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Process optimization for the recovery of silver from waste X-ray photographic films

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A novel, simple, fast, cheap and pollution free method for utilizing waste X-ray film for silver recovery using sodium hydroxide and sodium sulfide by the stripping and precipitation processes, respectively has been reported. The yield of silver by this process is 1.07% w/w at a stripping temperature of 70.88°C, 10.97 min and NaOH concentration of 1.5M. The composition of recovered silver has been determined by XRF and the results are compared with existing literature for the purity of silver. The study warrants the application of NaOH and Na_2S to recover silver from used X-ray photographic film.

Keywords: Silver recovery, Waste photographic film, Sodium hydroxide, XRF

Silver is one of the most precious metals used particularly in the photographic industry. Among metals, pure silver has the highest thermal conductivity highest optical reflectivity. Silver is rare, but occurs naturally in the environment as a soft “silver” colored metal.Ores of silver are argentite (Ag_2S), chlorargyrite (AgCl), and pyrargyrite (Ag_3SbS_3). Commercial-grade fine silver is at least 99.9% pure, and purities greater than 99.99% are available[1]. The most common oxidation state of silver are +1 ($AgNO_3$), +2 (AgF_2), +3 ($KAgF_4$) and +4 (K_2AgF_6). Naturally occurring silver is composed of two stable isotopes, ^{107}Ag and ^{109}Ag, with ^{107}Ag being more abundant[2,3]. The most common applications of this metal are to make currency, jewelry, silverware, dentistry, Photography, electronics, mirrors, optics, other industrial applications include in biology, medicine, investing, clothing**.**

Silver is found in abundance in the waste X-Ray photographic films. Researches claim that silver-containing wastes like used X-ray photographic film are toxic and considered as hazardous wastes. The hospitals, clinics and medical laboratories in the country dispose these wastes without the knowledge of their toxicity into land and water bodies.The primary sources of recoverable silver are present in the ‘fix’ and the ‘bleach-fix’ solutions[4]. Most photographic and X-ray wastes contain silver thiosulfate. Wastes having a silver concentration of 5 parts per million (ppm) including the fixer solution, Rinse water following water baths, Solution from cleaning developer tanks (cleaner dissolved precipitated silver), Film, negative and paper are hazardous because they display the characteristic of toxicity[5].

Methods applied to recover silver from photographic waste are important in reducing cost, time, and environmental pollution. X-ray photographic film contains about 2.0% silver by weight in the emulsion on the polyester film base, after the developing and fixing processes. Silver recovery has been significant since it reduces the toxic effect on the aquatic organism and promotes the reuse of silver. In large doses, silver and compounds containing it can be absorbed into the circulatory system and become deposited in various body tissues, leading to argyria, which results in a blue-grayish pigmentation of the skin, eyes, and mucous membranes[6]. Several technologies exist to recover silver from used X-ray photographic film such as burning the film, electrolysis, metal replacement, bacterial, and enzymatic methods and chemical precipitation[7]. Except chemical methods, the other methods are expensive and time consuming to recover the silver. However, using the chemical method does not need much time, not expensive technology, fast and simple. The use of chemicals, sodium cyanide, nitric acid or organic compounds cause environmental problems, whereas the decomposition by microorganism is slow.

Ion exchange is used for effective recovery of silver from rinse water or other dilute solutions of silver, reduce the silver concentration in photographic effluent to levels in the range of 0.5 to 2 mg/L[8]. Reverse osmosis (RO) that uses high pressure to force the silver-bearing solution through a semipermeable membrane to separate larger molecules. In the distillation recovery process, the photographic processing effluent is captured in a vessel and heated to evaporate the water. This research reports on a novel method for recovering high-purity silver from waste x-ray films using sodium hydroxide. The research also focuses on the optimization of the parameters that affect the process of silver recovery.

