Silver Recovery from X-ray Film Waste by Leaching and Precipitation Method Using Sodium Hydroxide and Sodium Sulfide

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Abstract

Silver recovery study from X-ray film waste by leaching and precipitation method using NaOH and Na_2S aims to determine the optimum conditions in silver recovery. The parameters optimated in this study were concentration of the precipitants, leaching temperature and effect of the type of precipitants on the precipitation time. The results showed that the NaOH and Na_2S precipitants were able to recover silver optimally at the concentration of 1.5 M. The optimum leaching temperature of the film with the Na_2S to recover silver was at 25 ^{o}C, whereas in the NaOH the film leaching temperature only affected time of precipitation. Therefore, the formation of precipitate using Na_2S was more efficient than NaOH, however the acquisition of silver was better in the use of NaOH than Na_2S.

1. INTRODUCTION

X-ray film has important role in medical use, especially in radiology. This film is widely used in providing a description of the anatomy of the body to diagnose whether there are abnormalities in the body or not. To get its picture, film processing is required. Icky (2011) stated that the processing of x-ray films consists of several stages, namely generating, rinsing, fixing, washing and drying. Among those stages, a very important stage in the formation of images on X-ray films is the Fixation.

The fixation stage in the processing of film, causing the silver halide compound (AgBr) in the film bound and formed shadows on the film. This fixation process uses a binding solution named Fixer. Fixer solution is a chemical in the form of concentrated liquid which function is to dissolve silver halides in films that are not activated by light (Goaz and White, 1982). The X-ray film that has been processed leaves quite a lot of unexposed silver halide compounds. X-ray film is a double emulsion film consisting of transparent base material with adhesive coating, light sensitive emulsion, and protective coating on both surfaces (armymedical.tpub.com). Every 1 m^2 of X-ray film that has been used or has been exposed to light contains about 3-3.5 g of silver. Whereas intact or unexposed X-ray films have an average silver content of 4-6 g / m^2 (Khunpraset, 2008). This relatively high silver content would be beneficial if recovered perfectly with high percent recovery.

The relatively high silver content in the fixer solution and in the X-ray film can be grouped as B3 waste if it is discharged into the environment. The maximum limit of silver waste that can be discharged into the environment is 5.0 g / L (PP no.85, 1999 about TCLP). Therefore, a recovery of fixer solution or x-ray film waste is needed.

There are several methods to recover silver from waste fixer solution including: metal replacement, electrolysis, and precipitation. The precipitation method is carried out by mixing fixer waste or x-ray film with precipitant material (Kesumayadi, 2015). Some precipitant that can be used consist of

Oxalic Acid, NaOH, and Na_2S (Kesumayadi, 2015; Syed, 2002; Nakiboğlu, 2003).

The results of Kesumayadi's research (2015) showed that the precipitation method using NaOH and Na_2S with each 2M concentration, produced 16 g and 25 g silver respectively from 5 liters of saturated fixer solution waste. The use of NaOH or Na_2S as precipitating agent is due to the ability of sulfide and hydroxide which are effective for depositing silver (Lange and Triebel, 2000). The advantages of precipitation method using sodium hydroxide and sodium sulfide is because of its economical value (Kesumayadi, 2015), and its ease in the formation of deposits with silver elements based on the value of the results of its solubility (Chang, 2005). However, there is still few research conducted on the application of this deposition method to X-ray films, especially for the use of Na_2S as precipitating material. In fact, based on the Ksp Na_2S value which is very small (Svehla, 1985), Na_2S is considered to be very effective for depositing silver.
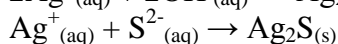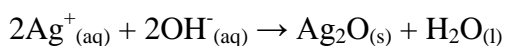
Other research conducted by Syed (2002) and Canda (2017), focused on the leaching method in recover silver from X-ray films. Syed (2002) reported that from 4 kg of X-ray film silver recover was successfully performed with recovery percentage of 97% (41 g) under optimal condition using oxalic acid. However, the use of oxalic acid as a precipient in this leaching method can cause the formation of dangerous and explosive compounds, namely silver oxalate. Canda *et al.,* (2017) conducted a study to recover silver from X-ray films using Aqueous NaOH Solution. The silver obtained was 6.54 g from 1 kg of X-ray film. However, this study only focused on using one reagent, NaOH. Beside that, his research also focus on the effect of NaOH concentration to the film's leaching time.

