Review of Silver Recovery Techniques from Radiographic Effluent and X-ray Film Waste

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Abstract— **This paper highlights the techniques for silver recovery from radiographic waste; effluent and X-ray films. The decline in silver natural resource has increased the cost of sourcing for pure silver. The ecological problems caused by the disposal of radiographic waste is a huge motivation for increased recovery, regeneration and recycling process. The negative impact of pure silver on human and the environment is low but its soluble salt and emission from its recovery process pose a great risk to the ecosystem. Pyro-metallurgical processes of silver recovery requires heat >950°C which also destroys the polymer substrate. Hydrometallurgical processes such as electrolysis, metallic replacement, chemical precipitation and adsorption, are often used and provides high purity and efficiency. A proposed research work for silver recovery based on chemical precipitation using oxalic acid has been presented.**

Keywords—**Hydrometallurgy, Pyro-metallurgy, Radiographic waste, Silver recovery**

I. Introduction

INCREASING demand for precious metals in industrial activities has increased intensive studies for their extraction from every form of waste and ores. Industries produces large amount of solid and liquid waste which are primarily of two components; organic and inorganic [1]. Organic wastes which are biodegradable can be reduced to less harmful substances before disposal into the environment. Inorganic waste consist of metallic and non-metallic components [1]. The metallic part consist of some precious metals such as silver, the recovery of which is of interest to this study, and other form of heavy metals. Silver (Ag), a precious metal, is generally obtained from natural sources also as a by-product of metallurgical and industrial processes and has been applied in different forms including electronic, pulp, jewellery and radiographic industries [2], [3]. Its antimicrobial and anti-inflammatory properties in the medical field has been useful in managing burns, roles in antibiotics, surgical and wound dressing [2]. Silver is used in radiographic industries due to its high photosensitivity characteristics [4]. World silver production was reported to be insufficient to meet the demand which is steadily increasing by ~2-2.5% yearly [5]. Due to the decreasing amount of silver natural resources as well as the high cost of regenerating silver from waste, the cost of silver production has risen rapidly [4]. Syed, et al. [1] reported that most methods for silver recovery are not cost effective thus creating economic and ecological problems. The ecological problems caused by the disposal of silver enriched effluent is driving factor for increased recovery, regeneration and recycling of this particular effluent and other industrial waste [1]. The ecological acceptance concentration is <5mg/l Ag [6].

Radiographs, still and motion industry wastes are excellent sources for silver recovery. Approximately 2 billion radiographs per year are taken around the world which include chest X-rays, mammograms and CT scan [7]. 94-98% of the X-rays taken are in the medical fields producing photographic chemicals and scrap films as waste [7]. Radiographic films used in the medical field are polyester sheets coated on both sides by radioactive materials which are light sensitive [7]. Abdel-Aal and Farghaly [8] reported that 1kg of developed X-ray film contains 14-17g of silver. Most photographic chemicals for developing X-ray films are made from silver salt. Due to the high photosensitivity of silver halide, about 8.3% of silver is used in photography [5]. The effluent of X-ray films processing facilities can reach a silver content of 1-12g/l [5]. The method for silver recovery in broad terms are either hydrometallurgical or pyro-metallurgical processes [8]. The hydrometallurgical processes are through electrolysis, metallic replacement, chemical precipitation, adsorption and liquid membrane [2], [3], [5]-[7]. Biosorption is also a possible technique for silver recovery which is a physico-chemical & metabolic process based on absorption, adsorption, ion exchange and precipitation mechanisms [9]-[13]. Pyro-metallurgical process which is the traditional method for silver recovery from X-ray films include incineration, smelting, drossing, sintering and melting at high temperature [14]. This technique has been reported to be less efficient with a recovery <95% and temperature >950°C at which X-ray film polymers are destroyed [7], [8]. During the process, the produced silver is covered with carbon reducing the purity that can be achieved. Apart from low purity, the process if not controlled can pollute the air with ~3-25% silver emission into the atmosphere [4]. The hydrometallurgical processes, which will be discussed briefly have >99% recovery efficiency and heat requirement could be as low as 100°C depending on the method chosen. The essence of silver recovery is focused more importantly to reduce emission of pollutant from the recovery processes and for economic benefit. However some health and environmental impact of exposure to silver also exist and therefore will be discussed. Fig. 1 shows a process cycle for silver recovery [15].

