Recovery of Silver from Waste Radiographic Films by Chemical Leaching

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The major sources to recover silver are photo-processing solutions, spent rinse water, scrap film and scrap printing paper. As much as 80 % of the total silver processed for black and white positives and almost 100 % of the silver processed in colour work will end up in the fixer solution. The waste radiographic films used in the experiments were taken from Cukurova University, Balcali Hospital, Adana, Turkey and cut into small pieces. The film pieces (1-9 g) were boiled with 100 mL of various quantities of oxalic acid, nitric acid and sodium hydroxide solutions for about 2.5, 5.0, 7.5 and 10 min at boiling temperature ($\cong$ 97 ℃). The aim of the study is to recover silver from waste radiographic films by HNO_3 leaching. To optimize the results of the experimental work, variance analysis was used. The statistical tests (F-tests) showed that nitric acid gave the best results compared with the other agents. Under optimum leaching conditions (radiographic films quantity, 50 g/L; nitric acid concentration, 30 g/L; stirring speed, 180 rpm; leaching time, 15 min) 89 % silver recovery was obtained.

Key Words: Waste radiographic films, Silver recovery, Acid leaching, Variance analysis, F-Test.

INTRODUCTION

There was a little study on the recycling of silver from the radiographic films and its environmental effects in Turkey. The recovery of silver process depends on heating the films with oxalic acid, nitric acid and sodium hydroxide solutions to boiling temperature to separate the inorganic component from the polymer substrate. Silver, a precious metal, is used in photo film because of its photosensitive properties. Film development causes photographic waste of spent fixer and rinse water containing 1000-10000 and 50-200 mg Ag/L, respectively, in the form of silver-thiosulphate complexes[1]. Silver in the photographic industry is recovered from two main sources *i.e.*, photographic solutions and scrap films. Basically, two types of solutions are used in the photographic industries. They are the fixer and bleach solutions. The fixer solutions consist of chemical substances which have the ability to dissolve sensitized salts on films on which photographic images could be developed. Fixer solutions dissolve the opaline silver compounds on the film and cause the picture to remain unchanged when exposed to light. Bleach solutions are used to rinse the negatives on which the photographic images are formed. The photographic wastes comprise mainly fixer and bleach solutions contain high concentrations of dissolved silver and other chemicals such as sulphates and nitrates[2]. Much

of the silver consumed annually in the world is used in photographic and radiographic applications. Small operations such as local doctors' and dentists' offices, veterinary clinics and 1 h film developers consume the bulk of this silver during the photographic/radiographic developing process. Once used, the majority of this silver ends up as waste, typically as sediment in our nation's waterways or as solid waste in landfills. Although this silver could easily be recovered and recycled, the current regulatory environment makes disposal an easier, less costly option for this small generator[3-6].

The photographic processing industry has four options in silver recovery *i.e.*, electrolytic plating, metallic replacement, ion exchange and chemical precipitation[7]. Four factors limit the extent to which photographic processing solutions can be recovered, regenerated, or reused. The ability to collect the solutions efficiently, dilution by water or other solution carried over from the preceding processing step, exhaustion of some of the chemical components in the solutions contamination of the solutions by reaction products or carryover[2]. 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. The ever-growing ecological considerations and stringent laws are driving the whole world to a system of increased recovery, regeneration and recycling of industrial wastes. Moreover, the

principle focus of recycling effort has been post-consumer products. Industries constitute a formidable source of pollution and radiographic industries produce large amounts of solid and liquid wastes. The wastes consist primarily of two components-organic and inorganic that makes regeneration and/or recycling worthwhile. Organic wastes can be further categorized into small molecules, such as hydroquinone and large molecules consisting of polymer substrate. The inorganic component consists of metallic and non-metallic parts. The latter comprises mainly fixer and bleach solution containing high concentrations of sulphates and nitrates. The metallic part consists of silver, the recovery of which is of paramount importance. Table-1 shows methods to recover silver from processed radiographic films[15]. Reagents were discovered dissolution of silver halides in photographic fixing process using ammonium thiosulfate (ATS) and sodium thiosulfate solutions (STS) as fixing baths in 1837[21]. Conventional fixing of AgX in photographic and medical X-ray films has been extensively used in the photo-industry for more than 2 centuries. The dissolution of silver halides by thiosulfates and thiocyanates are usually rapid and do not need any catalytic influence. Hence they are highly soluble in these lixiviant and are considered to be thermodynamically stable at slightly alkaline pH[22].

