



## Recovery of the fixing solution waste and silver, as well as the direct synthesis of silver nanoparticles from the solution waste

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### Article Info

**Article type:**

Research Article

**Article history:**

Received: 29 Sep 2022

Revised: 28 Jan 2023

Accepted: 19 May 2023

**Keywords:***Recovery**Silver nanoparticles**The fixing solution**Chemical reduction**Cementation*

### ABSTRACT

Radiology and photography films are mainly made of silver halides, which are very sensitive to light. The developer-fixing solution reduces silver salt crystals and turns them into black metallic silver on film and a stable and clear image appears on the film. After several uses of the fixing solution, its efficiency is reduced due to the decrease in the concentration of sodium thiosulfate and finally, it cannot be used since there is not enough awareness regarding its harm, so it enters the environment through wastewater. In this study, the recovery of fixing solution waste has been investigated. The recovery of the solution waste, silver extraction, and direct synthesis of nanoparticles have been performed by chemical reduction method from the waste. The obtained samples were analyzed and studied by EDX, XRD, and SEM techniques. The results showed that the fixing solution waste and silver metal were recovered properly with a purity of 99.81%. Also, AgNPs were synthesized by chemical reduction. Recovery of the fixing solution waste -for the first time- and metallic silver, as well as the synthesis of AgNPs by chemical reduction method, is an economical method and free of any contamination.

**Cite this article:** Azordeh Molkabadi, S., and Asadi, M. (2023). Recovery of the fixing solution waste and silver, as well as the direct synthesis of silver nanoparticles from the solution waste. *Pollution*, 9 (3), 1074-1082. <https://doi.org/10.22059/poll.2023.349294.1640>



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Publisher: University of Tehran Press.

DOI: <https://doi.org/10.22059/poll.2023.349294.1640>

## INTRODUCTION

Due to its sensitivity to light, silver has many applications in various industries, especially in radiology and photography (Zhouxiang et al., 2008). This metal is heavy and it is harmful. In addition, it is a nonrenewable resource of mineral resources (Asadi and Azordeh, 2020). Therefore, all countries would like to recover used silver in industry due to high cost of silver mining and its environmental damage. The radiology and photography are industries in which the used silver can be recovered (Zhouxiang et al., 2008; Azarkhalil and Keyvani, 2016). In other words, 20% of the used silver in these industries remains on radiology and photography films and 80% of it enters the environment by fixer solution (Zhouxiang et al., 2008).

The radiology and photography films are mainly made of silver halides, especially silver bromide, which are highly sensitive to light. When light is emitted into an emulsion (virgin film), its surface changes to form an image. At this stage, the image is hidden and it requires to be appeared by chemical reactions (developing process) (Lupi and Pasquali, 2008; Jacobson et al., 1980; Abbasi, 2006; Gol Golab, 1991).

Within the developing procedure, those silver salt crystals that have been exposed to radiation of light are reduced to black metallic silver on film (Jacobson et al., 1980; Time life

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editors, 1976; Eaton, 1986). After stopping the process of developing by another weakly acidic solution - mainly 30% acetic acid solution or a solution containing sodium sulfite, potassium metabisulfite, and hydrochloric acid (Horenstein, 2005; Suess, 2003) the process of fixing is done to stabilize the permanent and clear image on the film. Within the fixing procedure, sodium thiosulfate in the fixing solution is responsible for doing the chemical reaction and fixing the image. In this way, silver bromides that have not been exposed to radiation are reacted with sodium thiosulfate, and a permanent and clear image is fixed on the film by the formation of  $\text{Ag}(\text{S}_2\text{O}_3)\text{Na}$  salt (Time life editors, 1976).



After using the fixing solution several times, its efficiency is reduced due to the decrease in the concentration of sodium thiosulfate and finally, it cannot be used; since there is not any awareness regarding its harm, it enters the environment through wastewater. Studies show that the solution can be recovered for preventing biological pollution; moreover, solved silver can also be recovered for reuse.

