# APPROPRIATE TECHNOLOGY FOR SILVER REMOVAL AND RECOVERY FROM SPENT BLEACH-FIX PHOTOGRAPHIC SOLUTION

Chavalit Ratanamskul, Komsan Lertviriyaprapa and Pirun Saiyasitpanich

*Department of Environmental Engineering,Chulalongkorn University*
*Payatai Road, Patumwan, Bangkok 10330, Thailand*

## ABSTRACT

Two methods of silver removal and recovery from spent bleach-fix photographic solution containing a very high silver concentration of 5,500 mg/.l were investigated here. They were a chemical precipitation method using sodium hydroxide and a metallic replacement method using an iron waste from industrial manufacturing process. It was found that in the case of chemical precipitation, the percentages of silver recovery were 25, 63.98, 74.24, 84.89 and 95.94 at pHs of 9, 10, 11, 11.5 and 12, respectively. In the case of application of steel wool as waste from industrial manufacturing process, it was found that The recovery percentages of silver were in the range of 98.8 to 99.8 % at a steady state condition of the operation. The mechanism of silver recovery by the iron waste was expected to be a metallic-replacement mechanism.

In summary, two methods for silver recovery were feasible to be applied. However, the metallic replacement method using iron waste is preferable since it does not need any chemical addition and can achieve higher silver recovery percentage. Moreover, another advantage of this method is that it can be a possible way for recycling the waste from industrial process as a waste-minimization strategy.

**Keywords:** Silver recovery, spent bleach-fix photographic solution, chemical precipitation, metallic replacement, steel wool

## INTRODUCTION

Nowadays, an appropriate disposal method for spent bleach-fix photographic solution from photographic business is still needed to be investigated for a practical application in Thailand. The spent solution is either disposed into public water sources without an appropriate treatment or collected by waste buyers, who do not have a systematic knowledge of waste recovery and disposal methods. Since the spent solution has a concentration of silver as high as 2,000-5,5000 mg/l, an appropriate treatment technology to recover silver in the wastewater for further reuse and recycle before discharging into the environment is considered to be an urgent issue. Here, silver is in the form of silver halide, used as a light-sensitive emulsion. In this research two methods of chemical precipitation and metallic replacement using steel wool were selected to know the treatment feasibility for silver recovery from the spent bleach-fix photographic solution.

## MATERIAL AND METHODS

*Bleach-fix photographic solution characteristics*: the solution obtained from a photographic shop has a main composition of potassium ferricyanide, potassium ferrocyanide, potassium bromide and silver. Silver concentration in the solution was in the range of 2-6 g/l. the variation depends on the reuse of solution and light-sensitivity of film and paper. The pH of the solution was about 5.9.

*Jar-test experiment*: The jar-test experiment was done after pH adjustment of the spent solution. The mixing speed was controlled to be a rapid mixing of 100 rpm for 15 minutes, following by a slow mixing of 40 rpm for 20 minutes.

*Chemical precipitation method*: The experiment was done with the jar-test experiment. Sodium hydroxide is used to adjust pH of the solution to the pH range of 9-12, which is expected to be an optimum pH range for silver precipitation. The effluent was collected after steady state to measure the concentration of residual silver.

Metallic replacement method: Steel wool was employed to cause the replacement reaction between iron and silver in the bleach-fix photographic solution. The study with this method was carried out into three experiments as follows:

1) *Effect of mass of steel wool on silver recovery:*

The feed pH of the spent bleach-fix photographic solution was 5.9 as the original feed pH value. The mass of steel wool was varied to be 25, 50,75 and 100 g iron, however, the volume of the spent solution was always kept at 500 ml.

2) *Effect of operating pH on silver recovery:*

Amount of steel wool used in this study was fixed at 100 g iron: volume of the spent solution at 500 ml with variation of feed pH values in the range of 3-9.

3) *Effect of dissolved oxygen concentration on silver recovery:*

The iron mass of steel wool was 50 g iron. The spent solution of 500 ml having the original feed pH of 5.9 was prepared with the variation of dissolved oxygen concentration to be 0.75,2.2, 3 and 4 mg/l.

## RESULTS AND DISCUSSION

### 1) Chemical precipitation method for silver recovery

The principle of chemical precipitation applied here is to form a precipitate of Ag(OH)2 by sodium hydroxide for pH adjustment. Fig.1 shows that an increase in pH of the spent solution from 9 to 12 resulted in an increase in silver-removal percentage from 25 to 94. The optimum pH for the treatment of spent solution by this method should be higher than 11 to achieve removal percentage of higher than 80%. Moreover, the amount of sludge production did not increase higher than 560 ml when the pH of the spent solution was higher than 11 as shown in Table 1.

