

## **Fabrication And Characterization Of Highly Pure And Fine Copper Powder By Electrodeposition**

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### **Abstract**

*Electrodeposition is a candidate method for producing fine and pure copper powder, which have a wide range of uses in different fields such as in applications of aerospace, atomic energy, defense, electronics, paints, plastics, cutting tools, ...etc.*

*This work focusing on studying some working variables such as voltage, temperature, copper sulfate concentration, sulfuric acid concentration, circulation velocity and lanoline addition on fineness and producebility of deposited copper powder.*

*Optimum conditions concluded for copper powder fineness were at (1.6V, 30°C, 25g/ L of copper sulfate, 150g/ L of sulfuric acid and circulation velocity of 150 rpm. Addition of 0.075g of lanoline increase the fineness of deposited copper powder, but did not affect clearly the dendritic shape of deposited particles.*

**تحضير ودراسة خصائص مسحوق النحاس عالي النقاوة  
والنعومة بطريقة الترسيب الكهربائي**

### **الخلاصة**

*يعتبر الترسيب الكهربائي من الطرق الواحدة في مجال تحضير وانتاج مسحوق نحاس ناعم ونقي والذي بدوره يستخدم وبشكل واسع في مجالات عديدة مثل التطبيقات الفضائية والطاقة الذرية والدفاعية والالكترونية والاصباغ والبلستيك وعدد القطع... الخ.*

*يركز هذا العمل على دراسة بعض المتغيرات التشغيلية مثل الفولتية ودرجة الحرارة وتركيز كبريتات النحاس وحامض الكبريتيك وسرعة تدوير محلول الخلية الالكتروليتي وازضافة مادة اللانولين على نعومة وكمية مسحوق النحاس المترسب.*

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الظروف المثلى المستحصلة من هذه الدراسة لتحضير مسحوق نحاس عالي النعومة كانت عند (٧١,٦، ٣٠ م، ٢٥ غمًا لتر كبريتات النحاس، ١٥٠ غمًا لتر حامض الكبريتيك وسرعة تدوير المحلول الكهربائي ١٥٠ دورة دقيقة. وبينت الدراسة ان إضافة ٠,٠٧٥ غمًا لتر من مادة اللاتولين أدت إلى زيادة نعومة المسحوق المترسب ولكن إضافة هذه المادة لم تؤثر وبشكل واضح على شكل الدقائق الشجيرى لمسحوق النحاس المترسب.

## 1. Introduction

Metal powders can be produced, by electrodeposition from an aqueous solutions and fused salts. This method is a reversed adaptation of electroplating, this, technique is mainly employed for the commercial production of metal powders such as copper, beryllium, iron, zinc, tin, nickel, cadmium, antimony, silver and lead. Such a process provides a high degree of purity excellent compatibility and sinter ability for produced powders.

However drawbacks in such technique include, time consuming, high cost of powders due to low productivity of the process and high operating cost. So, electrolytic powders are employed only for the production of important parts. The conditions favoring the production on a cathode of powders easily removable and pulverizable, are high current density, low metal - ion concentration, high acidity,

addition of colloids, low temperature, high viscosity and circulation of electrolyte to avoid and suppress convection.

The crystalline electrolytic powders deposited are generally characterized by their dendrites or fern like shape of low apparent density and flow rate, favorable for pressing due to the tendency for individual particles to readily interlock.

The particle size is largely dependent on the conditions obtained during deposition. The low specific gravity of these powders is greatly improved by subsequent heat treatment and grinding.

Copper powder is produced commercially on large scale by electro deposition, at which the electrolyte employed is copper sulphate and sulfuric acid. The copper concentration has a considerable effect on cathode current efficiency, apparent density, and particle size of the powder.

Crude copper is used as the anode material and formation of spongy deposit of copper takes place which adheres only loosely to the cathode [1, 2, 3, 4].

Our study concern in fabrication of copper powder, because of its wide applications that cover automotive applications, aerospace, atomic energy, self defence, pharmacy and chemical industries, electronic industries, petrochemical industries, paints, plastics industries and cutting tools [5, 6, 7].

This work focuses on studying the effect of some variables like (electro - potential, temperature, concentration of copper sulphate and sulfuric acid, electrolyte circulation, connection model, and additives), on the fines and

produceability of electrodeposited copper powder.

