

# **RECOVERY OF SILVER FROM SPENT PHOTOGRAPHIC SOLUTION**

**BY**

**NWOKO CHRISTOPHER IKPE AMADI**

**FEBRUARY, 2008**

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*(B.Sc. UNN; M.Sc. FUTO)*

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**A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL,  
FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR  
THE AWARD OF THE DEGREE OF DOCTOR OF PHILOSOPHY  
(Ph.D) IN PHYSICAL CHEMISTRY**

**FEBRUARY, 2008**

## CERTIFICATION

This is to certify that the report in this thesis titled "Recovery of Silver from Spent Photographic Solution" is the result of investigations carried out by Mr. Christopher Ikpe Amadi Nwoko in the Department of Chemistry, Federal University of Technology, Owerri; under the supervision of the under listed supervisors. It is also certified that no part of this work has been submitted to any other institution for a degree.

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## **DEDICATION**

To the blessed memory of my parents – Mr. Paul Amadi Nwoko and Mrs. Roseline Ihuoma Nwoko; and to all those people who have fought the good fight of faith.

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## ABSTRACT

Recovery of silver from spent photographic solutions was investigated by electrogravimetric technique. The silver content of the effluent was determined using both Volhard titrimetric method and atomic absorption spectrophotometry. The results of the analysis showed that rinser has least amount of silver, while bleach – fix and fixer have appreciably larger amounts of silver. The study was carried out to determine the operating conditions for optimum recovery of silver from these photographic waste solutions. The results showed that at a pH of 5, 45°C, 0.15A and a voltage of 6Volts; 2,530mg Ag/200ml bleach-fix and 3,496mg Ag/200ml fixer were recovered at a cathode efficiency of 62.87% and 86.88% respectively with current density of 342.5/m<sup>2</sup> in each case. In the case of the rinser only 72.4mgAg/200ml was recovered when the same optimum conditions were applied. This recovery was recorded at a cathode current efficiency of 1.80%, indicating that most of the applied current went into unwanted chemical reactions such as sulphide precipitation and hydrogen evolution at the cathode surface. A plot of amount of silver deposited against quantity of electricity showed linear relationship, which validated Faraday's first law of electrolysis. It was however observed that despite the linearity of the plot, an intercept was included which made it impossible for the line to pass through the origin in contrast to Faraday's plot. This development led to a proposal to modify the mathematical equation of Faraday's first law of electrolysis by introducing a constant to represent the intercept. Thus, instead of having  $m = k Q$ , we now have  $m = k Q + C$ . The intercept 'C' is approximately the mass deposited when Q tends to zero. This shows that the electrode immersed into the electrolyte is capable of generating charging current even in the absence of externally applied voltage. Diffusion and the electrical double layer played very significant role. The project is relevant in terms of its contribution towards waste management and environmental protection as well as economically viable because silver is a highly precious metal.

# CHAPTER ONE

## INTRODUCTION

### 1.1 BACKGROUND

Many arguments can be presented to indicate that technological development is responsible for much environmental degradation. Production of waste has accelerated in the period since industrial revolution and an increase in the global population of human beings has as well created increasing volumes of wastes that need to be disposed of [1]. Wastes are produced by living things, excreted by organisms or thrown away by society because they are no longer useful and if kept may be harmful.

These wastes which are materials resulting from various industrial processes should be treated in order to reduce their toxicity, and to avoid contamination of the desired product as well as the environment. The wastes usually become harmful and in the extreme cases lethal and therefore should be properly managed. Such management procedures may be sophisticated and may involve recycling for re-use and other economic purposes [2].

However, some of these wastes may contain valuable raw materials for some other industries and hence it is necessary to find solutions on how to utilize the waste products.

The photographic processing industry produces waste that contains silver, which could both be toxic or useful to humans. Most wastes exhibit toxicity

even at low concentration and their release into the environment creates some health hazards. There are various levels of toxicity. Lethal levels cause death by direct poisoning, acute levels cause traumatic effects usually death within a short period; chronic levels cause effects over a prolonged time period, or cumulative toxicity result in effects that increases by successive doses.

The large number of photographic industries in Nigeria is an indication that a large amount of these wastes is being disposed into the drainage system or onto the surface soil. Photographic industry effluents contain the following substances: non-biodegradable, some heavy metal(s) as well as organic compounds.

It is therefore necessary to design an efficient waste management technique that will be suitable for a photo-processing industry.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

#### 2.1 PREVIOUS WORK

Among all the precious metals, silver [2] is frequently recovered from process streams of other industrial activity.

A good number of scientists have done impressive work covering the area of wastes reduction in photo processing industries.

Arthur D. Little [3] who carried out a research captioned, "Waste Audit Study of Photoprocessing Industry" reported the environmental health hazard of silver as a result of photoprocessing activities. This work pointed out that photoprocessing wastes are serious pollutants to the ecosystem.

Thomas P. Cribbs and Thomas J. Dagon [4] undertook a review of waste reduction programs in the photoprocessing industry. Their report suggested various methods of photographic waste reduction techniques such as metallic replacement, ion exchange, electrolytic method and reverse osmosis that could be used in solving the pollution problem.

Monica E. Campbell and William M. Glenn[5] in their work titled "pollution probe", highlighted some profit from pollution prevention. The authors showed that economic valuable substance such as silver could be recovered from the photographic waste solutions.

In a similar work, Eastman Kodak Company [6] reported on the disposal and treatment of photographic processing solutions in support of clean water. This work showed that silver could be recovered from both the liquid and

solid photographic wastes using electrolytic waste recovery technique or through any of the other recovery methods.

### **2.1.1 Electrolytic Method**

Electrolysis of the waste effluents was shown to remove up to 95% of silver from such effluent streams at optimum conditions [7]. It was also pointed out by some notable researchers [14,15,16] that electrolytic silver recovery remained the most efficient technique for recovering silver from silver-rich photographic solutions. During electrolysis, an electric current reduces the silver thiosulphate complex and plates almost pure silver metal onto the cathode. In this process, it was disclosed that silver concentration could range between 5mg/L and 12,000mg/L depending on the processing state from which the waste originated and the type of film processed. These researchers went further to state that efficiencies approaching 90% were possible when recovering silver from bleach-fix and fixer solutions from colour processing machines.

Additional information from literature revealed that electrolytic plating can give about 95% recovery [17,18,19]. It can therefore be said that silver recovery by electrolytic technique may range between 90 – 95% as optimum value if properly operated. The time duration [7] for good deposition of silver on the cathode was also reported to be 9 hours for large scale work.

### **2.1.2 Ion Exchange Methods**

Ion exchange is recovery technique generally used for effective recovery of silver from rinse water or other dilute solution of silver. The ion exchange method involves the exchange of ions in the solution with ions of a similar charge on an exchange resin. In this process soluble silver thiosulphate complex is exchanged with the ion on the resin. The silver is then removed from the resin column with a silver complexing agent such as ammonium thiosulphate. Finally, silver is recovered from the thiosulphate regenerant with an electrolytic recovery cell [9, 10].

Lindsted, John and Doyle, Michael [13] in their own investigation, attempted bench scale studies which examined the effectiveness of thiocyanate regeneration of saturated resin for silver recovery.

Factors which affect recovery efficiency in an ion exchange system for silver recovery are resin type, flow rate of silver bearing solution, column configuration and selection of the regenerant. The use of ion exchange can reduce the silver concentration in photographic effluent to levels in the range of 0.5 to 2mg/L and can recover up to 98% of available silver. This method suffers the disadvantage of having to subject the recovered metal to further purification.

### **2.1.3 Reverse Osmosis**

Reverse Osmosis (RO) is a recovery method which is used for dilute solutions. Reverse osmosis uses high pressure to force the silver – bearing solution through a semi permeable membrane to separate molecules, such

as salts and organic compounds from smaller molecules like water. The extent of separation is determined by membrane surface chemistry and pore size, fluid pressure and waste characteristics. This method encounters some operating problems as fouling of the membranes and biological growth [6].

#### **2.1.4 Recovery by Evaporation**

Photographic waste effluents can also be treated by evaporation. The effluents are collected and heated to evaporate all liquids. The resulting sludge is collected in filter bags which can be sent where silver is being recovered. The major advantage of the evaporation technique is it achieves 'zero' water discharge. A disadvantage is that the organics and ammonia in the waste solution may create air pollution when evaporated [11]. This problem can be controlled to a large extent by incorporating a charcoal filter into the heating unit in order to capture the organics.

#### **2.1.5 Recovery by adsorption**

The use of alfalfa biomass to recover silver was reported by Herrera et al [12]. The work was based on finding a cost effective and environment safe technique, which could be adopted for silver recovery by adsorption.

## **2.2 PHOTOGRAPHY**

### **2.2.1 Silver Halide Photography**

Photography is an area of interest in photochemistry which can be defined as the science and art of producing pictures by the action of visible light on

chemically prepared silver compounds[20]. Photography depends on the sensitiveness of silver compounds to light. Photographic processes include the production of black and white and coloured photographs.

A photographic film is a thin sheet of cellulose acetate or other polymeric material that can be cast into films coated with a photographic emulsion. A photographic emulsion consists of silver halide such as silver bromide suspended in gelatin. The silver halide salts are commonly referred to as grains. The suspension of these grains in a gelatin matrix result in a gelatin dispersion. This dispersion is referred to as the photographic emulsion because of the following properties:

- (a) An emulsion is a system in which droplets of a liquid, 0.1 to 1 $\mu$  in diameter, are dispersed in another liquid dispersion medium.
- (b) They contain very minute sized particles which ionize in aqueous electrolyte to yield a small cation and a large anion.
- (c) The dispersion contains particles whose dimensions are less than those of suspension but larger than those of solutions (ie from 1 – 10nm). Hence, photographic emulsion contains grains of silver halide suspended in gelatin.

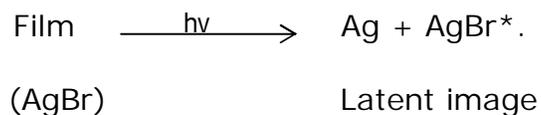
## **2.3 PROCESSING AN EXPOSED FILM**

### **2.3.1 Film Exposure**

When a film is exposed to visible light reflected from an object to be photographed, the silver bromide, AgBr, grains are activated as a result of its interaction with visible light.

### 2.3.2 Formation Of Latent Image

The activation of silver bromide leads to the formation of a latent image [20,23]. The latent image consists of minute particles of silver, which serve as catalyst when the exposed silver bromide is treated with a reducing agent called developer. Activation of exposed film is the first process towards picture production. Thus:

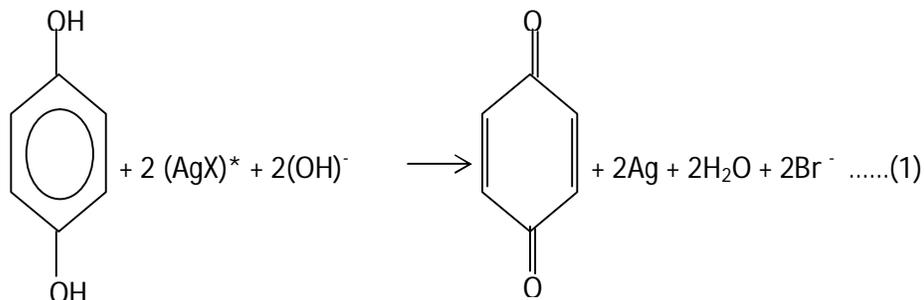


### 2.3.3 Developing The Latent Image

The exposed silver bromide is treated with a developer and became reduced to silver. However, inside the system remained some unexposed silver bromide, which will not be affected by the action of the developer. This process can be represented as follows:



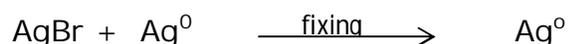
The developer is an alkaline solution of a reducing agent such as 1,4-dihydroxybenzene, which is also known as hydroquinone. This reduces the activated AgBr\* grains to silver at an appreciably greater rate than the unexposed and underexposed silver bromide. This is illustrated with the reaction below [20]:



### 2.3.4 Fixing process (removal of excess AgBr)

After developing, the alkali is removed by immersion in 0.5% acetic acid for a short time and the excess of AgBr is removed by treatment with sodium thiosulphate which is technically called "hypo".

The process of removal of the excess AgBr is called fixing. This process can be represented as follows:



(unexposed

silver bromide)

It is important to remove the unexposed AgBr so that the fidelity of the picture is not marred during the subsequent positive printing stage. Silver halides are only slightly soluble in water, therefore there is need to convert it to soluble complexes, which can be removed by washing. The active ingredient in fixer is either sodium thiosulphate or ammonium thiosulphate. The film is washed and dried to give the negative.

### 2.3.5 Printing Stage

The negative is printed in order to obtain a positive picture. The printing of the negative involves placing it in contact with a photographic paper and exposing to light. After the exposure, the photographic paper is developed, fixed, washed and dried to give the positive photograph.

### **2.3.6 Photographic Process Effluents**

There are three main sources of the effluent silver under study. The first source of effluent silver is the developing stage where the unexposed silver bromide remained in solution. This effluent is called the bleach-fix or simply the developer. The second source of effluent silver is as a result of the fixing process where soluble silver thiosulphate complex is formed. This type of effluent is called fixer or the washing source.

The third source of the effluent silver is the rinse water or rinser.

## **2.4 THE PHOTOGRAPHIC GELATIN**

Gelatin is a protein extracted from animal hides, bone, and sinews. Photographic grade gelatin is usually produced by alkaline extraction process using bovine bones; however some acidic processes have been developed [6,17].

Some special gelatins are also used that are derived from pigskins. A jelly-like, non rigid mass which is formed as a result of the coagulation process of the lyophilic sols of gelatin is called a gel. The process of gel formation is known as gelation and this is accompanied by an increase in viscosity. The gels can be classified as elastic and non elastic depending on their behaviour.

Gelatin is a typical example of an elastic gel and it is obtained by cooling the lyophilic sol, prepared by warming gelatin with water [20]. The isoelectric point [20] of gelatin occurs at a pH 4.7. The isoelectric point of the disperse phase is the intermediate pH, the sol will not exhibit any electrophoretic

movement.

Nevertheless, the pH for the isoelectric point can be altered by adding electrolytes.

Similarly, addition of alcohol can bring about flocculation of gelatin over a certain range of pH probably due to dehydration. Dehydration appears to be the important factors for stability.

Photographic gelatin is much purer than that used in food industries. It is important to point out that gelatin solutions have the useful property of behaving as a liquid when warm and setting to a relatively hard gel when cool. The gelatin swells rapidly, absorbing water and dissolved development chemicals.

However, it does not dissolve at normal temperatures. These properties are harnessed in the preparation of photographic emulsion, in coating it on film base or paper and in the processes of development, fixation and washing [21]. The gelatin serves as an anti-coagulant and stabilizing colloid during the preparation of a photographic emulsion. The gelatin is an indispensable parameter in determining the dispersity or range of grain sizes of the silver halide.

#### **2.4.1 THE PHOTOGRAPHIC EMULSION**

An emulsion, according to Becher[24] is a heterogeneous system consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter in general exceeds  $0.1\mu$ . The type of emulsion formed appears to depend on the relative amounts of the phases.

Photographic emulsion is a light sensitive coating on paper or film, consisting of fine grains of silver halide suspended in a gelatin [25].

The preparation of the emulsion has gone through a continuous evolution. The number of ingredients has steadily increased with the diversification in the use of photography.

There are two general classes of emulsions and they are the negative emulsion and the paper emulsions. The negative emulsions are used for exposure in cameras and produce a reversed or negative image and print images that produce the final photograph. The emulsions used for developing papers are different from the negative emulsions in a number of ways. In the preparation of the paper photographic emulsion, the silver may be added to the gelatin solution containing the soluble halide, as in the preparation of a negative emulsion the halide may be added to the gelatin silver solution, or the silver and soluble halide may be added simultaneously. The paper emulsions are generally not heat ripened, as are negative systems since that will result in large crystal sizes which tends to increase the sensitivity.

The speed or sensitivity of an emulsion can be adjusted in many cases by the use of colour sensitizing dyes. Antiseptics, such as phenol or thymol are added to inhibit the growth of micro-organisms. Alum serves as hardener; the physical characteristics of the emulsion particularly during storage and development, is improved by the addition of formaldehyde and glyoxal, while wetting agents, such as saponin or other surfactants are used to reduce surface tension and accelerate the coating of the emulsion.

Negative emulsion can further be differentiated from paper emulsion in terms of the concentration of silver halide grains [26]. Thus, the silver halide grains in a paper emulsion seldom exceed 0.01 to 0.02 microns as compared with negative emulsion from 1.0 to 2.0 microns. Likewise, the amount of silver halide in the coated paper per unit area is about one-fifth that of a negative material.

## **2.5 THE ELEMENTAL SILVER**

The name originated from the Latin word-Argentum, meaning silver. Silver occurs in massive sulphide ores [27], in mineralized veins as the native ore[28], and in various natural alloys.

Silver also occurs very frequently as a secondary component of a great variety of minerals. Argentiferous galena is the most common of these, but association with Sb, As, Te and Se also occur. Galena and sphalerite are often enriched in Ag, following its isomorphous substitution into the crystal lattice [29].

Halide minerals are less common sources of silver AgCl, found in oxidized zones of deposits and shallow surface depth.

Igneous rocks contain on average 0.1 ppm Ag, sedimentary rocks 0.05-0.25ppm, organic rich shales up to 1ppm [30]. Sediments may contain slightly higher concentrations than soils and are prone to enrichment near mineralized zones or anthropogenic sources. The highest reported value is 154ppm for a grossly polluted section of the river Rhine [31].

Elevated silver levels have also been reported in anthropogenically derived

media such as sewage sludges and municipal wastes. A concentration of up to 960ppm has been reported [31,32,33].

It should be noted that this extraordinarily high value for one sewage sludge sample is influenced by discharges from a photographic works in the catchment area of the sewage treatment plant.

The normal range of silver in soils varies from <0.01 to 5ppm with an average of 0.1ppm [34].

It is also interesting to note that data on silver in plants have mainly been gathered to aid biogeochemical exploration for ores [34,35,36].

Copper, silver and gold belong to group 1B in the transition series and are known collectively as the coinage metals.

Copper, silver and gold are unreactive heavy metals in group 1B and their physical and chemical properties are very different from the highly reactive, light easily fusible metals of group 1A, such as sodium[37]. The unreactive metals are amongst the least electropositive of the metals and are unable to discharge hydrogen ions from solution. They are therefore used in coinage and referred to as such.

The univalent chlorides of copper, silver and mercury are all white insoluble solids. The oxide of mercury, silver and gold are thermally unstable.

### 2.5.1 PHYSICAL PROPERTIES OF SILVER.

The major physical properties of silver are as shown in the table below[38].

**Table 2.1: Physical parameters of Silver**

Parameters	Values
Symbol of Element	Ag
Atomic Number	47
Atomic Mass	107.87
Covalent Radius ( $\text{A}^0$ )	1.34
Atomic Radius ( $\text{A}^0$ )	1.44
Ionic Radius ( $\text{A}^0$ )	1.26
Atomic Volume (W/D)	10.3
1st Ionization Energy (Kcal/g-mol)	175
Electronegativity (Pauling's)	1.9
Heat of vaporization (K-cal/g-atom)	60.7or 255.1kJ/mole
Heat of fusion (K-cal/g/atom)	2.70 or 11.3kJ/mol
Electrical conductance (micro-Ohms)	
(Most conducting of that group-Gp.IB)	0.616
Thermal conductance (Siemens, S)	0.98
Specific heat (cal/g/ $^0\text{C}$ )	(0.056 or). $235\text{Jg}^{-1}\text{K}^{-1}$
Crystal structure	cubic, face centered cubic
Radioactive isotope	Ag <sub>110</sub> (24sec.) B-, <sub>111</sub> (7.5days) B-, Y
Transition element	Partially filled 4 d-orbital
Colour (when pure)	White lustrous metal

Boiling point ( $^{\circ}\text{C}$ )	2210
Melting Point ( $^{\circ}\text{C}$ )	960.8
Density or specific gravity ( $\text{g}/\text{cm}^3$ )	10.5
Electron structure (most stable config.)	(Kr) $4d^{10}5s^1$
Optical reflectivity	97%
Coefficient of linear thermal expansion	$1.862 \text{ E cm}/^{\circ}\text{C}$
Crystal structure at room temperature	face centre cubic (fcc)
No of atoms per unit cell	4
Common lattice defect	Frenkel defect
Mohs hardness	2.5

### 2.5.2 CHEMICAL PROPERTIES OF SILVER

Silver is inert to many chemical substances. However, it is the most reactive of the noble metals forming three cationic species,  $\text{Ag}^+$ ,  $\text{Ag}^{2+}$  and  $\text{Ag}^{3+}$  of which the monovalent form is environmentally significant. Silver as  $\text{Ag}^+$  is among the most toxic of heavy metals to a range of life forms [39,40].

The principal chemical reactions of silver are discussed as follows [41].

#### Reaction with dilute hydrochloric acid



A white precipitate is obtained when silver ion is treated with dilute hydrochloric acid.

### Reaction with concentrated hydrochloric acid.

A soluble dichloroargentate complex is formed.



By diluting with water, the equilibrium shifts to the left and the precipitate reappears. The silver chloride precipitate thus formed can be dissolved by the addition of ammonia solution.



Also, potassium cyanide dissolves the precipitate with the formation of the dicyanoargentate complex.

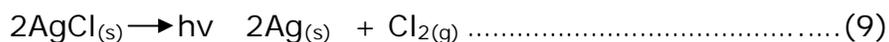


The precipitate of AgCl is also soluble in sodium thiosulphate.



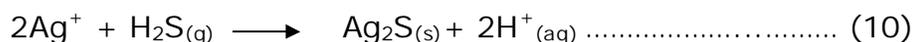
This is an important reaction because it is used during processing of photographic impression by fixing [20].

Sunlight or ultraviolet irradiation decomposes the silver chloride precipitate, which turns to grayish or black owing to the formation of silver metal.

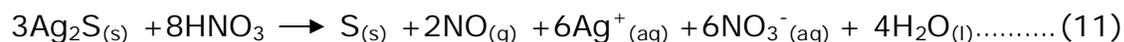


The reaction is usually slow. Photography is based on these reactions. The processes are initiated in the camera and the reaction gets to completion when the photographic film has been developed to get a negative image. The excess of silver halide has to be removed to make the negative insensitive to light by fixation[20].

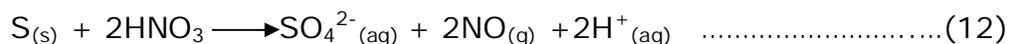
### Reaction with hydrogen sulphide



The reaction of silver (1) ion with hydrogen sulphide results to a black precipitate of silver sulphide. When hot concentrated nitric acid is added to the precipitate it decomposes the silver sulphide and sulphur remains in the form of white ppt.



If the mixture is heated with conc.  $\text{HNO}_3$  acid for a considerable time, sulphur is oxidized to sulphate and the precipitate disappears.

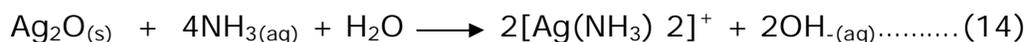


The precipitate of sulphur is insoluble in ammonium sulphide, ammonium polysulphide, ammonia, potassium cyanide, or sodium thiosulphate. Silver sulphide can be precipitated from solutions containing diammine –, dicyanato –, or dithiosulphato argentate complexes with hydrogen sulphide.

### Reaction of silver with ammonia solution.

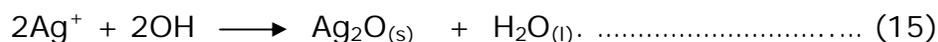


The brown precipitate of silver oxide dissolves in excess of the reagent, and diammineargentate complex ions are formed.

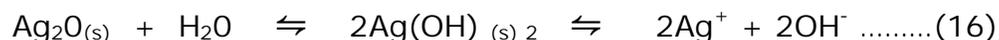


The solution should be disposed of quickly because when set aside silver nitride  $\text{Ag}_3\text{N}$  precipitate is formed, which explodes readily even in a wet form.

**Reaction of silver with sodium hydroxide to give brown precipitate of silver oxide.**

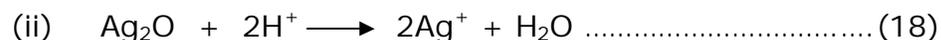
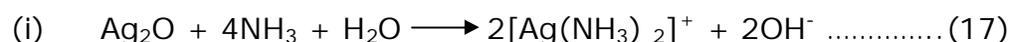


A well washed suspension of the precipitate shows a slight alkaline reaction owing to the hydrolysis equilibrium:



The precipitate is insoluble in excess reagent. The precipitate dissolves in

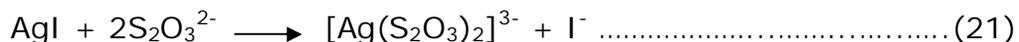
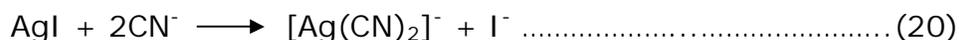
(i)  $\text{NH}_3$  solution and (ii) Nitric acid.



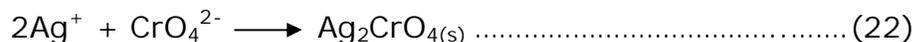
**Reaction with potassium iodide to give yellow precipitate of silver iodide.**



The precipitate is insoluble in dilute or concentrated ammonia, but dissolves readily in potassium cyanide and sodium thiosulphate.

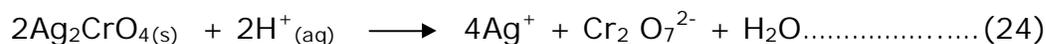
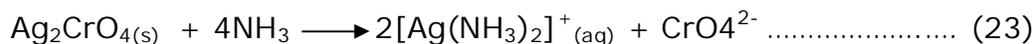


**Reaction with potassium chromate in neutral solution to give red precipitate of silver chromate.**



The precipitate formed is a needle-like red crystals of silver chromate. The reaction can serve as a spot test for silver.

The precipitate formed is soluble in dilute nitric acid and in ammonia solution.



The acidified solution turns to orange because of the formation of dichromate ions in the reaction.

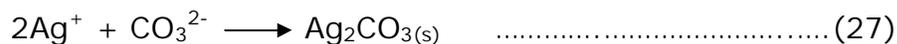
**Reaction with potassium cyanide to yield a white precipitate of silver cyanide.**



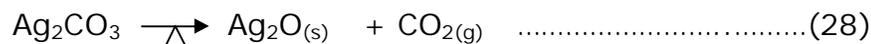
When potassium cyanide is added in excess the precipitate disappears owing to the formation of dicyanoargentate ions.