TABLE-1
METHODS TO RECOVER SILVER FROM PROCESSED
RADIOGRAPHIC FILMS

Method	Reagents used	Temperature of operation	pH Range	Ref. No.
Inorganic chemicals				
1	$FeCl_3$ (10–26% w/v)	35-40	2	8
2	$FeCl_3$	Not reported	n.r.	9
3	NaOH (1% w/v)	5-50	Alkaline	10
4	NaOH (in ethanol)	Boiling solution	Alkaline	11
5	H_2O_2/NaCN	Room temperature	–	12
6	EDTA-Fe^{3+}, $(NH_4)_2S_2O_8$	–	–	13
Organic chemicals				
1	$RCONH_2$+HNO_3	60-100	Acidic	14
2	Oxalic acid	97	Acidic	15
Biological chemicals				
1	Bacillus Zimet-11262	70	Min.salts	16
2	*Streptomyces grisens*	15-70 (wash)	6-9	17
3	Gelatin decomposing microorganisms	n.r.	n.r.	18
Mechanical chemicals				
1	High shear	60-93	–	19
Mechanical + chemicals				
1	High shear + NaOH	60-93	alkaline	20

EXPERIMENTAL

The processed radiographic films (with an average content of 6.85 g of silver/kg) were procured from Cukurova University Hospital, Turkey and cut into small pieces. Three different

reagents (nitric acid, sodium hydroxide and oxalic acid) were used of commercial grade for leaching. The first step, the best reagent was determined with means using to same test conditions (acid concentration: 20 g/L; radiographic film quantity: 50 g/L; temperature: 97 °C; mixed time: 10 min at 180 rpm stirring speed).

Secondly, the concentration of the best reagent was determined. In this step, the film pieces (5 g) were boiled with 100 mL of various quantities (5, 10, 20, 30 and 50 g/L) reagents solutions for about 10 min at boiling temperature at *ca.* 97 °C. After that, the effect of pulp density was investigated. For this aim, the film pieces (1, 3, 5, 7 and 9 g) were boiled with 100 mL of 30 g/L nitric acid solution for about 10 min at boiling temperature at *ca.* 97 °C. Finally, the film pieces (3 g) were boiled with 100 mL of 30 g/L nitric acid solution for 5, 10, 15, 20 and 25 min at boiling temperature of about 97 °C for the determination of optimum stirring time. The completion of the peeling process is indicated by the disappearance of the black colour of the film and appearance of clear blue of the polyester or triacetate film. The sludge was separated by filtration, dried and further subjected to melting to recover pure silver. The determination of the silver content of the processed radiographic films was carried out by atomic adsorption spectrophotometer (AAS). The resultant Ag_2SO_4 was measured potentiometrically with solution of NaCl.

RESULTS AND DISCUSSION

Reliability of the data depends upon the reproducibility. Hence replicates (n = 4) were carried out and the means and standard deviations of 4 tests at the same conditions (acid concentration: 20 g/L; radiographic film quantity: 50 g/L; temperature: 97 °C; stirring time: 10 min) are presented in Table-2. The results showed that the silver recovery, 72.30 % Ag recovery, could be achieved using nitric acid. Ajiwe and Anyadiegwu[23] studied that recovered silver from X-ray films by dissolving the silver compounds with concentrated nitric acid. They stated that silver recovery by internal electrolysis gave better recovery. Similar results were in conformity with the reports of Loto[24].