## 2. Experimental Procedure:-

### 2.1. Material Preparation:-

The electrolyte used in this study was based on the bath mixture of nominal composition of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , concentrate  $\text{H}_2\text{SO}_4$ , distilled water (for electrolyte preparation and powder washing) [8]. Also,  $\text{Na}_2\text{CO}_3$  and  $\text{C}_4\text{H}_4\text{NaO}_6$  were used for powder washing [9].

Additives, such as  $\text{Na}_2\text{SO}_4$  and lanoline ( $\text{C}_{30}\text{H}_{50}\text{O}$ ), were examined for their effect on powder fineness.

Table (1) explain the purity of materials used in this study, also indicates the purity of raw copper plate that used in this study which are lazed with atomic absorption.

Table. (1).

Explain the Chemical results of the prime used materials.

Lemoline	Sodium sulfate	Sodium tartarate	Sodium carbonate	Disteld water	Sulfuric acid	Copper sulfate	Anode copper plate	Cathode copper plate
99%	98%	98%	98.5%	99%	96.7%	98.8%	9.52%	99%

### 2. 2. Electrolytic Cell Preparation:-

A vessel made of poly vinyl chloride (PVC) with dimensions of (42 × 15 × 20)

cm to represent the electrolytic cell. Anode and cathode of the cell were made of crude and pure copper respectively with

dimension of (10 × 14 × 0.9) cm [4, 8, 10].

Bipolar connection were used in this study which after getting the optimal condition for producebility and fineness of copper powder it is compared to Betts connection. The immersed areas of anode were (10× 12)cm<sup>3</sup>.

### 2. 3. Measurements:-

The calculation rates of copper powder deposition were based on faradays laws (I & II) as follows [8, 9, 10]:-

$$N=M/Z \quad (1)$$

Where

N = equivalent weight of the element (g)

M = atomic weight (g).

Z = equivalent No.

$$g = IMt/FZ \quad (2)$$

Where

I = Passed current (A).

g = mass of deposited (g).

M = atomic weight (g).

t = time of at which the current passed.

F = faraday's constant (96500).

$$C = I \times t \quad (3)$$

Where

C = amount of electricity (coulomb).

I = passed current (A).

$$h = \frac{C}{96500} \quad (4)$$

Where: - h = faraday's No.

$$g = h \times N \quad (5)$$

While the current efficiency was determined by the formula:-

$$\eta = p/g \quad (6)$$

Where

η = current efficiency.

P = practical deposited mass.

g = theoretical deposited mass.

The deposited powder was characterized for some properties. The particle shape of deposited powder was examined by optical microscope. While its, surface area and particle size distribution was tested by using [laser analyzer [22]. Apparent density was measured according to the following formula [1]:-

$$P_p = \frac{W_2 - W_1}{W_p} \quad (7)$$

Where

W<sub>1</sub> = weight of empty flask (g).

W<sub>2</sub> = weight of filled flask (g).

V<sub>p</sub> = volume of powder (cm<sup>3</sup>).

P<sub>p</sub> = Apparent density (g/ cm<sup>3</sup>).

Identify such characteristics, will be useful to evaluate the stage of powder compaction and sintering.

The fineness of powder was measured according to powder that passed through

sieve (<53), and its percent determined as follows:-

$$\% \text{Powder fineness} = \frac{\text{Amount of passed powder through sieve (< 53}\mu\text{m),}}{\text{total amount of deposited powder}}$$

### **3. Results and discussion:-**

#### **3. 1. Effect of Voltage:-**

Effect of voltage on fineness and producebility of copper powder, have been studied at arrange of (0.4 – 1) volt, as shown in fig. (1a & b).

Higher percent of particles size of (< 53 $\mu$ m) was 70% at total voltage of (1.6) V, and maximum deposition of (18) g. As total voltage increase the percent of fine particle decrease, this related to the increase of electrochemical voltage, makes the electrolyte saturated with ions which cause the increase in the rate of passed current i.e. the separation of copper ions will be stronger enough to hit each other, so particles will tend to agglomerate and their size will increase [11, 12, 13].

For the same reason i.e. as voltage increase the reducibility increase because of high pass of current, and it will reach maximum amount at total voltage (4V), i.e. (69)gm with 17% of fine particles of (< 53 $\mu$ m).