Different methods such as electrolysis (Moeglich, 1977; Onlin et al., 1993), acid deposition (Masebinu and Muzenda, 2014), electrochemical reactor (Ramirez et al., 2011), ion exchange (Goshima et al., 1994), cementation (Aktas et al., 2010), electrical deposition (Satyanarayana and Ramesh, 2020), etc. can be applied to recover silver from fixing solution and radiographic film.

Valdivieso et al. recovered silver from radiology fixing solution waste with zinc powder in the cementation method. The results of this study show that the amount of recovered silver is related to the pH level. So that, the rate of recovered silver rises with pH. Furthermore, existing of oxygen in the reactor is effective on the type of recovered silver. They have shown that metallic silver recovered at all ranges of pH in the absence of oxygen, whereas silver and silver sulfide formed at the acidic ranges of pH (<7.5) in the presence of oxygen, and at the alkaline ranges metallic silver formed (>7.5) (Valdivieso et al., 2009).

Shu et al. recovered silver metal from fixing solution waste with an 8-hour electrolysis method that the most yield (100%) of silver recovery performed for a current of 0.9 A at pH=8. The results of their study show that there is high concentration of chemical oxygen demand (COD) in the treated solution that 42% and 99.3% of COD can be removed respectively by 30 ml sulfuric acid per liter of the treated solution and distillation method. Although the distillation method is high yield than COD removing by acid method, but the distillation method is costly (Shu et al., 2012).

Mekurialem, et al. were able to recover silver with a purity of 98.29% from X-ray films which were collected from the hospital, by using sodium hydroxide and sodium sulfide. The results indicated the efficiency of this method is 57% and the effective parameters are the temperature of the reaction, time of silver separate from the film, and the concentration of sodium hydroxide, respectively (Erku et al., 2017).

In the other study, Galarpe and Leopoldo used the chemical method of alkaline treatment with sodium hydroxide to recover silver from the fixing solution. During this study, 8-10 g of sodium hydroxide was used per 600 ml of the fixing solution, and also the quantity of recovered silver was calculated to be 0.88- 2.46 g at pH = 9-12 (Galarpe and Leopoldo, 2017).

In another study, Serdar calculated the amount of recovered silver more than 99%, by cementing method, where the copper powder was used by weight ratio (Cu/Ag) 5.23 and 2.64 g in the presence of air and Ar gas for 30 and 10 minutes, respectively. Meanwhile, the use of Ar gas prevents the silver from redissolution in the fixing solution. In the current method, it should be noted that the use of highly acidic pH levels degrades thiosulfate and causes the production of toxic gases as well as the deposition of the undesirable elements such as sulfur and silver sulfide (Aktas, 2008).

In the present study, a green and harmless method for preventing bio-pollution has been investigated. In order to do this, copper metal (blade) has been used to recover the fixing solution and silver extraction, and in the other experiment, silver nanoparticles have been synthesized by a chemical reduction method, in which the dissolved silver ions in the fixing solution were as a source of silver ions. The most prominent difference between this study and the same studies is that a green route has been presented with a neutral range of pH because the highly acidic level can cause the emission of toxic gases, and an alkaline range completely prevents recovering and reusing the fixing solution waste. Hence, for the first time, the recovery of fixing solution waste to reusing have studied successfully in this study. As well as, the most important novelties of this study are the recovery and reusing of the fixing solution as a virgin solution, and the direct synthesis of AgNPs from fixing solution waste by chemical reduction method, without producing COD and no need for oxidizing.

## MATERIAL AND METHODS

Sodium citrate with a purity of 99.0% (CAS No.6132-04-3) was purchased from Sigma-Aldrich as a reduction agent, and a copper blade (>99.99%) purchased from the metal market was used in the reduction of silver ions. Also, the fixing solution waste was collected from X-ray and photographic laboratories.

