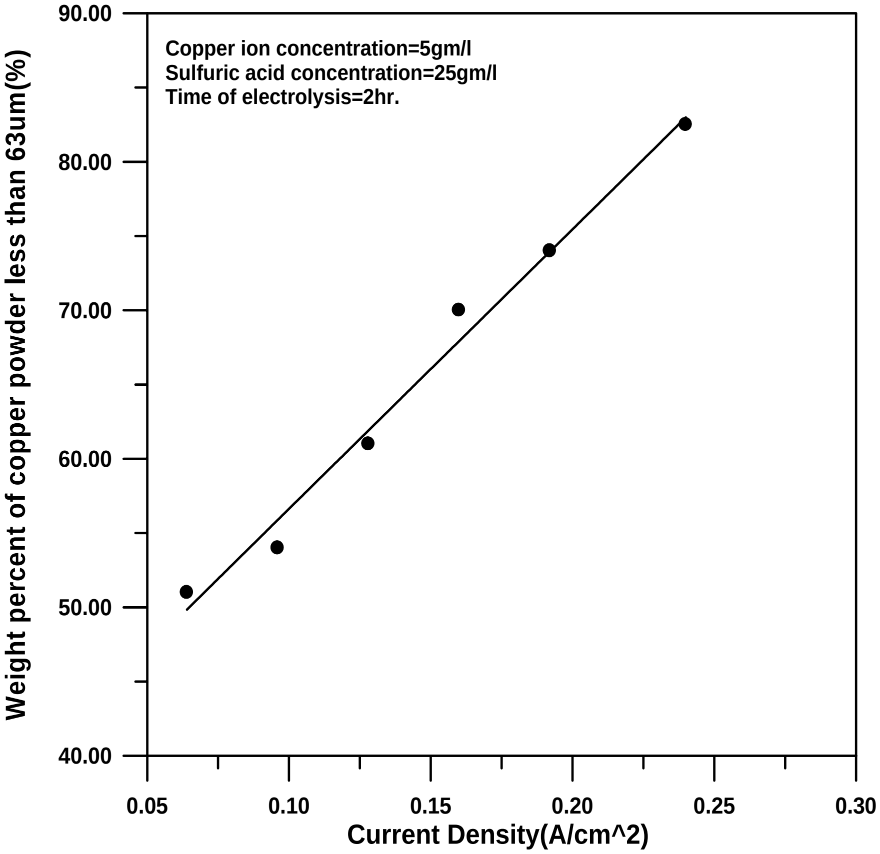

Figure (2): Effect of current density on the weight percent of copper powder less than 63µm

