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Silver recovery from radiographic film processing effluents by hydrogen peroxide: Modeling and optimization using response surface methodology

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Abstract−The recovery of silver from X-ray film processing effluents by precipitation using hydrogen peroxide as the precipitating agent was studied. Response surface methodology (RSM) and central composite design (CCD) were applied to achieve optimum conditions. Linear, square and interactions effects between parameters to study of a second order polynomial equation were obtained. Optimum condition included the volume of H_2O_2 0.8 ml/min, pH=5.5, ethylene glycol 9 ml in the experimental condition. In these conditions silver recovery percentage was predicted as 92.8%. The experiment was conducted in triplicate under optimized conditions. Silver recovery percentage and average of precipitate were obtained as 91.5% and 423.19 mg, respectively, which were close to the predicted amount achieved by the model.

Keywords: Silver Recovery, Optimization, Radiographic Film, Response Surface Methodology

INTRODUCTION

Approximately 8.3% of silver is used in photography due to silver halides photosensitivity [1]. Silver-halides such as AgBr or AgCl on photographic films are reduced to metallic silver when exposed to light. During the development and fixing of film, silver-halide crystals that are not exposed to light are leached by thiosulphate from the film into the processing solution [2]. A photoprocessing solution is used repeatedly, but despite this the effluent contains high amount of silver. Silver is one of the most toxic metals [3] and the film processing effluents are classified as hazardous waste that will cause soil and water pollution if released to the environment without treatment [4,5].

While silver is not as expensive as gold or platinum, it is present in limited amounts in nature, and world silver production is not sufficient to meet the demand, this indicates the need for recycling of silver from waste of industries and hospitals. So these wastes can be a useful resource for silver [6,7]. Therefore, treatment of these effluents for reclamation of silver provides significant economic as well as environmental benefits.

Methods that have been applied to the recovery of silver from its solutions include electrolysis, metallic replacement (cementation), chemical precipitation, ion-exchange and reverse osmosis [8-12]. The most widely used methods for recovery of silver from photographic waste are metal replacement and electrolysis. Electrolysis is capable of producing silver with high purity by suitable control of operating conditions. However, it is suitable only for silver-rich effluents and it is unable to reduce the silver levels below 100 mg/L. Electrolysis needs further treatment by ion exchange or metallic replacement to be acceptable [11,13]. Metallic replacement based on the use of more active metals than silver such as Fe, Al, Zn and Cu is an effective method for the recovery of silver [14,15]. A drawback of metal replacement is that the solution being recycled becomes contaminated by metal ions [16]. This method introduces metal impurities (e.g. Fe^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}) into the effluent and silver sludge produced is not pure and needs costly refinement processes [11]. Several chemicals including sodium sulphide (Na_2S), sodium dithionate ($Na_2S_2O_4$), potassium borohydride (KBH_4) and 2,4,6-trimercapto-*s*-triazine (TMT; C3N3S33-) have been used as precipitating agents to recover silver from waste photoprocessing solutions [17]. Silver can be readily recovered from the waste solutions by sulfide precipitation leading to the effluent silver levels as low as 0.1-1 mg/L. However, careful control of the precipitation process and sulphide dosing are essential to prevent the release of noxious hydrogen sulfide gas (H_2S) [11]. Consequently, there is a need for methods of silver recovery that are efficient, selective, and use environmentally benign materials or processes. A variety of new approaches are currently being explored, including adsorption onto agricultural by-products [18] and combining ultrasound with electrochemical methods [19]. Hydrogen peroxide with oxidizing and reducing properties under appropriate conditions is often regarded as a green chemical with no hazardous by products since it decomposes into only oxygen and water [20]. In addition, recently some simple procedures which benefit from simultaneous generation and applying hydrogen peroxide have been investigated [21,22]. Reduction of silver ion to metal by hydrogen peroxide appears to be thermodynamically feasible.

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Also, inorganic compounds, e.g., thiosulphate and sulphite, and organic compounds, e.g., formaldehyde and hydroquinone, which are abundantly present in the photoprocessing effluents [13], can be readily destroyed by hydrogen peroxide [23]. These environmental and technical attributes make hydrogen peroxide a potential alternative for the treatment of photoprocessing effluents.

In this work, the optimum conditions of pH, amount of H_2O_2 (ml/min), and ethylene glycol concentration for recovery of silver from radiographic film effluents were investigated using response surface methodology.