Therefore, based on those problems this study aims to recover silver from X-ray film waste by using NaOH and Na_2S reagents.

2. MATERIALS AND METHODS
Materials and Instrumentation
The Instrumentation used in this study are beaker glass and magnetic stirrer. Analysis of silver content (ppm) in the filtrate are using Atomic Absorption Spectroscopy (AAS). Analysis of silver content in precipitate was determined using XRF. The material used in the study was X-ray film waste from one of the clinical laboratories in Bandung.

Procedures
The study of silver recovery from X-ray film waste consists of 3 stages. The first stage was the leaching of X-ray film $2x2$ cm^2 using precipitating reagents. The film was dissolved with 2 different types of reagents, NaOH and Na_2S. The concentration of NaOH used was 1M; 1.5M; 2M; 2.5M, and the concentration of Na_2S used was 1.5M; 2M; 2.5M; 3M; 3.5M. The second stage was the deposition of leaching product for 48 hours. Then the separation of precipitated solution was carried out to obtain precipitate and filtrate. The third stage was analysis. These experiment was one time repeated because the limitation of materials.

The precipitate was weighed to determine its mass then burned, while the filtrate was analyzed with AAS to determine the remaining silver content. Part of the precipitate from each reagent was used for the analysis of the silver content using XRF.

The maximum concentration and leaching temperature was determined based on precipitate mass, while the optimum concentration and leaching temperature is determined based on the remaining silver content in the filtrate.

3. RESULT AND DISCUSSION
Theoretically the silver recovery method in this study is based on the precipitation reaction between NaOH and Na_2S with silver which can produce silver (I) oxide (Ag_2O) and silver (I) sulfide (Ag_2S) (Svehla, 1985), according to the following reaction equation 1 and 2.

This precipitation method is used based on the fact that silver compounds easily precipitate in the presence of hydroxide and sulfide ions in water at 25 ^oC (Chang, 2008).

$$2Ag^+_{(aq)} + 2OH^-_{(aq)} \rightarrow Ag_2O_{(s)} + H_2O_{(l)}$$
$$Ag^+_{(aq)} + S^{2-}_{(aq)} \rightarrow Ag_2S_{(s)}$$

$$K_{sp} = 1.52 \times 10^{-8} \qquad (1)$$
$$K_{sp} = 6.0 \times 10^{-50} \qquad (2)$$

Leaching Results

The perfect leaching of the film by the precipitating reagent marked by colour changing of the film from purple to transparent blue (Canda *et al.,* 2018). Based on experiment conducted on the process of leaching 2x2 cm^2 x-ray film using Na_2S reagent at various concentrations and temperatures, the results showed the time required to leach 2x2 cm^2 X-ray film has tendency to be faster as concentration of Na_2S reagent and leaching temperature increased. However, the leaching time was not affecting the obtained silver or precipitate. This was because the leaching only produces brownish black suspension of silver halide with precipitant, not producing a precipitate or silver. The time of dissolution of X-ray films with Na_2S on various concentrations and temperature is presented in Tables 1 and 2. The data was obtained by making one of the variable constant. The time of dissolution of X-ray films with NaOH at various concentrations and temperatures is presented in Tables 3 and 4.

Table 1. Time data of the X-ray films leaching using Na_2S with variation of concentration in room temperature

Film mass (g)	Na_2S Concentration (M)	Leaching time (Minutes)
50	1.5	42
50	2	32
50	2.5	15
50	3	14
50	3.5	13

Table 2. Time data of X-ray film leaching using 1.5M Na_2S with variation of temperature

Film mass (g)	Temperature (^{o}C)	Leaching time (Minutes)
25	25	15
25	40	12
25	60	11
25	80	10
25	25	15

Based on table 1 to table 4, in NaOH reagent, the leaching time also offered the same tendency with the Na_2S reagent, the increased concentration and temperature offered the faster time required to leach the X-ray film. Based on the result of Canda's research (2017), the optimum concentration and leaching temperature using NaOH reagent was 1.5M with the temperature above 60 ^{o}C. However, Na_2S could leach film slightly more efficient than NaOH. This is due to the smaller Ksp of Na_2S, so that the formation of precipitate is more efficient. In addition, in the formation of Ag_2O where Ag_2O is also formed from AgOH equilibrium, the ability of OH^- to bind Ag is smaller than the ability of S_2^- bind Ag as shown in the equations (1) and (2).

