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Recovery of pure silver from spent silver electroplating solutions via electrochemical process and zinc cementation

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Abstract

Recycling of spent silver electroplating solutions has been investigated via electrowinning and electrorefining in comparison to zinc cementation technique in this research. Two different compositions of transparent and dark waste solutions were used having the remaining silver contents of 17.71 $g \cdot L^{-1}$ and 33.36 $g \cdot L^{-1}$ respectively. The waste solutions were used as an electrolyte in the first step of electrowinning at low current density of 0.015 $A \cdot cm^{-2}$. It was found that increasing electrowinning time from 4 h to 24 h increased the recovery of silver cathode for both types of waste solutions. The optimum electrowinning time was higher than 8 h, giving the recovery of higher than 97.5% and 98.5% purity for 24 h electrowinning. Through the subsequent electrorefining, the electrowon silver cathode was set as the anode, while $HNO_3 + AgNO_3$ electrolyte containing high silver content of 120 g Ag/L was used. By controlling the potential at 0.8 V, silver crystal of high purity > 99.9% was obtained. The highest recovery was 99.11% when using silver cathode obtained from electrowinning of the transparent waste solution. Zinc cementation however led to loss of silver in the precipitate form on the zinc metal surface, giving only 86.16% recovery.

1. Introduction

Electroplating of silver is of significant in a range of industries, i.e., jewelry for decorative purposes, electronic devices for electrical conduction and automotive parts for friction control. In electroplating, an electrolytic cell is set where the part is set as the cathode, and the more noble material is set as the anode. Initially, the electroplating solution contains silver in a range of 20 $g \cdot L^{-1}$ to 45 $g \cdot L^{-1}$ in sodium or potassium cyanide base in the forms of $KAg(CN)_2$ or $NaAg(CN)_2$, used in conventional plating following ASTM B700-20 [1]. The cyanide solution requires careful handling and regulated treatment after use. Related reactions for silver electroplating are as follows [2]:

$$NaAg(CN)_2 \rightarrow Na^+ + Ag^+ + 2CN^- \tag{1}$$

$$HCN \rightarrow H^+ + CN^- \tag{2}$$

$$H_2O \rightarrow H^+ + OH^- \tag{3}$$

reaction at cathode:

$$Ag^+ + e^- \rightarrow Ag \tag{4}$$

reaction at anode:

$$Ag \rightarrow Ag^+ + e^- \tag{5}$$

As the amount of silver reduces after being used in the electroplating process, the solution becomes waste. Also, spent silver electroplating solution may be caused by impurities that interfere with metal deposition at the cathode. Silver containing waste solutions can be categorized as (i) plating solution, (ii) rinsing water, and (iii) drag-out [2]. However, these wastes still contain significant amounts of silver, particularly the first one containing the highest amounts of silver, that can be recovered as pure metal.

Recovery and refining of silver from waste solution can be carried out based on extraction from ores; for example, solvent extraction, precipitation, ion exchange, cementation, electrocoagulation, electrochemical techniques as well as membrane separation and carbon absorption [3-8]. Research by N. G. K. Ramesh Bapu, *et al.*, indicated that electrowinning of low silver concentration (200 $mg \cdot L^{-1}$ to 1000 $mg \cdot L^{-1}$) cyanide spent plating solution could be achieved by controlling the current density of 0.04 $A \cdot dm^{-2}$ to 0.20 $A \cdot dm^{-2}$ [4]. The electrolytic cell was set such that stainless steel and platinum were used as the cathode and anode respectively. Investigation by V. Väzquez, *et al.* [6], applied Merrill – Crowe process to recover silver from cyanide solution containing silver and gold in a vacuum de-aeration tank using zinc dust via cementation according to Equation (6) [5]. The obtained precipitate was leached with sulfuric acid to dissolve zinc, leaving silver precipitate for remelting. Refining of silver is subsequently applied when high purity of silver is required, typically via electrorefining using 1) Balbach−Thum cell, and 2) Moebius cell [3].