**Reaction with sodium carbonate to give a yellowish – white precipitate of silver carbonate.**

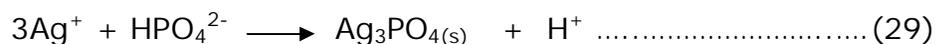


When heated, the precipitate decomposes and brown silver oxide precipitate is formed.



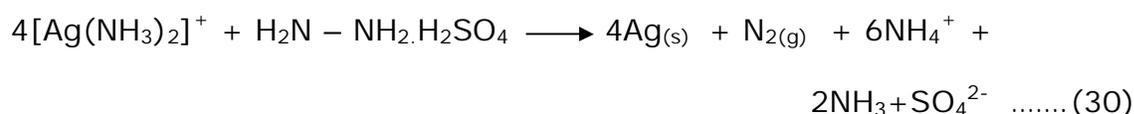
Nitric acid and ammonia solution dissolve the precipitate.

**Reaction with disodium hydrogen phosphate in neutral solution to yield yellow precipitate of silver phosphate.**



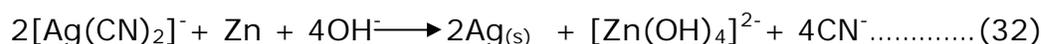
The precipitate is also soluble in nitric acid and ammonia solution respectively.

**Reaction of diammineargentate ions with hydrazine sulphate to form finely divided silver metal, with the evolution of gaseous nitrogen.**



**Cyanidation Reaction:**

The process of recovering silver by treatment with cyanide is called cyanidation reaction. In the cyanide process, the silver – bearing rock is crushed and agitated with an alkali cyanide solution through which a current of air is blown. The metal passes into solution as a complex ion. The free metal can be precipitated from its solution by treatment with zinc in the presence of alkali.



**Another form of cyanidation reaction:**



The complex salt is treated with zinc so that silver is precipitated by electrochemical displacement.



The group IB elements all have  $d^{10}s^1$  electron configurations and form the +1 oxidation state, a point of similarity with the group 1A elements. Group 1B metals such as copper, silver and gold are much less reactive than the alkali metals, they exhibit higher oxidation states, and they form complex ions.

The +1 ions of the group IB elements are colourless like  $\text{Na}^+$  in group 1A, but they differ from  $\text{Na}^+$  in that they form many insoluble salts including the halides. Silver and gold have unstable +2 oxidation states.

All the group IB metals have excellent thermal and electrical conductivities similar to group 1A, the alkali metals. Silver is a transition metal with  $[\text{Kr}]d^{10}s^1$  as its most stable electron configuration. The electrons per shell is 2,8,18,18,1.

### 2.5.3 TOXICITY OF SILVER

Laboratory experiments have shown  $\text{Ag}^+$  to be one of the most toxic elements to micro organisms and biochemical processes in the soil. It has been reported that  $6 \times 10^{-9} \text{g Ag}^+/\text{ml}$  kills *Escherichia coli* in 2 – 24 hours, depending on the numbers of bacteria [42]. It has also been reported that silver nitrate a compound of silver at a concentration of  $10 \times 10^{-9} \text{gAg per ml}$  killed 50% of the fungus *Alternaria tenuis* [43].

Hoffman and Hendrix [44], showed that soluble Ag had an adverse effect on *Thiobacillus ferro oxidans* at  $0.1 \mu\text{g}/\text{ml}$  or more. However, reports have shown some bacteria such as *pseudomonas* and *thiobacillus* which have a

great capacity for Ag accumulation and tolerance, probably due to reduction of the Ag ion to metallic Ag or Ag<sub>2</sub>S [45]. The release of silver into the environment as the case with other heavy metals is strictly regulated. Many of the heavy metals are significant as pollutants of ecosystems throughout the world. Heavy metals are, however, important in several ways: many are used industrially in technologically advanced countries, and are physiologically essential for plants and animals, and thus have direct bearing on human health as well as agricultural productivity.

Surveys carried out since the 1960s have indicated that soils in many parts of the world, especially in urban and industrial areas, contain anomalously high concentrations of heavy metals [46]. Additional information pointed out that in most cases the levels of these heavy metals are not high enough to cause acute toxicity problems. However, increased concentrations in the food chain may cause significant health effects in the long term. Heavy metal polluted soils constitute a major environmental problem because many of the elements will persist in the soil for hundreds or even thousands of years, and already polluted soil therefore require careful management.

The absorption of colloidal silver into human system results in an illness called argyria which is darkening of the skin [47]. Soluble silver salts are also, poisonous. This is why analyst handling small quantities of any form of silver should take sufficient precaution and observe normal good house keeping. Another health hazard associated with prolonged contact with silver is a lung condition marked by shortness of breath known as emphysema.

#### **2.5.4 USES AND APPLICATIONS OF SILVER.**

Silver is a precious metal of considerable economic and historical importance. By 400BC, the Assyrians had established a system of trade based on silver. Other uses mentioned in old manuscripts include the fabrication of idols, shrines, bowls, vases, flasks and jewellery [46]. Major contemporary uses include the production of very thin films for electroplating, manufacture of reflecting mirrors, electrical contacts, alloys, coinage, and jewellery, and various uses in density, optics, photography and medicine. Silver is also used in creaming and paint production. Certain compounds of silver are also of industrial importance; for instance, silver nitrate. Silver perchlorate can be used as an accelerant in rocket propellants. The halides of silver particularly silver bromide and chloride are important in the photographic and photocomposition fields[43,44,45]. Silver is known to be used in construction of astronautics devices such as solar cells. Silver finds use in the printing industry. Silver is also used for cloud seeding [48,49] which is one of the techniques used by rain makers to cause cloud by exposing silver iodide (AgI) into the air.

An important alloy of silver which is most widely used in silver jewelry is sterling silver which is 92.5% silver and the remaining is iron[50]. Silver can also be used as a catalyst example is formaldehyde catalyst – which is silver screens or silver crystals.

## **2.6 DETERMINATION OF SILVER**

Analysis of the silver content in the spent photographic emulsion is a necessary step towards ascertaining the amount of silver present initially and after the recovery process. Several analytical methods of determining the amount of silver exists. These include: gravimetry, titrimetry, colorimetry (used for determining major amounts of silver). Instrumental methods include the use of atomic absorption spectroscopy, flame emission spectroscopy and the use of ion specific electrodes<sup>[51,52]</sup>. X – ray fluorescence spectroscopy (XRFS) is a multi – element method of analyzing for silver.

### **2.6.1 ATOMIC ABSORPTION SPECTROSCOPY**

Atomic absorption spectroscopy is a sensitive means for the quantitative determination of more than 60 metals or metalloid elements[52,53,54].

The development of source element in atomic absorption spectroscopy which results in its ability to spectrally select the radiation of choice is an overwhelming step to its global recognition and general preference to other analytical procedure.

The atomization is done by a nebulizer or burner which converts the liquid to an aerosol. The aerosol is fed into the flame where the metallic element is converted to vapour containing the atoms. The source (Hollow cathode lamp) emits a characteristic radiation of the element of choice. The dispersed atom will absorb the radiation energy and thereby emit spectral lines when radiation is passed through the vapour. The monochromator will

isolate the energy wavelength of the choice atom from other emitted wavelengths and the response is measured in the signal processor. Atomic absorption spectrometry is a single element method of analysis. It should be emphasized that in AAS, analysis is usually carried out in solution, i.e. with dissolved samples. While as in XRFS method; solid samples are analysed directly.

The choice of method for a particular application should take account of those factors as well as their sensitivity, precision and accuracy. The choice of method may well be dominated by the relative cost of the instrumental techniques current in use. Absorption of radiation by a given amount of sample is quantitatively interpreted by Beer – Lambert’s Law. This law can also serve as a guide to monitor the detection limits for several different methods of analysis categorized as solution or solid sample methods.

Thus;

$$\text{Absorbance} = \log I_0/I_t = ECl \dots\dots\dots (36)$$

Where:  $I_0$  = the intensity of the incident beam

$I_t$  = the intensity of the beam transmitted by the atoms.

$C$  = the concentration of the atoms in the atomizer, and

$EI$  = a constant.

Beer – Lambert’s Law is extremely useful in determining the concentration of a solution from the measurement of the absorbance of a standard solution used for preparation of standard calibration curve. The concentration of the analyte is then determined by interpolation procedure[55].

### 2.6.2 TITRIMETRIC METHOD

Titration is an important step in volumetric analysis. Volumetric analysis is a method used by chemists to determine the quantity or concentration of a substance by measuring the volumes of some solutions [56]. A standard solution is usually prepared during a titration.

Titrations may involve precipitation, complexation, redox or acid-base reactions. The end point of a titration can be detected by using a suitable indicator. The end point of titrations can alternatively be identified through changes in pH value, electrical conductivity or temperature variations.

By titrating a solution containing  $\text{Ag}^+$  with standard potassium cyanide or potassium thiocyanate solution as described by Vollard [57,58], the concentration of the  $\text{Ag}^+$  ion present in solution can be determined. Thus



Ferric alum indicator is used for this precipitation titration to determine the end point value. This operation must be carried out in a well ventilated fume cupboard as copious fumes of hydrocyanic acid are evolved.

### 2.6.3 ELECTROGRAVIMETRY

Electrogravimetry[58] is a method which involves quantitatively electroplating a metal onto an electrode that is dimensionally stable. A dimensionally stable electrode (DSE) is the electrode that does not dissolve in the electrolyte in which it is immersed during electrolysis.

The amount of metal deposited is determined by the weight difference of the cathode before and after electrolytic deposition. The details of electrolytic

deposition will be discussed under “recovery of silver by electrowinning”.

## **2.7 SURFACE PASSIVITY**

Some metals produce protective films on their surface. The metals that readily form an adherent coating which resists further chemical action are said to become passive[59]. Passive metals are corrosion resistant to a large extent.

However, this phenomenon of surface passivity poses a problem to electroplating process because it is difficult to deposit other metals satisfactorily on the surface of a passive electrode. An active surface is necessary for a reasonable adherent during electroplating process.

## **2.8 SURFACE ACTIVATION**

Cathode surfaces are thoroughly cleaned in order to allow adhesion of discharged metal atoms into such surfaces. The importance of perfect cleaning cannot be over emphasized, since upon the efficiency of this operation depends the adhesion of the deposited metal.

Preliminary cleaning or degreasing of the electrodes involves the removal of heavy oils, greases with trichloroethane. This is followed by the removal of oxide and scale by pickling and dipping the electrode into hot alkaline solution, or immersion in dilute acid. The electrode is subsequently rinsed with copious amounts of distilled water. These stages will remove all traces of grease. And any passive film to give an active surface to which the electroplated deposit will adhere. Trichloroethane is a good solvent to

remove greases. It is environmentally friendly.

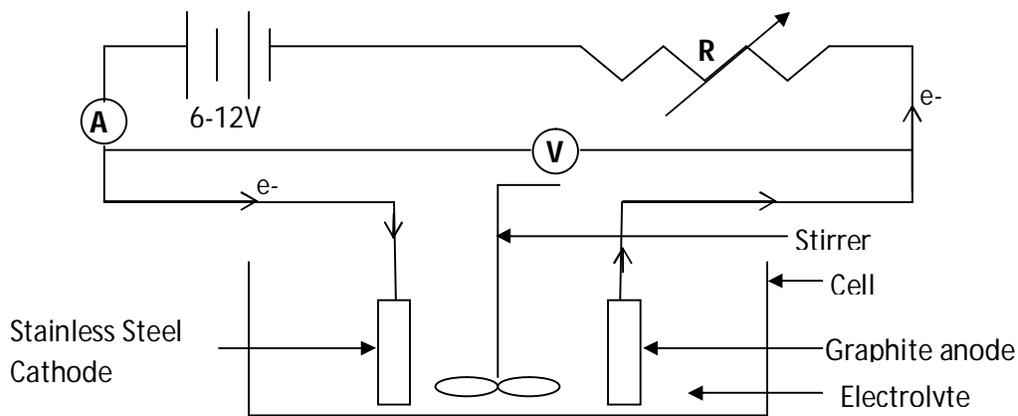
## **2.9 RECOVERY OF SILVER BY ELECTROWINNING.**

The most widely used silver recovery method for large operation is electrolytic or electrowinning technique. In this method, the silver is recovered from the solution by electroplating it on a cathode which is used as the negative electrode.

A controlled, direct electrical current is passed between two electrodes suspended in the emulsion as the electrolyte. Silver is deposited on the cathode in the form of nearly pure silver plate. The cathodes are removed periodically and the silver is stripped off for sale and reuse [60] .

This method yields entirely pure silver. The fixer or developer can be reused after the extraction of silver. An efficiently operated electro – winning technique can give about 95 percent of potentially available silver.

**FIG 2:1 ELECTROLYTIC SILVER RECOVERY CELL**



The battery or A.C converter (where A.C is used) acts as an electron pump, pushing electrons into the cathode and removing them from the anode. At the cathode silver ion undergoes reduction by accepting an electron, while oxidation takes place at the anode. Stirring is effected to reduce concentration polarization. Current and voltage are indicated by an ammeter and voltmeter respectively. Electro-deposition is governed by Ohm's law and Faraday's laws of electrolysis [62].

According to Ohm's law, the strength of an electric current flowing through a conductor, i.e., the quantity of electricity flowing per second, is determined by the difference in potential applied across the conductors and by the resistance offered by the conductor to the current.

Thus; 
$$I = \frac{V}{R} \dots\dots\dots(38)$$

Where  $I$  = current flowing (ampere)

$R$  = resistance (Ohm)

$V$  = applied potential (volt)

Faraday's first law of electrolysis states that the mass of a substance which undergoes a reaction at the electrodes is directly proportional to the quantity of electricity passed through the solution. This law applies to both molten electrolytes and solution of electrolytes.

Faraday's second law of electrolysis states that the masses of different substances produced during electrolysis are directly proportional to their equivalent weights. From the second law, it follows that during electrolysis 96500 coulombs of electricity will yield one equivalent weight of any substance.

The potential applied between anode and cathode is the driving force for the transfer of charge across the metal/solution interface, its value determines the rate of charge transfer. The potential for commercial deposition processes is usually between 2 and 16 volts direct current applied between anode and cathode and derived from a transformer – rectifier set. For small scale laboratory scale plating, accumulators or dry cells may be used.

The desired qualities of a deposit include adherence, dense and smoothness. These conditions enable the deposit to be washed without undue loss. As a rule, more satisfactory deposits are obtained when the metal is deposited from a solution in which it exists as a complex [41, 62].

As the applied potential is increased the rate at which the metallic ions are discharged measured by the current density, increases. There is the tendency for hydrogen co-discharge to occur at the cathode as a result of increase in applied potential up to a given point. It is dangerous to the

quality and quantity of the deposits obtained during electrolytic reaction.

Most of the hydrogen is evolved from the cathode surface as a gas and only a small portion is built into the cathode structure. Hydrogen absorbed into the deposit can give rise to hydrogen embrittlement.[63].

A number of natural agencies transport metal ions from the body of the bath to the cathode, to replace the ions deposited.

These agencies are diffusion, convection and electrical migration. Electrical migration, which involves the transport of ions under an applied electric field. Positive ions being attracted to the negative electrode and vice versa. This mode of transportation contributes little to the total transport of ions. This is because the speed of the ions is very small.

The other two agencies, convection and diffusion transport most ions. Convection means, essentially, the mass transport of electroactive material to the electrode by gross physical movement. This is simply fluid or hydrodynamic flow of the solution. Generally, fluid flow occurs because of natural convection caused by density gradients. This could also be forced convection caused by stirring or agitation of the solution.

Diffusion on the other hand, is the natural transport or movement of a substance under the influence of a gradient of chemical potential, that is, due to the concentration gradient. In other words, substances move from regions of high concentration to regions of low concentration in order to minimize or eliminate concentration differences.

The effect of diffusion is most pronounced in the regions of the electrolyte next to the cathode, called the cathode diffusion layer, from which ions are

continuously removed by deposition and replaced by transport from bulk of the bath. Both diffusion and convection play a major role in the transport of complex ions from body of the bath to the cathode.

The contemporary theory of deposition from complex ions is that metal is deposited by direct discharge from the complex ion [64,65]. The complex ion is thought not to undergo further dissociation, for example to give silver ions and cyanide ions or thiosulphate ions as the case may be.

The ions are believed to be surrounded by an atmosphere of other ions of opposite charge or water molecules known as hydration sheath in the case of water. Under the influence of an applied electric field, this sheath distorts to give one part of the molecule positively charged and another negatively charged to produce a dipole. The positively charged end is aligned towards the cathode, and the negative end towards anode.

The metal ion is stripped from its distorted sheath as it passes through the double layer within the diffusion layer, and is neutralized by accepting electrons, and is deposited on the cathode [66,67]. The double layer is the charged layer at metal/solution interface.

The released water and anions then migrate by diffusion, convection or electrical attraction away from the cathode to the body of bath.

## **2.10 CATHODE EFFICIENCY**

Cathode current efficiency is the proportion of the total cathode current, which is used in depositing the metal concerned. The wasted current can also be defined as the portion of current flowing, which is not used in

depositing metal. This wasted current is used primarily in depositing hydrogen, an unwanted by-product of the deposition process. The cathode current efficiency can also be defined as the ratio of the amount of wanted product, which is actually obtained by Faraday's first law of electrolysis [65, 68] to the quantity of electricity supplied.

A coulometer is a small electroplating cell in which the deposition process is carefully chosen so that all the current flowing through the cathode is used in one electrode process only. A process like this, is said to have a cathode efficiency of 100%. The cathode current efficiency is calculated as follows:

$$\text{Atomic weight of silver} = 107.87$$

$$\text{Valency of silver} = 1$$

$$\text{Chemical equivalent of silver} = 107.87$$

$$\text{Valency of silver} = 1$$

$$\text{Chemical equivalent of silver} = \frac{\text{Atomic weight}}{\text{Valency}}$$

$$= \frac{107.87}{1} = 107.87$$

One ampere hour is 1 ampere flowing for  $60 \times 60 = 3600$  sec.

Weight of silver deposited per ampere hour at 100% efficiency

$$= \frac{107.87 \times 3600}{96500}$$

$$= 4.024 \text{g Ag.}$$

$$= 4.024 \text{g Ag.}$$

Therefore, 4.024g Ag would be deposited per ampere hour at 100% efficiency.

Efficiency varies with operating parameters of an electrolytic cell and therefore it is necessary to define the current density, pH, temperature and metal ion content of the cell.

## **2.11 CURRENT DENSITY**

Current density is the quantity of current on a specific area, and is usually expressed in terms of amperes per square decimeter, or as ampere per square metre. This is an important electroplating parameter which must be carefully determined in order to obtain a uniform deposit on the cathode.

As a general rule, the distribution of the deposit is more uniform at low current densities. However, low current densities need long depositing times to achieve a reasonable thickness of deposit. High current densities cause the deposit to build up excessively on prominent edges or extremities of the cathode while recessed areas may receive less than adequate coverage.

Therefore while it is desirable for economic reasons to work as fast as possible, one should also take into consideration the other facts when deciding what current densities to employ for particular electrodeposition.

The higher the current density the greater the cathode efficiency.

## 2.12 TEMPERATURE CONTROL

It is essential for the success of the operation of many plating processes, that the solution temperature is kept within the recommended range. A temperature indicator is required for this purpose. It is important to enclose a temperature-sensing element, which will serve to eliminate the possibility of D.C. electrical leakage. It will also contribute in preventing the possibility of unsatisfactory work being produced due to accidental rise or fall in operating temperature.

Mechanical agitation is used for solutions, which contain wetting agents or easily oxidisable constituents, which prevent the employment of air agitation. It is also used to supplement air agitation. The solution may be stirred mechanically, circulated by means of a pump or by the use of magnetic stirrer.

## 2.13 THE IMPORTANCE OF pH AND BUFFERS.

The pH value is a measure of the active acidity or alkalinity of a solution. It is important that the pH value be maintained at value specified. In electrodeposition it is advantageous to use solutions of known and steady pH value. pH is a most important factor in the control of electroplating solutions[65]. The formula used to calculate pH is given as:

$$\text{pH} = -\text{Log}_{10} [\text{H}^+]\dots\dots\dots(39)$$

where  $[\text{H}^+]$  = active hydrogen ion concentration.

It is the hydrogen ion activity, which forms the fundamental basis of the pH scale in aqueous media. The actual value of hydrogen ion concentration is

however extremely low, and for convenience is expressed as its negative logarithm.

Buffers are added to a solution in order to resist the effect of additions of acid or alkali on its pH value. This is most easily accomplished by adding buffer salts to solution, usually a mixture of weak acid or base and one of its salts. This process resists changes in hydrogen or hydroxyl ion concentration in solution by corresponding dissociation or association. Buffering of the layer of electrolyte at the cathode surface is important in a number of electroplating processes.

Evolution of hydrogen gives an excess hydroxyl ions in the cathode layer and in the absence of a buffer, the pH rises.

With increase in pH at the cathode there is the possibility that hydroxide will be precipitated on the cathode surface.

Examples of buffer salts are boric acid/borate buffer system, and citric acid/citrate system. Ethanoic acid and sodium ethanoate can serve as a good buffer system too.

The methods suitable for the determination of pH of electroplating solutions are briefly summarized here.

- (i) Colorimetric methods using indicators
- (ii) Electronic method using a pH meter.
- (iii) Comparator papers.
- (iv) Disc comparator.

The indicators employed for the colorimetric determination of pH value are dyestuffs which give differing colours in acid and alkaline solutions. A wide

range of indicators is now available and by their use it is possible to determine with considerable accuracy the pH value of a solution.

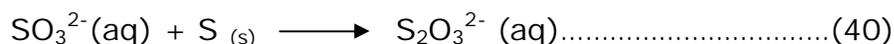
The pH meter is an electronic voltmeter with a specially calibrated scale. This instrument is now widely used where pH values are required with high accuracy. A glass electrode and a calomel reference electrode are immersed in the solution under test and the pH value is obtained from the difference in potential of the two electrodes.

The comparator papers provide the simplest method of testing the pH of solutions. They are supplied in strips similar to litmus paper. However, the comparator has a plain white background. The colour strips correspond to a definite pH value, which is indicated by the printed scale on the side of the box. In the case of a disc comparator, the pH value corresponding is indicated by figures on the disc, which appear in the front of the case.

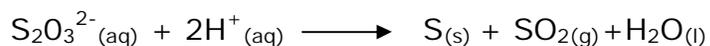
#### **2.14 THE THIOSULPHATE AS A COMPLEXING AGENT**

The thiosulphate ion,  $S_2O_3^{2-}$  is related to the sulphate ion ( $SO_4^{2-}$ ). The difference between the two anions is the replacement of one oxygen atom in the sulphate ion by a sulphur atom in the thiosulphate. The prefix 'thio' is used to indicate a substitution of sulphur for oxygen in a species.

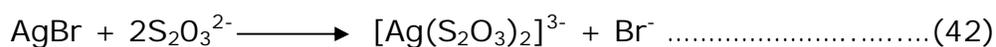
The thiosulphate ion is produced when an alkaline solution of a sulphite is boiled with elemental sulphur, as shown in the reaction:



In acid media the thiosulphates decompose to give elemental sulphur dioxide gas ( $SO_2$ )



The pentahydrates of sodium thiosulphate is used in photography under the name "hypo". The excess AgBr not reduced by the developer is usually removed by treatment with sodium thiosulphate solution. Thus, it exhibits a complexing property.



## 2.15 DESTRUCTION OF CYANIDE

Cyanide can be present in an effluent from a number of sources within the plating environment. It can be present either as AgCN or as a soluble cyanide complex such as NaAg(CN)<sub>2</sub> or Ag (CN)<sub>2</sub><sup>-</sup>. Cyanide in silver is as a result of sodium cyanide used in processing argentite (Ag<sub>2</sub>S) an ore of silver. There are a number of different methods of destroying cyanide, each with its own advantages and disadvantages. Two basic methods are discussed here.

### 2.15.1 Chlorination Method:

In chlorination method either gaseous chlorine or sodium hypochlorite solution may be used. At pH of 11, chlorination of cyanide containing solutions results in rapid detoxification by the hydrolysis of cyanate into nitrogen and carbonate.

At this pH value, cyanogens chloride is not produced at an intermediate stage. An excess of chlorine is always needed for complete removal of the cyanide in the presence of sodium thiosulphate or sulphur dioxide.

### **2.15.2 Electrolytic Method**

In electrolytic oxidation process, all cyanide complexes may be oxidized at the anode without an addition of any other chemical agents. The technique is best used for concentrated solutions and the procedure is to recycle the effluent continually through an electrolytic cell where the anodes of graphite and cathodes of titanium are interleaved.

The advantage of this process is that it enables the metallic content to be recovered as a deposit on the cathodes which are collected for purification or and reuse.

The process is carried out at a minimum temperature of 90<sup>0</sup>C and at an anode current density of 3.0 to 6.5 amp/dm<sup>2</sup>. The electrolytic process is carried out in a steel tank fitted with air agitation, fume cupboard and preferentially covered.

### **2.16 THE OBJECTIVE OF THIS WORK**

At present, information on the operating conditions for optimal recovery of Silver from photographic waste solutions are quite inadequate. It is therefore the objective of this research to establish process variables which will enhance optimal recovery of Silver from spent photographic solutions.

It is also intended to evaluate the application of the classical law of Faraday to a system that involves competing electrolyses.

## 2.17 THE SCOPE OF THE STUDY

In order to realize the above objective , the following steps will be followed.

- Sampling of the effluent solutions
- Determination of the concentration of silver in the effluent by Volhard titrimetric method
- Spectrophotometric analysis for metallic content of the effluent.
- Determination of the non metallic content of the effluent.
- Conductivity and pH measurement of the effluent.
- Preparation of stripping solution.
- Choice of electrodes
- Construction of the electrolytic cell
- Determination of polarity
- Effect of concentration of the effluent on quantity of Silver recovered
- Determination of the optimum temperature, pH and current density for Silver precipitation
- Determination of cathode efficiency.

## CHAPTER THREE

### 3.0 EXPERIMENTAL MATERIALS/METHODS

#### 3.1 SOURCES OF SAMPLES

Samples of spent photographic emulsion were sourced from the following photo-processing industries within and outside Imo state, Nigeria.

- a. Lixil colour photo laboratory; Rotobi/School Road, Owerri, Imo – State
- b. Eurocolours photoprocessing laboratory; Uwani Enugu, Enugu State.
- c. Obi's Commercial Photos; Lagwa Okwuato, Aboh-Mbaise, Imo State.
- d. Photowash Nigeria Ltd., 13 Mission Rd, Uromi, Edo State.

Hyondae Photo Laboratories Ltd; 17 Aba-Owerri Road, Aba, Aba State.

From each of the above photoprocessing laboratories, three sources of photographic effluents which include rinser, developer and fixer were collected in sufficient quantity for the project.

