Optimization of Silver Recovery from Used Radiograph Films (URF) via Sodium Hydroxide Stripping

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Abstract - The optimum conditions for the recovery of silver from used radiographic (X-ray) films (URF) by sodium hydroxide stripping was attempted using response surface methodology (RSM). From atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF) analyses, the URF had a silver purity of about 30.91% and a recoverable silver of 0.5845g Ag per 100g URF. Initial 2^k factorial experiments showed that NaOH concentration, reaction temperature and contact time were significant factors at 5% significance level. RSM-designed experiments confirmed the significance of these factors, and a quadratic model was obtained to relate the factors to the responses (silver recovery and silver purity). Numerical optimization on the model to maximize both silver recovery and purity yielded an optimum solution of 90^{o}C temperature, 1.75M NaOH concentration and 194 seconds contact time. Experimental verification showed 69.69% silver recovery with a reasonable difference of 12.62% from the predicted value. At optimum conditions, preliminary cost analysis showed that the recovery process costs ₱54.72, with profit of ₱39.26 per kilogram of film processed.

Keywords: *Silver Recovery; NaOH Stripping; Radiograph Films; Response Surface Methodology; Optimization*

I. INTRODUCTION

The use of x-ray radiation for visualizing the internal parts of the human body is an important tool for diagnosis, and an important milestone in modern medicine. The visualization of the image produced after x-ray radiation is made possible by the use of photosensitive radiographic films which contain an emulsion of silver bromide molecules.

Used radiographic films (URFs) after an x-ray procedure are produced in large quantities by hospitals and health institutions. These are usually incinerated after use. An estimated of two billion URFs are generated annually around the world; and these still contain about 1.5% to 2% of recoverable silver (Nakiboglu *et. al.*, 2003). The resource recovery of silver from these discarded wastes as a value-added product can be considered as an economic opportunity, as well as a sustainable alternative to managing a waste problem.

Two sequential steps are generally involved in the recovery of silver from URFs: (a) silver extraction from film via leaching to form silver-ion-rich solution, and (b) conversion/recovery of metallic silver from the silver-rich solution. Recovery methods range from mechanical, biological and chemical methods. Mechanical extraction is reported to be inefficient and impractical due to relatively low recovery yields. Biological and chemical processes, on the other hand, are more efficient and are widely used; however, these methods are slow and they generate toxic by-products (Jadhav & Hocheng, 2012).

To address these drawbacks, a novel approach was developed to recover silver from URFs via sodium hydroxide stripping (Nakiboglu *et. al.*, 2003). In this method, sodium hydroxide acts as a solvent for the dissolution of the silver ion impregnated in the film. At the same time, it acts also as a reducing agent in order to sequentially convert is into solid metallic form present as black solid residues. Mixing coagulates the silver residue into larger masses, which can easily be collected by decantation.

Being a novel process, limited amount of literature is available to develop the technology into a marketable and commercial scale; and certain research areas are yet to be explored, one of which is the optimization of silver recovery conditions. The optimization aspects of silver recovery from this novel process is the focus of this study.

In summary, the study intends to optimize the recovery of silver from used radiograph films using sodium hydroxide stripping; specifically, it aims to:

1. prepare and characterize used radiograph films in terms of silver content, and presence of other impurities;
2. conduct a two-level factorial experiment to determine the effects and level of significance of temperature, NaOH concentration, contact time, and films to NaOH volume ratio on the silver recovery yield;
3. generate statistical model equations that will describe the process via response surface methodology ;
4. determine the optimum conditions that will potentially give the highest silver recovery efficiency;
5. verify experimentally the predicted optimum conditions for the recovery of silver from URFs via NaOH stripping; and
6. provide a preliminary cost analysis based on the material balance of the process.

II. EXPERIMENTAL

The experimental design was done in two phases: (1) factorial experiments to assess factors that may significantly affect silver recovery, and (2) response surface methodology (RSM, via central composite design), in order to obtain a validated statistical model that can be used for numerical optimization. The factors considered were (1) temperature (70^{o}C and 90^{o}C), (2) sodium hydroxide dosage (0.5M and 2.5M), (3) contact time 60s and 210s), and number of films to NaOH volume ratio (37 and

44). The silver recovery response was quantified as percent solids recovery.