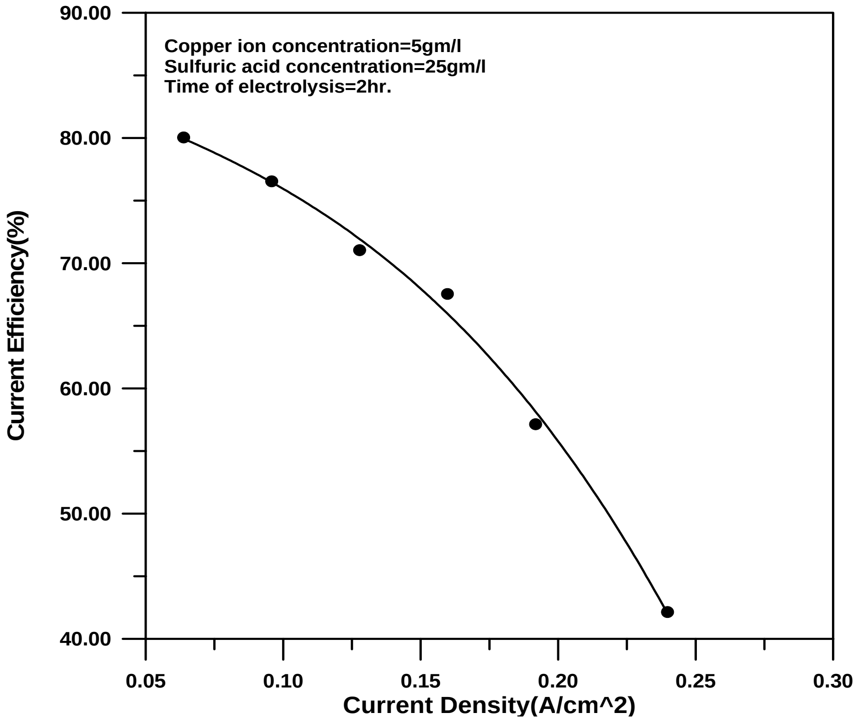

Figure (3): Effect of current density on the current efficiency

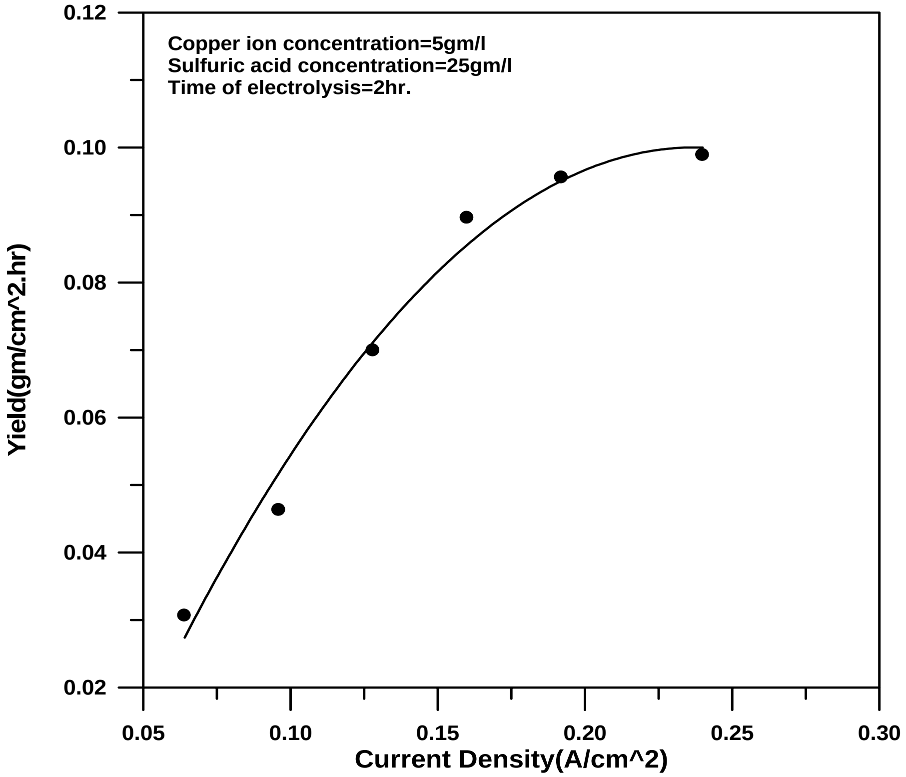

Figure (4): Effect of current density on the yield

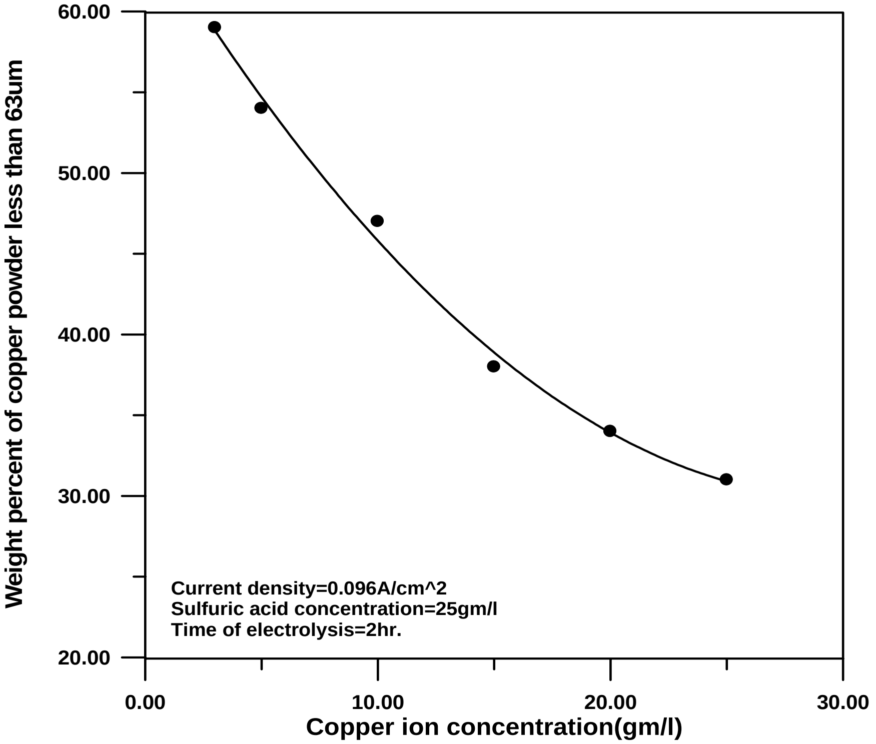

Figure (5): Effect of copper ion concentration on the weight percent of copper powder less than 63µm