Experimental Section

Chemicals and reagents

Sodium hydroxide, NaOH; Sodium sulfide, Na_2S; Ethanol, C_2H_5OH; Hydrochloric acid, HCl; Borax decahydrate, $Na_2B_4O_7{\cdot}10H_2O$; Sodium carbonate, Na_2CO_3 was procured from Sigma-Aldrich, USA. All other analytical grade reagents were supplied by Merck, Germany. The used X-ray photographic films were collected from Black Lion medical faculty, Addis Ababa University, Addis Ababa, Ethiopia.

Processing the films

The collected X-ray photographic films were washed with distilled water and wiped with ethanol. These films were cut into 1 cm pieces and dried in an oven at 40°C for 30 min[7]. NaOH at various concentrations (0.5M, 1.5M and 2.5M) were prepared to strip the gelatin-silver layer from the base of the film. Na_2S was prepared to precipitate the silver from the stripped solution[7]. HCl (11.65M) was prepared to validate the completion of stripping and presence of silver in the solution. An equal mixture of Borax and sodium carbonate was also prepared for the processing.

Silver recovery

Silver stripping experiments were carried out as follows. Twenty pieces (25 cm × 29 cm) for each run of prepared films were measured, cut, weighed and treated with 0.5 M, 1.5 M and 2.5 M NaOH in a 3L container placed in an oil bath. The temperature was varied at three levels (50, 70 and 90°C)[8]. The experiments were carried out by fixing the time at three levels (1, 10.5 and 20 min). After the stripping process, the residual solution containing the colloidal black metallic silver was mixed with a proportionate amount of a precipitating agent, Na_2S with Na_2S to NaOH ratio (1:2). Stirring the solution resulted in the precipitation of the silver as a black sludge due to the common ion effect[7]. This was followed by decantation and filtration. The black sludge was washed with distilled water till neutral *p*H, followed by drying. The sludge was dried in a muffle furnace at 500°C for 30min. Equal amounts of $Na_2B_4O_7{\cdot}10H_2O$ and Na_2CO_3, was mixed with the dry black sludge in a ratio of 2:1. The mixture were placed in the graphite crucible and heated for 90 min at 950°C. The molten pure silver was collected in a mould and its purity was measured.

Process variables and optimization

Response surface methodology using Design Expert Software (version 9.0.0) was used to evaluate the effect of several process parameters and their interactions on the response variable[9,10]. The effects of the NaOH concentration, temperature and time of the stripping operation on the yield of silver recovered and its purity were studied. The three factors were analyzed against three levels (low [-1], medium [0] and high [+1]), the 3^3 design. 27 runs were performed to study the interaction among the factors and their effect on the amount of silver recovered using the response surface methodology[11,12].

Analytical methods

The purity of silver recovered and the impurities present in them were measured using EDXRF Spectrometer (Sky Ray Model: EDX2800).

Results and Discussion

Yield of silver

All the experimental sequences were performed in triplicate. The coded values of independent variables were found from equation (1)

$$x_i = \frac{X_i - X_0}{\Delta X}, \ \text{i=1,2,3,...,k} \quad \text{...(1)}$$

where x_i is the dimensionless value of an independent variable, X_i is the real value of an independent variable, X_0 is the value of X_i at the center point and ΔX is the step change[13]. A second-order quadratic model was used to fit the quadratic equation (2)

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_5 x_1^2 + \beta_6 x_2^2 + \beta_7 x_3^2 + \beta_8 x_4^2 + \beta_9 x_1 x_2 + \beta_{10} x_1 x_3 + \beta_{11} x_1 x_4 + \beta_{12} x_2 x_3 + \beta_{13} x_2 x_4 + \beta_{14} x_3 x_4 \quad \ldots (2)$$

where Y is the measured response (silver recovery), x_1, x_2, x_3, x_4 are the coded independent input variables, β_0 is the intercept term, β_1, β_2, β_3, β_4 are the linear coefficients showing the linear effects, β_5, β_6, β_7, β_8 are the quadratic coefficients showing the squared effects and β_9, β_{10}, β_{11}, β_{12}, β_{13}, β_{14} are the cross product coefficients showing the interaction effects[14,15]. The optimum values of the factors were obtained by solving the regression equation, analyzing the surface of the three-dimensional response surface plot and also by the setting up of constraints for the levels of the variables[16,17]. The recovered silver yield was calculated as follows for each run and recorded (Table 1)

$$\%\ \text{yield or recovery} = \frac{(\text{weight of pure silver obtained from each run})}{(\text{weight of prepared film for each run})} * 100 \quad \ldots (3)$$

During the measurement of the yield, the weight of used x-ray film is taken as input and the amount of pure silver recovered is used as output. There was a considerable variation in the amount of silver recovered irrespective of the size and type of the x-ray film. This fact is due to the dependency of the area covered by the x-ray image on the surface of the entire film. The data has been randomized during Design expert software (Table 2).

