



Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 7(6), 2012 [233-238]

Extraction of silver from spent x-ray and photographic fixer solution in Tigray region, Ethiopia

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Received: 31st May, 2012 ; Accepted: 8th August, 2012

ABSTRACT

Spent fixer solution from photographic industries and X-ray machines cause water and soil pollution if drained out without any treatment. This solution contains about 2 - 4 g of silver per liter. The maximum permitted level of silver in the waste solution is only 3 ppm. It is clear that concentration of silver in spent fixer solution may be thousand times greater than maximum stipulated limit. Moreover silver is precious and noble metal. So recovery of silver from waste fixer solution will not only prevent water and soil pollution but also prove to be profitable process. A survey in most of the places in Tigray Region shows that spent fixer solution is drained out without any treatment. The photographic industry is fast growing industry and this may lead to soil and water pollution. Two methods are identified as economical and simple without involving complicated procedures for extraction of silver. One is chemical method and the other an electrolytic method. Both methods are found to be successful; however electrolytic method is the preferred one because of its simplicity, economical and environmentally friendly. In photographic fixer solution about 2 gL⁻¹ and in X-ray solution, about 3 gL⁻¹ of silver were recovered.

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KEYWORDS

Silver;
Spent;
Fixer;
Tigray;
Electrolytic method;
Chemical method.

INTRODUCTION

Silver is a metal of commercial importance for use in high strength and corrosion resistance alloys and jewelry. In addition, owing to its excellent properties of electrical and thermal conductivity and ductility, silver

has been widely applied in fields of aerospace, communications, chemical industry (for instance as catalyst, conductor and chemical sensors), medical equipment, electroplating, photographic materials and electronic industries^[1-5]. Silver has been used for its antimicrobial properties at least since the ancient Romans used silver

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coins to treat drinking water. However, silver resources in the world are extremely scant and mainly associated with lead, copper and antimony deposits^[4].

There are risks associated with the use of silver. High levels of silver are toxic to human cells, which can slow healing in the case of wound care. Other problems associated with silver include argyria, which is a condition characterized by a permanent blue-gray discoloration of the skin^[6]. Studies show that toxicity of silver depends on its chemical form, concentration, salinity, redox potential and pH of the receiving water^[7]. Globally, large quantities of silver are not recycled or recovered, as most of the methods are not cost effective, thus creating important economic, management and ecological consequences^[8]. Regulations for recommended allowable silver discharge levels from 0.1–1.0 mgdm⁻³ are expected^[1].

For decades the medical sectors and film industries extensively use high quality photographic films and X-ray films where both of them depend heavily on silver. Nothing has been found to equal it as a light sensitive material capable of forming photographic images because of the unique qualities of silver. The cost of silver has risen considerably in recent years mainly due to price increase on the international market compounded with a world of shortage of silver. Fortunately, much of the silver used by the photographic industries and hospitals for X-ray machine can be recovered from the photographic and X-ray solutions and reused. The photographic wastes which comprise mainly fixer and bleach solutions contain high concentrations of dissolved silver and the chemicals such as sulfates and nitrates^[9]. Several waste streams are generated in hospital radiology departments, such as wastewater containing photographic chemicals, scrap films such as those purged from old files, or chemicals and silver removed from the film generated from poor photographs during processing, fixer solutions and spoiled chemicals^[10]. From an environmental point of view, the best way of reducing the undesirable wastes would be to reuse the major part of the fixing solution or to recover the silver from the waste solution^[1,11].

The methods used for silver recovery methods mainly from the fixing bath have been sharing common steps. Primarily, the silver was regenerated through burning waste photosensitive films. The produced silver was covered with a layer of carbon that led to dif-

ficulty in silver recovery. Syed et al.^[8] described a process for the recovery of silver in processed radiographic films. It is based on heating the films with an oxalic acid solution to separate the inorganic component from the polymer substrate, but the temperature must reach the boiling point of the solution. Adani et al.^[12] used sodium thiosulfate to dissolve the silver halide on the waste films, but elemental silver cannot be dissolved. Ajiwe and Anyadiegwu^[13] used concentrated nitric acid to dissolve silver from X-ray films. The produced nitrogen oxides are the major air pollutants.

