CHAPTER I
INTRODUCTION

1.1 Background

Electrodeposit coating metals such as chromium (Cr), copper (Cu), nickel (Ni) 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) which if not managed properly can cause environmental pollution. High levels of heavy metals in water can be toxic materials that can damage aquatic organisms (Pratiwi, 2020). The plating of the above metals is generally carried out in an 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 have a negative impact on environmental components, thereby reducing their quality. According to Government Regulation of the Republic of Indonesia Number 18 of 1999 concerning 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 waste treatment methods to separate heavy metals from liquid waste. However, these heavy metals are often difficult to precipitate, so they must be reduced first to achieve high efficiency.

Research on the reduction of heavy metals in metal plating industrial waste and the 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 work is known. In order for the reduction and precipitation to run perfectly, an excess concentration of reducing agent is required.

1.2 Objectives

1. Determining the effect of contact time on the electroplating performance.
2. Determining the effect of electric current on the electroplating performance.
3. Determining the effect of solution concentration on the electroplating

performance.

4. Determining 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 the reduction and precipitation of Cu^{2+} in a copper sulphate ($CuSO_4$) solution electrochemically.

CHAPTER II
LITERATURE REVIEW

2.1   Basic Concepts of Electrochemical Reactions

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 cells or galvanic cells, while electrochemical cells in which non-spontaneous redox reactions occur so that they use an electrical energy source to change chemical reactions are called electrolytic cells (Harahap, 2016). Changes that occur in a chemical system due to electrolysis reactions and redox reactions are discussed in electrochemical reactions.

Electrochemical reactions are very important in studying chemistry and daily activities. Through electrochemical reactions can be obtained information about changes in chemical energy so as to help analyze chemical systems. Until now, electrochemistry still plays an important role in industry and households. The influence of electrochemical reactions on modern society is almost everywhere. In the field of chemical analysis, electrochemistry is applied to the processes of electroanalysis, electrosynthesis, electrocoagulation, electrodialysis, electrowinning, electrorefining, and electroplating. Chemical products such as Al, Cl_2, and NaOH are also produced through the electrochemical process of electrolysis. In addition, all small electrical energy sources (batteries) are obtained from oxidation-reduction electrochemical reactions.

Before understanding the electrochemical system, it is also necessary to understand the process of electrical conduction occurrence. The process of conducting electricity differs between metals and chemical systems. Metals are conductors which capable of moving their electric charge (electrons) from one place to another if an electron is added or removed at one end. 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 electrons 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.

If there is electricity from the battery (DC current source), then:

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 (-) from 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 migration of ions 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 reaction at the electrode as long as an electrolytic conduction is present is called an electrolytic reaction. The place where the electrolysis reaction occurs is called an electrolytic cell. One of the uses of electrolysis is refining copper metal (Cu). After being separated from the ore, the purity of copper metal (Cu) is 99% with the main impurities Fe, Zn, Ag, Au, and Pb. In the refining process, impure Cu is used as anode in the copper sulphate (CuSO4) electrolytic cell, while the cathode is made of high-purity copper (Cu). The electrolysis process is carried out by adjusting the voltage where only copper (Cu) and ore active metals, such as iron (Fe) and zinc (Zn), are oxidized. Silver (Ag), gold (Au), and platinum (Pt) metals are insoluble but fall and precipitate on the bottom of the electrolysis cell. At the cathode, only copper ions (Cu2+) that is reduced to form copper (Cu) deposits. The overall results of this electrolysis 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 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.

A redox reaction is a combination of chemical reactions that occur in electrochemical cells. 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 electrochemical cells, oxidation occurs at the anode, while reduction occurs at the cathode. In a redox reaction, the substance that oxidizes is called the oxidizing agent, while the substance that reduces another substance is called the reducing agent. A reduction reaction can give rise to a certain electric potential called the electrode potential (E). The easier it is for an element to be reduced, the greater its electrode potential (Kurniasari *et al*., 2019). The actual the electrode potential value in a reduction reaction cannot be calculated because no reduction reaction takes place without an oxidation reaction being followed. Therefore, the electrode potential used is the standard potential value, more precisely called the standard electrode potential (E0). The electrode used as the standard for determining the electrode potential is the hydrogen electrode. How to obtain it by flowing pure hydrogen gas on a platinum electrode (Pt) in contact with acid (H^+ ions) so that the following balance occurs:

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

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

Based on the value of E_0, a series of elements starting from the smallest to the largest E0 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 right sided in the voltaic series have the higher E_0 value, which means the metals to the right of H are easy to reduce or difficult to be oxidized. These are called passive metals or noble metals.

