

A Novel Silver Recovery Method from Waste Photographic Films with NaOH Stripping

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A novel, simple, fast, cheap and pollution-free method was developed for recovering the silver from waste X-ray photographic films with NaOH stripping. The method has a number of advantages because it obviates the need for burning, oxidizing, electrolysis or purifying steps. Moreover, all experiments were carried out in the same flask, unlike other techniques. Silver recovery conditions were optimized and silver a purity level of 99% was recovered. The metal impurities (Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Sn) in the recovered silver were determined using the ICP-MS method. The results were compared with results in the literature for high-purity silver using the same method.

Key Words: Silver recovery, waste photographic films, sodium hydroxide

Introduction

Silver, one of the precious and noble metals, is used in large quantities for many purposes, particularly in the photographic industry. It has been reported that 25% of the world's silver needs are supplied by recycling and that 75% of this is obtained from photographic waste¹. For this reason, the methods applied to recover silver from photographic waste are important in reducing cost and time, and have a positive effect on environmental pollution.

Compared to other films, waste X-ray photographic film contains a great deal of silver to enhance its sensitivity to transmitted X-rays and 1.5% to 2.0% silver by weight survives in the emulsion on the polyester film base, even after the developing and fixing processes. These waste films are a good source of silver that is reused for a variety of purposes including light-sensitive materials. Various studies have been carried out over a long period of time to recover the silver from these wastes, and most of them have been patented. The silver recovery methods from waste films can be classified as (a) burning the films directly², (b) oxidation of the metallic silver following electrolysis³⁻⁸, and (c) stripping the gelatin-silver layer using different solutions⁹⁻²¹. The second and third methods have been used more extensively for the recovery of

silver than the first method. In general, the methods reported for the recovery of silver from films involve two steps; the first is the separation of the silver from the film base, and the second the recovery of the silver by smelting or electrolysis. The first step is commonly leaching, which may be either chemical³⁻¹⁶ or microbiological¹⁶⁻²¹. Table 1 shows the existing silver recovery methods from waste photographic films. The use in chemical methods of reagents such as sodium cyanide, nitric acid or organic compounds causes environmental problems. Microorganisms can be used, but this process is slow. On the other hand, all of the existing methods are time-consuming, since they involve two separate steps. This paper reports on a novel method for recovering high-purity silver from waste X-ray films using sodium hydroxide. The method is based on combining the stripping step with the recovery step of the silver recovery process without electrolysis or smelting.

Table 1. Methods of recovering silver from waste X-ray films.

Method	Reagents used	Operation temperature (°C)	Recovery or purification method	Ref. No
A-Chemical				
1	NaCN + H ₂ O ₂	room temp.	electrolysis	3
2	Ce(SO ₄) ₂	nr	electrolysis	4
3	NaClO	room temp.	electrolysis	5-6
4	FeCl ₃	35-40	electrolysis	7
5	HNO ₃	room temp.	electrolysis (in the presence of cyanide)	8
6	RCONH ₂ + HNO ₃	60-100	smelting	9
7	urea nitrate (15-20%)	90-95	smelting	10
8	NaOH + high shear	60-95	nr	11
9	KOH (saturated) + KCl	80	nr	12
10	H ₂ C ₂ O ₄ (1% w/v)	97	smelting	13
11	NaOH (in ethanol)	boiling solution	smelting	14
12	NaOH or KOH + Na dinaphtyl methane sulfonate (5 g/L)	70-80	smelting	15
13	Hot water	nr	electrolysis	16
B-Microbiological				
1	<i>Pseudomonas B132</i>	45	smelting	17
2	<i>Streptomyces rimosus oxytetracycline</i>	15-70	smelting	18
3	<i>Gelatin-decomposing microorganisms</i>	40, 50-60, 85	smelting	19-21

nr: not reported

Experimental

All of the chemicals and reagents were of analytical grade. Distilled water was used throughout the study. Triply distilled water was used during the determination of metal impurities. NaOH solutions (0.5-2.5 M) and standard NaCl solution (0.1000 M) were prepared. The used X-ray photographic films were supplied by the Radiology Department of the Medical Faculty Hospital, Ege University, İzmir (Turkey).

A Chiltern HS 31 magnetic stirrer and heater was used. A Tacussel TS 60/N potentiometer with an AgCl/Ag electrode and saturated calomel electrode connected to a KNO₃ (saturated) salt bridge was

used to determine the purity of the recovered silver. Trace metal impurities were determined by an HP 4500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in the laboratory of the İzmir Regional Sanitation Institute. Photographs of the recovered silver were taken by a Canon 500 camera.

