SILVER RECOVERY FROM WASTE X-RAY PHOTOGRAPHIC FILMS COLLECTED FROM HOSPITALS IN ADDIS ABABA

Mekurialem Demelash Erku[1], Anuradha Jabasingh S [1,*], Abubeker Yimam[1]
[1]Process Engineering Division, School of Chemical and Bio Engineering, Addis Ababa Institute of Technology, Addis Ababa University, Ethiopia
*Corresponding author's E-mail: anu3480@gmail.com

ABSTRACT

The present research reports a simple and efficient method for silver recovery using sodium hydroxide and sodium sulfide from the waste x-ray film. Response surface methodology was used to evaluate the effect of process parameters. The yield of silver by adopting this method was 1.07% at a stripping temperature of 70.88°C, at 10.97 min and NaOH concentration of 1.5M. The composition of recovered silver was determined by X-Ray Fluorescence (XRF).

Keywords: Photographic film, sodium hydroxide, XRF, Silver recovery

INTRODUCTION

Silver is rare, but occurs naturally in the environment. Ores of silver are argentite, chlorargyrite, and pyrargyrite [1]. The most common oxidation state of silver are +1, +2, +3 and +4 for $AgNO_3$, AgF_2, AgF_4 and K_2AgF_6 respectively [2]. Naturally occurring silver is composed of two stable isotopes, ^{107}Ag and ^{109}Ag, of which the former is more abundant [3,4]. Silver has more renowned applications. One of its most significant application is in the photographic industry. With the highest thermal conductivity and highest optical reflectivity it is found in abundance in the waste X-Ray photographic films [5]. Research claim that silver-containing wastes like used X-ray photographic film are toxic and considered as hazardous wastes [6]. In large doses, silver and compounds containing it lead to argyria, which results in a blue-grayish pigmentation of the skin, eyes, and mucous membranes [7]. Most households dispose these wastes into land and water bodies. The recoverable silver in the x-ray films are mostly present in the 'fix' and the 'bleach-fix' solutions. Most photographic and X-ray wastes contain silver thiosulfate with silver at a concentration of 5 parts per million (ppm). They are found in the fixer solution, rinse water, water baths and cleaning developer tank solutions [8].

Several technologies exist to recover silver from X-ray photographic film such as burning the film, electrolysis, metal replacement, bacterial, enzymatic methods and chemical precipitation. Except chemical methods, the other methods are expensive and time consuming to recover the silver [9]. The use of chemicals, sodium cyanide, nitric acid organic compounds cause environmental problems, whereas the decomposition by microorganism is slow [10]. Ion exchange processes, reduce the silver concentration in photographic effluent to levels in the range of 0.5 to 2 mg/L. Reverse osmosis (RO) and distillation recovery process are amongst the others used [11]. The present study explores the feasibility of high-purity silver recovery from waste x-ray films using sodium hydroxide with a focus on the optimization of the parameters that affect the process of silver recovery.

MATERIALS AND METHODS

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. The above listed chemicals were of Laboratory grade. Silicone oil was used in the oil bath. X-ray photographic films were collected from Black Lion medical faculty of Addis Ababa University, 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 at 40°C for 30 min. 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. HCl (11.65M) was prepared to validate the completion of stripping and presence of silver in the solution. An equal mixture of Borax (5g/dL) and sodium carbonate(anhydrous) was prepared for the processing[9].

Silver recovery

Twenty pieces (25 cm × 29 cm) for each run of prepared films were measured, cut, weighed and treated with 0.5M, 1.5M and 2.5 M NaOH in a 3L container placed in a silicone oil bath. The temperature was (50, 70 and 90°C) varied at three levels. The experiments were carried out by fixing the time (1, 10.5 and 20 min) at three levels. After the stripping process, the residual solution containing the colloidal black metallic silver was mixed with a proportionate amount of Na_2S to NaOH in the ratio (1:2). Stirring the solution resulted in the precipitation of the silver as a black sludge due to the common ion effect [11,12]. This was followed by decantation and filtration.

The black sludge was washed and 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 and the mixture was 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 by XFS using EDXRF Spectrometer (Sky Ray Model: EDX2800) at the Ethiopian geological survey, Addis Ababa. The process adopted for the recovery of silver is given in Fig. 1.

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 [13]. The effects of the NaOH concentration, temperature and time of the stripping operation on the yield of silver recovered and its purity were studied.