#### **3. 2. Effect of temperature:-**

The effect of temperature on fineness and producebility of deposited copper powder by electrodeposition, have been studied at a range of (20 – 50) °C, as shown in fig. (2a & b).

Higher percent of fine particles size of (< 53 $\mu$ m) was 73% at a temperature of (30)°C, with maximum deposition of (20) g. Then the mechanism of electrolyte conductivity depends basically on the exsistance of ions in the solution, and through the laws of electrolyte dissociation it is found that an increase in electrolyte solution temperature, will tend the electrolyte to dissociate into ions, which in turn, will increase the total amount of electrical carriers, that provide higher conductivity, so that fine copper particles will obtained as temperature raise from (20)°C to (30) °C. As temperature raise higher than (30) °C, particle size increase, this is due to higher chemical and higher conductivity of electrolyte cell, which results in

higher current rate because of highly immigration of cell ions that resulted from electrolyte dissociation that leads to impment of ions and fine particles, causing agglomeration and increase the particle size [2, 12, 14, 15].

While the amount of deposited copper powder increase as temperature increase up to (50) °C, i.e. (26) gm with 20% of fine particles of ( $-53\mu\text{m}$ ). This is due to higher current rate passing through the cell.

### **3. 3. Effect of Copper Sulfate Concentration:-**

The effect of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) concentration, have been studied at a range of (25 – 100) g/L on the fineness and producebility of copper powder deposition. As shown in fig. (3a & b).

The highest percent of fine particle size of ( $< 53\mu\text{m}$ ) was 83% at a concentration of (25) g/L, with a maximum deposition of (165) g. As the addition amount of copper sulfate increase the particle size of deposited copper powder on cathode increase. This related to the increase in copper sulfate concentration which represents the main constituent of electrolyte. The exist of much

copper ions in the solution will increase the impact between these ions which in return cause agglomeration of deposited particles of copper powder on cathode, so the particle size will increase [2, 12, 15].

While the amount of deposited powder will increase as the concentration of copper sulfate increase, and reaches its maximum amount (26) g at a concentration of (100) g/L of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . with a fine particle size of ( $< 53\mu\text{m}$ ) of 5% only.

This is due to the an increase in  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration, which will increase the conductivity. Thus, the pass current through the cell will increase, raising the amount of deposited copper powder.

### **3. 4. Effect of Sulfuric Acid Concentration:-**

The effect of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) concentration have been studied at a range of (80 – 180) g/L on the fineness and producebility of copper powder deposition as shown in fig.(4a & b).

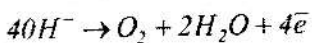
As the ( $\text{H}_2\text{SO}_4$ ) concentration increase the amount of fine particles increase until it reaches a maximum percent of 84% of ( $< 53\mu\text{m}$ ) with a maximum



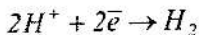
deposition of (16)g at a concentration of  $H_2SO_4$  of (150)g/L. then as the concentration increase the percent of fineness decrease.

The  $H_2SO_4$  added to decrease the ohmic resistance an improve the electrolyte electrical conductivity [3, 13].

As  $H_2SO_4$  concentration increase after 150 g/ L, hydrogen ions in the solution will increase causing the collision between ions, which force the particle to agglomerate, that result is an increase in particle size of deposited powder. While the amount of copper powder deposition increase as the  $H_2SO_4$  concentration increase and reaches a maximum amount of (21.5) g at (180) gm/L of  $H_2SO_4$  with a fine particle size of ( $< 53\mu m$ ) of 56%. It is found that electrical deposition depends on (pH) of electrolyte solution. When (pH) is high we have the following reaction:-



while at low (pH) we have the following reaction:-



the cathode reactions for hydrogen ions affect the electro deposition, where the release of hydrogen with a mean velocity require an amount of cathode reaction, so that the needed reactivity for deposition in t6he case of hydrogen ions exist, require a higher polarization, than in the case of hydrogen ions absence, so that the fineness of deposited copper powder increase until we reach the concentration of  $H_2SO_4$  of 150 g/ L [9].

### 3. 5. Effect of Circulation Velocity:-

The effect of circulation velocity on fineness and producebility of deposited copper powder have been studied at a range of (150 – 450) rpm as shown in fig.(5a & b).

It's found, that as circulation velocity increase the particle size of deposited copper powder decrease, and the best percent of fine particles was 57% of ( $< 53\mu m$ ) at a velocity of (150) rpm, with a maximum deposition of (21)g.

