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**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTION OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIOENGINEERING**

# Electrolytic Silver Recovery from Photographic Fixer Solution: Berhanena Selam Printing Enterprise

**A thesis submitted to the school of chemical and Bio Engineering, Addis Ababa Institute of Technology in partial fulfillment of the requirement for the Degree of Master of Science in Chemical Engineering**

**(Environmental Engineering)**

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## Declaration

I thus certify that, to the best of my knowledge, this thesis submission is my original work for the MSc program; it does not contain any material that has already been published by another individual or that has been partially or fully submitted for any other professional or academic degree.

Author: Signature, Date:

Name of student advisor: Signature, Date:

## Abstract

The goal of the study is to develop an electrolysis process for recovering silver from waste photographic fixer. Brehanena Selam Printing Enterprise provided the samples for the investigation. The experimental runs are randomized, and suitable software is used for the analytical process. Portal for Design Expert 6.0.8: Box-Behnken Design was used during this study statistical method of surface response methodology (SRM) was used for analyzing of laboratory result of silver recovery. The amount of the variable used in the study was selected after considering the effects of each parameter on the results. Ph (4-8), current density (2-5), and time (20-90).17 different laboratory experiments were carried out within these specified ranges. ANOVA results, fitness graphs, and 3D graphs of operational parameters were examined using BBD (Box-Behnken Design) of RMS (Response Surface Methodology) and fit summery and also XRD analysis and XRF analysis. The three parameter investigated that the result showed pH at 6 and current density at 5A and contact time at 1:30hr gives silver yield of 97.295%. This is my optimum result. So the result of the study showed that electrolysis process on silver recovery from photographic waste is technically feasible.

## Acknowledgment

First of all, I went to convey my appreciation to the All-Powerful God for allowing me to survive during this challenging period of the COVID-19 epidemic and for assisting me in finishing my thesis work. Then I would want to thank you very much for everything to Advisor Dr Ing. Abubeker Yimum for follow-up and understanding me throughout this study and also for his suggestion and guidance throughout this investigation. I also appreciate all labs. Assistants for their technical support especially Mr. Aklilu and Mr Sami. Additionally I would want to convey my appreciation to the management and staff at the Brehan ena Selam Printing Company. Finally I am sincerely grateful to my family especially my Mom (Aster Amda) and my friend for belief me and for giving love, mortal and support.

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## Abbreviation

| | |
|---|---|
| Ag | Silver |
| Ppm | part-per-million) |
| OSHA | Occupational Safety and Health Administtration |
| EDTA | EthyleneDiamine Tetraacetic acid |
| PDTA | PropyleneDiamine Tetraacetic acid |
| MRCs | Metallic Recovery Cartridges |
| TMT | tri-mercapto-S-triazine |
| CRCs | Chemical Recovery Cartridges |
| ER | Electrochemical Reaction |
| SCE | Saturated Calomel Electrode |
| DC | Direct Current |
| RSM | Response Surface Miscellaneous |
| RMS | Response surface methodology |
| LOD | Lower Detection limit |

# 1. INTRODUCTION

## 1.1 Backgrounds

Global urbanization and industry are growing, and this has led to major pollution worldwide, particularly in the aquatic environment [1]. Human-produced wastewater frequently contains hazardous heavy metals including copper, silver, mercury, and so forth. Among the wastes generated by the paper and printing industries, photographic waste is one that mostly consists of iron, silver, sodium, and potassium.

The two main sources of silver released during photographic processing are bath fixing and bath and rinse water bleaching. Therefore, the primary goal of the work described in this research was to identify a straightforward and effective procedure for extracting silver from this silver thiosulfate complex ($Ag_2\ S_2\ O_3$ ).

The literature mentions several methods for recovering silver, but the electrolytic procedure is the most effective and produces a pure product. It was also hoped that the experimentation detailed in this paper would also lead to the construction of low-cost equipment that the tiny camera store might utilize.

The recovery of silver from photo-processing waste is interesting for a number of reasons. Silver has monetary value as a recovered product, is a valuable natural resource with limited supply, and its release into the environment is highly restricted. Silver compounds are the fundamental light-sensitive substance utilized in the majority of today's photographic films and sections in photo processing. Throughout the processing process, silver is extracted from the film or paper and processed in the solution, typically as a silver thiosulfate complex, especially in the fixing bath or bleach-fix.

Photo-processing solutions, spent rinse water, scrap film, and scrap printing paper are major sources of recoverable silver. The cost of the initial equipment, the quantity and value of silver recovered, and the return on investment are all economic factors.

## 1.2 Where is Silver to be found?

Silver is present in films and papers that have not been exposed to light in the form of small silver halide crystals that transform when exposed. These light-struck crystals turn black and create the picture on the film or paper when it is developed. Without exposure to light, crystals are unable to develop.

They can't be left in the film or paper since they would darken and distort the picture as they grew older. These crystals are eliminated by dissolving them in a fixing bath since the image needs to be stabilized. The "fix" consists of a number of components, but sodium or ammonium thiosulphate (hypo), which dissolves silver halides, is the main component. The silver compounds build up in the fixing bath as the hypo completes this task, and the fixer's capacity is depleted. At that point, the bath is useless and needs to be thrown out.

Sodium thiosulphate fixers, which are often provided in powder form, have wash qualities that are comparable to those of ammonium thiosulphate fixers; nevertheless, they are more susceptible to building up of silver and, hence, more sensitive to its removal. The fixing time is shortened and, more crucially, the fixing bath's lifespan is greatly extended when silver is removed from this kind of fixer.

Most of the silver that can be recovered is dissolved in the bleach solution during the processing of black and white reversal type films. Silver image is removed using bleach, but silver halide is not removed. Due to the bleach's need for a comparatively high replenishment rate in order to retain its effect on the silver image, the concentration of silver in a used bleach bath is not as high as that found in a conventional fixing bath.

The silver in color processing does not dissolve into the bleach solution, in contrast to the black and white reverse procedure. Instead, during the film emulsion, the silver is changed into a silver salt. Next, in the fixing bath, this silver salt is dissolved. In the process of applying color, nearly all of the silver may be recovered from the fixing bath.

It is also possible to recover silver from used processed films, sheets, and some printing plates, as was previously indicated. You can use almost any black and white paper or film for recovery. A significant amount of silver is also produced by some printing plates.

## 1.3 Statement of the Problem

A larger portion of the silver halides migrates to the fixer solution while the remaining portion stays on the film to form the image when creating black and white photographs, to name just one example. Nearly 100% of the silver processed for color work and up to 80% of the total silver treated for black and white positives will end up in the fixer solution. Because of carry-over, silver is also found in the rinse water after the bleach-fix or fixerBecause it is more readily available to plants and animals and can be transferred with ease, the soluble form of these heavy metal wastes is extremely harmful [2].

Human toxicity from these metals can cause serious problems with the kidney, reproductive system, liver, brain, and central nervous system [3]. Therefore, there has been a greater focus on eliminating the hazardous heavy metals from wastewater.

Furthermore, according to reports, 25% of the world's recycling needs are met by the 75% of silver needed to produce jewelry that comes from photographic garbage. Because of this, recovering valuable metals like silver has the potential to be profitable in addition to providing a solution to the environmental issues. The techniques used to extract silver from photographic waste are therefore crucial for cutting expenses and time, as well as for minimizing environmental impact [4].

Because there are numerous varieties of photography processes and no two processing laboratories are same, photographic effluents differ in composition. The dimensions, amount of wash water used, number of hours worked per day, amount of effluent produced, and use of chemical recovery systems in processing laboratories vary widely.The most effective way to ascertain the true effluent characteristics of any photographic processing studio is to gather a representative wastewater sample and have it examined by a qualified analytical laboratory.

From this point of view we can understand that the suggested methodology for efficiently treating the effluents from one photographic processing technology cannot work effectively for all photographic effluents generated from different technologies. So the waste generated from each company’s must be studied individually for effective treatment of the waste they generated.

Previously in Ethiopia there is no research work was not been done in Berhanena Selam printing enterprise but the idea is already done in another place.

## 1.4 Objective

### 1.4.1 General Objective

- To analyze the electrolytic silver recover method from waste fixer solution generated from Berhan Ena Selam printing company.

### 1.4.2 Specific Objective

- Characterizations of the collected photographic fixer waste.
- To investigate a more-efficient and cost-effective method for the electrolytic way of silver recovered method.
- To examine how various circumstances affect silver's electrolytic recovery.
- To characterize characterization of the recovered product.

## 1.5 Scope of the research

The research focus was on the extraction of silver from photographic waste from Berhanena Selam printing enterprise waste by using electrolysis method and laboratory setup, sample preparation and finally to investigating the effect of pH, current density and time using lab scale under controlled condition.

## 1.6 Significance of the Study

The research will give detailed information about the advantage of using electrolysis method instead of using other methods. Therefore, upon successful completion of this research task, the result of the analysis will be expected to be used for further study. By doing so it contributes to the reduction of environmental problem caused by this waste.

Recovering the silver has a number of significant advantages including:

- Preserve civilization from harm and risk by steering clear of water contamination.
- To decrease silver's harmful impact on the aquatic environment.
- Take advantage of the silver to print paper.

# 2. LITRATURE REVIEW

On the recovery of metallic silver from solutions containing silver ions, a great deal of study has been done and documented in the literature. Electrolytic techniques are often better than solely chemical techniques, according to a review of the literature.

## 2.1 Silver extraction from waste

The chemical symbol for silver is Ag, and its atomic number is 47. It is among the fundamental substances that comprise our world. It is the element with the highest electrical conductivity and the highest metal with the highest thermal conductivity. Pure forms of the metal, devoid of native silver, as well as alloys with other metals like gold and minerals like argentite and chlorargyrite, can all be found in nature. Refining copper, gold, lead, and zinc produces most of the silver that is produced as a byproduct.

Silver is one of the essential components of our universe. Despite being rare, silver does occur naturally as a soft metal with a silver hue. There are no artificial sources of silver because it is an element. Silver in its metallic form is used to manufacture jewelry, cutlery, electrical devices, and dental fillings.

**Figure 1 Silver**

Moreover, it is present in powdered white (silver nitrate and chloride) or dark-gray to black compounds (silver oxide and succinic acid). In the form of these compounds combined with soil or water, silver may be found in hazardous waste sites.

Market of Silver is both Industrial metal as well as a precious metal. Silver is critical in photographic printing and paper industry. Silver investments are steadily increasing as a result the price of silver is raising steadily over the years. Production of silver from wastes must be increased in order to keep up with the increased demand.

## 2.2 Silver in the environment

There are trace amounts of metallic silver in Mexico, Germany, and Norway. It usually appears in the form of a compact mass rather than as crystals. Acanthite, which is mined in Mexico, Bolivia, and Honduras, and stephanite, which is mined in Canada, are the two main sources of silver ores. Nevertheless, the majority of silver is produced as a byproduct during the refining of other metals. Of the 17.000 tons of newly mined silver produced year worldwide, only roughly 25% originates from silver mines. The residual amount is a result of refining other metals. [5]

Depending on the concentration and chemical alterations connected to the disposal site, silver and its salts have different effects on the environment. All surface waters contain silver, albeit in quite small amounts. Compared to freshwater, seawater has less harmful levels of silver nitrate.[5]

## 2.3 Chemical properties

Silver is an extremely inert metal. Normal conditions prevent it from reacting with airborne oxygen. With sulfur compounds in the air, it does react slowly. Silver sulfide, or Ag 2 S, is the dark chemical that results from this reaction. Silver sulfide is the tarnish that appears on cutlery and other items that are plated in silver over time. Water, acids, and a variety of other substances do not react well with silver. Except as silver powder, it doesn't burn. There are two isotopes of silver that occur naturally: silver-107 and silver-109. An element can exist in two or more forms as isotopes. Approximately sixteen radioactive silver isotopes are also known.[6]

Silver compounds are utilized by photographers to capture images. The primary source of silver emitted the surroundings is photographic materials. Another source are mines that produce silver and other metals. The phrase "silverware" refers to the expensive tableware and utensils that are made of silver, which is also used as a precious metal that is prized for its lengthy history. Silver is also used as an investment in the form of coins and bullion.

## 2.4 Environmental Effects of Silver

There are various terms for silver that is soluble in water and remains free of atoms when in solution, such as hydrate silver ion, ionic silver, and free silver. The most hazardous type of silver is usually the free form. The rules governing the release of silver compounds are based on this toxicity. Some silver compounds emit ionic silver very slowly because of their limited solubility (like silver sulfide) or composition (like silver thiosulfate).

When it comes to aquatic organisms, these substances are more than 15,000 times less harmful than silver nitrate. Long-term effects on organisms are unlikely due to silver's propensity to create nearly insoluble compounds in natural streams and sediments.

Up to 2g of concentrations (0.070 ounce) of soluble silver salts, particularly AgNO3, are fatal.Agiriia, or blue-black skin pigmentation, is caused by the gradual absorption of silver compounds by human tissues. Skin, eyes, throats, and lungs may become irritated by liquid or mist. Intentional misuse of this product, such as concentrating and breathing its contents on purpose, can be lethal.

On the recovery of metallic silver from solutions containing silver ions, a great deal of study has been done and documented in the literature. Electrolytic techniques are often better than solely chemical techniques, according to a review of the literature.

- Weiner[7], describes a procedure for producing brilliant silver electrodeposits from a solution containing 40 grams of silver (as silver chloride), 170 grams of sodium thiosulfate crystals, 20 grams of sodium bisulfite, and 50 grams of sodium sulfate per liter at a current density of 0.3 to 0.5 amperes per square decimeter. Silver thiosulfate complexes are prevented from decomposing oxidatively by sodium bisulfite, and the anode's solution is facilitated by sodium sulfate.[7]

- Kare Heiberg [8]
  - Faraday's first law states that the amount of metal deposited at the cathodes is proportionate to the current flowing through the bath. This is true, at least in part, when fixing bath is utilized as the electrolyte. Conversely, electrodeposition experiences impart that there is a relationship between the electrolyte's metal content and the maximum current density that may be employed safely; in general, a higher metal concentration allows for a higher current density and faster rate of deposition.

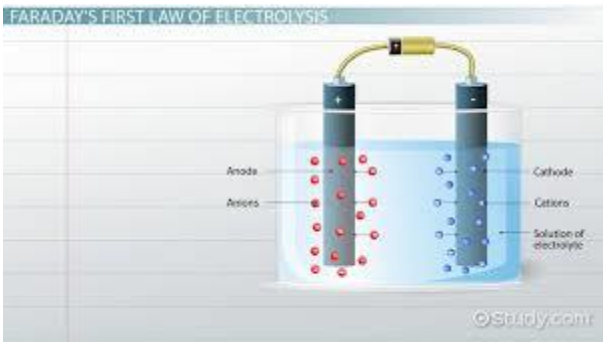



**Figure 2 Faradays Law**

- One square meter. About 20 grams of silver are present in the unprocessed film in the form of silver halides; of these, 4-5 grams are reduced to metallic silver in the developer to generate the image, and the remaining 15 grams are dissolved in the fixing bath. Nevertheless, the silver can be recovered by electrolysis as highly pure metallic silver, and the fixing bath will continue to have its fixing qualities longer if this technique is used while the fixing bath is being used.