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$$2Ag(CN)_2^- + Zn \rightarrow 2Ag + Zn(CN)_4^{2-} \qquad (6)$$

This research therefore focused on the recovery of high purity silver metal from spent silver electroplating solutions. Two types of spent silver electroplating solutions were used: (i) transparent and (ii) dark solutions, having different compositions of silver and other metal contents. Parameters on electrowinning and electrorefining were controlled for the two waste solutions to determine % recovery and % purity of the recycling product, and to compare with those obtained from zinc cementation.

2. Experimental

2.1 Waste characteristics

The spent silver electroplating (transparent and dark) solutions were obtained from an electronic part plating industry in Northern Thailand as shown in Figure 1(a) and 1(b) respectively. Composition analysis via ICP-OES (Optima 8000, Perkin Elmer) is listed in Table 1. The amount of silver in the transparent solution is 17.71 $g{\cdot}L^{-1}$ which is noticeably lower than 33.36 $g{\cdot}L^{-1}$ obtained from the dark solution. The transparent solution became waste due to a low silver content, and it contained some amounts of copper (0.2391 $g{\cdot}L^{-1}$), zinc (0.0280 $g{\cdot}L^{-1}$) and aluminium (0.0463 $g{\cdot}L^{-1}$) as the material substrates in the electroplating process. The dark solution contained significantly higher content of silver of 33.36 $g{\cdot}L^{-1}$, with less metal impurity contents, except for phosphorus. The dark appearance caused by the oxidation process lowered the electroplating efficiency, making it became waste. Both plating solutions were based on sodium cyanides.

2.2 Recovery of silver

Recovery of silver from the transparent electroplating solution was carried out via two routes for comparative results; (i) route I: cementation using zinc metal, and (ii) route II: electrowinning followed by electrorefining, whereas the dark solution was via route II only, as demonstrated in Figure 2. For route I: cementation, zinc metal was used for an amount of 500 g Zn/ 1 L of waste solution. The cementation was carried out in a normal atmospheric condition for 3 h (where no further precipitation was observed). The precipitate was filtered and rinsed with DI water or NH_4Cl for 3 h. Sampling of the waste solution was carried out on 10 min to180 min for composition analysis by ICP-OES. The obtained precipitates were subject to melting using oxyacetylene to obtain silver metal. Analysis on SEM (JEOL-JSM-6010LV) coupled with EDS analyzer was carried out on the obtained silver precipitate and the final silver metal.

Comparatively, for route II, an electrowinning cell was set using Pt-Ti and 304 stainless steel plates as the anode and cathode respectively. The spent silver electroplating solution was used as an electrolyte at 200 mL for each trial. Due to limited wastes provided, preliminary test was conducted to obtain the controlled parameters, which were set at the current density of as low as 0.015 $A{\cdot}cm^{-2}$ to obtain high recovery yield, at pH of 11 to 12. Electrowinning time was varied from 4 h to 24 h. Weight and composition of silver deposited at cathode was measured to give % recovery and purity of the electrowon silver (EW Ag). In the refining step, electrorefining of the silver cathode obtained from the electrowinning process was carried out to obtain high purity silver. Resembling the Moebius cell [3], the anode was the silver plate obtained from electrowinning, while 304 stainless steel was used as the cathode. Electrolyte was prepared using nitric acid (HNO_3) at 10 $g{\cdot}L^{-1}$ and silver nitrate ($AgNO_3$) solution, controlled at 120 g Ag/L, to ensure silver ion saturation in the electrolyte [9]. The electrorefining was carried out at a controlled potential of 0.8 V for 2 h and 30 min. The silver crystal deposited at cathodes and in the electrolyte was collected and subject to ultrasonic cleaning. Weight of the silver crystal was measured to determine % recovery and its composition was analyzed by ICP-OES for purity. For cyanide-based silver electroplating solutions, the samples were prepared by adding DI water to dilute at 100, 1000, 10000 times for the analysis of silver, aluminium, copper, zinc, phosphorus, and sodium elements. For silver plates obtained after electrowinning and silver crystal achieved from electrorefining, 65% HNO_3 solution of 20 mL to 30 mL was used to dissolve silver plates/crystals under heat using an alcohol lamp. After a complete dissolution, the solution volume was adjusted to 100 mL using DI water, followed by adding 5%v/v HNO_3 solution to dilute at 10 time and 50 time for the analysis of aluminium, copper, zinc, phosphorus, and sodium elements. Experimental set-up schematics of zinc cementation along with electrowinning and electrorefining are illustrated in Figure 3.