Table 1 — Factors and corresponding ranges and levels

Factors	Range	Levels		
		Low (-1)	Medium(0)	High(+1)
Temperature (°C)	50-90	50	70	90
Concentration (M)	0.5-2.5	0.5	1.5	2.5
Stripping time (min)	1-20	1	10.5	20

Table 2 — Factors and determined responses

Run No.	Factors Concentration (Mol/L)	Time (min)	Temp (°C)	Average film weight (g)	Average pure silver weight (g)	Average yield or recovery (%)
1	0.50	1.00	50.00	354.70± 0.46	1.45± 0.08	0.41±0.02
2	0.50	10.50	50.00	354.10± 1.15	2.16± 0.32	0.61±0.06
3	0.50	20.00	50.00	353.20± 0.36	2.15± 0.27	0.61 ±0.04
4	0.50	1.00	70.00	345.37± 0.55	2.56± 0.70	0.74 ±0.02
5	0.50	10.50	70.00	347.50± 0.79	3.09± 0.09	0.89 ±0.03
6	0.50	20.00	70.00	352.60± 2.34	3.07± 0.35	0.87 ±0.03
7	0.50	1.00	90.00	353.70± 0.46	2.30± 0.28	0.65 ±0.06
8	0.50	10.50	90.00	351.40 ± 1.65	2.85± 0.29	0.81 ±0.04
9	0.50	20.00	90.00	354.20± 1.31	2.55± 0.34	0.72 ±0.04
10	1.50	1.00	50.00	352.00± 1.41	2.50± 0.51	0.71 ±0.02
11	1.50	10.50	50.00	348.70± 0.10	2.96± 0.40	0.85 ±0.04
12	1.50	20.00	50.00	353.80± 0.26	2.76± 0.13	0.78 ±0.07
13	1.50	1.00	70.00	348.80± 0.72	3.31± 0.49	0.95 ±0.04
14	1.50	10.50	70.00	358.10± 0.36	3.87± 0.08	1.08±0.01
15	1.50	20.00	70.00	347.60± 1.08	3.30± 0.29	0.95±0.06
16	1.50	1.00	90.00	355.50± 0.79	2.81± 0.16	0.79 ±0.04
17	1.50	10.50	90.00	353.90± 0.20	3.15± 0.27	0.89 ±0.08
18	1.50	20.00	90.00	348.20± 0.26	2.71± 0.15	0.78 ±0.04
19	2.50	1.00	50.00	355.80± 0.95	2.46± 0.04	0.69 ±0.02
20	2.50	10.50	50.00	352.10± 0.62	2.75± 0.16	0.78 ±0.02
21	2.50	20.00	50.00	349.70± 2.04	2.13± 0.25	0.61±0.05
22	2.50	1.00	70.00	347.70± 0.35	2.78± 0.21	0.80 ±0.04
23	2.50	10.50	70.00	358.60± 0.80	3.14± 0.38	0.88 ±0.03
24	2.50	20.00	70.00	350.30± 0.75	2.52± 0.24	0.72 ±0.07
25	2.50	1.00	90.00	350.40± 0.95	2.06± 0.34	0.59 ±0.09
26	2.50	10.50	90.00	349.70± 0.85	2.20± 0.23	0.63 ±0.02
27	2.50	20.00	90.00	354.90± 0.96	1.60± 0.32	0.45 0.01