#### 3.2 REAGENTS

3.2.1 Nitric acid (BDH grade)

3.2.2 Sulphuric acid (BDH grade)

3.2.3 Sodium chloride (May and Baker Ltd)

3.2.4 Ammonium chloride(May and Baker Ltd)

3.2.5 Potassium chloride (BDH grade)

3.2.6 Conc. Ammonia (Analar grade)

3.2.7 Silver nitrate (Analar grade)

3.2.8 Methanol (BDH)

3.2.9 Ferrous ammonium sulphate hexahydrate (BDH)

3.2.10 Ammonium thiocyanate (Analar grade)

3.2.11 Granulated zinc (Zinc dust).

3.2.12 Deionized water.

### **3.3 EQUIPMENT**

3.3.1 Atomic Absorption Spectrophotometer (Pye Unicam sp 1900)

3.3.2 Flame photometer (Model EEC M866150)

3.3.3. Digital pH metre (Labtech model)

3.3.4 Electronic balance (Metler PN163)

3.3.5 Ammeter (Milliammeter-Philip Harris Ltd)

3.3.6 Rheostat (Philip Harris Ltd)

3.3.7 Voltmeter (Anders Ltd)

3.3.8 Stop Watch (Junghans)

3.3.9 Thermometer (Celcius type)

3.3.10 Electric plate (NI.115, NPL)

3.3.11 Thermostated water bath (Kottermann)

3.3.12 Magnetic stirrer

3.3.13 Conductivity Metre (dipping cell type; Hanna Ec215 model) 3.3.14

Wires and crocodile clips

3.3.15 DC power source (12 volts battery)

3.3.16 pH paper and filter paper.

3.3.17 Dimensionally stable electrodes (stainless steel and graphite)

### **3.4 PREPARATION OF BUFFER SOLUTIONS**

Buffer solutions were prepared using freshly boiled and cooled distilled water. This should be kept in bottles made of alkali – free glass and used not later than three months after preparation. The type of buffer prepared depends on the pH range of the working solution. The method of preparation adopted in this work is as described in British Pharmacopia[55].

#### **3.4.1 ACETATE BUFFER pH 3.5.**

This Acetate buffer was prepared by dissolving , 25g of ammonium acetate in 25ml of distilled water and adding 38ml of 7M hydrochloric acid to the solution. The pH was then adjusted to 3.5 with either hydrochloric acid or 5M ammonia and diluted to 100ml with deionized water.

#### **3.4.2 ACETATE BUFFER pH 5.0**

In the preparation of acetate buffer pH 5.0, 13.6g of sodium acetate and 6ml of glacial acetic acid were dissolved in sufficient distilled water to produce 100ml of solution.

#### **3.4.1 CITRO – PHOSPHATE BUFFER pH 7.0**

Buffer solution of pH 7.0 was prepared by mixing 82.4ml of a 7.15% w/v solution of disodium hydrogen orthophosphate with 17.6ml of a 2.1% w/v solution of citric acid.

#### **3.4.4 BORATE BUFFER pH 9.0**

This buffer solution is prepared by dissolving 0.6189g of boric acid and

0.7456g of potassium chloride into 50ml of deionized water. To the mixture, 21.30ml of 0.2M sodium hydroxide was added and diluted to 200ml with deionized water.

#### **3.4.5 AMMONIA BUFFER pH 10.9**

Ammonia buffer pH 10.9 was prepared by dissolving 13.5g of ammonium chloride in 130ml of 13.5M ammonia. This was subsequently diluted to 200ml with deionized water.

#### **3.5 CHOICE OF ELECTRODES**

Based on some electrochemical parameters such as nature of the electrolyte, inertness of the electrode, availability and cost considerations; stainless steel (cathode) and graphite (anode) were used for the electrogravimetric work.

#### **3.6 SAMPLING OF SOLUTIONS**

It is essential that the sample taken be truly representative of the solution in the tank [69]. The solution was thoroughly mixed by stirring. A representative sample was obtained by immersion of a glass sampling tube into the solution with the upper end open, and covering this end before withdrawing the tube. The content of the tube was then allowed to drain into a glass beaker. This procedure was repeated at different depths and in different parts of the tank until sufficient solutions was removed for analysis.

### **3.7 CONCENTRATION OF EFFLUENTS BY EVAPORATION**

Evaporative recovery technique was used to enhance the concentration of silver ion present in the photographic waste solution. Evaporation of liquid is the loss of molecules from surface of solid or liquid.

The photoprocessing waste solution was boiled until an appreciable volume was evaporated. The amount of water evaporated out for a given volume of effluent and the resultant percentage evaporation or concentration was recorded in table 3.1

**Table 3.1: Effluent Concentration by Evaporation.**

<b>S/No</b>	<b>Initial volume of effluent (cm<sup>3</sup>)</b>	<b>Volume evaporated (cm<sup>3</sup>)</b>	<b>Volume after evaporation (cm<sup>3</sup>)</b>	<b>% Evaporation (concentration)</b>
1	1000	-	1000	0 (as discharged)
2	1000	100	900	10
3	1000	200	800	20
4	1000	300	700	30
5	1000	400	600	40
6	1000	500	500	50
7	1000	600	400	60
8	1000	650	350	65
9	1000	700	300	70
10	1000	750	250	75
11	1000	800	200	80
12	1000	900	100	90

### **3.8 SPECTROPHOTOMETRIC ANALYSIS OF PHOTOGRAPHIC EFFLUENTS**

Samples of coloured photographic effluents used for this analysis were collected from sources already mentioned. The reagents used are analytical grade and thus required no further purification. All preparations involving water were done with deionized water. Atomic absorption spectrophotometer and flame photometer were used for the determination of metals accordingly. Gravimetric and volumetric analyses were also applied at appropriate places.

#### **3.8.1 PREPARATION OF STANDARD SOLUTIONS**

Standard solutions of the elements to be investigated were prepared following the descriptions stated by Whitehead [49] and Skoog .A. Douglas [55,70] .

#### **3.8.2 STANDARD SOLUTION OF SILVER (Ag)**

To prepare 1000ppm stock solution of silver (Ag). 1.575g silver nitrate salt  $\text{AgNO}_3$  was weighed and dissolved in  $200\text{cm}^3$  of deionized water. This was diluted to  $100\text{cm}^3$  or 1litre in a volumetric flask using deionized water. The stock solution was stored in a darkened or amber colour bottle with a stopper. Aliquots solutions of 1.0ppm, 2.0ppm, 3.0ppm, 4.0ppm and 5.0ppm were made from serial dilutions using deionized.

### **3.8.3 DETERMINATION OF METAL IONS WITH ATOMIC ABSORPTION SPECTROPHOTOMETER**

#### **3.8.3.1 DETERMINATION OF SILVER**

The wavelength was set at 328.1nm using air/acetylene ( $C_2H_2$ ) flame. The stock solution of the standard silver nitrate was aspirated into the Pye Unicam SPI900 Atomic Absorption spectrophotometer equipped with silver, single elemental hollow cathode lamp and digital display read out. Absorbance readings were taken for each of the working solutions, and calibration curve was plotted using the standard values.

Following the same process, the unknown solutions (analyte) were aspirated into the Atomic Absorption spectro photometer and the absorbance readings were taken and then extrapolated from the standard curve the corresponding concentrations. Three separate absorption readings were made with each solution, and an average value taken.

#### **3.8.4 STANDARD SOLUTION OF SODIUM (Na).**

25g of sodium chloride (NaCl) which was dried in an oven at  $120^{\circ}C$  for 2hours was weighed and dissolved in  $5cm^3$  of deionized water to give 1000ppm of sodium (Na). The solution was diluted to  $1000cm^3$  (1litre) in a volumetric flask. From the stock solution, aliquots solutions of 1.0ppm, 2.0ppm, 3.0ppm, 4.0ppm and 5.0ppm were made by serial dilutions using deionized water. Standard plot was obtained by plotting the given concentrations versus the corresponding absorbances. Sodium content of the photographic waste solution was determined by using the absorbance

value to extrapolate the corresponding concentration from the standard calibration curve for sodium. The result recorded was the mean value of three separate absorption readings. The wavelength was set at 589nm.

### **3.8.5 DETERMINATION OF POTASSIUM (K).**

To prepare 1000ppm potassium (K), 1.9g of potassium chloride, KCl was weighed after drying in oven at 120°C for 2 hours. This was then dissolved in 5cm<sup>3</sup> of deionized water and subsequently diluted to 1000cm<sup>3</sup> (1litre) in a volumetric flask.

Aliquot solutions of the stock solution were prepared by serial dilution to obtain 1.0ppm, 2.0ppm, 3.0ppm, 4.0ppm and 5.0ppm. Calibration curve was plotted with absorbance values against concentrations in ppm. Hence, the concentration of unknown was determined by extrapolation.

### **3.8.6 DETERMINATION OF MERCURY (Hg)**

1000 ppm stock solution of mercury was prepared by dissolving 1.3520g of mercury (ii) chloride (HgCl<sub>2</sub>) in 250cm<sup>3</sup> of deionized water.

This was diluted to 1 litre (1000cm<sup>3</sup>) in a volumetric flask with deionized water. The stock solution was stored in a polythene bottle. Aliquot solutions were prepared from the stock solution to produce working solutions of 1.0ppm, 2.0ppm, 3.0ppm, 4.0ppm and 5.0ppm. Using these standard concentration values, absorbance readings were obtained by setting the atomic absorption spectrophotometer at a wavelength of 253nm using mercury cathode lamp. All the results were mean values of triplicate

determination of each sample.

The standard calibration curve was plotted, and the unknown concentration was determined by extrapolation[55,70].

### **3.8.7 DETERMINATION OF IRON (Fe)**

7.1g of ferrous ammonium sulphate hexahydrate salt  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$  was dissolved in  $25\text{cm}^3$  of deionized water with the addition of  $4\text{cm}^3$  of concentrated sulphuric acid,  $\text{H}_2\text{SO}_4$ [55,86]. The solution was further diluted with deionized water in a volumetric flask to  $1000\text{cm}^3$ .

Aliquot solutions of the stock solution were prepared by serial dilutions to obtain 1.0ppm, 2.0ppm, 3.0ppm, 4.0ppm and 5.0ppm working concentrations. Absorbance readings were taken and standard calibration curve was plotted with the values obtained. The absorbance of the test sample was also taken and the concentration determined by extrapolation from the standard calibration curve[55,89].

### **3.8.8 DETERMINATION OF CHLORIDE( $\text{Cl}^-$ ) [VOLUMETRIC METHOD]**

10ml of standard  $\text{AgNO}_3$  solution was added to the photographic effluent solution in slight excess. This was stirred well, filtered, and washed the  $\text{AgCl}$  ppt thoroughly. 5ml ferric indicator and 2ml  $\text{HNO}_3$  acid was added to the filtrate. The excess silver was titrated with thiocyanate standard solution to permanent light brown. From the volume of  $\text{AgNO}_3$  used, the percentage of chloride ion was calculated [55].

### 3.8.9 DETERMINATION OF SULPHUR (GRAVIMETRIC METHOD)

To 200ml of the test sample, 2ml 50% NaOH and 2ml 30% NaOH were added. The beaker was covered with watch glass and heated for 1hour, 1ml increments H<sub>2</sub>O<sub>2</sub> was added as reaction subsided.

The watch glass was washed and removed after 1 hour. This was diluted to about 175ml with deionized water, acidified with about 10ml dilute HCl.

About 15ml of 10% BaCl<sub>2</sub> solution was added slowly in slight excess with constant stirring. This was digested over a hot plate at 45°C for 1hour making sure that the solution did not boil. This was allowed to stand at room temperature overnight. The resulting precipitate was filtered through pooch crucible containing glass fibre paper previously dried at 250°C, cooled and weighed.

The precipitate obtained was washed with hot deionized water. Crucible and contents were dried for 1hour at 2500C. It was again cooled and weighed.

The percentage sulphur was then determined by applying the formula:

$$\% \text{ sulphur} = \frac{\text{g BaSO}_4}{\text{g sample}} \times 0.1374 \times 100$$

Where 0.1374 is the volumetric factor of BaSO<sub>4</sub>.

### 3.8.10 DETERMINATION OF TOTAL NITROGEN

#### (Kjeldahl Method)

The sample was digested with H<sub>2</sub>SO<sub>4</sub> to convert organic nitrogen to ammonia. It was distilled after alkalization with an excess of 40% aqueous NaOH to make the solution strongly alkaline. Ammonia was liberated out of

the solution by distillation into a vessel containing boric acid indicator and ammonium borate.

The bluish colour of the boric acid at end point was regenerated by titrating the borate anion with 0.01M HCl.

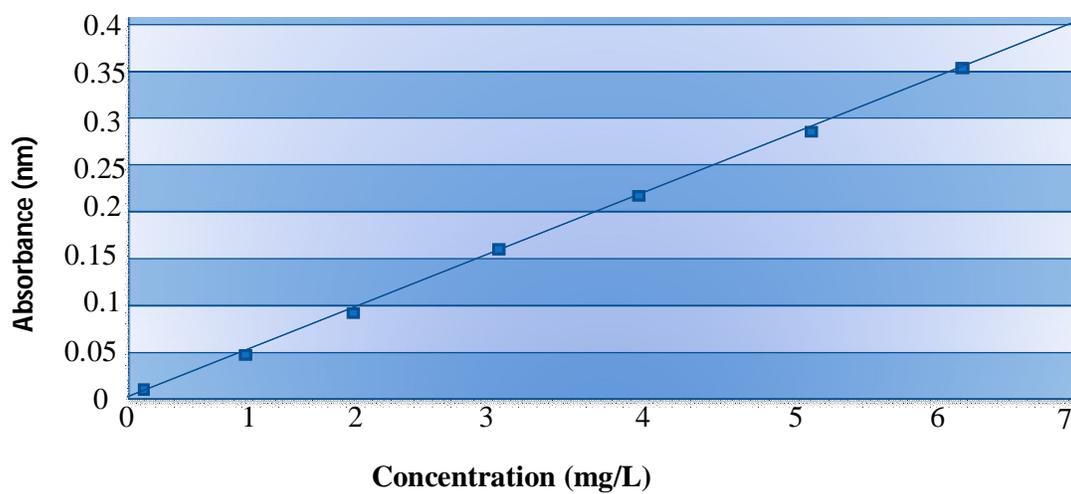
The amount of nitrogen, nitrogen compounds in the effluent sample expressed as a percentage was then determined.

The results of the analyses were as recorded on table 3.3

**Table 3.2: Data for standard calibration curve for silver determination at 328.1nm.**

Concentration (mg/L)	Absorbance (nm)
1.0	0.054
2.0	0.110
3.0	0.170
4.0	0.225
5.0	0.280
6.0	0.340

**Fig 3.1: Standard Calibration curve for silver determination at 328.1nm**



**Table 3.3: Results of Analysis of Photographic effluent solutions collected from Eurocolours photoprocessing laboratory Uwani, Enugu State.**

<b>Parameter Analysed</b>	<b>Developer</b>	<b>Fixer</b>	<b>Rinser</b>
Silver (mg/ L)	16,000	22,000	500
Sodium (mg/ L)	42.4	649.0	245.8
Potassium (mg/ L)	4.8	74.1	7.1
Iron (mg/L)	22.4	82.4	2.6
Mercury (mg/L)	0.2	0.8	0.1
Chloride (mg/L)	104.3	42.6	8.0
Bromide (mg/L)	177.0	ND*	ND
Sulphur (mg/L)	ND	449.5	173.4
Thiosulphate (mg/L)	ND	1,104.1	ND
Nitrogen (mg/L)	ND	92.0	ND
Cyanide (mg/L)	200.6	ND	ND
Conductivity (mscm <sup>-1</sup> )	126.6	167.3	75.4
PH (at 29 <sup>o</sup> C)	8.2	4.8	6.4

\* ND = Not detected

\*\* Analysis of the sample was conducted at the laboratory of Agricultural Research Institute, Umudike Abaia State.

### 3.9 DETERMINATION OF SILVER CONCENTRATION IN THE EFFLUENT BY CHEMICAL ANALYSIS.

The chemical assay of the samples for silver content determination was carried out using the method described by Volhard[58,71,72].

This was carried out in two stages viz:

- (a) Estimation of the silver equivalent in waste solution by determining the volume of  $\text{NH}_4\text{SCN}$  used.
- (b) Determination of silver concentration in waste solution.

#### 3.9.1 Estimation of Silver Equivalent of Ammonium thiocyanate

##### Procedure:

7.6lg of ammonium thiocyanate was accurately weighed. The weighed substance was dissolved in 100ml of deionized water and subsequently diluted to 1 liter (1000ml) to give 0.1M  $\text{NH}_4\text{SCN}$ .

0.3g of silver nitrate was weighed and dissolved in a 250ml Erlenmeyer flask using a solution of 4M nitric acid. 3ml of ferric alum indicator solution was added. This solution was titrated with ammonium thiocyanate solution to a permanent reddish colour. The titration was done four times to determine the average titre value.

Silver equivalent of the ammonium thiocyanate was calculated using the formula state below.

$$\text{Silver equivalent of the } \text{NH}_4\text{SCN (D)} = \frac{A \cdot x}{B}$$

Where A = weight of silver nitrate(g) used

$$x = \frac{\text{molecular weight of silver}}{\text{Molecular weight of silver nitrate}}$$

B = Volume of NH<sub>4</sub>SCN solution used (i.e. titre value).

### 3.9.2 PREPARATION OF FERRIC ALUM INDICATOR

The ferric alum indicator (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) was prepared by dissolving 40g of the salt in 100ml of solution and adding nitric acid until brown colour disappeared. The preparation gave exactly 1M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution.

The use of Fe<sup>3+</sup> as the indicator in titrating silver ion with a standard thiocyanate solution was indicated by the end point, which resulted in the formation of a soluble, highly coloured complex.

A deep coloration formed due to complexation of Fe (iii).

Thus; this could be explained by the following equations:



### 3.9.3 Determination of Silver Concentration in waste photographic solution.

20ml of the waste photographic solution was transferred to a 500ml flask. 50ml of 4M HNO<sub>3</sub> acid was added to the flask and this was heated slowly on a hot plate until the solution became colourless. The solution was heated further to boiling point to expel nitrogen oxides. It was subsequently cooled and diluted to 200ml using deionized water. 3ml of the ferric alum indicator

was added and the resulting mixture was titrated using ammonium thiocyanate solution already prepared to obtain a permanent reddish colour as the endpoint. Four titrations were performed in order to determine the average titre value. The formula stated below was used to obtain the concentration of silver in the photographic effluent.

$$\text{Silver concentration in the effluent} = \frac{[C] \cdot [D]}{W}$$

Where C = Volume of  $\text{NH}_4\text{SCN}$  solution used (titre value)

D = Silver equivalent of  $\text{NH}_4\text{SCN}$  solution (g/ml)

W = Volume of photographic effluent used (20ml).

The procedures described above were used to analyze each of the three different samples of the photographic waste solutions viz: rinse water, developer and fixer collected from Euroclours photoprocessing laboratory and the results obtained were tabulated in tables 3.4, 3.5, 3.6 and 3.7.

**Table 3:4: Estimation of Silver equivalent using a known amount of silver, to obtain the volume of NH<sub>4</sub>SCN used.**

No of Readings	Initial Vol. (ml)	Final Vol. (ml)	Titre Value (ml)
1	0.50	20.50	20.00
2	20.00	38.50	18.50
3	1.00	19.30	18.30
4	19.00	37.50	18.50

$$\text{Average titre} = \frac{18.50 + 18.30 + 18.50}{3}$$

$$\therefore \text{Average titre NH}_4\text{SCN} = 18.43\text{ml}$$

$$\begin{aligned} \text{Hence, silver equivalent of the NH}_4\text{SCN} &= \frac{A \cdot X}{B} \\ &= \frac{0.30\text{g} \times 108/170}{18.43\text{ml}} \\ &= 0.010\text{g/ml.} \pm 0.005 \end{aligned}$$

**Table 3.5: Determination of Silver concentration in waste photographic solution of rinse water (rinser) source.**

No of Readings	Initial Vol. (ml)	Final Vol. (ml)	Titre Value (ml)
1	0.50	1.40	0.90
2	1.50	2.20	0.70
3	2.50	3.30	0.80
4	4.00	4.75	0.75

$$\begin{aligned} \text{Average titre} &= \frac{0.70 + 0.80 + 0.75}{3} \\ &= 0.75\text{ml} \end{aligned}$$

Substituting the titre value into the expression for silver concentration; the amount of silver was thus calculated.

$$\begin{aligned} \text{Amount of silver in rinser} &= \frac{[C] \cdot [D]}{W} \\ &= \frac{0.75\text{ml} \times 0.010\text{g/ml}}{20\text{ml}} \\ &= 3.8 \times 10^{-4} \\ &= 0.080\text{gAg}/200\text{ml rinser}. \end{aligned}$$

**Table 3.6: Determination of silver concentration in developer/bleach – fix photographic effluent solution.**

No of Readings	Initial Vol. (ml)	Final Vol. (ml)	Titre Value (ml)
1	2.00	29.60	27.60
2	10.00	37.30	27.30
3	5.00	32.10	27.10
4	10.00	36.80	26.80

$$\begin{aligned} \text{Average} &= \frac{27.30 + 27.10 + 26.80}{3} \\ &= 27.07\text{ml} \end{aligned}$$

$$\text{Hence, amount of silver in the developer effluent} = \frac{[C] \cdot [D]}{W}$$

$$= \frac{27.07\text{ml} \times 0.010/\text{ml}}{20\text{ml}}$$

$$= 0.014\text{g/ml Ag}$$

$$= 2.8\text{g Ag}/200\text{ml}$$

**Table 3.7: Determination of silver concentration in fixer photographic effluent solution**

No of Readings	Initial Vol. (ml)	Final Vol. (ml)	Titre Value (ml)
1	0.50	43.00	38.00
2	2.00	39.50	37.50
3	2.00	39.30	37.30
4	2.00	39.20	37.20

$$\text{Average titre} = \frac{37.50 + 37.30 + 37.20}{3}$$

$$= 37.33\text{ml}$$

$$\text{Concentration of silver in the fixer solution} = \frac{[C] \cdot [D]}{W}$$

$$= \frac{37.33\text{ml} \times 0.010\text{g/ml}}{20\text{ml}}$$

$$= 0.018665\text{g/ml Ag in fixer solution}$$

$$\approx 0.019\text{g/ml Ag}$$

Or 3.8g/200ml Ag fixer solution

**Table 3.8 Summary of analysis of silver concentration in the effluent solution by Volhard titrimetric method.**

<b>Source of effluent</b>	<b>Rinser</b>	<b>Fixer</b>	<b>Developer</b>
<b>a. Eurocolours Laboratory</b>	<b>0.080gAg/200ml</b>	<b>3.8gAg/200ml</b>	<b>2.8gAg/200ml</b>
<b>b. Lixil photolaboratory</b>	<b>0.050gAg/200ml</b>	<b>3.4gAg/200ml</b>	<b>2.6gAg/200ml</b>
<b>c. Obi's commercial photos</b>	<b>0.10gAg/200ml</b>	<b>4.0gAg/200ml</b>	<b>2.9gAg/200ml</b>
<b>d. Photowash laboratory</b>	<b>0.060gAg/200ml</b>	<b>3.6gAg/200ml</b>	<b>2.6gAg/200ml</b>
<b>e. Hyondaee Photo Laboratory</b>	<b>0.070gAg/200ml</b>	<b>3.6gAg/200ml</b>	<b>2.7gAg/200ml</b>

**Table 3.9: Electrochemical Series [62,73]**

K		OH <sup>-</sup>
Na		I <sup>-</sup>
Ca		Br <sup>-</sup>
Mg		Cl <sup>-</sup>
Al		NO <sub>3</sub> <sup>-</sup>
Zn		SO <sub>4</sub> <sup>2-</sup>
Fe		F <sup>-</sup>
Sn		
Pb		
[H]		
Cu		
Hg		
Ag		
AU		

**(Increasing electrodeposition character)**

**Increasing ease of ions to accept electrons**

**Increasing preference to deposit at the anode or decreasing electronegative character)**

### **3.10 PREPARATION OF STRIPPING SOLUTION FOR SILVER DEPOSITS**

There are many methods for the removal of silver deposits from the surface of the cathode. The methods include the immersion process and the electrolytic process [65].

In this experiment, the immersion process was used to strip silver from the surface of the cathode after electrodeposition process.

#### **Procedure:**

The solution for immersion process of silver removal was prepared by mixing together 19 parts by volume of concentrated sulphuric acid with 1 part by volume of concentrated nitric acid [65]. The preparation was done in a tank made of stainless steel placed in a fume cupboard fitted with a functional fume extractor. The tank was also covered when not in use to prevent absorption of moisture from the atmosphere.

The mixed solution was used at temperature of 50 to 60°C. The cathode was dried before it was immersed in the stripping solution and removed and washed thoroughly with water as soon as the silver had been removed.

### **3.11 DETERMINATION OF POLARITY**

The polarity of the electrodes used in this experiment was determined by the immersion of the exposed ends of two insulated copper wires in a beaker containing acidified 1M Na<sub>2</sub>SO<sub>4</sub> solution. The opposite ends of the two wires were connected to each busbar. The two wires were held apart in the

electrolyte solution with about 6 volts maintained across the busbars. Gas was caused to evolve at the free ends of the wires. The wire at which most gas is liberated is the negative electrode [65].

### **3.12 DETERMINATION OF OPTIMUM VOLTAGE**

The choice of the optimum voltage for optimum recovery of silver by electrode position was carried out by electrolyzing the effluent at varying voltage values and fixed resistance.

The effluent was used at a concentration of 60% of the initial volume, pH 7 and temperature of 29°C. It was conditioned with zinc dust and sodium carbonate to enhance the throwing power of the solution. The stainless steel cathode was properly activated to support efficient adhesion of the silver metal. The electrolyte was continuously stirred until electrodeposition of the silver metal was optimally recovered.

The percentage recovery of silver determined from the mass deposited on the cathode for a given voltage were plotted and from the graph, the optimum voltage was determined. This voltage value became the working voltage for the rest of experiment done [65].

### **3.13 DETERMINATION OF OPTIMUM CURRENT**

The effluent was electrolysed at various current 0.025 – 0.175A applied using the D.C. power source from a 12 volt battery. The experiment was conducted at 60% effluent concentration, pH5 and temperature of 45°C. The reostat was used to regulate the current in the electrolytic circuit.

The values of the amount of silver recovered and the corresponding current as shown in Table 4.10, 4.24 and 4.36 were used to plot graphs depicted by Figures 4.11, 4.26 and 4.38. Using the graph, the optimum current was determined. The experiment was repeated and mean values were recorded.

