



EXTRACTION OF SILVER FROM WASTE RADIOGRAPHIC FILM BY LEACHING AND PRECIPITATION

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ABSTRACT:

One of the most expensive noble metals known to mankind is silver (Ag). Mining is the major method for obtaining silver. Apart from mining, a potential source for silver recovery is possible from radiographic waste films as well. The waste photographic films, X-ray contains 1-2% (worldwide) black metallic silver which can be recovered and reused. Methods for recovery of silver from x-ray waste include Chemical Precipitation, Electrolysis, Metal replacement cartridges, Biological method by enzyme production and extraction of silver by glucose, Electrolysis Process. In our project, silver from the used radiography films was recovered by Leaching and Precipitation. This method is one of the most efficient processes while compared to other methods of extracting silver from waste radiographic films. The photographic film was initially leached, Precipitated and heated to get silver metal. The resulting silver then had to have several stages of purification. The method was efficient and environmentally friendly to obtain silver compared to other methods.

Keywords: Absorption, Effluent, Electrolysis, Photographic film, Radiation, Silver recovery, Waste, X-ray films.

1. INTRODUCTION:

Silver is the most valuable metal with the symbol of Ag, after the Latin word and atomic number 47(one of the noble metal).It occurs in elemental form in nature which is mostly used and costliest next to gold. Silver is a white, lustrous, soft, ductile, malleable metal. It also combines with other elements like oxygen, nitrogen, sulphur, chlorine, etc., The silver metal is widely used in electrical, electronics, photographic, jewellery and also in most chemical industries manufacture coin. Silver was one of the metals of antiquity which were known as prehistoric humans. It is a rare precious, naturally occurring metal, often found deposited as a mineral ore in association with other elements. 50% of the silver produced is used in photographic and imaging materials, for decades the medical sector and film industry has been using the high-quality photographic films and X-ray films where both of them depend mainly on silver. It is one of the highly photosensitive materials which made it useful in photographic imaging as a unique quality of silver. The cost of silver has been increasing constantly in recent years due to increase of price in international market compounded with the shortage of silver. Extraction of silver from the ore is expensive and harmful to the environment and low efficiency [1]. The current price of silver is

around ₹63,750.00 per kilogram. Radiographic applications get 45% of the silver used in the photography industry alone, however the silver is totally destroyed after usage. The silver content in X-ray and photographic films is mostly removed using the electrochemical and chemical precipitation procedures. Due to silver's special properties, nothing has been discovered that compares to it as a light-sensitive substance capable of producing photographic pictures. Luckily, a lot of the silver used in the medical and photography industries can be recycled. Silver emissions from the production and disposal of some photographic and X-ray films are significant. A plastic sheet (polyester film) covered with a thin layer of gelatin (a protein) impregnated with silver grain is used to create the X-ray films utilised in medical applications. The 25% of the world's silver needs are supplied by recycling, out of which 75% is obtained from photographic waste. Silver is mostly obtained through mining. In addition to mining, radiography waste films represent another potential source for the extraction of silver [2]. Since research on recovering silver from exposed radiography films must be focused on achieving a maximum recovery and a high purity silver, with technologies that will result in by-products that are less harmful to the environment, radiographic films represent a significant global consumer.

2 MATERIALS AND METHODS:

2.1. CHEMICAL PROPERTIES OF SILVER:

Silver is a highly inactive metal. Under ordinary circumstances, it doesn't react with ambient oxygen. The ambient sulphur compounds do, however, only react slowly with it. Silver sulphide (Ag_2S), a black chemical, is the end result of this process. Silver sulphide is the tarnish that forms over time on cutlery and other items with silver plating. Water, acids, and a variety of other chemicals do not readily react with silver. Except for as silver powder, it does not burn. Silver has two naturally occurring isotopes: 107 and 109. Isotopes are two or more different forms of the same element. There are also about 16 radioactive isotopes of silver identified [3].