Silver recovery method

The used X-ray films were washed with distilled water and wiped with cotton impregnated with ethanol, and were cut into 4 x 4 cm² pieces after being dried in an oven at 40°C for 30 min. Each of the films was weighed and stirred in series in a beaker containing 80 mL of 1.0-1.5 M NaOH solution at 70-80°C in a water bath until the gelatin-silver layer was stripped off completely. The resulting solution containing colloidal black metallic silver was stirred vigorously in a water bath at 90-95°C until coarse-grained silver was observed. The solution was easily decanted and the residue washed with distilled water, dried and weighed. The basicity of the used washing water was checked with a phenolphthalein indicator. The purity of the recovered silver was determined by potentiometric titration with a standard solution of NaCl using Ag/AgCl and a saturated calomel electrode as an indicator electrode and reference electrode respectively.

Determination of trace metal impurities in the recovered silver

Sample cleaning

The recovered silver was transferred to a 100 mL PTFE beaker, and then 2.5 mL of cold 0.1 M HNO₃ was added and shaken for approximately 10 min. This was followed by a thorough rinsing in distilled water. It was then dried and stored in a desiccator²².

Sample pre-treatment

The cleaned silver was weighed and 3 mL of triply distilled water and 3 mL of concentrated nitric acid were added to it in a PTFE beaker. The sample was heated at temperatures below boiling point, and then 4 mL of 2.3 M HCl was added progressively to form a fine precipitate of silver chloride. After the addition of 2 mL of concentrated HCl and some 20 h of agitation, the solution was filtered by a G4 crucible under vacuum. The filtrate was made up to 25 mL triply distilled water in a calibrated flask, and then trace metals in the filtrate were determined by ICP-MS method²².

Results and Discussion

The appropriate stripping temperature range for gelatin-silver layer from the used photographic films was 70-80°C (Figure 1). We observed that the blackish metallic silver in colloidal form in NaOH solution had been converted to coarse-grained and bright metallic silver due to the effects of heating and stirring, especially at high temperatures. It was noted that the number of silver particles in solution is important and that 30-35 of the films (6-7 cm² film/mL NaOH soln.) had to be stripped in 80 mL of 1.0-1.5 M NaOH solution to obtain coarse-grained, bright metallic silver. The average silver content of the waste X-ray films was 0.38 mg/cm². This result is supported by the 0.37 mg/cm² results from our previous enzymatic method¹⁹. The average yield of the method was 66% according to silver content based on the finding of 0.38 mg/cm². The variations of the yields in the different NaOH concentrations were attributed to the differences in silver content of the waste photographic films.

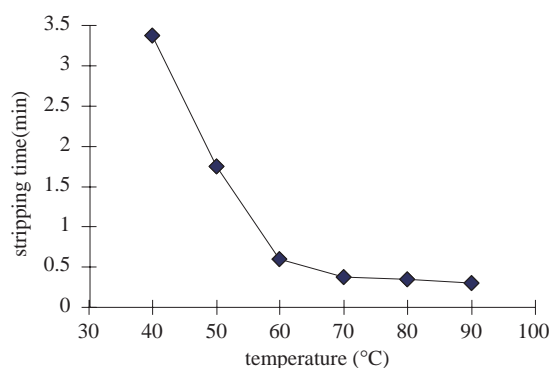


Figure 1. The temperature effect on the stripping times of the used films in 1 M NaOH.

Table 2 shows the results and observations for various concentrations of NaOH solutions for stripping the metallic silver from the film base and coagulation. The purity of the recovered silver for all concentrations of NaOH solutions was $\geq 99\%$ using the average of five potentiometric measurements. However, coarse-grained and very bright silver was recovered for 1.0 and 1.5 M NaOH solutions, while somewhat bright fine, black particles were observed for the other concentrations. The coagulation of the colloidal metallic silver particles can be explained by mechanisms such as coagulation of the precipitates. The particles remain suspended in the solution owing to a persistent particle charge that causes a mutual electrostatic repulsion of the particles. These become charged due to the adsorption of the ions in the surrounding solution. These particles have zeta potential, which gives an indication of the potential stability of the colloidal system. Particles with a zeta potential of ± 30 mV positive or negative are normally considered to be stable²³. On the other hand, the most important factors affecting zeta potential are pH, ionic strength and concentration of any additives such as surfactants. The zeta potential of silver colloidal solutions is negative in alkaline medium²⁴ and its value is approximately -50 mV²⁵. Factors affecting the zeta potential of the silver particles in NaOH solution containing hydrolysis products of gelatin can be established from the information above. We have not detected any significant pH difference during and after the silver recovery process. On the other hand, gelatin produced amino acids during its hydrolysis with NaOH. Thus, it can be speculated that excess NaOH, amino acids or the remaining unhydrolyzed gelatin could be the effective factors on the zeta potential of silver particles. Solutions containing Na^+ ions (NaOH in this case) are called indifferent electrolytes, since they can compress the electrical double layer, causing a shift of the zeta potential towards positive values²⁴ (double layer compression). In addition, the hydrolysis products of gelatin, i.e, amino acids, can behave as collectors by adsorbing on the colloid surface, and this neutralizes the negative charge of the silver colloid, resulting in a near-zero net charge (charge neutralization). From these points of view, we conclude that the zeta potential of silver particles draws closer to the zero point of charge through the effects of both excess NaOH and the hydrolysis products of gelatin during heating with vigorous stirring at 90-95°C. Furthermore, heat treatment is itself an efficient way of solution breaking. This causes the coagulation of silver particles at all concentrations of NaOH.