### **3.14 DETERMINATION OF EFFECT OF CONCENTRATION ON RECOVERY OF SILVER**

The electrodes were activated by thorough cleaning and degreasing before use. They were first weighed before use. The electrodes were dipped into the electrolyte, which covered about 2/3 of the length. The automated stirrer was used to ensure that the solution was well circulated during the process of electrode position. The experiment was carried out at ambient temperature and pH 7. At the end of deposition, the stainless steel cathode was dried in the oven for five minutes at 100<sup>0</sup>C and allowed to cool. The cathode was then weighed and the weight of silver was determined. Starting with the rinsers, the experiment was repeated for wastes from developer and fixer, and the results were appropriately recorded.

200ml of the effluent solution as discharged was electrolysed for periods ranging from 10mins to 80min at 10 minute intervals. A corresponding current range of 0.025A to 0.175A were used. A resistance box of 40 ohms was incorporated in the circuitry.

The effluents were filtered and treated with zinc dust and sodium carbonate in order to condition the electrolyte.

### **3.15 EFFECT OF pH ON MASS OF SILVER DEPOSITED.**

The various effluents were subjected to electrolysis as earlier described. The pH of the solution was varied by the use of aqueous nitric acid and dilute ammonia. The working pH was buffered by acetate buffer for the acidic solutions and ammonia buffer for the alkaline solutions. The pH reading was obtained by using the digital pH metre.

At the end of the electrolysis, the amount of silver deposited was determined and recorded.

A plot of % recovery of silver against pH was used to determine the optimum pH. The experiment was repeated for all the various effluent solutions under investigation and the results recorded accordingly

### **3.16 EFFECT OF TEMPERATURE ON % RECOVERY OF SILVER**

The effluent was electrolysed at different temperatures and with fixed pH and concentration values using the same experimental set up already described. The electrolytic cell was placed into the thermostated water bath in order to maintain constant temperatures.

The amount of silver deposited at various temperature ranges were determined and tabulated. The temperature of the solution was measured by the thermometer.

A plot of amount of silver recovered versus temperature used gave an indication of the optimum temperature required for optimum silver recovery. The results are recorded in the tables and figures under result presentation.

### 3.17 DETERMINATION OF OPTIMUM CURRENT DENSITY.

Effect of current density on cathode deposition of silver was investigated using the electrolytic cell described in Fig. 2.1. The effluent under investigation was electrolysed after appropriate treatment and conditioning of the solution [62]. Electrolysis was carried out at various current values for 60 minutes. The surface area of the cathode was calculated in  $m^2$  and the value was used to divide the current applied for a given deposition of silver to obtain the current density ( $A/m^2$ ).

A graph of % recovery of silver obtained was plotted against the cathode current density. From the graph, the optimum current density was determined. This experiment was repeated for each effluent. The results are recorded in the result section.

The following procedure was followed in calculating the current density.

$$\begin{aligned} \text{Length of stainless steel cathode} &= 8.20\text{cm} \\ \text{Width of stainless steel cathode} &= 0.80\text{cm} \\ \text{Length of cathode in contact with electrolyte} &= 5.47\text{cm} \\ \text{Width of cathode in contact width electrolyte} &= 0.80\text{cm} \\ \text{Surface area of cathode in contact with electrolyte} &= 5.47\text{cm} \times 0.80\text{cm} \\ &= 4.38\text{cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Since } 10,000\text{cm}^2 &= 1\text{m}^2 \\ \therefore 4.38\text{cm}^2 &= \frac{4.38}{10,000} = 4.38 \times 10^{-4}\text{m}^2 \end{aligned}$$

Hence, surface area of cathode in contact with the electrolyte is

$$4.38 \times 10^{-4} \text{m}^2$$

Therefore, the cathode current density =  $\frac{\text{Current (Amp)}}{\text{Surface area (m}^2\text{)}}$ .

The results obtained were recorded in appropriate table.

### 3.18 DETERMINATION OF CATHODE CURRENT EFFICIENCY

Cathode efficiency calculation is based on the theoretical yield of silver metal at 100% efficiency according Faraday's first law of electrolysis.

Using the experimental set up for current density determination, the cathode current efficiency was also determined.

Thus, gram deposited per ampere hour at 100% efficiency (theoretical yield)

$$= \frac{\text{equivalent wt. of silver} \times \text{time (seconds)}}{1 \text{ Faraday.}}$$

$$= \frac{107.87 \times 3600}{96500} = 4.024 \text{gAg.}$$

$$\therefore \text{Actual cathode efficiency} = \frac{\text{Mass deposited} \times 100\%}{\text{Theoretical yield.}}$$

The results obtained were recorded in the appropriate tables.

### 3.19 CONVERSION OF RECOVERED SILVER INTO SILVER NITRATE.

The recovered silver metal was converted into silver nitrate according to a method cited in literature [48,78]. The silver metal was dissolved in 65% concentration of aqueous nitric acid. The solution was heated to evaporation

and silver nitrate crystals were recovered. The equation of reaction is represented as follows:



Silver nitrate crystal is white solid substance with a molecular mass 169.9g/mol. It was a density of 4.35g/cm<sup>3</sup> and solubility in water of 219g/100ml at 20<sup>o</sup>C.

## CHAPTER FOUR

### 4.0 RESULTS AND DISCUSSION

#### 4.1 PRESENTATION OF RESULTS

The results obtained from the experimental section of this thesis are sequentially presented in Tables 3.1 to 3.8 and from Tables 4.1 to 4.40; and Figures 3.1 ranging from 4.1 to 4.41. The results are the mean values of four replicate samples in each case.

Table 3.1 is a presentation of effluent concentration by evaporation. By subjecting the photographic effluent solution to evaporation through heating, a lot of the water content is removed and thus reduce the level of dilution of the chemical species. This will enhance the quantitative measurements of silver metal from the effluent.

Table 3.2 and Figure 3.1 are data for standard calibration curve for silver determined at 328.1nm and the standard calibration plot respectively. The concentration of silver in the effluent was extrapolated from the standard calibration plot.

The results of analysis of the photographic effluent solutions collected from Eurocolours photoprocessing laboratory, Uwani Enugu are shown in Table 3.3. Among other things, the Table shows that the silver content in rinser, bleach-fix and fixer solutions are 500mg/L , 16,000mg/L and 22,000mg/L respectively.

Similar results are obtained in the case of determination of silver concentration in the effluents by Volhard titrimetric method as presented in

Tables 3.4, 3.5, 3.6 and 3.7 respectively. The summary of similar results from the various effluent solution sources are also presented in Table 3.8. The difference in the results of the two methods of analysis in favour of Atomic Absorption spectrophotometry can be explained in terms of the high precision of instrumental analysis, Nevertheless, the two results are comparatively close. From the results obtained using these two different analytical techniques, it is obvious that the concentration of silver in the effluents is highest in the fixer and least in the rinser. Based on economic consideration it is not viable to recover silver from the rinse water. The bleach-fix and the fixer solutions are silver-rich solutions as evidenced in the results.

The electrochemical series data which served as a guide in electrogravimetric process is presented in Table 3.9. This Table provides information in determining the ion that is deposited in preference to the other in a complex electrolytic system.

The results of electrodeposition of silver from the effluents as-discharged at ambient temperature and pH 7 are reported in Tables 4.1, 4.14, 4.27 and Figures 4.1, 4.16 and 4.29 respectively. At the electrodeposition time of 60minutes a maximum of 16.0mgAg representing 20% is recovered from the rinse water effluent. In the case of bleach-fix and fixer solutions, 605mgAg (22%) and 912mgAg (24%) are recovered. It was also noticed that beyond the electrolysis time of 60minutes the amount of silver deposited begins to diminish. This is an indication of exhaustion of silver concentration thereby giving way to other ions to compete for cathodic

deposition. Apart from the low yield that characterized deposition beyond the optimum electrodeposition time, contamination of the product and poor adhesion are additional indicators.

Tables 4.2, 4.3, 4.4, 4.5, 4.6, 4.7 and the corresponding Figures 4.2, 4.3, 4.4, 4.5, 4.6 and 4.8 are the summary of results for electrolyzing concentrated rinsing effluent under the stated conditions.

The results of electrowinning silver from concentrated bleach-fix photographic effluent solution are presented in Tables 4.15, 4.16, 4.17, 4.18, 4.19, 4.20 and Figures 4.17, 4.18, 4.19, 4.20, 4.21 and 4.22 consecutively.

The electrodeposition of silver at various concentration of fixer solution are presented in Tables 4.28, 4.29, 4.30, 4.31, 4.32, 4.33 and Figures 4.30, 4.31, 4.32, 4.33, 4.34 and 4.35, as well.

The results of the studies on the parameters which affect the performance of the cathode such as effect of pH, temperature, current and current density are reported in Tables 4.8, 4.9, 4.10, 4.11, 4.21, 4.22, 4.24, 4.25, 4.34, 4.35, 4.36 and 4.37. The data shown in these Tables are used to make plots and these plots are Figures 4.9, 4.10, 4.11, 4.12, 4.23, 4.24, 4.26, 4.27, 4.36, 4.37, 4.38 and 4.39 respectively.

The data generated from assessment of cathode efficiency are presented in Tables 4.12, 4.26 and 4.38 which are also shown in Figures 4.13, 4.28 and 4.40 respectively. The effects of voltage on percentage recovery are shown in Tables 4.23 and 4.39. The corresponding plots of these data are displayed in Figures 4.25 and 4.41.

## 4.2 EFFECT OF CONCENTRATION OF THE EFFLUENTS

A comparison of the electrolysis of unconcentrated samples with the concentrated types shows a tremendous difference in the amount of silver recovered favouring the concentration of effluents to some extent prior to electrowinning the desired mineral. The amount of silver deposited at the cathode was highly enhanced by concentrating the effluents.

Optimal recoveries are attained at 60% concentration of the effluents. Thus, the rinser gave 62.40mgAg (78%), bleach-fix gave 2200mgAg (80%) and fixer gave 3,116mgAg (82%) as cathode deposits.

The concentration factor started exhibiting diminishing effect beyond 60% sample concentration as can be seen in Tables 4.7, 4.20, 4.33 as well as Figures 4.8, 4.22 and 4.35.

This observation of decrease in the amount of silver deposited at 70% concentration of the sample against expectation could be interpreted in terms of colloidal interactions and aggregate formation due to highly reduced volume of solvent. As the concentration of the sample progresses, the aggregation of finely divided solids in suspension also increases.

These substances function as bonding agents by adsorbing on and bridging between surfaces of more than one primary particle as reported by Rutherwein and Ward[82].

This view was substantiated by the work of Michaels[83] who studied the flocculation of fine suspensions of soils and clays. These interactions are especially important for small particles, where they can easily out weigh other forces such as hydrodynamic drag and gravity which become dominant

for larger particles[84]. The most important types of interaction include: van der Waals interaction, electrical interaction, hydration effects, hydrophobic interaction, steric interaction and combined interaction. The universal attractive forces between atoms and molecules, known as van der Waals forces are known to operate between macroscopic objects and also play an important part in the interaction of colloidal particles.

Practically all particles in aqueous suspensions carry a surface charge due to ionization of surface groups or specific adsorption of ions. The nature of the electrical double layer formed can greatly influence the interaction between charged particles. At higher electrolyte concentrations, the diffuse layer is less extensive and particles need to approach quite close before repulsion is felt.

Some particles have quite large amounts of 'bound water', which plays a part in the interaction of such particles. The approach of two particles with hydrated surfaces will generally be hindered by an extra repulsive interaction, distinct from electrical double-layer repulsion.

All these interactions highlighted give rise to formation and stability of larger particles known as flocs or aggregates. These substances require more time and larger energy to decompose during electrolysis in order to liberate the encapsulated desired metal.

A linear relationship exists between a plot of amount of silver deposited and the quantity of electricity applied as can be seen in Figures 4.6, 4.8, 4.21, 4.22, 4.34 and 4.35. The linearity of these plots is in agreement with Faraday's first law of electrolysis which states that the mass

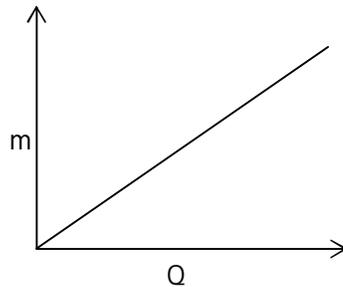
of substance involved in reaction at the electrode is directly proportional to the quantity of electricity passed through the solution[85]. However, a critical examination of Figures 4.8, 4.22 and 4.35 pointed out additional information of which the original Faraday's first law needs to be modified to accommodate the electrolysis of a system consisting of competing electrolytes. In a general electrolytic reaction, the reactions at the electrodes are forced to occur by the imposition of an external voltage from a battery. However, the initial cathodic deposits recorded during the electrolysis of the competing electrolytes system without externally applied voltage of to a momentary spontaneous cell reaction. The presence of zinc dust as an additive helped to initiate the reaction and thus facilitated the flow of electrons from the anode to the cathode. The inclusion of intercept in these plots is in contrast with Faraday's first law of electrolysis, which has a plot running through the origin.

#### **A MODIFICATION OF FARADAY'S FIRST LAW USING ELECTROLYSIS OF A MULTI-COMPONENTS SYSTEMS**

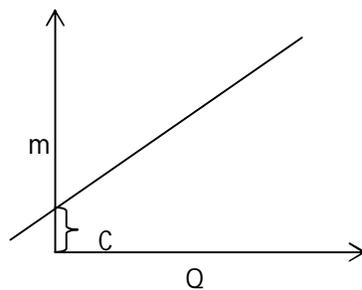
Given that  $Q$  = quantity of electricity,  $M$  = mass deposited and  $x$  = constant of proportionality or the electrochemical equivalent.

Thus:  $Q \propto m$

$$m = Q$$



$Q = m \times \dots\dots\dots$  (1) Faradaic Process



$$m = X Q + C$$

$Q = mx + c \dots\dots\dots$  (2) Spontaneous process.

When  $m = 0$ ,  $x = 0$ .

$$\therefore Q = C$$

Hence  $C$  is approximately the mass deposited at real  $m = 0$  when  $m x + c$  is when there is no externally applied voltage (change); as a result of insitu charging which is a function of electrical double layer, mass was deposited at

zero voltage.

Thus, Faraday's Law

$$M_0 \propto Q \quad \text{OR} \quad M_0 = zQ$$

$$M = zQ + C$$

Where  $x = z$

$$M_0 \approx C$$

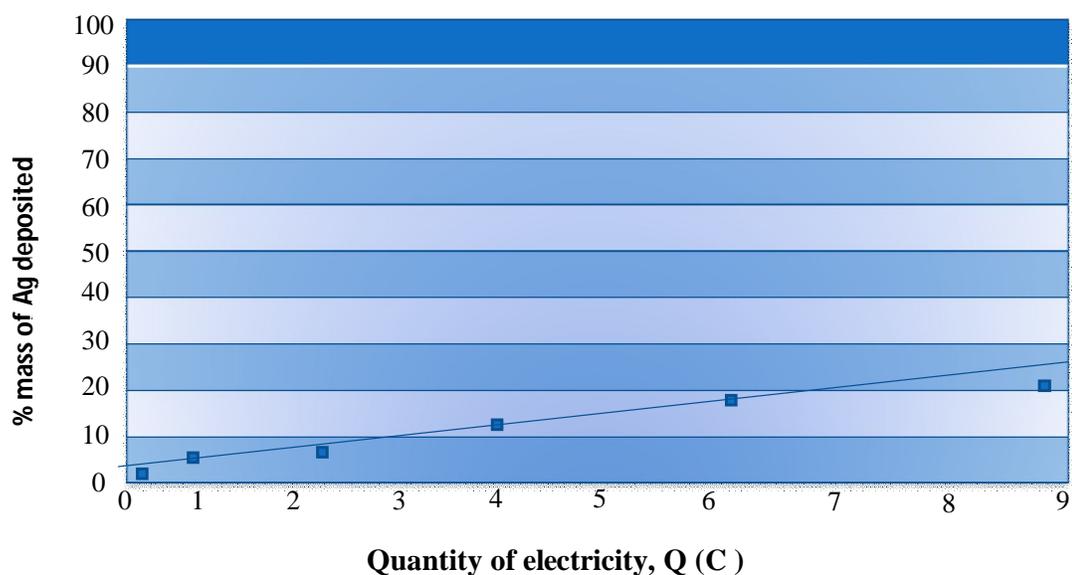
$$\therefore \boxed{MQ = C}$$

$C$  = mass deposited at zero applied voltage.

**Table 4.1: Variation of mass deposited with quantity of electricity using as discharged effluent at pH 7, and an ambient temperature, using rinser as the source of effluent.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	0.8	1.0
2	20	40	0.050	2.0	1.00	2.8	3.5
3	30	40	0.075	3.0	2.25	4.0	5.0
4	40	40	0.100	4.0	4.00	8.4	10.5
5	50	40	0.125	5.0	6.25	12.0	15.0
6	60	40	0.150	6.0	9.00	16.0	20.0
7	70	40	0.175	7.0	12.25	12.8	16.0
8	80	40	0.200	8.0	16.00	8.0	10.0

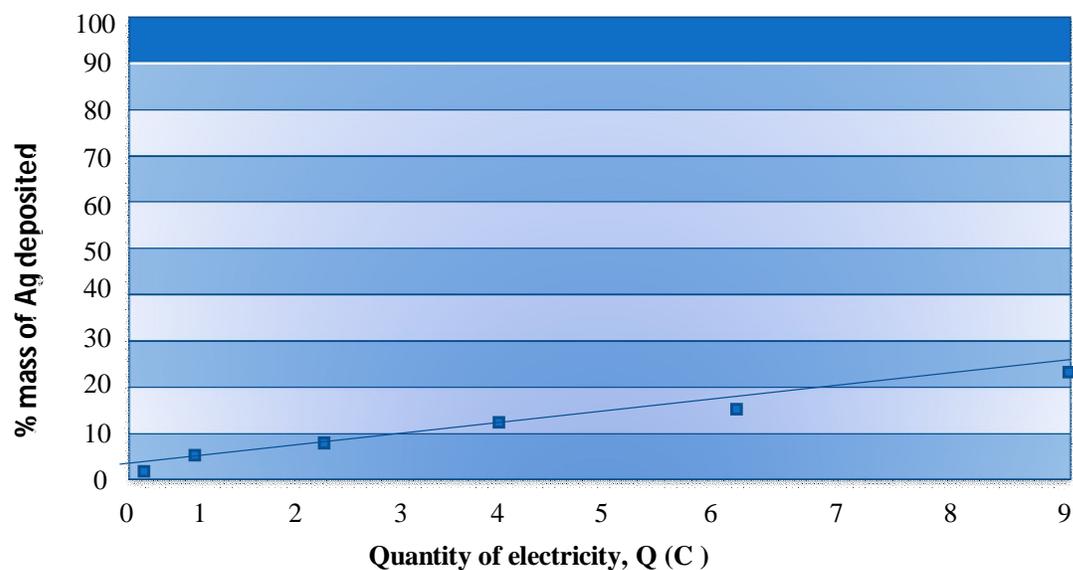
**Fig. 4.1: Variation of mass deposited with quantity of electricity using as discharged effluent at pH 7, and an ambient temperature.**



**Table 4.2: Variation of mass of silver deposited with quantity of electricity at 10% effluent concentration and pH 7, and an ambient temperature, using rinser.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	1.60	2.0
2	20	40	0.050	2.0	1.00	4.00	5.0
3	30	40	0.075	3.0	2.25	6.40	8.0
4	40	40	0.100	4.0	4.00	10.40	13.0
5	50	40	0.125	5.0	6.25	13.84	17.3
6	60	40	0.150	6.0	9.00	20.08	25.1
7	70	40	0.175	7.0	12.25	15.60	19.5

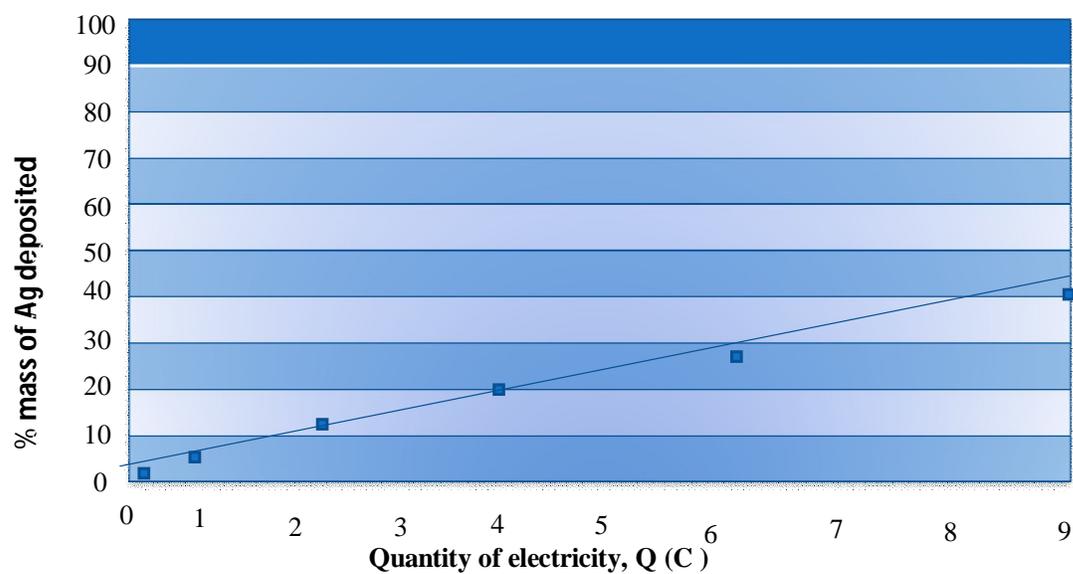
**Fig. 4.2: Variation of mass of silver deposited with quantity of electricity at 10% effluent concentration and pH 7**



**Table 4.3: Variation of mass of silver deposited with quantity of electricity at 25% effluent concentration, and pH of 7, and an ambient temperature using rinser.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	2.40	3.0
2	20	40	0.050	2.0	1.00	4.80	6.0
3	30	40	0.075	3.0	2.25	10.56	13.2
4	40	40	0.100	4.0	4.00	16.08	20.1
5	50	40	0.125	5.0	6.25	22.40	28.0
6	60	40	0.150	6.0	9.00	32.00	40.0
7	70	40	0.175	7.0	12.25	24.40	30.5

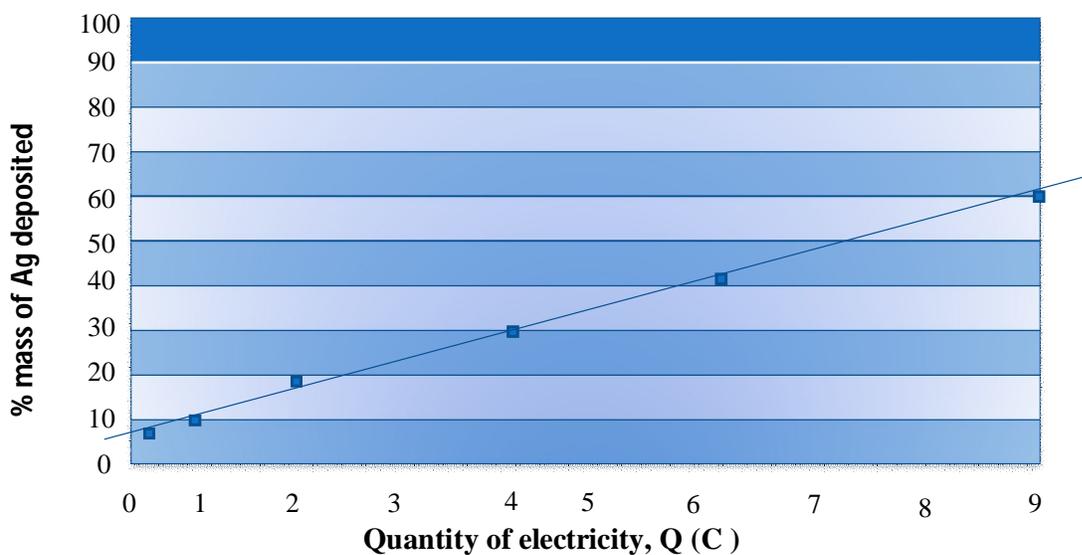
**Fig. 4.3: Variation of mass of silver deposited with quantity of electricity at 25% effluent concentration, and pH of 7**



**Table 4.4: Variation of mass of silver deposited with quantity of electricity at 50% effluent concentration, pH 7, an ambient temperature using rinser.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	4.80	6.0
2	20	40	0.050	2.0	1.00	8.05	10.0
3	30	40	0.075	3.0	2.25	16.10	20.0
4	40	40	0.100	4.0	4.00	24.10	0.0
5	50	40	0.125	5.0	6.25	33.60	42.0
6	60	40	0.150	6.0	9.00	48.00	60.0
7	70	40	0.175	7.0	12.25	36.80	46.0

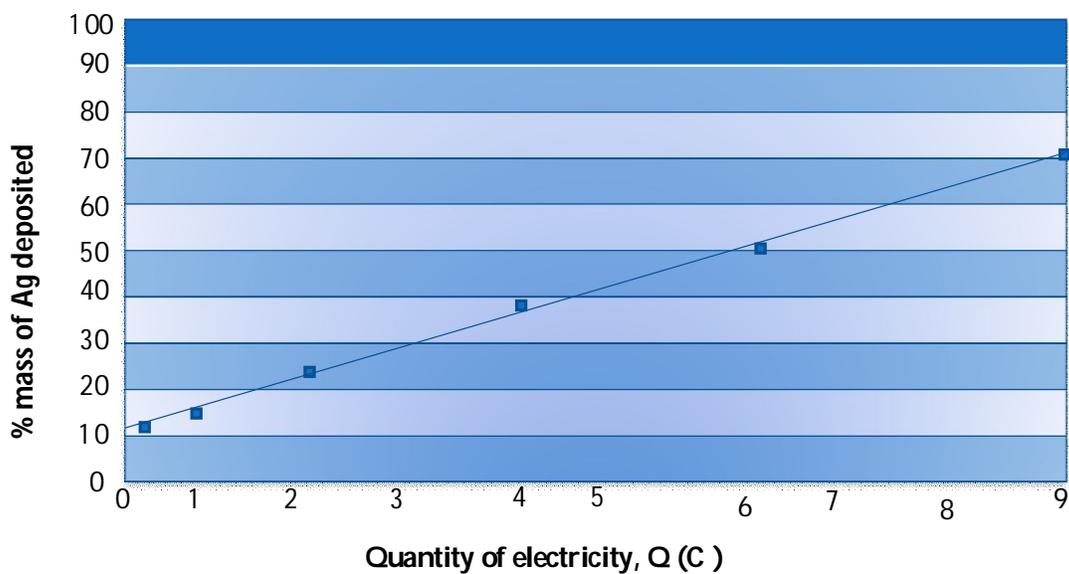
**Fig. 4.4: Variation of mass of silver deposited with quantity of electricity at 50% effluent concentration, pH 7**