- When the fixing solution has silver content of two to three grams per liter, it is a good idea to begin silver recovery and then work to maintain this level of silver content. There is no chance that the silver concentration will fall below the essential limit in a single night and cause an undesired breakdown if it stays above 2 grams per liter. The fixing bath has a silver concentration of roughly 2.5 grams per liter when it is used up 1/3 of the way to its limit. We are already beginning the recovery of silver.[8]
- When using electrolytical units, the size of a unit needs to be calculated based on the amount of silver that dissolves on a daily average in the fixing bath. This means that 1 sq. m. of film leaves 15 grams of silver in the bath. One ampere hour will deposit 4.024 grams of silver under ideal deposition conditions (100% efficiency). When fixing bath is used as the electrolyte, we typically get between 80 and 85 percent current efficiency. A current efficiency of 80% means that 3.2 grams will be deposited in an hour at 1 amp. It takes 15: 3.2 = 4.6 ampere hours to deposit 15 grams. In 18 hours, that equates to roughly 250 milliamperes. The fixing solution wastes some silver, so it is best to calculate 200 m.A. The silver content of the

solution shouldn't be allowed to diminish; it is safer if it rises gradually. 200 m.A. is equivalent to 20 sq.dm. when calculating the cathode surface at 10 m.A. per sq.dm.

- We have been utilizing a 16 x 30 cm zinc plate as the anode, or a carbon stick if an external current source is being used. This unit has been running at 1 ampere, corresponding to 12 m.A. per sq.dm. (At 14 m.A. per sq.dm. the cathodes turn dark). This unit has been in action 18 hours of the twenty-four and has produced about 1.5 kg. silver per month. The concentration of the fixing bath has been'restored by addition of dry fixing salt to spec. grav. 1.17 once after 8 to 10 days' use, and the pH has been kept below 6 by addition of potassium metabisulphite. The fixing bath has been in use 2-3 weeks. Without regeneration it can be used 1 week.[8]
- When an electrical current is transferred between two un corrodible electrodes (a carbon anode and a platinum cathode) immersed in a water solution of a metallic salt, oxygen gas is generally evolved at the anode and At the cathode, the metal is deposited. Depending on the conditions, the metal may be powdery, crystalline, dull or bright, loose or adherent. If, however, a current of normal plating density is passed through a thiosulfate solution containing silver, no gases are evolved, both the oxygen and hydrogen being absorbed by the solution. In general, tetrathionates are liberated at the anode and a black deposit of silver sulfide at the cathode[9].
- A study of Mellor's discussion of thionic acids [10] exposes that the presence of hydrogen sulfide, sulfur dioxide, thiosulfate, the four thionic acids, sulfite, hydrosulfurous, and sulfoxylic acids can all be found in a basic thiosulfate solution exposed to air. When a silver-containing thiosulfate solution is electrolyzed under standard laboratory conditions, the complicated situation leads to the creation of colloidal silver sulfide at the cathode. [10]

## 2.5 The photographic waste

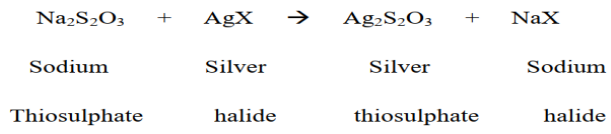
Photographic waste is the waste that is generated by the photographic processing machinery used in the paper and printing industries. One of the photographic wastes produced by medical facilities and biochemical laboratories is X-ray film. Photographic waste contains silver that serves as the primary medium for image transfer. It has a lower concentration of silver sulfite and soluble silver thiosulfate complex. Most photographic processes focus on the light-sensitive characteristics of silver compounds, which also serve as the foundation for the majority of trash generated. Because of their severe toxicity, these molecules, like those of many other heavy

metals, are classified as special wastes. The cost of producing silver has increased dramatically, and the price of silver on the market has been rising significantly along with the decline of natural silver supplies. Every nation has concentrated on recovering silver from garbage that contains silver. [11].

### 2.6 Formation of photographic waste

Much of the waste generated in photography can be related to the light-sensitive qualities of silver compounds, which are also necessary to most photographic processes. In addition to being categorized as special wastes, they share many other heavy metal compounds' high toxicity. Recycling has long had a financial foundation thanks to the high value of silver.

The fixer solution, or sodium thiosulfate solution, is the primary component of photographic waste. Fixer solution is used to wash out the silver halides from used photographic films and paper. Following its usage in washing, silver thiosulfate is the primary ingredient in the fixer solution. The reaction is




Since the fixer solution is no longer useful, it is seen as waste. Additionally, after processing and washing, photographic films that contain a trace quantity of silver can be collected and used as waste.

### 2.7 Silver in Photographic Waste

The "fix" (diluted aqueous Na2s203/NaHSO3) and "bleach-fix" (diluted aqueous Na2S203/NHS03/NaFeEDTA) solutions are the main sources of silver that can be recovered from photographic processing solutions. [12]. Silver thiosulfate is present in many photographic and x-ray waste materials. Because they exhibit toxicity, wastes with a silver concentration of 5.0 parts per million (ppm) or above are dangerous. Waste that generally has amounts of silver above 5 parts per million (ppm) includes:

- A fixer solution
- After a water bath, rinse the water.
- Film, negative, and paper;
- Solution from development tanks cleaned (precipitated silver is dissolved by cleaner)

Silver halides embedded in a coating of gelatin are used as light-sensitive agents in photographic films and sheets. 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. The photographic and x-ray wastes have to manage well to prevent harm to human health and the environment [13].

## 2.8 The photographic process

**General processes are:-**

Exposure ⟶ Developer ⟶ Stop Bath ⟶ Fixer ⟶ Color Vs Black & white process ⟶ Bleaching ⟶ Bleach-Fixes ⟶ Washes ⟶ Stabilizers Solution Cary over & Replenishment

### 2.8.1 Exposure

A photographic material consists of a base made of a sheet of plastic film, glass, or paper coated with a photographic emulsion (consisting of a polymeric material such as gelatin containing numerous fine crystals of light-sensitive silver halide). Silver halides used in photographic emulsions include silver bromide, silver chloride, silver iodide, or mixtures of these. Exposure of this photographic emulsion to light results in the formation of a “latent image”.

In simplified terms, light striking molecules of silver halide (AgX) in the emulsion causes some of them to be reduced to metallic silver (Ag0) atoms.
This can be represented by the following simplified equation:

$$\mathbf{AgX + Light \longrightarrow Ag^{\circ} + X_2}$$

**(Silver halide) (metallic silver latent image) (dielectronic halide)**

This latent image is invisible to the naked eye, because it consists of only a minute portion of the total amount of silver halide available in the emulsion. The number of atoms converted to silver depends on the intensity of the light and the duration (time) of exposure, as well as several other factors not discussed here.

### 2.8.2 Development

In order to be useful, this nearly invisible latent image must be enhanced or "amplified" by converting other surrounding silver halide molecules to silver metal, until the metallic image becomes fully visible. This is done chemically by a process step known as development. The latent image is developed by immersing the emulsion into a solution (the developer) containing a mild chemical reducing agent (the developing agent) in water, usually at an alkaline pH. The developer may include other ingredients added to enhance the process. A chemical reaction takes place in which the developing agent furnishes an electron (e2) to reduce the silver halide molecule (AgX) to a metallic silver atom (Ag0), releasing halide ion (X2) in the process. The reaction describing this step can be summarized as follows:

$$\underset{\text{(silver halide surrounding latent image)}}{AgX} + \underset{\text{(electron from developer)}}{e^-} \rightarrow \underset{\text{(metallic silver image)}}{Ag^0} + \underset{\text{(free halide ion)}}{X^-} \qquad \text{eqn 3}$$

This chemical reduction proceeds as an autocatalytic chain reaction, enhanced or catalyzed by the presence of already formed metallic silver atoms. Thus, the silver halide molecules in the immediate vicinity of the latent image react more quickly than those that are farther away. Those sites in the latent image that were originally exposed to the most intense light will contain the largest concentration of metallic silver atoms.

Therefore, development will proceed faster around these areas than around other locations where weaker light had exposed fewer silver atoms. The chain reaction thus proceeds at different rates within the silver halide crystal and among crystals, producing groups of dark metallic silver "grains," with the groupings sized roughly in proportion to the amount of light that struck the area. If the emulsion were allowed to remain in the developer for a long time, eventually the reaction would proceed to completion and all the silver halide crystals would be reduced to metallic silver, leaving a fully developed black surface.

Thus, time of development is an important factor in this step, with time (among other factors) being carefully controlled to yield a photographic image of a desired "density," "contrast," "grain," "sharpness," "resolution" and other characteristics that are discussed further in most standard photographic texts.

Another very important factor is developer temperature. As the temperature is increased, a silver image is produced in a shorter time, but may have less sharpness and contrast than if the reaction were conducted at a lower temperature.

Other factors influencing the results include pH, the measure of acidity or alkalinity of a solution (developers are usually strongly alkaline, in a pH range of 9–12); strength of the developer solution, with more dilute solutions producing finer developed silver particles (i.e., less grain) but at a slower rate; the type of emulsion used (emulsions have varying thickness and are often combined in multiple layers, with each layer containing various additives to modify the process and achieve certain desired results); agitation or mixing (to remove unwanted development byproducts from the emulsion and allow fresh developer to access the silver halide crystals); and other factors.

In the real world of the photo processing laboratory, developer stability is an important factor. Because the developing agent is a chemical reducing agent, it is easily oxidized by oxidizing agents, including air, and must be protected. Thus, certain advantages one could gain by running the process one way may be traded off for other advantages gained by operating it under slightly modified conditions.

A chemical known as a preservative, usually sodium sulfite, is added to protect the developer from unwanted aerial oxidation; it does this by sacrificing itself and being oxidized instead, generally to sulfate. This is summarized by the reaction equation

$$SO_3^{2-} + \tfrac{1}{2}O_2 \longrightarrow SO_4^{2-} \qquad \text{eqn 4}$$

**(Sulfite ion) (Oxygen from air) (Sulfate ion)**

During development, unwanted byproducts form in the developer that gradually decrease the activity of the developing agent and begin to retard development. One of these is the free halide ion (chloride, bromide, or iodide) that is released to the solution when the developer converts the silver halide to metallic silver. Another is the oxidized (used) developing agent itself. When it reduces (i.e., gives up an electron to) the silver halide molecule, it in turn becomes oxidized (i.e., it has lost an electron).

Thus, it can no longer enter into the development reaction and, in the case of black and white developer, becomes a useless, less-soluble molecule that impedes the action of its unused

neighboring developer molecules. It can also form an objectionable brown scum or stain on the surface of the emulsion.

Fortunately, a rapid chemical reaction occurs between the oxidized developing agent and the sulfite preservative to produce a sulfonated form of the spent developing agent that is less reactive and more soluble in water.

This helps prevent stain or scum formation on the emulsion by keeping the spent developer in solution, and also helps reduce interference with the unused developing agent. At some point in the development cycle, the amount of spent reaction products could build up to a point where they would begin to seriously interfere with developer activity if not controlled. This buildup of unwanted development products has historically been remedied by discarding a portion of the solution and reconstituting the remainder with fresh developer (known as "replenishment"). In order to produce the highest quality result with the desired characteristics in the final developed image, it is necessary to be able to stop the development reaction quickly.

This can be done in one of several ways: quickly lowering the pH, rapidly reducing the concentration of developer, or abruptly decreasing the temperature to a low value (the latter way is usually not practical, too expensive, and therefore generally not used). pH and developer concentration can be lowered in one of two ways: with the use of an acid solution (in either an appropriately named stop bath or an acidic fixer), or by dilution with water (which is generally not as sudden or precise) using a water wash.

### 2.8.3 Stop Bath

The stop bath (or "stop") is generally an organic acid in water. Acetic acid is used most of the time because it is relatively inexpensive, nontoxic, commercially available, and has good buffering capability (i.e., the ability to remain at a relatively fixed acidic pH even though a certain amount of alkali may be added to it). As described above, it stops the action of the developing agent when the film is immersed in this bath. Today the stop bath is frequently combined with the next solution in the process, the fixer, to form a fixer in the pH range 4–6 (sometimes known as "acid fix") that combines the action of stopping development with that of fixing, described next. This economizes on the number of separate steps and, correspondingly, the number of processing tanks or trays needed to process the emulsion.

### 2.8.4 Fixing

After the latent silver halide image has been developed into a metallic silver image, the remainder of the emulsion still contains undeveloped silver halide. Because this is an opaque, pinkish-to-grayish material that will not pass light (and will eventually turn into metallic silver if exposed to light or heat for too long a time), it must be removed from the emulsion. The fixer is a solvent that will selectively dissolve silver halide molecules from the emulsion while leaving adjacent metallic silver atoms relatively untouched. It is generally composed of thiosulfate, $S_2O_3$ (usually the sodium, potassium, or ammonium salt, depending on certain processing considerations).

Fixer is also sometimes known in the photographic trade as “hypo,” an abbreviated version of “hyposulfite,” the now obsolete chemical term for thiosulfate. This is an inexpensive, nontoxic, commercially available, quick-acting solubilizing agent (also known as a “complexing agent” or “sequestrant,” because it tends to form a stable chemical complex with the metal ion it dissolves). The thiosulfate fixer dissolves the unused silver halide from the emulsion, forming a tightly bound silver thiosulfate complex, $Ag(S_2O_3)$. This is a stable, Treatment of Photographic Processing Wastes water-soluble chemical complex that has very low toxicity compared to free silver ion (Ag); thus, it is relatively safe for photographic personnel to handle and does not create toxicity problems if discharged to a sewer for biological treatment.

### 2.8.5 Colour versus Black and White Processes

The above description adequately portrays the typical black and white negative process, in which the final desired image is a black metallic silver image on a transparent or white background. Color processes follow approximately the same steps, but with some important variations. A black and white developing agent is a mild reducing agent, usually a rather simple organic molecule like hydroquinone, which has no further value to the photographic process once it has become spent (oxidized) in developing the silver atom. In contrast, the color developing agent is a more complicated molecule, usually a para-phenylenediamine-based compound, which comprises one-half of a dye-forming molecule.

The emulsion of a color film or paper is also more complex than its black and white counterpart. In addition to the profusion of fine silver halide crystals, the gelatin matrix also contains a

dispersion of tiny globules of the other half of the dye-forming molecule, known as the "coupling agent" or coupler. Whereas the developer half of the final dye molecule is always the same regardless of color, the coupler half of the molecule is a different type of compound, depending on the particular color (cyan, magenta, or yellow) to be formed in that emulsion layer. When the color developing agent reduces the silver halide molecule (AgX) to metallic silver (Ag°) by supplying an electron ($e^2$), it in turn becomes oxidized by losing an electron, as described above. However, instead of becoming a waste product as in the case of the black and white developing agent, the oxidized color developing agent now seeks to join up (couple) with the nearest coupler molecule, to form a dye. This dye, being a large bulky molecule and relatively insoluble in water, has no tendency to migrate from its position in the matrix but remains in place. Thus, the image at this point consists of tiny globules of dye sharing space with clusters of developed silver grains, with both surrounded by a dispersion of transparent, unused coupler globules and undeveloped silver halide crystals in a gelatin matrix. The reactions can be described as follows:

$$\underset{\text{(silver halide surrounding latent image)}}{AgX} + \underset{\text{(electron from developer)}}{e^-} \longrightarrow \underset{\text{(metallic silver image)}}{Ag^0} + \underset{\text{(free halide ion)}}{X^-}$$

$$\text{Color developing agent} - \underset{\text{(electron lost to silver)}}{e^-} \longrightarrow \text{Oxidized color developing agent}$$

$$\text{Oxidized color developing agent} + \text{Coupler} \longrightarrow \text{Colored dye image} \qquad \text{eqn 5}$$

The emulsion now contains both developed metallic silver and undeveloped silver halide, neither of which is wanted in the final product. Fixing at this point would remove only the silver halide but not the silver metal. Thus, it is necessary to convert the silver metal back to silver halide before both can be satisfactorily dissolved from the emulsion by the same fixing step.