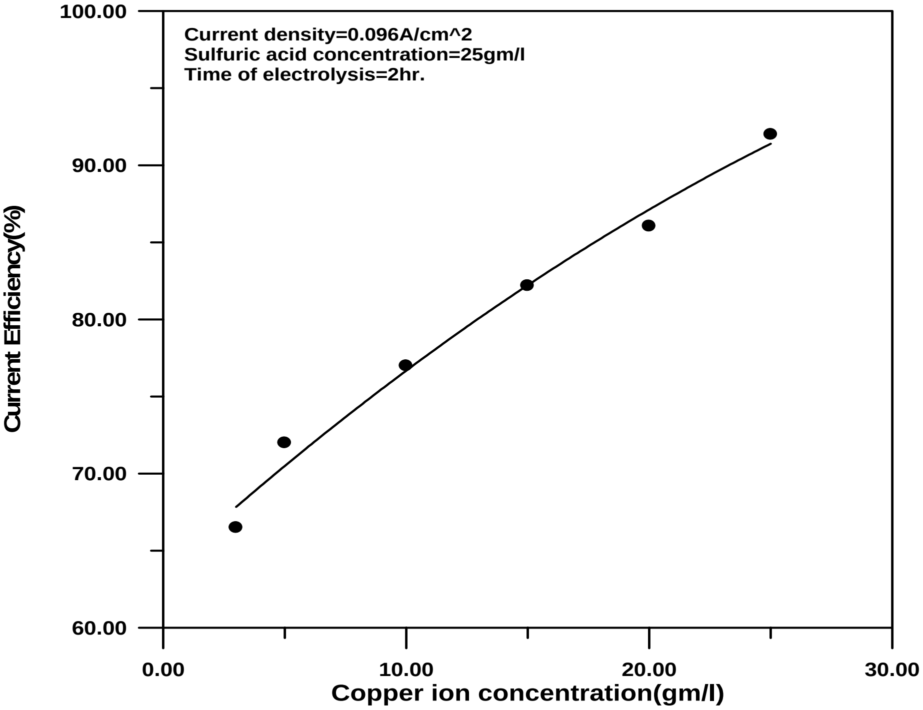

Figure (6): Effect of copper ion concentration on the current efficiency

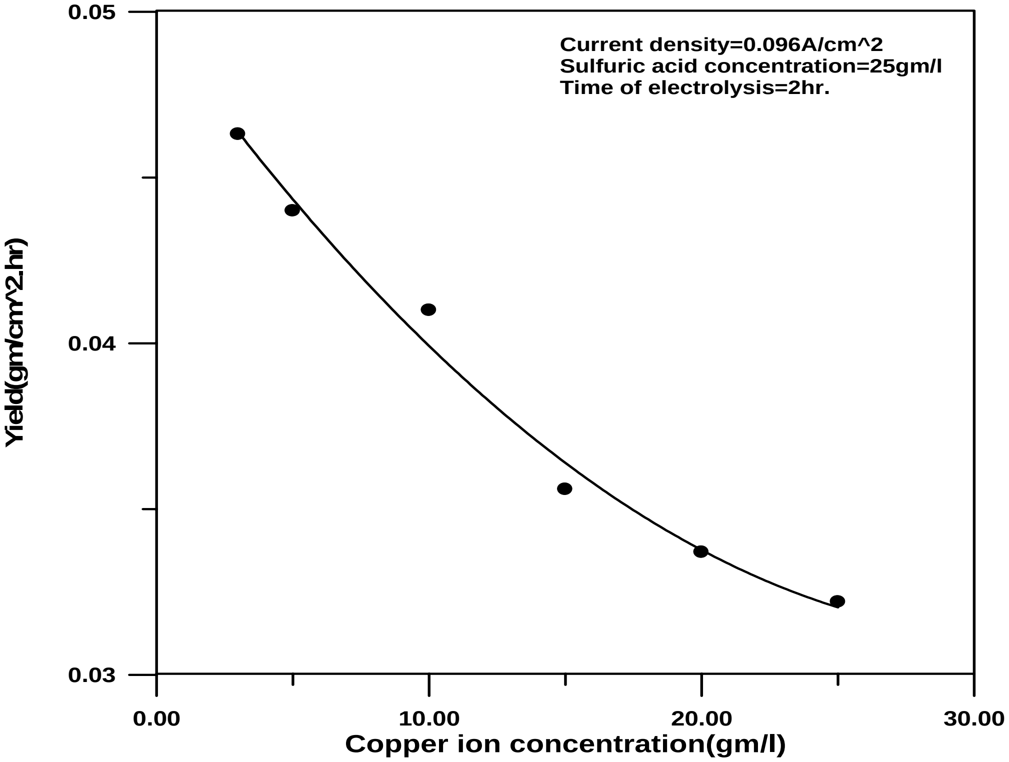