**Table 4.5: Variation of mass of silver deposited with quantity of electricity at 55% effluent concentration, and pH 7, ambient temperature using rinser.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	9.0	11.3
2	20	40	0.050	2.0	1.00	12.9	16.1
3	30	40	0.075	3.0	2.25	20.0	25.0
4	40	40	0.100	4.0	4.00	30.6	38.2
5	50	40	0.125	5.0	6.25	40.8	51.0
6	60	40	0.150	6.0	9.00	56.0	70.0
7	70	40	0.175	7.0	12.25	40.0	50.0

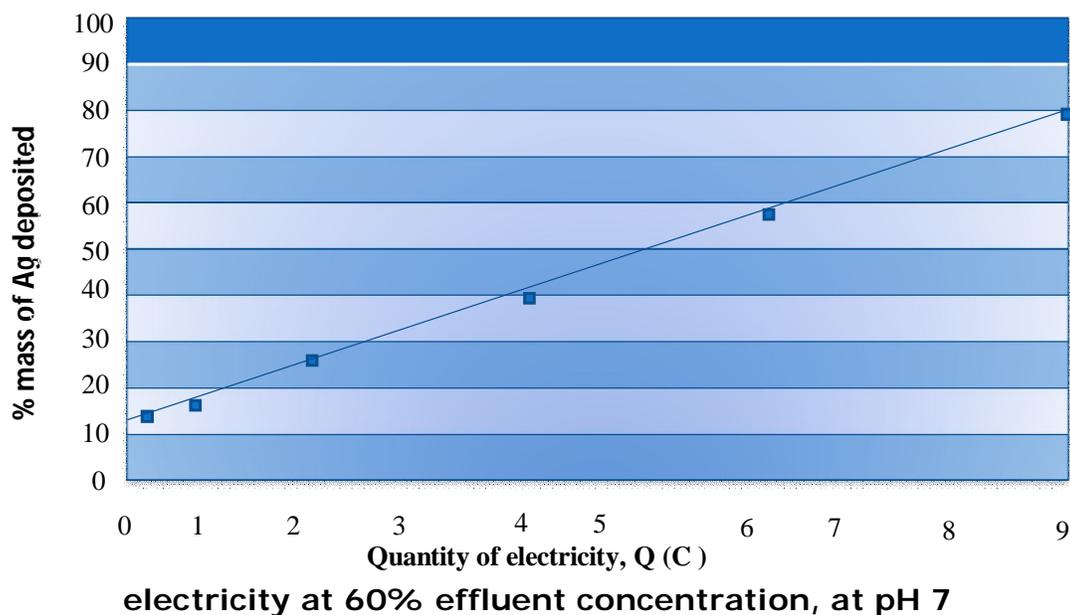
**Fig. 4.5: Variation of mass of silver deposited with quantity of electricity at 55.0% effluent concentration, and pH 7**



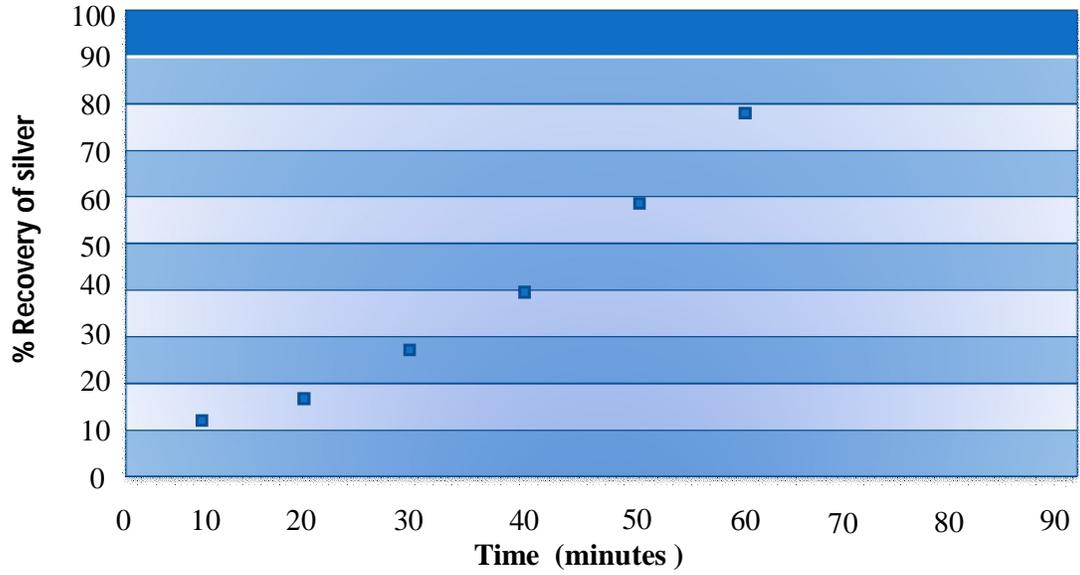
**Table 4.6: Variation of mass of silver deposited with quantity of electricity at 60% effluent concentration, at pH 7, an ambient temperature using rinser.**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	9.60	12.0
2	20	40	0.050	2.0	1.00	12.96	16.2
3	30	40	0.075	3.0	2.25	22.40	28.0
4	40	40	0.100	4.0	4.00	31.28	39.1
5	50	40	0.125	5.0	6.25	46.80	58.5
6	60	40	0.150	6.0	9.00	62.40	78.0
7	70	40	0.175	7.0	12.25	50.56	63.2

**Table 4.6: Variation of mass of silver deposited with quantity of**



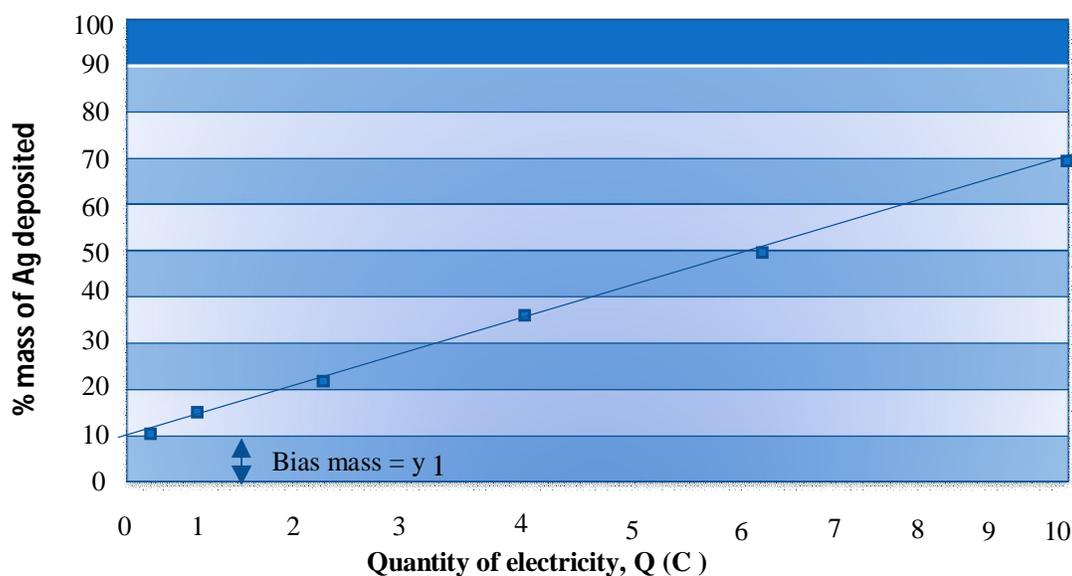
**Fig. 4.7: Variation of % recovery of Ag with time**



**Table 4.7: Variation of mass of silver deposited with quantity of electricity at 70% effluent concentration, at pH 7, an ambient temperature using rinser.)**

No. of expts	Time (mins)	Resistance (ohms)	Current (A)	Voltage (V)	Quantity of electricity (C )	Mass of silver deposited (mg)	% mass of silver
1	10	40	0.025	1.0	0.25	8.80	11.0
2	20	40	0.050	2.0	1.00	13.60	17.0
3	30	40	0.075	3.0	2.25	19.20	24.0
4	40	40	0.100	4.0	4.00	29.60	37.0
5	50	40	0.125	5.0	6.25	40.40	50.5
6	60	40	0.150	6.0	9.00	55.04	68.8
7	70	40	0.175	7.0	12.25	48.00	60.0

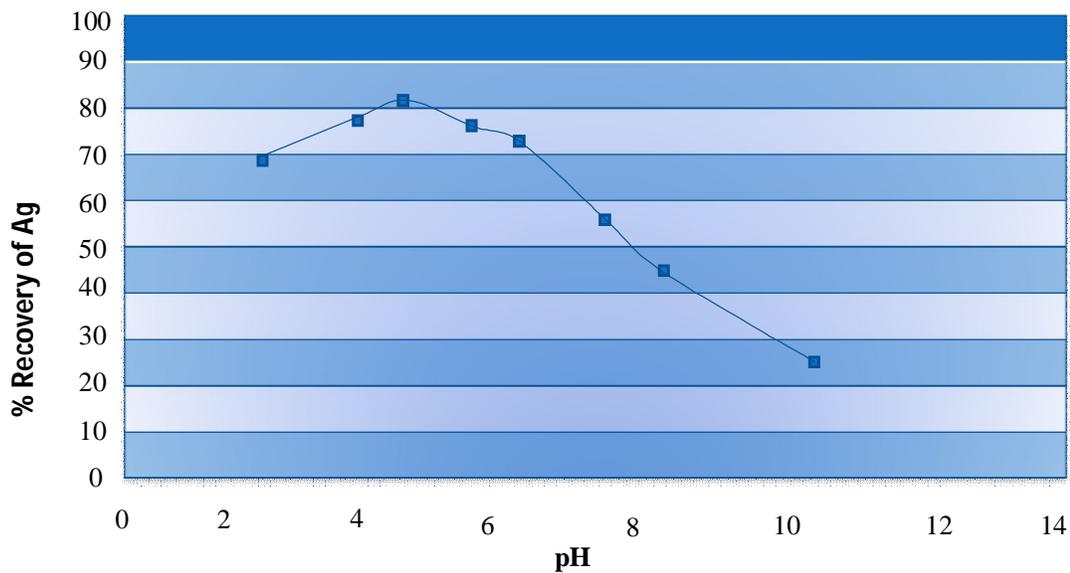
**Table 4.8: Variation of mass of silver deposited with quantity of electricity at 70% effluent concentration, at pH 7**



**Table 4.8: Effect of pH on % mass of silver recovered using rinse water or rinsers at ambient temp.**

pH	3	4	5	6	7	9	10	12
Mass of silver deposited (mg)	56.0	62.4	66.4	61.2	58.4	44.8	36.0	20.8
% Recovery of silver	70	78	83	76.5	73	56	45	26

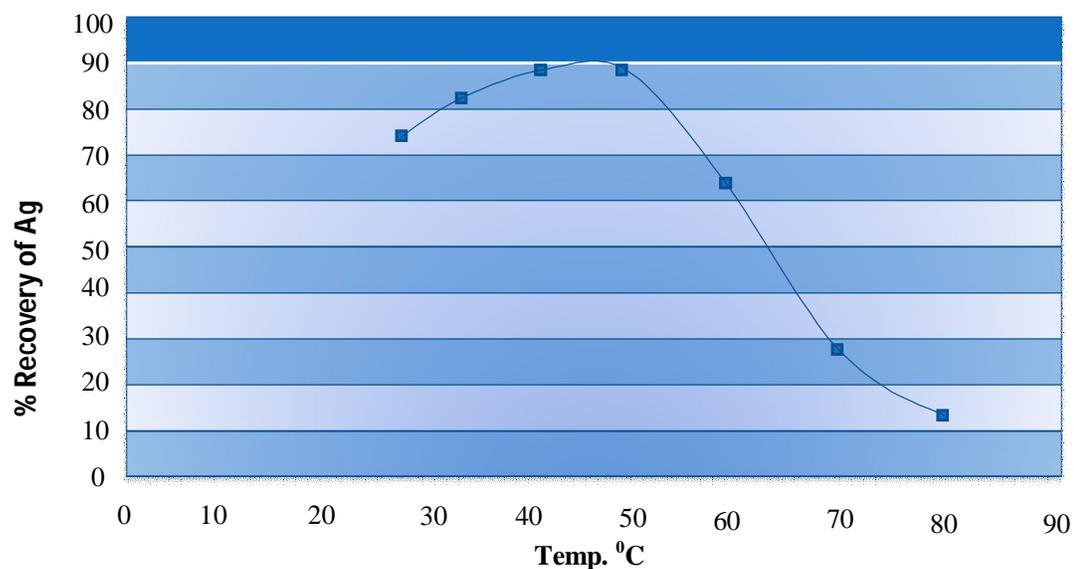
**Fig. 4.9: Effect of pH on % recovery of silver using rinsers water as source of effluent**



**Table 4.9: Effect of temperature on mass of silver deposited using rinse water, at pH 5.0**

Temperature °C	29	35	40	50	60	70	80
Mass deposited (mg)	60.0	65.6	70.4	70.4	52.0	22.4	12.0
% Recovery	75	82	88	88	65	28	15

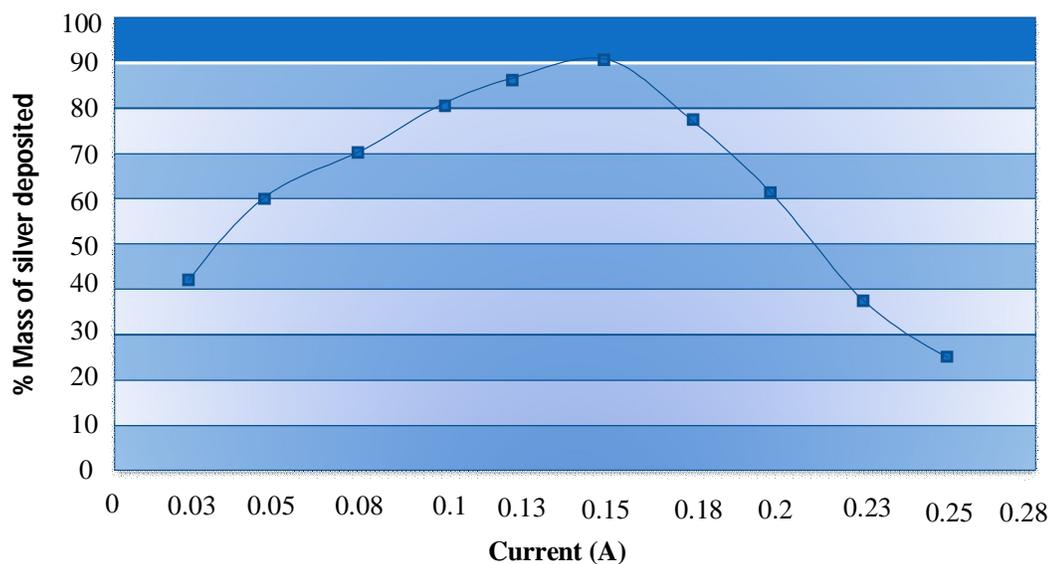
**Fig. 4.10: Effect of temperature on mass of silver using rinse water as source of effluent**



**Table 4.10: Effect of current on cathode deposition of silver using rinsing as the electrolyte at pH 5.0, temperature of 45°C**

Weight of cathode (g)	Weight of cathode+ weight of silver deposited (g)	Weight of silver deposited (mg)	% Recovery of silver	Current Applied (A)
17.60	17.6344	34.4	43.0	0.025
17.60	17.6480	48.0	60.0	0.050
17.60	17.6564	56.4	70.5	0.075
17.60	17.6640	64.0	80.0	0.100
17.60	17.6684	68.4	85.5	0.125
17.60	17.6724	72.4	90.5	0.150
17.60	17.6628	62.8	78.5	0.175
17.60	17.6496	49.6	62.0	0.200
17.60	17.6304	30.4	38.0	0.225
17.60	17.6200	20.0	25.0	0.250

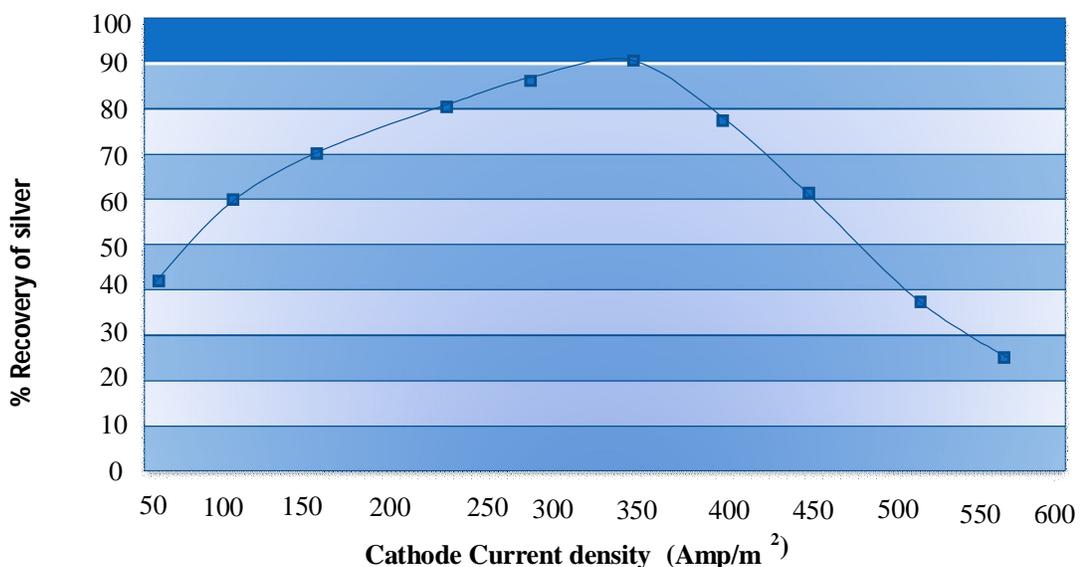
**Table 4.11: Effect of on cathode deposition (Effluent used: rinsing or rinse water)**



**Table 4.11: Effect of current density on cathode deposition of silver using rinsers as the electrolyte at pH 5.0 and temperature of 45°C**

Current Applied (A)	Weight of silver deposited (mg/200ml rinsers)	% Recovery of silver	Surface area of cathode in contact with rinsers (m <sup>2</sup> ) x 10 <sup>-4</sup>	Cathode Current Density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
0.025	34.4	43.0	4.38	57.1	0.85
0.050	48.0	60.0	4.38	114.2	1.09
0.075	56.4	70.5	4.38	171.2	1.04
0.100	64.0	80.0	4.38	228.3	1.59
0.125	68.4	85.5	4.38	285.4	1.70
0.150	72.4	90.5	4.38	342.5	1.80
0.175	62.8	78.5	4.38	399.5	1.56
0.200	49.6	62.0	4.38	456.6	1.23
0.225	30.4	38.0	4.38	513.7	0.76
0.250	20.0	25.0	4.38	570.8	0.50

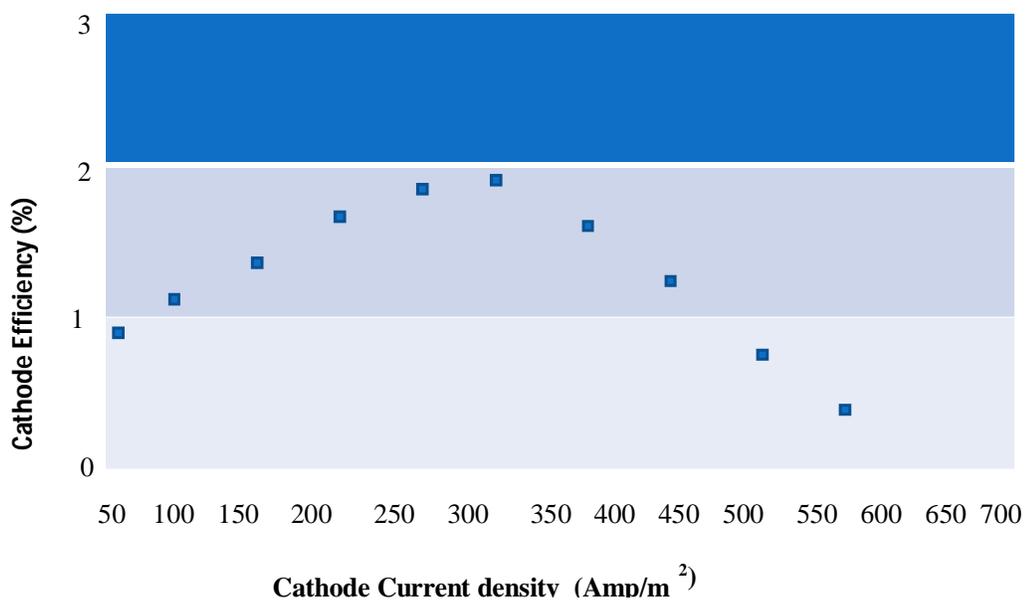
**Table 4.12: Variation of current density on cathode deposition of silver using rinsers as the electrolyte at pH 5.0 and temperature of 45°C.**



**Table 4.12: Variation of current density with cathode efficiency using 60% rinser concentration at pH 5.0 and 45°C**

Weight of silver deposited (mg/200ml rinser)	% Recovery of silver	Cathode Current Density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
34.4	43.0	57.1	0.85
48.0	60.0	114.2	1.09
56.4	70.5	171.2	1.04
64.0	80.0	228.3	1.59
68.4	85.5	285.4	1.70
72.4	90.5	342.5	1.80
62.8	78.5	399.5	1.56
49.6	62.0	456.6	1.23
30.4	38.0	513.7	0.76
20.0	25.0	570.8	0.50

**Fig. 4.13: Variation of current density with cathode efficiency using 60% rinser concentration at pH 5.0 and 45°C**



**Table 4.13: Relationship between voltage and current on mass of silver deposited, using rinsers at 60% concentration, pH 7, and an ambient temperature of 29°C.**

Voltage (V)	Current (A)	Resistance ( $\Omega$ )	Mass of Ag deposited (mg)	% Recovery of Ag
1.0	0.025	40	9.60	12.0
2.0	0.050	40	12.96	16.2
3.0	0.075	40	22.40	28.0
4.0	0.100	40	31.28	39.1
5.0	0.125	40	46.80	58.5
6.0	0.150	40	62.40	78.0
7.0	0.175	40	50.56	63.0
8.0	0.200	40		

**Fig. 4.14: Voltage-current graph**

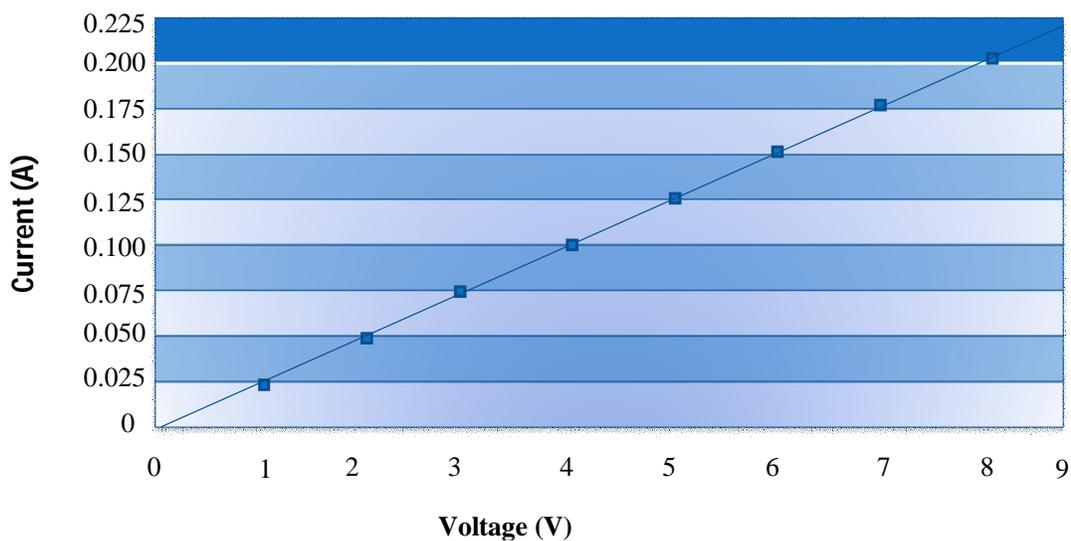
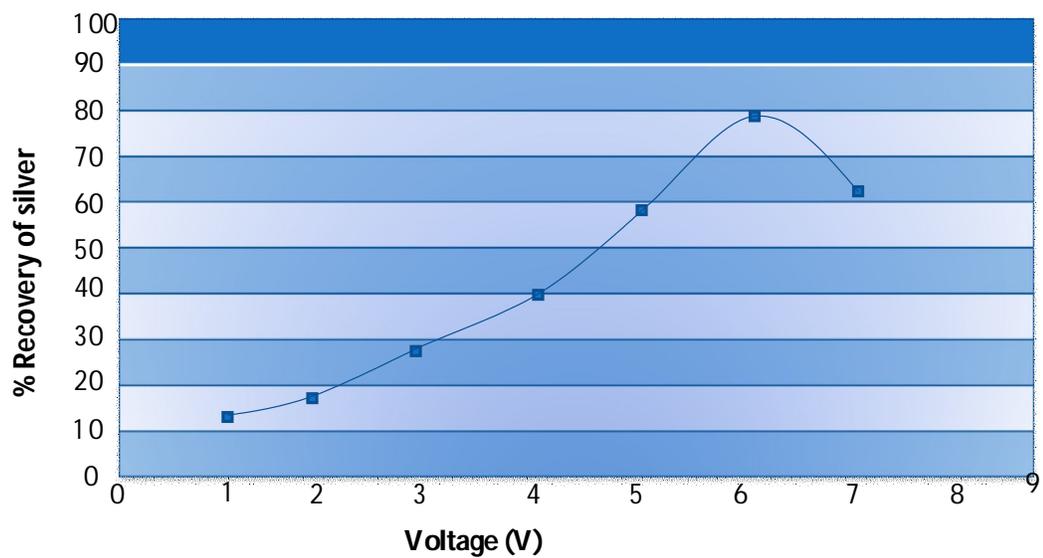


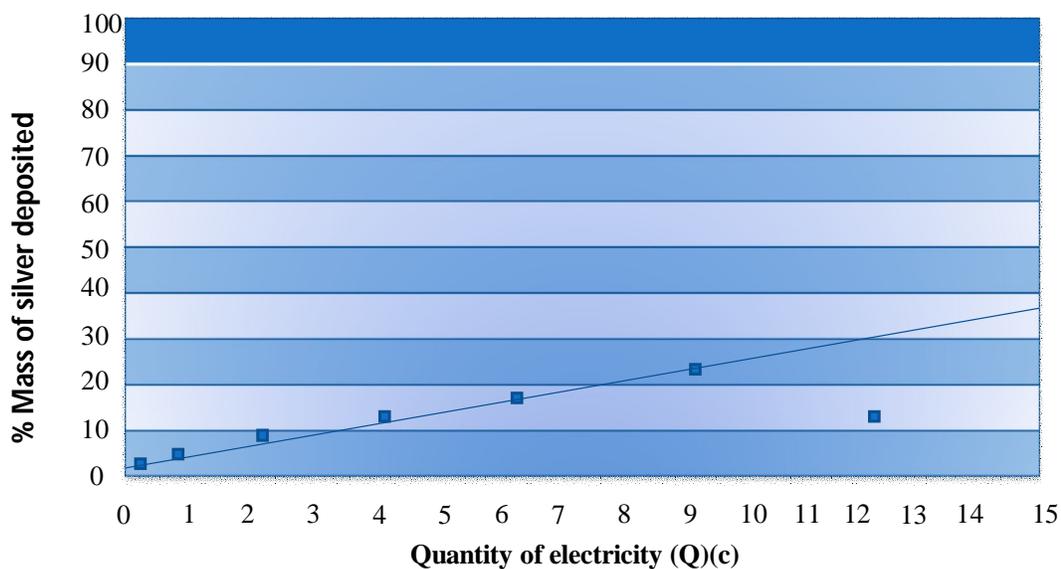
Fig. 4.15: Variation of % recovery of silver with voltage using the rinsers at 60% concentration. pH 7, and temperature of 29°C.