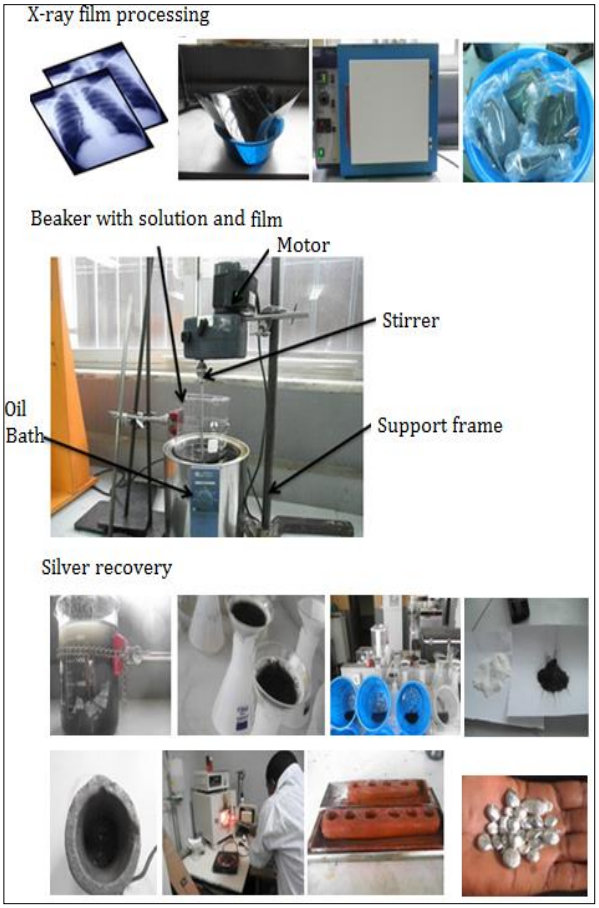

Fig. 1. Silver recovery from X-Ray films

The three factors were analyzed against three levels, 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. All the experimental sequences were performed in triplicate. The coded values of independent variables were found from equation (1)

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

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

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

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]. 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 [15].

RESULTS AND DISCUSSION

Yield of silver

The recovered silver yield was calculated as follows for each run and recorded (Table 1)

$$\%\ \text{yield} = \frac{(\text{weight of pure silver})}{(\text{weight of prepared film})} * 100 \quad (2)$$

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 levels

Factors	Range	Levels		
		-1	0	+1
A: Conc. (Mol/L)	0.5-2.5	0.5	1.5	2.5
B:Time (min)	1 - 2 0	1	10.5	20
C: Temp. (°C)	50-90	50	70	90

Effects of process parameters

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 was favorable at short stripping time at high NaOH concentration [16].

But increasing NaOH concentration beyond 1.5 M resulted in a difficulty of silver recovery due to precipitation. Fig.2a -Fig.2c shows that 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 contact between the reagent and film base was the key factor responsible for the stripping away of the silver from the film base. 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. Very high temperatures are not suitable for the silver stripping, due to the disintegration of stacked gluten employed in the manufacture of x-ray films. 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.3a-Fig.3c). 3D surfaces show the interaction effects of concentration and time with respect to the yield of silver. The interaction plots show the increasing yield of silver until 15 min at 1.5M NaOH concentration and yield was found to decrease after this treatment time. 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 it settling, making the subsequent decantation and separation processes difficult and also resulting in degradation. Higher yields of silver are obtained at 1.5M NaOH and 70° C. All the three factors were significant as found from the ANOVA results. All the factors had values of "prob> F" less than 0.05, thus proving the significance of the results (Table 3).

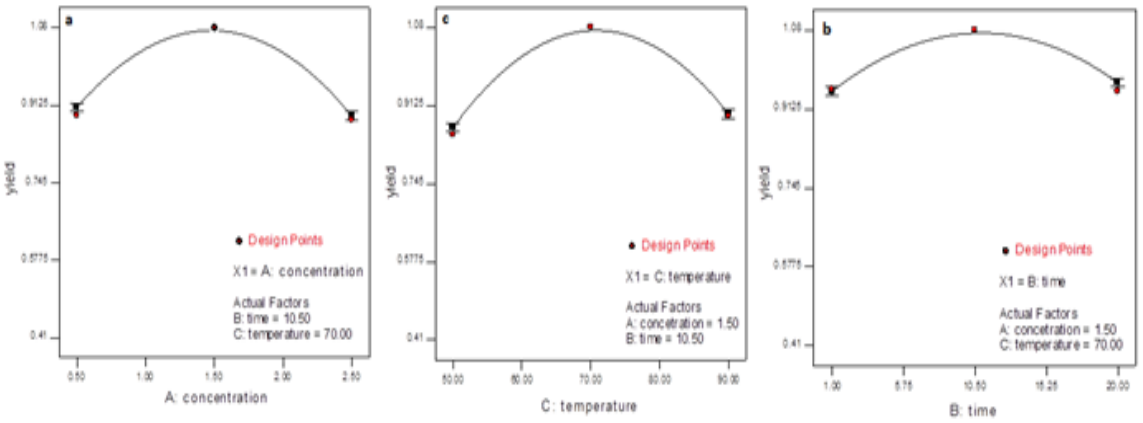

Fig. 2. (a) Effect of NaOH concentration (b) Effect of time (c) Effect of temperature.