The Analytik Jena Model: Nova AA400 Atomic Absorption Spectroscopy (AAS) to determine the concentration of remaining  $\text{Ag}(\text{S}_2\text{O}_3)_2\text{Na}$ , VEGA/TESCAN-LMU Energy-Dispersive X-ray spectroscopy (EDX) to determine the purity of extracted silver and synthesized AgNPs, Siemens D500 X-ray Diffraction (XRD), and TESCAN MIRA3-FEG Scanning Electron Microscopy (SEM) TESCAN MIRA3-FEG to study the structure and morphology of synthesized AgNPs were used.

### *Recovery of the fixing solution waste and dissolved silver in that*

In this part of the experiment, the dissolved silver ions in the fixing solution waste were extracted by a blade of copper metal (cementing method) at the neutral pH range, after that the remaining of the fixing solution was recovered by a chemical reaction and reused. To do that, a blade of copper (with dimensions of  $10 \times 40 \times 250$  mm) entered into 1 liter of the fixing solution waste at  $27^\circ\text{C}$ . According to the potential difference between  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  ( $\text{Ag}^+$ : +0.8 and  $\text{Cu}^{2+}$ : +0.337), the potential difference of copper ions in the comparison with silver ions is lower; therefore, the copper metal ( $\text{Cu}_{(s)}$ ) is oxidized to  $\text{Cu}^{2+}$  ions (slowly corroded) and electrons were released into the solution, that causes to reduce  $\text{Ag}^+$  to  $\text{Ag}_{(s)}$  (Aktas, 2008; Syed, 2016).

### *Synthesis of silver nanoparticles from the fixing solution waste.*

In the second part of this study, the dissolved silver ions in the fixing solution waste were used as a source of silver ions for the synthesis of silver nanoparticles by a chemical reduction method. Moreover, to reduce silver ions to AgNPs sodium citrate ( $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3$ ) was used as a reducing and stabilizing agent (Mohaghegh et al., 2020). Due to high surface energy and van der Waals' attractive force, atoms accumulate together to grow nanoparticles.

To do so, firstly the concentration of remaining  $\text{Ag}(\text{S}_2\text{O}_3)_2\text{Na}$  in the fixing solution was determined by Atomic Adsorption Spectroscopy (AAS) (0.02M). To start, one liter of the fixing solution waste is heated to  $80^\circ\text{C}$  as a source of silver ions, then 100 ml of 2% sodium citrate solution was added drop by drop and heated and stirred until the color of the solution changed to brown. After that, the heating stopped and was stirred until it reached to  $27^\circ\text{C}$ . Finally, the obtained depositions, which were the same as AgNPs were filtered and washed by deionized water, and dried at  $27^\circ\text{C}$  (Mohaghegh et al., 2020). The amount weight of the synthesized AgNPs was 4.86 g/L.

## RESULTS AND DISCUSSION

### *The EDX pattern of extracted silver and the synthesized AgNPs*

The purity of extracted silver is determined by EDX, which is more than 99.8% as shown in Figure 1. 0.19% of the copper element as it can be observed due to the used copper metal to extract silver from the fixing solution has entered the sample as powdered copper while there is not any percentage of the copper element in the synthesized sample of AgNPs because copper metal did not use in the process of nanoparticle synthesis (Figure 2). As shown in Figure 2, the EDX pattern of the synthesized AgNPs shows a strong peak in the 3keV area, which confirms that the obtained sample is AgNPs.

### *XRD pattern of AgNPs*

The X-ray diffraction pattern of the synthesized sample in Figure 3 shows the crystal structure