### 2.8.6 Bleaching

The conversion of silver metal back to silver halide is accomplished by using a mild oxidizing agent known as a bleaching agent together with a water-soluble halide salt, such as potassium bromide, in a water solution. Together these are known as photographic bleach. The bleaching agent is mild enough to not adversely affect the gelatin or dye in the emulsion, yet strong enough to take electrons from the silver metal in the presence of the halide, thus converting the silver back to silver halide.

Typically, iron complexes such as iron EDTA (ethylene-diamine tetraacetic acid), iron PDTA (propylene-diamine tetraacetic acid) or less commonly ferricyanide [$Fe(CN)_6$ ] are used since

they can supply the proper bleaching activity without harming the emulsion. These are all relatively nontoxic salts that are cheap, commercially available, and safe to handle. Two are commonly used in food products: EDTA is found in bread, baked goods, and pharmaceuticals whereas ferricyanide is used to prevent table salt and foods from caking and as a blue pigment in cosmetics, inks, and paints [14]. Ferricyanide was formerly the photographic bleaching agent of choice because it was relatively easy to recover and reuse, but was largely removed from the marketplace because of public concern over the word "cyanide." However, ferrocyanide, or hexacyanoferrate, is an extremely stable, complex iron salt with very low toxicity compared to simple cyanide.

The reaction between the bleach and the metallic silver halide can be described in simplified fashion as:

$$\underset{\text{(ferric iron salt)}}{Fe^{3+}} + \underset{\text{(metallic silver)}}{Ag^{0}} + \underset{\text{(halide ion)}}{X^{-}} \longrightarrow \underset{\text{(silver halide)}}{AgX} + \underset{\text{(ferrous iron salt)}}{Fe^{2+}} \qquad \text{eqn 6}$$

After the metallic silver is converted back to silver halide, the entire emulsion can be fixed to remove all the silver, leaving only an image of finely divided colored dye globules in a transparent matrix.

### 2.8.7 Bleach-Fixes

In some processes, particularly paper processes, which are more easily bleached than film processes, the bleach and fixer, can be combined into a single solution known as bleach-fix (also commonly known in trade jargon as a "blix" or a "bleach-fixer"). Some chemical synergy is achieved by mixing the two solutions; therefore, the concentration of each can be lowered slightly to achieve the same photographic effect. The gentle oxidizing action of the bleach component is insufficient to damage the fixer component; therefore, they are able to survive together for a reasonable period of time in a single solution.

This single solution saves time in processing and simplifies the processing machine. It may also save money in shipping processing chemicals and may produce environmental benefits since it may result in less chemical usage. Bleach-fixes were first introduced commercially in the late 1960s for color paper, specifically for their environmental features as well as reduced processing steps. They remain as a predominant processing solution in color print processes today.

### 2.8.8 Washes

Before finally drying a photographic emulsion, residual chemicals from processing solutions and reaction byproducts must be eliminated to avoid future interactions that would limit the life of the product. In conventional processing, a final water wash is most often used for both color and black and white products. Also, at certain critical junctures in various processes, it may be desirable to introduce an intermediate wash to remove residual chemicals and/or alter the pH or chemical balance before entering the next solution. Water washes generally contain much lower concentrations of the same chemicals found in the preceding tank.

In the past, all water washes were usually discarded. In more recent years, because of environmental and energy concerns as well as economic considerations, many schemes for purifying and reusing wash waters were proposed and in some cases were successfully implemented to accomplish at least partial recycling and reuse. In some of these cases, when an additional chemical was needed to treat the water or rejuvenate a purification bed, disposal of the treatment chemical may have posed a separate problem. However, water conservation techniques such as countercurrent washes, and mechanical devices known as “water savers” to turn off the water when it is not needed; have generally been shown through practical experience to be much more economical and environmentally beneficial than more complicated recovery techniques.

### 2.8.9 Stabilizers

Historically, at the end of the process, the gelatin emulsion, having undergone a series of swelling and shrinking cycles as it passed from one processing solution to another, may have lost some of the hardness and physical strength it originally had, which could make it susceptible to scratching or damage. Also, some of the newly formed dyes in the emulsion needed to be further chemically protected against aging and light fading. Both of these tasks can be performed by treating the emulsion with a stabilizer, usually the last solution in a color process.

However, through the use of modern fore hardened emulsions and other chemical modifications, a number of newer processes have been reformulated to eliminate the need for an emulsion hardening agent in stabilizers. Currently many processes are designed to save or eliminate water. “Washless minilab” processes are intended to provide processing for a customer in 1 hour or less, and may be located in department store, drugstore, or storefront locations not having

sewers. Increasingly, such processes are also being found in professional and commercial photography houses.

In these cases the stabilizer may also serve the function of a wash, by eliminating residual chemicals in the emulsion prior to the drying step, which is necessary for image stability upon long-term keeping. Throughout much of the history of color films and papers, the most common and effective stabilizer was a water solution of formaldehyde, sometimes containing additional ingredients such as citric acid. However, in recent years, because of heightened medical concerns over the handling of formaldehyde plus its annoying lachrymatory odor, most processes today use alternative materials.

### 2.8.10 Solution Carryover and Replenishment

If each of the above steps could be carried out under ideal, pristine conditions, there would be few unwanted reactions or byproducts and therefore waste would be minimal. Unfortunately, in actual practice this is not the case. Oxygen from the air is the primary cause of unwanted reactions. It slowly oxidizes components such as the developing agent and fixer upon long-term standing or solution agitation, both of which tend to promote dissolving of air, and during attempts to reuse solutions or recover silver. As previously mentioned, this oxidation necessitates adding preservatives such as sulfite and other ingredients needed to counter the effects of oxidation. These preservatives are also eventually consumed by oxidation, thereby forming byproducts of their own. Solution carryover is the second major cause of chemical loss, since a solution is carried on the surface and within the saturated emulsion from one tank to the next, thereby losing the solution from the first tank and contaminating the second. To protect against the undesirable effects of contamination, each succeeding solution must be chemically bolstered to contain more of the active ingredient than might be needed strictly to react with components in the film or paper, if carryover did not occur.

## 2.9 Photo processing effluent

The photo processing industry is very diverse. It includes photofinishing laboratories, x-ray processing at medical and dental facilities and industrial sites, professional photographic operations, motion picture laboratories, processing systems for scientific uses such as astronomy and geology, aerial mapmaking and satellite photography, microfilm processors, graphic arts

operations, and others. Photographic effluents vary in composition because there are many different types of photographic processes and no two processing laboratories operate in the same manner. Processing laboratories vary greatly in size, wash water usage, daily operating time, volume of effluent, and the use of chemical recovery systems. The actual effluent characteristics for any photographic processing laboratory can best be determined by collecting a representative sample of the photo-processing wastewater and having it analyzed by a certified analytical laboratory. However, although concentrations will vary, the effluent from most photo-processing laboratories will generally be quite similar in chemical composition. It is not within the scope of this section to provide the actual processing effluent characteristics of every photographic process.

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 [11].

## 2.10 Silver Recovery Methods

In fixers, thiosulfate (hypo) is used to fix the image by converting the undeveloped, insoluble silver halide to a soluble complex. This soluble complex diffuses out of the Emulsion into the fixer. Halides [X = bromide or chloride ion) also diffuse from the film.

$$AgX + 2[S_2O_3]^{-2} - Ag\,[s_2o_3]_2^{-3} + x- \qquad \text{eqn 7}$$

As the fixer is used, it becomes a very complex mixture. In addition to its original Components, a used fixer contains Ferro cyanide, sodium sulfate, sodium bromide, sodium chloride, gelatin, complex silver salts, and varying amounts of practically all the chemicals used in processing.

Therefore, any method of silver recovery has to make allowances for these interfering Substances. Fortunately, silver is far removed in the electromotive series from any other Metallic ion in the solution. Most silver recovery methods take advantage of this fact. If silver is continuously recovered, the fixer can be reused until the halides, Ferro cyanide, etc., build up to concentrations high enough to retard fixing. Usually, enough fixer over low is discarded to prevent this from occurring.

The most common silver recovery method from fixer is electrolytic. An electrolytic method is fundamentally an electroplating process in which the silver in the fixer is deposited on a set of stainless steel plates that serve as the Cathode in an electrolytic cell. The primary cathode reaction is a reduction of complex Silver into silver. The thiosulfate is released from the complex to react with other silver ions. The cathode is removed from the cell periodically to strip off the plated silver.

This Technique has the advantage of being clean, allowing reuse of the fixer, and yielding silver metal with a high degree of purity (90-99 percent). The most effective method of recovery of silver from fixer wash waters or dilute fixers is by using ion-exchange resins [15]Silver from photo processing operations is much less toxic than free silver ion. Silver is generally removed from photographic products during processing in the form of silver thiosulfate complex, $Ag(S_2O_3)$. This complex has a dissociation constant of thus, it is virtually impossible for free silver ion (Ag) to be present at any significant concentration levels in photo processing effluents. In black and white products, because the final image is metallic silver, the amount of silver removed during processing will depend on the amount of exposed image area. In color products, processing removes essentially all the silver from the emulsion. Although primarily found in fixers and bleach-fixes, small quantities of silver will also have seasoned the developer and bleach, and some will be carried over into solutions following the fixer or bleach-fix. (In modern minilabs, the stabilizers or final rinses often contain approximately 25% of the silver available for recovery.

The most commonly used **silver recovery methods** will be discussed in detail below.

### 2.10.1 Electrolytic Methods

In the process of electrolysis, or 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. In a simultaneous reaction at the anode, an electron is taken from some species in solution. In most silver-rich solutions, this electron usually comes from sulfite.

An overview of the reactions is

**Cathode:**

$$Ag(S_2O_3)_2^{-3} + e^- \longrightarrow Ag^\circ + 2(S_2O_3)^{-2} \text{ or}$$

Silver thiosulfate complex + electron ⟶ metallic silver+ thiosulfate eqn 8

**Anode**

$$SO_3^{-2} + H_2O \longrightarrow SO_4^{-2} + 2H^+ + 2e^- \text{ or}$$

***Sulfite+ water ⟶ sulfate + hydrogen ions + electrons*** eqn 9

*2.10.1.1* Electrolytic silver recovery

Electrolysis, or more specifically electro winning, is the most widely used and universally applicable method for silver recovery in the photo processing industry. An electrolytic silver recovery cell consists of a cathode and an anode. Oxidation occurs at the anode (positive electrode) and reduction at the cathode (negative electrode). Silver deposits on the cathode during electrolysis when a direct current is passed through the silver-bearing photo processing solution. After sufficient silver has been plated, the cathode is removed from the system and the silver stripped off (91,92). The primary reaction occurring at the cathode is:-

$$Ag(S_2O_3)_2^{3-} + e^- \longrightarrow Ag^\circ + 2S_2O_3^{2-} \quad \text{eqn 10}$$

If the cathode voltage is allowed to become too high, thiosulfate could be reduced at the cathode as shown in the following equation:

$$S_2O_3^{2-} + 8e^- + 8H^+ \longrightarrow -2HS^- + 3H_2O \quad \text{eqn 11}$$

The production of sulfide is undesirable, because it will react with the silver complex to produce insoluble silver sulfide (known as “sulfiding”). Although from a recovery standpoint a small amount of silver sulfide can be tolerated, too high a level will result in a poor plate [93]. Additionally, if in-line fixer desilvering were being done, silver sulfide formation would contaminate the fixer and could damage the photographic product. Therefore, it is necessary to

compromise on the voltage applied, to obtain optimum current efficiency while minimizing sulfide production.

Electrolytic silver recovery requires a larger capital expenditure than the use of MRCs and also necessitates an electrical connection. However, it has the advantage of yielding nearly pure silver, resulting in lower refining and shipping costs. A primary advantage from an environmental viewpoint is that it allows fixer reuse for many processes because it does not contaminate the fixer when properly controlled.

There are essentially two ways in which electrolytic silver recovery can be applied [92]. One involves its use in a terminal manner, and one concerns its application for the in-line desilvering of fixer. When used in a terminal manner, the silver-bearing solution is passed through the electrolytic cell to recover the silver and the desilvered solution is slowly discharged to the drain, perhaps through a secondary metallic replacement cartridge or using chemical precipitation for additional low-level silver recovery. An alternate terminal approach is to mix the electrolytically desilvered solution with silver-containing wash waters and pass the mixture through an ion-exchange system for further silver recovery.

Finally, part of the desilvered fixer or bleach-fix, if not mixed with other solutions or otherwise contaminated or altered during silver recovery, may be reused in making fresh replenisher, thus minimizing the environmental impact.

It is also possible to operate electrolytic equipment for the in-line desilvering of the fixer solution. Although careful control is essential to preclude the formation of silver sulfide, this method offers several environmental benefits. Additionally, the lower silver level in the tank means that significantly less silver (only about 5–10% as much) will carry over to the washwaters, thus assuring that, overall, more silver is recovered and less is lost.

Several factors are involved in choosing and operating an electrolytic silver recovery unit.

The amount of current that a device delivers is important: low current density units can be used for desilvering fixers, but high current density is needed for bleach-fixes. Some method of agitation is required to keep the fresh silver-containing fixer in contact with the cathode, but too much turbulence that produces a vortex will whip air into the solution, consuming sulfite

preservative and promoting sulfiding. A rotating cathode unit provides its own agitation, whereas a pump or impeller may be needed for a stationary cathode.

Some method for controlling the current is also important. Several methods are available, including timers, selective ion electrodes for online monitoring, and constant voltage operation including the more complicated use of potentiostatic control with IR (voltage) compensation.

The current density relative to the solution silver concentration should be high enough to desilver the solution in a reasonable time, yet low enough to prevent sulfiding. Well-designed controls step the current down in stages as silver is depleted from the solution.

In addition to the time, voltage, and current, pH is an important factor affecting electrolytic silver recovery. As the pH of the bleach-fix increases, a side reaction involving the reduction of iron is inhibited and the electrolytic silver-recovery efficiency increased.

Electrolysis produces nearly pure metallic silver, contaminated only slightly some Surface reactions that also take place. The plated silver should be greater than 90 percent Pure [16].

#### 2.10.1.2 Terminal Electrolysis

In solutions high in iron, such as bleach-fixes, the sliver plating proceeds more efficiently in a slightly alkaline state; In other words, at a higher pH. You may need to add sodium Hydroxide, sodium carbonate, or sodium bicarbonate. Do this in a well-ventilated area and do not exceed a pH of 8, as ammonia may be released.

The electrolytic recovery process is efficient and cost effective, utilizing reusable equipment and little or no chemical additions. The efficiency of the system is dependent among other things, on the availability of silver-rich solution at the cathode surface. In current commercial recovery equipment, this is accomplished in one of two ways

- ❖ The cathode is moved within the solution.

The most common application is the rotary cathode cell. The negative current is applied to a rotating drum in the solution and the silver plates onto the drum. Because of the high mass-transfer efficiency of electrolytic cells of this design, they can be used successfully to treat iron-rich bleach-fixes that are traditionally difficult to de-silver.

- ❖ The liquid is rapidly pumped over tie stationary cathode.

This design often tends to be somewhat less efficient than rotating cathode cells; however, these units usually require less maintenance. Electrolytic Silver recovery has its disadvantages. The

equipment can be relatively Expensive. Also, attempts to accelerate the recovery process, or to desilver to silver Concentrations below 200 mg/l-by extending the residence time in the cell or increasing the Current density (amperage/cathode surface area) on the cathode-will produce an inferior, black, crumbly silver sulfide- contaminated plate, which reduces the cell efficiency dramatically.

