

1. Introduction:

Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode.

The process used in electroplating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity.

A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode.

The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.[1]

Copper element:

Copper is a chemical element with the symbol Cu (from Latin: cuprum) and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish-orange color.

It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys.

The metal and its alloys have been used for thousands of years. In the Roman era, copper was principally mined on Cyprus, hence the origin of the name of the metal as cyprium (metal of Cyprus), later shortened to cuprum.

Its compounds are commonly encountered as Copper(II) salts, which often impart blue or green colors to minerals such as azurite and turquoise and have been widely used historically as pigments.

Architectural structures built with copper corrode to give green verdigris (or patina). Decorative art prominently features copper, both by itself and as part of pigments.

Copper is essential to all living organisms as a trace dietary mineral because it is a key constituent of the respiratory enzyme complex cytochrome c oxidase. In mollusks and crustacean copper is a constituent of the blood pigment hemocyanin, which is replaced by the iron-complexed hemoglobin in fish and other vertebrates. The main areas where copper is found in humans are liver, muscle and bone.[2] Copper compounds are used as bacteriostatic substances, fungicides, and wood preservatives.

Copper does not react with water but it does slowly react with atmospheric oxygen to form a layer of brown-black copper oxide which, unlike the rust which forms when iron is exposed to moist air, protects the underlying copper from more extensive corrosion.

There are 29 isotopes of copper. ^{63}Cu and ^{65}Cu are stable, with ^{63}Cu comprising approximately 69% of naturally occurring copper; they both

have a spin of $3/2$. [4] Copper is synthesized in massive stars [5] and is present in the Earth's crust at a concentration of about 50 parts per million (ppm), [6] where it occurs as native copper or in minerals such as the copper sulfides chalcopyrite and chalcocite, the copper carbonates azurite and malachite, and the copper(I) oxide mineral cuprite. [3]

Copper physical properties:

-Melting point: 1357.77 [or 1084.62 °C (1984.32 °F)] K.

-Boiling point: 3200 [or 2927 °C (5301 °F)] K.

-Density of solid: 8920 kg m⁻³

Atomic properties:

-Oxidation states +1, +2, +3, +4 (a mildly basic oxide).

-Electronegativity 1.90 (Pauling scale).

-Ionization energies 1st: 745.5 KJ.mol⁻¹

2nd: 1957.9 KJ.mol⁻¹.

3rd: 3555 KJ.mol⁻¹.

-Atomic radius empirical: 128 pm.

-Covalent radius 132±4 pm.

-Van der Waals radius 140 pm

Copper Electro Plating:

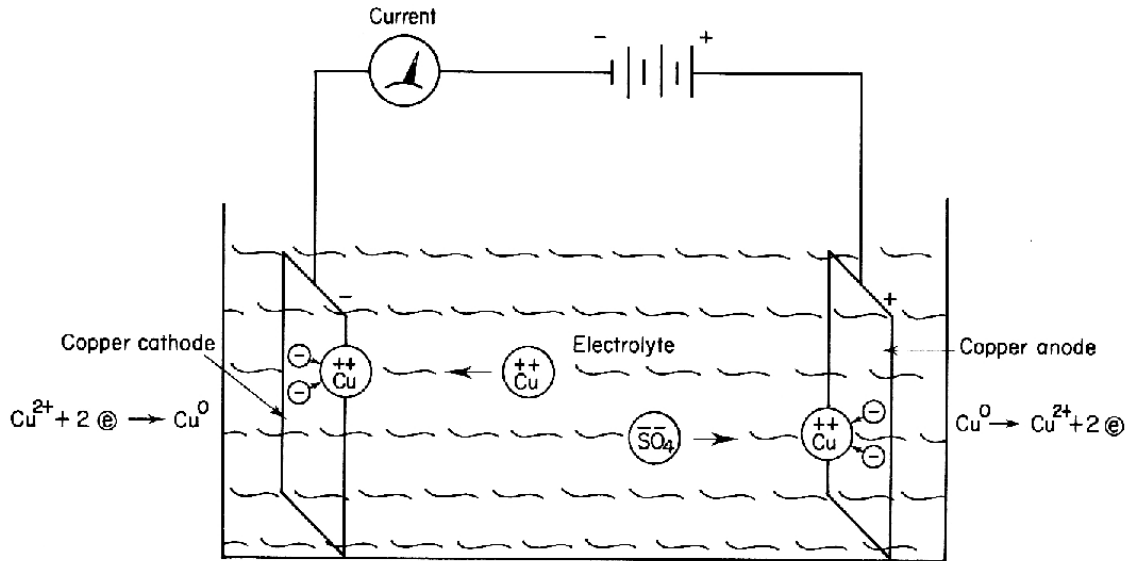
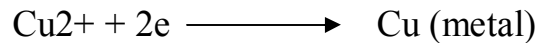
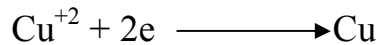


