CHAPTER I
INTRODUCTION

1.1 Background

Electrodeposition of coating metals such as chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), and others are widely used in industry in terms of performance improvement. The metal plating industry will produce waste containing heavy metals such as chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb), which, if not properly managed, can cause environmental pollution (Rajoria et al., 2021). High levels of heavy metals in water can be toxic materials that harm aquatic organisms (Yan et al., 2022). The plating of the above metals is generally carried out in electroplating bath. Retrieval of these metals from the rest of the electroplating bath solution needs to be done in order to reduce the adverse effects on the environment.

Disposal of metal plating industrial waste without prior processing will negatively impact environmental components, thereby reducing their quality. According to Government Regulation of the Republic of Indonesia Number 18 of 1999 concerning the Management of Hazardous and Toxic Waste, heavy metal waste discharged into the environment must not exceed the stipulated threshold. Deposition is one of the most widely used methods for treating waste, as it separates heavy metals from liquid waste. However, heavy metals are often difficult to precipitate, so they must be reduced first to achieve high efficiency. The mechanism mainly refers to oxidation and reduction at the anode and cathode, respectively, when a current is introduced to the electrodes. Heavy metal ions in the electrolyte will be reduced to their elemental forms and will be deposited on the surface of the cathode due to the chemical reaction. This mechanism offers several advantages in that no chemical reagent is required and it has a low operating cost (Babilas et al., 2024).

Research on the reduction of heavy metals in metal plating industrial waste and their deposition process through the electrolysis process needs to be learned by Chemical Engineering students. It is also necessary to understand the kinetics of the reduction and deposition of heavy metals so that the performance of the process and how to improve its works is known. In order for the reduction and deposition to run perfectly, an excess concentration of reducing agent is required.

1.2 Objectives

1. Studying the effect of contact time on the electroplating performance.
2. Studying the effect of electric current on the electroplating performance.
3. Studying the effect of solution concentration on the electroplating performance.
4. Studying the effect of solution concentration on the electroplating constant rate.

1.3 Benefits

1. Students are able to understand the process of reduction and precipitation of Cu^{2+} contained in a copper sulphate ($CuSO_4$) solution by electrochemistry or electrolysis.
2. Students are able to understand the kinetics of reduction and precipitation of Cu^{2+} in a copper sulphate ($CuSO_4$) solution electrochemically.

CHAPTER II
LITERATURE REVIEW

2.1 Basic Concepts of Electrochemical Reaction

The study of the relationship between chemical reactions and the electric current by applying the principles of redox reactions is called electrochemistry. Electrochemical cells that convert chemical energy into electrical energy, where redox reactions take place spontaneously are called voltaic cell or galvanic cell. In contrast, electrochemical cells where non-spontaneous redox reactions occur so that they use an electrical energy source to change chemical reactions are called electrolytic cells (Marcus, 2022). The changes that occur in a chemical system due to electrolysis and redox reactions are discussed in electrochemical reactions.

Electrochemical reactions are very important in studying chemistry in daily activities. Through electrochemical reactions, information about chemical energy changes in the world can be obtained, which helps in analyzing chemical systems. Until now, electrochemistry still plays an important role in industry and households. The influence of electrochemical reactions in modern society can be found almost everywhere. In the field of chemical analysis, electrochemistry is applied to the process of electroanalysis, electrosynthesis, electrocoagulation, electrodialysis, electrowinning, electrorefining, and electroplating. Chemical products, such as $AlCl_3$ and $NaOH$ are also produced through electrochemical electrolysis processes. In addition, all small electrical energy sources (batteries) are obtained from reduction-oxidation electrochemical reactions.

Before understanding electrochemical systems, it is necessary to understand the process of electrical conduction. The process of electrical conduction differs between metals and chemical systems. Metals are conductors which capable of moving their electric charges (electrons) from one place to another if an electron is added or removed at one end. This metal conductor is called an electrode. The electrode connected to the positive terminal (+) is called the anode and the one connected to the negative terminal (-) is called the cathode (Parthasaradhy, 1989). The conduction of electricity due to the transfer of electrons is called metallic conductivity. Melted ionic compounds and solutions called electrolytes can also conduct electricity, although in this system there are no free electron that can move easily. Therefore, it is necessary to learn how this system can generate electricity by

testing the phenomena in solutions and electrodes in the arrangement of electrolysis equipment.