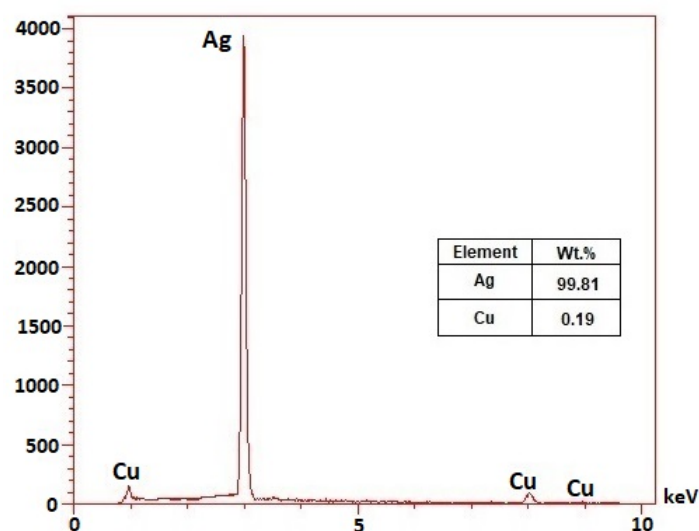


Fig. 1. The EDX pattern of extracted silver

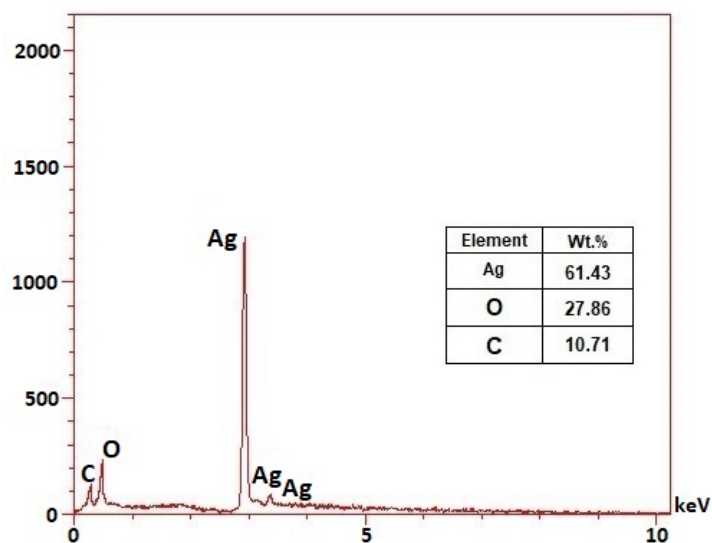


Fig. 2. The EDX pattern of synthesized AgNPs

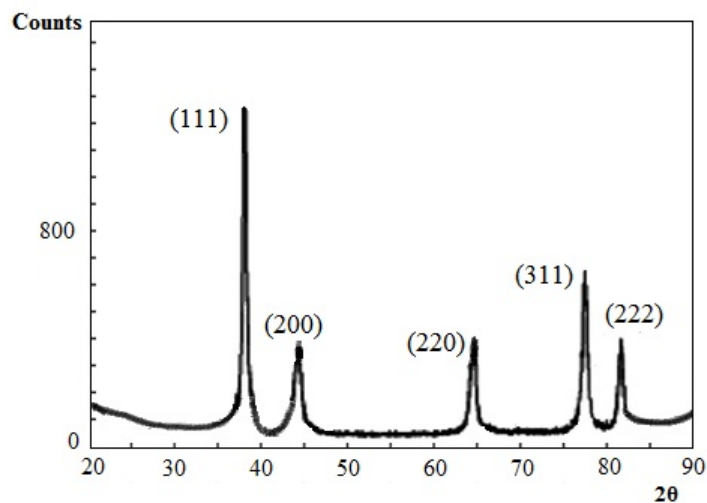


Fig. 3. The XRD pattern of synthesized AgNPs

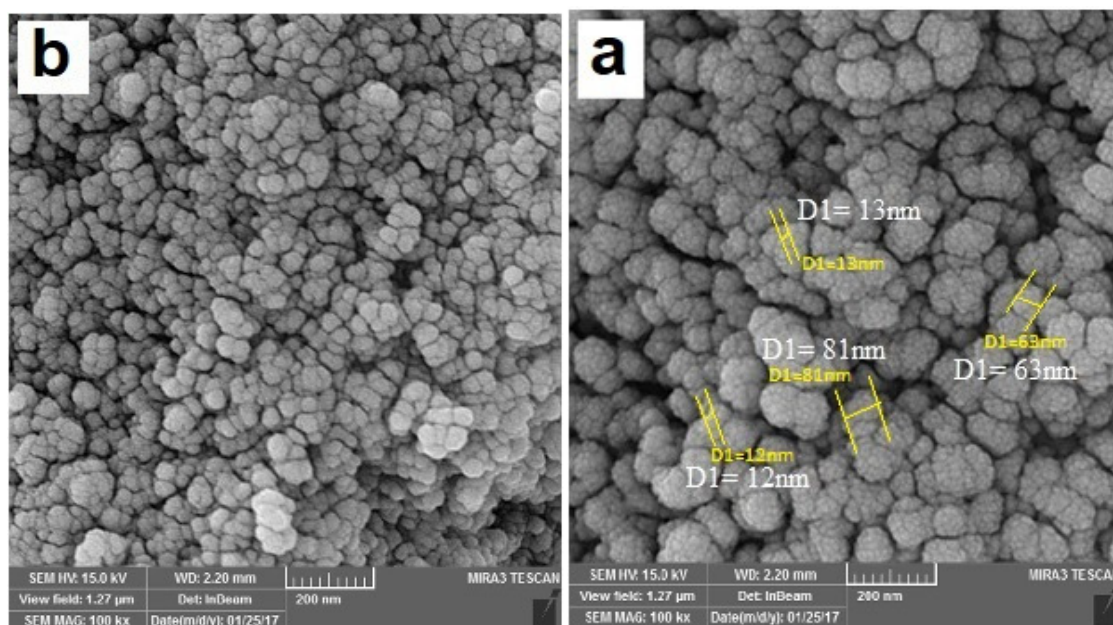


Fig. 4. SEM images of synthesized AgNPs: magnification: a) X50000 and b) X100000

of AgNPs. The peaks in  $2\theta = 37.6, 44.5, 64.8, 77.1$  and  $81.8$  correspond to the Miller Index Value (111) and (200), (220), (311), (222) (JCPDS No. 04-0783), respectively (Yerragopu et al., 2020; Lanje et al., 2010). Supported by studies, and consistent with the mentioned Miller index value, it is determined that AgNPs have been crystallized within the Face Centered Cubic structure (FCC) (Rautela, 2019; Kamali, 2012).

