Silver Recovery from used X-Rays and Other Silver-Rich Diagnostic Radiography Films: A Review

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Abstract: ***Silver is a precious metal and is used in electronics, industrial catalysis and biomedical sector because of its physiochemical properties. The present work focuses on techniques that are used in recovering silver from waste X-ray films, radiographic films and photographic films. Due to decrease in natural resources, there is increase in prices of pure silver. Direct decomposition of these films causes several environmental concerns therefore it becomes important to recover and regenerate silver. Toxiferous nature of silver depends on its redox potential, salinity and chemical form. The soluble salts of silver cause a serious effect to humans as well as ecosystem. Hydrometallurgical processes provide silver with highest purity. Approaches that must be adopted towards recovering silver should be economical and less harmful to the environment.SEM and XRD techniques confirm that silver recovered in metallic form. Hydrometallurgical techniques are the best route to recover silver that needs strong acid solution. Alternative method for recovering solution is through leaching solution. Silver recovered through UV-visible light driven process involves photolytic deposition of pure metallic silver over ZnO photolytic. This is the novel green process for silver recovery. ZnO photolytic is dissolved through acidic solutions and pure silver is recovered with very low cost and no harm to the environment. It needs mild operating conditions and is economically viable. Thiosulphate solutions are now widely used to recover silver from photovoltaic cells and electric vehicles through precipitation using TriMercapto-s-Triazine (TMT).TMT is a nontoxic organo-sulphide reagent. Researchers have shown that concentration of TMT has highest impact on silver precipitation.***

Keywords: Silver recovery, Semipermeable membrane, dimethyl formamide, hydroquinone, Thiosulphate solutions, Trimercapto-S-triazine, Hydrogen Peroxide

1. Introduction

Silver, with atomic number 47, is white and shiny element [1]. Standard atomic weight of silver is 107.8682, its density is 10.5 g.cm^{-3} at 20°C and boiling point is 2212°C.Silver is used in bullion coins, solar panels, water filtration, jewellery, ornaments and utensils. It is widely used in medical field and is used in managing burns, surgical and wound dressing [2]. It is widely used in production of mirrors along with mercury. Along with other metals such as Cu and Cd, it is used for welding purpose [3]. Sources of silver and other metals are mines. Silver is a valuable metal and is used in photographic and X-ray films. The improper management of these films leads to contamination of environment and straight away causes adverse effects on living beings. Silver gets stick to gills of fish and that leads to choking and finally to death. It also creates problem during sewage cleaning as silver interferes with bacterial activity [4]. Therefore, it is imperative to recover toxic, vital metals from waste [5]. Silver is recovering using the following techniques:

- Leaching into sodium hydroxide
- Using bromelain enzyme [5]
- Using borax compound [10]
- Using activated carbon [5]

Pyro-metallurgical process is traditional methods, that includes sintering, smelting and incineration. Pyro-metallurgical processes are expensive because of high demand of energy requirement [6]. Hydro-metallurgical processes are done with the help of metallic replacement, electrolysis, and chemical precipitation [6, 7]. Radiographic films are made up of polyester sheets that are coated with radioactive materials and are light sensitive on both the sides [8].Silver halides at alkaline pHare considered to be thermodynamically stable [9]. In recent years, study of developing nanoparticles is put forward although it is difficult to achieve [10].Samples are determined through spectrophotometer and XRD analysis.

Silver recovery techniques

There are a number of techniques through which silver can be recovered from photographic films. The following section discusses various techniques for silver recovery.

1) Electrolytic recovery

It works on the principle of electrolysis. Current is passed through solution that contains carbon anode and stainless steel cathode. Silver in its ionic form, dissociates and high purity silver gets plated onto cathode. Amount of silver that deposits on cathode depends on the rate of silver thiosulphate ion reaching cathode. Rotating cylindrical electrodes and 3D electrodes are used to increase deposition rate [11]

Thiosulphate ions undergo reaction to form sulphide ions [13].

$(S_2O_3)_2^{3-} + 2e- \rightarrow (SO_3)^{2-} + S_2$

Free sulphur is precipitated from sulphide ions.

$S_2O_3^{2-} + H^+ \rightarrow HSO^{3-} + S_2Ag^+ + S^{2-} \rightarrow Ag_2S(s)$

As soon as free sulphur is produced, yellowish sludge gets stick to electrodes.

This needs large scale cleaning and silver efficiency is also reduced. Along with this, if high current is supplied to sulphide ions, it may result into evolution of hydrogen sulphide gas which is a very poisonous gas.

$S^{2-} + 2H^+ \rightarrow H_2S(g)$

To manage with these problems, recovery units are checked regularly to decrease current flow if silver concentration lowers. Recovery units cannot be checked regularly, so microprocessor-controlled units are employed but this increases the cost of silver recovery.

Electrolytic recovery process is expensive for large volume generators. Equipment cost is high along with this electricity cost, maintenance cost and labour skill is also important to operate this. Silver flakes are hazardous waste.