Figure (7): Effect of copper ion concentration on the yield

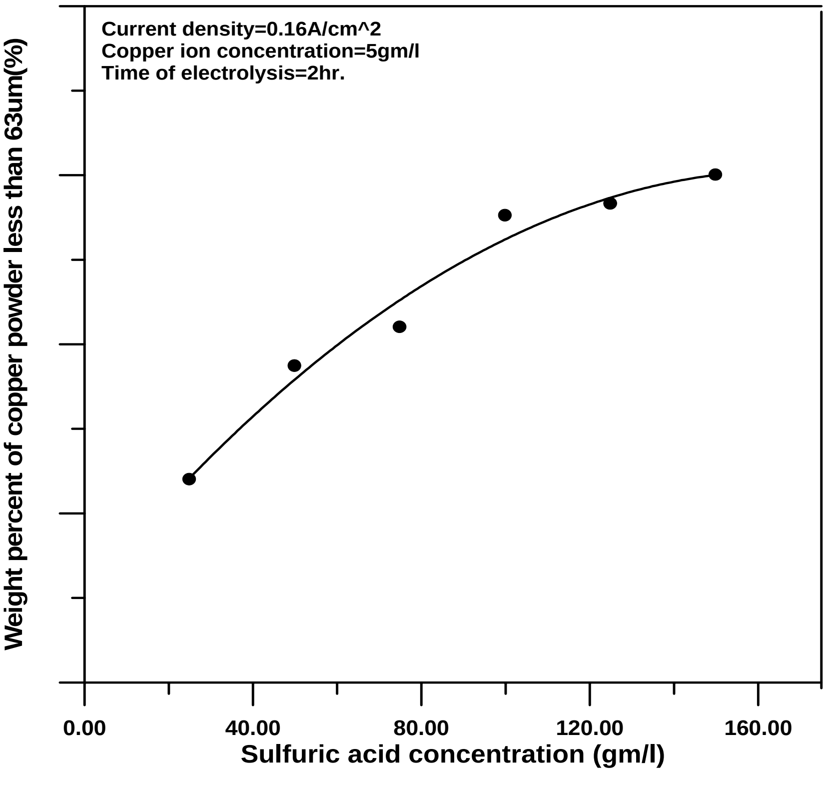

Figure (8): Effect of sulfuric acid concentration on the weight percent of copper powder less than