Electrolyte circulation will increase the rate of anodic dissolution and electrochemical effect, i.e. remove the ions that cause polarization which leads to the increase in the rate of electrochemical deposition.

As the circulation velocity increase, ions shoot will be stronger because of the fastening of chemical reactions, which leads to particles collision and their agglomeration, so the particle size will increase.

Since the chemical reactions fasten at higher velocities, associated with an increase in the rate of passed current through the cell, so the deposited amount of copper powder, will increase, and reaches a maximum amount of (24)g at a velocity of (450) rpm with (28.5 %) fine particles of (< 53µm).

**Table (2). Results concluded by bipolar and Betts methods.**

RESULTS OF COMPARISON	BIPOLAR	BETTS
Amount of deposited copper powder (gm)	23	88
Fineness % of (-53µm)	24	86

Table (2) explains that results almost equal, but we can recommend bipolar connection method, because of low cost i.e. no busbars are used, less junction points will reduce current losses and total resistance of the cell, which enhance the energy save. Also at the case of short circuit cuts the cell still working [2, 3, 18, 19].

### **3. 6. Effect of Connection**

#### **Method:-**

Comparison between bipolar Method series connection and Betts method (parallel connection) and their effect on fineness and producebility of deposited copper powder have been studied depending on the optimum conditions concluded from the latest variables. i.e. (1.6V, 30°C, 25g/L of CuSO<sub>4</sub>.5H<sub>2</sub>O, 150g/L of H<sub>2</sub>SO<sub>4</sub> and 150rpm) and as shown in table (2).

### **3. 7. Effect Lanoline**

#### **Addition:-**

the effect of lanoline (C<sub>30</sub>H<sub>50</sub>O) addition on fineness and producebility of deposited copper powder have been studied at a range of (0.035 - 0.1)% as show in fig.(6a & b).

The experiments were done depending on the optimal conditions that concluded from the study of latest variables. i.e. (1.6V, 30°C, 25g/L of CuSO<sub>4</sub>.5H<sub>2</sub>O, 150g/L of H<sub>2</sub>SO<sub>4</sub>



and circulation velocity of 150rpm).

It was found that as lanoline addition increase, the fineness of deposited copper powder increase, and reaches 94% of particle size ( $< 53\mu\text{m}$ ) with a maximum deposition of copper powder of (21)g at (0.075%) of lanoline addition. Then further increase in lanoline addition will increase the particle size of deposited powder.

This related to, that an addition of lanoline will increase the number of clustering centers that will enhance the formation of fine deposited particles, but at higher amount of lanoline addition will produce much fine particles (high surface area), so, the chance of collision between particles will increase, resulting in their agglomeration, associated by an increase in particles size of deposited copper powder [20, 21].

The addition of (0.035%) of lanoline will provide higher amount of deposited copper, i.e. (26)g with 91% fine particles of ( $< 53\mu\text{m}$ ). But further increase in

lanoline addition will decrease the amount of deposited copper powder.

### **3. 8. Physical Evaluation of Electrodeposited Copper Powder:-**

#### **3. 8. 1. Particle Shape:-**

Optical microscope results in fig.(7a & b), shows a dendritic particle shape of copper powder. This may related to that hydrogen may discharged at the cathode, form bubbles or dissolve in the metal and diffuse through it, which makes the composed powder layer brittle and irregular [1, 22].

#### **3. 8. 2. Particles Size Distribution and Surface Area:-**

laser analyzer system results, in table (3) shows particle size distribution of copper powder, at which (80%) of particles were smaller than ( $20.65\mu\text{m}$ ), i.e. the precipitated powder was fine, and this could be attributed to the addition of (lanoline), that increase the nucleus for crystallization, which results in fine copper powder particles.

**Table (3).explain the particles size distribution of deposited copper powder at an optimum condition.**

Fixed Percentage (%)	Volumes (under size) ( $\mu\text{m}$ )
20	< 9.30
40	< 12.54
60	< 16.2
80	< 20.65
100	< 47.68

The surface area recorded by laser analyzer was  $(3.47)\text{m}^2/\text{g}$ . That's related to the fine powder and its dintritic shape.