The metal composition of the URFs was analyzed by subjecting a batch of film samples to X-ray fluorescence (XRF) analysis. On the other hand, pre-weighed 4 cm x 4 cm strips of URF samples were immersed in NaOH solution under different conditions. After extraction, the spent films were removed from the solution. Whereas, the black residue in the resulting mixture was coagulated to form coarse solids using slow mixing under a water bath (90 to 95^{o}C). After coagulation, the liquid was decanted and the solid containing silver was transferred in a container. They were dried in an oven at 50^{o}C for one day and were weighed.

The dried solids were then contacted with ten milliliters of 10% v/v HNO_3 to completely dissolve the silver until bubbling stopped. The resulting solution was analyzed through atomic absorption spectrophotometry (AAS).

A statistical analysis software was used for the statistical analysis of the experimental data (Design Expert Version 10, Statease, Minnesota, USA, Serial Number: 1565-6362-7387-EVAL). Analysis of variance (ANOVA) was used to assess the significant factors affecting the silver recovery response in the factorial experiment. Numerical optimization was done to obtain possible optimum conditions. The selected optimum conditions were experimentally verified and were compared with the predicted response using ANOVA.

Preliminary costing was done through material balance and cost-benefit analyses. Among the factors considered were the cost of energy, input to heat the mixture, cost of reagents used, and the value of silver recovered in the current market.

III. RESULTS AND DISCUSSION

III. 1. Characteristics of used radiograph films

Characterization using AAS showed that 505 ppm of silver in the solution corresponds to 0.5845 g of silver per 100 g of films. This value differs from existing literature (1.5% to 2%) by 61.03%. Whereas, the XRF analysis reported that silver purity in the films was 30.91%, showing that silver was the dominant heavy metal in the URF sample. Potassium had the highest composition because it is present in the film base of the URF as part of the protein-rich layer of the gelatin.

Table. 1. X-ray fluorescence analysis of the radiograph films.

Element	Percent Composition (%)
Potassium	64.33
Silver	30.91
Zinc	2.06
Rubidium	1.38
Molybdenum	0.51
Thorium	0.39
Zirconium	0.30
Strontium	0.12

III. 2. Qualitative observations on silver recovery from URF via NaOH stripping

There were three observed stages in the extraction of silver from URF samples using NaOH stripping: (a) formation of the homogenous blue transparent films, (b) formation of black spent NaOH solution, and (c) coagulation of black residue from spent NaOH solution.

The black material from the URF samples were stripped off and this formed a black spent NaOH solution. The black suspension, afterwards, formed agglomerates which may be an indication of the coagulation of silver metals due to the presence of amino acids in the solution.

The coagulation was possible because of the amino acids produced from the hydrolysis of protein-rich gelatin layer in URF samples upon addition of NaOH. Particularly, the hydrolysis of amide group under basic conditions happens during coagulation via nucleophilic bimolecular substitution reaction (S_N2) (Stack Exchange Inc., 2016). The reaction produces negatively charged amino acids that serve as the coagulant for the positively charged silver suspension. The amino acids may also have been responsible for the black and gelatinous form of the aggregate solids.

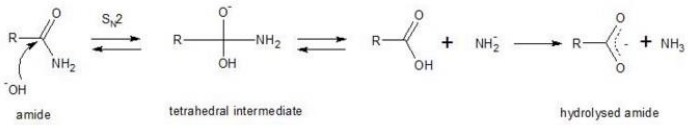


Fig. 1. Nucleophilic bimolecular substitution reaction of proteins (Stack Exchange Inc., 2016).

The dissolution of the solids with nitric acid caused intense bubbling until fine black solids were left in the test tube. The remaining fine black solids may have been composed of hydrolysed amino acids, thus cannot be dissolved by nitric acid. Images of the dissolution of solids with HNO_3 are shown in Figure 2.

(a) (b)

Fig. 2. Recovered solids (a) while and (b) after dissolution with 10% v/v HNO_3.

The decrease in the quantity of solids observed in Figure 2 may be attributed to the dissolution of silver into liquid phase. This was accompanied by the production of the colourless gas, nitrogen oxide, as indicated by the intense bubbling (Ozmetin *et. al.*, 2000). The corresponding reaction to support these observations is shown in equation 1.

$$4\ HNO_{3(aq)} + 3Ag_{(s)} \rightarrow 3\ AgNO_{3(aq)} + NO_{(g)} + 2\ H_2O_{(l)} \qquad (1)$$

III. 3. Results of the 2^k Factorial Experiment.

The analysis of variance of the factorial experiments showed that the process followed a square root model, with desirably insignificant lack of fit. The coefficient of determination (R^2) was found to be 0.9520, while the adjusted and predicted R-squared values of 0.9428 and 0.9273, respectively, were in reasonable agreement.

