Methods of silver recovery from radiographs - comparative study

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Abstract. Management and recovery of waste are activities with multiple impacts: technologically (by using waste on current production flows, thus replacing poor raw materials), economically (can substantially reduce manufacturing costs by recycling waste), social (by creating new jobs where it is necessary to process the waste in a form more suited to technological flows) and ecologically (by removing waste that is currently produced or already stored - but poses a threat to the health of the population and / or to the environment). This is also the case for medical waste, for example radiographs, which are currently produced in large quantities, for which replacement solutions are sought, but are currently stored by archiving in hospital units. The paper presents two methods used for this kind of waste management, the result being the recovery of silver, material with applications and with increasing price, but also the proper disposal of the polymeric support. This analysis aims at developing a more efficient recycling technology for medical radiographs.

1. Introduction
Silver is an important precious metal, due to its unique thermal conductivity, optical reflectivity and its photosensitivity. Its countless, medical and industrial application, have made studies on silver to be an attractive area of research related both extraction, and recovery from different waste.

Although global legislation places a growing underlining on controlling the dispersion of hazardous waste into the environment, significant amounts of waste reach it. Radiographs and effluents resulting from processing are such examples. Provided the X-rays reach patients, it is difficult to control their management, requiring a system to manage them either before reaching patients or through subsequent, controlled, safe collection, while ensuring health monitoring of patients.

The number of radiographs is rising, on one hand due to population growth and extended access to modern investigative methods (even in countries where access was formerly limited) and on the other hand, due to the increasingly intense pollution of the environment, resulting in a deterioration in the life quality, which leads to the necessity of more frequent medical investigations.

Processed radiographs contain a significant amount of silver that can be recovered. There have been several studies on its recovery from processed radiographs and their effluents [1-5], but the generally proposed methods have many disadvantages, vulnerabilities, one of which is that most of them involve high costs. Researches in this area need to reveal simple and effective techniques, both economically and ecologically. It is therefore necessary to improve these methods, as natural resources are limited and unceasingly.
In the recent years, a particular accent has been put on the purity and the form of recovered particles, although difficult to achieve, in addition to recovering silver itself, thus developing the study of nanoparticles.

The pharmaceutical industry uses silver more frequently. The shape, size, and distribution of nanoparticles depend on the methods applied in the recovery process. Electro-refining is a very important process because, in all areas, it is necessary to use silver as purely as possible. Adjusting the parameters in the electrochemical method makes it possible to control the particle size. However, it is still difficult to establish a well-defined, quantitative relation between the reaction parameters and the resulting particulate form.

Generally, not few chemical and physical methods are used for the synthesis of silver nanoparticles. For the cluster growth, it needs an energy, at a particular size, so more silver atoms diffuse in solution and captured to the surface.

Typical anisotropic forms result in the presence of a stabilizing polymer that binds preferentially to one of the faces of the crystal faster than the other does [6].

Most part of particles obtained are spherical, pyramidal, cubic, rods, octagonal or thin sheets shaped. Spherical particles are thermodynamically the most stable because of their minimum surface at a certain volume [7]. At first, in chemical methods, usually, a strong reducing agent produces small silver particles, and then a weaker reducing agent enlarges them. For example, the following reducing agents can be used: glucose, ethylene glycol, hydrazine hydrate and citrate of sodium [8], ultrasonic irradiation as a green reducing agent [9], sodium borohydride in the presence of sodium citrate (Na$_2$Cit) at room temperature [10], hydroxylamine. Normally the second selective reducing agent may be add about one mole $+$/$-$5% of silver reducing agent for each mole of silver. When sodium formate is utilised as the second selective reducing agent, however, it is preferable that at least two moles of sodium formate per mole of silver should be added [11].

The research of silver recovery from exposed X-ray films has been oriented towards several directions over time. Pyrometallurgical methods are inadequate, and energy-intensive. Studies on silver recovery by enzymatic methods are in a relatively incipient phase, with inconclusive and uncertain results, assuming a long time-span of separation of the emulsion film [12], [13].

Although seemingly harmless, some of these methods can give rise to dangerous secondary products, unless there is a clear strain on processes. Therefore, it seems that the best results regarding silver recovery from radiographs are those obtained by hydrometallurgical methods.

The migration of the emulsion from the radiological film is a relatively simple process, but a particular attention should be paid to the favourable factors, which can usually be: the dissolution temperature, the concentration of the solutions and the speed of rotation if an electromagnetic stirring is used.

2. Experimental data's

In this research, base outline of the process is the separation of inorganic component from the polymer layer by solubilisation with NaOH [5] and HNO$_3$ [3], respectively. The radiographic film contains gelatine, a protein derived from sacrificed animals leather and bones, containing glycine, proline and 4 hydroxyproline residues, in which are dispersed very fine silver bromide granules [14], [15].

Within the first experimental method, there were used aqueous NaOH solutions, to extract the polymer deposited substrate. The film was sequentially treated with NaOH solutions of various concentrations: 1M, 1.25M, 1.5M and 2M, respectively. For each 250g of solution, there were used 250g of radiographs. There were also used laboratory glassware with large base areas, so the dimensions at which the film was cut could be larger, 5x5cm$^2$. To avoid the sticking to each other, radiographic films have been introduced at a time. In order to increase the leaching speed, mechanical agitation of the aqueous solution was continually carried out with a stirrer rod.