Figure 1. Transparent (left) and dark (right) waste solutions.

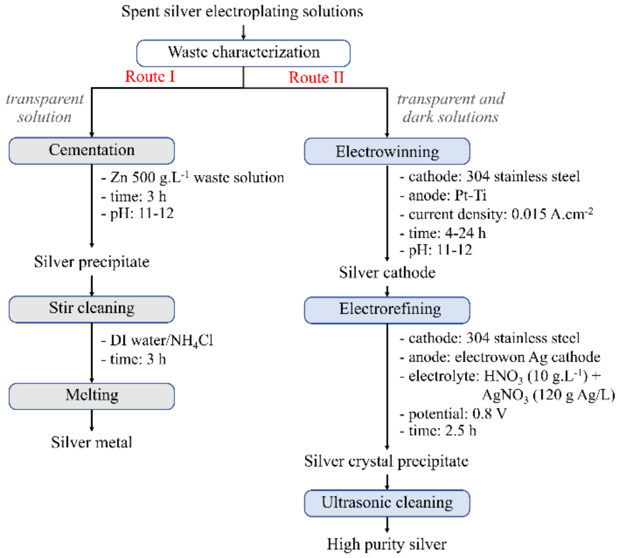
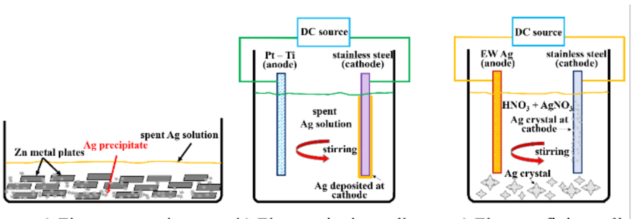


Figure 2. Experimental flow chart on silver recovery from spent electroplating solutions.

Table 1. Chemical composition of spent silver electroplating solutions (by ICP-OES).

Spent solution	Element ($g \cdot L^{-1}$)					
	Ag	Cu	Zn	Al	Na	P
Transparent	17.71	0.2391	0.0280	0.0463	1.0110	0.0337
Dark	33.36	0.1230	0.0180	0.0420	1.1750	1.3330



a) Zinc cementation b) Electrowinning cell c) Electrorefining cell

Figure 3. Experimental setups for route I: a) zinc cementation, route II: b) electrowinning and c) electrorefining.