TABLE-2
RESULTS OF SELECTED REAGENTS
USED FOR SILVER RECOVERY

Test No	Oxalic acid (%)	Nitric acid (%)	Sodium hydroxide (%)
1	1.49	71.68	7.00
2	1.65	71.81	6.72
3	1.72	72.99	6.86
4	1.53	72.70	7.00
Mean	1.60	72.30	6.90
SD*	0.11	0.65	0.14

*SD: Standard deviation

The analysis-of-variance statistical technique was adopted to facilitate interpretation of the experimental results. Total sums of squares for reagents (12405.345) test, reported in Table-3 was partitioned into a sum of squares due to the effect of the different reagents used, (among reagents) and a sum of squares due to the experimental error involved in the test (within reagents). The different effect of the reagents on the selectivity was represented by the different silver recovery averages[15-27].

TABLE-3
ANALYSIS OF VARIANCE FOR REAGENTS

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Among reagents	12404.000	2	6202*	
Within reagents	1.345	9	0.149**	41500
Total	12405.345	11		
*MS1, **MS2.				

The variance MS1 is associated to these averages, while the variance MS2 represents the experimental error involved in the experiments and was calculated by pooling the variances coming from each test of 6 replicates of each reagent tested. These two variances are obtained by dividing the sum of the squares by the associated degrees of freedom. The null hypothesis H_0 -to be proved or otherwise-is that all the silver recover ratio averages μ belong to the same statistical population, that is H_0: $\mu_1 = \mu_2 = \mu_3$ for reagents. The alternative hypothesis is that they do not belong, so the reagents behave in a different manner regarding selectivity. In this case it is said that a statistical difference exists among the reagents. If MS1 differs significantly from MS2, $i.e.$, the ratio MS1/MS2 is significantly different from 1, the null hypothesis H_0 is rejected and the effect of the reagents, as a whole, differs one from another. The ratio between the two variances MS1 and MS2 constitutes a ratio between the explained variance due to the reagents and the unexplained variance generated by the experimental error and follows an F-statistic[28].

The critical threshold value of F with the appropriate degrees of freedom, associated with the numerator and the denominator, at a given level of confidence, is found in an F-table. If the computed value of the F statistic is smaller than that obtained from the F-table, there is no evidence that the two variances are different. Hence the difference of the silver recovery ratio averages obtained by the different reagents is only due to experimental error and the null hypothesis cannot be rejected. If the computed value of F is greater, it means that the null hypothesis has to be rejected and a statistical difference exists in the performance of the reagents. Statistical significance is decided by the level of probability associated with F. If it is desired to be on safer ground regarding acceptance of the hypothesis that the reagents act differently, it is necessary to choose a higher level confidence and as a consequence the calculated F should be higher to pass the test. In the work reported here the level of confidence was established at 95 %, that is the level of confidence commonly used as a threshold for statistical decision-making. Its adoption means that the experimenter does not want to be wrong more than once in 20 times, hence the risk of falsely rejecting the null hypothesis is 5 % at most. The high value of F (41500) reported in Table-3 shows that the null hypothesis cannot be accepted, hence it can be stated that the reagents on the whole have a different effect on the recovery of silver and experimental results indicated that nitric acid was the best reagent studied for silver recovery.

Effect of pulp density: The leaching efficiency for silver recovery from the radiographic films was pulp density dependent. Under higher pulp density conditions (3 % w/v), the recovery reaches its maximum value as seen in Fig. 1. After that, it is approximately stable case. Therefore, in further tests, 3 % w/v was used the best pulp density values.
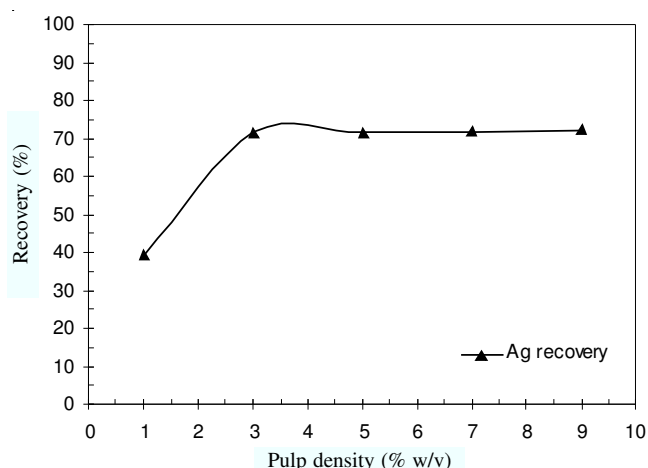