2.2 Reaction Mechanism of Electrolysis

The mechanism of electrolysis involves a complex interaction between ions in the electrolyte solution, the flow of electrons through an external circuit, and the redox reactions that occur at the electrode surfaces. The phenomena in the electrolyte solution and the electrodes within an electrolysis setup powered by direct current, can be explained as follows:

1) The cathode gets an electric charge e (-)
2) Due to the excess electric charge e (-), the cathode attracts ions (+) from the solution.
3) At the same time, the anode lacks electrons thereby attracting negative ions (-) form the solution.
4) Due to the presence of electricity, a chemical reaction (redox reaction) occurs at the electrode.
5) At the anode, the surrounding (-) ions release e- causing oxidation to become metal. Whenever oxidation occurs, the (-) ions are replaced by other (-) ions in the vicinity so that there is a flow of (-) ions from the solution to the anode.
6) The electrons released from the (-) ions flow to a DC current source and then forwarded to the cathode where there are (+) ions which then undergo reduction.
7) As a result of this reduction, other (+) ions present in the vicinity replace them, resulting in a flow of (+) ions from the solution to the (+) electrode.

So, if a redox reaction occurs, the electrons move through the circuit cable (DC current), and the ions move in the solution. The flow of ions in the solution is called electrolyte conduction. In electrolyte conduction, the instability that occurs due to ions migration and the difference in the number of (+) and (-) ions causes the solution to tend to maintain a neutral electrical charge through the flow of ions.

The chemical reactions that occur at the electrode as long as an electrolytic conduction present is called an electrolytic reaction. The place where electrolysis reaction occurs is called an electrolytic cell. An ideal electrolyte should have several properties, including high ionic conductivity over a wide temperature range, contain electrically charged particles,

environmental friendliness, low-cost, and easy to process (Yi *et al.*, 2024). In determining the reactions that occurs in electrolysis, there are several factors such as the type of electrode and the type of electrolyte solution. Based on its oxidizing properties, electrodes can be divided into two types, inert and non-inert electrode. Inert electrode is a conductive material that does not participate in the chemical reaction of an electrochemical cell. It serves as a surface for electron transfer without undergoing any redox reaction. Inert electrodes are used to conduct electrons in the electrolysis process without reacting with the solution or reactants involved in the process. Examples of inert electrodes include platinum, carbon, and gold, which are chosen for their non-reactive properties. Meanwhile, non-inert electrodes are electrodes that participate in the electrolysis reaction (Lestari *et al.*, 2022).
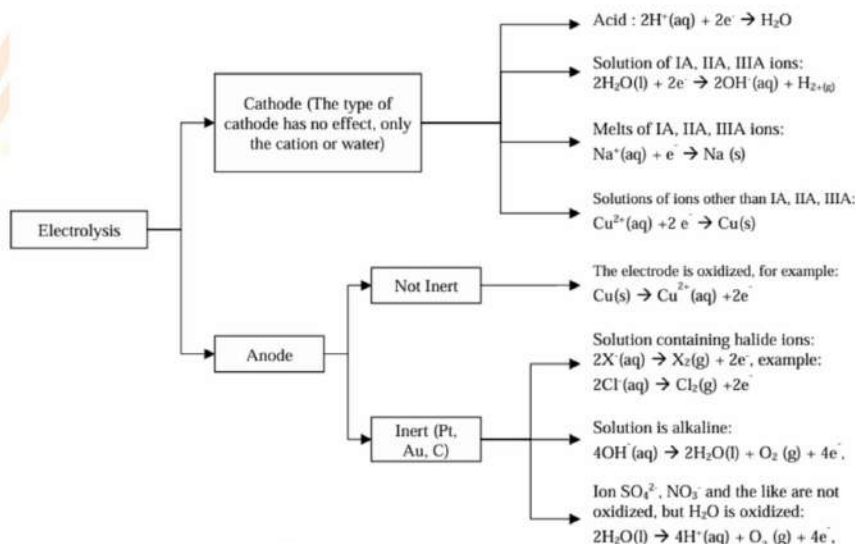