Bleach-fix solutions, In particular, should be adjusted to the alkaline PH range of 7.8 to 8.0 to prevent the iron complex from oxidizing and resolubilizing the plated silver. (You should not leave bleach-fix in a cell when it is turned off, Since the Solution may resolubilize or dissolve the silver off the cathode.). You can use electrolysis only as a primary treatment. Post-electrolysis silver concentrations are generally in the several hundred-milligram per- liter (ppm) range. If you must achieve a low regulatory limit, use some other type of secondary silver recovery such as metallic replacement or precipitation using TMT (tri-mercapto-s-triazine) [17]

#### 2.10.1.3 In-Line Electrolysis

In-line electrolytic fixer recirculation is used in some photographic processing facilities. With this technology, fixer is recirculated between the processing tank and a specially Designed electrolytic silver-recovery unit. Some of these units have electronic or sensors that automatically control the silver concentration in the recirculating solution, usually in the range of 750 to 1000mg/l. since the silver concentration in the fixer is significantly decrease; silver in the following wash tank is also reduced due to less silver ‘’carry-out’’ with the film or paper to the wash during processing.

#### 2.10.1.4 Metallic replacement process

Additional methods for silver recovery from photo processing solutions include electrolysising the silver to replace it with another metal, such as zinc, or precipitating it chemically using substances like sodium hydroxide or sodium sulfide. [21]. The fundamental method of metallic replacement is the conversion of the silver thiosulfate complex to elemental silver by metallic iron, which is typically found as "steel wool." Commercial recovery equipment is commonly referred to as Metallic Recovery Cartridges (MRCs) or Chemical Recovery Cartridges (CRCs). Fine steel wool is the most popular source of iron because of its large surface area. The steel wool is either broken up and placed into a cartridge, or it is twisted around a core. The solutions

rich in silver are gradually poured into the cartridge and pass through the iron layer. While the iron is taken out and solubilized by the solution, the silver remains in the cartridge. Similar to the electrolytic process, metallic replacement is a reduction oxidation process.

The ultimate concentration of silver is affected by various factors such as flow velocity, iron surface area, pH, contact time, initial silver concentration, thiosulfate concentration, and volume passing through the cartridge. It is possible to lower the silver concentration to less than 5 mg/l if the MRC is functioning well.

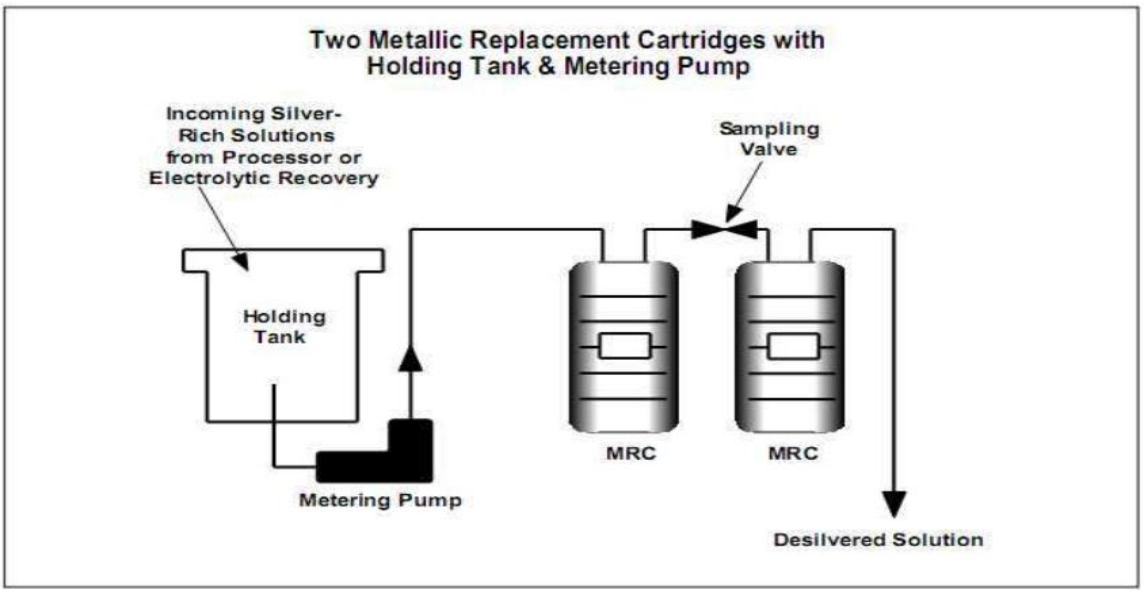



**Figure 3 Schematic diagram for metallic replacement process using MRCs**

Kodak states, "The majority of fixes fall within the pH (a measure of acidity) range for optimal steel wool use. The steel wool dissolves far too quickly at pH values below 4. When the pH level is above 6, the replacement reaction becomes extremely sluggish, leading to a prolonged reaction time and potential loss of silver [22]. Generally, a steel wool-filled cartridge is either filled with hypo or runs through it. Cartridges are packed and sent to refiners once they have gathered as much silver as they can.

The fixing bath is heavily iron-contaminated following the removal of the silver by metallic replacement. It needs to be thrown away because it is no longer useful for taking pictures.

Knowing how much solution goes through the cartridge, at what concentration of silver, and for how long is all that is necessary for system monitoring in this kind of situation. To find out

whether the system is operating correctly, all that is needed is a basic test paper that is utilized in a similar manner to a litmus paper. Usually, the company provides this exam paper.

## 2.11 Electrolysis process

There are two ways to achieve metal recovery by electrolysis from an aqueous solution of their salts. The first approach uses insoluble anodes to concentrate the appropriate metal from ores and then electrolyzes the solutions that are left over. The metal is refined electrolytically as part of the second technique[21]. A direct current is run between a positive electrode (the anode) and a negative electrode (the cathode) through a silver-rich solution in the electrolysis process, also referred to as electrolytic silver recovery[24] The positively charged silver receives an electron from the cathode during this electrolytic process, which changes it into a metallic form that sticks to the cathode.At the anode, a simultaneous reaction occurs where an electron is.

# 3. MATERIALS AND METHODS

## 3.1 Raw material collection preparation

Periodically and process-to-process, the amount of silver in the hypo/fixer solution fluctuates. Silver thiosulphate complex ions are created during the processing of photographic film when silver flakes into the fixer solution (sodium thiosulphate). This is metal displacement process; the silver concentration can be checked using 'silver estimation paper'.

## 3.2 Chemicals and instrumentation used

a) Chemicals
   - Photographic fixer waste collected from Berhan Ena Selame Printing Company
   - Distilled water for dilution.
   - Commercially available analytical grade NaOH for ph adjustment of waste fixer solution,
   - analytical grade Borax and sodium carbonate for refining of the final recovered silver,

b) The lab's tools and equipment contained the following:
   - Stainless steel
   - Silver estimation paper(difficult to find still)
   - Graphite
   - electrode holder (stand and clips)
   - direct current power supplier, wires with
   - Crocodile clips.
   - Motor with Stirrer
   - pH meter
   - Beakers, pipettes, burettes, desiccators, volumetric flasks, PH meters, analytical weigh balances with two-digit precision, filter paper watt man 540
   - Volumetric flask
   - Furnace

## 3.3 Methodology

Both the experiment runs' randomization and the proper analysis method using the right software Design expert 6.0.8 portal: Box-Behnken Design was used during this study statistical method of surface response methodology (SRM) was used for analyzing of laboratory result of silver

recovery. Based on how each parameter affected the outcomes, the amount of the variable used for the study was selected. Ph (4-8), current density (2-5), and time (20-90).17 different laboratory experiments were carried out within these specified ranges. ANOVA results, fitness graphs, and 3D graphs of operational parameters were examined using BBD (Box-Behnken Design) of RMS (Response Surface Methodology) and fit summery and also XRD analysis and XRF analysis.

## 3.4 Experimental procedures

To start the electrolysis process, we put the cathode and anode inside the electrolysis tank. Then we added the fixer waste in the tank connecting electricity on the current supplier. We started the process and we need to control the time by using timer. When the black flake of silver collects on the cathode and the time approaches the settled value, then we stopped the process and recycled the silver and desilvered fixer discharged to sewer.

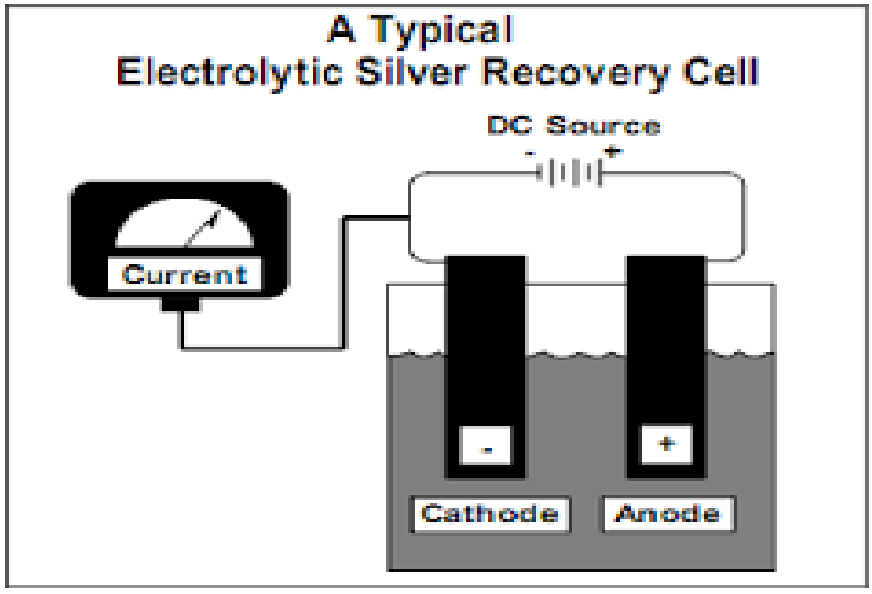



**Figure 4 A Typical silver recovery cells**

**Experimental procedure**

- Although electrolysis seems appealing in theory, I chose to investigate the usefulness of this strategy first. These are the actions I did and the outcomes I got.

**Steps**

1. Find out the silver concentration of the waste solution using silver estimation paper if we get this silver estimation paper.
2. Adjust pH value of the waste fixer solution at 4, 6 and 8 using 1M of NaOH solution then transferred to the Electrolytic tank.
3. Direct current was supplied according to the concentration of silver of the waste solution using the formula formulated using Faraday's law (the amount of Ag deposit = the current passed through it).
4. After some duration the DC power source turned off as a result the electrolysis process will be stopped.
5. The cathode was taken out from the electrolytic tank and the recovered silver was scraped using a scrapper then put in the crucible for further refining.
6. Equal amounts of borax and sodium carbonate were made and mixed with the scrapped silver in a 2:1 ratio prior to the scrapped silver being placed into the furnace. Due to the fact that sodium carbonate and borax, respectively, increased the sample's heat capacity and purity.
7. Following that, the mixture was placed inside the furnace using a graphite crucible, and the furnace's temperature was maintained at 9500C for 1:30 hours. In order to gather the pure silver, the melted black silver was finally put into the molder.

In laboratory describe in figure form**,**

1. Make sure the fixer solution PH ranges from 4, 6 and 8 respectively by using NAOH used for adjusting PH. Because the solution is acidic.




To make NAOH solution, we use 250 ml of water and add sodium hydroxide pellets 10g and mix very well.

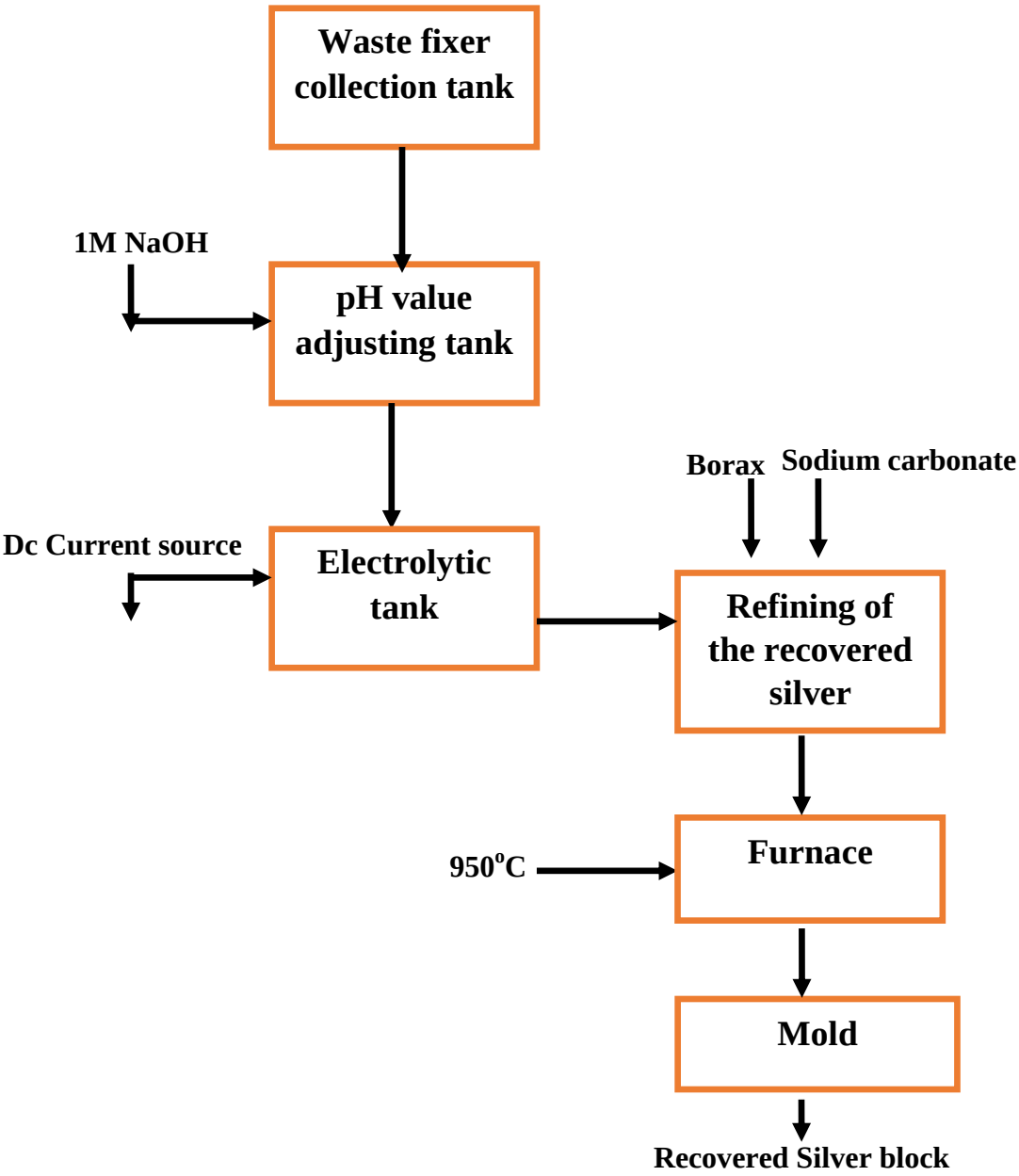
2. **First steps is adjust PH=4 by adding NAOH and mix it very well.**


3. **Then I am started the procedure as you see in the figure below.**

## 3.5 Electrolysis Process Description

To recover silver electrolytically, a solution rich in silver is poured over two electrodes. Nearly pure silver metal is deposited on the cathode, or negatively charged electrode, by electric current, which also decreases the silver thiosulfate complex in the solution. Stainless steel is commonly used for the cathode. Both the operating amperage and the duration of the solution's current exposure determine how much and what kind of silver plating is produced. The cathode rotates in the solution in the first type of electrolytic apparatus, and the solution circulates around a stationary cathode in the second type. An appreciable quantity of silver can be extracted from the silver-rich solutions using either kind of apparatus. Utilizing electrolytic units alone is not an option. [25]

**Experimental frame work.**



## 3.6 Experimental Factors and Responses

### 3.6.1 Study Factors:

The selection of the study factors was done by examining relevant literature, and preliminary tests were conducted to verify the selection. The parameters, their ranges, and their influence on the amount of silver recovered were noted during the preliminary studies. Consequently, there was no reason to move further this point.