Table 1: ELEMENTAL PROPERTIES OF SILVER:

S.NO.	PROPERTIES	DATA
1.	Atomic Number	47
2.	Atomic Mass	$107.87 \text{ g.mol}^{-1}$
3.	Electro Negativity	1.9
4.	Density	10.5 g.cm^{-3} at 20°C
5.	Melting Point	962°C
6.	Boiling point	2212°C
7.	Oxididtion states	+1, +2, +3

2.2. COMPOSITION OF RADIOGRAPHIC FILM:

A flexible, transparent, blue-tinted base and an emulsion-gelatin containing radiation-sensitive silver halide crystals, such as silver bromide or silver chloride, make up Radiographic film films for general radiography. Although Radiographic film films are sensitive to light, the emulsion used in other types of photography films is different in order to account for the specific features of gamma rays and Radiographic films. On both sides of the base, the emulsion is typically coated in layers that are about 0.0005 inch thick. The amount of radiation-sensitive silver halide is doubled when emulsion is applied to both sides of the base, which also speeds up the film. The emulsion layers are thin enough to allow for reasonable turnaround times for developing, fixing, and drying[4,5].

COMPOSITION OF RADIOGRAPHIC FILM

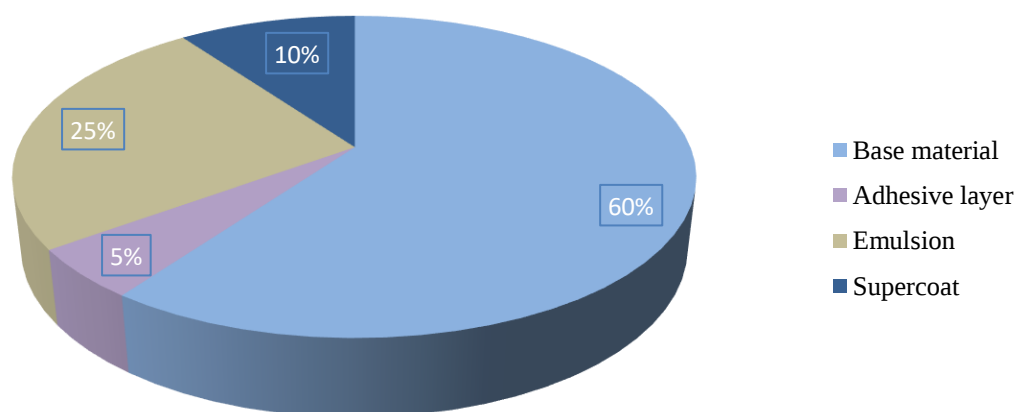


Figure 1: COMPOSITION OF RADIOGRAPHIC FILM

2.2.1. BASE MATERIAL:

The base material is a transparent supporting material with a thickness of 0.18 mm and is made of polyester, polyethylene, and terephthalate resin. It occupies 60% of the radiographic films combination[6].

PROPERTIES AND FUNCTIONS OF BASE MATERIAL:

- Structural support for fragile emulsion.
- Low light absorption: should not produce visible pattern on the radiograph.
- Flexible, thick and strong.
- Dimensional stability: maintain size and shape during processing, handling and storage.
- Non-Flammable.
- Provide support for emulsion layer.
- To transmit light.