**3. 8. 3. Apparent Porosity:-**

The measured apparent porosity of copper powder was  $(1.57)\text{g}/\text{cm}^3$ , this result is coincide with the standard range of powders produced by electrodeposition i.e.  $(0.5 - 4)\text{g}/\text{cm}^3$ . This may related to the small size of copper powder and because of irregular shape i.e. (dendritic).

**4. Conclusion:-**

1. Higher percent of fine deposited copper powder of ( $< 53\mu\text{m}$ ) are produced at (total voltage 1.6V,  $30^\circ\text{C}$ ,  $25\text{g}/\text{L}$  of  $\text{CuSO}_4.5\text{H}_2\text{O}$ ,  $150\text{g}/\text{L}$  of  $\text{H}_2\text{SO}_4$  and circulation velocity of  $150\text{rpm}$ ).
2. Higher amount of deposited copper powder was

produced at (total voltage 4V,  $50^\circ\text{C}$ ,  $100\text{g}/\text{L}$  of  $\text{CuSO}_4.5\text{H}_2\text{O}$ ,  $180\text{g}/\text{L}$  of  $\text{H}_2\text{SO}_4$  and circulation velocity of  $450\text{rpm}$ ).

3. Addition of 0.075% of lanoline increases the particles fineness while 0.035% of lanoline will increase the producebility.
4. Variation of connection method i.e. (bipolar and Betts) has no obvious effect on the fineness and producebility of deposited copper powder.
5. Chemical analysis shows that purity of deposited copper powder had increased from 96% to 99.5%.
6. Physical observations shows, that 80% of deposited copper powders are smaller than  $(20.65\mu\text{m})$ , also the deposited powder particles are of dintritic shape.