MATERIAL AND METHODS

1. Materials

A sample of X-ray film processing effluent obtained from *Shohada* Hospital (Tabriz, East Azerbaijan, Iran), Sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2, 33% w/w), ethylene glycol ($C_2H_6O_2$, ≥99%) was prepared from Merck, Germany.

2. Method of Silver Recovery

Experiments were conducted in 100-ml Erlenmeyer flasks. 50 ml of sample with the initial concentration of 9.25 g/L was used in each experiment. pH of the waste solution was adjusted using 4 M NaOH and H_2SO_4. Then first, 5 ml of hydrogen peroxide (33% w/w) was added and the flask sealed carefully. The flask was placed in a shaker incubator operating at 140 min^{-1} and 10 °C. After this step, due to the exothermic nature of the reactions, hydrogen peroxide was added at a predetermined rate of 0.2, 0.5, 1.0, 1.5, and 1.8 ml/min (according to the experimental design) for ten min. Precipitates were collected via filtration and washed twice with deionized-distilled water and then dried at 105 °C for 6 h [24]. The X-ray diffraction (XRD) pattern of the precipitate was determined using a D5000 diffractometer (Siemens German) with Cu K_α radiation source (λ=1.54056 Å) for study the kind and particle size of precipitate.

3. Experimental Design

A five-level, three-factor CCD was employed in this investigation. For three variables (n=3), the central composite design could be represented by points on a cube, with eight cubic points, six center points, and six axial points. In this case 20 experiments comprised the CCD and were performed in one block. Table 1 and Table 2 show the complete design matrix. In this study CCD design has been constructed using Design Expert (version 7) and Statistica (version 7). The factors in this experiment were amount of H_2O_2 (x_1) amount, pH (x_2), and ethylene glycol concentration (x_3). The mathematical relationship of the response (y) on the three significant independent variables x_1, x_2, and x_3 can be approximated by a nonlinear polynomial model including 3 linear, 3 squared, and 3 interaction of two factor terms

Table 1. The experimental factors and levels in the silver recovery

Factors	Parameter values				
	$-\alpha$	−1	0	+1	$+\alpha$
x_1: Amount of H_2O_2 (ml/min)	0.2	0.5	1	1.5	1.8
x_2: pH	3.37	4	5	6	6.63
x_3: Ethylene glycol concentration (ml/100 ml)	1.1	3	6	9	10.9

α=1.63

Table 2. Central composite experimental design

No.	X_1	X_2	X_3	Experimental response	Predicted response
1	1.0	5.0	6.0	92.0	89.7
2	0.5	4.0	9.0	82.5	82.3
3	0.5	6.0	9.0	85.0	85.9
4	1.5	6.0	3.0	72.0	73.9
5	1.0	5.0	6.0	85.0	85.7
6	1.0	5.0	6.0	85.2	85.7
7	1.0	5.0	6.0	85.5	85.7
8	1.5	4.0	9.0	70.0	68.6
9	0.5	4.0	3.0	56.0	53.5
10	1.5	4.0	3.0	53.0	54.3
11	0.5	6.0	3.0	59.0	60.3
12	1.5	6.0	9.0	72.0	78.8
13	1.0	5.0	1.1	67.5	65.6
14	1.0	5.0	6.0	85.5	85.9
15	1.8	5.0	6.0	65.0	64.4
16	0.2	5.0	6.0	59.0	61.2
17	1.0	5.0	10.9	92.0	92.9
18	1.0	5.0	6.0	85.1	85.9
19	1.0	6.6	6.0	80.0	78.6
20	1.0	3.7	6.0	55.0	56.9

and 1 intercept term, which have been shown in (Eq. (1)) [25,26]:

$$y = \beta_0 + \sum_{i=1}^{3}\beta_i x_j + \sum_{i=1}^{3}\beta_{ii} x_i^2 + \sum_{i=1}^{3}\sum_{j=i+1}^{3}\beta_{ij} x_i x_j \quad (1)$$

where y is the silver recovery percentage; β_0 is the constant coefficient; β_1, β_2, and β_3 are the linear effects of coded variables x_1, x_2, and x_3, respectively; β_{11}, β_{22}, and β_{33} represent quadratic effects; and β_{12}, β_{13}, and β_{23} represent the cross product effects or two factor interaction effects.