COMPOSITION OF RADIOGRAPHIC FILM

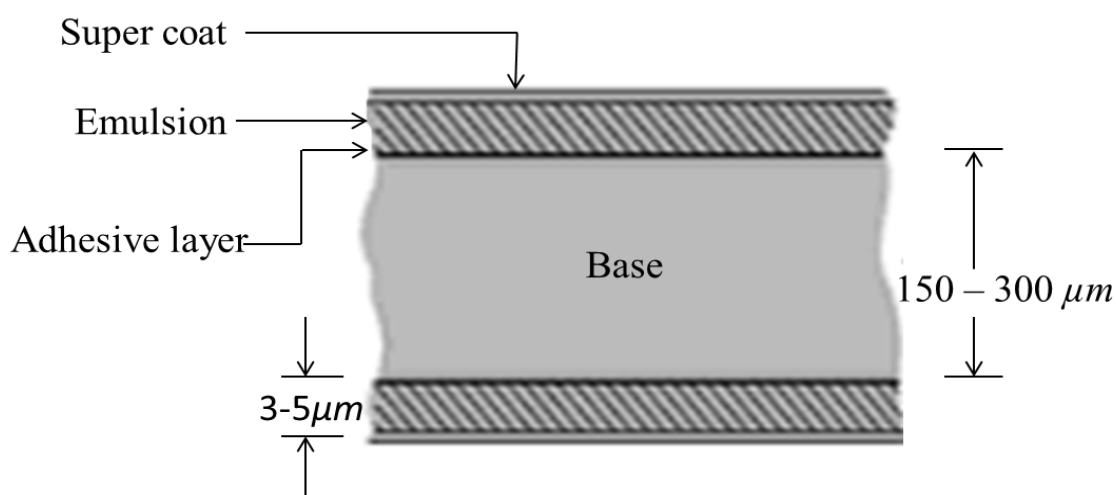


Figure 2: COMPOSITION OF RADIOGRAPHIC FILM

For the recovery of valuable silver from the waste radiographic film, a certain amount of radiographic films were collected from different places (The collected radiographic films are double coated emulsion since they contain more silver content than single coated emulsion film). The radiographic films are stored as small pieces in a borosilicate glass. A solution of concentrated nitric acid (HNO_3) is taken which acts as a leaching agent (Other leaching agents like cyanides, thiosulfates can also be used.) by acid leaching in removing the emulsion of the radiographic film which contains silver in the form of silver nitrate. An atomic absorption spectrophotometer can be used to analyse the concentration of elements present in the solution. A precipitant like Sodium hydroxide (NaOH) or sodium sulphide (Na_2S) is used. A furnace was required for heating the solution to a high temperature to obtain the product [7,8,9].

3. METHODS FOR RECOVERY OF SILVER FROM WASTE RADIOGRAPHIC FILM:

There has been several methods that has been used to recover the valuable silver from the waste radiographic films, like