3. Results and discussion

3.1 Recovery via zinc cementation

Metal concentration analyzed by ICP-OES of the transparent waste solution after cementation is illustrated in Figure 4. The amount of silver reduced from 17.71 $g \cdot L^{-1}$ for the original waste to 0.33 $g \cdot L^{-1}$ after 3 h of cementation using zinc metal. Concentrations of other metals such as copper, and aluminium remained very small, while that of zinc was found to increase to 3.78 $g \cdot L^{-1}$ after 180 min. However, SEM analysis showed that dark precipitates obtained after cementation appeared mostly in a dendritic form along with globules and metallic bands, as shown in Figure 5. Elemental analysis by EDS technique indicated that dendrites and globules contained around 94 wt% to 98 wt% of silver. Other elements such as copper, zinc, aluminium, and sodium in trace amounts were present. Point analysis on silver bands detached from zinc metal surfaces revealed significantly higher silver of around 98.91 wt%. Comparative tests on stir-cleaning of the silver precipitate using DI water and NH_4Cl showed slightly different results. Extensive EDS analysis on various locations of precipitates revealed that stir-cleaning via DI water gave slightly lower purity of silver of higher than 95 wt% while that from NH_4Cl stirring gave > 97 wt%. Moreover, results from ICP-OES of DI water after stir-cleaning showed 0.0311 $g \cdot L^{-1}$ of silver whereas only 0.0087 $g \cdot L^{-1}$ of silver was obtained by NH_4Cl stirring for 3 h. This indicated that NH_4Cl stirring gave slightly better silver purity. However, the recovery yielded only 86.16%, according to Equation (7), where $W_{\text{Ag precipitate}}$ and $W_{\text{Ag in waste solution}}$ are weights of silver precipitate and in the original waste solution respectively.

$$\% \text{ Recovery (cementation)} = (W_{\text{Ag precipitate}}/W_{\text{Ag in waste solution}}) \times 100 \quad (7)$$

Investigation on silver loss on the zinc metal surface, as illustrated in Figure 5(e) and (f), indicated very fine precipitates in the thin-plate form of around 2 µm size containing 28.18 wt% of silver, 34.11 wt% of oxygen, and 30.90 wt% of zinc. It was therefore assumed that silver loss might be due to silver oxide formation since the cementation was under the normal atmospheric condition, not in a vacuum or de-aeration atmosphere. After melting the silver precipitates using oxy-acetylene gas, silver metal was achieved as shown in Figure 6. Due to the small amount of silver metal attained, and not sufficiently high % recovery, purification has not been carried out in this case.

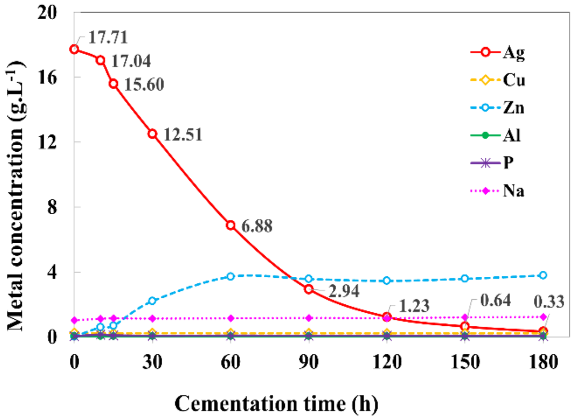
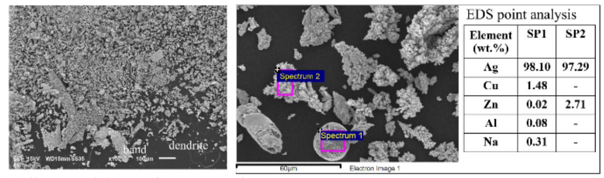
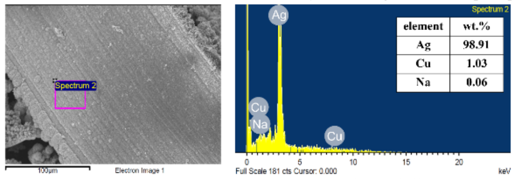


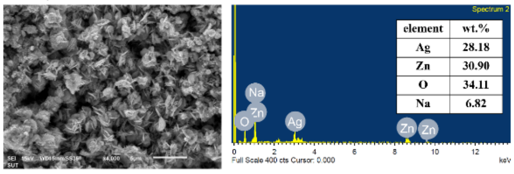
Figure 4. Metal concentrations of waste solution after 3 h cementation (by ICP-OES).



a) Silver precipitates after cementation b) EDS analysis of silver precipitates



c) Silver band d) EDS analysis of silver band



e) Precipitate left on zinc surface f) EDS analysis of silver band

Figure 5. Silver precipitates after 3 h cementation using zinc metal (SEM + EDS analysis).

