RECOVERY OF SILVER FROM PHOTOGRAPHIC WASTE: ELECTROLYSIS BEHAVIOR

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ABSTRACT

Photographic waste is one of the wastes produced by the paper and printing industries. Photographic waste usually contains metal ions mostly silver, sodium, potassium and iron. Since silver is photosensitivity material and its valuable increasing price, people tends to recover the silver from photographic waste to reuse it in paper and printing industries. A lot of research had been done to effectively recover the silver from photographic waste. This research is to investigate the ability of electrolysis process to recover the silver from photographic waste. In the process of electrolysis, or commonly known as electrolytic silver recovery, a direct current is passed through a silver-rich solution between a positive electrode (the anode) and a negative electrode (the cathode). During the process, an electron is transferred from the cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode. There are two parameters that have been focused on; the effects of current supply to the electrolysis process on the yield of silver and the effects of distance between two electrodes on the yield of silver. The results show that the electrolysis is able to recover silver from photographic waste. For the current supply variable, the best current supply for the electrolysis process is 40 mA and variable of distance between electrodes contribute minor effect to the process. Electrolysis process is one of the cheapest processes since it is able to recover silver from photographic waste.

ABSTRAK

Sisa buangan fotografi adalah salah satu sisa buangan yang dihasilkan oleh industri kertas dan percetakan. Sisa buangan fotografi biasanya mengandungi ion logam seperti perak, natrium, kalium dan besi. Oleh kerana perak adalah bahan sensitive cahaya dan nilai harganya yang sentiasa meningkat, industry mula cenderung untuk mengekstrak semula perak dari sisa buangan fotografi untuk digunakan semula dalam industri kertas dan percetakan. Banyak kajian telah dilakukan untuk mengekstrak semula perak dengan efektif dari sisa fotografi. Penelitian ini bertujuan untuk mengetahui kemampuan proses elektrolisis untuk mengekstrak semula perak dari sisa fotografi. Dalam proses elektrolisis, atau biasanya dikenali sebagai elektrolisis pengekstrakan semula perak, arus elektrik dialirkan menerusi larutan yang kaya dengan ion perak di antara elektrod positif (anod) dan elektrod negatif (katod). Selama proses tersebut berjalan, elektron dipindahkan dari katod ke perak yang bercas positif, mengubahnya menjadi logam, yang akhirnya melekat pada katod. Terdapat dua pembolehubah yang telah difokuskan dalam kajian ini; kesan bekalan arus elektrik kepada proses elektrolisis terhadap pembentukan perak dan pengaruh jarak antara dua elektrod terhadap pembentukan perak. Keputusan kajian menunjukkan bahawa elektrolisis mampu mengekstrak semula perak. Untuk pembolehubah bekalan arus elektrik, bekalan arus elektrik terbaik untuk proses elektrolisis adalah 40 mA dan pembolehubah jarak antara elektrod hanya memberikan kesan kecil pada proses. Proses Elektrolisis adalah salah satu proses termurah kerana kemampuannya untuk mengekstrak semula perak dari sisa fotografi.

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LIST OF SYMBOLS

$Na_2S_2O_3$	-	Sodium Thiosulfate
$NaHSO_3$	-	Sodium Sulfite
NaFeEDTA	-	Sodium Iron EthyleneDiamineTetraAcetate
$AgNO_3$	-	Silver Nitrate
$Ag(S_2O_3)_2^{-3}$	-	Silver Thiosulfate Complex
Ag_2S	-	Silver Sulfide
Fe^0	-	Metallic Iron
Ag^0	-	Metallic Silver
Fe^{+2}	-	Ionic Iron
$S_2O_3^{-2}$	-	Thiosulfate
e^-	-	Electron
SO_3^{-2}	-	Sulfite
H_2O	-	Water
SO_4^{-2}	-	Sulfate
H^+	-	Hydrogen Ion
mg/L	-	milligram per liter
CRCs	-	Chemical Recovery Cartridges
MRCs	-	Metallic Recovery Cartridges
TMT	-	tri-mercapto-s-triazine
mA	-	miliampere
kΩ	-	kiloOhm
cm	-	centimeter
mm	-	millimeter
V	-	Volt
SS	-	Stainless Steel
AAS	-	Atomic Absorption Spectroscopy

oz	-	ounce
g	-	gram
L	-	Liter
DC	-	Direct Current
Ppm	-	part per million
USD/oz	-	US Dollar per ounce