Fig. 1. Effect of pulp density on the silver recovery

Effect of acid concentration: The effect of various nitric acid concentrations on the silver recovery was investigated. In Fig. 2, it is seen that the silver recovery initially increased with increasing acid concentration reached to the optimum value around 30 g/L. The improved silver recovery was observed when the pH was lowered from pH 7.5 to 3.0 at 30 g/L nitric acid in the solution. This indicated that improved silver recoveries could be achieved under acidic conditions. Very small changes in the content of silver recovery were observed when nitric acid was added extra 20 g/L. Therefore, 50 g/L gave approximately the same value as 83.94 % silver recovery.
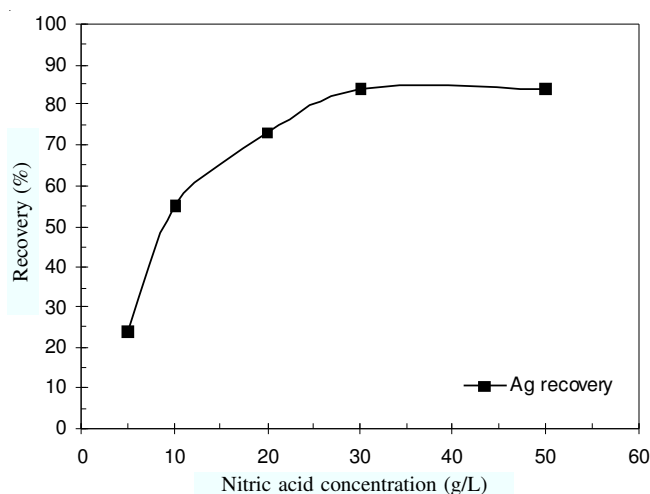

Fig. 2. Effect of nitric acid concentration on the silver recovery

Effect of leaching time: In order to determine the effect of the leaching time on the silver recovery, a series of experiments were conducted at 3 % w/v pulp density and 30 g/L nitric acid concentration. As it was seen in Fig. 3, the silver recovery increased with increasing leaching time. There was no effect on silver recovery over the 15 min leaching time. Therefore, the optimum leaching time was determined 15 min.

Conclusion

(a) The recovery of silver from processed radiographic films can be easily carried out by treatment with nitric acid solution. It is a low cost reagent, the process is simple and the consumption is low. Nitric acid is commonly used for silver recovery.
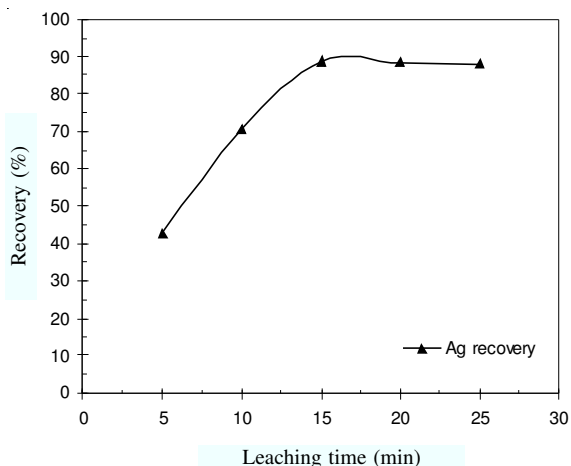
Fig. 3. Effect of leaching time on the silver recovery

(b) Using nitric acid resulted in the formation of nitrogen groups that resulted in the improved silver recovery *i.e.*, 1.60 % Ag recovery over oxalic acid and sodium hydroxide 6.90 % Ag recovery.

(c) The silver recovery was pulp density dependent.

(d) The presence of excess NO_3^- ions (> 30 g/L HNO_3 in solution) was observed not to improve silver recovery.

(e) Optimum leaching time caused a remarkable increase in the silver recovery at 15 min.

(f) The study shows that there is a strong relationship between pulp density, acid concentration and leaching time. The best silver recovery was determined as 89 % using optimum test parameters.

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