Among the factors, ANOVA also showed that the significant factors were temperature (A), concentration (B), and time (C) while the significant interactions were temperature's interaction with concentration and time (AB and AC). This relationship was further observed from the coded and actual equations generated from the statistical analysis shown in equation 2.

$$\sqrt{\%\ \text{Solids Recovery}} = 5.7561 + 1.0558A + 1.5224B + 1.7106C - 0.6701AB + 0.3622AC \quad (2)$$

Based on the equation, temperature, NaOH concentration, time, and interaction of temperature and time had positive effects on percent silver recovery, i.e., factors were directly proportional to the square root of the percent solids recovered. The interaction of temperature and concentration, on the other hand, decreased the recovery of solids. Among the factors, time had the highest level of significance, while the number of films to NaOH volume ratio was found to have insignificant effect on solids recovered. As a result, the number of films to NaOH volume ratio was removed in the response surface experimental design.

The findings from the ANOVA and coded equations may be explained by the collision theory, which states that the effectiveness of a chemical reaction is dependent on the number of collisions of reactant species and kinetic energy of the reactants in the system, as well as the reaction time (Levenspiel, 1999). Increasing the concentration of NaOH increased the number of particles to collide with the silver ion, thus increasing the silver recovered. The reaction temperature dictates kinetic energy of the molecules, thus, an increase in temperature increased the movement of the particles resulting to higher number of collisions, as well. Lastly, a longer reaction time will tend to promote collisions and thus more silver produced.

The positive interaction effect of time and temperature is also in agreement with the collision theory. However, despite the increasing trends of the main effects, the interaction of temperature and concentration was found to have a negative impact. This may have been affected by the heat released from exothermic reactions during the stripping process that raised the temperature of the liquid. For this we may consider that the final reaction temperature is associated with (a) the heat released from the reaction and (b) that associated external heating. If the change in temperature is proportional to the increase of concentration, then it may follow that the externally added temperature is unique for each treatment, i.e. for lower NaOH concentrations, more external heat should be added to raise the temperature in the reaction vessel, while lower external heat is added to higher NaOH concentrations. Therefore, even at higher NaOH concentrations, higher temperatures will not increase the formation of silver significantly. This may also have been the reason why temperature is ranked last based on the level of significance of the main effects.

Among the factors, the number of films to NaOH volume ratio was found to be insignificant. This may be due to the differences in the initial amount of recoverable silver present in every films since silver may not be homogenously distributed in URFs. Consequently, increasing the films to NaOH volume ratio may not necessarily ensure that the amount of recoverable silver also increases.

III. 3. Results of the response surface method experiments on silver recovery and solids purity.

Using the significant factors in the 2^k factorial experiments (temperature, time, and concentration), response surface experiments were conducted to determine the main effects, their interactions, and quadratic effects on silver recovery and purity.

The generated quadratic model was found to significantly best fit the data with a desirably insignificant lack of fit. The coefficient of determination (R^2) was found to be 0.863, while the adjusted and predicted R-squared, which were 0.800 and 0.667, respectively, were in reasonable agreement with each other.

The ANOVA showed that the significant factors were temperature (A), concentration (B), and time (C), while the significant quadratic interactions are concentration (B^2) and time (C^2). All interaction effects were found to be insignificant, too.

The quadratic model equations were determined using coded and actual values. The coded equation below was used to determine to assess relative dominance and magnitude of the factors on the responses.

$$\%\ \text{Silver Recovery} = 56.754 + 14.159A + 13.108B + 16.325C - 7.850BC - 8.121B^2 - 8.812C^2 \quad (3)$$

Based on the coded coefficients, the main effects (temperature, NaOH concentration, and time) gave positive effects on the response, which agreed with the factorial experiments. Meanwhile, the quadratic terms of concentration and time negative effects on silver recovery.

The negative impacts of the quadratic terms of concentration of sodium hydroxide and contact time may be due to the limiting conditions of the sodium hydroxide concentration, and the reaction time that can indicate the complete recovery of silver from the URF samples. Hence, silver in this case became the limiting reactant species.