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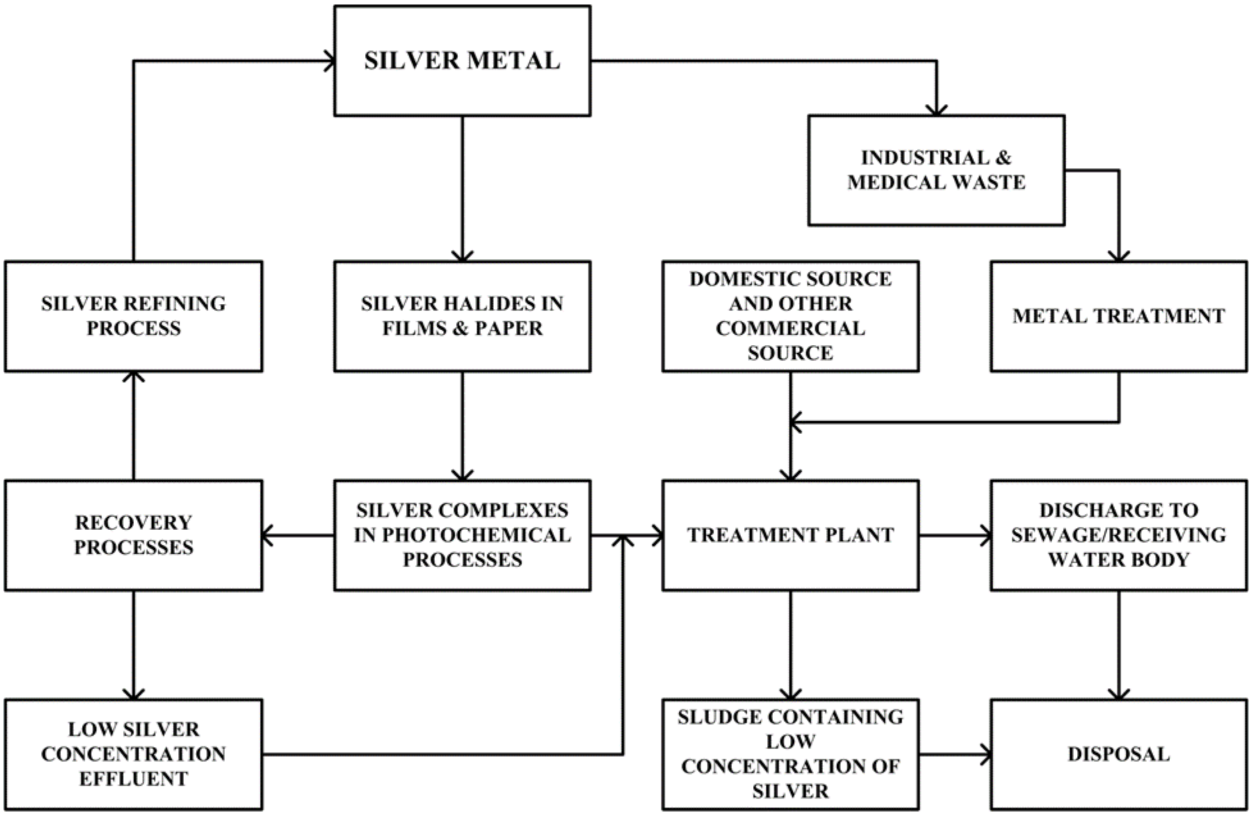

Fig. 1 - Process cycle for silver recovery

II. Health & Environmental impact of Silver

The health impact of pure solid silver on human beings is low due to its almost completely biological inert nature, hence if ingested in moderate quantities, it would pass through the human body without being absorbed into tissues. However, soluble silver salts are lethal in concentration which can cause organ failure and skin pigmentation [16]. The Occupational Safety and Health Administration (OSHA) of the United State permissible exposure limit for silver is 0.01mg of Ag/m^3 of air over an eight-hour work shift [17]. TABLE I summarises the effect of silver on human health [16], [17]. The environmental impact of silver and its salts varies depending on the concentration and chemical changes associated with the disposal body [15]. Silver is present in all surface water but in extremely low concentrations. Silver nitrate is less toxic in seawater than in fresh water. Ionic silver is extremely toxic to aquatic life and aqueous concentration of 1-5µg/liter can kill sensitive species of aquatic organisms [18]. Sensitive aquatic plants were reported to grow poorly at 3.3–8.2 µg Ag/litre during exposure for 5 days and consequently died when concentration is >130 µg Ag/litre [18]. At nominal water concentration of 0.5-4.5µg Ag/liter, accumulation in most exposed species retards their growth [18]. The accumulation of silver by terrestrial plants from soil is low hence waste with concentrated silver from agricultural processes is low [6], [18]. Ratte [19] reported that the germination stage of plants is the most sensitive stage at which exposure to silver needs to be controlled. A concentration greater than 0.75mg Ag/liter affect lettuce adversely and 9.8mg Ag/liter would kill corn (Zea mays). A spray containing 100-1000mg Ag/liter will kill tomato (Lycopersicon esculentum) and bean (Phaseolus spp.) plants. However, the yield of some crops has been reported to be higher on soil amended by silver laden waste [18], [20], [21].