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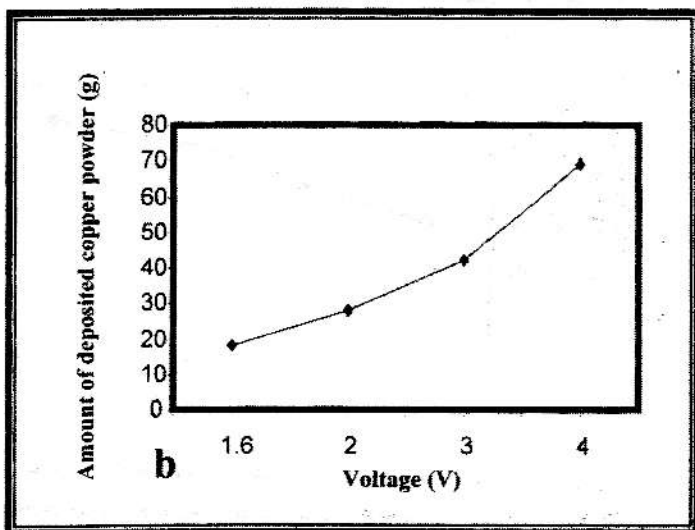
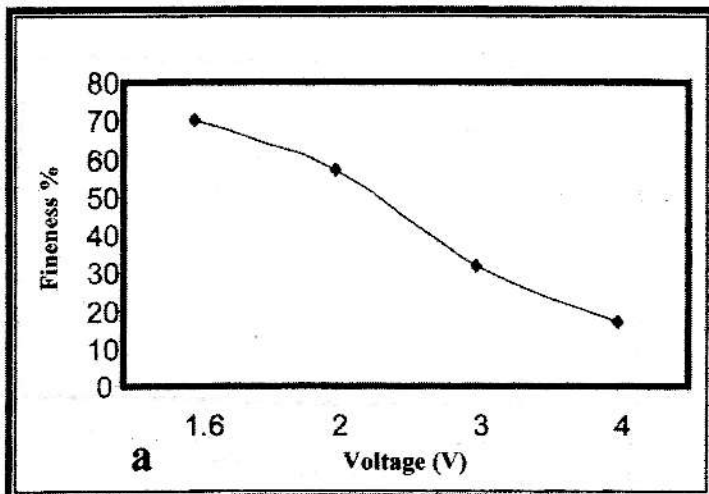
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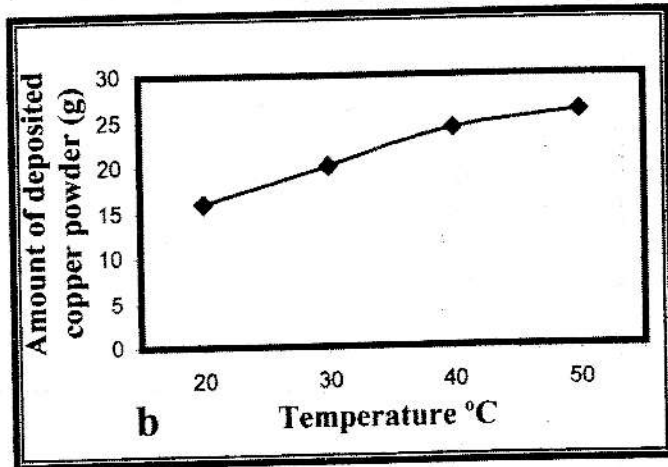
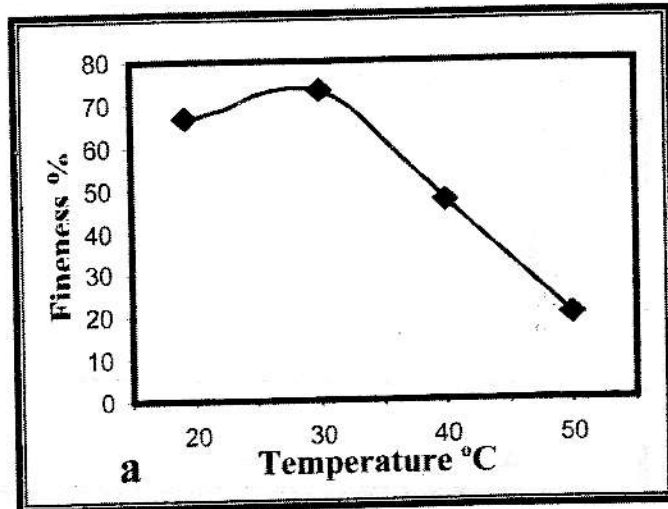
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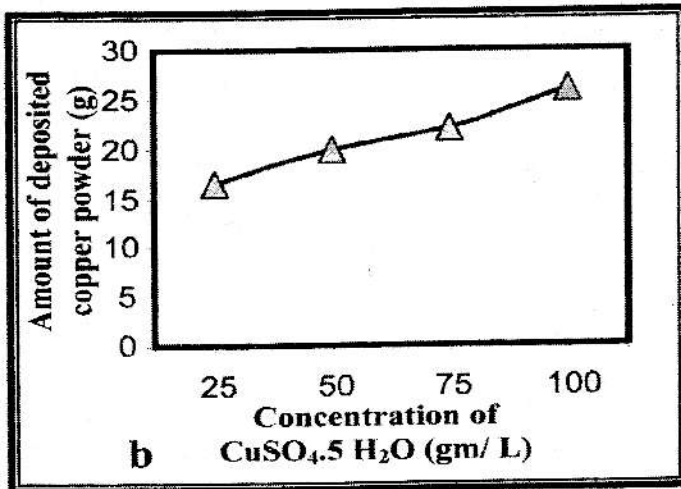
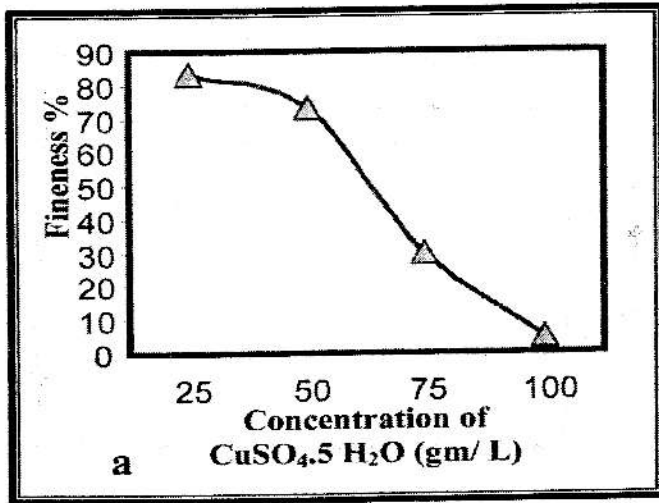