Figure (1.1) shows a simple electroplating system for the deposition of copper from copper sulphate solution

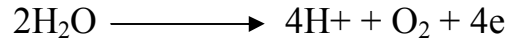
The electrolytic solution contains positively charged copper ions (cations) and negatively charged sulphate ions (anions). Under the applied external electric field, the cations migrate to the cathode where they are discharged and deposited as metallic copper.



Copper from the anode dissolves into the solution to maintain the electrical neutrality.



The overall process is known as electrolysis. If some noble metal (such as platinum) is used as the anode, the overall reaction at the anode is the oxidation of water.



The sulphate ions remain unchanged in quantity during the electrolysis. However, if noble metal is used as the anode, the concentration of Cu^{2+} ions will decrease and that of H^+ ions will increase with time. Under this situation, extra copper sulphate must be added into the solution from time to time and the hydrogen ions must be removed by neutralization with an alkali or by using a buffering solution.

In practical electrodeposition processes, the chemical reaction around the electrode area occurs in a more complicated way than that shown in Figure 1. Under the influence of an Figure (1.1) applied potential, rearrangement of ions near the electrode surface results in an electrical double layer called the Helmholtz double layer, followed by the formation of a diffusion layer as shown in Figure (1.2).

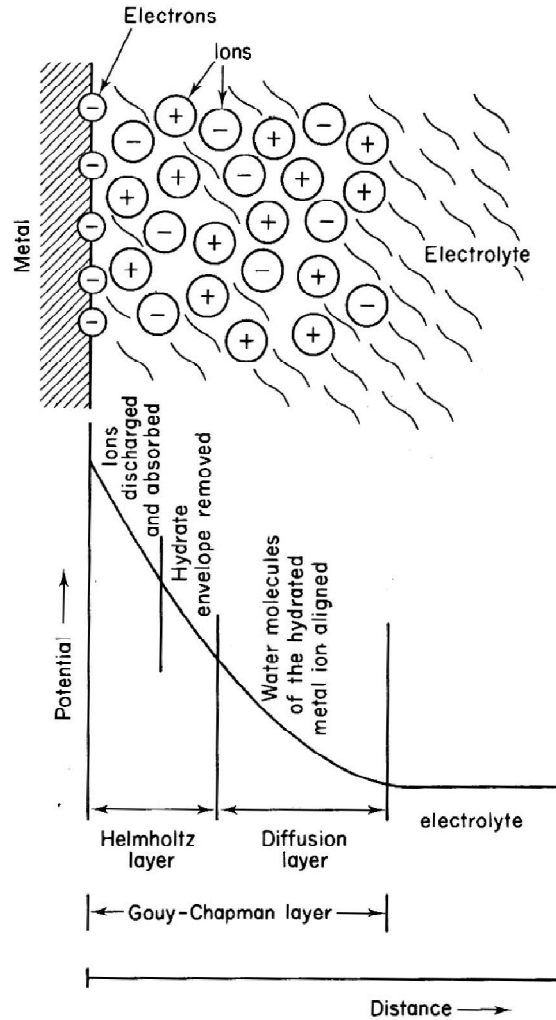


Figure (1.2). Electrical double layer

These two layers are referred as the Gouy-Chapman layer. The process is as

Follows:

- **Migration:**

The hydrated metal ions in the solution migrate towards the cathode under the influence of impressed current as well as by diffusion and convection.

- **Electron transfer:**

At the cathode surface, a hydrated metal ion enters the diffused double layer where the water molecules of the hydrated ion are aligned. Then the metal ion enters the Helmholtz double layer where it is deprived of its hydrate envelope.

- The dehydrated ion is neutralized and adsorbed on the cathode surface.
- The adsorbed atom then migrates or diffuses to the growth point on the cathode surface.