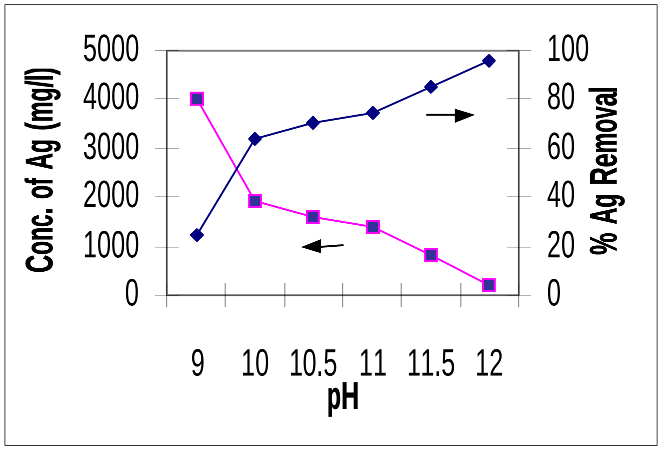


Fig.1 Effect of pH on Ag recovery by chemical precipitation method

Table 1 Sludge production of silver hydroxide as a function of pH

| pH | Amount of sludge prodution (ml) |
|---|---|
| 9 | 100 |
| 10 | 350 |
| 10.5 | 550 |
| 11 | 560 |
| 11.5 | 560 |
| 12 | 560 |

## 2) Application of steel wool in metallic replacement method

### 2.1) Effect of mass of steel wool on silver recovery

Since iron in steel wool is responsible for silver recovery by metallic replacement mechanism, increasing iron mass tends to increase silver recovery as the residual concentration of silver decreased significantly as shown in Fig.2. A very high removal percentage of more than 99% could be achieved with this method, though the spent solution pH was as low as 5.9. Therefore, the metallic replacement using steel wool does not require pH adjustment as required by chemical precipitation.

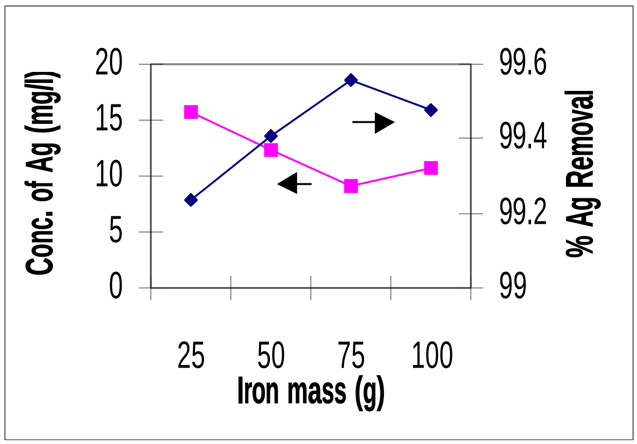


Fig.2 Effect of iron mass on Ag recovery using steel wool

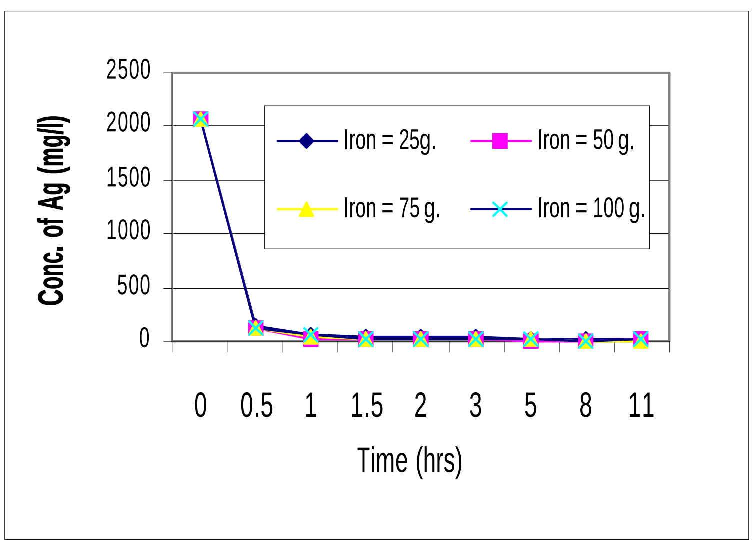


Fig.3 Time scale of Ag reduction in the spent solution

Moreover, the time scale of silver reduction in the spent solution with the metallic replacement method is shown in Fig.3. It was found that silver concentration decreased very rapidly within 0.5 hours with all range of iron mass from 25 to 100 g iron in the spent solution of 500 ml. This means that the reaction between silver and iron in steel wool is a very fast reaction. It seems that iron mass of at least 25 g iron was rather enough for the spent solution of 500 ml.

### 2.2) Effect of operating pH on silver recovery

The effect of operating pH on silver recovery by metallic replacement using steel wool is shown in Figs.4 and 5.