Silver recovery studies

Effects of NaOH Concentration, stripping time and temperature on silver yield

The process adopted for the recovery of silver is given in Fig. 1. The yield of silver was determined at each combination of the process settings. NaOH concentration emerged to be the most important factor during stripping and recovery of silver. Stripping of silver from the film base needed a shorter time with increasing NaOH concentration[18]. It was highly impossible to strip the silver particles from the film base at low concentrations. Further, increasing the NaOH concentration would make difficult the recovery of the silver from the solution due to its high corrosiveness resulting in a difficulty of silver precipitation. The NaOH concentration of 1.5 M provided a maximum yield of silver. The concentration of sodium hydroxide had a large impact on the yield of silver. Increasing NaOH concentration until 1.5M increases the yield rapidly, but further increasing the concentration decreases the yield by the same rate.

The silver yield was observed to increase slightly as there was an increase in the stripping time until 15 min. The intense contact between the reagent and film base was responsible for the stripping away of the silver from the film base. At extended time, a slight decrease of the yield was observed due to the corrosive nature of NaOH. Temperature has a significant effect on the yields of the silver. Increasing the temperature until 70°C, increases the yields of silver. Increasing temperatures above 70°C decrease the yield due to the interaction effects of the factors. The temperature is the most important factor to make the silver more exposed to stripping. This is because the stacked gluten would be loosened at high temperature, making it to detach from the surface. The 3-D response surfaces were plotted to understand the interaction between the variables and to determine the optimum levels of each variable for maximum response (Fig. 2a-2c). 3D surfaces show the interaction effects of concentration and time with