Thickness of the electroplated layer on the substrate is determined by the time duration of the plating. In other words, the longer the time the object remains in the operating plating bath, the thicker the resulting electroplated layer will be. Typically, layer thicknesses may vary from 0.1 to 30 microns. An electroplated layer is usually composed of a single metallic element.

Co-deposition of two or more metals is possible under suitable conditions of potential and polarization, such as a Cu-Zn alloy or a Au-Sn alloy.

Properties of deposited film:

ADHESION:

As one of the most important requirements, adhesion is mostly dependent upon the substrate. For proper adhesion, the substrate must be thoroughly cleaned and free of any surface films. It is desirable that the substrate and the deposited metal interdiffuse with interlocking grains to give a continuous interfacial region. Alloy formation by the interdiffusion of

the substrate and the deposited metals provides good adhesion. However, an intermetallic compound is undesirable since it behaves like inorganic salts and results in poor adhesion.

MECHANICAL PROPERTIES:

Mechanical properties of the electrodeposited film depend to a considerable extent on the types and amounts of growth-inhibiting substance at the cathode surfaces. The purpose of using a growth-inhibiting substance is to obtain fine-grain structure of the deposited film, in which the grain boundaries act as the main obstacles to dislocation motion, leading to a higher yield strength and hard surface. Hardness of the deposited film can also be increased by introducing lattice strain through incorporating impurities into the film-growth process.

Electroplating processes frequently result in the development of internal stresses. The reasons for internal stresses relate to coalescence of three-dimensional, epitaxial crystallites, dislocation configurations, hydrogen incorporated into the crystal lattice, or other factors.

Tensile stress is more detrimental than compressive stresses since it easily causes cracks of the deposited film, reducing the fracture strength and ductility. Certain addition agents for some electroplating solutions have been developed to reduce tensile stress.

BRIGHTNESS:

Brightness of deposited film is critical for decoration applications. The brightness of thin deposited films depends on the surface finish of the substrate. Thicker bright deposited films are produced by additional agents in the plating solution which result in elimination of protrusions or crevices which deviate from the surface plane by about the wavelength of visible light. The addition agents are mostly organic compounds such as dextrose, saccharine, lactose, formalin, citrates, tartrates, etc. However, most good brighteners are sulphur compounds, especially thiourea and its derivatives and organic sulphonic acids. Brightening agents are foreign inclusions in the deposited film.

Overdosage of these additives can cause brittleness and lead to cracks and peeling off of the deposited film from the substrate.[#]

1.2 The Earlier Studies:

"**Acid Copper**" deposition was referred to as early as 1810 [7]. In 1831 Bessemer [8] copper plated steel casting of frogs, insect, and tray. In 1836 the Daniell cell was first used for electrodepositing copper [9] and technical report was published by De La Rue [10]. In 1843 Jacobi made Russian bank notes using copper-plated electrotypes, and in 1840 he received the first patent for making electrotypes [11]. Smee discussed commercial copper plating processes in 1843 [7]. During the next 70 years progress was directed principally toward developing specific application for acid copper electrodeposition. Most of the efforts dealt with Cu^{2+} sulfate-sulfuric acid solution, but oxalate, nitrate, acetate, flu silicate, and Cu^{1+} chloride solutions were also investigated.

Before 1915 "**copper cyanide**" solution were invariably prepared by dissolving copper carbonate in alkali cyanide. The use of tartrates is mentioned in early references [12, 13], but their value apparently was not fully recognized. An exception was the combination cleaning and plating solution described by Watts [14] in 1915. Deposits from these early solutions were relatively thin and were used largely as bases for oxidized and other decorative types of finishes. The first commercially successful high-efficiency solution was introduced in 1938. It was used extensively throughout the automotive industry in subsequent years for plating zinc die castings as well as steel parts. Alkali thiocyanate was used by Wernlund [15] in 1941 to brighten the deposits.

"Alkaline non-cyanide copper"plating solution have found increasing popularity since the mid-1980, because of environmental issues The cost of using and disposing of cyanides and associated environmental concerns have led to efforts to replace cyanides. Besides the obvious plus of elimination of cyanide from the waste water stream, these new solution are safe to work with and easily waste treated with lime in the same treatment process used for nickel, acid Copper, and acids [16].