Figure 2.1 Electrolysis Cell Reaction

One of the uses of electrolysis is refining copper (Cu) metal. After being separated from its ore, the Cu metal is 99% pure, with the main impurities being Fe (iron), Zn (zinc), Ag (silver), Au (gold), and Pb (lead). In the refining process, the impure Cu is used as anode in the copper sulphate ($CuSO_4$) electrolytic cell, while the cathode is made of high-purity copper (Cu). The electrolysis process is carried out by adjusting the voltage where only Cu and more active metals, such as Fe and Zn, are oxidized. Ag, Au, and Pt metals are insoluble but fall and precipitate on bottom of the electrolysis cell. At the cathode, only copper ions (Cu^{2+}) that is reduced to form copper (Cu) deposits. The overall result of this electrolytic process are:

1)   Copper (Cu) is transferred from the anode to the cathode.

2) Iron (Fe) and zinc (Zn) impurities remain in solution as ferrous ion (Fe^{2+}) and zinc ion (Zn^{2+}).

3) Other metals such as silver (Ag), gold (Au), and platinum (Pt) settle to the bottom of the cell.

If Ag, Au, and Pt are taken and then sold, the proceeds can cover the electricity costs required for the electrolysis. The copper (Cu) metal obtained through this process has a purity of 99.96%.

If in the manufacture of pure copper (Cu), the cathode is replaced with iron (Fe), it will still form copper (Cu) deposits at the iron (Fe) cathode. The cathode coating process with another metal by electrolysis is called electroplating. This process is widely used commercially in coating car bumpers with chromium (Cr) in order to prevent corrosion and improve aesthetics.

2.3 Electrode Potential

Electrode potential forms the basis of understanding in electrochemical cells, particularly those related to redox reactions. A redox reaction is a combination of chemical reactions occurring in an electrochemical cell. An oxidation reaction is a chemical change in which a substance loses electrons. A reduction reaction is a chemical change in which a substance gains electrons. In an electrochemical cell, oxidation occurs at the anode and reduction occurs at the cathode. In a redox reaction, the substance that oxidizes another substance is called the oxidizing agent, while the substance that reduces another substance is called the reducing agent. A reduction reaction can produce a certain electrical potential called the electrode potential (E). The easier it is for an element to be reduced, the greater its electrode potential. In fact, the electrode potential in a reduction reaction cannot be directly measured because a reduction reaction never occurs without an accompanying oxidation reaction. Therefore, the electrode potential used is the standard potential value, more precisely called standard electrode potentials (E_0). The electrode used as the reference standard for determining electrode potentials is the hydrogen electrode. This is achieved by passing pure hydrogen gas over a platinum (Pt) electrode in contact with acid solution (H^+ ions), creating an equilibrium as follows:

$$H_2 \rightarrow 2H^+ + 2e$$

The value of electrode potential for this reaction is set to 0 volts. The standard electrode potential of all reduction reactions is the value compared

to the standard hydrogen electrode (SHE).

Based on the value of E_0, a series of elements starting from the smallest to the largest E_0 values can be arranged which is called the "voltaic series" as follows:

Li – K – Ba – Ca – Na – Mg – Al – Mn – Zn – Cr – Fe – Cd – Co – Ni – Sn– Pb – H – Cu – Hg – Ag – Pt – Au

The properties of the voltaic series are:

1) The metal to the right of H has a positive E_0 value, while the metal to the left of H has a negative E_0 value.

2) The metals on the right side of the voltaic series have higher E_0 value, which means they are easy to reduce or difficult to oxidize. These are called passive metals or noble metals.

3) The metals on the left side of the voltaic series have lower E_0 value, which means they are difficult to reduce or easy to oxidize. These are called active metals.