Purification of rinse waters is expedient both for environmental reasons and for the recovery of silver as precious metal^[14,15]. The liquid wastes, originate from several sources such as photo-processing and X-ray medical laboratories contains silver which exists mainly as insoluble silver halide, soluble silver thiosulfate complex, silver ion or elemental silver, depending on the type and the stage of the process, where this element is to be recovered^[12,16]. There are many methods to recover silver from photographic wastes such as cementation or metallic replacement, electrolytic recovery, chemical precipitation, ion exchange combined with or without preliminary physico-chemical treatment, biosorption, membrane processes, crystallization, alkaline saponification of film substrate and filtration of the insoluble silver and selective solvent extraction, reductive exchange, adsorption, ozonation, physico-chemical or biological treatment^[1,10,16-18].

Electrolysis is commonly used to recover silver from photographic wastes^[18,19]. Recovery of metals from aqueous solution of their salts by electrolysis can be realized by two methods. The first method consists of the electrolysis of solutions obtained after leaching of the corresponding metal from ores or concentrated with the use of insoluble anodes. The second method consists of the electrolytic refining of the metal. Here the crude metal to be refined serves as the anode and the pure metal is deposited at the cathode. This is a better method for noble metal recovery. Internal electrolysis is a form of electrode deposition without an applied external voltage while external electrolysis is a form of electrode deposition with an applied external voltage^[13]. Silver is recovered from used photographic film by dissolving the silver with nitric acid, precipitated with sodium chloride and then filtered^[13]. The precipitation

method would not achieve the required discharge level although it has provided an effective technique for silver recovery and also faced several other problems such as formation of silver complexes in the effluent. This silver complex is sometime very stable and difficult to be precipitated by the precipitation process^[18].

There is no information on the geographic distribution and environmental effects of silver discharges in Ethiopia particularly in Tigray Region. Moreover, up to our knowledge, there is little information on retrieving silver from used films in the region in particular and the country in general. Here used photographic and X-ray waste fixer solutions are managed carelessly. The main objective of this study is to develop a method for the recovery of silver from photographic and X-ray waste fixer/spent solutions and extraction of silver from them from selected places in Tigray Region, Ethiopia. By doing this, in one way the recovered silver used again while the environment will be protected from pollution of unwise disposal of liquid wastes from them.

Study area

The study area, Tigray Region, is the northern most National State (Region) of Ethiopia with estimated surface area of 50,078.64 Km². The following towns were selected for the collection of spent fixer solution: Maychew (12°47'2" N 39°32'2" E, 2479 m elevation), Mekelle (13°29'2" N 39°28'2" E, 2084 m elevation), Wukro (13°47'2" N 39°36'2" E, 1972 m elevation), Adigrat (14°16'2" N 39°27'2" E, 2457 m elevation), Axum (14°7'2" N 38°44'2" E, 2131 m elevation) and Shire (14°6'2" N 38°17'2" E, 1953 m elevation) as shown in Figure 1. From all the photographic printing sectors and government and private hospitals in these areas are having X-ray machines waste fixer solutions were collected. A survey in these areas very clearly reveals that the waste fixer solution is completely poured into drainage channels without any treatment.