The temperatures at which the leaching took place varied between ambient temperature and 90°C. The solutions of NaOH containing black colloidal silver were decanted and filtered – Figure 1. The
residue was washed with distilled water (3-4 times) and then dried – Figure 2. The silver particles were visualized at the stereo-microscope (x60) – Figure 3, Stereo-microscope from the Physical Metallurgy Laboratory within Hunedoara Engineering Faculty, Politehnica University of Timisoara.

Figure 1. Resulting solution after leaching

Figure 2. The solid residue before and after settling and washing

Figure 3. View by microscope after filtration and drying
The second method used involves the passing of the silver deposited with the emulsion on the polymer support into a solution of HNO₃ [16]. Three beakers, each containing 250g HNO₃ aqueous solution (68%) were used: the first beaker contained 30% HNO₃, the second 25% HNO₃ and the third 20% HNO₃ respectively. Every beaker was leached an amount of 350g film. Dissolving results in silver nitrate and impurities. During the transfer of silver to the HNO₃ solution, evaporation occurs. Thus, distilled water was added, when necessary, to the completion of the 250ml. When the leaching time increased, the solution was considered to lead to saturation.

The solutions, with different concentrations, were cooled, filtered with the Büchner funnel and subjected to several silver recovery processes by cementation.

The general chemical cementation reaction can be explained by the formula (1) [17]:

\[
Ag^{+z_1} + \frac{z_1}{z_2} Me \Leftrightarrow \frac{z_1}{z_2} Me^{+z_2} + Ag
\]  

(1)

where Me is the metal used for cementation (in our case Cu, Zn, Al or Fe);

- \( z_1 = 1 \) - valence (electro-valence);
- \( z_2 \) - the valence of the metal used for cementation.

Process for cementing a metal from an acidic, aqueous solution is based on the capacity of some metals that are higher in the electromotive series than the metal to be recovered, to reduce the ions of more noble metals. Metals such as Cu, Zn, Al or Fe can cement the silver from AgNO₃ solutions. Copper cementation has been preferred for a better visualization of recovered silver since the initial phase. Zn and Fe tests have also been performed – Figure 4.

The higher initial nitric acid concentration was required to increase the silver flow rate in the solution. If the solution is not saturated with silver ions, Copper nitrate (Cu (NO₃)₂) will be formed concurrently with Cu – Figure 5. In the cementation process, a very small amount of copper is consumed by diluting the solution. After the copper cementation test was carried out, the solution was
filtered, the silver metal remained on the filter paper – Figure 6, which was washed with distilled water to avoid further chemical reactions.

Figure 5. Complex solution of nitrate silver and copper

Figure 6. Copper cementation and Ag highlighting by filtration

To streamline the process, the resulting solution, after the filtration is reused in the silver leaching process, upon a new series of radiographs.

3. Results analysis
The equilibrium and kinetics of chemical reactions at the passage of silver in the solution from X-ray films depends on several factors, regardless the method used. These are:
- concentration of reagents;
- type of radiography (silver content and age after archiving);
- leaching time in the solution;
- stirring rate;
- leaching temperature;
- solid / liquid rate.

In order to study this equilibrium and kinetics of chemical reactions, the concentration of aqueous NaOH solutions was taken into account, for each experiment measuring the leaching time and the temperature. Concerning the rate of stirring, it can be considered a constant factor in the experiments carried out, considering that the mechanical agitation performed in order to decrease the leaching time.

Figure 7 shows the dependence between leaching time and temperature at different concentrations of aqueous NaOH solution.

![Graph showing the dependence between leaching time and temperature at different NaOH solution concentrations](image)

**Figure 7.** Dependence of leaching time and temperature at different concentrations of aqueous NaOH solution

The graph analysis in Figure 7 shows that an increase in the concentration of the solution at 2M does not lead to a significant decrease in 80-90°C the silver transition time, which is why the increase in concentration is pointless (especially from an economic and environmental point of view). The minimum leaching time, at 80-90°C, occurs at a 1.5M concentration.

A good purity silver is obtained by borax treatment and heating at high temperature, 500-600°C, by calcination [18].

Regarding the parameters characterizing the leaching process of the Ag-containing the emulsion from the radiographic films - presented in the graph of Figure 8, the following were found:

- the leaching is carried out at very low speeds, which leads to a decrease of the yield, at ambient temperature;
- the temperature has a relatively low influence, at temperatures above 40°C, which leads to the conclusion that an average temperature of 60-65°C would be sufficient for a good solubility;
- either a very high concentration of HNO₃ in the aqueous solution is not recommended and can be solubilized at the lower limit of the range, respectively a 20% HNO₃ concentration in the aqueous solution.
Figure 8. The dependence between dissolution time and temperature at different concentrations of HNO₃ solution

4. Conclusion

As a result of running under laboratory conditions the two different methods for recovering silver from radiographic films, the following conclusions can be drawn:

- the obtained silver has sufficiently high purity, in both experiments. Electrically refining can be performed for a high purification of silver;
- both methods are relatively simple and silver was successfully recovered with low costs;
- regarding the leaching of radiographic films in aqueous NaOH, the following process parameters are recommended: concentration of aqueous 1.5M NaOH solution, 80-90°C process interval;
- it has been found that in the method of solubilisation with HNO₃, a lower concentration of acid in the aqueous solution can also be employed; In addition, the resulting solution can be recycled for a new leaching of silver from the X-rays. Recommended parameters: concentration of 20% HNO₃ at a working temperature of max. 65°C.

Subsequent research will focus on recovering silver from X-ray films by sodium and ammonium thiosulphate [2], [19], [20] oxalic acid [1], establishing a quantitative relation between the recovered silver, solution concentration and agitation rate, as well as recovering silver from the effluents resulting from the development process [21].

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