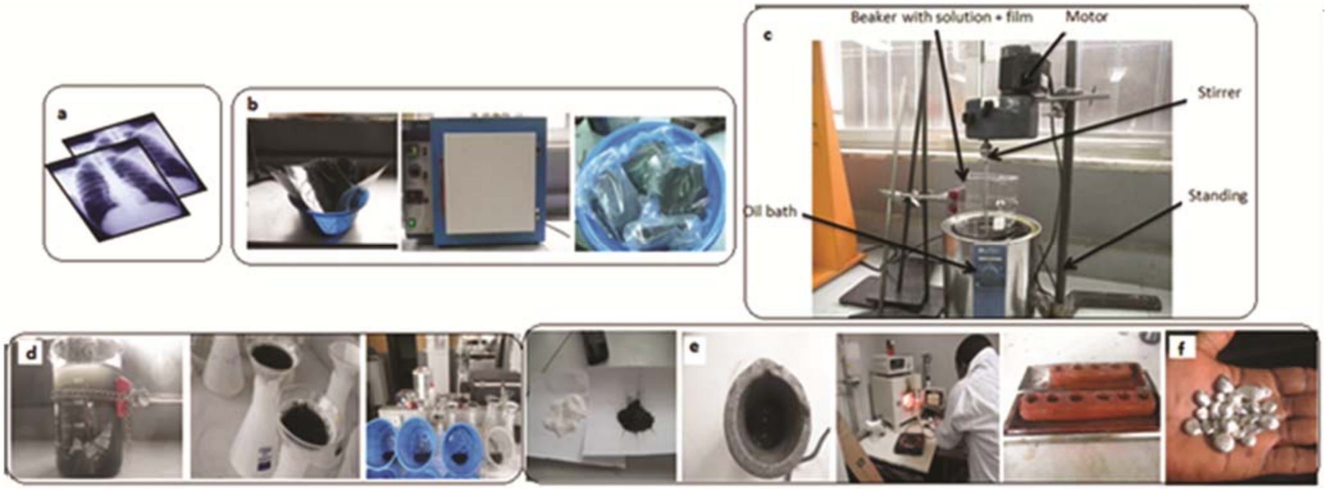

Fig. 1 — Silver recovery from X-ray films

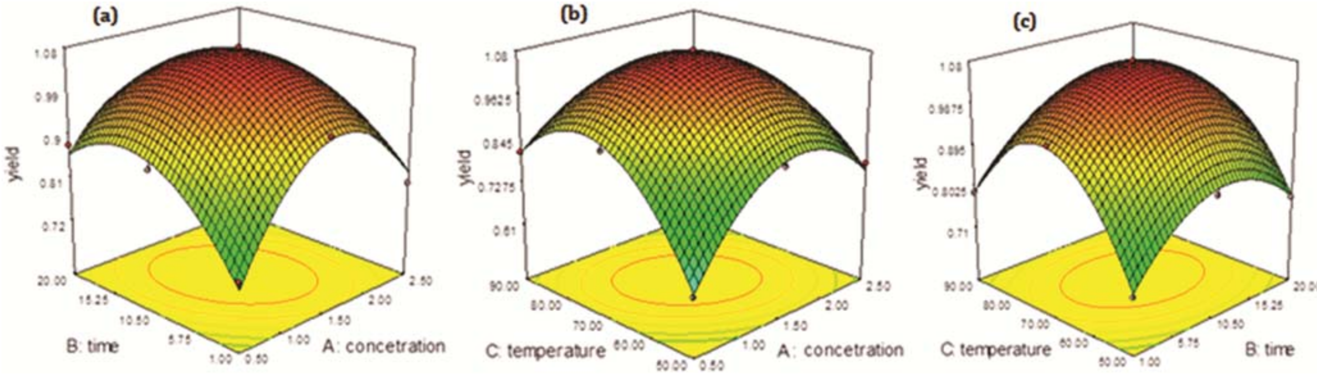

Fig. 2 — Interaction effects on silver yield (a) Effect of NaOH concentration and time; (b) Effect of temperature and NaOH concentration and (c) Effect of temperature and time.

respect to the yield of silver. The interaction plots show the increasing yield of silver until 15 min at 1.5 M NaOH concentration and yield was found to decrease after this treatment time[19]. Higher stripping time, favor complete stripping of silver from the film into the stripping solution. Longer times of exposure resulted in the suspension of silver rather than its settling. This condition makes it difficult to decant and separate the silver from the solution and also result in its degradation.

Higher yields of silver are obtained at 1.5 M NaOH and 70°C. Higher temperatures favors higher recovery of silver, but when the temperature exceeds 70°C, recovery decreases mainly due to NaOH corrosiveness. Higher temperature and time increased the yields of silver, because the silver completely strips from the film base. All the three factors were significant as found from the ANOVA results[20]. All the factors had values of “prob> F” less than 0.05, thus proving the significance of the results (Table 3). The Model F-value of 603.68 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A2, B2, C2 are significant model terms. Values greater than 0.1 indicate the model terms are not significant[14]. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Pred R-Squared" of 0.9899 is in reasonable agreement with the "Adj R-Squared" of 0.9943. "Adeq Precision" measures the signal to noise ratio[15,16]. A ratio greater than 4 is desirable. The ratio of 84.527 indicates an adequate signal. This model can be used to navigate the design space. Based on the above significant factors, the coefficients for the model were estimated.The final equation in terms of coded factorsis given as follows:

$$\mathit{SilverYield} = 1.07 - 0.0092A + 0.0095B + 0.015C - 0.059AB$$
$$- 0.080AC - 0.022BC - 0.18A^2 - 0.11B^2 - 0.19C^2$$

The positive coefficients were found to maximize the yield, whereas, the negative coefficients drastically minimized the recovery of silver. Thus, increasing the concentration had an inverse relationship with the silver yield. However, the parameters including the time and temperature with positive cofficients had a direct proportionality with the yield. Increasing time would allow the silver stripped completely from the film base and high temperatures were found to activate and expose the sticked silver to be leached out. The interaction and square of these factors have inverse proportionality with the yield.