RESULTS AND DISCUSSION

1. X-ray Diffraction Pattern Analysis

X-ray diffraction pattern of the precipitate which was recorded at 2θ=5-70 degree has been depicted in Fig. 1. Four distinct peaks

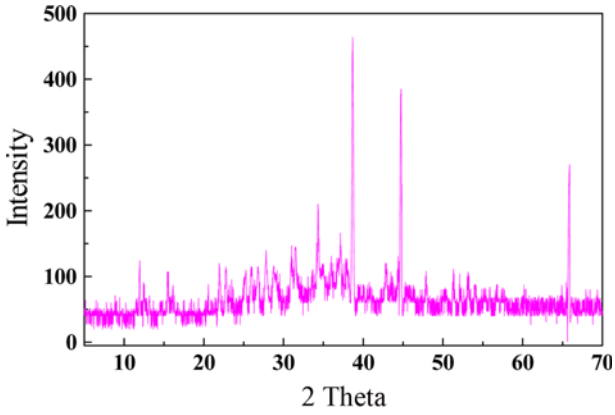

Fig. 1. XRD patterns of the silver particles.

are seen at 2θ=33.0, 38.0, 44.0, and 65.0. A peak at 2θ=33 is related to Ag_2S, and peaks at 2θ=38, 44, and 65 represent silver. So precipitate contains Ag_2S and Ag, but the intensity of Ag_2S peak is low; therefore, the most amount of precipitate is silver. Also, X-rays show the material to be highly crystalline. The average size of the silver particles was calculated from X-ray patterns by the Scherrer equation.

$$d=K\,\lambda/b_{hkl}\cos\theta \quad (2)$$

where d (nm) is the particle size, θ is the Bragg angle, K, is the constant of diffraction, λ (1.54056 nm), is the X-ray wavelength and b_{hkl} is the peak width at the half-maximum, corrected for instrument broadening. The average size of the silver particles was obtained around 20 nm.

2. Analysis of Variance and Pareto

The experiments were performed according to the central composite design arrangement considering amount of H_2O_2 (ml/min), pH, and ethylene glycol concentration as the selected variables. The design matrix by CCD and the experimental and theoretical results have been presented in Table 2. The application of the response surface methodology for these values yielded regression equation in coded form as follows:

$$y=86.21+4.66x_1+3.89x_2+3.52x_3-3.27x_1^2-2.11x_2^2 -0.57x_3^2+2.95x_1x_2-0.15x_1x_3+0.26x_2x_3 \quad (3)$$

where y is the response, silver recover percentage and x_1, x_2, and x_3 are the coded forms of variables referring to amount of H_2O_2 (ml/min), pH, and ethylene glycol concentration respectively. A positive sign for the coefficients in the fitted models indicates that the response increases by increasing the amount of that factor. Or on the other hand, response and that variable are consistent. A negative sign for the regression coefficient indicated that the ability of the reaction system was decreased with increasing that value [27].

The obtained experimental results were statistically treated using an analysis of variance (ANOVA) to study the goodness of fit. ANOVA results of this quadratic model are in Table 3. The probability-value (P-values) was used as a tool to check the significance of each coefficient. A commonly used cut-off value for the P-value was 0.05 (due to the 95% confidence level). A small probability-value suggests that the influence of the corresponding coefficient was significant. A P-value less than 0.05 at 95% confidence level indicates that term is effective in the model. The P-value analysis of the experimental design demonstrated that the linear, square, and interactive model terms were significant.

The test of reliability for predicting equation was carried out by Fisher's variance ratio test known as the F-test. The F-test is a hypothesis test that examines the ratio of two variances to determine their equality. If the model is a good predictor of the experimental results, the F-Value should be greater than the calculated value for a certain number of degrees of freedom in the model at determined level of significance [28,29]. Comparing calculated and tabled F-value (5.56< 19.42) implied the model was adequate. The F-ratio is given by the following form [30]:

$$F=\frac{\sigma_{res}^2}{\sigma_{rep}^2}\text{ with }\sigma_{res}^2=\frac{\sum_{i=1}^{N}(y_i-\hat{y}_i)^2}{N-L}\text{ and }\sigma_{rep}^2=\frac{\sum_{i=1}^{n_0}(y_i-\hat{y}_0)^2}{n_0-1} \quad (4)$$

Where σ_{res}^2 is the residual variance; σ_{rep}^2 is the replication variance; N is the total number of observations (N=20); L is the number of coefficients in the regression equation (L=9); y_i is the observed response for each observation and $\hat{y}_i$ is the estimated value of response for each observation; $\hat{y}_0$ is the average value of response for the central point and n_0 is the repetition number of experiments at the center work domain.