#### SEM images of synthesized AgNPs

Figure 4 shows the SEM images of the synthesized sample and also the size distribution of the nanoparticles. Further, as it can be observed the particles are arranged in an exceedingly spherical and regular pattern. In keeping with Figure 4-a, the dimensions of nanoparticles are about 12-13 nm, which due to high surface energy and van der Waals attractive force (Endres

et al., 2021; Henry et al., 2013), have formed regular and uniform clusters with a size of about 63 nanometers (Figure 4-b).

In the first part of the study (recovery of the fixing solution waste and extraction of silver from that) by copper metal, silver ions in the fixing solution were extracted as silver metal from the fixing solution. In this section, chemical reactions are as follows:



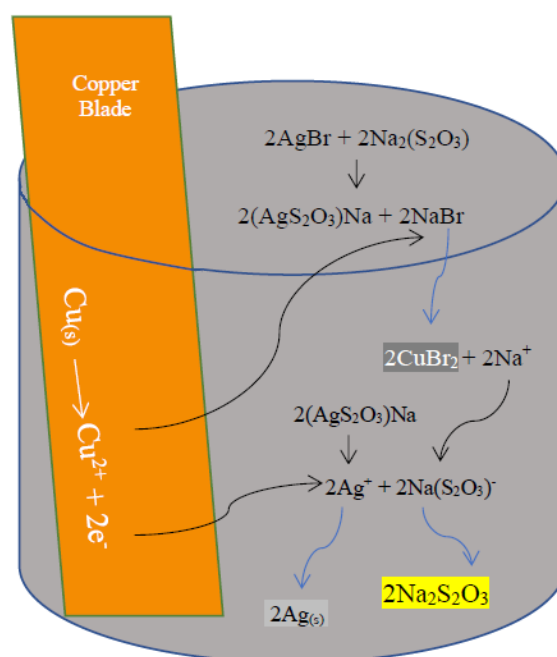
On the other hand,  $\text{Cu}^{2+}$  ions with  $\text{NaBr}$  cause the production of  $\text{CuBr}_2$  and the released  $\text{Na}^+$  also reacts with  $\text{Na}(\text{S}_2\text{O}_3)^{-}$  and causes the recovery of the fixing solution:



Finally, after 7-9 hours, silver metal depositions with  $\text{CuBr}_2$  and to separate that, due to the difference in melting point ( $\text{Ag}_{(s)} = 950^\circ\text{C}$ ,  $\text{CuBr}_2 = 900^\circ\text{C}$ ) silver metal with a purity of 99.81% with weight 5.8 g/L is separated at  $950\text{-}960^\circ\text{C}$ . Schematic 1 shows how the silver ion is reduced to metallic silver and also the fixing solution is recovered.

#### *Reusability of recovered fixing solution*

The fixing solution is used several times until the fixing process stops. During this study, the recovered solution was used repeatedly within the fixing process to verify the successful recovery of that. Table 1 shows the average results of the reusing of the recovered solution in the radiology laboratory, photography laboratory, and dental laboratory, where the recovered solution can be reused as the virgin solution.



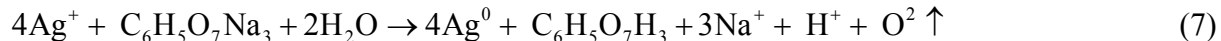
**Schematic 1.** Process of the silver ions reduction to metallic silver and fixing solution recovery

**Table 1.** Comparison of the performance of the virgin fixing solution with the recovered fixing solution

Tests	Virgin Solution			Recovered Solution		
	Radiology Laboratory	Photography Laboratory	Dental Laboratory	Radiology Laboratory	Photography Laboratory	Dental Laboratory
Fixing time	14-15 minutes	20-22 minutes	2-3 minutes	14-15 minutes	20-22 minutes	2-3 minutes
reused times	70-75 times	35-40 times	90-100 times	70-75 times	35-40 times	90-100 times
Quality of Fixing process	Standard			The quality of the recovered solution is the same as the virgin solution		

It should be mentioned, the virgin fixing solution has a neutral pH. The preliminary experiments show that an alkaline pH solves all existing silver halides at the surface of X-ray and photographic films in the fixing process and the recorded images fade. So, recovering silver at the alkaline range from fixing solution waste causes destroy features of the solution and that is non-reusable.

In the second part of this study (synthesis of AgNPs from soluble silver ions in the fixing solution), dissolved silver ions in the fixing solution waste by chemical reduction method and using sodium citrate as reducing and stabilizing, in the form of cluster nanoparticles with size 63 -81 nm were synthesized. The performed chemical reactions are as follows (Zhang et al., 2018; Nandatamadini et al., 2019):



## CONCLUSION

Recovery of the fixing solution waste and metallic silver, as well as the synthesis of AgNPs by chemical reduction method, is an economical method, green route and free of any contamination. The amount of extracted silver depends on the concentration of  $\text{Ag}(\text{S}_2\text{O}_3)\text{Na}$  in the fixing solution waste and the average amount of  $\text{Ag}_{(s)}$  5.8 g/L with a purity of 99.81% can be extracted. On the other hand, in this process, the fixing solution waste was recovered and reused as the same as the virgin fixing solution. Also, ions in the fixing solution waste can be used as a source of silver ions for the synthesis of cluster AgNPs with a particle size of 63-81 nm by chemical reduction method and using sodium citrate as a reducing and stabilizing agent.

The present study has shown the results of the recovery of the fixing solution for reusing for the first time. According to the results, the recovered solution can be used as the virgin fixing solution. The alkaline level of pH for the recovery of silver ions from the fixing solution is not appropriate because the alkaline range can destroy the features of the fixing solution and completely prevent recovering and reusing the fixing solution waste. On the other hand, rising acidic level cause degrades thiosulfate and eventually toxic gases emission. That this will result in the deposition of undesirable elements such as sulfur and silver sulfide.

## ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support of this study by Bio Future World LLC. Co.

## CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication &/or falsification, double publication &/or submission, and redundancy has been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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