**Table 4.14: Variation of mass of silver deposited with quantity electricity As-discharged effluent (bleach fix) at pH 7, and an ambient temperature.**

No. of expts	Time (mins)	Resistance ( $\Omega$ )	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.055	2.0
2	20	40	0.050	2.0	1.00	0.138	5.0
3	30	40	0.075	3.0	2.25	0.206	7.5
4	40	40	0.100	4.0	4.00	0.303	11.0
5	50	40	0.125	5.0	6.25	0.468	17.0
6	60	40	0.150	6.0	9.00	0.605	22.0
7	70	40	0.175	7.0	12.25	0.371	13.5

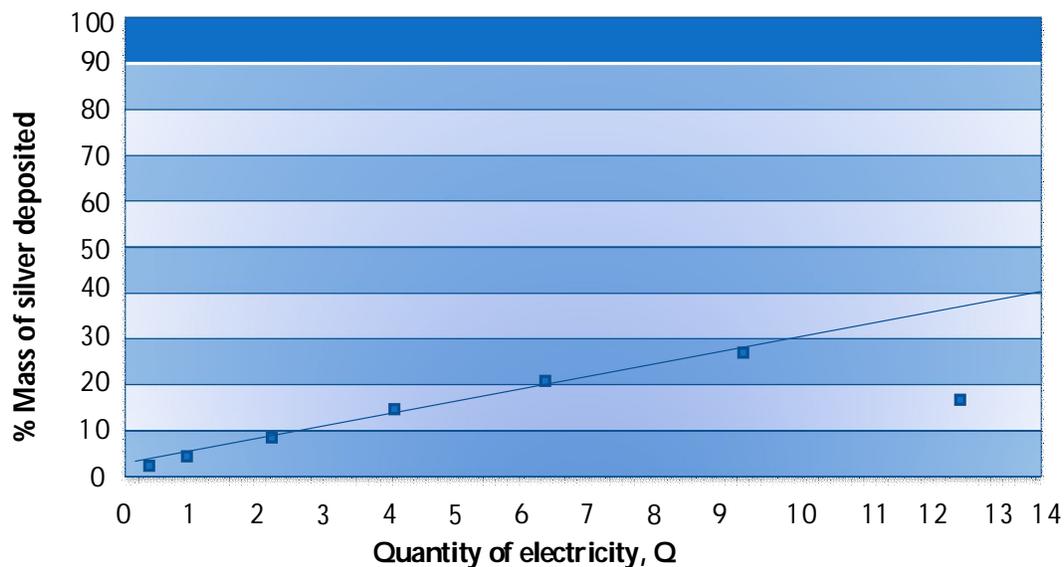
**Fig. 4.16: Variation of mass of silver deposited with quantity electricity As-discharged effluent (bleach fix) at pH 7, and an ambient temperature.**



**Table 4.15: Variation of mass of silver deposited with quantity electricity at 10% concentration of the effluent developer source/bleach fix; pH 7 and an ambient temperature of 29°C.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.069	2.5
2	20	40	0.050	2.0	1.00	0.165	6.0
3	30	40	0.075	3.0	2.25	0.248	9.0
4	40	40	0.100	4.0	4.00	0.413	15.0
5	50	40	0.125	5.0	6.25	0.550	20.0
6	60	40	0.150	6.0	9.00	0.756	27.5
7	70	40	0.175	7.0	12.25	0.468	17.0

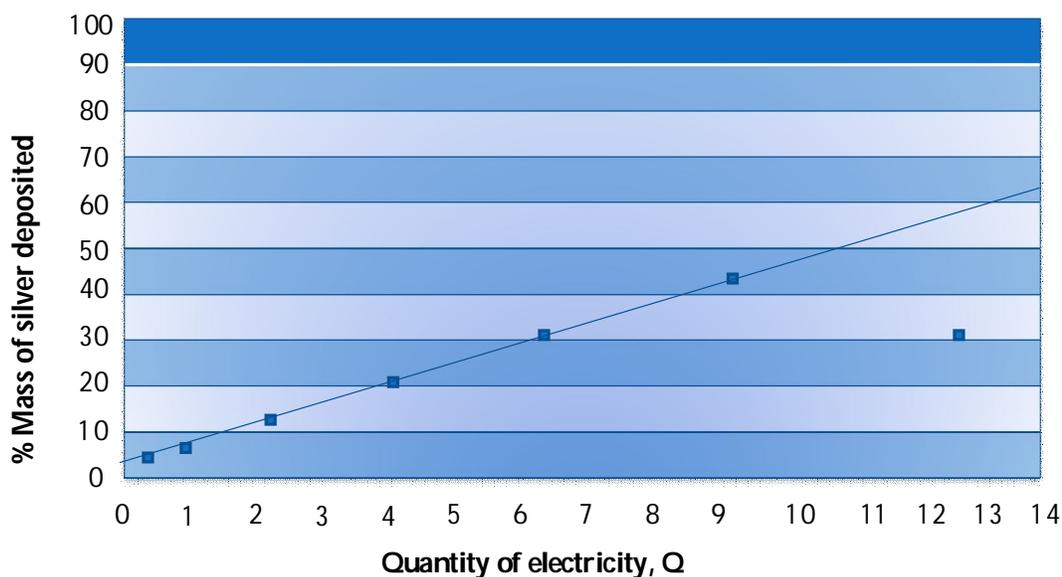
**Fig. 4.17 Variation of mass of silver deposited with quantity of electricity at 10% concentration of the effluent-developer/bleach fix; pH 7 and an ambient temperature.**



**Table 4.16: Variation of mass of silver deposited with quantity electricity of at 25% concentration of the effluent bleach fix pH 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.11	4.0
2	20	40	0.050	2.0	1.00	0.21	7.5
3	30	40	0.075	3.0	2.25	0.36	13.0
4	40	40	0.100	4.0	4.00	0.56	20.5
5	50	40	0.125	5.0	6.25	0.83	30.0
6	60	40	0.150	6.0	9.00	1.18	43.0
7	70	40	0.175	7.0	12.25	0.87	31.5

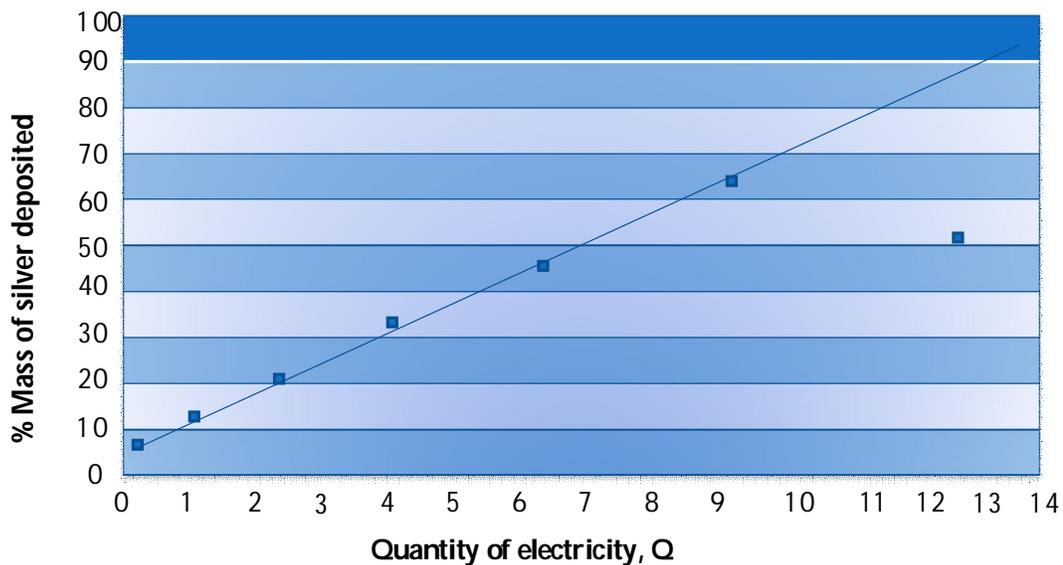
**Fig. 4.18: Variation of mass of silver deposited with quantity of electricity at 25% concentration of the effluent bleach fix; at pH 7 and an ambient temperature**



**Table 4.17: Variation of mass of silver deposited with quantity of electricity at 50% concentration of the effluent bleach fix; pH 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.193	7.0
2	20	40	0.050	2.0	1.00	0.316	11.5
3	30	40	0.075	3.0	2.25	0.550	20.0
4	40	40	0.100	4.0	4.00	0.880	32.0
5	50	40	0.125	5.0	6.25	1.265	46.0
6	60	40	0.150	6.0	9.00	1.788	65.0
7	70	40	0.175	7.0	12.25	1.430	52.0

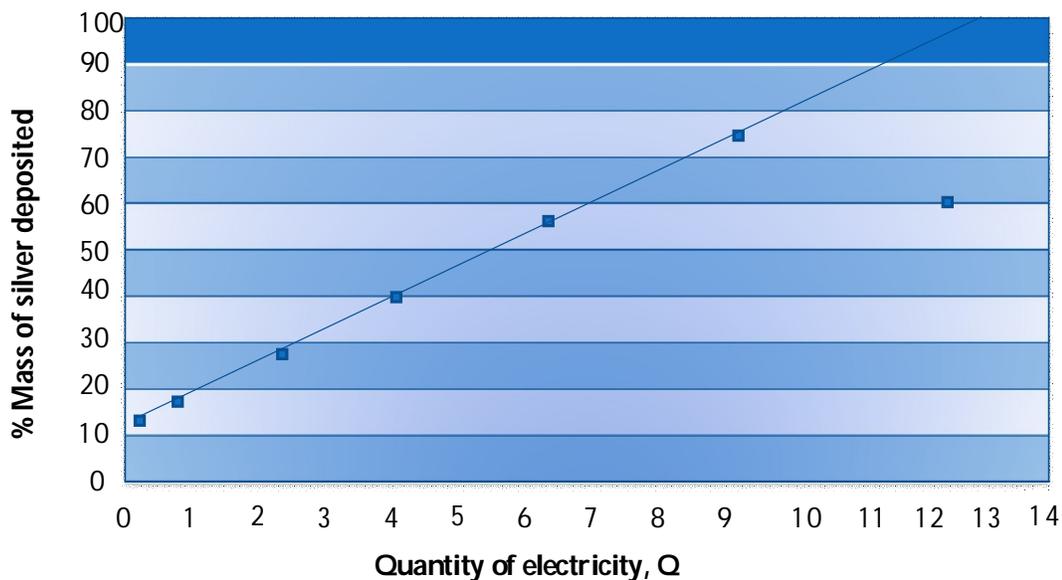
**Fig. 4.19: Variation of mass of silver deposited with quantity electricity at 50% concentration of the effluent bleach fix; at pH 7 and an ambient temperature.**



**Table 4.18: Variation of mass of silver deposited with quantity of electricity at 55.0% concentration of the effluent bleach fix; at pH 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.358	13.0
2	20	40	0.050	2.0	1.00	0.523	19.0
3	30	40	0.075	3.0	2.25	0.770	28.0
4	40	40	0.100	4.0	4.00	1.100	40.0
5	50	40	0.125	5.0	6.25	1.513	55.0
6	60	40	0.150	6.0	9.00	2.063	75.0
7	70	40	0.175	7.0	12.25	1.650	60.0

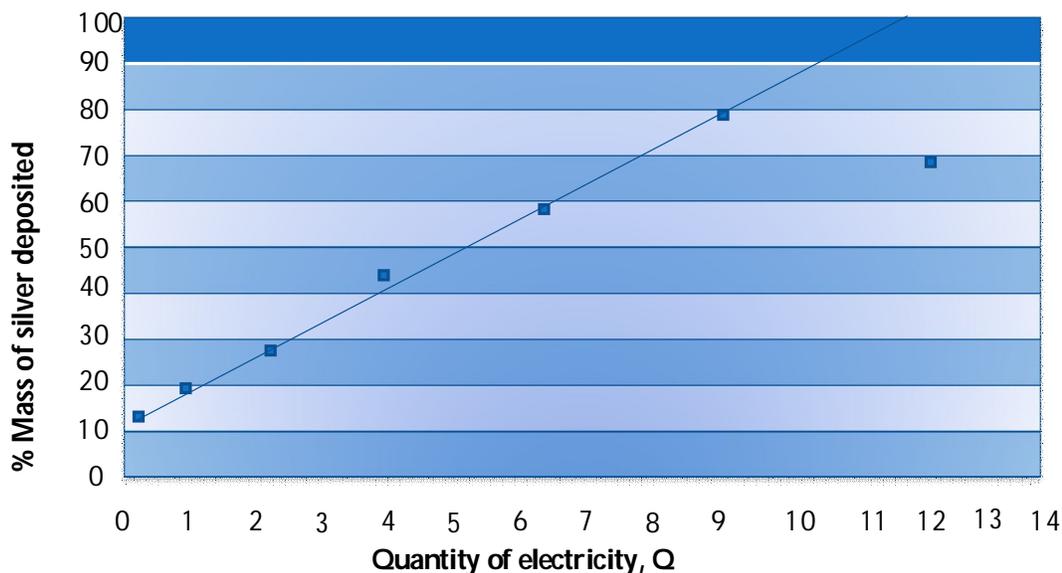
**Fig. 4.20: Variation of mass of silver deposited with quantity electricity at 55.0% concentration of the effluent bleach fix; at pH 7, and an ambient temperature.**



**Table 4.19: Variation of mass of silver deposited with quantity electricity of at 60% concentration of the effluent bleach fix; at pH 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.363	13.2
2	20	40	0.050	2.0	1.00	0.536	19.5
3	30	40	0.075	3.0	2.25	0.770	28.0
4	40	40	0.100	4.0	4.00	1.169	42.5
5	50	40	0.125	5.0	6.25	1.603	58.3
6	60	40	0.150	6.0	9.00	2.200	80.0
7	70	40	0.175	7.0	12.25	1.870	68.0

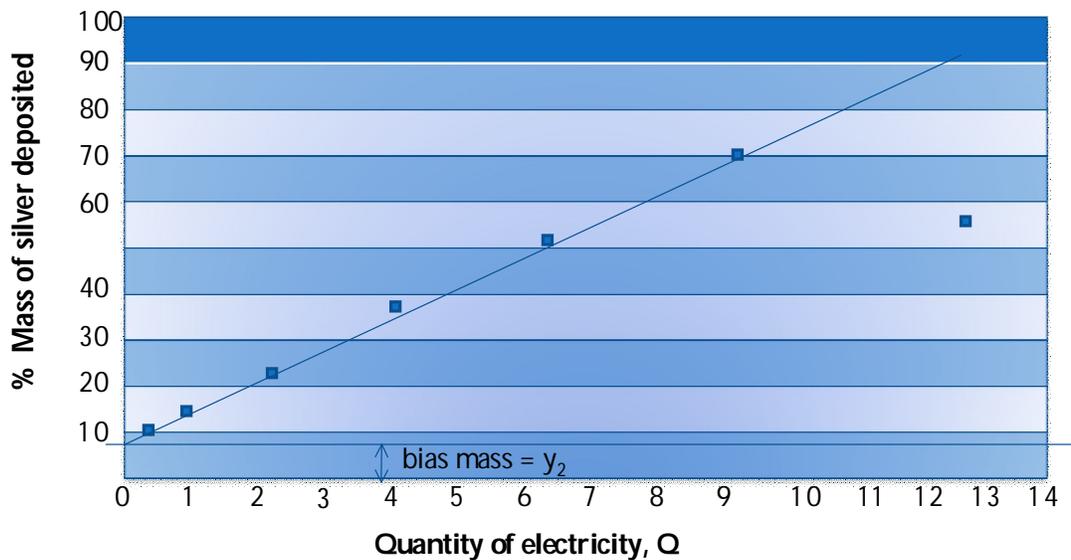
**Fig. 4.21: Variation of mass of silver deposited with quantity electricity of at 60% concentration of the effluent bleach fix; at pH 7 and an ambient temperature.**



**Table 4.20: Variation of mass of silver deposited with quantity electricity of at 70% concentration of the effluent (developer source/bleach fix); at pH of 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.275	10.0
2	20	40	0.050	2.0	1.00	0.413	15.0
3	30	40	0.075	3.0	2.25	0.633	23.0
4	40	40	0.100	4.0	4.00	0.990	36.0
5	50	40	0.125	5.0	6.25	1.43	52.0
6	60	40	0.150	6.0	9.00	1.898	69.0
7	70	40	0.175	7.0	12.25	1.513	55.0

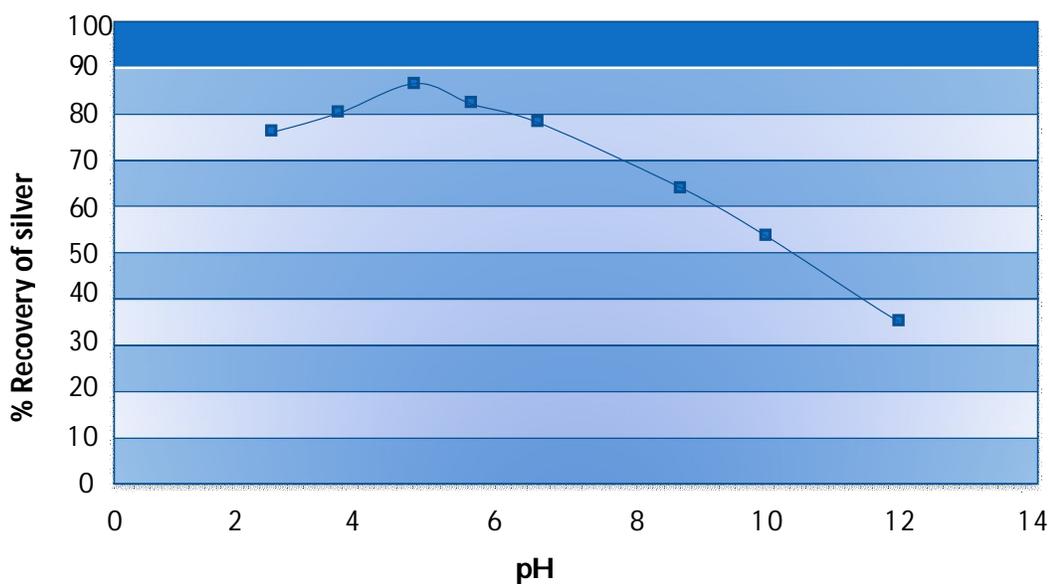
**Fig. 4.22: Variation of mass of silver deposited with quantity electricity at 70% concentration of the effluent (developer source/bleach fix); pH 7, and an ambient temperature.**



**Table 4.21: Effect of pH on mass of silver deposited, using developer/bleach fix, at an ambient temperature.**

pH	3	4	5	6	7	9	10	12
Mass of Ag deposited (g)	2.09	2.255	2.338	2.228	2.145	1.788	1.485	0.99
% Recovery of Ag	76	82	85	81	78	65	54	36

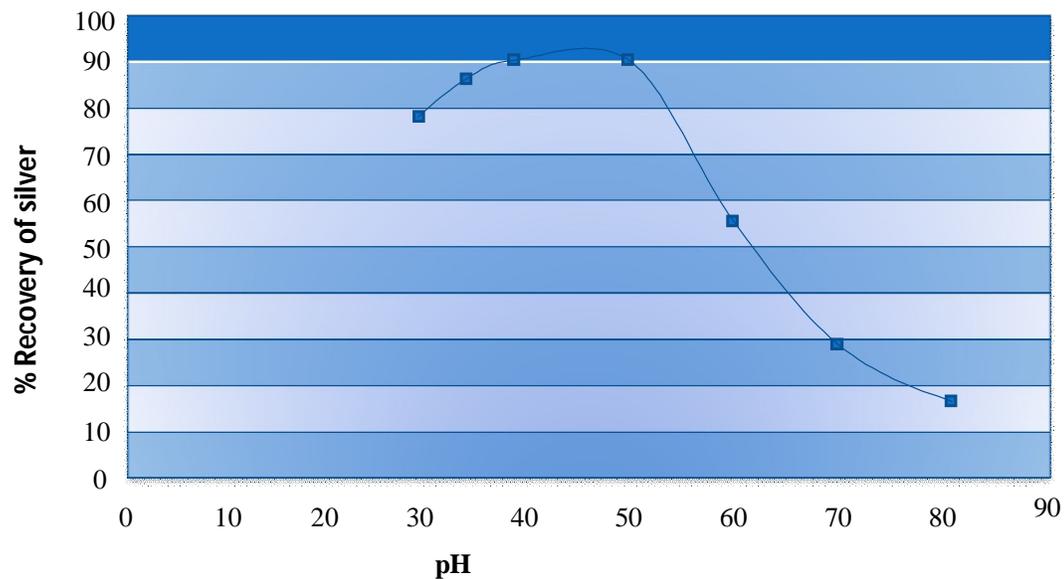
**Fig. 4.23: Effect of pH on mass of silver deposited using developer source at 60% concentration.**



**Table 4.22: Effect of temperature on mass of silver recovered from developer source or bleach fix at pH 5.0**

Temperature, °C	29	35	40	50	60	70	80
Mass of Ag deposited (g)	2.145	2.365	2.461	2.461	1.513	0.811	0.413
% Recovery of Ag	78	86	89.5	89.5	55	29.5	15

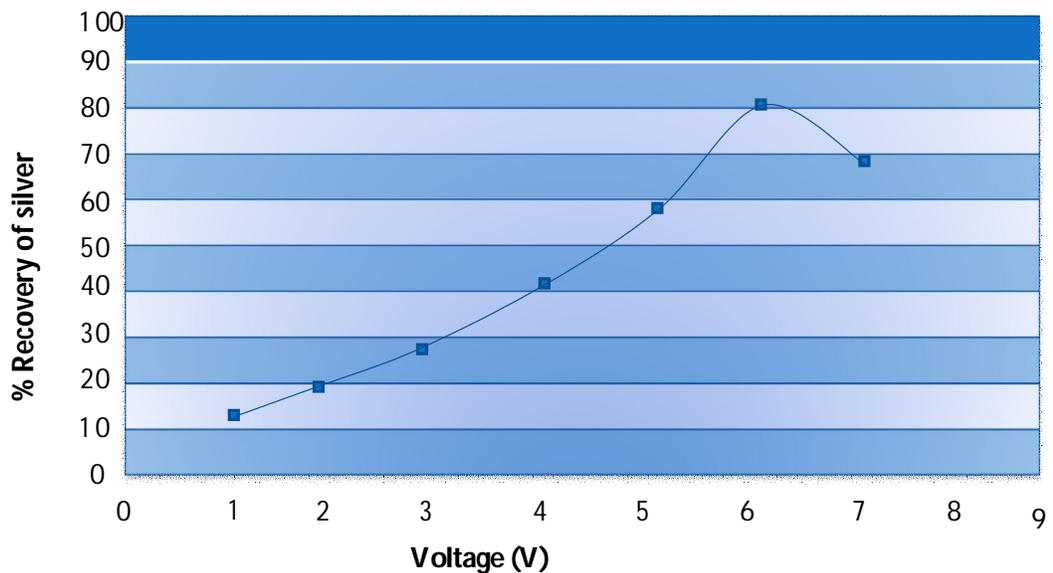
**Fig. 4.24: Effect of temperature on mass of silver recovered from developer source at 60% concentration and at pH of 5.0**



**Table 4.23: Relationship between voltage and current on mass of silver deposited using the developer source at 60% concentration, pH 7 and at an ambient temperature of 29°C.**

Voltage (V)	Current (A)	Resistance ( $\Omega$ )	Mass of silver deposited (g)	% mass of silver
1.0	0.025	40	0.363	13.2
2.0	0.050	40	0.536	19.5
3.0	0.075	40	0.770	28.0
4.0	0.100	40	1.169	42.5
5.0	0.125	40	1.603	58.3
6.0	0.150	40	2.200	80.0
7.0	0.175	40	1.870	68.0

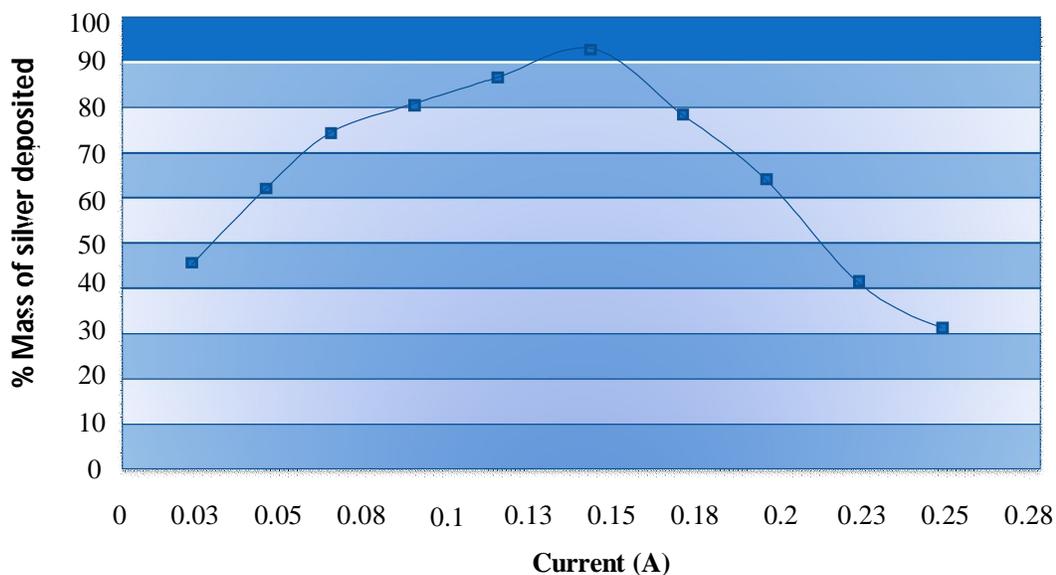
**Fig. 4.25: Variation of % recovery of silver with voltage using the developer source at 60% concentration, pH 7 and at an ambient temperature of 29°C.**