Table 2. Factors and responses

Run No	Factors			Film Weight(g)	Pure Silver Weight(g)	Yield(%)
	A	B	C			
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

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
A	0.0015	1	0.0015	7.78	0.0107
B	0.0016	1	0.0016	8.35	0.0085
C	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		
Pure Error	0.000	5	0.000		
Cor Total	1.06	31			

There is only a 0.01% chance that a "Model The Model F-value of 603.68 implies the model is significant 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, A^2, B^2, C^2 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]. 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 factors is given as follows

$$Yield = 1.07 - 0.0092A + 0.0095B + 0.015C - 0.059AB - 0.080AC - 0.022BC - 0.18A^2 - 0.11B^2 - 0.19C^2$$

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.

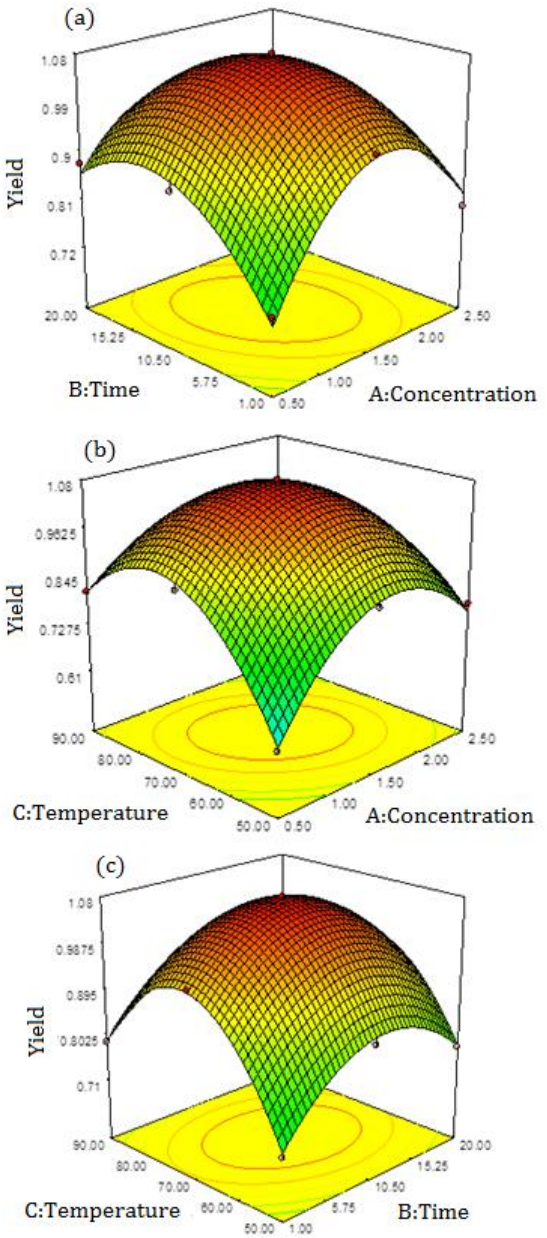

Fig. 3. (a) Effect of NaOH concentration and time (b) Effect of temperature and NaOH concentration (c) Effect of temperature and time.

However, the parameters including the time and temperature with positive coefficients 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 silver to be leached out [12]. The interaction and square of these factors have inverse proportionality with the yield.

Parity plot was prepared to investigate the agreement between experimental (actual) values

and model predictions (Fig. 4). The actual values and the predicted values were compared. 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 controllable independent variables 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 maximum. The optimum yield of silver was 1.07% at a NaOH concentration of 1.46 Mol/L, stripping time of 10.97 min and 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. 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.

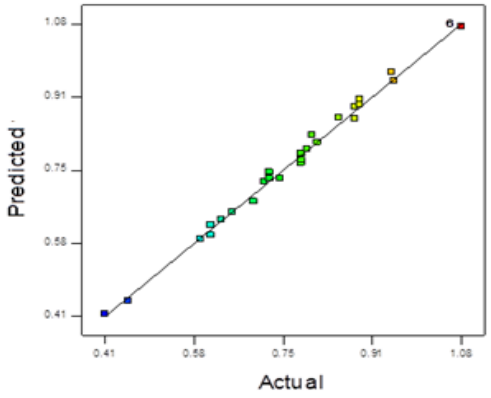

Fig. 4. Parity plot

Product characterization

The purity and the trace impurities present in the recovered silver were quantified and provided in Table 4. The X-Ray Fluorescence (XRF) machine sampled silver product of about 0.8 mm diameter and 15 mm depth (Fig 5).