(Hartaya *et al.*, 2023)

2.4 Quantitative Aspects of Electrochemical Reactions and Electrolysis

Michael Faraday has explained that there is a quantitative relationship between the amount of chemical change in an electrochemical reaction and the amount of current. The amount of chemical change is proportional to the number of moles of electrons used in the oxidation-reduction reaction. An example of a cathodic reaction is:

$$Ag^+_{(aq)} + e \rightarrow Ag_{(s)}$$
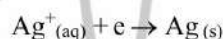
When cathode supplies 1 mole of electrons, 1 mole of Ag deposit is produced. In the SI system, 1 mole of electrons corresponds to 96,494 coulombs (C) and is commonly taken as 96,500 C. Coulomb is the amount of electric charge that passes through a single point in an electrical circuit when 1 ampere (A) current flows for 1 second (s), which is expressed as:

$$1\,C = 1\,A.\,1\,S$$

The number of Coulomb charges (Q) can be determined by measuring the current strength (I) and the duration of the current (t). Also, the number of substance moles can be determined by the number of electron moles from Coulomb charges. In the law of electrolysis, Michael Faraday discovered:

1) The amount of decomposed material during electrolysis is directly proportional to the current (I) and time (t) in electrolyte solution.

2) The amount of chemical change by a unit of electric current is

proportional to the amount of electric current (I).

The statement is formulated as:

$$W = \frac{e.I.t}{96500}$$

Where:

W : deposit mass (g)

I : electric current (A)

t : time (second)

e : chemical equivalent weight (atomic mass divided by valence)

The deposit volume is obtained by using this formula:

$$\text{Volume (cm}^3) = \frac{\text{Deposit mass (g)}}{\text{Density } (\frac{g}{cm^3})} = \frac{W}{\rho}$$

Where:

W : deposit mass (g)

ρ : coating metal density (g/cm^3)

So, to get the thickness value:

$$\text{Thickness (cm)} = \frac{\text{Volume (cm}^3)}{\text{Surface area (cm}^2)}$$

Faraday's law can explain the effect of increasing time on the electroplating process. The longer the time used, the greater the metal layer produced. The thickness of the metal layer is also affected by the chemical equivalent weight of a chemical element used as the anode. In the equation above, it can also be seen that the greater the amount of metal layer deposit (the total weight of the deposit), the greater the thickness of the layer. Hence, it can be concluded that the time used in the coating process and anode variations affect the amount of layer deposit and also the thickness of the layer formed.

2.5 Electrochemical Reaction Kinetics and Electrolysis

Reaction kinetics studies the rate of chemical reactions quantitatively and the factors that affect it. The rate of a chemical reaction is the number of moles of reactants per unit volume that react in a given unit of time. If a curve is made for decreasing the concentration of a reactant as a function of time, then the slope of the curve at any point will always be negative because the reactant concentration continuously decreases. So, the rate of reaction at any point along the curve is $-\frac{dC}{dt}$. If the reaction rate is written as the rate of formation of products, then the reaction rate will be positive. If the concentration of the product after the reaction has taket place t seconds is x

mol/dm³, then the reaction rate is $+\frac{dC}{dt}$. The reaction rate at each time is proportional to the concentration of the reactant (C) remaining at that time. It can be written mathematically as:

$$-\frac{dC}{dt} = k.C$$

Where:

$\frac{dC}{dt}$: differential rate expression

k : reaction rate constant

A general rate equation for a reaction is:

$$v = k[A]^x[B]^y[C]^z$$

with total reaction order $= x + y + z + ...$

$$\text{The rate of reaction} = \frac{\text{Concentration changes}}{\text{Time changes}} = \pm\frac{\Delta X}{\Delta t}$$

The negative sign is used when X is a reactant, and the positive sign is used when X is a product of the reaction. In general, the rate of a chemical reaction increases when the concentration of one of the reactants is increased. The relationship between reaction rate and concentration can be obtained from experimental data.

For the reaction:

$$A + B \rightarrow Product$$

It can be found that the reaction rate is directly proportional to $[A]^x$ and $[B]^y$.

$$\text{The rate of reaction} = k[A]^x[B]^y$$

x and y are integers that represent the order of x with respect to A and the order of y with respect to B, while $(x + y)$ represents the overall reaction order. The rate law of the reaction is determined experimentally and does not depend on the stoichiometric equation. The order of reaction is the sum of the powers of concentration in differential form. Theoretically, the order of reaction is a small whole number, but in some cases, it can be a fraction or even zero. The order of reaction refers to the relationship between the rate of a chemical reaction and the concentration of the species involved. In general, the reaction order of a particular substance is not the same as the coefficient in the stoichiometric equation of the reaction (Zhen *et al.*, 2024).