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CHAPTER 1

INTRODUCTION

1.0 Introduction

Waste consumption is one of the major environmental problems in Malaysia. As Malaysia progresses towards becoming a developed country in 2020, consumption of waste will correspondingly increase. Consumption however, produces some undesirable impacts on the environment and climate (Liew, 2008). Photographic waste is one of the wastes produced by the paper and printing industries. Photographic waste usually contains metal ions mostly silver, sodium, potassium and iron. Since silver is photosensitivity material and its valuable increasing price, people tends to recover the silver from photographic waste to reuse it in paper and printing industries. A lot of research had been done to effectively recover the silver from photographic waste. This study is to investigate the ability of electrolysis process to recover the silver from photographic waste.

1.1 Research Background and Problem Statement

Silver is both an Industrial Metal and a Precious Metal. As an industrial metal, Silver has many thousands of uses due to its outstanding qualities. Silver has the highest electrical and thermal conductivity of any element. Silver was critical to the photographic industry as well as paper and printing industry. Although over the past ten years the supply through production and scrap of silver has increase by 26 percent, the demand has expanded by only 10 percent. But a good percentage of this production is irrecoverable through photographic paper and other industrial use. Yet silver bullion inventories have fallen dramatically while silver investments are increasing steadily with a consequent silver price now looking bright as reflected in the steadily rising silver price. Production will have to hurry to keep up with the increased demand.

Figure 1.1: 1 year silver price in USD/oz (www.silverprice.com)

Figure 1.1 show that the price of silver is not stable but it shows a dramatically increase from May 2009 to March 2010. In May 2009 the price is about 13 USD/oz and the current price of silver is about 18.4 USD/oz. These values give a figure of increasing price of silver that put a concern to recover the silver.

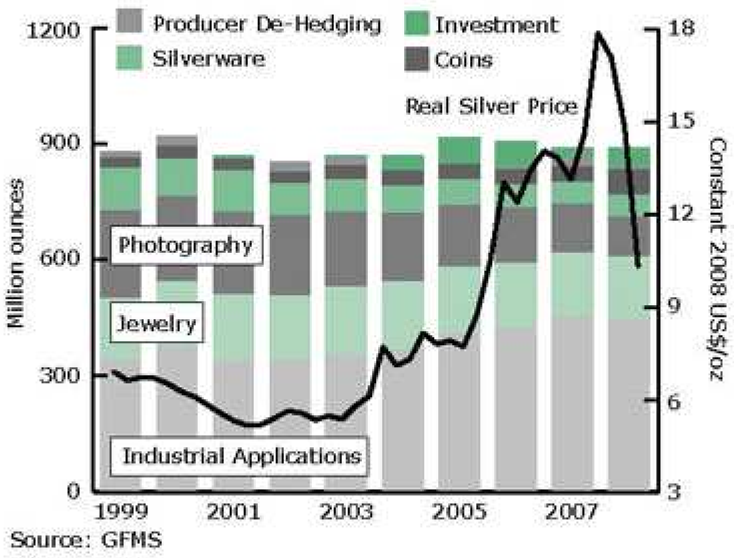

Figure 1.2: World silver demand until 2008 (www.silverprice.com)

From figure 1.2, the demand increased in industrial application and jewelry. The industrial application demand of silver had increased to about 400 million ounces meanwhile the jewelry show stable demand.

In Malaysia, photographic waste consumption is about 11969 cubic meters in 1987. The amount of photographic waste generated by electronic and semiconductor sector is estimated at 5% per annum (Ahmat et al, 2000). About 5000 kg per annum of photographic waste generated by paper and printing industries which are the major producer of photographic waste.

There are silver recovering activities in Malaysia, but still not widely practiced. Electrolysis process is a basic method to recover silver which produces nearly pure metallic silver. This study is to investigate the electrolysis behavior in silver recovery process.

1.2 Objective

i. To investigate the ability of electrolysis process in recovering silver from photographic waste.

1.3 Scopes

i. To investigate the effects of distance between two electrodes on the yield of silver.
ii. To investigate the effects of current supply to the electrolysis process on the yield of silver.