2) Metallic displacement

Silver do not dissolve as base metal. Silver thiosulphate and metal contacts each other. Metallic filaments are used in the form steel wool. So, when silver thiosulphate comes in contact with other metals (ex: -copper, zinc filament. etc.), exchange occurs. Exchange takes place between silver and other metal, sludge formed is taken for refinement. This unit is easy to operate and can easily handle smaller volumes. [14, 15]. Redox reaction takes place. pH of range 5-7.6 was considered for optimal performance. Abdel-Aal and Farghaly claimed 98% of silver in 50 minutes retention time at 90°Cusing zinc metal and nitric acid [15, 16].

3) Electrodialysis

In this process both electric current and semipermeable membrane (ion selective) are used. Sometimes, membranes used are ion exchange resins having both cation and anion that are alternately arranged to form compartment and is maintained between electrodes. When current is passed, ions start moving into opposite direction in compartment [17].

4) Chemical precipitation

This method is employed for large generators. In this method Sodium Sulphide is added to fixer, then silver precipitates as Silver Sulphide, and is refined. This method requires operating skill. Formed as by product should be cleared immediately. This technique is applicable to silver plating baths [18]. Ethylene Glycol was used as a stabilising agent on hydrogen peroxide for obtaining silver [20].Due to Addition of ethylene glycol, volume reduced and 95.8% of silver recovered from Xray films with 99.5% purity. Khunprasert, et al. investigated that by using oxalic acid, recovery as well as efficiency of silver was maximum.

5) Continuous ion exchange

Waste water is allowed to pass over ion exchange resins that have charge sites. So, when this waste water passes over, silver ions are removed from passed solution. Silver ions get replaced by ions present om resins. Silver is washed with dimethyl formamide (acts as regenerant) Resins are expensive.

6) Reverse osmosis

Solution having silver is passed through semipermeable membrane (SPM) at high pressure. Clear water retains on one side and Ag concentrated liquid on the other side. As silver is in concentrated form, it can be recovered easily. Membranes need to be replaced every time for effective result.

7) Batch ion exchange resin

The resins are fitted into one box so that it acquires less area. Spent developer of fixed volume is mixed with resin. Developer contains polymeric based materials that absorbs water and expands and ionically bonds with silver by displacing original ions. Developer (hydroquinone) is continuously added till containers get occupied with filtrate solid part. The method suits for less volume production [23].

Macro-economic aspects of Silver Recovery

Silver if directly dumped into aquatic system, silver is impossible to recover as it is a non-renewable resource. World's silver reserves are finite. So, recovering silver is challenging. As supply of silver is limited, this will drive up the prices of silver and in turn prices of photographic films will rise. If X-ray films are recycled, this will stabilize the increasing price of silver. Indirectly it will create more job and business opportunities. Rise in recycled silver would increase the supply and it will lower the price, demand will increase. So, the mines that are sensitive to such changes will be affected.

Silver losses to the environment

In other countries, silver loss is due to photographic processing facilities. In India, loss of silver is due to mining and smelting process, waste disposal. The use of silver in photographic films accounts only for 0.62%. This is not that much harmful but dumping this amount of waste directly river bodies cause deposition of silver in rivers and oceans. Proper disposal of effluent should be done to prevent effects on the environment and marine animals.

Toxicity of Silver

It is important to know the form of silver in which it is present in aquatic and terrestrial environment. Silver sediments mainly silver sediments remains in freshwater for longer period of time. In humans' skin, it induces a blue-grey colouration called Argyria. Residence time of silver is long in estuaries and silver binds with the sediment particles that are available with shellfish. [25]Silver nitrate is one of the most toxic compounds. The free silver cation is leads to toxicity and these free ions after coming in contact with nanoparticles, becomes toxic. To detect the toxicity of silver ion, special types of equipment need to be designed. Still longevity of nanoparticles is not known. The toxicity depends upon silver's chemical form and its concentration. Toxicity can be altered by salinity, redox potential and pH of water. Table 1 shows exhaustive literature review of silver recovery from radiographic films by various techniques under different conditions and showing diverse recovery performance.

Table 1: Exhaustive literature review of silver recovery from radiographic films by different methods