J.C.Ballesteros, E. Chainet, P. Ozil, Y. Meas and G. Trejo were studied "Electrodeposition of copper from non-Cyanide Alkaline solution containing tartrate". A thermodynamic study of the aqueous Copper(II)-tartrate-chloride system is presented in this work with the view to better understand the electrodeposition of copper from a non-cyanide alkaline solution additionally, an electrochemical study onto the initial stages of copper electrodeposition on glassy carbon electrode (GCE) is presented in this work. Upon scanning in the negative direction, two cathodic peaks were observed, which are associated with two reduction processes with different energies that involve the same species of Copper(II). Analysis of chronoamperograms obtained indicates that the nucleation mechanism involved during the initial stage of Cu deposition is consistent with the model 3D diffusion-controlled nucleation.

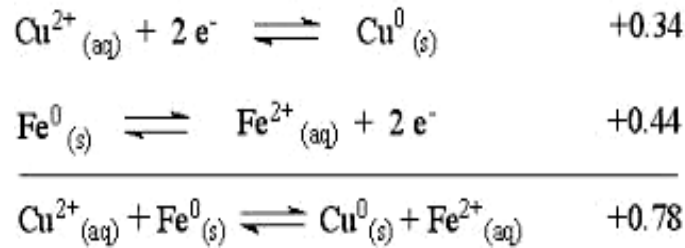
The earliest published reference to **"Copper pyrophosphate"** deposition was by Roseleur in 1847 [17]. In 1883 Gutensohn [18] was granted a patent for copper pyrophosphate plating on a number of substrate. Others associated with the early state of the art included Brand [19], Delval [20]

.....pioneering work by Stareck [21, 22] led to the development of commercial copper pyrophosphate in 1941.

DarkoGrujicic, BatricPesic [23*] Studied "**The reaction and nucleation mechanisms of copper electrodeposition from ammonical solution on vitreous carbon**". The reaction and nunleation mechanisms of the electrodeposition of copper from ammoniacal solution were investigated by cyclic voltammetric (CV) and chronoamperometric(Ca) techniques, respectively. Each experiment with both electrochemical techniques was followed by morpholgical studies by atomic force microscopy (AFM). With respect to PH,the studies were performed on ammoniacal solution at PH 4, PH 6, and PH 8, each representing acharacteristicpredominance region in E-PH diagrams. The experimental parameters were copper concentration, scanning rate, deposition potential, and electrode conditioning.

1.3 Aimof the Research:

Is to electroplating iron with Copper deposit.



1.4 Copper Plating Uses:

Electroplating is widely used in various industries for coating metal objects with a thin layer of a different metal. The layer of metal deposited has some desired property, which the metal of the object lacks.

Copper plating are a protection to the iron surface from corrosion-resistant, are one part of the sequence for decoration plating of aluminum and iron wheels for automotive application, electroformed copper articles include band instrument heat exchangers reflectors and avidity of articles from military and aerospace application.

Electroplating has wide usage in industries. It is also used in making inexpensive jewelry. Electroplating increases life of metal and prevents corrosion.

1.4.1 Other uses of Copper:

Copper compounds in liquid form are used as a wood preservative, particularly in treating original portion of structures during restoration of damage due to dry rot. Together with zinc, copper wires may be placed over non-conductive roofing materials to discourage the growth of moss.[citation needed] Textile fibers use copper to create antimicrobial protective fabrics,[24][25] as do ceramic glazes, stained glass and musical instruments. Electroplating commonly uses copper as a base for other metals such as nickel.

Copper is one of three metals, along with lead and silver, used in a museum materials testing procedure called the Oddly test. In this procedure, copper is used to detect chlorides, oxides, and sulfur compounds.

Copper is used as the printing plate in etching, engraving and other forms of intaglio (printmaking) printmaking.

Copper oxide and carbonate is used in glassmaking and in ceramic glazes to impart green and brown colors.

Copper is the principal alloying metal in some sterling silver and gold alloys. It may also be used on its own, or as a constituent of brass, bronze, gilding metal and many other base metal alloys.

Experimental

For this Iron Electroplating with copper on Different Electroplating conduction were studied like the concentration of copper, current, Temperature, time and PH. To investigate the relation between the wight, density of copper electrodeposition.

2.1 Material

2.1.1 Chemical:

-Copper sulphate.

-Sulfuric Acid (concentration).

-Distilled water.

-Sodium hydroxide.

(All the chemical used in this research were analytical grade type).