1.4 Rationale and Significance

Silver recovery activities become a major concern nowadays to recover silver from photographic waste for industrial application use. There are some advantages of recovery the silver which are:

i. Contribute to the society in preventing the community from any harm and danger for instance water pollutions.
ii. To reduce the toxicity effects of silver on the aquatic organism.
iii. Reuse the silver in paper and printing industry.

CHAPTER 2

LITERATURE REVIEW

2.0 What is Silver?

Silver is one of the basic elements that make up our planet. Silver is rare, but occurs naturally in the environment as a soft, "silver" colored metal. Because silver is an element, there are no man-made sources of silver. People make jewelry, silverware, electronic equipment, and dental fillings with silver in its metallic form. It also occurs in powdery white (silver nitrate and silver chloride) or dark-gray to black compounds (silver sulfide and silver oxide). Silver could be found at hazardous waste sites in the form of these compounds mixed with soil and/or water. Photographers use silver compounds to make photographs. Photographic materials are the major source of the silver that is released into the environment. Another source is mines that produce silver and other metals (ATSDR, 1990)

2.1 Photographic Waste

Photographic waste is the waste generated by the photographic processing machine in paper and printing industries. X-ray film also is one of the photographic wastes generated by hospital and biochemical lab. Photographic waste contains silver that is the main material use to transfer image. It contains soluble silver thiosulfate complex and smaller amount of silver sulfite. The light-sensitive properties of silver compounds are the key to most photographic processes, and the basis of most of the waste produced. Like the compounds of many other heavy metals, they are highly toxic, and classified as special wastes. Along with the decreasing amount of silver natural resources, the cost of silver productions has risen rapidly and the price of silver in the market has increased constantly. Every country has focused on the recovery of silver from silver-containing waste (Zhouxiang, 1999).

2.2 Silver in Photographic Waste

The primary sources of recoverable silver from photographic processing solutions are the 'fix' (dilutea queous $Na_2S_2O_3/NaHSO_3$) and the 'bleach–fix' solutions (dilute aqueous $Na_2S_2O_3/NaHSO_3/NaFeEDTA$) (Pollet et al, 2000).Many photographic and x-ray wastes contain silver thiosulfate. Wastes having a silver concentration of 5.0 parts per million (ppm) or more are hazardous because they display the characteristic of toxicity. Waste that typically contains silver in concentrations greater than 5 ppm includes:

i. Fixer solution
ii. Rinse water following water baths
iii. Solution from cleaning developer tanks (cleaner dissolve precipitated silver)
iv. Film, negative and paper

Most photographic films and papers carry as light sensitive agents silver halides embedded in a layer of gelatin. In this "emulsion" a single photon of light can sensitize by catalytic action a billion silver atoms. The sensitization of the silver halide, predominantly silver bromide, is accomplished by exposing the emulsion to light through the lens of a camera or by mean of a projector or a transparency, to x-rays or as accomplished only recently by means of computerized laser beams (Messerschmidt, 1988). The photographic and x-ray wastes have to manage well to prevent harm to human health and the environment.

2.2.1 Environmental Effects of Silver

Toxicity is the measure of adverse chemical effects on an organism and is governed by several factors, including the form and amount of the chemical present in the organism. Different form of silver display different degree of toxicity. Silver that is soluble in water, and unattached to any other atoms while in soluble, is known by several names including free silver, ionic silver, and hydrate silver ion. In general, it is the free silver that is the most toxic form. This toxicity is the basis of regulations on discharge of silver compounds. Some silver compounds release ionic silver very slowly due to very low solubility (e.g., silver sulfide) or complexation of the silver (e.g., silver thiosulfate). These compounds are over 15,000 times less toxic than silver nitrate to aquatic organisms. Because of the tendency for silver to form nearly insoluble compounds in natural waters and sediments, the chance for organism to be affected long term is minimal (KODAK, 2003).

Soluble silver salts, especially $AgNO_3$, are lethal in concentrations of up to 2g (0.070 oz). Silver compounds can be slowly absorbed by body tissues, with the consequent bluish or blackish skin pigmentation (argiria). Liquid or vapor may be irritating to skin, eyes, throat, or lungs. Intentional misuse by deliberately concentrating and inhaling the contents of this product can be harmful or fatal.