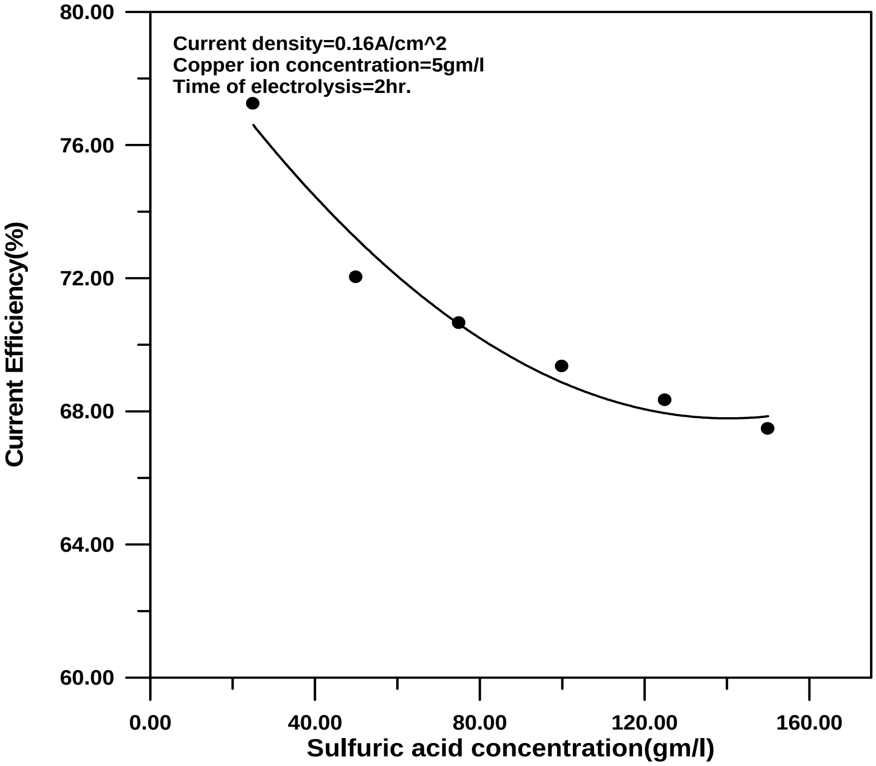

Figure (9): Effect of sulfuric acid concentration on the current efficiency

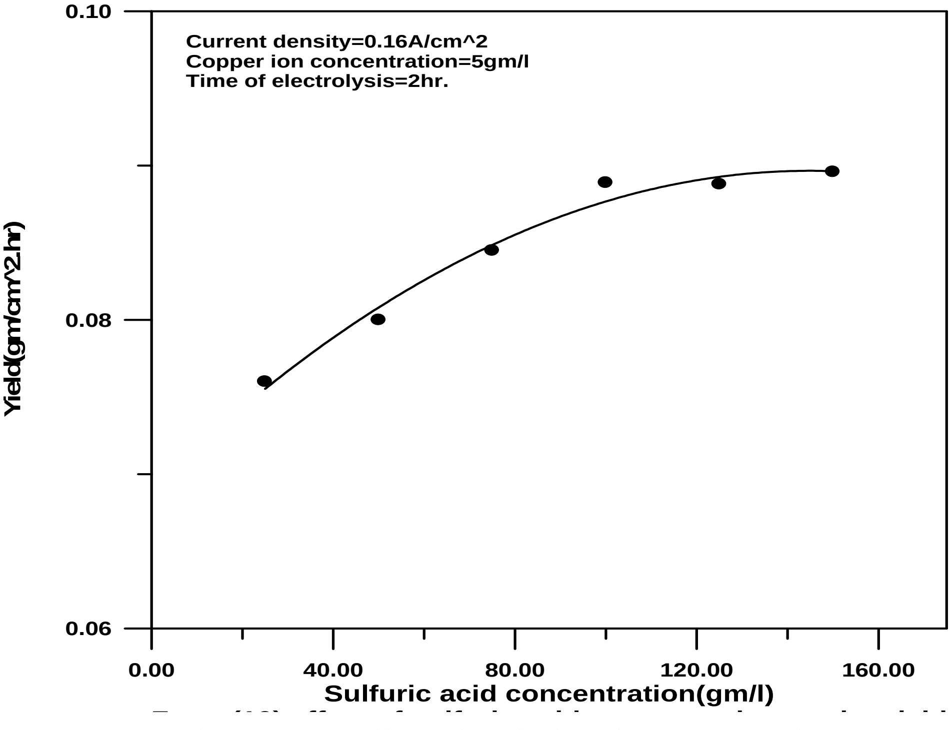