2.1.2 Apparatuses:

-Power supply.(Low voltage power supply AC/DC 2Amps.)

-Ammeter.

-PH meter (HANA. Pocket size)

-Sensitive Balance.

-(Volumetric Flask 50 cm³- glass road- glass)

1.1.3 Samples:

Were obtained from Sudanese local market, were prepared at the Black Smith by cutting and shaping as a substance (plate) of iron. The sizes were (2× 2 cm) and the thicknesses were (0.05 cm).

1.1.4 Electroplating Copper's Cell:

The cell was connected by insuring the electrode (Fe), and anode (Cu) author. Using restateammeter and power supply as electric current connected directly. The plating paths contain Cu SO⁴, distilled water and sulphuric acid.

2.2 Experimental Procedure:

The concentration of the ingredient on the plating bath and different operating conditions were shown on table (1).

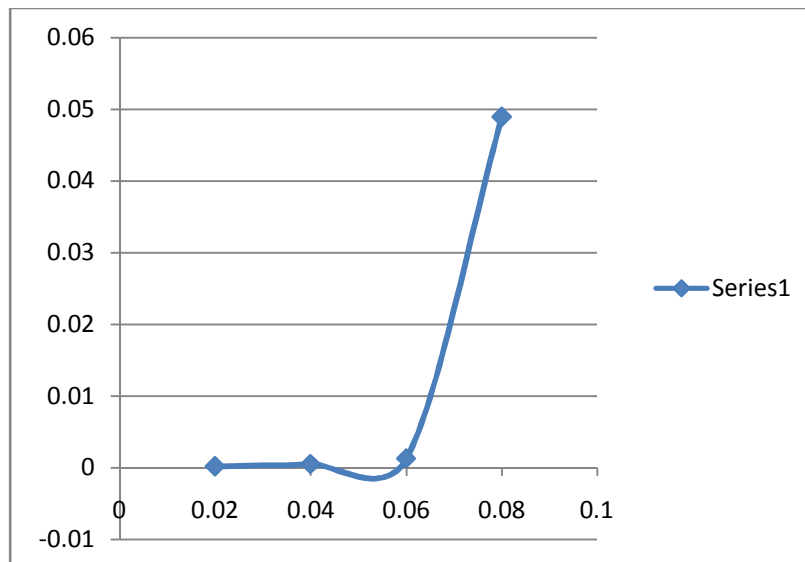
Cu So ₄	0.02-0.08 M
Sulphuric acid	Diluted
Current	0.1-0.6 ampere
PH	1-5
Time	10-60 min
Stirrer	150rpm

Results and Discussion

3.1 Effect of copper concentration on the deposited layer: table (2):

Concentration \M	Wight of the deposit layer
0.02	0.0002
0.04	0.0005
0.06	0.0013
0.08	0.0489

Table (2) shows increase of the Wight of deposited layer on cathode (Fe) with the increase of CuSo4 concentration in the bath.

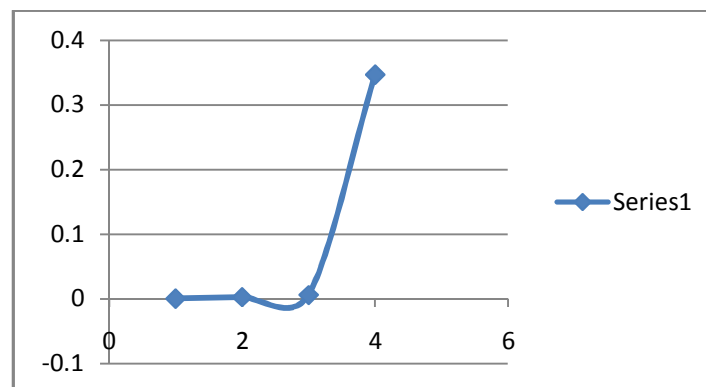
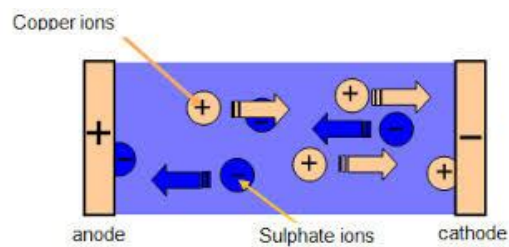


3.2 Effect of (PH) on the deposited layer: table (3):

PH	Wight of the deposit layer
1	0.0002
2	0.0024
3	0.00575
4	0.3465

Changes in sulphuric acid concentration have more influence than changes in CuSo₄ concentration on anode (Cu), cathode (Fe), and solution conductivity.