**Table 4.24: Effect of current on cathode deposition of silver using developer source as the electrolyte at pH 5 and temperature of 45°C.**

Weight of cathode (g)	Weight of cathode + weight of silver deposited (g)	Weight of silver deposited (mg)	% Recovery of silver	Current applied (A)
17.60	18.838	1.238	45.0	0.025
17.60	19.33	1.733	63.0	0.050
17.60	19.663	2.063	75.0	0.075
17.60	19.800	2.200	80.0	0.100
17.60	19.993	2.393	87.0	0.125
17.60	20.130	2.530	92.0	0.150
17.60	19.745	2.145	78.0	0.175
17.60	19.360	1.760	64.0	0.200
17.60	18.700	1.100	40.0	0.225
17.60	18.725	0.825	30.0	0.250

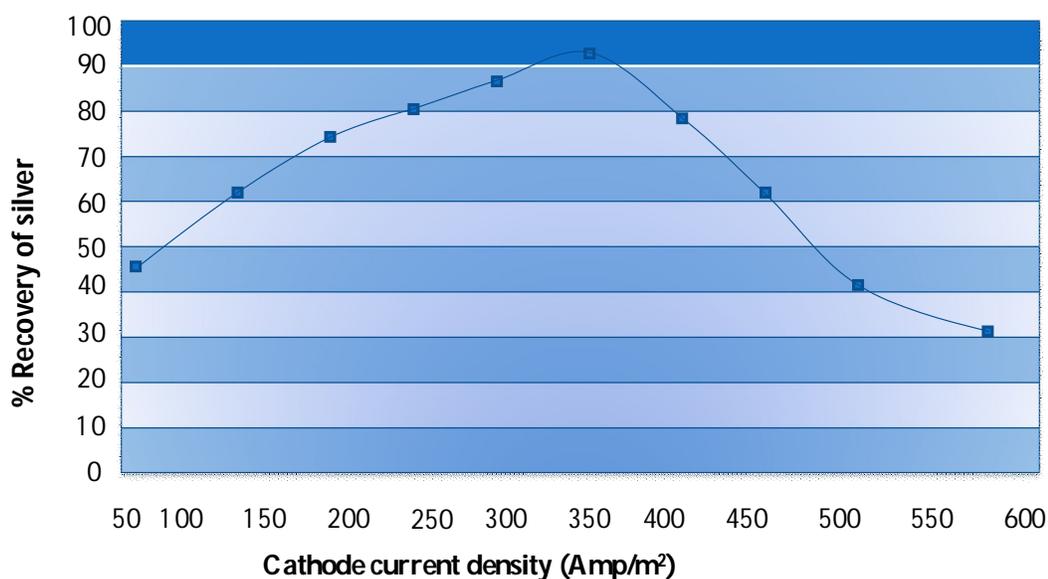
**Fig.4.26: Effect of current on mass of silver recovered at pH 5.0, temperature of 45°C using developer source.**



**Table 4.25: Effect of current density on cathode deposition of silver using developer source as the electrolyte at pH 5.0 and at temperature of 45°C**

Current (A)	Weight of silver deposited (mg)	% Recovery of silver	Surface area of cathode in contact with developer (m <sup>2</sup> ) x 10 <sup>-4</sup>	Cathode current density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
0.025	1.238	45.0	4.38	57.1	30.77
0.050	1.733	63.0	4.38	114.2	43.07
0.075	2.063	75.0	4.38	171.2	51.27
0.100	2.200	80.0	4.38	228.3	54.67
0.125	2.393	87.0	4.38	285.4	59.47
0.150	2.530	92.0	4.38	342.5	62.87
0.175	2.145	78.0	4.38	399.5	53.31
0.200	1.760	64.0	4.38	456.6	43.74
0.225	1.100	40.0	4.38	513.7	27.34
0.250	0.825	30.0	4.38	570.8	20.50

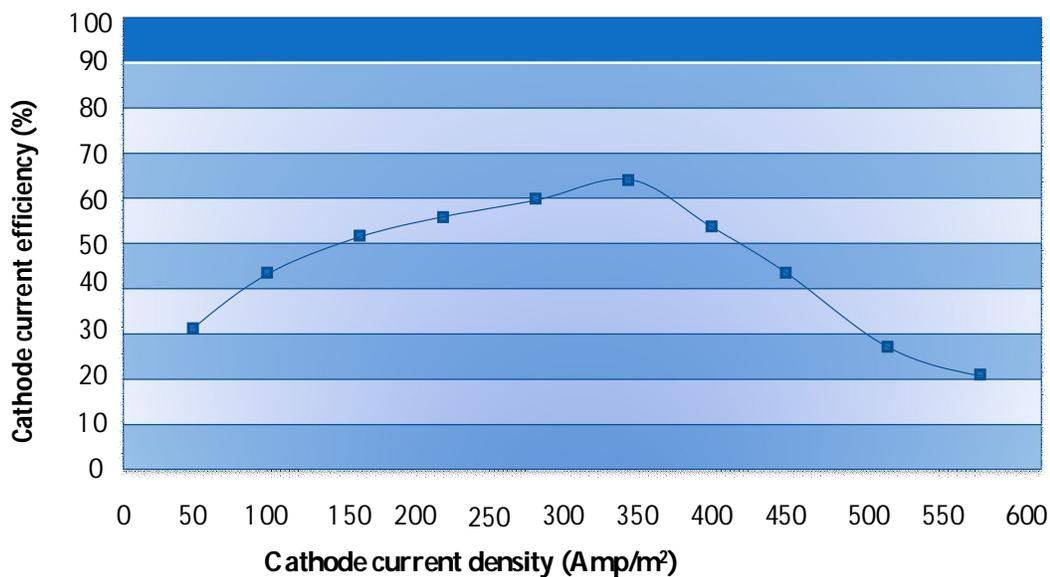
**Fig. 4.27: Effect of current density on cathode deposition of silver using developer source as the electrolyte at pH 5.0 and at temperature of 45°C**



**Table 4.26: Variation of cathode current density with cathode efficiency using 60% concentration of developer at pH 5.0 and 45°C**

Weight of silver deposited (mg)	% Recovery of silver	Cathode current density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
1.238	45.0	57.1	30.77
1.733	63.0	114.2	43.07
2.063	75.0	171.2	51.27
2.200	80.0	228.3	54.67
2.393	87.0	285.4	59.47
2.530	92.0	342.5	62.87
2.145	78.0	399.5	53.31
1.760	64.0	456.6	43.74
1.100	40.0	513.7	27.34
0.825	30.0	570.8	20.50

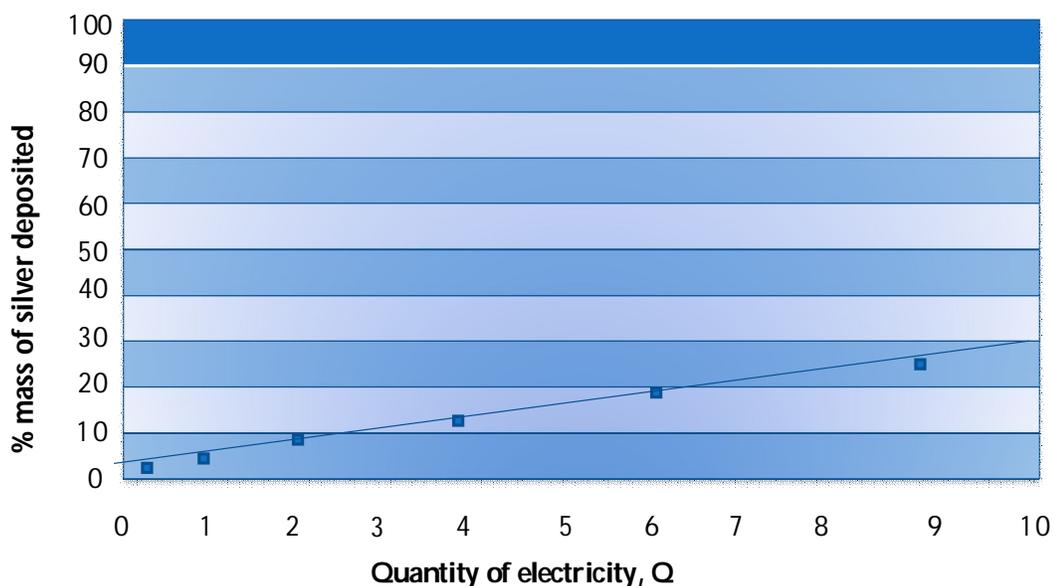
**Fig. 4.28: Plot of cathode efficiency versus cathode current density using 60% concentration of developer at pH 5.0 and 45°C.**



**Table 4.27: Variation of mass of silver deposited with quantity of electricity using As–discharged effluent fixer, at pH 7 and at an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.114	3.0
2	20	40	0.050	2.0	1.00	0.190	5.0
3	30	40	0.075	3.0	2.25	0.342	9.0
4	40	40	0.100	4.0	4.00	0.494	13.0
5	50	40	0.125	5.0	6.25	0.684	18.0
6	60	40	0.150	6.0	9.00	0.912	24.0
7	70	40	0.175	7.0	12.25	0.608	16.0

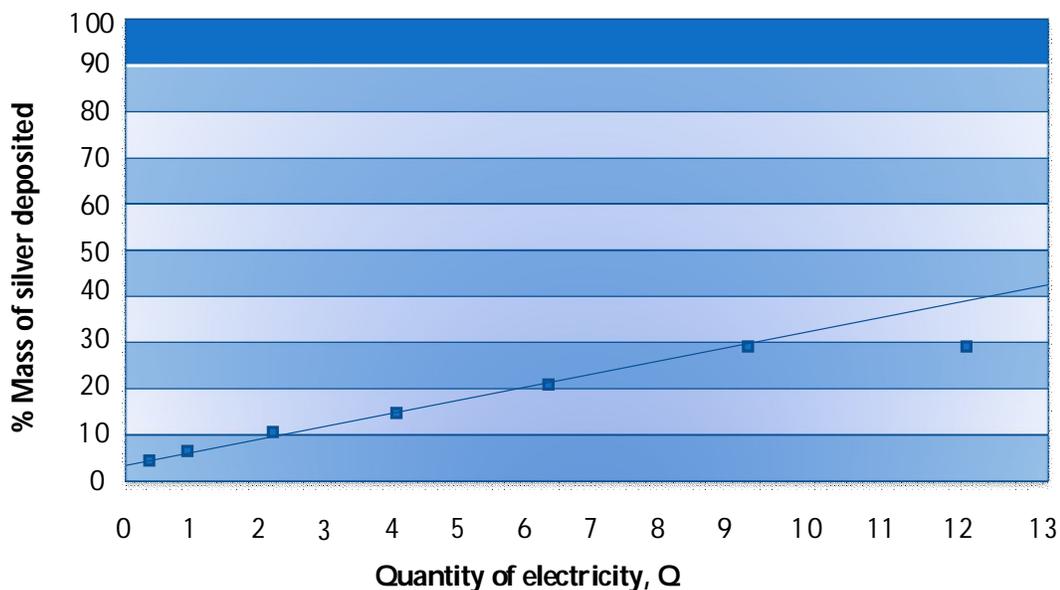
**Fig. 4.29: Variation of mass of silver deposited with quantity of electricity using As–discharged effluent fixer, at pH 7 and at an ambient temperature.**



**Table 4.28: Variation of mass of silver deposited with quantity of electricity at 10% concentration of the effluent (fixer or washing source), at pH 7, and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.152	4.0
2	20	40	0.050	2.0	1.00	0.247	6.5
3	30	40	0.075	3.0	2.25	0.380	10.0
4	40	40	0.100	4.0	4.00	0.608	16.0
5	50	40	0.125	5.0	6.25	0.798	21.0
6	60	40	0.150	6.0	9.00	1.140	30.0
7	70	40	0.175	7.0	12.25	0.722	19.0

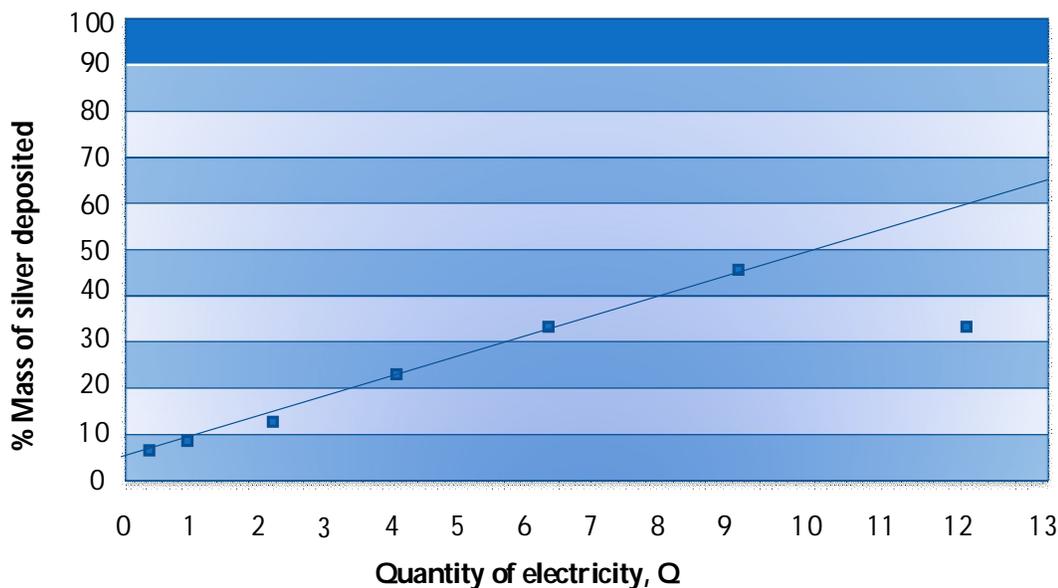
**Fig. 4.30: Variation of mass of silver deposited with quantity of electricity at 10% concentration of the effluent fixer or washing source, at pH 7, and an ambient temperature.**



**Table 4.29: Variation of mass of silver deposited with quantity of electricity at 25% concentration of the effluent (fixer or washing source), pH of 7 and at an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.190	5.0
2	20	40	0.050	2.0	1.00	0.304	8.0
3	30	40	0.075	3.0	2.25	0.494	13.0
4	40	40	0.100	4.0	4.00	0.836	22.0
5	50	40	0.125	5.0	6.25	1.235	32.0
6	60	40	0.150	6.0	9.00	1.672	44.0
7	70	40	0.175	7.0	12.25	0.292	34.0

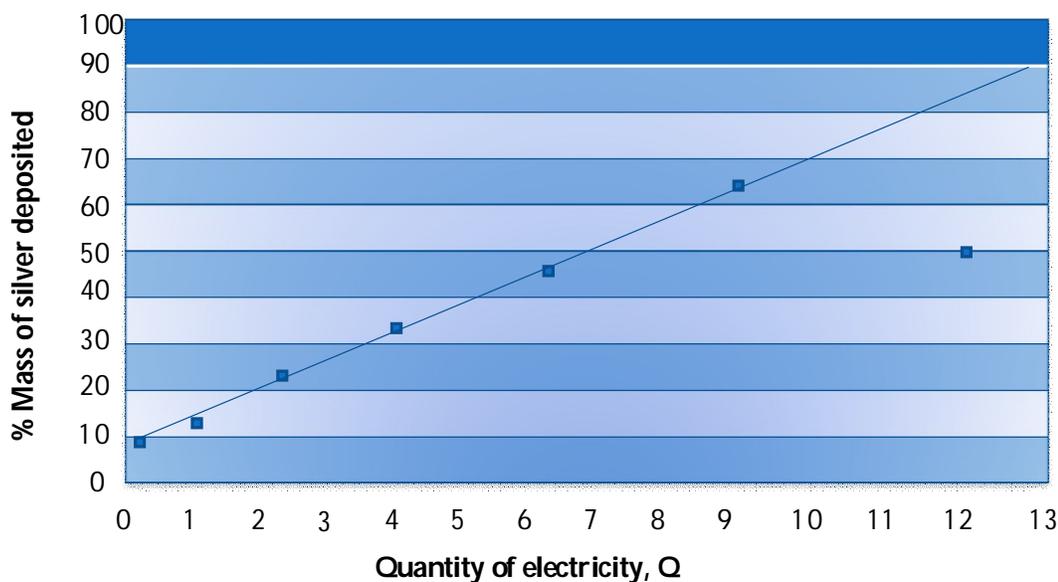
**Fig. 4.31: Variation of mass of silver deposited with quantity of electricity at 25% concentration of the fixer or washing source, pH of 7 and at an ambient temperature.**



**Table 4.30: Variation of mass of silver deposited with quantity of electricity at 50% concentration of the effluent (fixer or washing source), pH of 7 and at an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.304	8.0
2	20	40	0.050	2.0	1.00	0.494	13.0
3	30	40	0.075	3.0	2.25	0.836	22.0
4	40	40	0.100	4.0	4.00	1.216	32.0
5	50	40	0.125	5.0	6.25	1.786	47.0
6	60	40	0.150	6.0	9.00	2.470	65.0
7	70	40	0.175	7.0	12.25	1.900	50.0

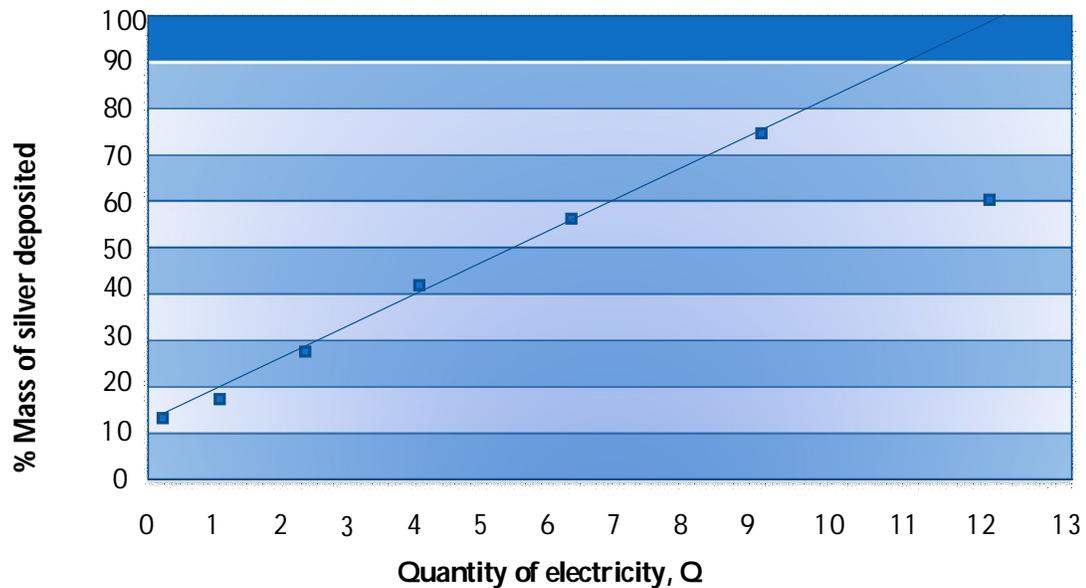
**Fig.4.32: Variation of mass of silver deposited with quantity of electricity at 50% concentration of the fixer or washing source, pH of 7 and at an ambient temperature.**



**Table 4.31: Variation of mass of silver deposited with quantity of electricity at 55% concentration of the effluent (fixer or washing source) at pH of 7, and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver deposited
1	10	40	0.025	1.0	0.25	0.475	12.5
2	20	40	0.050	2.0	1.00	0.703	18.5
3	30	40	0.075	3.0	2.25	1.026	27.0
4	40	40	0.100	4.0	4.00	1.55.8	41.0
5	50	40	0.125	5.0	6.25	2.166	57.0
6	60	40	0.150	6.0	9.00	2.888	76.0
7	70	40	0.175	7.0	12.25	2.356	62.0

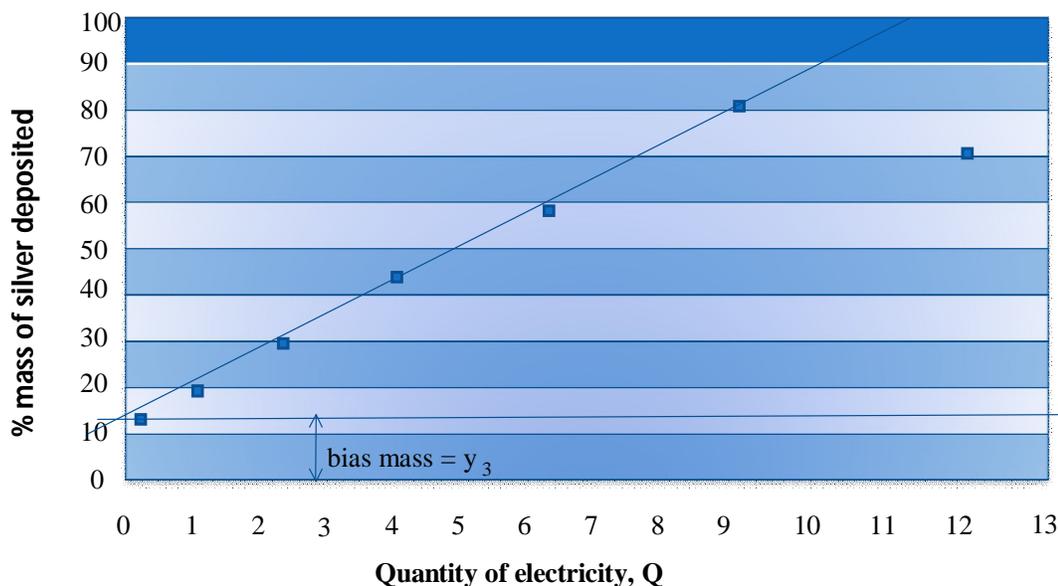
**Fig. 4.33: Variation of mass of silver deposited with quantity of electricity at 55% concentration of the fixer or washing source at pH of 7, and an ambient temperature.**



**Table 4.32: Variation of mass of silver deposited with quantity of electricity at 60% concentration of the effluent (fixer or washing source); at pH of 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver deposited
1	10	40	0.025	1.0	0.25	0.532	14.0
2	20	40	0.050	2.0	1.00	0.760	20.0
3	30	40	0.075	3.0	2.25	1.140	30.0
4	40	40	0.100	4.0	4.00	1.672	44.0
5	50	40	0.125	5.0	6.25	2.242	59.0
6	60	40	0.150	6.0	9.00	3.116	82.0
7	70	40	0.175	7.0	12.25	2.660	70.0

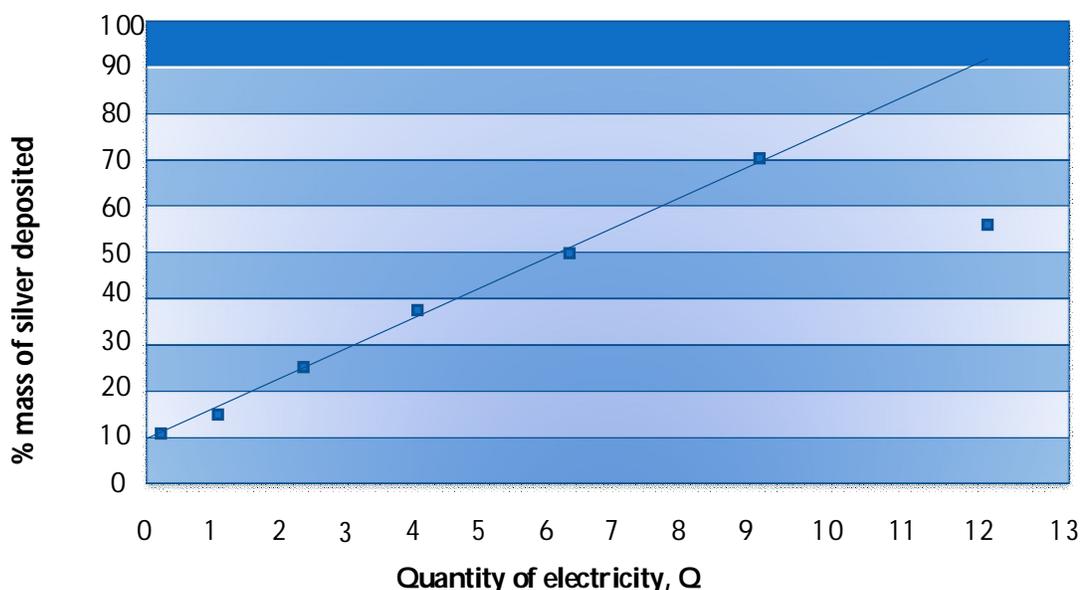
**Fig. 4.34: Variation of mass of silver deposited with quantity of electricity at 60% concentration of the fixer or washing source; at pH of 7 and an ambient temperature.**



**Table 4.33: Variation of mass of silver deposited with quantity of electricity at 70% concentration of the effluent (fixer or washing source); at pH of 7 and an ambient temperature.**

No. of expts	Time (mins)	Resistance (ohmn)	Current (A)	Voltage (V)	Quantity of electricity (C)	Mass of silver deposited (g)	% mass of silver
1	10	40	0.025	1.0	0.25	0.418	11.0
2	20	40	0.050	2.0	1.00	0.570	15.0
3	30	40	0.075	3.0	2.25	0.950	25.0
4	40	40	0.100	4.0	4.00	1.406	37.0
5	50	40	0.125	5.0	6.25	1.938	51.0
6	60	40	0.150	6.0	9.00	2.660	70.0
7	70	40	0.175	7.0	12.25	2.147	56.5