The effects of the factors listed below on the amount of silver recovery and its purity studied.

- Current density
- pH of waste fixer solution
- time

### 3.6.2 Experiment for current density determination

The selected current density was supplied based on the silver concentration using Frady's law. One ampere hour of deposition will deposit 4.024 grams of silver under ideal circumstances. When fixing bath is used as the electrolyte, we typically get between 80 and 85 percent current efficiency. When 80% current efficiency is calculated, 1 amp hour will deposit 3.2 grams.

To apply different current density we use the next steps formulated based on the faradays law.

a) Determining the current needed in ampere hour.

$$\textbf{Current supply (ampere hour)} = \frac{\textbf{Silver concentration } (\frac{\textbf{g}}{\textbf{l}})}{\textbf{3.2}} \qquad \text{eqn 13}$$

b) fixing the electrolysis time using the ampere hour required

$$\textbf{Current supply (milliamper)} = \frac{\textbf{Current supply (ampere hour)}}{\textbf{electrolysis time(hour)}} \qquad \text{eqn 14}$$

c) cathode surface determination based on the required current density

$$\textbf{Cathod surface (sq.dm)} = \frac{\textbf{Current supply (milliampere)}}{\textbf{current density supply}(\frac{\textbf{milliamper}}{\textbf{sq.dm}})} \qquad \text{eqn 15}$$

So using the above formula adjusts and supplies the required current density. So based on the literature three current density are selected and supplied on the electrolysis. These are 2A , 3.5A and 5A.

### 3.6.3 Experiment for pH value determination

The impact of pH on silver recovery efficiency was determined by changing the pH value of the waste fixer solution before electrolysis was performed. PH at 4, 6 and 8 are selected based on literatures. The pH value is adjusted using 1M NaOH diluted solution.

### 3.6.4 Experiment time determination of cathode

The effect of cathode time on the electrolytic silver recovery was determined by selecting three times, Based on literature time of cathode at 20, 55 and 90 min are selected.

So using the above experiment The 33 design was used to assess the three components versus the three levels (low [-1], medium [0], and high [+1]). A total of around (3*3*3 = 27) runs were completed, and analysis was performed to determine how the components interacted and how much silver was collected. Only 27 duplicated runs were completed despite the Response Surface Miscellaneous (RSM) design for three levels duplicating the central point five times, making the run 32. The lower, medium, and higher values from the above ranges were selected because there were only 27 duplicated runs with three levels completed. This was due to the fact that notable responses were only noted in cases where there was an obvious distinction between the lower and higher levels. It would be difficult to determine whether the reaction had increased or decreased if there was a greater difference between the lower and higher levels. As a result, the medium level had been taken into account to view the response profile.

## 3.7 Silver purity and Trace metal impurity determination

The purity of the recovered silver and any trace metal contaminants were assessed using the Ethiopian Geological Survey's DXRF Spectrometer (XRF). The most recent device to identify roughly 78 elements in a sample in the forms of ore, dirt, and bars is this one. Consequently, this device made it simple to identify purity and trace contaminants in recoveries of precious metals like gold and silver. Initially, the samples—which included ore, dirt, and bar—were placed on the analyzer's slide. The sample's detection area measured 8 mm in diameter and 15 mm in depth. Since the goal of this research is to recover valuable metals, the instrument software was configured to handle bar-shaped samples of precious metal.

## 3.8 Experimental design and interaction effect of parameter

It is crucial to look into the interaction effect of all three operational factors at once, after screening studies have been performed to identify the effects of each parameter separately

(current density, pH, and time). As a result, a statistical model was developed using a three-variable Box-Behnken design (BBD) for response surface methodology (RSM), and the suitable range of these parameters was determined using the data from the screening trials. The BBD can be utilized to investigate stable quadratic response surfaces, and this design can be applied to the construction of an optimization-useful second-degree polynomial model. By creating alternative order models to represent the data, it is a strategy that is frequently used to explain the behavior of experimental data. Statistical analyses were then performed to ascertain the model's correctness. With that particular set of operational settings, the model was further applied to optimize and attain the greatest feasible result. Its purpose was to provide information about possible interactions between the operating parameters. The fact that the variables are not changed one at a time while the others are kept constant gives Design of Experiment (DOE) a significant advantage over alternative methods. The amounts of each parameter on which this research focused were determined based on the preliminary experiments carried out, as indicated in this table.

**Table 1 Factors and the corresponding ranges and levels**

| Factor | unit | Level | | |
|---|---|---|---|---|
| | | Low(-1) | Medium(0) | High(+1) |
| Current density | Ampere | 2 | 3.5 | 5 |
| pH of waste fixer solution | | 4 | 6 | 8 |
| time of the cathode | Min | 20 | 55 | 90 |

A total of 17 runs were conducted with various combinations of time, pH and current density. For a three-factor system, as shown in table below,

**Table 2 Experimental design matrix of factor and label**

| Std | Run | Block | Factor 1 A:pH | Factor 2 B: current Density(A) | Factor 3 C:Time(min) | Response 1 Recovery solid (g) | Response 2 Recovery silver (g/250ml) |
|---|---|---|---|---|---|---|---|
| 16 | 1 | Block 1 | 6.00 | 3.50 | 55.00 | 4.23 | 3.17 |
| 6 | 2 | Block 1 | 8.00 | 3.50 | 20.00 | 3.15 | 1.78 |
| 15 | 3 | Block 1 | 6.00 | 3.50 | 55.00 | 4.14 | 3.17 |
| 12 | 4 | Block 1 | 6.00 | 5.00 | 90.00 | 5.01 | 3.85 |
| 11 | 5 | Block 1 | 6.00 | 2.00 | 90.00 | 4.07 | 3.14 |
| 2 | 6 | Block 1 | 8.00 | 2.00 | 55.00 | 3.44 | 2.53 |
| 5 | 7 | Block 1 | 4.00 | 3.50 | 20.00 | 3.25 | 2.12 |
| 10 | 8 | Block 1 | 6.00 | 5.00 | 20.00 | 4.21 | 2.88 |
| 9 | 9 | Block 1 | 6.00 | 2.00 | 20.00 | 3.45 | 2.25 |
| 8 | 10 | Block 1 | 8.00 | 3.50 | 90.00 | 3.56 | 2.76 |
| 1 | 11 | Block 1 | 4.00 | 2.00 | 55.00 | 4.09 | 2.85 |
| 4 | 12 | Block 1 | 8.00 | 5.00 | 55.00 | 4.65 | 2.98 |
| 17 | 13 | Block 1 | 6.00 | 3.50 | 55.00 | 4.3 | 3.06 |
| 3 | 14 | Block 1 | 4.00 | 5.00 | 55.00 | 4.16 | 3.62 |
| 13 | 15 | Block 1 | 6.00 | 3.50 | 55.00 | 4.44 | 3.54 |
| 14 | 16 | Block 1 | 6.00 | 3.50 | 55.00 | 4.68 | 3.35 |
| 7 | 17 | Block 1 | 4.00 | 3.50 | 90.00 | 3.99 | 3.13 |

# 4. RESULTS AND DISCUSSION

## 4.1 XRD Analysis

An effective technique for studying nanomaterials (materials with structural characteristics of at least one dimension in the range of 1-100 nm) is X-ray diffraction (XRD). Since X-rays have an atomic-scale wavelength, X-ray diffraction (XRD) is a key technique for examining the structure of nanomaterials.

The XRD pattern of the silver recovered from fixer waste showed the presence of a single phase, face-centered cubic (fcc) silver. The average grain size of the silver was calculated to be 20 nm using the Scherrer equation.

The XRD results indicate that the silver recovered from fixer waste is of high purity and has a nanocrystalline structure. Nanocrystalline silver has a high surface-to-volume ratio, which makes it more reactive and suitable for applications such as catalysis and water purification.

The formation of nanocrystalline silver from fixer waste is most likely due to the reduction of silver thiosulfate ions by hydrogen gas. Hydrogen gas is produced in fixer waste by the reaction of sodium thiosulfate with sodium sulfite.

The high purity and nanocrystalline structure of the silver recovered from fixer waste make it a valuable resource. The silver can be used in a variety of applications, such as jewelry, electronics, and catalysis.

The XRD pattern of a silver sample have four peaks at 2θ values of approximately 38.1°, 44.3°, 64.4°, and 77.5°. These peaks correspond to the (111), (200), (220), and (311) crystallographic planes of face-centered cubic (fcc) silver, respectively.

As for another related element, let's consider copper. The XRD value of copper is usually observed at 2θ angles of 43.3, 50.4, 74.1 and 89.6. These peaks correspond to (111), (200), (220), and (311) crystallographic planes of copper, respectively.

Please note that XRD patterns may vary slightly depending on the specific sample and experimental conditions used.

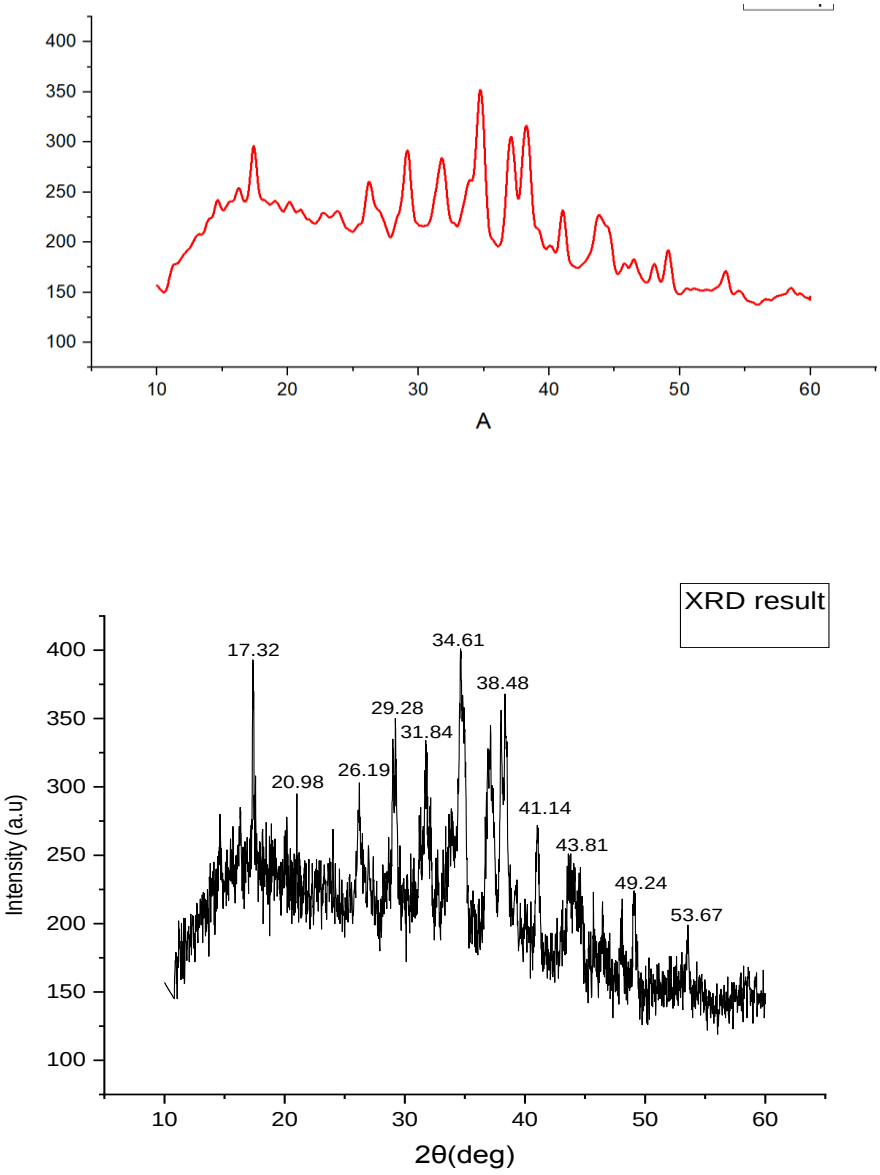



**Figure 5 X-ray diffraction of the recovered silver**

## 4.2 XRF Analysis

The results of the XRF analysis show that the silver recovered from fixer waste is very pure, with a purity of 97.295%. The only impurities detected were sulfur and oxygen, which were present in very small quantities. The presence of sulfur and oxygen in the silver sample is most likely due to the fixer solution. Fixer solutions typically contain thiosulfate ions, which are sulfur-containing ions. The thiosulfate ions can react with the silver to form silver sulfide. Silver sulfide is a black powder that is insoluble in water. The oxygen in the silver sample is

most likely due to the presence of silver oxide. Silver oxide is a white powder that is formed when silver is exposed to air. The high purity of the silver recovered from fixer waste makes it suitable for a variety of applications. For example, the silver can be used to make jewelry, coins, and electronic components.

**Table 3 XRF analysis**

| Elements | | error | CPS/ua |
|---|---|---|---|
| Sb | <LOD | 0.042 | 0.622 |
| Sn | 0.754 | 0.071 | 79.592 |
| Cd | 0.179 | 0.012 | 3.05 |
| Pd | 0.278 | 0.01 | 7.435 |
| Ag | 97.295 | 0.266 | 591.963 |
| Ru | <LOD | 0.006 | 1.852 |
| Mo | 0.03 | 0.005 | 6.579 |
| Nb | 0.096 | 0.004 | 4.213 |
| Zr | 0.008 | 0.002 | 1.364 |
| Bi | 0.913 | 0.013 | 5.206 |
| Pb | <LOD | 0.009 | 0.6 |
| Se | <LOD | 0.004 | 0.51 |
| Au | <LOD | 0.002 | 0.436 |
| W | <LOD | 0.024 | 0.537 |
| Zn | <LOD | 0.009 | 0.261 |
| Cu | <LOD | 0.018 | 0.657 |
| Ni | <LOD | 0.043 | 1.759 |
| Co | <LOD | 0.036 | 0.268 |
| Fe | 0.351 | 0.03 | 0.66 |
| Mn | <LOD | 0.055 | 0.192 |
| Cr | <LOD | 0.096 | 0.23 |
| V | <LOD | 0.216 | 0.218 |
| Ti | <LOD | 0.446 | 0.271 |
| Al | <LOD | 80 | 0.896 |

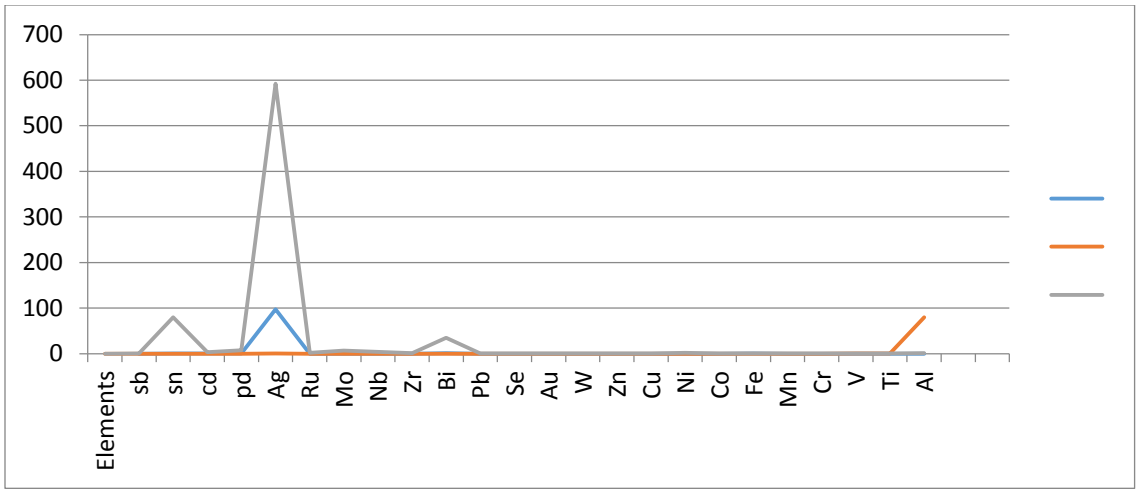



**Figure 6 XRF result using Excel sheet**

As shown from the experiment, the purity of the silver recovery is higher compare to the other metal impurities. Its result shows about 97.295% silver was recovered.