Also, the regression between experimental and theoretical responses confirms the model (Fig. 2). The value of the determination coefficient (R^2=0.972) showed a good t to the model and indicated that only 2.8% of the total variations were not explained by the model. The value of the adjusted determination coefficient (Adj. R^2=0.919) also conrmed that the model was highly signicant. A very low value of coefficient of the variation (C.V.) (5.3%) clearly indicated a very high degree of precision and a good deal of reliability for the experimental values.

The adequacy of the model was also evaluated by the residuals. The interpretation of the residual plots relevant to silver recovery would help to assess the strengths of the estimated model. The residuals provide a measure of the quality of the data analysis. The emphasis in the use of residual plots is usually on the use of some simple graphical techniques, which makes it possible to detect and explain the departures from assumptions used in developing the regression equations. The pattern of the straight line in the normal plot of the residuals implies the following: a normal distribution of the errors and

Table 3. Analysis of variance for silver recovery

Source	DF[a]	Seq SS[b]	Adj MS[c]	F	P
Regression	9	3027.57	336.39	19.22	0.000
Liner	3	1288.63	429.54	21.78	0.000
Square	3	1512.57	504.19	13.82	0.060
Interaction	3	226.38	75.46	4.07	0.005
Residual	9	328.25	36.47		
Lack-of-fit	5	293.70	58.74	2.94	0.920
Pure error	4	34.55	8.64		
Total	19	3358.71			
R^2=97.2%		R^2 (adj)=91.9%			

[a]DF=degree of freedom
[b]Sum of squares
[c]Adjusted mean square

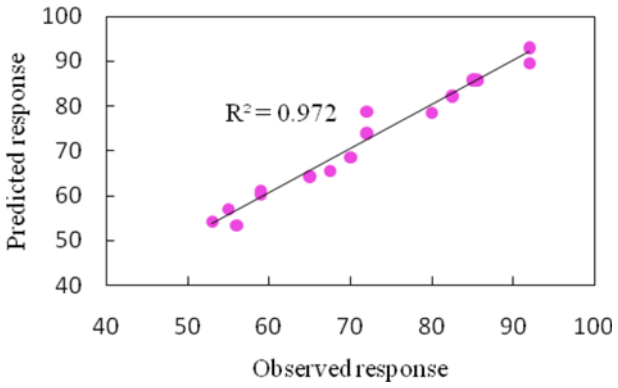

Fig. 2. Relation between predicted responses vs. experimental responses.