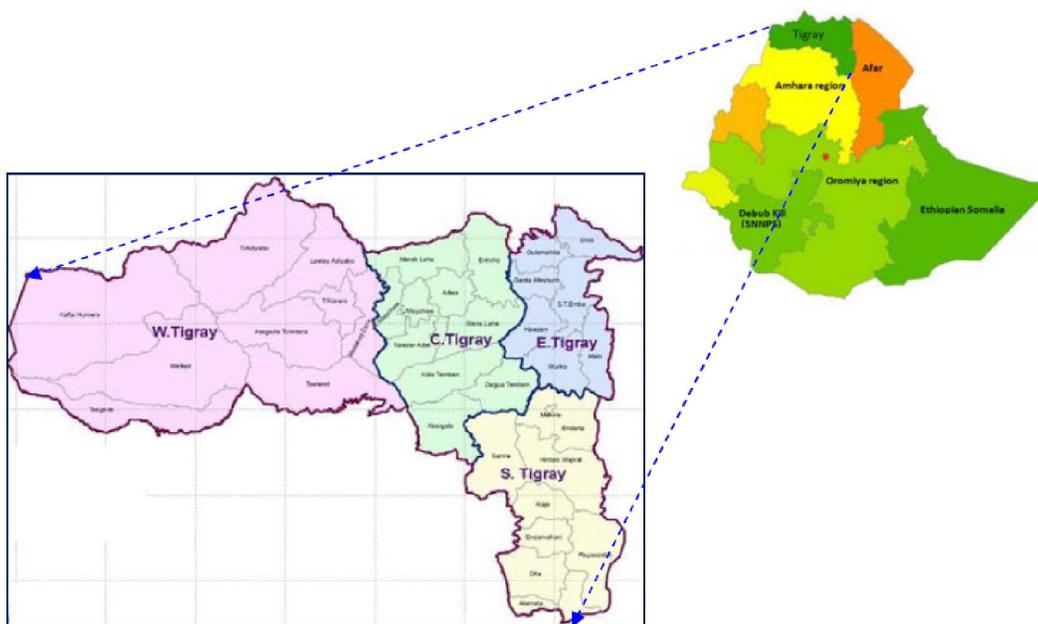


Figure 1 : Map of the study area.

Chemical and apparatus/instruments

All reagents were analytical reagent grade unless otherwise stated. All plastic and glassware were cleaned by soaking in dilute HNO₃ (1:9) and rinsed with distilled water prior to use. The following chemicals were used for the analysis: sodium sulfide, sodium chloride, sodium carbonate, nitric acid and hydrochloric acid

where all were analytical grade reagents from Merck, Germany. The apparatus used for the whole procedures were oven ("industrial furnace" Supreme Enterprises, India make), DC power supply (6 V, 10–20 A) and ammeter DC (0–25 A).

Recovery and analysis of silver

Two methods, a chemical and an electrolytic method

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were attempted for the recovery and analysis of silver from waste fixer solution.

Chemical method

Using 1 L spent fixer solution the silver was precipitated as silver sulfide by adding 6 to 7 g of sodium sulfide. The separation of the precipitate from the liquid was facilitated by the addition of cheap electrolytes namely sodium chloride and then digesting the precipitate in an oven at 150 °C for 1 h. After decanting the solution, the precipitate was washed with distilled water and kept at high temperature. Then a calculated amount of sodium carbonate was mixed thoroughly with silver sulfide and heated to about 600 °C for about 3 h. At the end the mass was ground and washed with water several times and collected. The black residue was heated in a furnace to about 1100 °C and poured into a die.

Electrolytic method

The fixer solution (25 L) was taken in the plastic bucket tank and a carbon rod anode and a stainless steel cathode (40 cm x 10 cm) were immersed in the bath where care was taken not to make the two electrodes in contact with each other. The electrodes were connected to the DC power supply by means of appropriate connecting wires, switched on and the current was adjusted to 5 A. The time was taken and the electrolysis was continued for about 10 h with continuous stirring and then the power supply was switched off. The solution was allowed to stand for about 30 minutes for the particles to settle, decanted carefully and the precipitate was separated. The electrodes were washed thoroughly, removed from the bath, dried and weighed and recorded before desilvering as follows: the cathode was removed carefully from the mounting tank. The cathode was placed on a clean surface (a polythene sheet or tin foil) and was carefully brushed to remove silver plating. The cathode was then re-cleaned with a wire brush several times before replacement into the plating solution. In a furnace this was converted into bar and estimated by gravimetric analysis, where a known amount of silver piece was dissolved in nitric acid and then precipitated as silver chloride by the addition of hydrochloric acid. The precipitate was filtered in a sintered crucible, washed, dried in an oven at 120 °C, weighed and the amount of silver present in the whole sample was calculated.

RESULTS AND DISCUSSION

In a typical film developing operation, fixer solution is continuously added to maintain solution strength. As a result, there is generally an overflow of fixer from the bath. The concentration of silver in the overflow may vary greatly depending on the type and amount of film processed, frequently exceeding 3 gL⁻¹. Because of this high silver concentration, silver recovery from the fixer solution is very cost effective. In addition to this when the fixer solution is totally exhausted; it is drained out to drainage channels which causes a concern for environment since it creates water and soil pollution. Silver is extremely toxic to fish and other aquatic life. Even small quantities of silver are known to induce oligodynamic effect. This deactivates the enzyme action and the toxic effect is fully developed often only after a long time. Waste recycling is always an encouraging and advantageous idea in the global level. There are two benefits in this concept, namely, the recovery of a substance and the prevention of pollution. Since silver is a precious metal of exceptionally wide range of applications, recovery of silver from spent fixer solution will prove to be not only a profitable job but also prevents soil and water pollution to a greater extent.