2.3 Silver Recovery Process

The silver to be recovered may be present in different forms: as insoluble silver halide, a soluble silver thiosulfate complex, a silver ion, or elemental silver, depending upon the type of process and the stage at which it is recovered (Messerschmidt, 1988). A number of techniques are available to remove silver from silver rich photographic processing solution. Of these, three are used in virtually all practical methods of silver recovery. They are:

i. Precipitation
ii. Metallic Replacement
iii. Electrolysis

Additionally, ion-exchange technology can be used to treat washwaters to remove silver. This technology is typically used when we must meet stringent discharge requirement, and capital and operating coast are a secondary concern. Other technologies such as reverse osmosis, distillation, and evaporation can produce a silver sludge. However, they only alter the silver concentration and do not actually remove silver from solution. Methods that are successfully used in other industries to recover silver, such as electrowinning, may not be applicable to photographic processing solution, as they tend to cause significant solution decomposition (KODAK, 1999)

2.3.1 Precipitation Process

Precipitation can remove silver from silver-rich solutions, reducing it to very low levels. Properly applied, levels can be reduced to the low ppm range. Until recently, precipitation has not been as widely used as a silver-recovery technique. Common precipitating agents classically have been alkali metal salts of sulfide (sodium sulfide, potassium sulfide, etc) which will form silver sulfide in solution. The silver sulfide is removed by filtration (KODAK, 1999).

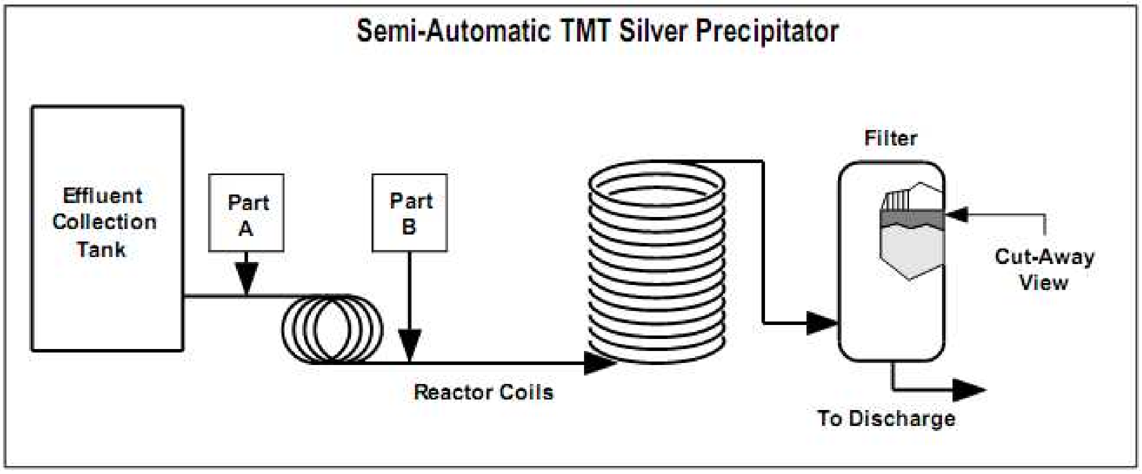

Figure 2.1: Schematic Diagram for Semi-Automatic TMT Silver Precipitator (Kodak, 1999)

Figure 2.1 shows a Schematic Diagram for Semi-Automatic TMT Silver Precipitator. This silver precipitation technique utilized a chemical called TMT (tri-mercapto-s-triazine). TMT produces an insoluble silver compound that is more easily filtered than silver sulfide. For many processes, silver levels may be reliable and consistently reduces to an average of less than 1.5 ppm. Advantages of TMT include consistent low silver discharge and reduce cost (Kodak, 1999).