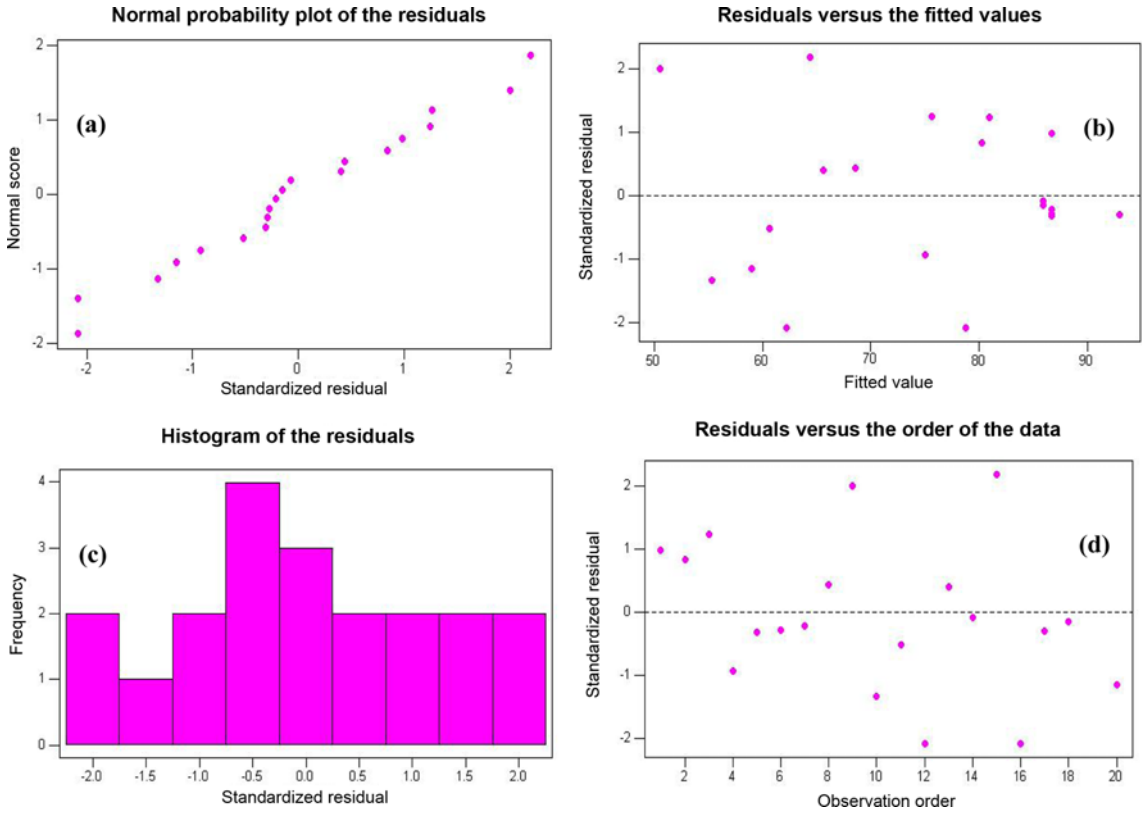

Fig. 3. Normal probability plots of the residuals.

adequacy of the least squares technique was confirmed; the data supported the constructed model (Fig. 3(a)). Residuals against the predicted values of the response showed an almost equal scattering pattern above and below the axis (Fig. 3(b)). The histogram of the residuals had approximately normal distribution (Fig. 3(c)) and the residuals versus the run order of the experiments according to the design of the experiment are helpful to show the random scattering of the residuals around zero (Fig. 3(d)). This informative approach implies that the constructed model was adequate [31].

The Pareto analysis was carried out to check the percentage effect of each factor. This analysis gives more significant information to interpret the results. This analysis calculates the effect of each factor according to following equation [32]:

$$P_i = \frac{(\beta_i)^2}{\sum(\beta_i)^2} \times 100 \mathrm{i} \neq 0 \quad (5)$$

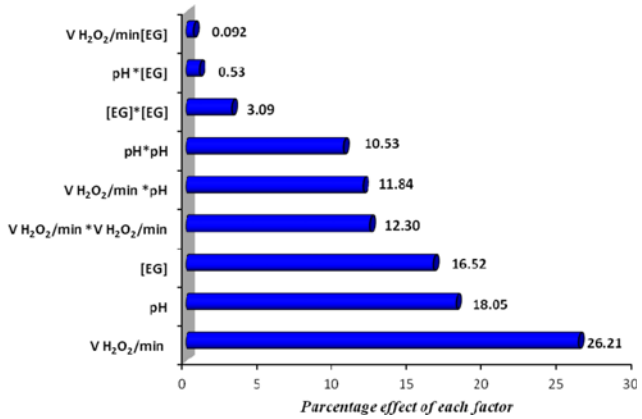

Fig. 4. Pareto analyses (percentage effect of each factor) for silver recovery.

All factors are not equally important; the amount of H_2O_2 is the most effective factor in silver recovery (Fig. 4).

The Bonferroni test, also known as the Bonferroni correction or Bonferroni adjustment, is a type of multiple comparison test used in statistical analysis. The degree of freedom for residuals according to the ANOVA table is 12. In this case, the critical t-value is 2.1788. A more conservative t-value, named after its inventor Bonferroni, takes the desired probability for the value of alpha (α) into account by dividing it into the number of estimated effects (Eq. (6)) [30]. For this research, nine effects are estimated, so the Bonferroni corrected P-value and according to the P-value, Bonferroni t-value was calculated by following equation and using the t-value chart:

$$t\left[\frac{(\alpha_2 - \text{tail} = 0.05)}{9}, \mathrm{DF} = 12\right] = t_{(0.006,12)} = 3.5824 \quad (6)$$

Based on Bonferroni limit and t value limit (Fig. 5), it was decided which terms are highly significant, which are reasonably significant, and which are not at all significant and may be removed from the model [33]. This analysis indicates linear terms and square effect of volume of H_2O_2 and interaction between volume of H_2O_2 and pH are highly significant, pH×pH is reasonably significant, and square effect of ethylene glycol concentration and interactions of pH× ethylene glycol concentration and ethylene glycol concentration× volume of H_2O_2 are not at all significant and should be removed