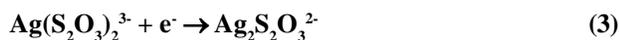
Using the chemical method, about 10 g of silver sulfide was obtained per liter of the from X-ray waste fixer solution while from color photographic solutions it was about 8 g only. The advantage of this method is that large quantities of spent fixer solution need not be transported to the working centre from the sampling centers. Instead of 25 L of fixer solution, only 1 L of concentrated silver sulfide residue needs to be transported. However silver sulfide is relatively a stable compound and does not decompose even at 1100 °C. The process is very difficult to extract silver from silver sulfide in a small scale level. The separation of the precipitate from the liquid was facilitated by the addition of cheap electrolytes namely sodium chloride and sodium carbonate in presence of heating to form black residue of Ag₂O as follows:



The black residue contains pure silver and silver oxide where silver could be obtained by heating black

residue in a furnace to about 1100 °C and pouring into a die.

In case of electrolytic method care had been taken not to make the two electrodes in contact with each other since this will cause a short circuit which will affect the power supply. Ag is deposited at the cathode by the following reaction:



However the formation of such complexes may cause serious problems in the electrolysis of silver from fixer solutions. For example it has been reported that^[20] the majority of argento-thiosulfate complexes tend to migrate away from the cathode leading to a shortage of these complexes at the electrode surface which in turn leads the formation of silver sulfide^[20,21]. This reaction, often termed 'sulfiding', takes place as a result of the sulfide ion produced from the decomposition of thio-sulfate ions $\text{S}_2\text{O}_3^{2-}$ reacting immediately with the silver ions in solution to deposit insoluble silver sulfide at the electrode and thus preventing further electrodeposition of silver. However, if silver ions are kept at sufficiently high concentration near the cathode, sulfiding may be minimized. This can be achieved by vigorous agitation of the solution, i.e., by forced convection near the cathode and deciding the electrolysis time carefully^[22]. In the electrolytic method of extraction of silver from the waste fixer solution is the most simple and economical method. One time purchase of power supply is required with minimum power consumption, i.e., the rate of 10 V - 5 A current capacities, power consumption for the electrolysis of 25 L of fixer solution is only 0.5 KWH. No additional chemical pollution is involved. The operation is very easy. The silver powder can also be melted in private shops. The major disadvantage is the transportation of large volumes of waste fixer solution. In photographic and X-ray spent fixer solutions, the amount of silver depends on the number of fixings (developing) made, i.e., the more the number of fixings is, the more will be the amount of silver present in the fixer solution. The quantity of fixer solution available in a shop mainly depends on their business. In X-ray machines also the concentration of silver depends on the number of times the solution is used and the quantity of spent fixer solution depends on the usage of the machine. So it is very difficult to ascertain the quantum of business.

A long term statistics may provide an average estimation. However, in the photographic fixer solution about 2 gL⁻¹ and in X-ray solution, about 3 gL⁻¹ of silver were recovered.

CONCLUSION

In Tigray Region, almost in all selected centers the spent photographic and X-ray fixer solutions are simply poured into drainage channels without any treatment. The better way to control water and soil pollution is to highlight the benefits of the extraction of silver from these waste solutions. The choice of the method depends on the situation. For owner of photographic industry, the electrolytic method is the suitable one. In both the methods, the concentration of silver in the spent solution may be brought down by 3 ppm level. In the photographic fixer solution about 2 gL⁻¹ and in X-ray solution, about 3 gL⁻¹ of silver were recovered.

ACKNOWLEDGEMENTS

This research was done with the fund obtained from Mekelle University of 'MU-NoRad-II' collaboration with project registry FED/10/2007. So the authors duly acknowledge Mekelle University Norad fund (MU-Norad-II) for financial support to accomplish the project. The Department of Electrical Engineering of Mekelle University had borrowed the DC power supply and Department of Chemistry of Mekelle University allowed laboratory rooms to do the analysis.

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