Table 3. Time data of the X-Ray film leaching using NaOH with variation of concentration in room temperature

Film mass (g)	NaOH Concentration (^{o}C)	Leaching time (Minutes)
50	1	80
50	1.5	45
50	2	36
50	2.5	25

Table 4. Data on the time of X-ray film leaching using 1.5M NaOH with variation of temperature

Film mass (g)	Temperature (^{o}C)	Leaching time (Minutes)
25	25	24
25	40	20
25	60	15

Precipitation Results

The precipitation process with NaOH and Na_2S can produce Ag_2O and Ag_2S precipitate (Svehla, 1985), following the equation (1) and (2). In the study that has been done, two types of precipitate from the results of perfect precipitation and separation was obtained, one was black precipitate and other was gray colored precipitate.

Based on the literature (Svehla, 1985), the precipitate obtained is successively in accordance with the characteristics of Ag_2S and Ag_2O precipitate. The precipitate obtained was burned using a flame gun to obtain pure silver. In addition, some precipitate were

analyzed using X-ray fluorescene (XRF) to determine the silver content. The filtrate was then analyzed using Atomic Absorption Spectroscopy (AAS) to further analysis on the possibility of silver in the filtrate that might not precipitate.

The weighted mass of the precipitate obtained and the results of the analysis of the filtrate using AAS were used as a reference to determine the optimum concentration of the precipitation and the optimum temperature of the leaching.

Effect of NaOH Concentration on Silver Recovery

In determining the effect of concentration on silver recovery, the precipitate mass obtained and filtrate analyzed using AAS are the variables that determine the optimum concentration. In determining the optimum concentration of NaOH with variations of 1 M, 1.5 M, 2 M, and 2.5 M concentrations, the results showed that the most precipitate obtained was at 1.5 M concentration with a total precipitate of 1.9018 g from 50.0765 g of X-ray film, and based on analysis silver content in the filtrate using AAS, 1.5 M NaOH concentration is the most effective reagent also in recovering silver from the film, which leaves silver in the filtrate as much as 12 ppm. The results of the precipitate mass and silver content in the filtrate show the appropriate data alignment, so based on these results, the optimum concentration of NaOH for silver recovery is 1.5 M. This result was corresponding with the literature (Canda *et al*., 2017) that the optimum concentration is 1.5 M. Table 5 shows the data obtained from the precipitation and analysis of silver content in the filtrate using AAS.

Table 5. Data of precipitate mass and silver content in filtrate using NaOH with variations of concentration

Film Mass (g)	[NaOH] (M)	Precipitate Mass (g)	Silver in Filtrate (ppm)
50	1	0.8346	26.16
50	1.5	1.9018	12
50	2	1.7249	33.84
50	2.5	1.1611	30.16

The data obtained pointing to the deficiency that after concentration of 1.5 M NaOH the next precipitate mass will be decrease. Therefore, the optimal NaOH concentration which can obtain optimal precipitate mass is 1.5 M. The following plot data on the concentration of NaOH with the precipitate mass obtained.

Effect of Na$_2$S Concentration on Silver Recovery

In the use of Na$_2$S, the maximum precipitate mass was obtained at concentration of 2.5 M, which was 1.0499 g. While the minimum precipitate mass was obtained at the concentration of 1.5 M. However, based on the analysis of silver content in the filtrate using AAS, showed that the most recovered silver was at a concentration of 1.5 M not at the concentration of 2.5 M. This means that in the use of Na$_2$S reagents, the mass of precipitate obtained did not associate with recovered silver. This was because in the precipitate, it is possible to form sulfur precipitate as impurities, where the number of this imputrities affects the mass of the precipitate obtained. The existence of sulfur precipitate is also proven by the presence of yellow precipitate when the precipitate burned using a flame gun. Therefore, the optimum concentration of Na$_2$S reagent is at the concentration of 1.5 M. This result can not be compared with the literature (Kesumayadi, 2015), because the concentration of Na$_2$S used was one concentration (2 M). The following presented data shows the association between the mass of precipitate obtained and the silver content in the filtrate using Na$_2$S precipitant in table 6.