**Fig. (1). Effect of voltage on a) fineness and b) producebility of deposited copper powder.**



**Fig. (2). Effect of temperature on a) fineness and b) producebility of deposited copper powder.**





**Fig. (3).** Effect of copper sulfate concentration on a) fineness and b) producebility of deposited copper powder.

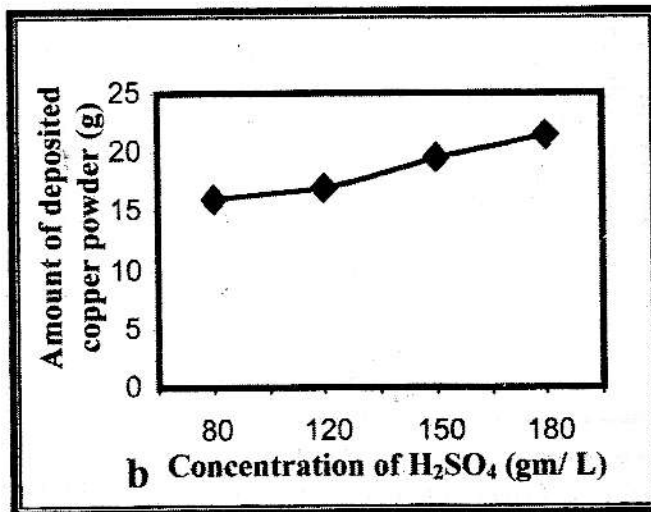
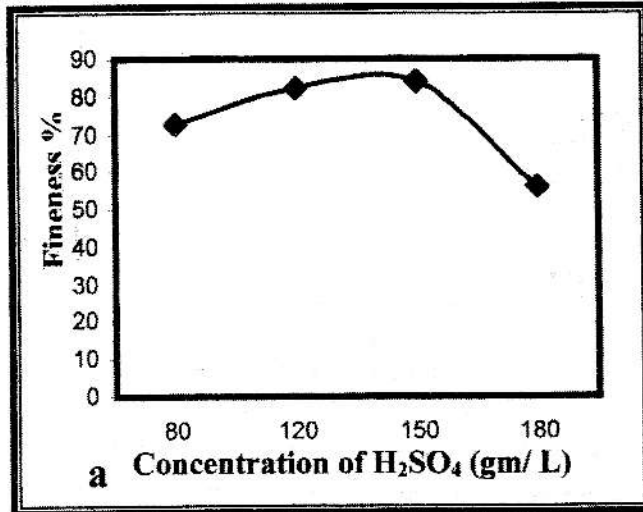
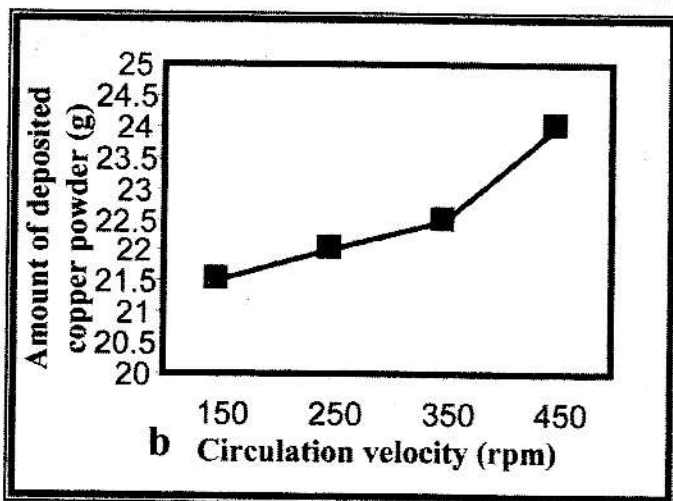
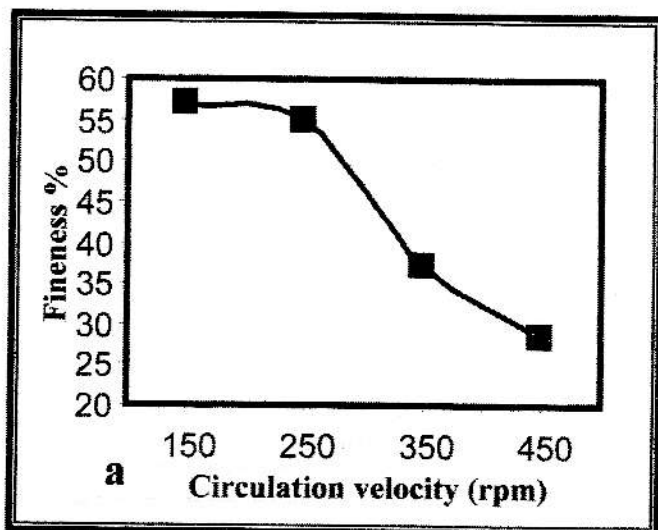


Fig. (4). Effect of sulfuric acid concentration on a) fineness and b) producebility of deposited copper powder.