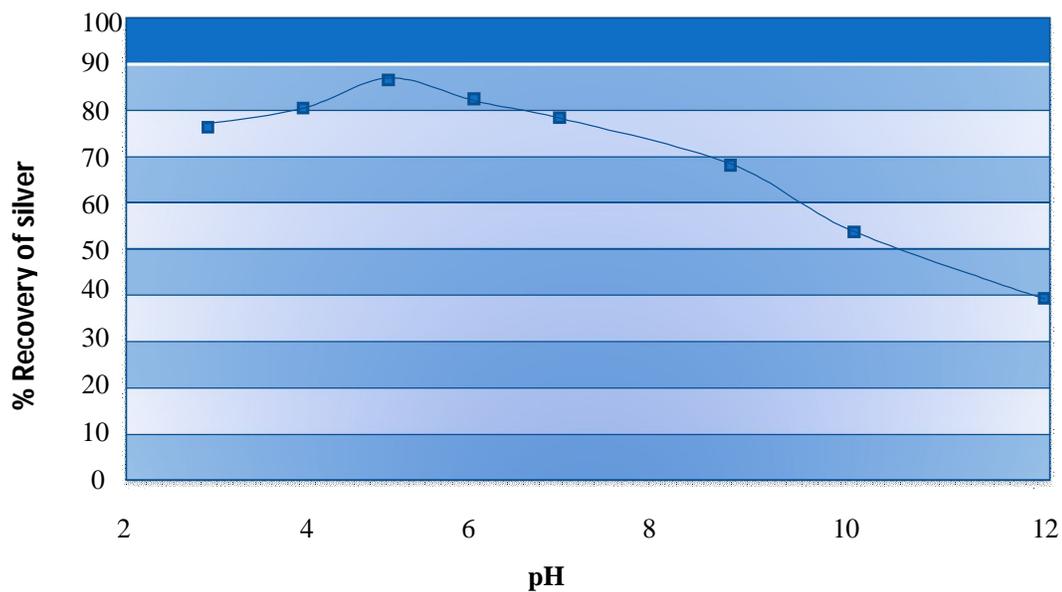
**Fig. 4.35: Variation of mass of silver deposited with quantity of electricity at 70% concentration of fixer or washing source; at pH of 5 and an ambient temperature.**



**Table 4.34: Effect of pH on mass of silver deposited using fixer or washing source, at ambient temperature.**

pH	3	4	5	6	7	9	10	12
Mass of Ag deposited (g)	2.964	3.097	3.268	3.154	3.002	2.584	2.128	1.520
% Recovery of Ag	78	81.5	86	83	79	68	56	40

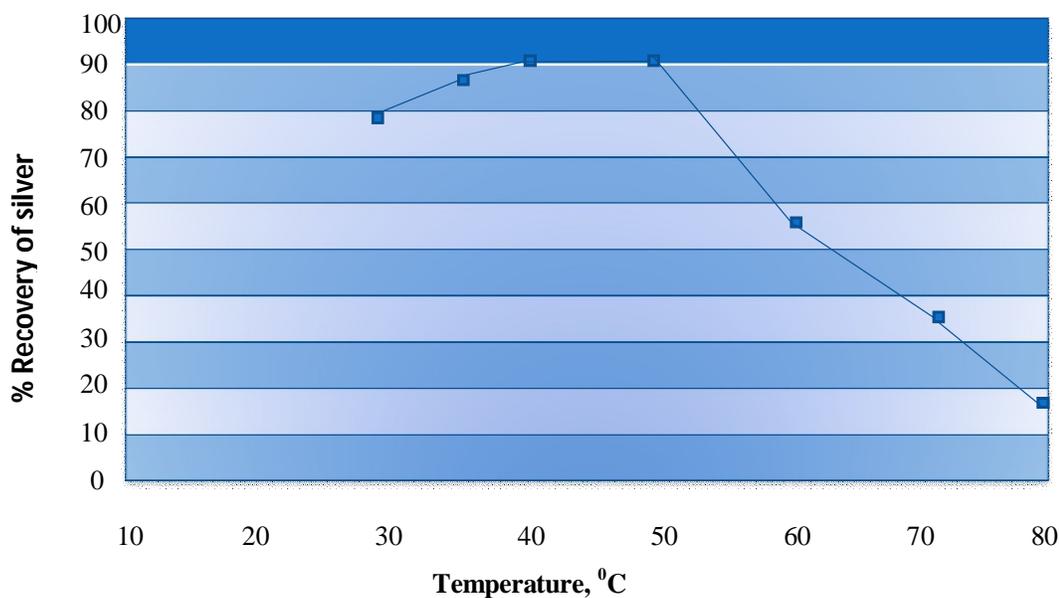
**Fig. 4.36: Effect of pH on mass of silver deposited using fixer or washing source at ambient temperature.**



**Table 4.35: Effect of temperature on mass of silver recovered from fixer or washing source at pH 5.0**

Temperature, °C	29	35	40	50	60	70	80
Mass of Ag deposited	2.983	3.306	3.420	3.420	2.166	1.387	0.665
% Recovery	78.5	87	90	90	57	36.5	17.5

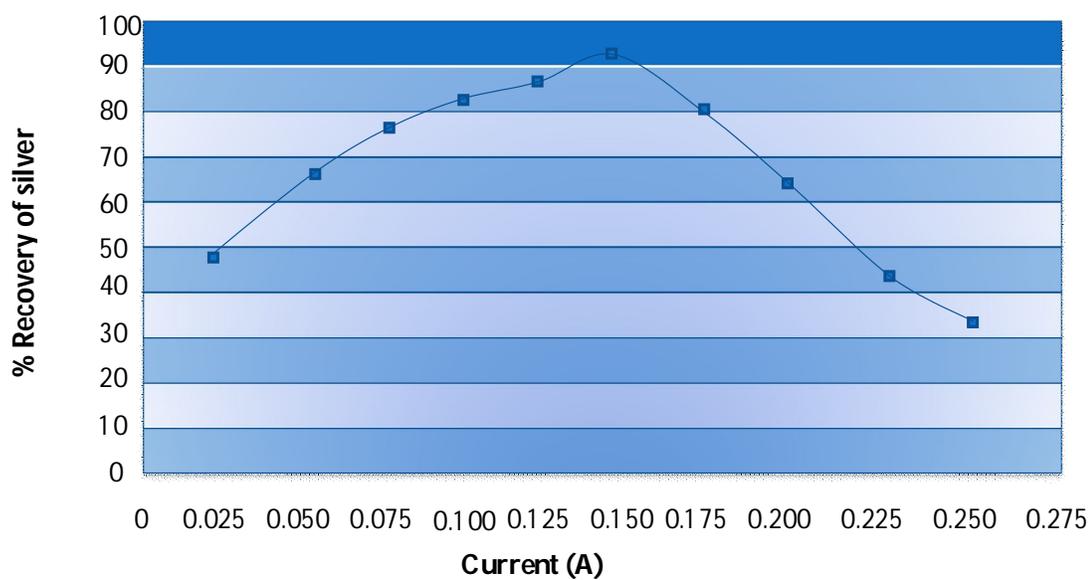
**Fig. 4.37: Effect of temperature on mass of silver recovered from fixer or washing source at pH 5.0**



**Table 4.36 :** Effect of current on cathode deposition of silver fixer source of effluent as the electrolyte at pH 5 and temperature of 45°C.

Weight of cathode	Weight of cathode + weight of silver deposited (g)	Weight of silver deposited (mg)	% Recovery of silver	Current applied (A)
17.60	19.424	1.824	48	0.025
17.60	20.070	2.470	45	0.050
17.60	20.450	2.850	75	0.075
17.60	20.716	3.116	82	0.100
17.60	20.944	3.344	88	0.125
17.60	20.096	3.496	92	0.150
17.60	20.640	3.040	80	0.175
17.60	20.070	2.470	65	0.200
17.60	19.310	1.710	45	0.225
17.60	18.930	1.330	35	0.255

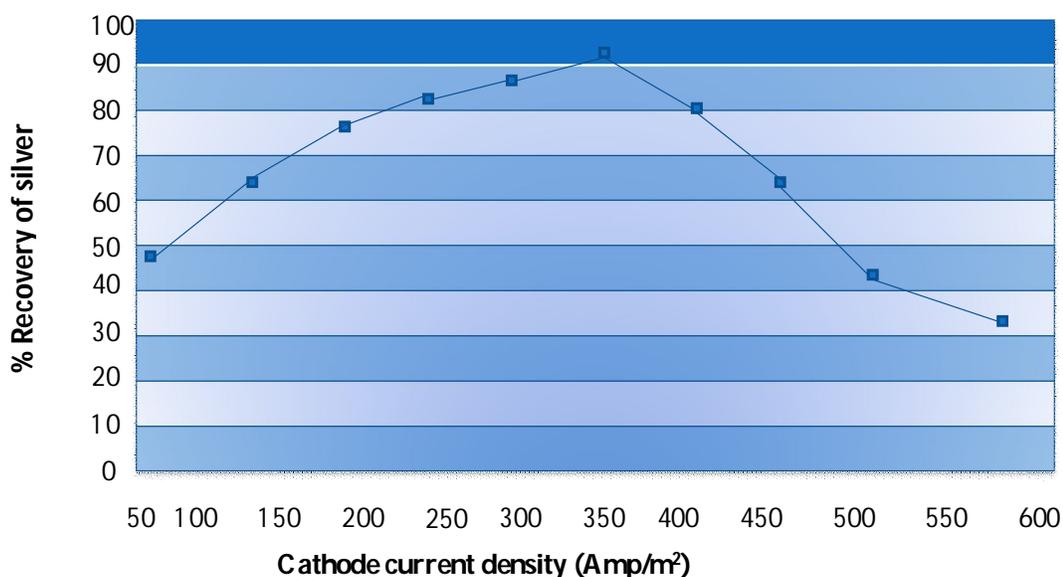
**Fig. 4.38:** Effect of current on silver deposited at pH 5.0, temperature using fixer source of the electrolyte



**Table 4.37: Effect of current density on cathode deposition of silver using fixer source as the electrolyte at pH 5.0 and temperature of 45°C**

Current	Weight of silver deposited (g/200ml)	% Recovery of silver	Surface area of cathode in contact with fixer	Cathode current density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
0.025	1.824	48.0	4.38	57.1	43.33
0.050	2.470	65.0	4.38	114.2	61.38
0.075	2.850	75.0	4.38	171.2	70.83
0.100	3.116	82.0	4.38	228.3	77.44
0.125	3.344	88.0	4.38	285.4	83.10
0.150	3.496	92.0	4.38	342.5	86.88
0.175	3.040	80.0	4.38	399.5	75.55
0.200	2.470	65.0	4.38	456.6	61.38
0.225	1.710	45.0	4.38	513.7	42.50
0.250	1.330	35.0	4.38	570.8	33.05

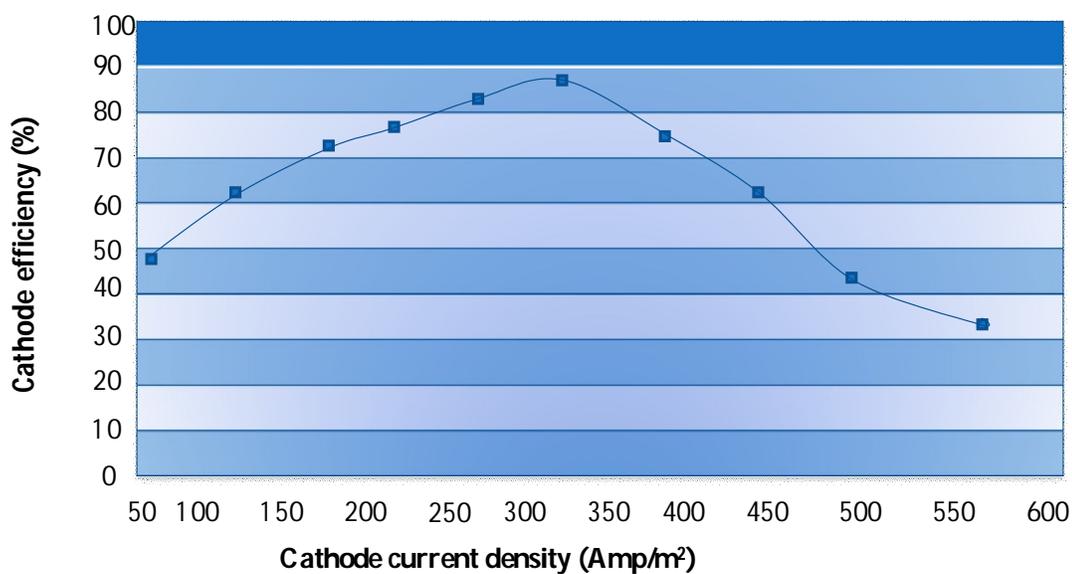
**Fig. 4.39: Effect of current density on cathode deposition of silver using fixer source as the electrolyte at pH 5.0 and temperature of 45°C**



**Table 4.38: Variation of cathode current density with cathode efficiency using 60% concentration of fixer at pH 5.0 and 45°C**

Weight of silver deposited (g/200ml)	% Recovery of silver	Cathode current density (Amp/m <sup>2</sup> )	Cathode current efficiency (%)
1.824	48	57.1	43.33
2.470	65	114.2	61.38
2.850	75	171.2	70.83
3.116	82	228.3	77.44
3.344	88	285.4	83.10
3.496	92	342.5	86.88
3.040	80	399.5	75.55
2.470	65	456.6	61.38
1.710	45	513.7	42.50
1.330	35	570.8	33.05

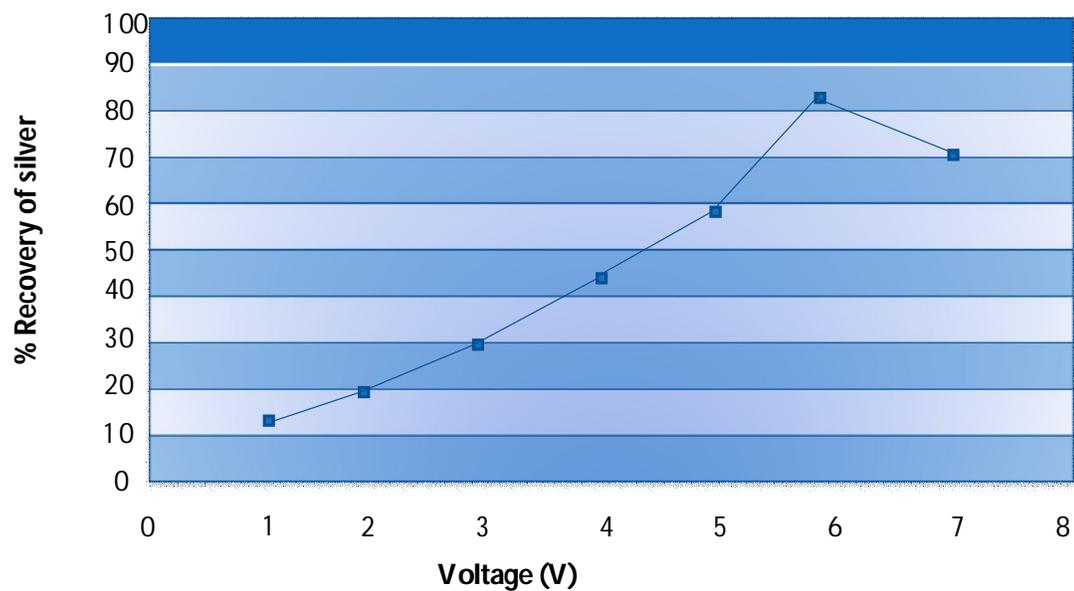
**Fig. 4.40: Variation of cathode current density with cathode efficiency using 60% concentration of fixer at pH 5.0 and 45°C**



**Table 4.39: Relationship between voltage and current on mass of silver deposited using the fixer at 60% concentration of the effluent, pH 7 and temperature of 29°C.**

Voltage (V)	Current (A)	Resistance ( $\Omega$ )	Mass of Ag deposited (g)	% Mass of silver recorded
1.0	0.025	40	0.532	14.0
2.0	0.050	40	0.760	20.0
3.0	0.075	40	1.140	30.0
4.0	0.100	40	1.672	44.0
5.0	0.125	40	2.242	59.0
6.0	0.150	40	3.116	82.0
7.0	0.175	40	2.660	70.0

**Fig. 4.41: Relationship between voltage and current on mass of silver deposited using the fixer at 60% concentration of the effluent, pH 7 and temperature of 29°C.**



### 4.3 EFFECT OF pH ON % MASS OF SILVER RECOVERED

The effect of pH on the mass of silver recovered was studied at several pH values between 3 and 12 at ambient temperature of 29°C. As shown in Table 4.8 and Figure 4.9, the rinse water yielded an optimal recovery of 66.4mgAg (83% recovery); in Table 4.21 and Figure 4.23, the bleach fix gave an optimal yield of 2.338gAg (85% recovery), and in the case of fixer solution an optimal recovery of 3.268gAg was recorded as shown in Table 4.24 and Figure 4.36. It is noted that the optimal recoveries of silver are obtained at pH 5 in each case. pH 5 is therefore chosen to be the optimum pH for electrodeposition of silver. In electroplating it is advantageous to use solutions of known and steady pH value. This is achieved by the use of buffers. With increase in pH at the cathode there is the possibility that hydroxide will be discharged on the cathode surface. Also increasing the pH leads to increase in the net negative charge which is expected to increase the binding affinity of cations such as silver ions ( $\text{Ag}^+$ ) in solution and hence interferes with the deposition of the silver metal. This explains the observation noted beyond pH 5 or precisely between pH 6 to 12, which suggests less discharge of  $\text{Ag}^+$  or poor-adhesion discharged  $\text{Ag}^+$ .

At low pH value, the production of hydrogen gas interferes with cathodic deposition. Most of the hydrogen is evolved from the cathode surface as a gas. Hydrogen absorbed into the deposit and substrate can give rise to hydrogen embrittlement which is a form of corrosion. This interference of cathodic deposition by hydrogen adsorption is responsible for the low yield recorded at low pH values as seen in Figures 4.9, 4.23 and 4.36. Excessive

acidity of the solution which is denoted by copious gassing due to evolution of hydrogen at the cathode surface is responsible for imperfect adhesion of deposits. This defect may be visible on removal of the article by the stripping or peeling of the deposit. Another possible cause of poor adhesion is the presence of grease on the cathode surface and contamination of the solution with other interfering metals. The choice of good pH value, suitable current density and appropriate complexing agent can remedy adhesion problems.

#### **4.4 EFFECT OF TEMPERATURE ON MASS OF SILVER DEPOSITED**

The effects of temperature on mass of silver recovered are presented in table 4.9, 4.22, 4.35 as well as Figures 4.10, 4.24 and 4.37 respectively. Increasing the temperature increases ionic mobility and thus allows more metal ions diffuse in and out of the electrodes, thus lowering the over potential. The effect of too low temperature on cathode deposition is that it leads to slow rate of deposition. Low temperature also leads to low current density.

As shown in tables 4.9, 4.22 and 4.35 highest recovery of silver from each of the effluents is achieved in 60min between 40-50oC. At this temperature range 70.4mgAg (88%), 2.461gAg (89.5%) and 3.42gAg (90%) are recovered from rinser, bleach-fix and fixer effluent solutions respectively.

Silver recovery declined rapidly beyond this temperature range indicating the high impurity level of the silver deposited as a result of the deposition of other ions in solution like thiosulphate to give sulphide because they are

decomposed by the high temperature. Sulphide precipitation as a result of high temperature is very good in rendering the cathode surface passive.

Thus, the use of temperature beyond 50°C must be avoided if a reasonable recovery is desired. These results also show that it is more beneficial to electroplate at temperature above the ambient temperature of 29°C but not more than 50°C.

#### **4.5 EFFECT OF CURRENT ON CATHODE DEPOSITION**

The optimum current of 0.15A is obtained during the electrolysis of each of the three effluent sources. While the rinser gave 72.4mgAg representing 90% recovery, the bleach-fix and fixer solutions yielded 2.53gAg and 3.496gAg representing 92% in each case.

The experiment was conducted at an optimum pH 5, 45°C and resident period of 60minutes. There is a sharp fall of cathodic recovery beyond the optimum current.

#### **4.6 EFFECT OF CURRENT DENSITY AND EFFICIENCY**

The effect of current density on cathode deposition of silver was studied and the results are presented in tables 4.11, 4.25, 4.37 and Figures 4.12, 4.27 and 4.39 representing three effluent sources from rinser, bleach-fix and fixer. From the graph of percent recovery against the current density, the optimum current density of 342.5Am<sup>-2</sup> was obtained in each case for the maximum recovery of 72.4mgAg/200ml of rinser, 2.53gAg/200ml of bleach-fix, and 3.46gAg/200ml fixer solutions.

These results showed also that the corresponding cathode current efficiencies were 1.8% (rinser), 62.87% (bleach-fix) and 86.88% (fixer).

At high cathode current densities evolution of hydrogen occurred. It is believed that it is as a result of reduction in the concentration of silver ions in the electrolyte that made it possible for hydrogen to evolve. This explains the reason for decreases in the mass of silver recovered beyond the optimum cathode current density of  $342.5\text{A/m}^2$ .

The very low current efficiency recorded in the case of rinser source is an indication that much of the current went into an unwanted electrochemical reactions like evolution of hydrogen, hydroxide and sulphide precipitation.

The current efficiencies for bleach-fix and fixer solutions are quite encouraging and give a good explanation for the relatively high recovery of silver metal in both cases.

#### **4.7 VARIATION OF CATHODE CURRENT DENSITY WITH CATHODE EFFICIENCY**

A study of the variation of cathode current density with cathode efficiency is reported in tables 4.12, 4.16, 4.38 and Figures 4.13, 4.28, as well as 4.40 accordingly.

These results show that the optimum cathode current density of  $342.5\text{A/m}^2$  is common to the three samples electroanalysed. The rinser gave a recovery of  $72.4\text{mgAg}/200\text{ml}$  at cathode efficiency of 1.80%. Bleach-fix yielded  $2.53\text{gAg}/200\text{ml}$  at efficiency of 62.89%, while fixer recorded

3.496gAg/200ml at 86.88% cathode efficiency. This relationship can be summarized in the table shown below.

**Table 4.40: Variation of cathode current density with cathode efficiency**

	Rinser	Bleach-fix	Fixer
Optimum cathode current density (Amp/m <sup>2</sup> )	342.5	342.5	342.5
Cathode efficiency (%)	1.80	62.87	86.88
Weighty of silver deposited (mg/200ml)	72.4	2,530	3,496
% Recovery	90.5	92.0	92.0

Table 4.40 shows that the three effluent sources are electroanalysed at an optimum cathode current density of 342.5 A/m<sup>2</sup> for various optimal recoveries.

This uniform optimum current density is because the surface area of the cathode in contact with the effluent is of the same dimension and the use of optimum current of 0.15A for the electrogravimetric work is the same throughout.

The low cathode efficiency of 1.80% observed with respect to the rinsing shows that there is very low concentration of silver ions around the cathode

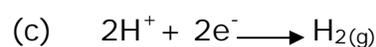
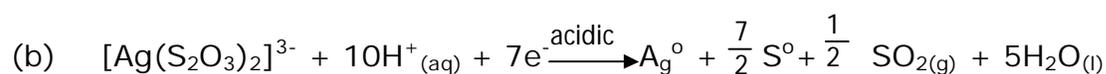
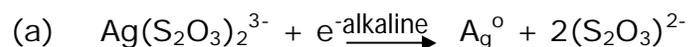
and hence the current was wasted in depositing unwanted materials at the cathode instead of silver. The 1.80% cathode efficiency means that 98.2% of the current supplied was wasted. Therefore it is not advisable to extract silver from rinsers by electrolysis.

The situation is however different in the case of bleach – fix and fixer solutions. These two effluents show good results when their efficiencies are compared with that of rinsers and hence recovering silver through these sources is a viable venture. The results obtained are comparable with literature range which stated that efficiencies approaching 90% are possible when recovering silver from bleach – fix and fixer solution from colour processing waste [10, 16, 86].

Silver is present in the photo processing effluent solutions as a silver thiosulphate complex ion with other interfering substances such as sodium, potassium, iron, chloride, bromide and sulphur being present. In the presence of alkaline solution the silver thiosulphate complex can easily be separated into silver metal and thiosulphate group when electric current is applied during electrolysis of the bleach –fix and fixer solutions.

Reduction of the complex silver into a silver metal is also possible in acidic medium during electrolysis. However, in acid solution the thiosulphates decompose to give elemental sulphur and sulphur dioxide gas. Since the project was electrolysed in both alkaline and acidic media, we expect to observe the two occurrences. With the use of good conditioning agents such as zinc dust,  $H_2O_2$ ,  $Na_2CO_3$  and ensuring effective filtration as well as

agitation, electrolyzing the effluent bearing silver – thiosulphate complex is expected to give a good result. In this respect the possible primary cathode reaction can be represented as follows:



The drop in pH observed during electrolysis as a result of sulphite consumption is maintained by buffering the sample prior to electrolysis.

Reaction (a) is tenable in an alkaline condition that is when the pH is maintained above 7.

Reaction (b) is predominant in acidic medium when the pH of the electrolyte is less than 7.

Reaction (c) is possible to occur in either (a) or (b) especially when the concentration of silver ion has depleted, hence there will be hydrogen evolution some of which adsorbs on the cathode surface.

#### **4.8 RELATIONSHIP BETWEEN VOLTAGE AND CURRENT ON MASS OF SILVER DEPOSITED**

In order to find the optimum voltage, the relationship between voltage and current on mass of silver deposited was studied and the results are

recorded in Tables 4.23, 4.39 and Figures 4.25, 4.41 respectively.

The plots show that optimum recovery of silver from both the bleach – fix (developer) and the fixer is tenable at voltage of 6. Thus the optimum voltage for the electrolytic study in this case is 6.0volts.

## CHAPTER FIVE

### 5.0 CONCLUSION AND RECOMMENDATION

#### 5.1 CONCLUSION

The importance of photography cannot be over emphasized. It is used to preserve memories of favourites and as a source of entertainment. Security agents use photography for surveillance, recognition, data storage and crime detection.

Inspite of all these advantages inherent in photography, the industrial waste from photographic processes is a serious threat to the environment and ecosystem because of the presence of hazardous substances such as silver. The absorption of silver by body tissue has been reported to target the intellectual sections of the brain, which may seriously affect the reasoning abilities. Other health hazards had been mentioned in the earlier chapter, hence there is need to desilver the effluent.

The economic benefit of silver as a precious metal is another motivating factor for its recovery from the photographic waste solution.

The beneficiation of silver from the photographic effluent is therefore an important and beneficial waste management technique for the overall interest of human being. The technique employed for the beneficiation process is quite simple and can be adapted as a teaching aid for practical classes in electrochemistry.

The process information has been obtained on the factors affecting the optimum recovery of silver and this has demonstrated the role of the

electrochemist in waste management issues.

The research work is very relevant, considering its role in waste management toward a safe environment. It is also economically viable and can generate a lot of income by sale of recovered silver and also re-use of the deslivered photoprocessing solutions such as bleach-fix and fixer solutions.

## **5.2 RECOMMENDATION**

I would recommend that further investigations be carried out on photographic waste solutions using locally available sea weeds as the adsorbent of the silver ions. This method will be useful in terms of cost reduction since the sea weeds are obtained free of charge. Apart from its cost effective advantage, it is believed to be an environmentally safe technique for the recovery of silver ions from aqueous solutions.

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