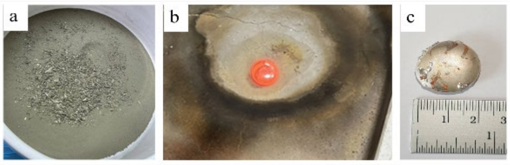
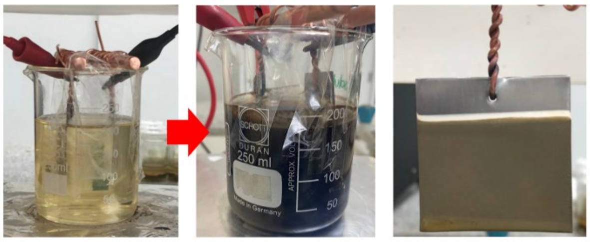


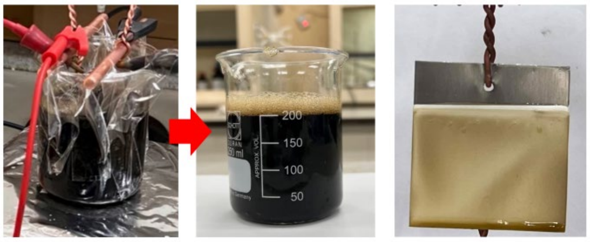
Figure 6. Silver precipitates after a) filtering, b) melting, and c) solidified silver metal.

3.2 Recovery via electrowinning and electrorefining

For the first step of electrowinning using 200 mL of the transparent waste solution, the silver appeared to deposit at the cathode, while the waste solution color changed significantly from light yellow to dark brown, same as the dark waste solution in Figure 7. This might be due to oxidation process taking place during electrowinning [10]. The dark appearance of the waste solution was studied by filtering the electrolyte after electrowinning and subjected to XRD (Bruker D2 PHASER) analysis. It appeared that the black residue was cyanide complex compound of sodium-nitrogen-carbon and sulfur, as shown in Figure 8.

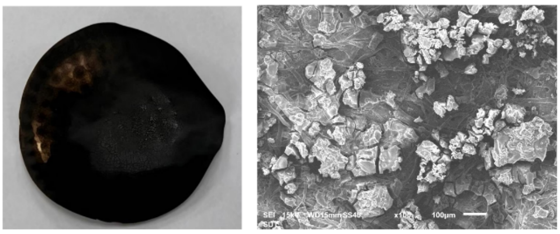


a) Electrowinning cell of transparent waste solution
b) Waste solution after electrowinning for 24 h
c) Silver deposited at cathode (from transparent solution)

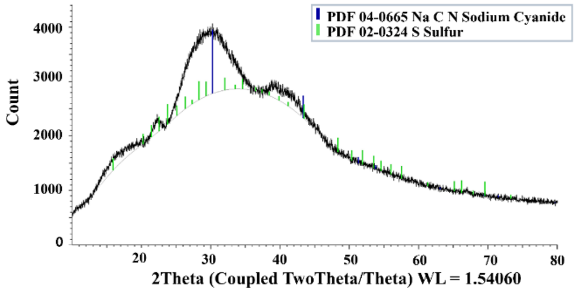


d) Electrowinning cell of dark waste solution
e) Waste solution after electrowinning for 24 h
f) Silver deposited at cathode (from dark solution)

Figure 7. Electrowinning cell setup to give silver deposited at cathode.



a) Black residue on filter paper
b) Black residue under SEM



c) XRD spectra of black residue

Figure 8. XRD spectra of black residue on filter paper after electrowinning of spent silver electroplating solution for 24 h.