2.3.2 Metallic Replacement Process

Silver is also recovered from photographic processing solution by replacing the silver with another metal such as zinc by electrolysis or by chemical precipitation with chemicals such as sodium hydroxide or sodium sulphide (Ajiwe and Anyadiegwu, 2000). The basic for metallic replacement is the reduction by metallic iron (usually present as “steel wool”) of the silver thiosulfate complex to elemental silver. The commercial equipment commonly used for the recovery is often referred to as Metallic Recovery Cartridges (MRCs) or Chemical Recovery Cartridges (CRCs). The most common source of iron is fine steel wool, chosen for its surface area. The steel wool is wound on a core or chopped up and packed into a cartridge. The silver rich solution are slowly metered into the cartridge and through the iron medium. The silver is left behind in the cartridge while iron is solubilized and carried out by the solution. Like the electrolytic process, metallic replacement is a reduction-oxidation process.

$$2Ag(S_2O_3)_2^{-3} + Fe^0 \rightarrow 2Ag^0 + Fe^{+2} + 4S_2O_3^{-2}$$ (Kodak, 1999)

Silver Thiosulfate Complex + Metallic Iron → Metallic Silver + Ionic Iron + Thiosulfate

The final silver concentration is affected by flow rate, iron surface area, contact time, pH, original silver concentration, thiosulfate concentration, and the volume passing through the cartridge. If the MRC is operating properly, the silver concentration may be reduced to less than 5 mg/L (Kodak, 1999)

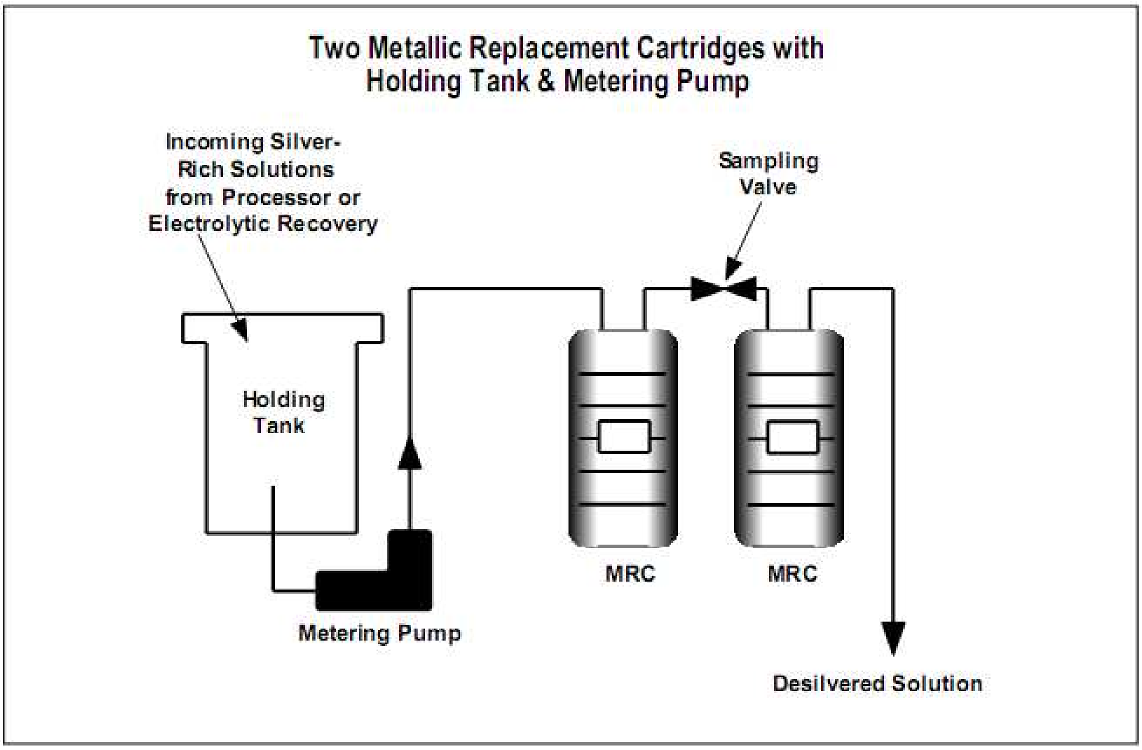

Figure 2.2: Schematic Diagram for Metallic Replacement Process Using MRCs (Kodak, 1999)

2.3.3 Electrolysis Process

Recovery of metals from aqueous solution of their salts by electrolysis can be realized by two methods. The first method consists of the electrolysis of solutions obtained after leaching of the corresponding metal from ores or concentrated with the use of insoluble anodes. The second method consists of the electrolytic refining of the metal (Ajiwe and Anyadiegwu, 2000). In the process of electrolysis, or commonly known as electrolytic silver recovery, a direct current is passed through a silver-rich solution between a positive electrode (the anode) and a negative electrode (the cathode). During this electrolytic process, an electron is transferred from the cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode (Kodak, 1999). In a simultaneous reaction at the anode, an electron is taken from some species in solution. In most silver-rich solution, this electron usually comes from sulfite.