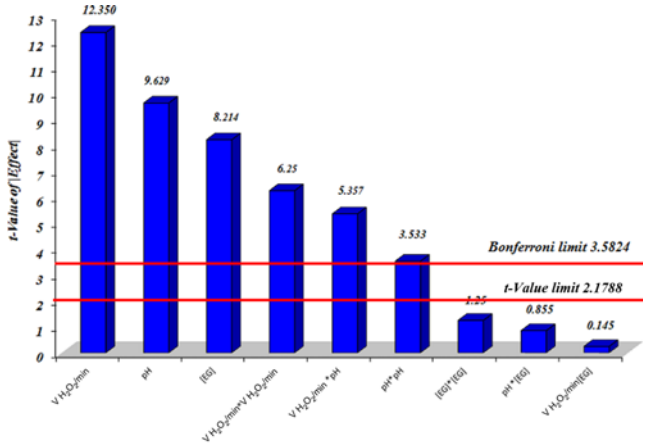

Fig. 5. Pareto chart: significance of factors by considering t-value.

from the model. Based on this analysis and P-values of terms, the model was refitted.

3. Refitted Model

Because terms of square effect of ethylene glycol concentration and interactions of pH× ethylene glycol concentration and ethylene glycol concentration×volume of H_2O_2 are not at all significant, they were removed. A reduced model was obtained. After refitting, the regression equation in coded form was as follows:

$$y=86.16+4.86x_1+3.91x_2+3.55x_3-3.28x_1^2-2.12x_2^2+2.97x_1x_2 \quad (7)$$

The new ANOVA analysis has been summarized in Table 4. P-value has been reduced and F test has been increased for the model but P-value and F test respectively increased and decreased for the lack of fit. R^2 increased to 0.979. These results indicate the adequacy of model has been improved.