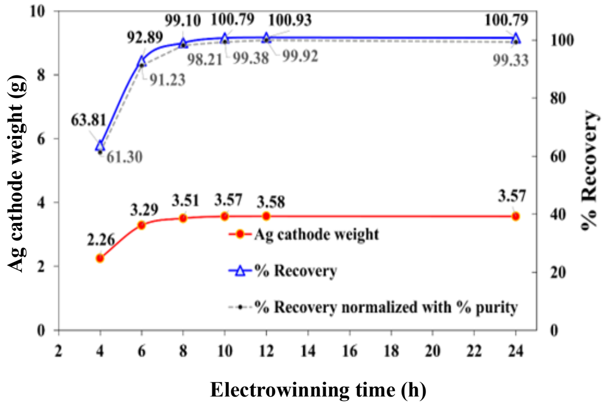


Figure 9. Effect of electrowinning time on silver recovery from transparent waste solution.

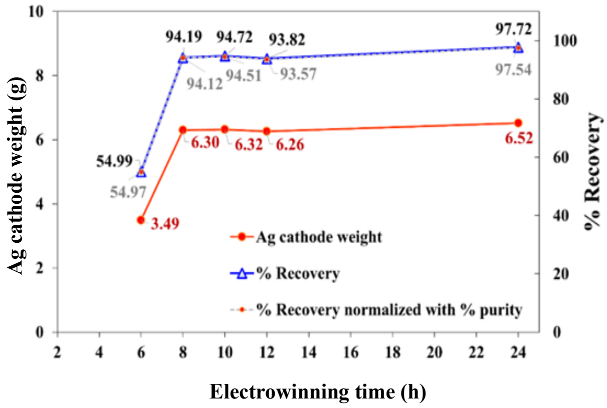


Figure 10. Effect of electrowinning time on silver recovery from dark waste solution.

The effect of electrowinning time on silver recovery at cathode from transparent waste solution is graphically shown in Figure 9. Weight of silver cathode increased from 2.26 g to 3.51 g when the electrowinning time increased from 4 h to 8 h. No significant increase in silver cathode weight till electrowinning time reached 24 h. In terms of silver recovery, electrowinning gave more effective results in comparison to that obtained via zinc cementation. Electrowinning for 8 h to 24 h gave high % recovery, according to Equation (8), where $W_{\text{Ag cathode}}$ and $W_{\text{Ag in waste solution}}$ are weights of silver deposited at cathode and in the original waste solution respectively.

$$\%\ \text{Recovery (electrowinning)} = (W_{\text{Ag cathode}}/W_{\text{Ag in waste solution}}) \times 100 \quad (8)$$

It should be noted that silver recovery of greater than 100% might result from minor impurities that also deposited at the cathode. A dashed line curve of silver recovery after being normalized with % purity of silver deposited at cathode (IPC-OES result) is provided, and it shows the greatest recovery value of 99.33% after electrowinning for 24 h.

Electrowinning of the dark waste solution for the same period of 24 h gave more weight of silver deposited at the cathode, as shown in Figure 10. After 6 h electrowinning, the silver weighed 3.49 g and increased to 6.30 g after 8 h electrowinning. This resulted from the greater amount of 33.36 g·L^{-1} of silver in the original dark waste solution, which was nearly double to 17.71 $g \cdot L^{-1}$ of silver in the transparent waste solution. Silver recovery normalized by % purity of the deposit gave the greatest value of 97.54% after 24 h electrowinning, which was slightly lower than that of the transparent type.

The metal concentration of the transparent and dark waste solutions after electrowinning is illustrated in Figure 11 and Figure 12 respectively. The silver contents reduced significantly from its original contents after electrowinning for 6 h. Other metal contents such as copper, aluminium, zinc, and sodium remained almost constant. By considering the silver purity, ICP-OES result indicated the values obtained were 98.22% to 99.95% (8 h to 24 h electrowinning), as listed in Table 2. Further purification was therefore required via electrorefining in the next step.

