

Recovery of Silver from X-ray Washings

Shakila Begum^{ab*}, Pir Aurang Zeb^a and Qazi Sharif^a

^aPCSIR Laboratories Complex, Jamrud Road, Peshawar-25120, Pakistan

^b717-186 King Street, N6A 1C7, London, Ontario, Canada

(Received May 22, 2008; revised December 2, 2008; accepted December 4, 2008)

Abstract. This paper presents the enhanced recovery of silver from polymers and gelatin in X-ray washings by treating with activated carbon at different temperatures and optimizing the parameters as temperature, pH and acid base concentrations. It was found that at pilot scale silver recovery increased through treatment with activated carbon and in comparison to the temperature of 20 °C, at 50 °C, the recovery increased from 82.57% to 94.04%.

Keywords: silver recovery, activated carbon, X-ray washings

Introduction

Recycling of secondary raw materials is an important part of the industries in developing countries like Pakistan. Silver is a valuable natural resource of finite supply; it is used as a component of various products. The discharged silver remains a pollutant of concern due to its aquatic toxicity and is subject to control by both hazardous waste and water quality regulatory programmes. Wastewashings containing silver at a concentration greater than 5 mg/l are regulated as hazardous waste (Paul, 1997) and cannot be discharged without first being rendered non-hazardous. Silver has monetary value as a recovered commodity as well. Harper and Siegel (2003) studied two different types of processes, electrolytic plating units alone and electrolytic plating units in combination with metallic replacement backup units and using them, they described the recovery of silver, down to concentrations of less than 5 mg/l.

Major source of recoverable silver is photo processing activity wherein the metal appears in different forms depending on the type of process. The photographic processing industry has four options in silver recovery i. e., electrolytic plating, metallic replacement, ion exchange and chemical precipitation. Chemical precipitation and recovery of silver by gravimetric methods is an effective technology. The precipitation process converts soluble metal compounds into relatively insoluble sulphide compounds through the addition of precipitating agents, such as sodium sulphide (Na_2S). Over a broad pH range, sulphides (S^{2-} , HS^-) are extremely reactive with heavy metal ions. Sulphide precipitation can be operated over a wide range of pH, typically from pH 2 to 12. Metal-sulphide precipitates are less amphoteric than the

corresponding metal-hydroxides and, therefore, less likely to resolubilize because of changes in pH.

Extraction of silver from industrial wash waters of film-printing plants has been the subject of interest of many investigators. Syed *et al.* (2002) obtained a high yield of silver on heating the films with oxalic acid solution to boiling temperature to separate the inorganic components from the polymer substrate. Lanzano *et al.* (2006) studied one year anthropogenic stocks and flows of silver as it progresses from extraction to final disposal. They concluded that in total 62% of all discarded silver is recycled and 38% is sent to landfills. Rivera *et al.* (2007) studied silver precipitation in elemental form in the $\text{S}_2\text{O}_3^{2-}$ - $\text{S}_2\text{O}_4^{2-}$ system and recorded recovery of more than 99%. Arsalan and Sayiner (2008) followed the process of thiosulphate leaching of precious metals and recovered 99.57% Au and 95.87% Ag at optimized conditions. Zhouxiang *et al.* (2008) reported total silver recovery from the spent fixing bath and waste X-ray films as 98.0% and 95.8%, respectively.

In the present investigation, X-ray washings, were treated with activated carbon under certain conditions prior to its precipitation as silver sulphide in a bid to separate the inorganic compounds from gelatin and polymer compounds to gain the maximum recovery of silver. Possibilities of application of the developed procedure for processing of secondary raw materials containing silver, at large scale, were also explored.

Materials and Methods

The present study was performed to study a process at large scale that was earlier made at the laboratory scale.

Laboratory scale experiment. In the laboratory, at first, X-ray washings with no activated carbon yielded 77.57% recovery at 25 °C. X-ray washings were then stirred with activated carbon, supplied by Merck, at 20 and 50 °C; pH

*Author for correspondence; E-mail: shakilakakakhel@yahoo.com

^bPresent address

was kept constant at 5.4 ± 0.1 and recorded with Corning pH-meter. The highest recovery of silver was obtained from washings treated with activated carbon at 50°C (Table 1). At each temperature the experiment was repeated in triplicate to optimize the parameters and the average value was reported. Analytical grade reagents were used for the optimization of parameters. Concentration of silver was determined by Zeeman 8000 atomic absorption spectrophotometer.