Diagnostics and optimization

Parity plots were prepared to investigate the agreement between experimental (actual) values and model predictions. The actual values and the predicted values were compared[14]. The actual value was the measured response data for the runs, y_i, and the predicted value was the value predicted from the model, generated by using the prediction equation. There was a satisfactory agreement between experimental and predicted values. Optimization may be interpreted as the way to find those values of

Table 3 — Analysis of variance for silver yield

Source	Sum of square	df	Mean square	F value	p-value	Prob > F
Model	1.06	9	0.12	603.68	< 0.0001	Significant
A-concentration	0.0015	1	0.0015	7.78	0.0107	
B-time	0.0016	1	0.0016	8.35	0.0085	
C-temperature	0.0039	1	0.0039	20.06	0.0002	
AB	0.041	1	0.041	212.97	< 0.0001	
AC	0.076	1	0.076	390.79	< 0.0001	
BC	0.0059	1	0.0059	30.09	< 0.0001	
A^2	0.22	1	0.22	1130.04	< 0.0001	
B^2	0.094	1	0.094	483.15	< 0.0001	
C^2	0.27	1	0.27	1378.80	< 0.0001	
Residual	0.0043	22	0.0002			
Lack of fit	0.0043	17	0.0003			Not significant
Pure error	0.000	5	0.000			
Cor total	1.06	31				

controllable independent variable that give the most desired value of the dependent variable. Numerical optimization was carried out considering each value of the response and the goal of silver recovery or yield is set to maximize. The optimum yield of silver was 1.07% at a NaOH concentration of 1.46 Mol/L, stripping time of 10.97 min and a temperature of 70.88°C. At these optimum values, the average silver content of the waste x-ray film was 0.26 mg/cm^2. This result was supported by the 0.37mg/cm^2 of silver recovered[20]. The average yield of the method was 54%, according to silver content based on the 0.26mg/cm^2, the average silver content of the waste x-ray film. The desirability output of the model was 0.992.

Product characterization

The recovered silver was identified and characterized at the Ethiopian geological survey, Addis Ababa using XRF (Supplementary file). The purity and the trace impurities were recognized and quantified. Table 4. Provides the composition of the recovered silver. The X-Ray Fluorescence (XRF) machine sampled silver product of about 0.8 mm diameter and 15 mm depth. The machine generated an average composition of the impurities in the samples. Table 4 shows the purity of the first sample as 98.28 % and the second sample as 97.77% purity. The average purity remained 98.03 %, these results were encouraging as the impurities in the samples were less than 2%. Literatures supported an average purity of 99.24%[19,20]. The proposed method was able to remove the trace metals other than the recovery of high grade silver. Metals including Zn, Au, Pd were detected during the testing processes.

Economic analysis

A preliminary economical analysis was made to scale up the laboratory result into industry level. The waste films deposited per day by the Black Lion Hospital, Addis Ababa was 5 kg and considering another 50 hospitals in Addis Ababa (Health indicators, FMOH: EFY 2001), each hospital generates 2 kg films per day and a total of 105 kg can be collected per day. Hence, the amount of pure silver that can be recovered is estimated as 1.117 kg/day. And for 300 working days a year and 8 working hours a shift, the amount recovered annually is estimated as 335.1 kg of pure silver. Annually, 31,500 kg can be used as can be used as an input raw material. The input- output data were calculated per batch. And within one hour, three bathes could be run (i.e. 10 min required to run one batch and 10 min to load, unload and clean) to start the next batch. The total cost of all the raw material was to be 3,308,023 ETB. The total product cost of 1 kg silver produced by this method, was 1531 ETB (69 USD) and the payout period is 1.6 years.

Table 4 — Composition of the recovered silver

Sample No.	Sample weight (g)	Cu%	Zn%	Ag%	Au%	Pd%	Cd%	Sn%
1	2.52	<0.01	0.30	98.28	<0.01	0.52	0.30	<0.01
2	1.61	<0.01	0.30	97.77	<0.01	0.52	0.30	0.54

Conclusion

Best conditions have been obtained to achieve high silver yield. The optimal recovery conditions of silver are stripping temperature of 70.88°C, stripping time of 10.97 min and NaOH concentration of 1.46 M. Under these conditions, the obtained silver 1.07% yield or 54% recovery. The order of factors that are influencing the stripping process of silver was stripping temperature > stripping time > and NaOH concentration. The rate of return and payback period for the process are 51.5 % and 1.6 years, respectively. This is to mean that 51.5% of the total capital investment will be returned within one year and it will take only 1.6 years to return the whole capital investment cost. It is concluded that silver from used X-ray film had 98.28% purity.

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