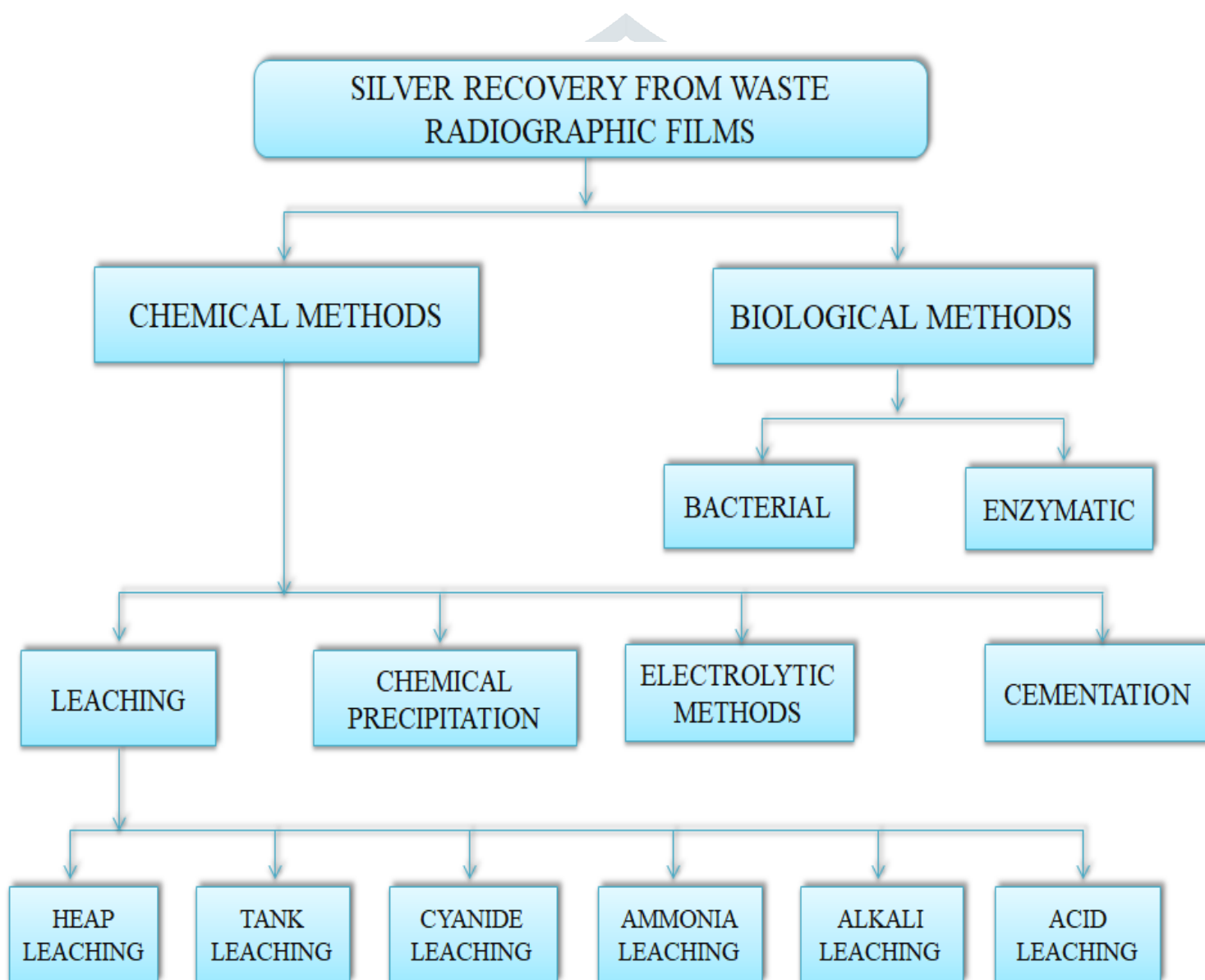


Figure 3: SILVER RECOVERY FROM WASTE RADIOGRAPHIC FILMS

For our interest we took the method of chemical treatment of the films without damaging the films since the latter is rather expensive because of the cost of maintaining the furnace and treating the soot and foul-smelling smoke. While the biological method is relatively a slow process hence consumes more time [10].

3.1. CHEMICAL METHODS OF REMOVING THE SILVER FROM THE WASTE RADIOGRAPHIC FILMS

3.1.1. LEACHING:

Leaching process describes the release of organic and inorganic contaminants or radionuclides from a solid phase into a water phase when influenced by processes such as desorption, complexation and dissolution[11].

Types of leaching:

➤ Heap leaching:

Heap leaching is a widely used method for extracting low-grade minerals, including copper, gold, silver, and uranium

➤ Tank leaching:

It is a process to extract trace metals from feed. The feed treated with lixivants inside large tanks, and the material is ground sufficiently fine to form a slurry.

➤ Cyanide leaching:

Cyanide process is widely used in extracting noble metals by dissolving them in a dilute solution of potassium cyanide or sodium cyanide. Ex:-sodium cyanide leaching.

➤ Ammonia leaching:

It is a process in which the feed is leached by a solution of aqueous ammonia under suitable pressure.

➤ Alkali leaching:

The leaching process in which the feed is treated using an aqueous alkali to form soluble complex.

➤ Acid leaching:

It is a process of dissolution of metals using an acid solution Ex:- Thiosulphite leaching, nitric acid leaching. The leaching process acts as a base for the recovery process.

3.1.2. CHEMICAL PRECIPITATION

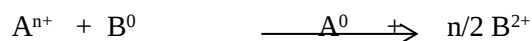
It is chemical reaction occurring in an aqueous solution where two ionic bonds combine, resulting in the formation of an insoluble salt. These insoluble salts formed in precipitation reactions are called precipitates. Precipitation reactions are usually double displacement reactions involving the production of a solid form residue called the precipitate. These reactions also occur when two or more solutions with different salts are combined, resulting in the formation of insoluble salts that precipitate out of the solution[12].

3.1.3. ELECTROLYTIC METHODS:

The process in which an electric current is passed through an electrode immersed in a silver bearing solution obtained from the radiographic films. This process is commonly known as electrolytic silver recovery. Electrolysis is usually done in a vessel named 'electrolytic cell' containing two electrodes (cathode and anode). A direct current is passed through a silver-rich solution between a positive electrode (the anode) and a negative electrode (the cathode). During this electrolytic process, an electron is transferred from the cathode to the positively charged silver, converting it to its metallic state, which adheres to the cathode[13].

3.1.4. CEMENTATION:

Cementation is the process of extracting the metals from a solution based on the electrochemical reaction between the cementing metal and the ion of the precipitated metal. Cementation process is also called as metal replacement reaction, cementation agents like zinc (Zn) and hydrogen (H) are commonly used for the recovering silver from the waste radiographic films[13].