Aside from silver recovery, the purity of the silver recovered was also investigated. A linear model was found to significantly best fit the data with insignificant lack of fit. The coefficient of determination (R^2) was found to be 0.649, while the adjusted and predicted R-squared, which were 0.584 and 0.500, respectively, were in reasonable with each other. In addition, the ANOVA, showed that the significant factors are temperature (A) and concentration (B) only. The coded coefficients are presented as an equation in equation 4:

$$\%\ \text{Silver Purity} = 39.61 + 10.64A + 16.67B + 7.36C \quad (4)$$

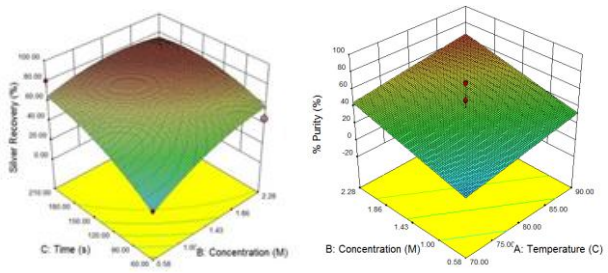
Temperature and concentration gave positive effects on the purity of silver. Amounts of silver in the solids increased due to the increase of concentration or temperature, which is true based on the collision theory. Whereas, increasing the temperature increases the acid dissociation constant (K_a) of amino acids, which decreases the pK_a values (Nelson & Cox, 2012). If the difference of the pH and pK_a expands, the deprotonated amino acids become more stable; hence, lesser amounts of amino acids are needed to coagulate the solids. Overall, the ratio of the silver to amino acids increases, as well as its purity.

III. 4. Numerical Optimization and Verification.

After having validated the statistical models for silver recovery and silver purity obtained from the RSM experiments, numerical

optimization was done with the following goal: maximizing silver recovery and purity.

The response surface graphs generated from the response surface are shown in Figure 4.



(a) (b)

Fig. 4. Response surface graphs for (a) silver recovery and (b) silver purity.

Among the forty-six possible optimum conditions, the treatment with the highest percent recovery and the lowest NaOH concentration was chosen: 90^{o}C, 1.75M, and 194s, which was predicted to yield 79.753% of silver recovery. The treatment was verified using a separate experiment in duplicate trials; they are summarized in Table 2.

Table 2. Verification experiments in silver recovery using optimum conditions.

Factors			Response (%)					
			% Silver Recovery			% Purity		
Temperature (^{o}C)	Concentration (M)	Time (s)	Actual	Pred	% Error	Actual	Pred	% Error
90.00	1.75	194	69.30 70.08	79.764	12.63	62.55 54.87	62.38	5.89

The optimum conditions recovered about 69.69% of the residual silver, with 58.71% purity. They are 12.63% and 5.89% different from the predicted value of the percent silver recovery and percent purity, respectively.

III. 5. Preliminary cost based on the material balance of the process.

The components considered for the preliminary costing were energy, NaOH and water. The costs considered were from sodium hydroxide and energy needed to heat the solution temperature from 25 ^{o}C to 90 ^{o}C. They are presented below as per mass basis in Table 2.

Table 2. Cost-benefit analysis of the optimized conditions of silver recovery.

Parameter	Price per kilogram of films (₱/kg)
Cost	
Energy	0.15
NaOH	7.01
Distilled water	47.56
Benefit	
Silver	93.97
Profit	39.26

The cost-benefit analysis showed that the process was very economical as it provided a high profit amounting to about ₱ 39.26 per kilogram of the films. However, there were still unaccounted costs to consider in this process. In industry scale, there are still costs coming from mixing, piping systems, and the fact that the output silver is still not ready for consumption.

IV. CONCLUSION

The 2^{k} full-factorial experiment showed that sodium hydroxide concentration, reaction temperature, and contact time were significant in the recovery process. Further, the response surface experiments show that the process can be represented in a quadratic model, which was used for optimization. Numerical optimization on the model to maximize both silver recovery and purity yielded an optimum solution of 90^{o}C temperature, 1.75M NaOH concentration and 194 seconds contact time. Experimental verification showed 69.69% silver recovery with a reasonable difference of 12.62% from the predicted value. At optimum conditions, preliminary cost analysis showed that the recovery process costs ₱54.72, with profit of ₱39.26 per kilogram of film processed.

The optimum conditions showed that the process is efficient and cost-effective in terms of silver recovery; however, recovery and purity can still be improved. Likewise, further studies must be conducted to support the limited amount of literature to develop it into a commercial scale. Nonetheless, this novel technology provides a high potential in assisting solid waste management systems, particularly on hospital wastes.

V. ACKNOWLEDGEMENT

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