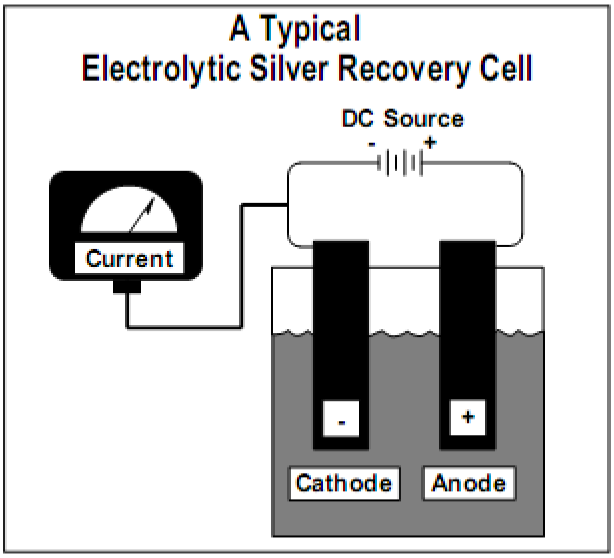

Figure 2.3: Schematic Diagram for Typical Electrolytic Silver Recovery Process (Kodak, 1999)

Figure 2.3 shows that the typical electrolysis cell for silver recovery process. An overview of the reactions is:

At Cathode: $Ag(S_2O_3)_2^{-3} + e^- \rightarrow Ag^0 + 2(S_2O_3)^{-2}$ (Kodak, 1999)

Silver Thiosulfate Complex + Electron → Metallic Silver + Thiosulfate

At Anode: $SO_3^{-2} + H_2O \rightarrow SO_4^{-2} + 2H^+ + 2e^-$ (Kodak, 1999)

Sulfite + Water → Sulfate + Hydrogen Ions + Electron

Here the crude metal to be refined serves as the anode and the pure metal is deposited at the cathode. This is a better method for noble metal recovery (Ajiwe and Anyadiegwu, 2000). Electrolysis recovery process produces nearly pure metallic silver, contaminated only slightly by some surface reactions that also take place. The plated silver should be greater than 90 percent pure (Kodak, 1999).

2.3.4 Other Recovery Process

There have some other recovery process such as reverse osmosis. Reverse osmosis is a concentration process by which ions are holding on one side of a semi-permeable membrane while the water is allowed to pass through the membrane. We may then treat the concentrated to recover silver. Even more than with ion exchange, cost, maintenance, and space requirements tend to make this technology impractical for most photographic processing facilities (Kodak, 1999).

In distillation recovery process, the photographic processing effluent is captured in a vessel and heated to evaporate the water. In some apparatus, the solution is actually boiled, the steam being condensed. In others, the solution is merely heated and released into the air (by a fan) to discharge evaporating moisture. Although some pieces of equipment may be capable of producing a solid block from the effluents, the energy requirements can be prohibitive, and heated photo processing effluents tend to give off pungent, unpleasant odors. We may need an air emission discharge permit for this type of equipment (Kodak, 1999).

For evaporation recovery process, vacuum distillation or cool temperature evaporation is a process by which a vacuum is drawn on a vessel containing the photographic processing effluents. At a sufficiently low pressure, the solution will boil and the water vapor is drawn from the vessel, condensed, and collected. These evaporators can generally reduce the effluent volume by up to 90 percent, but the initial equipment expense is relatively high (Kodak, 1999).

CHAPTER 3

METHODOLOGY

3.0 Electrolysis Process Description

In this research, we used electrolysis process as a research method. This method consists of two electrode plates connecting to the electric circuit for current supply. By taking variable of current supply and the distance between electrodes, some of the variable has to be constant such as pH value, electrode surface area, temperature of the waste solution, and the process duration.

3.1 Apparatus

The apparatus used in this research are 1L beaker, stainless steel electrode, electrode holder, retort stand, direct current power supply, wires with crocodile clips, and electric circuit.