Recovery of silver at large scale. Sampling. X-ray washings, 24 litres (9 l from Khyber Teaching Hospital and 15 l from Popular X-rays, a private organization) were collected in polyethylene bottles, prior washed, cleaned with dilute nitric acid and then rinsed with deionised water. Washings were poured in a large clean tub and were mixed thoroughly with a thick glass rod. Silver, 7 g/l, was detected in the aggregated solutions by atomic absorption spectrophotometer as well as by the standard method of chemical analysis.

Treatment of sample. To the washings in three different clean plastic tubs, each containing 8 l of washings, HNO_3 was added to bring the pH down to 5.4 ± 0.1 . Granular activated carbon, at 6 g/l, was added to the washings to increase the removal efficiency and tubs were placed in the incubator at 50°C .

Washings were stirred, from time to time, with a thick glass rod. After 6 h, washings were taken out and filtered through the suction pump. The filtrates were collected in large bottles.

Precipitation. Treated washings, 4 l, were taken at a time in a tub and made alkaline with 92 ml of 10N NaOH. The alkaline washings were then transferred to a steel bowl and heated to 60°C . Dissolved 160 g commercial grade sodium sulphide was added to each 4 l of washings while still hot. A substantial excess of sodium sulphide was preferred in order to ensure complete precipitation of silver as silver sulphide. The precipitate was massed for 2-3 h and then kept over night to cool down. As silver sulphide is a colloidal precipitate, it is extremely difficult to filter it. Therefore, excess water was decanted and the precipitate was oven dried.

Metallic silver. The precipitate was processed at pilot plant. A large graphite crucible was used for the gravimetric analysis. Silver was recovered from the black precipitate by smelting at 970°C utilizing commercial grade reagents for smelting. Natural gas was used as the source of heat.

The produced silver was again smelted in a furnace using analytical grade reagents.

Characterization of the produced silver. Specific gravity of the produced silver was determined using density meter

(Mettler Toledo model XS 203 S) as well as manually.

Used activated carbon. The organic substances and gelatin laden activated carbon was air dried and stored in a bottle, for treatment in a separate process to displace the organic substances and gelatin from it to render the carbon fit for reuse.

Results and Discussion

The parameters of the process, investigated for their influence on the recovery of silver, were temperature, pH, concentration of activated carbon and its stirring time.

On the first smelting 168 g metallic silver was obtained from the molten mass and on the second smelting, 158 g shining metallic silver was obtained. The density of the metal was 10.60 g/cm^3 and thus the purity of the product was 99.62%.

From 24 l of washings, 158 g silver were recovered at pilot scale which shows 94.04% recovery. Compared to the work carried out at laboratory scale (Table 1), the result achieved at the pilot scale was less by 0.50%; this amount of metal might have been lost during handling at large scale.

The activated carbon without absorbing the silver ions, sorbs organic substances, particularly gelatin from the solution and retains mechanical impurities, which makes the medium clear. It eventually results into the release of more silver ions from the washings and increases the recovery of silver. It could be concluded that through this process, silver recovery increases rapidly after treatment with activated carbon at high temperature whereas at lower temperatures and without treatment, silver recovery efficiency is insignificant.

The study shows technological justification of using activated carbon as a purifier for the removal of gelatin and organic compounds from X-ray washings, with high silver extraction efficiency and low reagent consumption. However, during the precipitation of silver as silver sulphide, H_2S gas is evolved, which is considered a broad-spectrum poison. At 0.0047 ppm H_2S gas has rotten egg smell. At

Table 1. Treatment of X-ray washings with activated carbon; dependence of temperature (lab. results)

Temperature ($^\circ\text{C}$)	Recovery of silver with no activated carbon (%)	Recovery of silver after treatment with activated carbon (%)
25	77.57	-
20	-	82.57
50	-	94.54

conditions: X-ray washings, 500 ml; pH, 5.4 ± 0.1 ; activated carbon, 4 g/l; stirring time, 6 h.

150-250 ppm the olfactory nerve is paralyzed after a few inhalations of the gas and the sense of smell disappears, giving signals of danger. Higher concentrations of 700-800 ppm of H_2S tend to be fatal. In addition to this, some causative chemicals have also been used with the risk of forming potential toxic fumes. This disadvantage was overcome by performing the precipitation experiment in the fuming chamber and sometimes in the very open air.

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