Table 6. Data of precipitate mass and silver content in filtrate using Na$_2$S with variations of concentration.

Film Mass (g)	[Na$_2$S] (M)	Precipitate Mass (g)	Ag in Filtrate (ppm)
50	1.5	0.3151	1140
50	2	0.4513	2560
50	2.5	1.0499	2212
50	3	0.5973	2411
50	3.5	0.7657	2179

Effect of NaOH Precipitation Temperature on Silver Recovery

Based on the results obtained in table 7, in the use of NaOH, the optimum silver recovey was at leaching temperature of 80 ^{o}C, with the remaining silver content of 2.6 ppm. These results are seen based on the silver content remaining in the filtrate only, the mass of the precipitate obtained using NaOH reagent with the film leaching temperature did not show significant effect. This result was corresponding with literature (Canda *et al.,* 2017) that the optimum temperature was above 60 ^{o}C. The following data on table 7 shows the association between precipitate mass and silver content in the filtrate at temperature variations.

Table 7. Data of precipitate mass and silver content in filtrate using NaOH with variation of leaching temperature

Film Mass (g)	Temperature (^{o}C)	Precipitate Mass (g)	Ag in Filtrate (ppm)
25	25	0.6509	3
25	40	0.6686	8
25	60	0.6336	4.17
25	80	0.6756	2.6

Effect of Na$_2$S Precipitation Temperature on Silver Recovery

Table 8. Data of precipitation mass and silver content in precipitate using Na$_2$S with variations of leaching temperature.

Film Mass (g)	Temperature (^{o}C)	Precipitate Mass (g)	Ag in Filtrate (ppm)
25.0060	25	0.5972	1019
25.0051	40	0.7269	1112
25.0041	60	1.0848	1146
25.0003	80	0.9881	1490

In the use of Na$_2$S reagent, the optimum leaching temperature was at 25 ^{o}C. Where based on the silver content in the filtrate at room temperature, the remaining silver was equal to 1019 ppm, while the optimum mass obtained by leaching was 60 ^{o}C with a mass of 1.0848 grams. However, the mass gain of these precipitate was not entirely proportional to the amount of silver recovered in the use of Na$_2$S reagent. That is because of the possibility of the formation of sulfur precipitate that affect the mass of the precipitate. Therefore the optimum leaching temperature with Na$_2$S precipitating was at 25 ^{o}C. Table 8 shows the association between the precipitate mass obtained and the remaining silver content in the filtrate with the Na$_2$S reagent with variations of temperature.

Effect of Precipitant Types on Precipitation Time

The precipitation time of the leaching product was affected by the type of precipitant used, that is NaOH and Na$_2$S. Based on the comparison results obtained, Na$_2$S reagent can precipitate faster than NaOH reagent, where the time required to completely precipitating product was two days for sodium sulfide, and 7 days for sodium hydroxide. The rate of precipitation was influenced by the Ksp of Ag$_2$S and Ag$_2$O, where the K$_{sp}$ Ag$_2$S value is smaller than the Ksp Ag$_2$O, which is 6.0 x 10^{-50} and 1.52 x 10^{-8}, respectively.

Table 9. Data comparison of precipitation time on NaOH and Na$_2$S

Reagent Type	Precipitation Time (days)	Precipitate Mass (g)	Ag in Filtrate (ppm)
NaOH	7	1.9018	1140
Na$_2$S	2	0.3151	12

The smaller K$_{sp}$ results in the faster formation of precipitate. However, faster precipitation time did not affect the amount of silver recovery in the use of Na$_2$S. If the silver was recovered based on precipitate mass and the remaining silver content in the filtrate, NaOH reagents are better than Na$_2$S reagents. That was because there is protonation in the Na$_2$S ionization reaction, which produces H$_2$S. So that the formation of Ag$_2$S precipitate is less than the formation of Ag$_2$O. Therefore, in the filtrate with Na$_2$S precipitant, the non-recoverable silver was still more than the NaOH precipitant. The following table 9 compares the precipitation time of optimum NaOH and Na$_2$S concentrations.