Figure (10): Effect of sulfuric acid concentration on the yield

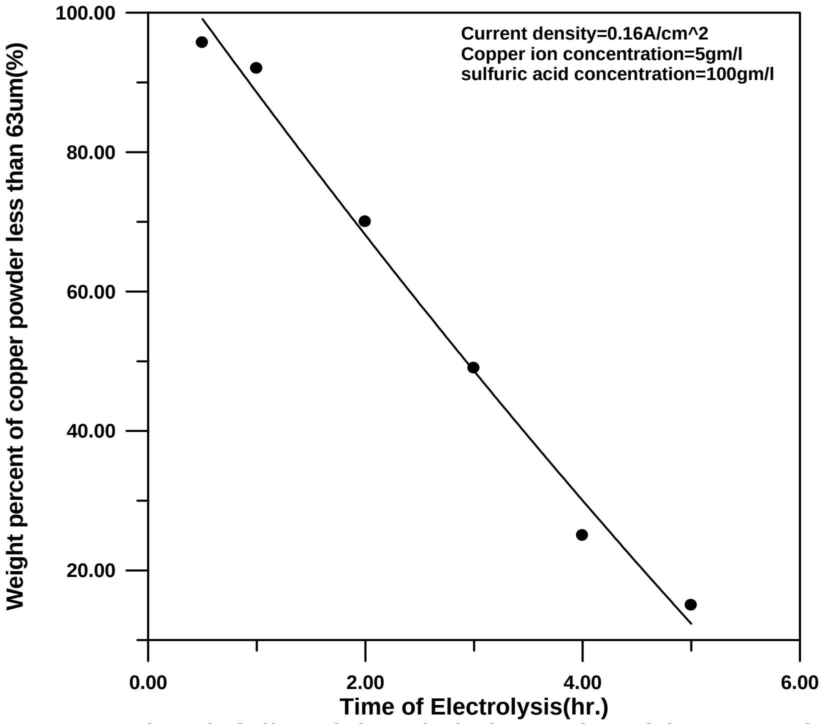

Figure (11): Effect of electrolysis time on the weight percent of copper powder less than 63µm