Table 3 shows the metal impurities in the recovered silver with a comparison to the high-purity silver in the literature^{19,22}. According to the data in Table 3, the silver recovered using the NaOH method contains fewer metal impurities than FS 14 and the silver recovered by the enzymatic method. On the other hand, the recovered silver can be described as high-purity silver containing 5'9-grade silver like EM 9465 at the least. The quantities of copper, magnesium, lead, manganese and cadmium in the recovered silver are lower than the quantities of these metals in EM 9343 while the quantities of aluminium and tin are similar.

Table 2. The observations and purity of the silver recovered by stripping 30 films in different concentrations of NaOH solutions.

C (mol/L)	W ₁ (g)	W ₂ (g)	W ₃ (g)	% Purity	% Yield	Observations
0.5	0.1046	0.1000	0.0990	99.04	57	Coagulation time: 3 h Somewhat bright and black, fine particles
1.0	0.1252	0.1001	0.0992	99.12	69	Coagulation time: 1 h 30 min Coarse-grained and very bright particles
1.5	0.1178	0.1009	0.1001	99.12	65	Coagulation time: 1 h 30 min Coarse-grained and vedy bright particles
2.0	0.1115	0.1012	0.1002	99.01	61	Coagulation time: 1 h 30 min Somewhat bright and black, fine particles
2.5	0.1381	0.1020	0.1013	99.31	76	Coagulation time: 1 h 30 min Somewhat bright and black, fine particles

W₁: The overall weight of the recovered silver, W₂: Silver weighed for potentiometric analysis, W₃: The results of potentiometric analysis.

Table 3. Results ($\mu\text{g/g}$) for the trace impurities in the recovered silver in comparison to some results for high purity silver in the literature²².

Element	Silver recovered using the proposed method	Silver recovered by the enzymatic method ²²	EM9465	EM9343	FS 14
Fe	2.3	20.01	1.85	0.26	47.6
Cu	0.047	1.714	0.132	0.078	61.8
Mg	0.011	0.033	0.087	0.0640	-
Cr	0.499	0.671	-	-	-
Pb	<0.001	0.010	0.597	0.011	33.8
Al	0.024	4.620	0.082	0.024	-
Mn	0.003	0.021	0.011	0.007	-
Co	1.16	20.89	0.0024	-	-
Ni	0.362	9.962	0.011	0.007	53.9
Sn	0.044	0.021	0.006	0.039	44.0
Cd	<0.001	<0.001	0.018	0.012	-

EM9465; high-purity silver containing 5'9 grade silver, EM9343; high-purity silver containing 6'9 grade silver, Fine silver FS 14: NIST SRM 8171.

In conclusion, silver was successfully recovered from photographic film using NaOH solution in both the stripping and recovering steps without any separation or purification. Being in colloidal form that cannot be filtered initially in NaOH solution, the metallic silver was obtained in the form of a coarse-grained and bright metallic silver with a purity level of $99.24\% \pm 0.03$ (for 95% confidence level, $N = 5$). The stripped silver is heated on a stirrer and can be separated from the solution simply by decanting. This eliminates some time-consuming steps such as filtering, centrifuging, smelting or electrolysis. Another advantage is that all the recovery steps are performed in the same NaOH solution and container. The recovered silver is high in purity, being of 5'9 or 6'9 grade with few impurities. The method can be applied to all kinds of

laboratory conditions (it is simple), contains fewer steps than the others (it is fast), does not require high temperatures of 900-1000°C so that it consumes little energy and is harmless because it lacks the burning, smelting and electrolysis steps (it is cheap and pollution-free).

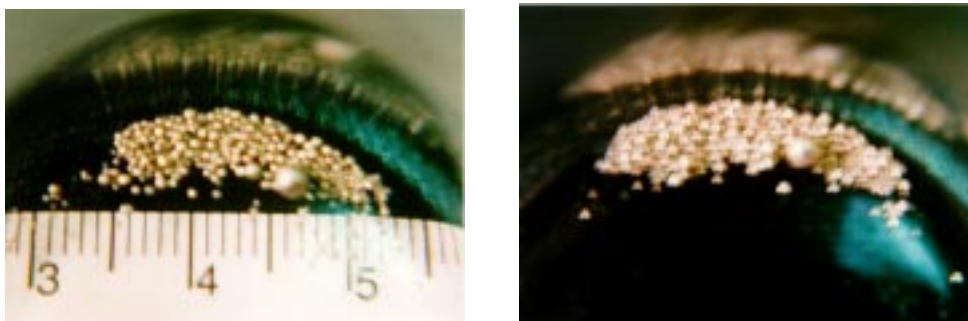


Figure 2. Two different views of the recovered silver.

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