Results of XRF Analysis on Solids of NaOH Reagents

The precipitate analyzed was the result of precipitation with the 2.5 M NaOH reagent. The analysis showed that in the precipitate there were no other elements besides Ag and Br. The mass percentages of Ag and Br were 58.09% and 41.91%, respectively. The following data shows the results of the precipitation analysis of the 2.5 M NaOH precipitant in table 10. These results state that there are no other impurities other than Br in the precipitate which interfere the precipitate mass.

Tabel 10. Data percentage of elemental masses in precipitate with NaOH precipitant

Element	Mass%	I-error%
Ag	58.09	1.01
Br	41.91	0.30

Results of XRF Analysis on Solids of Na_2S Reagents

In contrast to the results of XRF analysis on the precipitate using NaOH, the precipitates of Na_2S contained S element content as much as 47.85%, Ag 50.35%, and Br 1.80%. The existence of this element S is possible to form Ag_2S precipitate or Sulfur precipitate. Following are the results of XRF precipitation analysis and spectra with Na_2S precipitant in table 11 and figure 1.

Tabel 11. Data percentage of elemental mass in precipitate with Na_2S precipitant

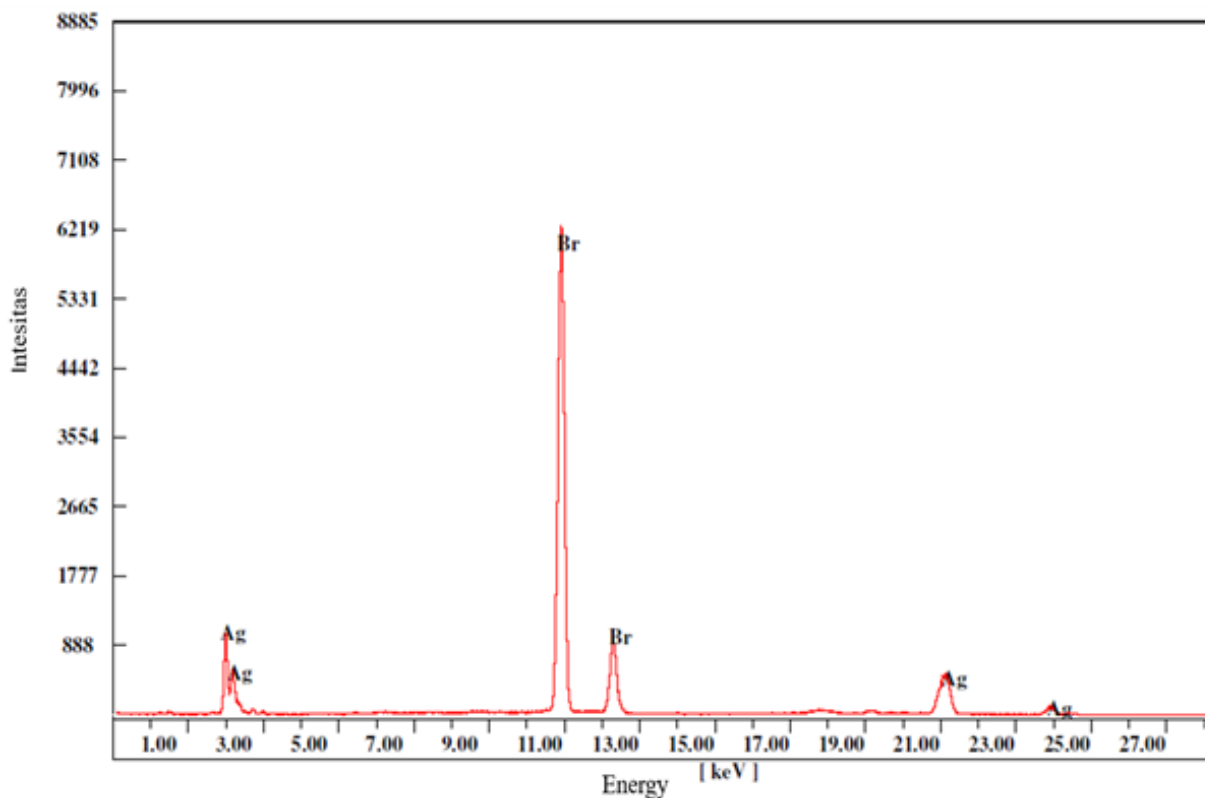| Element	mass%	I-error%
Ag	50.35	2.03
S	47.85	2.34
Br	1.14	2.98