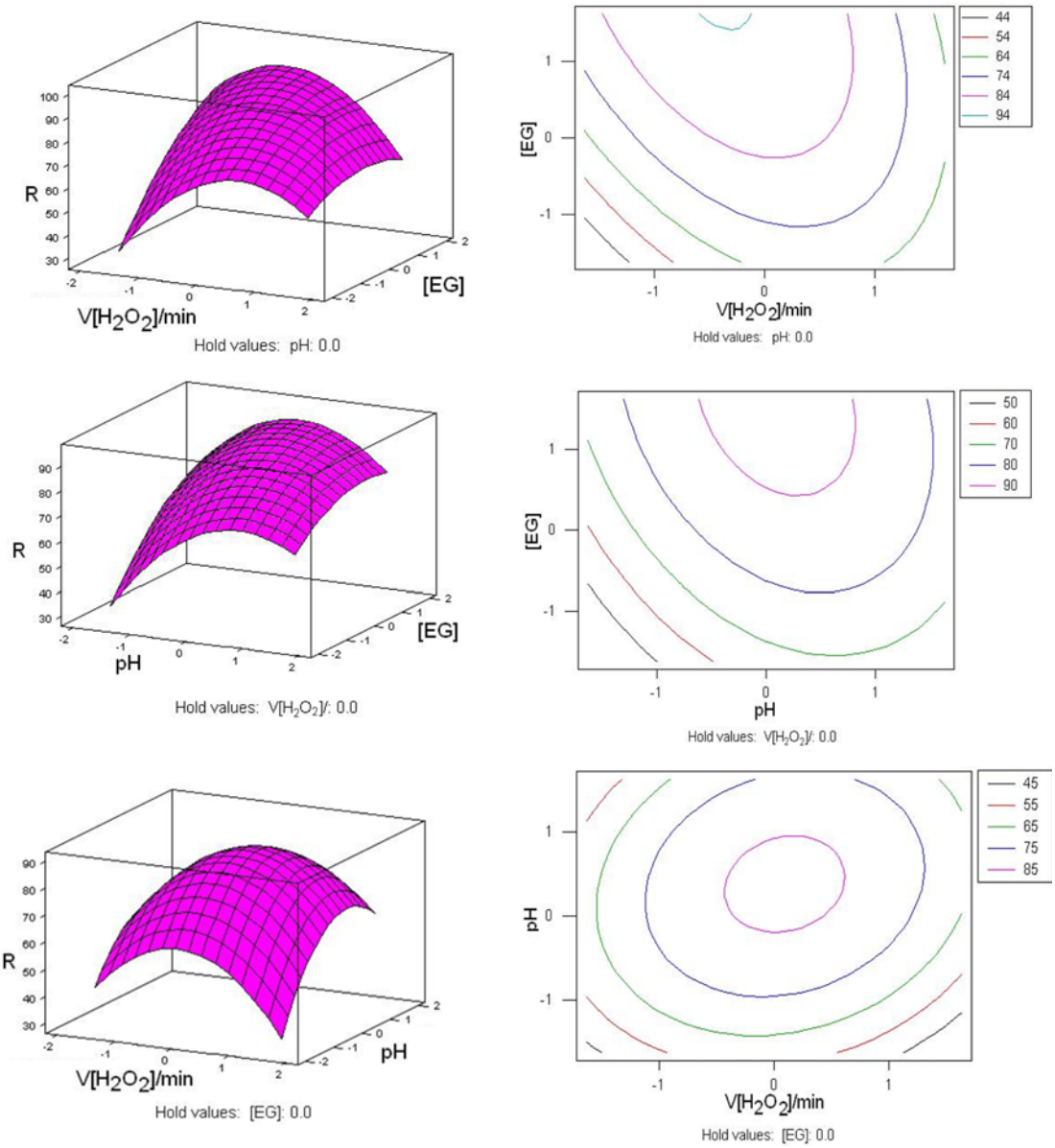

Fig. 6. Response surface (3-D) and contour (2-D) plots showing the effects of variables on response (in the plots two variables which don't exist on figure have been fixed in center level).

Table 4. Analysis of variance for silver recoveryafter refit

Source	DF[a]	Seq SS[b]	Adj MS[c]	F	P
Regression	6	2821.24	436.41	21.42	0.000
Liner	3	1241.33	413.91	22.71	0.001
Square	3	1579.45	516.48	13.92	0.002
Residual	12	405.30	33.77		
Lack-of-fit	8	317.76	57.24	2.65	0.966
Pure error	4	34.15	8.64		
Total	19	3232.67			
R^2=97.9%		R^2 (adj)=92.13%			

[a]DF=degree of freedom
[b]Sum of squares
[c]Adjusted mean square

4. Optimized Conditions

As we discussed in the previous section, the central composite experimental design and response surface methodology were used with three variables to evaluate their effects on investigating the effects of factors on the response [34]. Three three-dimensional surfaces and contour plots were drawn by considering two parameters variable at a time while keeping another at the central (0) level constant.

Graphical interpretation of three-dimensional and contour plots illustrated that the efficiency of silver recovery was increased in the volume of H_2O_2 0.8 ml/min, pH=5.5, 9 ml ethylene glycol.

Also, optimized conditions achieved by RSM were similar to the results of plots including volume of H_2O_2 1 ml/min, pH=5.5, ethylene glycol 9 ml in the experimental condition. In these conditions silver recovery percentage was estimated 92.8%. Experiments, with optimal parameters, were repeated three times. Silver recovery percentage was 91.5% and average of precipitate was 423.19 mg.

CONCLUSION

Hydrogen peroxide as a green chemical was used as a reagent for the treatment of X-ray photoprocessing effluents allowing the recovery of silver and removal of thiosulphate. Parametric optimization for recovery of silver from radiographic film effluents was done using response surface methodology and central composite design to determine the optimum conditions of pH, amount of H_2O_2 (ml/min), and ethylene glycol concentration. The optimum condition that was found isas follows: volume of H_2O_2 0.8 ml/min for 10 min, pH=5.5, ethylene glycol 9 ml in the experimental condition. In these conditions silver recovery percentage was estimated at 92.8%. Silver recovery experiments, with optimal parameters, were repeated in triplicate. Silver recovery percentage was 91.5% and average of precipitate was 423.19 mg, which was close to the predicted amount that was achieved by the model.

It was observed from the Pareto analysis that all of the variables do not have the same importance on response. The most important parameter is H_2O_2 volume, which was added to the reaction system per min. Square effect of ethylene glycol concentration, interactions of pH× ethylene glycol concentration and ethylene glycol concentration× volume of H_2O_2 are not at all significant in the silver recovery process.

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