TABLE I
HEALTH EFFECT ASSOCIATED WITH VARIOUS FORMS OF SILVER

Source of Silver	Health effects
Medicinal	
Silver nitrate - oral ulcerations; Silver nitrate solution - varicose veins; Silver nitrate - topical for gingival bleeding	Argyria*, silver deposits in organs, and abdominal pain
Silver acetate - antismoking gum, lozenges, and tablets	Argyria
Colloidal silver protein - allergy and cold medication	Argyria and high blood-silver levels
Silver protein - nose drops	Argyria
Colloidal protein - eye drops	Argyrosis
Colloidal silver and silver compounds	Argyria, argyrosis
Silver coated pills - mouth freshener; Silver coated acupuncture needles; Silver in water - hemodialysis therapy	Argyria
Occupational	
Soluble	Elevated blood-silver levels; Argyrosis; Argyria; abdominal pain; nosebleed; respiratory irritation; allergic response.
Metallic	Argyro-siderosis of the lungs
Insoluble	Severe circulatory and respiratory symptoms; Argyrosis

*Argyria is the impregnation of the mucous membrane, skin and eye with silver. It is generally recognised by pigmentation of the affected area [17].

III. Silver Recovery Techniques

The first step of the hydrometallurgical process is leaching. Leaching is carried out through the use of series of acidic or caustic solutions to remove the metal from the polymer substrate. Where X-ray films are used, the films are shredded and treated in reagents such as sodium hydroxide to liberate the metallic silver from the film into the solution [8]. The solution is subjected to separation and purification procedures such as precipitation, solvent extraction, adsorption and ion-exchange to isolate and concentrate the silver [14]. Consequently, the solutions are treated by electro-refining process, chemical reduction or crystallization for metal recovery [14].

A. Electrolysis

The electrolysis method, in which a direct current is applied between two electrodes, is capable of producing silver with purity greater than 98%. However, it is only used for silver rich effluent and incapable of reducing silver concentration below 100mg/l which is higher than the environmentally acceptable limit of 5mg Ag/l [5], [6]. Therefore, further treatment with other techniques is required to recover the remaining silver. Ajiwe andAnyadiegwu [22] investigated the recovery of silver from X-ray films. The crude metal to be refined serves as the anode and the pure metal is deposited on the cathode. It was recommended that silver be recovered by percolation of the effluent in ditches with immersed steel and copper electrode by internal electrolysis. To catalyse the process, cassava derived cyanide was added to the ditches. Electrolysis facilitates the continuous product removal and the silver depleted liquor can be recycled [23].

B. Metallic Replacement

Metallic replacement is also called cementation process. The process is based on the use of metals such as iron, zinc and copper which are more active metals than silver for effective recovery from effluent. Ion of the more active metals are released into the solution while atoms of the less active metal replaces them in solid state [6]. However, the method introduces impurities of the active metals e.g Fe^{2+}, Zn^{2+} and Cu^{2+} to the effluent and silver sludge which require a costly process for remediation [5]. The reaction is generally composed of two redox half reactions; reduction of the more active metal ion and oxidation of the less active metal [6]. For optimal performance of the process, a pH ~5-7.6 was recommended [6]. Abdel-Aal andFarghaly [8] reported a 98% silver recovery at 90°C within 50 minutes retention time using Zn metal powder with 6% nitric acid.

C. Chemical Precipitation

Chemical precipitation method is one of the widely used and researched method for silver recovery. Silver can be readily recovered from photographic chemical effluent by sulphide precipitation with concentration as low as 0.1-1mg Ag/l [5]. However, careful control of the precipitation process as well as the sulphide dosing process is required to prevent the release of poisonous hydrogen sulphide gas [5]. Several chemicals including sodium sulphide, sodium dithionate, potassium boro-hydride and 2,4,6-trimercapto-s-triazine have been used as precipitating agents to recover silver from photo chemical processing waste [5]. Bas, et al. [5] investigated the effect of ethylene glycol as a stabilizing agent on hydrogen peroxide in silver recovery process. The use of hydrogen peroxide only in silver recovery process was highly exothermic with high catalytic decomposition rate, making the process expensive. The addition of ethylene glycol reduced consumption rate to less than 25% and also improved recovery efficiency by 18.7%. Zhouxiang, et al. [4] investigated the effect of pH on potassium boro-hydride in silver recovery from effluent and X-ray films. Increasing pH reduced the volume of potassium boro-hydride required to achieve the desired purity and recovery. The experiment achieved 98% and 95.8% silver recovery from the effluent and X-ray film respectively with 99.5% purity. The use of oxalic acid has also been reported to be highly efficient in silver recovery process [1], [7]. Khunprasert, et al. [7] investigated the use of oxalic acid, malonic and acetic acid in silver recovery process. Oxalic acid achieved highest recovery and efficiency. At 100°C and 5% (w/v) oxalic acid, 100% recovery was achieved after 20mins. It was also observed that increasing the acid concentration and operating temperature increased efficiency of the process. The use of oxalic acid as a leaching agent has also been report to be economically viable as less than 1g/Kg of X-ray is required for the process. It can be used repeatedly and can be found naturally in plants like spinach and rhubard though at low concentration [1].