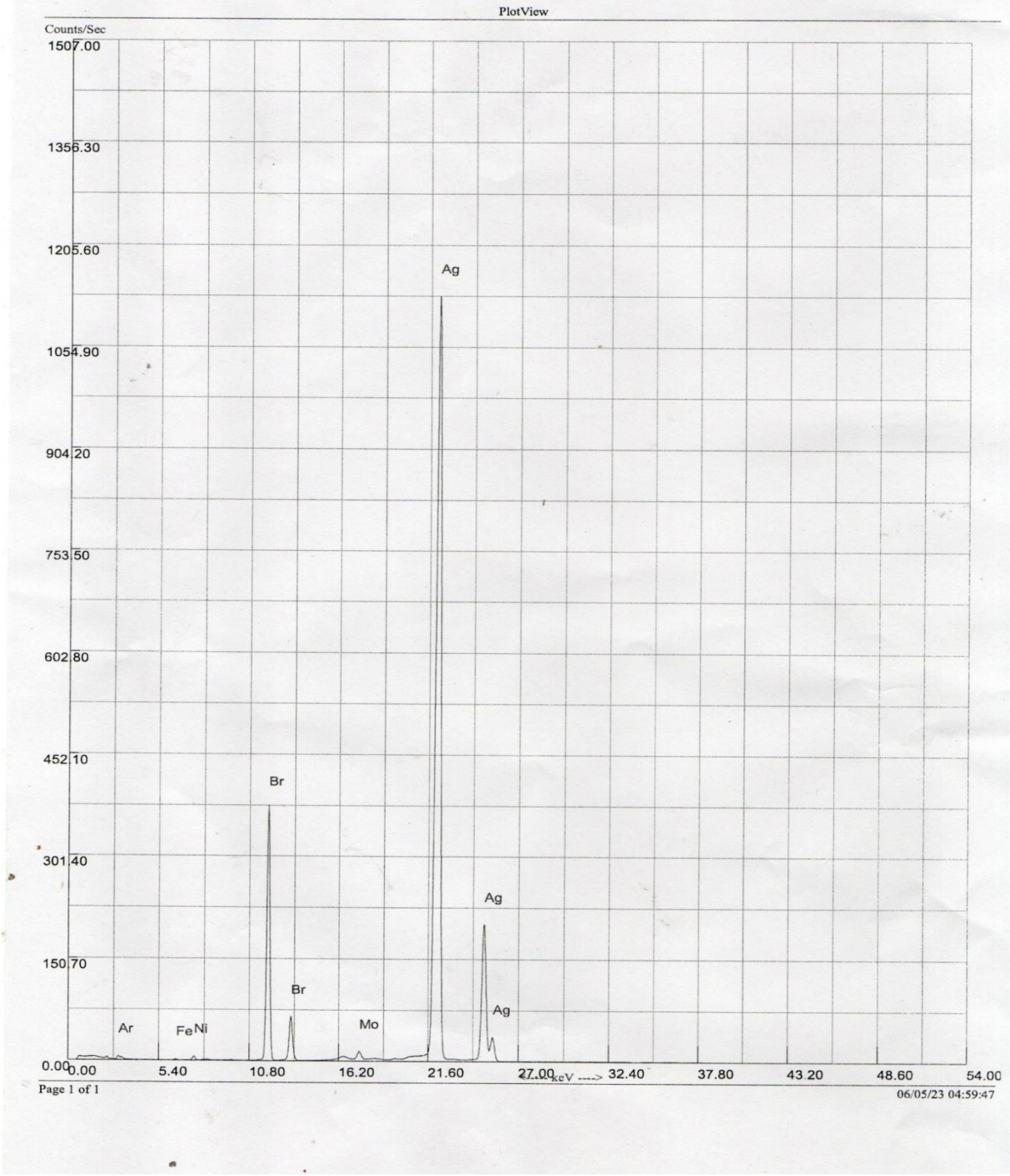



**Figure 7 XRF results analysis**

## 4.3 Interaction effects of parameters and optimization

### 4.3.1 Fitness of laboratory by RMS

Utilizing nonlinear regression and experimental data, the software design expert develops a mathematical model that shows the response as a function of the significant parameters. After that, this model is used to optimize the process parameters and produce the 3D surface plots. However, in light of the experimental results, the constructed mathematical model should be given a statistical evaluation to determine whether it accurately represents the process mathematically based on the variables taken into consideration. F-value and R-Square (determination of coefficient) are the metrics that describe how well the model fits, and how significant it is.

A model with an almost unity R-square and a p-value (prob > F) of less than 0.05 indicates significances as well as that the relationship between the model's and the experimental data's expected response is closed. As shown in the table, a quadratic model was determined to be the best match among the models suggested by the software, with prob>F value of 0.0010 and 0.0005 and R-square of 0.9486 and 0.9673 for recovery of solid and silver respectively.

Three components were used in a full factorial design for optimization (pH, current density and contact time) and two responses (recovery of solid material and recovery of silver). To determine the model's correlation coefficient as a function of the responses, statistical analysis was carried out.

The experimental data was analyzed to a multiple regression analysis in order to estimate the regression coefficient. The regression equations were obtained by fitting various models, including cubic, quadratic, interactive, and linear, to the experimental data. Two separate common tests—sequential model sum of squares and model summary statistics—were used to determine which of the many models to represent was adequate. [26].

The experimental runs are randomized, and suitable software is used for the analytical process. Box-Behnken Design was used during this study. Statistical method of surface response methodology (SRM) was used for analyzing of laboratory result of silver production. The amount the amount of the variables utilized for the study were chosen based on the finding of how each parameter affected the result. Furthermore, the fit summary below in Table 4 and Table 5

suggested quadratic model for recovery of solid material and silver removal was suggested to have maximum adjusted f-value and cubic model was found to be aliased. Therefore, quadratic model was chosen for further analysis

#### 4.3.1.1 Recovered solid material

fit summmery for Sequential Model Sum of Squares

**Table 4 fit summery for recovery of solid material**

| Source | Sum of squares | DF | Mean square | F value | Prob > F | |
|---|---|---|---|---|---|---|
| Mean | 278.60 | 1 | 278.60 | | | |
| Linear | 2.00 | 3 | 0.67 | 3.60 | 0.0433 | |
| 2FI | 0.36 | 3 | 0.12 | 0.59 | 0.6369 | |
| Quadratic | 1.82 | 3 | 0.61 | 18.77 | 0.0010 | Suggested |
| Cubic | 0.048 | 3 | 0.016 | 0.36 | 0.7848 | Aliased |
| Residual | 0.18 | 4 | 0.044 | | | |
| Total | 283.00 | 17 | 16.65 | | | |

*"Sequential Model Sum of Squares"*: Choose the highest order polynomial in which the model is not aliased and the additional terms are significant.

**Table 5 Lack of Fit Tests for recovery of solid material**

| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
|---|---|---|---|---|---|---|
| Linear | 2.23 | 9 | 0.25 | 5.57 | 0.0567 | |
| 2FI | 1.87 | 6 | 0.31 | 7.00 | 0.0403 | |
| Quadratic | 0.048 | 3 | 0.016 | 0.36 | 0.7848 | Suggested |
| Cubic | 0.000 | 0 | | | | Aliased |
| Pure Error | 0.18 | 4 | 0.044 | | | |

*"Lack of Fit Tests"*: It is desirable for the chosen model to have insignificant lack-of-fit.

**Table 6 Model statistic fit Summary for recovery of solid material**

| Source | Std.Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
|---|---|---|---|---|---|---|
| Linear | 0.43 | 0.4535 | 0.3274 | 0.0003 | 4.40 | |
| 2FI | 0.45 | 0.5354 | 0.2567 | -0.7877 | 7.86 | |
| Quadratic | 0.18 | 0.9486 | 0.8826 | 0.7613 | 1.05 | Suggested |
| Cubic | 0.21 | 0.9596 | 0.8384 | | + | Aliased |

*"Model Summary Statistics"*:Pay attention to the model that maximizes the "Adjusted R-Squared and the "Predicted R-Squared".

#### 4.3.1.2 Recovered silver

Fit summmery for Sequential Model Sum of Squares

**Table 7 fit summery for recovery of silver**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Mean | 148.12 | 1 | 148.12 | | | |
| Linear | 3.02 | 3 | 1.01 | 7.70 | 0.0033 | |
| 2FI | 0.027 | 3 | 9.142E-003 | 0.055 | 0.9822 | |
| Quadratic | 1.52 | 3 | 0.51 | 22.94 | 0.0005 | Suggested |
| Cubic | 0.012 | 3 | 3.908E-003 | 0.11 | 0.9501 | Aliased |
| Residual | 0.14 | 4 | 0.036 | | | |
| Total | 152.84 | 17 | 8.99 | | | |

*"Sequential Model Sum of Squares"*: Choose the highest order polynomial in which the model is not aliased and the additional terms are significant

**Table 8 Lack of Fit Tests for recovery of silver**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Linear | 1.56 | 9 | 0.17 | 4.85 | 0.0714 | |
| 2FI | 1.53 | 6 | 0.25 | 7.15 | 0.0389 | |
| Quadratic | 0.012 | 3 | 3.908E-003 | 0.11 | 0.9501 | Suggested |
| Cubic | 0.000 | 0 | | | | Aliased |
| Pure Error | 0.14 | 4 | 0.036 | | | |

*"Lack of Fit Tests"*: It is desirable for the chosen model to have insignificant lack-of-fit.

**Table 9 Model statistic fit Summary for recovery of silver**

| Source | Std.Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | |
|---|---|---|---|---|---|---|
| Linear | 0.36 | 0.6399 | 0.5568 | 0.3712 | 2.97 | |
| 2FI | 0.41 | 0.6457 | 0.4331 | -0.3009 | 6.14 | |
| Quadratic | 0.15 | 0.9673 | 0.9252 | 0.9130 | 0.41 | Suggested |
| Cubic | 0.19 | 0.9698 | 0.8791 | | + | Aliased |

*"Model Summary Statistics:* Pay attention to the model that maximizes the "Adjusted R-Squared and the "Predicted R-Squared ".

### 4.3.2 Analysis of variance (AVOVA)

Analysis of variance (ANOVA) allows us to examine particular operational parameters and determine whether or not their impacts were statistically significant. When the prob > F value is small and F-value is large, the effect was more significant. The ANOVA value for the recovery of solid material and recovery of silver as shown in the table below indicates that the mode of laboratory result was significant. The F-value of model was 14.13, 23 and prob < F value of 0.10%, 0.02%, respectively, which indicates that the chance of F-value this big could happen because the noise level is too low.

When the prob > F value less than 0.05 the term values are significant this means B, C and AB, $A^2$,$B^2$ and $C^2$ are significant models of term for recovery solid material. Similarly, A,B, C and $A^2$ and $C^2$ are significant models of term for recovering silver. The most significant from the term substrate Ph, current density and time has high significant effect on the recovery of silver. So, it is required to find there optimum operation. The model result for recovery of solid material and silver shows that no lack of fitness of model since 78.48% and 95.01% of chance that lack of fitness occurred. This all indicate that the laboratory result is statistically acceptable.

**Table 10 Analysis of variance for recovery of solid material**

| *Responce:* **recovery of solid material** | | | | | | |
|---|---|---|---|---|---|---|
| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
| Model | 4.17 | 9 | 0.46 | 14.36 | 0.0010 | Significant |
| *A* | *0.060* | *1* | *0.060* | *1.84* | *0.2167* | |
| *B* | *1.11* | *1* | *1.11* | *34.39* | *0.0006* | |
| *C* | *0.83* | *1* | *0.83* | *25.58* | *0.0015* | |
| $A^2$ | *0.99* | *1* | *0.99* | *30.71* | *0.0009* | |
| $B^2$ | *0.19* | *1* | *0.19* | *5.88* | *0.0458* | |
| $C^2$ | *0.62* | *1* | *0.62* | *19.36* | *0.0032* | |
| *AB* | *0.32* | *1* | *0.32* | *10.07* | *0.0157* | |
| *AC* | *0.027* | *1* | *0.027* | *0.84* | *0.3890* | |
| *BC* | *8.100E-003* | *1* | *8.100E-003* | *0.25* | *0.6318* | |
| Residual | 0.23 | 7 | 0.032 | | | |
| *Lack of Fit* | *0.048* | 3 | *0.016* | *0.36* | *0.7848* | *not significant* |
| *Pure Error* | *0.18* | 4 | *0.044* | | | |
| Cor Total | 4.40 | 16 | | | | |

The model has been determined significant based on its F-value of 14.36. There is justa 0.10% possibility that noise may be the cause of a "Model F-Value" this high."Prob > F" values less than 0.0500 suggest the significance of the model terms.B, C, A2, B2, C2, and AB are important model terms in this instance.The model terms are not significant if the value is bigger than 0.1000.Your model may be improved via model reduction if it has a large number of insignificant model terms (apart from those needed to support hierarchy).

Given the pure error, the "Lack of Fit F-value" of 0.36 suggests that the Lack of Fit is not significant. A significant "Lack of Fit F-value" has a 78.48% probability of being caused by noise. Good—we want the model to fit—is a non-significant lack of fit.