- Zero Order Reaction

    A reaction is said to be zero order to a reactant if the rate of the reaction is not affected by the concentration of that reactant. If [A] is the concentration and $[A]_0$ is the concentration at time $t = 0$, then:

$$\frac{-d[A]}{dt} = k$$

Then, it is integrated into:

$$[A]_0 - [A] = k \cdot t$$

- First Order Reaction

$$\frac{-d[A]}{dt} = k\,[A]$$

The integral results to obtain the correlation between the concentration of the reactants to time:

$$\ln\frac{[A]}{[A]_0} = k.t$$

- Second Order Reaction

$$\frac{-d[A]}{dt} = k\,[A]^2$$

The integral results to obtain the correlation between the concentration of the reactants to time:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k.t$$

- Third Order Reaction

$$\frac{-d[A]}{dt} = k\,[A]^3$$

The integral results to obtain the correlation between the concentration of the reactants to time:

$$\left(\frac{1}{[A]}\right)^2 - \left(\frac{1}{[A]_0}\right)^2 = 2k.t$$

CHAPTER III
PRACTICUM METHOD

3.1 Experimental Design

3.1.1 Experimental Scheme

3.1.2 Variables

1. Independent Variables
2. Controlled Variables

3.2 Materials and Tools Used

3.2.1 Materials

1. $CuSO_4$
2. Aquadest

3.2.2 Tools

1. DC power supply
2. Electroplating bath
3. Zinc plate (Zn)
4. Copper plate (Cu)
5. Alligator clip
6. Watch glass
7. Scales digital
8. Beaker glass 1000 mL
9. Beaker glass 500 mL
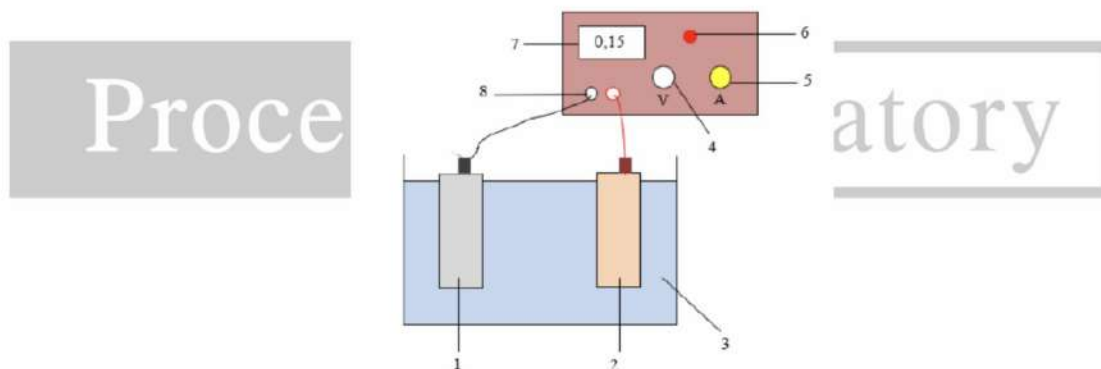10. Glass rod stirrer
11. Sandpaper

3.3 Instrument Design

Figure 3. 1 Electroplating instrument design

Where:

1) Cathode

2) Anode

3) The electroplating bath and the electrolyte solution

4) Voltage adjustment button

5) Current adjustment button

6) Maximum current marker

7) Current display

8) Power source cable

3.4 Procedure

1. Determine the optimum contact time

   The waste solution or synthetic solution in the electroplating bath was taken every ... minutes for ... minutes. Other variables are ... A current and ... g/L solution. The obtained sample were analysed and the efficiency of reducing copper content is being calculated. Variable with the highest efficiency is chosen to be the optimum contact time of the process and being used for further process.