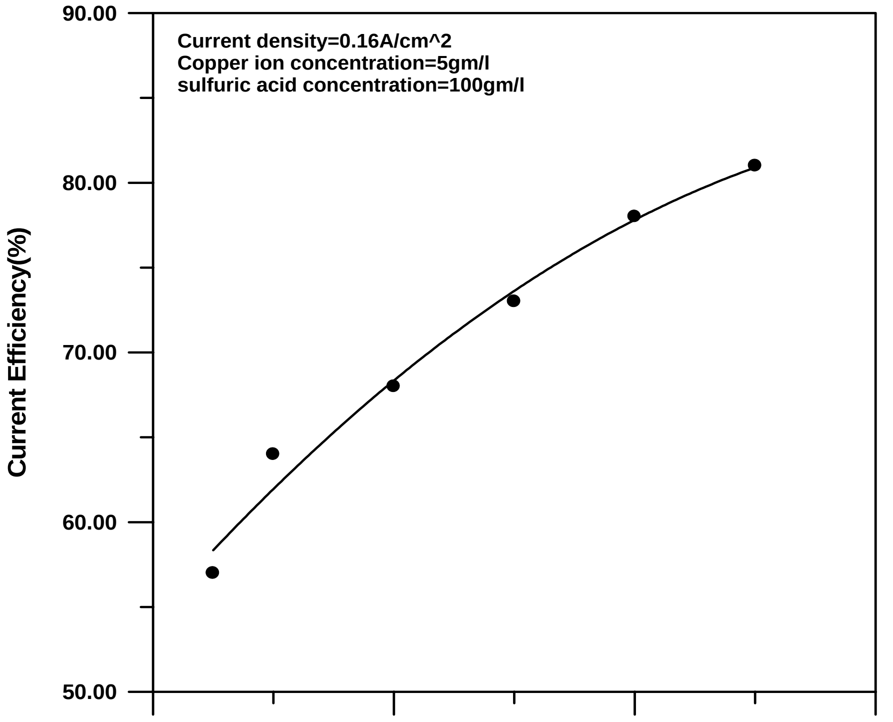

Figure (12): Effect of electrolysis time on the current efficiency

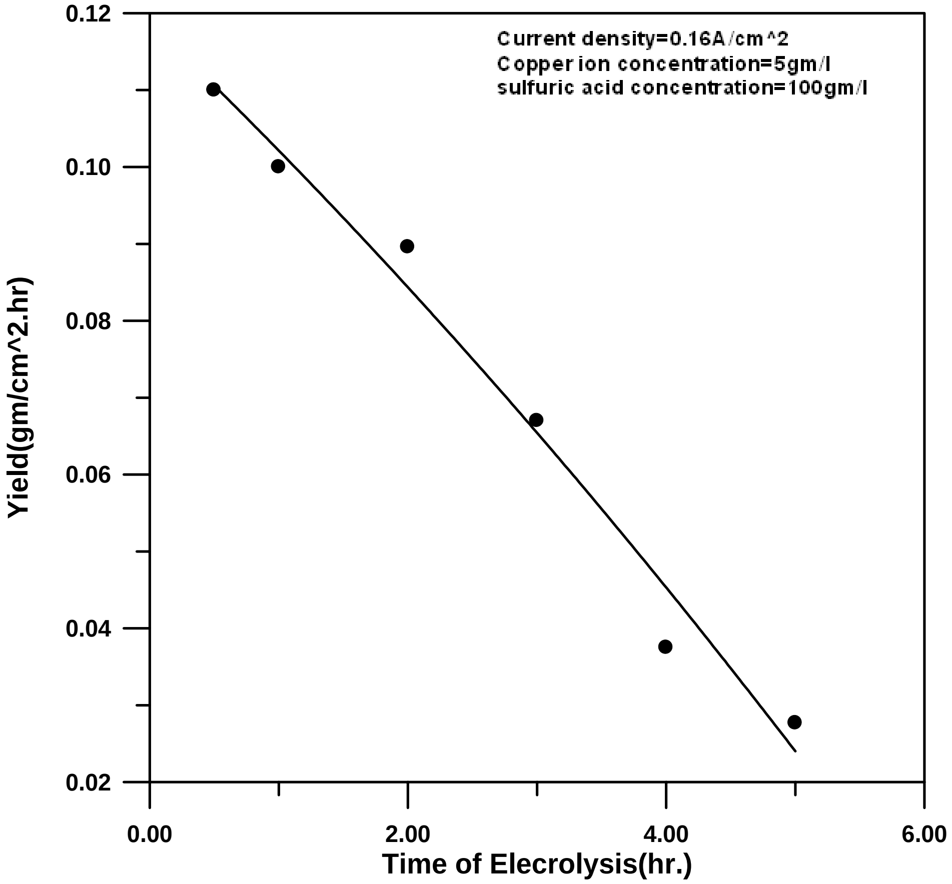

Figure (13): Effect of electrolysis time on the yield