**Table 11 Analysis of variance for recovery of silver**

| *Responce:* **recovery of silver** | | | | | | |
|---|---|---|---|---|---|---|
| **Source** | **Sum of Squares** | **DF** | **Mean Square** | **F Value** | **Prob > F** | |
| Model | 4.57 | 9 | 0.51 | 23.00 | 0.0002 | Significant |
| *A* | *0.35* | *1* | *0.35* | *15.80* | *0.0054* | |
| *B* | *0.82* | *1* | *0.82* | *37.14* | *0.0005* | |
| *C* | *1.85* | *1* | *1.85* | *84.00* | *< 0.0001* | |
| $A^2$ | *0.75* | *1* | *0.75* | *34.11* | *0.0006* | |
| $B^2$ | *0.11* | *1* | *0.11* | *4.87* | *0.0631* | |
| $C^2$ | *0.63* | *1* | *0.63* | *28.70* | *0.0011* | |
| *AB* | *0.026* | *1* | *0.026* | *1.16* | *0.3171* | |
| *AC* | *2.250E-004* | *1* | *2.250E-004* | *0.010* | *0.9224* | |
| *BC* | *1.600E-003* | *1* | *1.600E-003* | *0.073* | *0.7954* | |
| Residual | 0.15 | 7 | 0.022 | | | |
| *Lack of Fit* | *0.012* | *3* | *3.908E-003* | *0.11* | *0.9501* | *not significant* |
| *Pure Error* | *0.14* | *4* | *0.036* | | | |
| Cor Total | 4.72 | 16 | | | | |

The model has been considered significant based on its F-value of 23.00. Noise has a minimal 0.02% probability of producing a "Model F-Value" of this amount. "Prob > F" values less than 0.0500 suggest the significance of the model terms. A, B, C, A2, and C2 are important model terms in this instance.The model terms are not significant if the value is bigger than 0.1000. Model reduction could make your model better if it has a large number of insignificant model terms (apart from those needed to maintain hierarchy).
The "Lack of Fit F-value" of 0.11 indicates that, in comparison to the pure error, the Lack of Fit is not significant. A "Lack of Fit F-value" this large could be the result of noise, with a 95.01% chances. Good—we want the model to fit—is a non-significant lack of fit.

#### 4.3.2.1 Statistical fit

The other fit checked was statistical fit, table below indicate that the average mean value of laboratory result of solid recovery and silver recovery was 4.05 and 2.95. the predicted $R^2$ of 0.7613 and 0.9130 was reasonable consensus with the adjusted $R^2$ of 0.8826 and 0.9252 which

was less than 0.2 difference and adequate precision of 12.782 and 18.315 shows that the model is useful for navigating the design environment for recovery of solid and silver material.

**Table 12 Fit Statistical for solid recovery**

| | | | |
|---|---|---|---|
| Std. Dev. | 0.18 | R-Squared | 0.9486 |
| Mean | 4.05 | Adj R-Squared | 0.8826 |
| C.V. | 4.44 | Pred R-Squared | 0.7613 |
| PRESS | 1.05 | Adeq Precision | 12.782 |

The "Pred R-Squared" of 0.7613 is in reasonable consensus with the "Adj R-Squared" of 0.8826. "Adeq Precision" calculates the ratio of signal to noise. Ideally, the ratio should be higher than 4 is desirable. With a ratio of 12.782, you have an adequate signal. The design area can be navigated with the help of this model.

**Table 13 Fit Statistical for silver recovery**

| | | | |
|---|---|---|---|
| Std. Dev. | 0.15 | R-Squared | 0.9673 |
| Mean | 2.95 | Adj R-Squared | 0.9252 |
| C.V. | 5.03 | Pred R-Squared | 0.9130 |
| PRESS | 0.41 | Adeq Precision | 18.315 |

The "Pred R-Squared" of 0.9130 is in reasonable consensus with the "Adj R-Squared" of 0.9252. "Adeq Precision" calculates the ratio of signal to noise. Ideally, the ratio should be higher than 4 is desirable. With a ratio of 18.315, you have an adequate signal. The design area can be navigated with the help of this model.

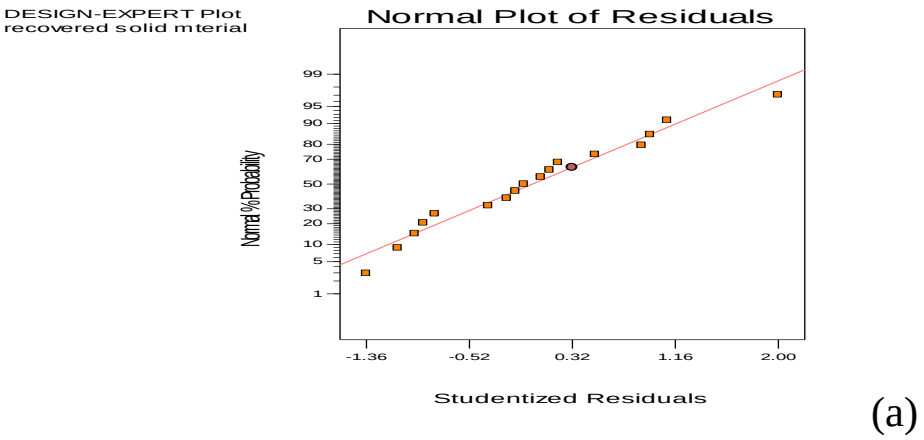
#### 4.3.2.2 Response surface plots

A normal plot of residuals, a predicted vs. actual plot for solid, and a predicted vs. actual plot for silver, predicted vs. actual for solid and predicted vs. actual for silver were used to examine the suitability of the experimental data.

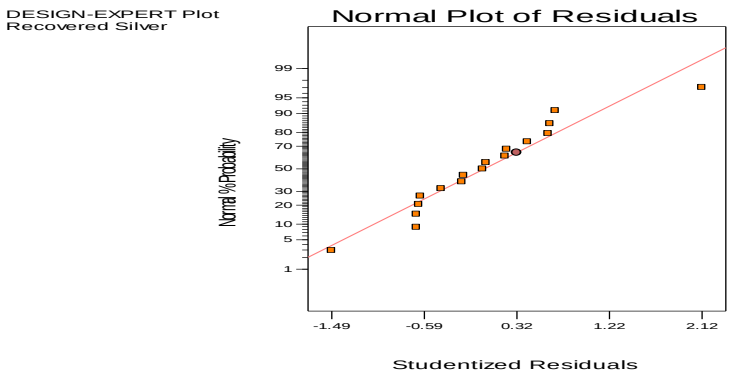
**Normal plot of residuals**

A method for determining whether or not a data set is roughly normally distributed is the normal plot of residual. Plotting the experimental data against the theoretical normal distribution resulted in an approximate straight-line formation between the locations.

There was no irregularity or no abnormality in this investigation, as shown by the normal probability plots of the accepted residuals in the plots.




(a)




(b)

**Figure 8 Normal plot of residuals**

## Predicted Vs Actual

It demonstrates that experimental values were distributed relatively near to the straight line. This proved that there is a good correlation between these values.

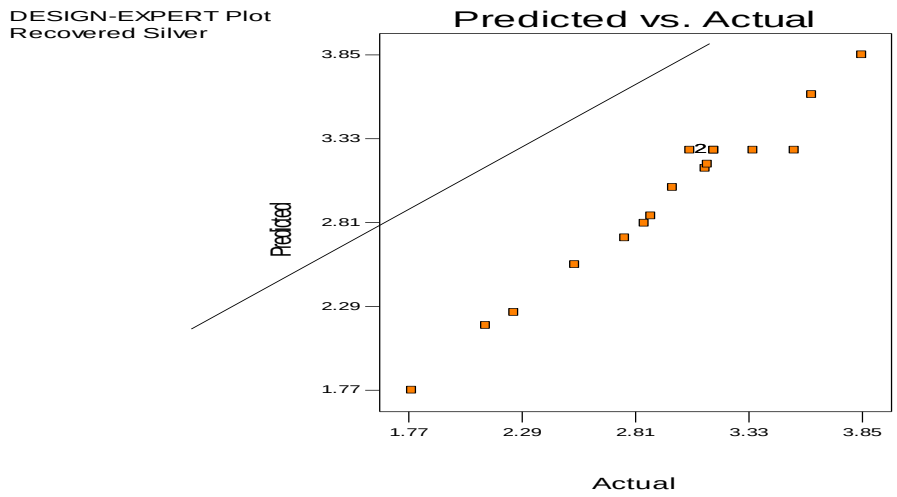
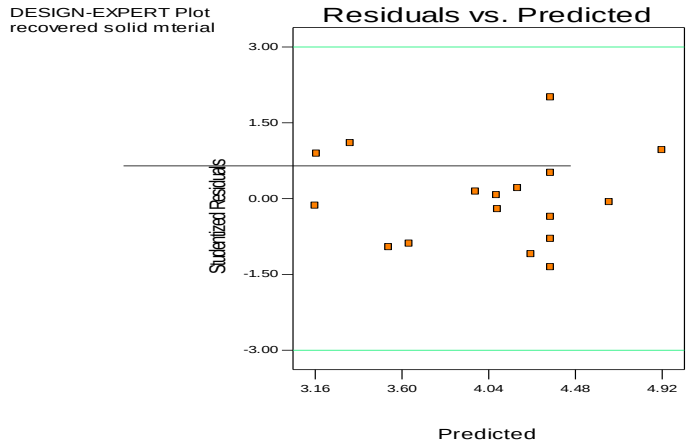


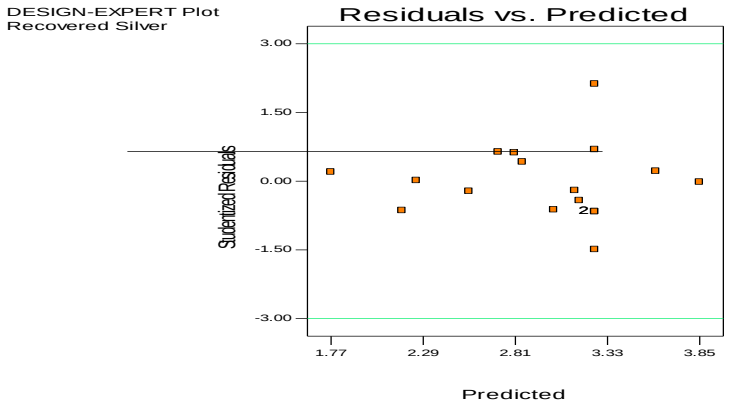

**Figure 9 predicted Vs Actual a) Silver material**

❖ **Residuals Vs predicted**

Which indicate that all the points of the graph are in between the maximum and minimum value of the given board point which is 3.00 and -3.00. It shows that the graph is acceptable and effect of residual on predicted value is acceptable.




(a)




(b)

**Figure 10 Residuals Vs predicted for (a) solid material and (b) Silver**

**Table 14 Experimental Design Matrix**

| Run | Factor 1 | Factor 2 | Factor 3 | silver | | Solid | |
|---|---|---|---|---|---|---|---|
| | PH | Current density | Time | Actual Value | Predicted Value | Actual Value | Predicted Value |
| 1 | 4.00 | 2.00 | 55.00 | 2.85 | 2.80 | 4.09 | 4.08 |
| 2 | 8.00 | 2.00 | 55.00 | 2.53 | 2.55 | 3.44 | 3.34 |
| 3 | 4.00 | 5.00 | 55.00 | 3.62 | 3.60 | 4.16 | 4.26 |
| 4 | 8.00 | 5.00 | 55.00 | 2.98 | 3.03 | 4.65 | 4.66 |
| 5 | 4.00 | 3.50 | 20.00 | 2.12 | 2.17 | 3.25 | 3.17 |
| 6 | 8.00 | 3.50 | 20.00 | 1.78 | 1.77 | 3.15 | 3.16 |
| 7 | 4.00 | 3.50 | 90.00 | 3.13 | 3.15 | 3.99 | 3.98 |
| 8 | 8.00 | 3.50 | 90.00 | 2.76 | 2.71 | 3.56 | 3.64 |
| 9 | 6.00 | 2.00 | 20.00 | 2.25 | 2.25 | 3.45 | 3.54 |
| 10 | 6.00 | 5.00 | 20.00 | 2.88 | 2.85 | 4.21 | 4.19 |
| 11 | 6.00 | 2.00 | 90.00 | 3.14 | 3.17 | 4.07 | 4.09 |
| 12 | 6.00 | 5.00 | 90.00 | **3.85** | 3.85 | 5.01 | 4.92 |
| 13 | 6.00 | 3.50 | 55.00 | 3.54 | 3.26 | 4.44 | 4.36 |
| 14 | 6.00 | 3.50 | 55.00 | 3.35 | 3.26 | 4.68 | 4.36 |
| 15 | 6.00 | 3.50 | 55.00 | 3.17 | 3.26 | 4.14 | 4.36 |
| 16 | 6.00 | 3.50 | 55.00 | 3.17 | 3.26 | 4.23 | 4.36 |
| 17 | 6.00 | 3.50 | 55.00 | 3.06 | 3.26 | 4.30 | 4.36 |

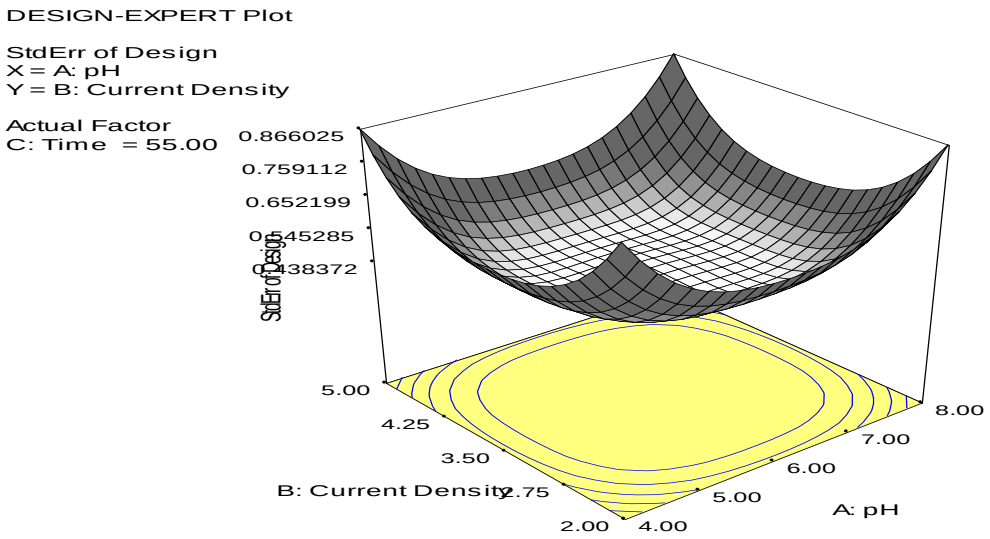



**Figure 11 Design Expert Plot**

## 4.4 Interaction effect of selected operational parameter

As we see from previous AVOVA table, selected operational parameters have interaction effects. Their effects were investigated by keeping on parameters contact and alternatively varying other two operational parameters since quadratic model was used for estimation. Their effect were more illustrated using contour and 3D graph model respectively as shown from figure below.

- Recovery solid material
- Recovery silver

Figure 13 shows the relationship between effect of pH and current density on time. It shows as current density increase, the recovery of solid increase but as increase of pH did not increase the recovery of solid that much.

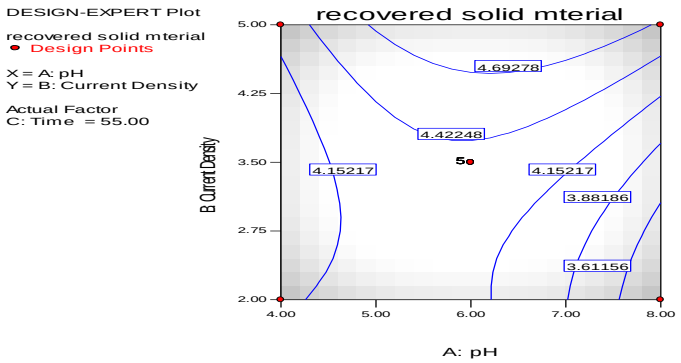



**Figure 12 Interaction effect of pH and current density on time**

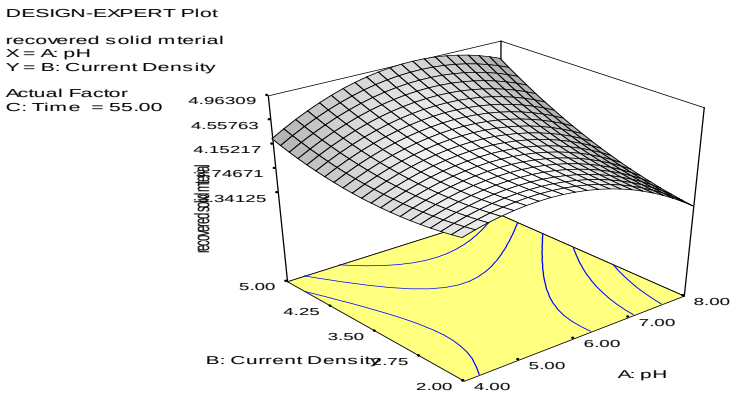



**Figure 13 3D Interaction effect of pH and current density on time**

Figure 15 shows the relationship between effect of pH and time on current density. It shows the response of recovery solid material as a function of pH and contact time under experimental conditions. The recovery of solid increased with an increase in contact time until 90min and pH of 6. But further increase in contact time did not lead to a significant increase in recovery solid.