**Fig. (5). Effect of circulation velocity on a) fineness and b) producebility of deposited copper powder.**

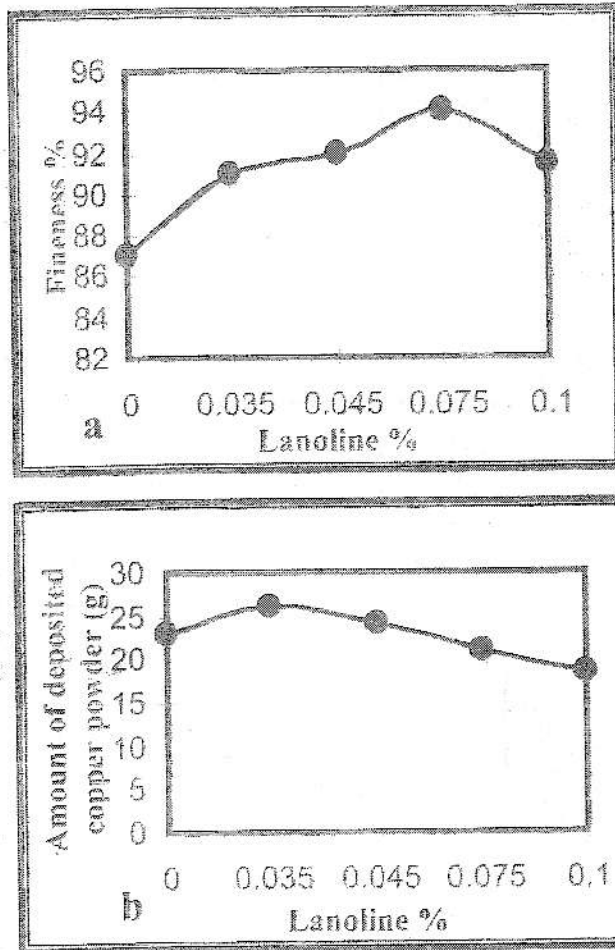
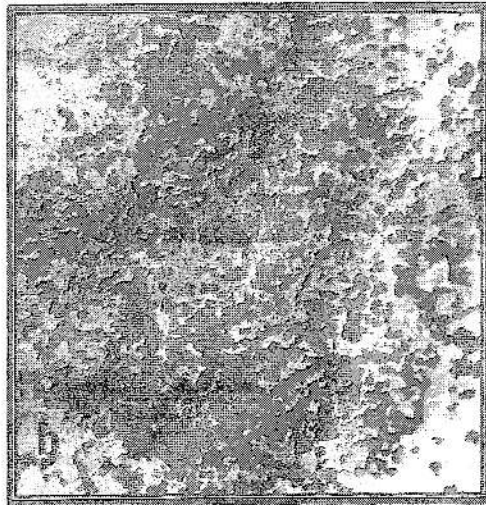
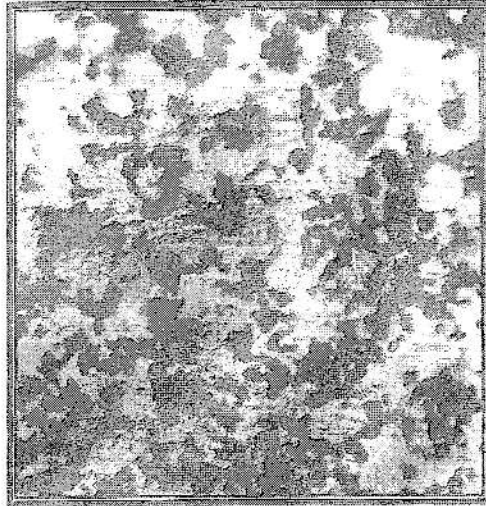


Fig. (6). Effect of lanoline addition on a) fineness and b) produceability of deposited copper powder.



**Fig. (7).** Shows the shape of deposited copper powder  
a. Before lanoline addition,  
b. After lanoline addition.