3) The left sided in the voltaic series have the lower E_0 value of the metal, which means the metal is difficult to be reduced and easy to oxidize. These are called active metals.

2.2 Quantitative Aspects of Electrochemical Reactions or 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. Examples of reactions at the cathode:

$$Ag^+_{(aq)} + e \rightarrow Ag_{(s)}$$
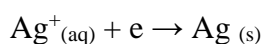
When the cathode supplies 1 mole of electrons, 1 mole of Ag deposits is produced. In the SI system, 1 mole e is equivalent to 96,494 Coulomb (C) and is usually considered 96,500

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 follows:

$$1C = 1A \cdot 1S$$

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.

2.3   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 reacts 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 is always negative because the concentration of the reactants always 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 taken place t seconds is x mol/dm^3, then the reaction rate is $+\frac{dX}{dt}$. The rate of reaction at each time is proportional to the concentration (C) remaining at each time. It can be written mathematically as:

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

Where:

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

k : reaction rate constant

A general rate equation for a reaction is:

$$v = k[A]^{\cdot}[B]^{-}[C]^{\cdot}$$

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

$$-\frac{\Delta \text{ concentration}}{\Delta \text{ time}} = \pm \frac{\Delta X}{\Delta t}$$

The negative sign is used if X is the reactant and the positive sign is used if X is the product of the reaction. The rate of a chemical reaction generally 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:

$$A + B \rightarrow \text{Product}$$
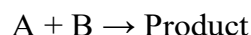
It can be found that the reaction rate is directly proportional to $[A]^{x}$ and $[B]^{y}$.

$$\text{Reaction rate} = k[A]^{\cdot}[B]^{-}$$

x and y are integers that represent the order of x to A and order of y to B, while (x + y) is the order of the overall reaction. The rate law of the reaction was obtained experimentally and does not depend on the stoichiometric equation. The order of the reaction is the sum of the powers of concentration in differential form. Theoretically, the order of a reaction is a small whole number, but in some cases form as a fraction or zero. In general, the reaction order of a particular substance is not the same as the coefficient in the stoichiometric equation of the reaction (Erawati & Marfiana, 2020).

- 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:

$$[A]_0 - [A] = k.t$$

- First Order Reaction

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

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

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

- 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:

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

CHAPTER III

PRACTICUM METHOD

3.1 Materials and Tools Used

3.1.1 Materials

1. $CuSO_4$
2. Distilled water

3.1.2 Tools

1. DC power supply
2. Electroplating bath
3. Zinc plate (Zn)
4. Copper plate (Cu)
5. Alligator clip
6. Watch glass
7. Beaker 2000 mL
8. Beaker 250 mL
9. Funnel
10. Glass stirring rod
11. Volumetric flask 500 mL
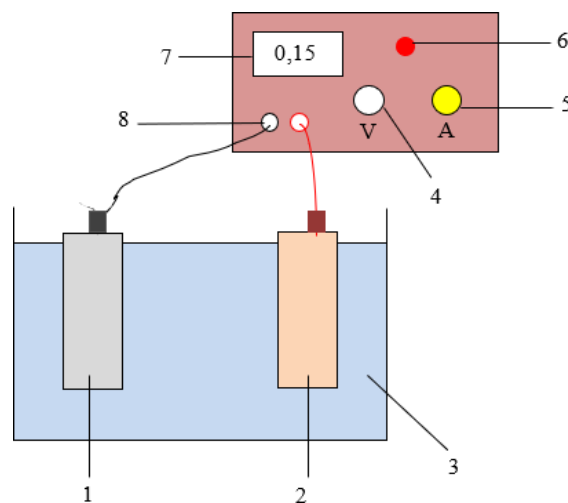12. Sandpaper

3.2 Instrument Design

Figure 3.1 Electroplating instrument design

Numbering:

(1)   Cathode

(2)   Anode

(3)   Electroplating bath and solution

(4)   Voltage adjustment knob

(5)   Current adjustment knob

(6)   Maximum current marker

(7)   Current display

(8)   Power source cable

3.3   Procedure

1. Determine the optimum contact time

    The waste solution or synthetic solution in the electroplating bath was taken every ... minutes for ... minutes. Another variables are … A current and ... g/L solution. The obtained sample were analyzed 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 process uses various electric current, i.e., … A, … A, and … A, each at the optimum contact time. All the efficiency of each variables are being analyzed 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

    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 variables are being analyzed 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   : the Faraday Constant (96,500 C/mole)

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