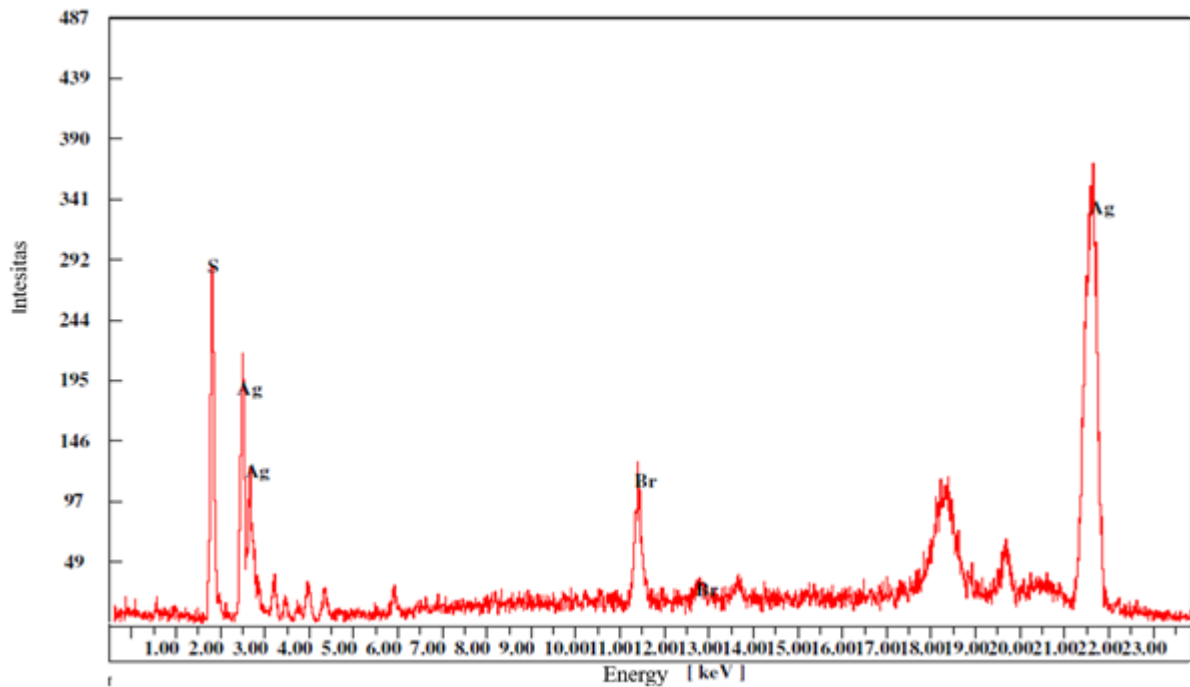**Figure 1.** The spectra resulting from XRF analysis on NaOH precipitant

Figure 2. XRF spectra of precipitate with Na_2S precipitant. XRF spectra of precipitate with Na_2S precipitant

4. CONCLUSION

The optimum concentration of NaOH and Na_2S in silver recovery from X-ray film waste by precipitation method was both at the concentration of 1.5 M with the leaching temperature of the NaOH precipitant did not significantly affect the silver recovery. Whereas in the Na_2S precipitation the leaching temperature significantly influences the recovery silver, it can precipitate the leaching product faster than NaOH, but resulted in the acquisition of less silver than the NaOH.

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