D. Others

Other techniques for silver recovery are adsorption on solid surface and use of membranes. Adani, et al. [24] investigated the adsorption of silver from photographic chemical waste on granulated activated carbon. When carbon was pre-treated with 0.5mol/dm^3 sulphuric and nitric acid at 25°C, it achieved silver recovery of 98.5% and 95% from sodium and ammonium thiosulphate solutions respectively. The optimal pH for the recovery was ~3-4. Condomitti, et al. [25] developed a super-paramagnetic carbon material (Cmag) functionalised with ethylenediaminepropyltriethoxysilane for capturing, concentrating and processing metal ions with the aid of an external magnet. This is an innovative electrochemical concept for precious metal recovery. Cmag exhibits a high affinity for Ag+ ions in aqueous solution and is capable of capturing a large amount of this element due to its large surface area. By using an external magnet, Cmag also provides an efficient way of transporting and concentrating the silver ions at the electrode surface generating a pure silver layer on the electrode. Tang, et al. [3] developed emulsion liquid membrane (ELM) crystallization process for silver recovery using hypophosphorous acid as reducing agent. 99.5% (wt.) of the silver ions was extracted by the ELM crystallization process, with an average recovery efficiency of 99.24% (wt.) and a purity of 99.92% (wt.). The membrane phase can be used repeatedly without loss of the efficiency of recovery. Table II gives a summarised comparison of the three major silver recovery techniques.

TABLE II
COMPARISON OF RECOVERY TECHNIQUES

	Recovery efficiency	Advantages	Disadvantages
Electrolysis	>90%	• 98% purity is achievable • The cathode can be cleaned and reused • Does not produce any new pollutant	• High capital cost of equipment • Operating cost due to electricity requirement • Special electrical and plumbing requirement • Requires monitoring and servicing to ensure high efficiency • Agitation is required to improve efficiency
Metallic replacement	>95%	• Low initial investment cost • Low operating cost • Low maintenance cost due to no mechanical parts and electrical connections • Relatively high recovery efficiency	• Not as efficient as other process • Impurities by presence of other metals in the silver sludge • Recovered silver in the form of sludge need further treatment • Unit must be replace each time it is expended
Chemical Precipitation	>99%	• Low silver concentration in effluent • Easy to monitor performance	• Require stringent control measure to avoid emission of poisonous hydrogen sulphide

Of the three major silver recovery techniques reviewed, chemical precipitation has been highly investigated and used because of the simplicity of the process and various leaching reagent available. The use of electrolysis techniques, which is also a common technique for large facilities, is limited if silver concentration is low in the effluent. Adsorption and membrane techniques are still at experimental/laboratory research stage.

IV. Proposed Research Work

The proposed work is to develop an integrated process using chemical precipitation technique for silver recovery which requires less heat. Used X-ray films, approximately a tonne, were obtained from a hospital in Zimbabwe for the proposed study while spent/used radiographic effluent will be obtained from the University clinic. Oxalic acid will be used as the leaching agent. The choice of oxalic acid over other leaching agents is due to possible 100% silver recovery; low toxicity; high efficiency on product purity; short retention time; reusability; low CO_2 emission; simple smelting process for the sludge. The research will investigate various leaching conditions such as pH; leaching time; mass to volume ratio; efficiency of reused leaching agent and temperature; on silver recovery and purity. A brief experimental procedure is highlighted below;

- X-ray films will be shredded into piece.
- The shredded X–ray film will be boiled in a known concentration of oxalic acid until a blue transparent polyester of the film is noticed which indicate a complete removal of the metal from the film.
- The sludge will be filtered, dried and heated further to recover pure silver
- Additive chemicals will be added to improve the efficiency of the process.
- Properties of the produce silver will be analysed.

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