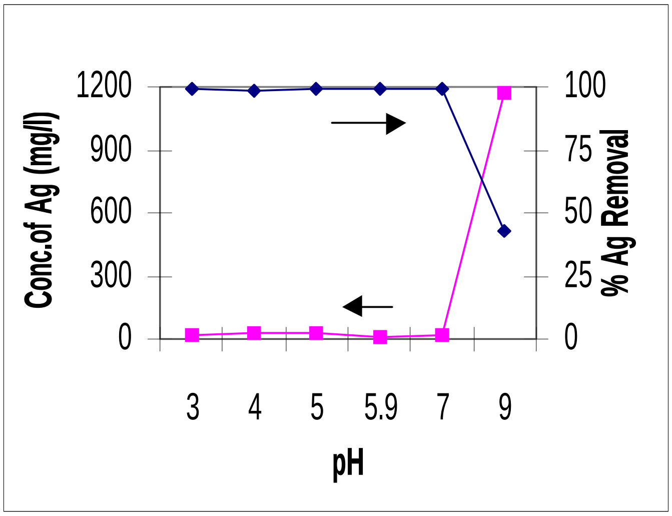


Fig.4 Effect of pH on Ag recovery by metallic replacement using steel wool

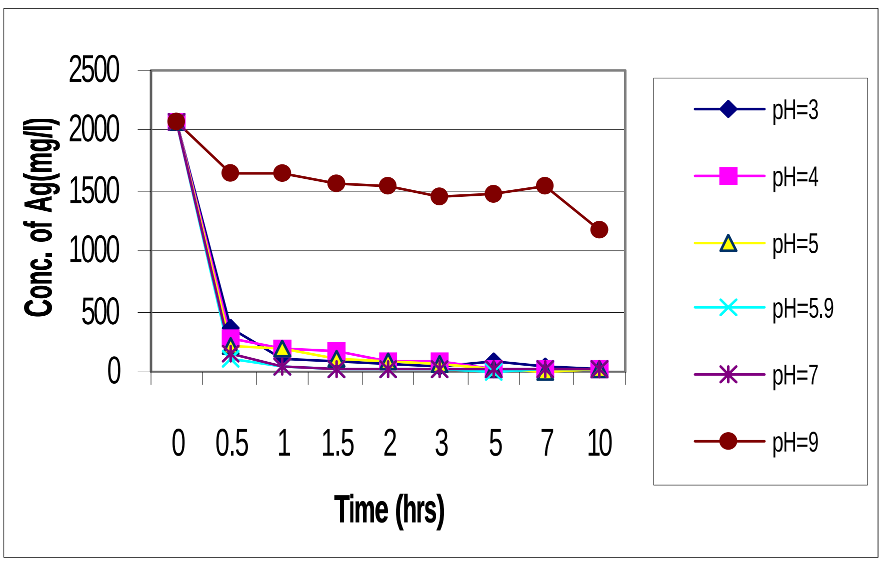


Fig. 5 Reduction of Ag concentration using steel wool as a function of time

The pH of spent solution ranging from 3 to 7 seems to be acceptable for the recovery of silver since silver removal percentages were considerably high without falling down. However, when the pH increased to 9, the silver removal percentage decreased sharply to less than 50%. Also, the time reduction of silver is rather constant for a 10 hour-period of contact time. Therefore, the metallic-replacement method using steel wool should keep the operating pH not to reach pH of 9 to maintain the silver-recovery performance.

**2.3) Effect of dissolved oxygen concentration on silver recovery**

Effect of dissolved oxygen concentration on silver recovery seems to be insignificant as shown in Fig. 6. An increase in DO concentration to 4 mg/l caused a little decrease in silver removal percentage. The mechanism of silver adsorption by the iron oxide might not be significant mechanism as no improvement of silver recovery by increasing dissolved oxygen in the spent solution. This phenomena is rather different from the case of phosphate sorption by the steel wool as studied by Chavalit et al. 1995. Therefore, the mechanism might be mainly a metallic-replacement mechanism.

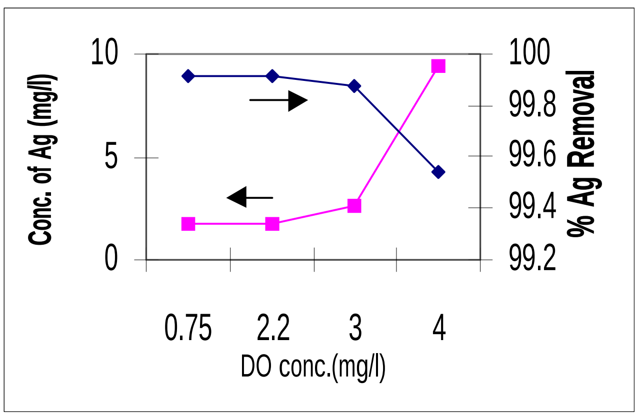


Fig.6 Effect of Dissolved oxygen on Ag recovery using steel wool

**CONCLUSION**

From the above-mentioned experimental results, it was found that both methods of chemical precipitation and metallic replacement methods were feasible to be applied in the real world application since high recovery of silver could be achieved with both methods. However, the metallic-replacement method is preferable since it does not need any chemical addition and it could achieve higher removal efficiency when compared to the results obtained in the case of chemical-precipitation method. Moreover, another advantage of this method is that it can be a possible way for reuse of the steel-wool waste from the manufacturing process.

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