2. Determine the optimum electric current

   The solution is fed into the electroplating bath with a fixed concentration. However, the porcess uses various electric current, i.e., ... A, ... A, and ... A, each at the optimum contact time. All the efficiency of each variable are being analysed and the highest one is chosen to be the optimum electric current. Hereinafter, the optimum current is being used for the next process.

3. Determine the optimum solution concentration

   The solutions that are fed into the electroplating bath come with various concentration, i.e., ... g/L, ... g/L, and ... g/L. process run at the optimum contact time and electric current conditions. All the efficiency of each variable are being analysed and the highest one is chosen to be the optimum solution concentration.

$$\text{Efficiency (\%)} = \frac{\text{Actual weight of cathode}}{\text{Theoritical weight of cathode}} \times 100$$

$$\text{Actual weight} = W_n - W_0$$
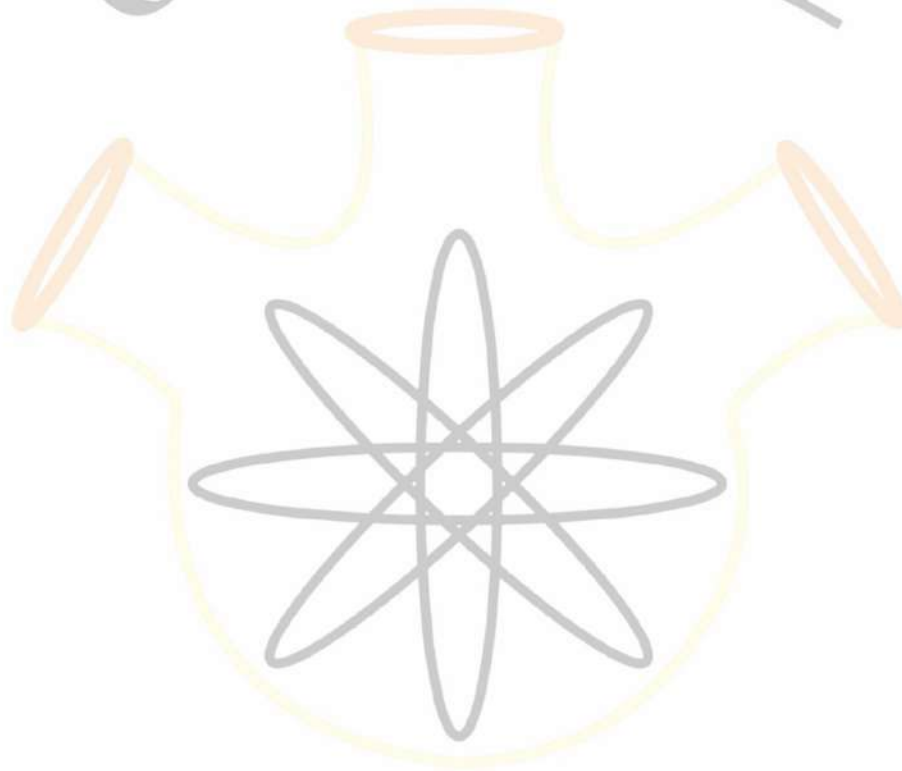
$$\text{Theoritical weight} = \frac{B \times i \times t}{E \times F}$$

Where:

B   = Anode molecular weight

I   = Electric current (ampere)

t   = Time (second)

E   = Atomic valency of anode

F   = Faraday Constant (96,500 C/mol)