Sr.No.	Type of film	Initial Composition	Method of extraction	Operating Conditions	Experimental Setup	Result	Cited References	References
1.	X ray, film	4196 mg/dm^3, 4050 mg/dm^3	Batch adsorption	25℃water bath pH= 3.5	Gold Carbon 207C & 208C	98.5% (STS), 91% (ATS	(Adani, 2005)	1
2.	Radiographic film	1.5 to 2.0% Ag by weight	1.Acid Digestion 2.Stripping with Oxalic acid solution.	Stripping time (5-10 min) & Temp. (90–100℃), Crucible temp. 110℃(Time =24hr), (Calcination =550℃), (Time =2 hr.) Acid Digestion, 2.Stripping with Oxalic acid	Oxalic acid, Nitric acid, XRF Spectroscopy	1. 1.84 wt.%, 2.Black residue obtained 3. 91.82% highest %recovery.	(Balela, 2020)	2
3.	Radiographic films	content ranging from 2–9g / kg, sometimes even higher: 15g / kg)	Leaching phenomenon based on NaOH conc.	1. Temp. at which the silver flow passed into the solution was 90°C.	1. Laboratory glassware with larger base areas were used. 2. Film treated with NaOH solutions conc: 1M, 1.25M, 1.5M and 2M. 3. 250g of radiographs were used.	1. Amount of silver obtained= 6.54g.	(Cânda, 2018)	3
4.	Xray film (SPENT FIXING BATH 2008)	-	Spent fixing bath solution.	1.Ph=8-9 2.Temp.1000 °C 3. ratio of mass to volume is 3:10.	1. Spent fixing bath containing 10 wt.% NaOH aqueous solution, then 10 wt.% KBH4	Purity= 99.6%, total recovery - 98%.	(Zhouxiang, 2008)	4
5.	Xray film	X-ray photographic films containing 1.5 - 2 % (w/w) black metallic silver.	Electro-deposition	1. Required voltage is 12volts.. 2 Optimum time is 120 min	Sodium hydroxides (NaOH), Silver Nitrate.		(rawat, 1986)	9
6.	Xray films(optimize surface methodology)	600 mg of Xray film was taken.	1. by using enzymes and chemical catalyst. 2 Hollow cathode lamp, SEM.	1.(bromelain) optimum temperature 45℃, pH6.5, stripping time 20 min. 2.(papain) pH6.9, 70℃	1. Bromelain, Papain enzyme were used as a biocatalyst. 2.NaOH as chemical catalyst.	1. 5.4 mg (from bromelain enzyme), 2. 4.8mg (from papain enzyme). 3. atomic absorption confirms 91.12% purity of silver.	(Urriquia, 2020)	6
7.	Xray film	NaClO(2%), NaOH(1mol/L), NaCl(1mol/L).	Volhard method	1000℃, 120 min.	Crucibles, Muffles, graphite photolyte fixative developer solution, desiccator.	0.51g for NaCl, 0.205 for NaOH and 0.00g for NaClO .	(Paraguassu-Chaves, 2019)	16
8.	Radiographic films	1. NaOH solutions of various concentrations : 1M, 1.25M, 1.5M and 2M.	1.Aqueous NaOH solutions, to extract the polymer deposited substrate.	- Ambient temperature, 90 ℃, - 1.5M conc.	1.Stereo Microscope,	1. high purity of silver Obtained.	(R Canda, 2007)	3
9.	Waste radiographic film	1.69wt %	heating the solution at 90–100 ◦C for 5–20 min.	1. 100-℃1. 2.time -20 min.	1.Oxalic acid and Nitric acid. 2. X-ray fluorescence spectrometer (XRF, XOS HD Mobile).	91.82% Ag purity.	(C, 2020)	22

10.	Xray film (IOP science) (2017)	100ml of 1.5M NaOH for 50 g of X-ray film.	Treatment with Nitric Acid	1. oven at 50°C. 2. NaOH solution of 1.5M concentration. 3. Leaching of silver layer at 70°C. 4. Time -1 hour.	steel electrode at cathode and a copper electrode at the anode.	98% purity	(Cânda L. R., 2017)	24
11.	Xray, Photographic films.	2% w/w	Using borax compound	Oven: 40℃ Heater temp: 60 -70℃	Ethanol, NaOH and Na_2CO_3	99% pure silver	(D.K.Chandre, 2017)	10
12.	Xray, Photographic films.	-	Recovery by AAS	hot air oven at 100ºC for 6 hours	AAS and EDX analysis	silver in the extractant was below the detection level of AAS	(Varghese, 2015)	23
13.	Xray film	-	Using Bromelian enzyme	pH 6 rpm 8000	AAS spectrophotometer	99% purity	(Engidayehu, 2020)	5
14.	Radiographic film	0.12 %	Leaching	Temp 77℃, 100g/L density	Hydrometallurgical treatment	90% recovery	(mishra, 2021)	26
15.	X-Ray	-	Leaching solutions	High temperature and highly acidic conditions	Hydrometallurgical	Pure metallic silver obtained	(marco, 2023)	27
16	Radiographic films	-	Leaching	0.69 mm TMT concentration	Thiosulphate solutions	94.7 % recovery	(yazici, 2022)	28
17.	Radiographic film	Initial conc – 100-1000 mg /litre (Ag)n	E waste leachates	Ambient temperature, 1 atm pressure	Catalytic process	Not mentioned	(Cânda L. , 2018) (RUCK, 2022)	29
18.	Photographic film	1.1 g/L Ag	Using Silver Halide	105℃, 5-6 hours	Hydrogen Peroxide, Ethylene glycol, Sodium Hydroxide, Distilled water	87.4% recovery	(BAS, 2012)	30

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