Table 4. Composition of the recovered silver

Weight (g)	Cu %	Zn %	Ag %	Au %	Pd %	Cd %	Sn %
2.52	<0.01	0.3	98.28	<0.01	0.52	0.3	<0.01
1.61	<0.01	0.3	97.77	<0.01	0.52	0.3	0.54

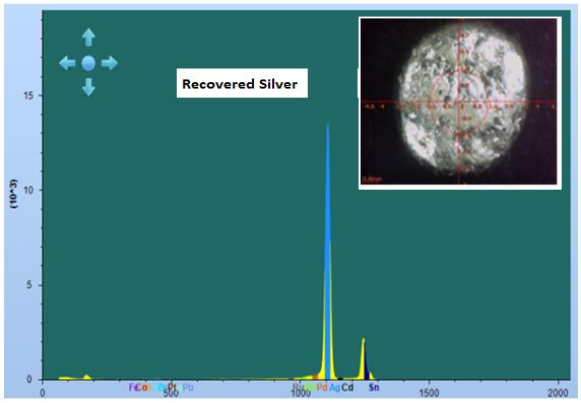

Fig. 5. Spectrum of recovered silver on XRF

The machine generated an average composition of the impurities in the samples. The 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% [12]. Metals including Zn, Au, Pd were also detected during the testing processes.

CONCLUSIONS

The optimal recovery conditions of silver were 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 had 1.07% yield and 54% recovery. The factors influencing the stripping process of silver were in the order of stripping temperature, stripping time and NaOH concentration. It is concluded that silver from used x-ray film had a purity of 98.28 %.

REFERENCES

[1] ATSDR., *"Toxicological profile for silver"*, Agency for Toxic Substances and Disease Registry U.S. Public Health Service, December 1990.

[2] **Riedel,** S., and **Kaupp,** M., "***The highest oxidation states of the transition metal elements",*** Coordination Chemistry Reviews 253 **(**5–6**), 2009,** 606-624**.**

[3] IUPAC., "*Atomic weights of the elements*", International Union for Pure and Applied Chemistry, Technical report, 2007.

[4] Bjelkhagen, H.I., "*Silver-halide recording materials: for holography and their processing*". Springer, 1995, 156-166.

[5] Masser, S.H., "*Method of recovering silver from waste photographic film and paper*", American patent, 4759914, 1988,CI 423-439.

[6] White, I.R., and Rycroft, R.J.G., "*Contact dermatitis from silver fulminate-fulminate itch"*. Contact Dermatitis, 8, 1982, 159-163.

[7] Samson, O.M., and Edison, M., "*Review of Silver Recovery Techniques from Radiographic Effluent and X-ray Film Waste*", Proceedings of the World Congress on Engineering and Computer Science, 2, 2014, San Francisco, USA.

[8] Kodak., "*Recovering silver from photographic processing solutions*", Publication no. J-215 Eastman Kodak Company, 1999.

[9] Rawat, J.P., and Iqbal, S., Kamoonpuri, M., "*Recovery of silver from laboratory wastes"*, Journal of Chemical Education, 1986, 63 (6), 537.

[10] He, J., and Kappler, A., "*Recovery of precious metals from waste streams*", Microbial Biotechnology, 10, 1194-1198, 2017.

[11] Goshima, T., Hori, K., Yamamoto, A., "*Recovery of silver from radiographic fixer*", Oral Surgery, Oral Medicine, Oral Pathology,77(6),1994, 684-688.

[12] Nikiboglu,N., Toscali, D., and Nisli, G., "*A novel silver recovery method from waste photographic films with NaOH stripping*". Turkish Journal of Chemistry 27, 2003, 127-133.

[13] Box, G.E.P., and Wilson, K.B., "*On the experimental attainment of optimum conditions*", J. R. Stat. Soc. Ser. B-Stat. Methodol.13, 1951, 1-45.

[14] Anuradha Jabasingh, S., Valli Nachiyar, C., "*Optimization of cellulase production by Aspergillus nidulans: application in the biosoftening of cotton fibers*", World Journal of Microbiology and Biotechnology, 27(1), 2011, 85-97.

[15] Anuradha Jabasingh, S, Valli Nachiyar, C., "*Utilization of pretreated bagasse for the sustainable bioproduction of cellulase by Aspergillus nidulans MTCC344 using Response surface methodology*", Industrial Crops and Products, 34(3), 2011,1564-1571.

Anuradha Jabasingh, S., "*Utilization of pretreated coir pith for the optimized bioproduction of cellulaseby Aspergillus nidulans*", International Biodeterioration and Biodegradation, 65 (1), 2011, 1150-1160.