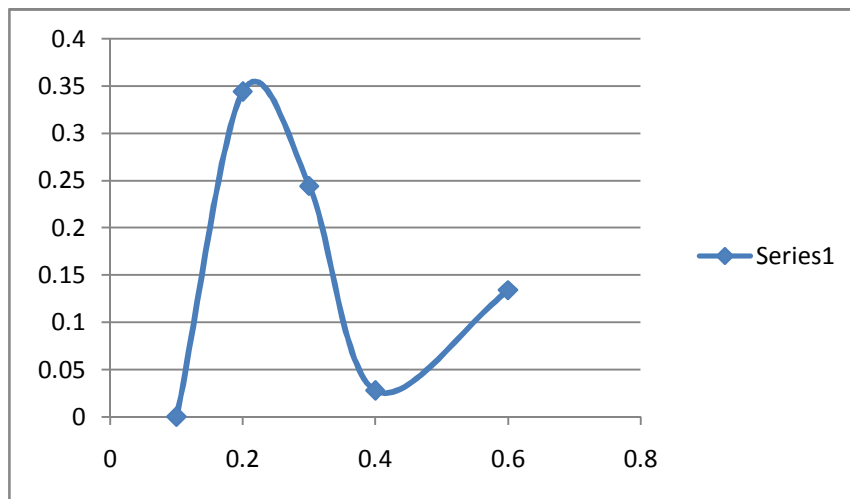
Table (3) shows increase of deposit layer Wight when reaches PH= 4, and decrease with a further increase in sulphuric acid PH=1.



3.3 Effect of current (I) on the deposited layer: Table (4):

Current/A/cm ²	Wight of the deposit layer
0.1	0.0002
0.2	0.344
0.3	0.244
0.4	0.0279
0.6	0.1339

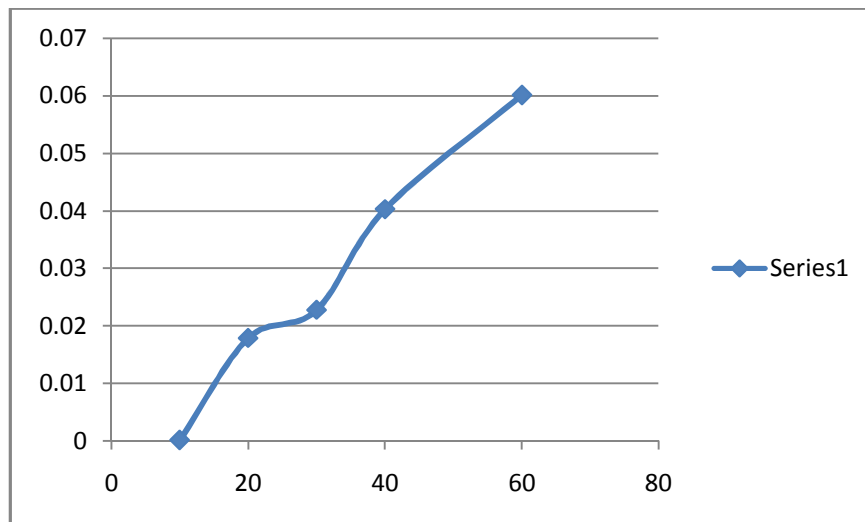
Table (4), shows increase in current (I) result (Wight of the deposit layer) are decreased when reach I=0.1, and increased again in I=0.6 A/cm².



3.4 Effect of the time (min) on the deposited layer: Table (5):

time \min	Wight of the deposit layer
10	0.0002
20	0.0179
30	0.0228
40	0.0403
60	0.0601

Table (5), shows increase in the Wight of deposited layer with the increase of time (min).



This study built on FARADAY'S law:

(The mass of a substance altered at an electrode during electrolysis is directly proportional of the quantity transferred at the electrode. Quantity of the electrical change typically measured in "coulomb".

$$m = (Q/F) (M/z).$$

Where:

m is the mass of the substance liberated at an electrode in grams

Q is the total electric charge passed through the substance

F = 96485 C mol⁻¹ is the Faraday constant

M is the molar mass of the substance

z is the valency number of ions of the substance (electrons transferred per ion).

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