3.2. BIOLOGICAL METHODS:

There are two types of biological methods for recovering silver from waste X-ray film. They are,

- ❖ Bacterial method
- ❖ Enzymatic method

3.2.1. BACTERIAL METHOD:

Biological method is one of the most crucial enzymes in the industrial sector; alkaline protease takes up a lot of space in the industry of enzyme manufacturing. It is extensively utilised in the preparation of animal nutrition, food processing, diagnostic procedures, silver extraction, and the leather sector. Now that it has such a broad range of uses, it is commercially manufactured. Additionally, it may recover this amount of silver by liquefying the gelatin layer in alkaline protease so that it can be utilised for other things[14].

3.2.2. ENZYMATIC METHOD:

The emulsion layer contains silver and the protein gelatin; it is possible to break it down using a photolytic enzyme protease which is extracellular enzyme produces by *Bacillus subtilis*. A protease (also termed peptidase or proteinase) breaks down proteins. A protease is any enzyme that conducts proteolysis, that is, begins protein catabolism by hydrolysis of the peptide bonds that link amino acids together in the polypeptide chain forming the protein. A protease is any enzyme that conducts proteolysis, that is, begins protein catabolism by hydrolysis of the peptide bonds that link amino acids together in the polypeptide chain forming the protein. Bacteria secrete proteases to hydrolyse (digest) the peptide bonds in proteins and therefore break the proteins down into their constituent monomers. The strips of radiographic film were dipped in the enzymatic protease solution and it results in slurry. The slurry is then smelted to get white powdered silver[14].

3.3.EFFICIENCY OF SILVER RECOVERED BY LEACHING:

Table 2: EFFICIENCY OF Ag YIELD FROM SOURCES

S.NO.	SOURCE (Material used)	EFFICIENCY OF SILVER YIELD
1.	X-Ray film	97%
2.	MRI scan film	84%

X-Ray film contains more amounts of silver ions than MRI scan films because X-ray film are double side super coated film while the MRI is single side super coated film. Hence yield of silver obtained from a X-ray is more than the MRI film. X rays when leached with Oxalic acid or Nitric acid results in greater silver recovery than MRI film[15].

3.4.VARIATION OF SILVER YIELD WITH RESPECT TO TEMPERATURE:

The precipitation of silver ions by the action of NaOH or Na₂S is increased with the increase in the temperature which in turns increase yield.

3.4.1. X-RAY FILM

The extraction process is taken for various temperatures as mentioned in the table for a standard amount of material used produces increase in production yield as we increases the temperature[16].

Table 3: VARIATION OF SILVER YIELD WITH RESPECT TO TEMPERATURE FROM X-RAY FILM

S.NO.	AMOUNT OF MATERIAL USED	TEMPERATURE	PERCENTAGE OF SILVER YIELD
1.	60g	25	58.7
2.	60g	40	65.6
3.	60g	60	78.3
4.	60g	80	86.5
5.	60g	95	97

3.4.2. MRI SCAN FILM

As we already discussed in above contents the MRI produces the less amount of silver yield than the X-Ray film[17].

Table 4: VARIATION OF SILVER YIELD WITH RESPECT TO TEMPERATURE FROM MRI SCAN FILM

S.NO.	AMOUNT OF MATERIAL USED	TEMPERATURE	PERCENTAGE OF SILVER YIELD
1.	60g	25	50.72
2.	60g	40	55.1
3.	60g	60	62.8
4.	60g	80	68.9
5.	60g	95	86.74

3.5. PERCENTAGE OF SILVER RECOVERY BY VARING THE CONCENTRATION OF THE LEACHING REAGENT (NITRIC ACID)

The leaching is carried out by using the various concentration of the leaching reagent while the other parameters are carried out same for all 5 trails (radiographic film quantity: 60 g/L; temperature: 97 °C; stirring time: 10).