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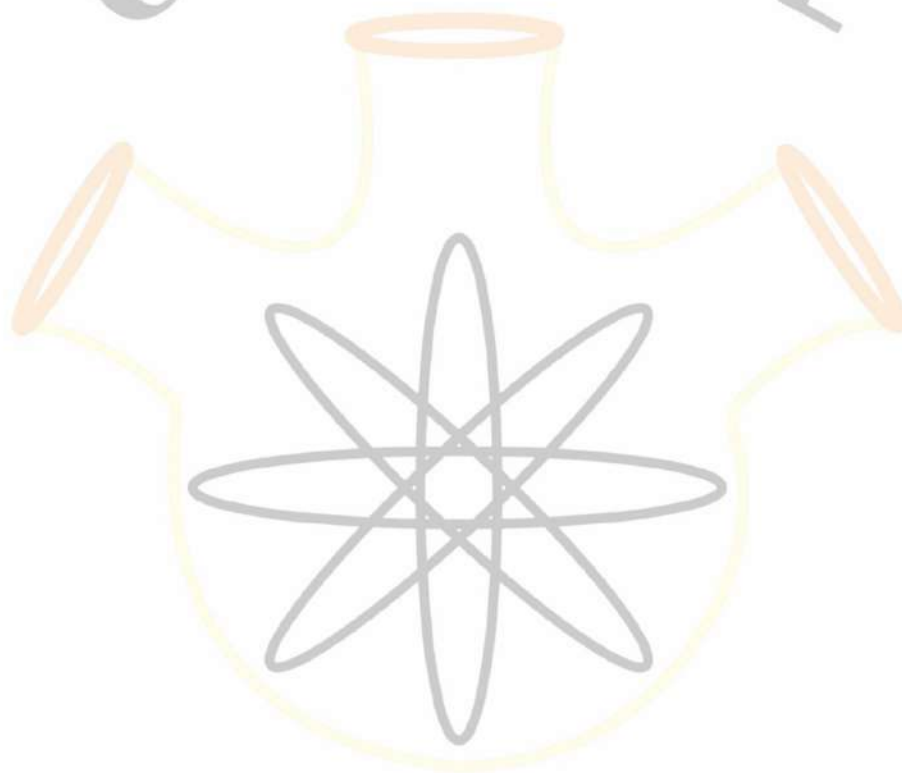
HAZARD IDENTIFICATION AND RISK ANALYSIS

MATERIAL: ELECTROPLATING

HAZARD IDENTIFICATION (HI)
A	**Mechanic**		**D**	**Environment**		**E**	**Chemical Materials**		**G**	**Another Hazard**	
A1	Manual handling	✓	D1	Noise		E1	Poison	✓	G1	Compressed gas	
A2	Moving parts		D2	Vibration		E2	Irritant	✓	G2	Ionizing radiation	
A3	Rotating parts		D3	Lighting		E3	Corrosive		G3	UV radiation	
A4	Cutting		D4	Humidity		E4	Carcinogenic		G4	Fatigue	
B	**Biology**		D5	Temperature		E5	Flammable		G5	Narrow space	
B1	Bacteria		D6	Danger journey		E6	Explosive		G6	Crowded	
B2	Virus		D7	Slippery surface	✓	E7	Cryogenic		G7	Thermometer	
B3	Mold		D8	Solid waste	✓	**F**	**Equipment**				
C	**Electricity**		D9	Air quality		F1	Pressure vessel				
C1	High voltage	✓	D10	Solitary work		F2	Hot equipment				
C2	Static electricity		D11	Splash/ drip/ flood	✓	F3	Laser				
C3	Cable	✓	D12	Powder spill	✓	F4	Glass vessel				

	RISK DETAILS						
HI	**Risk (After Control Action)**				**Risk Identification**	**Control Measures to Minimize The Risk**	**First Aid Measures**
	High	**Medium**	**Low**	**Minimum**			
1. PREPARATION/ FIRST STAGE							
			✓		When sanding the electrodes, there is a risk of scarping.	- Wear full PPE. - Sanding in one direction. - Make sure not to do sanding in a narrow space.	- Treat wounds with aid wound medicine.
2. MAIN EXPERIMENT							
		✓			When turning on the electricity, there is a risk of electric shock.	- Make sure the wires/ electrical terminals are not wet. - Wear full PPE.	- Cut off the power source. - Pushing the victim's body with insulating objects. - Seek medical help. - Treat burns.
		✓			When attaching and/ or removing alligator clips from the electrodes, there is a risk of electrocution.	- Make sure it doesn't come into direct contact with the cable or alligator clips. - Wear full PPE.	- Cut off the power source. - Pushing the victim's body with insulating objects. - Seek medical help. - Treat burns.
3. ANALYSIS/ FINAL STAGE							
			✓				