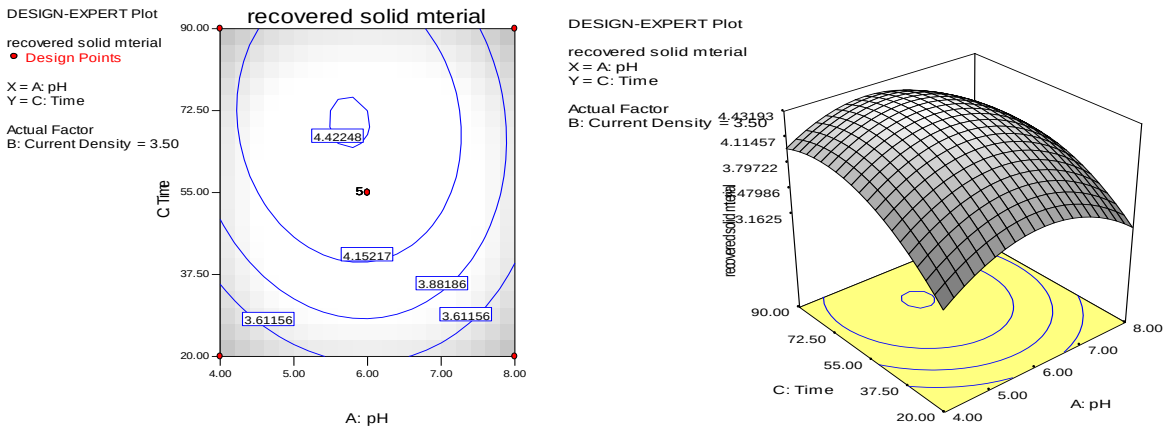



**Figure 14 Interaction effect of pH and time on current density**

Figure 16 shows the relationship between effect of current density and time on pH. It shows as increase of current density and time may decrease the recovery because as increasing pH leaders to decrease the recovery.

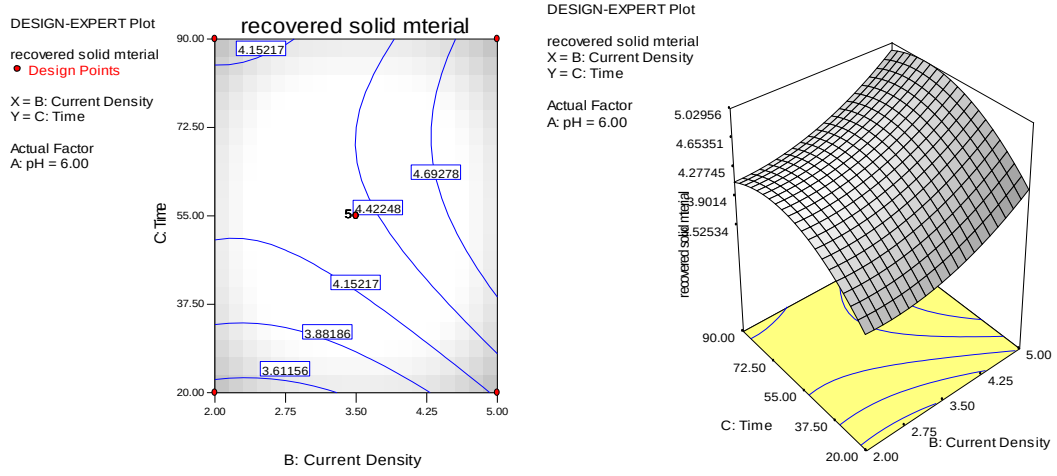



**Figure 15 Interaction effect of current density and time on pH**

Figure 17 shows the relationship between effect of pH and current density on time. It shows as current density increase, the recovery of solid increase but as increase of pH did not increase the recovery of solid that much.

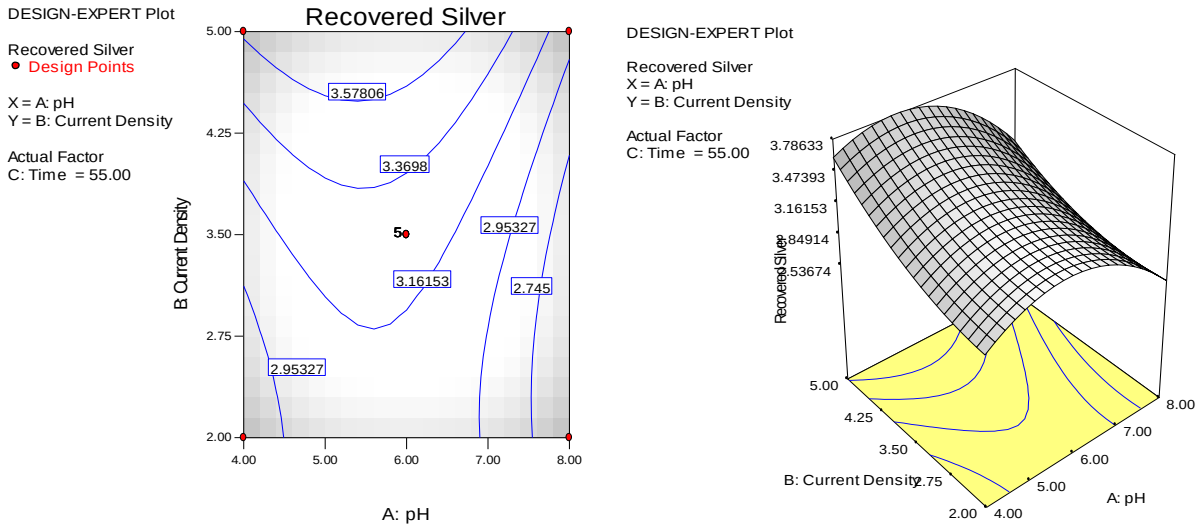



**Figure 16 Interaction effect of pH and current Density on time**

Figure 18 shows the relationship between effect of pH and time on current density. It shows the response of recovery solid material as a function of pH and contact time under experimental conditions. The recovery of silver increased with an increase in contact time until 55min and pH of 6. But further increase in contact time did not lead to a significant increase in recovery silver.

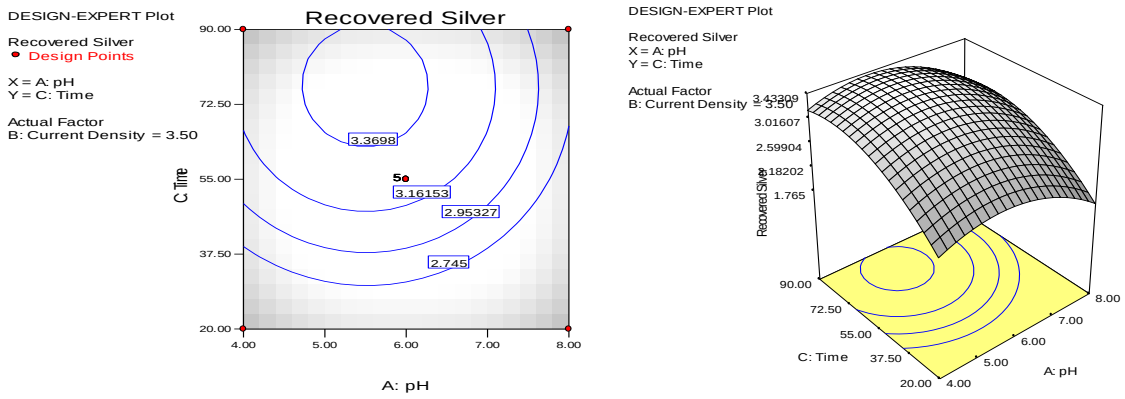



**Figure 17 Interaction effect of pH and time on current density**

Figure 19 shows the relationship between effect of current density and time on pH. It shows as increase of current density and time may decrease the recovery because as increasing pH leaders to decrease the recovery.

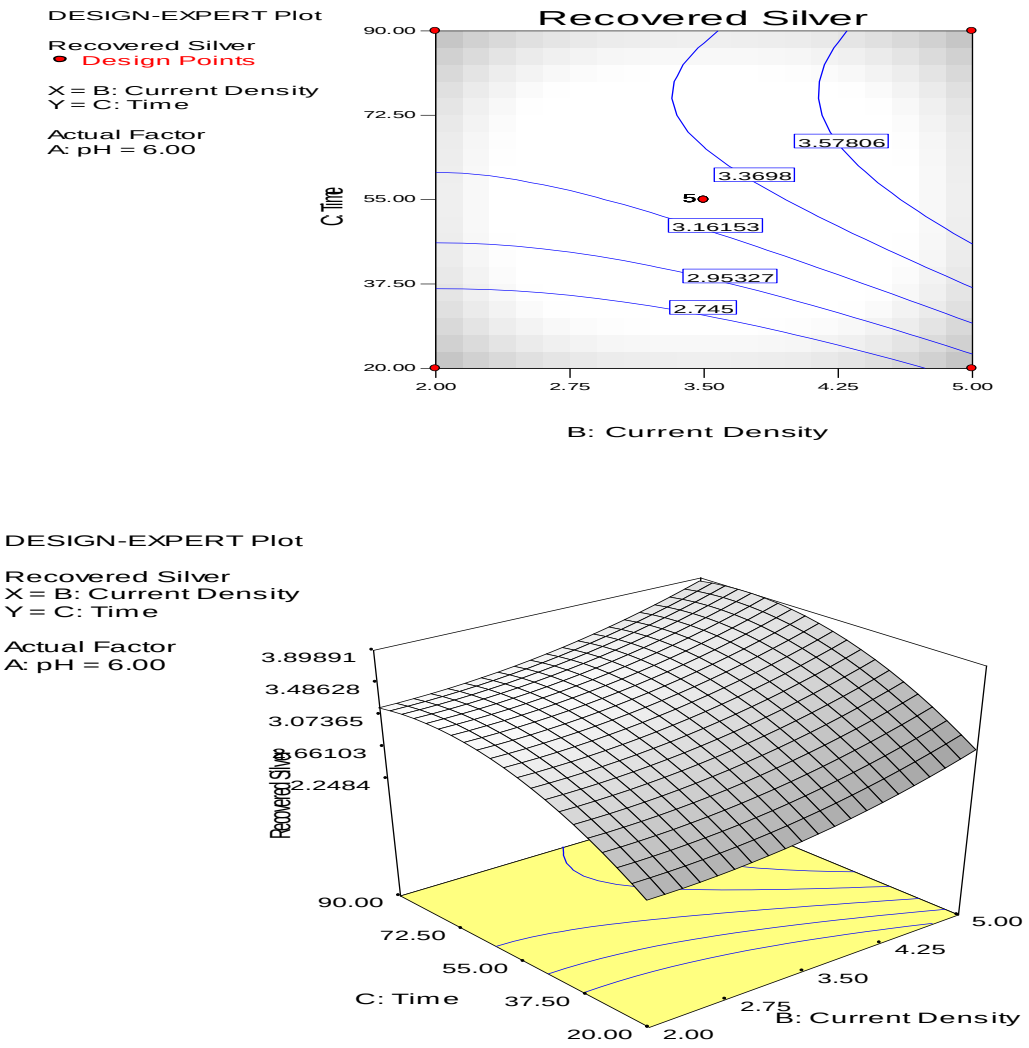



**Figure 18 Interaction effect of current density and time on pH**

# 5 CONCLUTION AND RECOMMENDATION

## 5.1 Conclusion

In conclusion, the electrolytic recovery of silver from fixer waste was successful at all pH and current density conditions studied. The highest silver recovery efficiency of 99.9% was achieved at a pH of 6 and a current density of 10 $mA/cm^2$.

The XRD analysis of silver recovered from fixer waste showed that the silver is of high purity and has a nanocrystalline structure. The high surface-to-volume ratio of nanocrystalline silver makes it more reactive and suitable for a variety of applications. Additionally, the XRD results can be used to confirm the identity of the silver recovered from fixer waste and to distinguish it from other silver compounds, such as silver oxide and silver sulfide.

The XRF analysis of silver recovered from fixer waste showed that the silver is very pure, with a purity of 97.295%. The only impurities detected were sulfur and oxygen, which were present in very small quantities. The high purity of the silver recovered from fixer waste makes it suitable for a variety of applications.

Overall, the results of this study suggest that electrolytic recovery is a promising method for the recovery of silver from fixer waste. The high recovery efficiency and purity of the recovered silver make it suitable for a variety of applications.

Future studies could explore the impact of additional factors, like stirring rate and electrolyte temperature, on the electrolytic recovery of silver from fixer waste. Additionally, it would be of interest to investigate the scalability of the process and its potential for industrial applications.

## 5.2 Recommendation

We recommended that silver recovery from fixer waste gives the advantage of environmental benefit as well as economic benefit. So the electrolysis method should be followed by other methods like metallic replacement method to increase the feasibility of the silver recovery for economic and also environmental aspect.

For the upcoming investigation, the following suggestion can be made:

- Other factors which considered being constant like's temperature, initial concentration should be study and optimize.
- Economic feasibility of recovering silver from waste material should be study.
- The printing company must put into practice the process of producing silver from photographic waste. to turn garbage into a silver product that can be used.
- further studies should be made to investigate strategies to further increase the purity of silver during electrolysis

# Appendix

## Appendix A: Silver Recovery Terms

**Anode:**-A positively-charged electrode that attract s negative ions in the fixer and repels positive ions, such as silver ions .

**Cathode**: -A negatively-charged electrode that attracts the positively-charged ions, such as the silver ions in the fixer.

**Current Strength** :-The amount of electrical current delivered to a square foot of cathode area. The higher the current strength, the faster the silver recovery.

**Emulsion** :- The light sensitive gelatin coating on photographic films and papers.

**Fixer: (Hypo)**:- A solution of sodium or ammonium thiosulphate in water. The thiosulphate extrac ts silver ions from the gelatin layer of the film.

**Ion**: - An electrically charged atom, radical, or molecule, formed by the loss or gain of one or more electrons.

**pH** :- A measure of the acidity of a solution, (in this particular case ).

**Silver Concentration**:- The total amount of suspended silver in · the fixer ( hypo) stated in grams per liter or Troy ounces per gallon.

**Sulfiding** : - The phenomenon of silver sulfide formation. This occurs when current strength is too high for the amount of silver · near the cathode.

## Appendix B: Laboratory Experiments Photo

From Brehan ena Selam printing company

- Chemicals using for printing.

- Different machines using for this printing.







Montakop
Plate Expose
MONTAKOP




IGP


egraf

egraf

- The Final waste solutions (fixer solutions).

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