Table 5: PERCENTAGE OF SILVER RECOVERY BY VARING THE CONCENTRATION OF THE LEACHING REAGENT (NITRIC ACID)

S.NO.	CONCENTRATION OF HNO ₃	RECOVERY (%)
1.	8	23.5
2.	10	55.1
3.	20	72.52
4.	30	85.3
5.	50	84

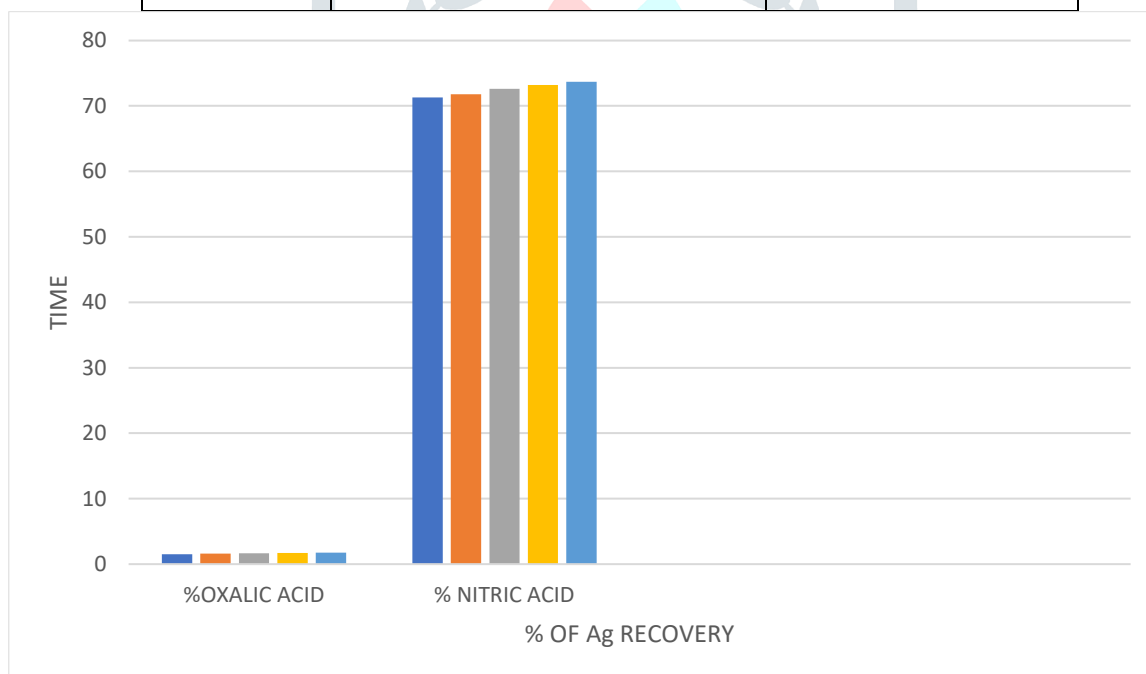
3.6. USING NITRIC ACID AND OXALIC ACID AS LEACHING ACID:

The silver halides from the radiographic films can be extracted by leaching them with oxalic acid or nitric acid which dissolves the gelatin. Reliability of the data depends upon the reproducibility [18,19]. Hence replicates ($n = 5$) were carried out and the means and standard deviations of 5 tests at the same conditions (acid concentration: 20 g/L; radiographic film quantity: 60 g/L; temperature: 97 °C; stirring time: 10 min) are presented in below Table. The results showed that the silver recovery, 72.52 % Ag recovery, could be achieved using nitric acid and 1.67% Ag recovery, could be achieved using oxalic acid. The recovered silver from X-ray films by dissolving the silver compounds with concentrated nitric acid and oxalic acid.

Generally, the recovery of silver is carried out using nitric acid as it is or low-cost reagent, low consumption of acid and it is a strong leaching agent [20,21].

Table 6 Ag RECOVERY USING NITRIC ACID AND OXALIC ACID AS LEACHING ACID

S NO.	OXALIC ACID (%)	NITRIC ACID (%)
1.	1.52	71.3
2.	1.63	71.8
3.	1.69	72.6
4.	1.71	73.2
5.	1.78	73.7
AVERAGE	1.67	72.52



GRAPH 1: % OF Ag RECOVERY

4. CONCLUSION

This is the study to introduce the concept of silver extraction from radiographic film by leaching and precipitation. This experimental work has been well proposed in this study. When compared to other processing methods this is the best method for silver extraction, where the yield is significantly higher the yield has been showed that the range of 72.52 % -73.16% Ag recovery, could have been achieved using nitric acid and 1.67% Ag recovery, could have been achieved using oxalic acid.

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