During electrorefining, silver crystal nucleated at cathode, grew to a dendritic form with time, and later dropped down to the beaker bottom. The silver crystal was subsequently retrieved from the electrorefining cell, and subject to ultrasonic cleaning as shown in Figure 13. The recovery of pure silver after electrorefining is expressed in Equation (8), where $W_{\text{Ag recovered}}$ is weight of silver recovered, and $W_{\text{Ag loss at anode}}$ is weight loss of silver at anode.

$$\%\ \text{Recovery (electrorefining)} = (W_{\text{Ag recovered}}) / W_{\text{Ag loss at anode}}) \times 100 \quad (8)$$

In the case of transparent waste solution, electrorefining of the electrowon silver cathode gave the recovery yield of 85.23% based on silver deposited on the cathode, as detailed in Table 3. However, if fine silver precipitate after filtering the electrolyte was included, and the amount of silver loss in the electrolyte was subtracted, the recovery then become 99.11%. For dark waste solution, the first run of electrorefining gave the recovery yield of 83.06%, which was comparable to the result obtained from the transparent waste solution. The second run of electrorefining (using the first run electrolyte) in the case of dark waste solution gave significantly reduced recovery of only 58.14%. This was due to the amount of silver in the electrolyte that has decreased around 16%, providing less silver saturation in the electrolyte system. Therefore, adjustment of the $HNO_3 + AgNO_3$ electrolyte should be done to reach silver saturation for electrorefining. In terms of silver purity, both cases gave greater purity than that obtained after electrowinning. High purity silver of greater than 99.99%, as listed in Table 4, was achieved as the final recycling product from both transparent and dark waste solutions.

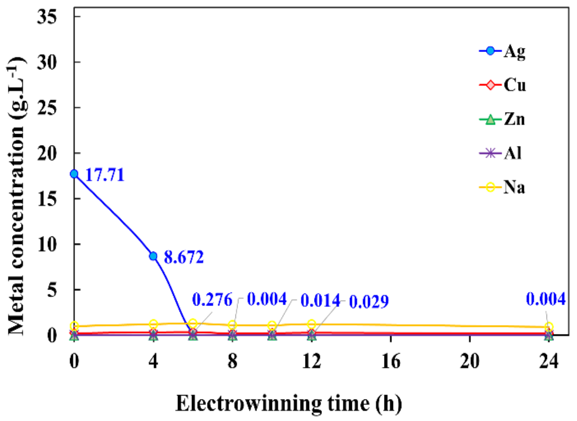


Figure 11. Metal concentration in transparent waste solution after electrowinning for 4 h to 24 h.

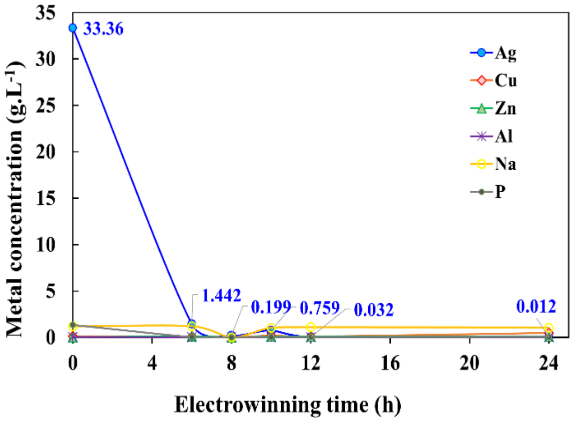


Figure 12. Metal concentration in dark waste solution after electrowinning for 6 h to 24 h.

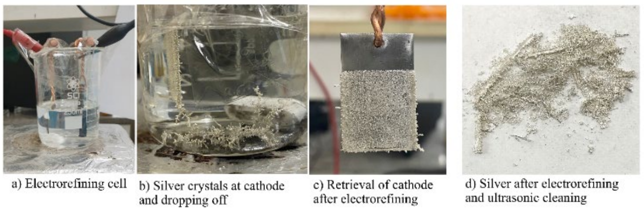

a) Electrorefining cell
b) Silver crystals at cathode and dropping off
c) Retrieval of cathode after electrorefining
d) Silver after electrorefining and ultrasonic cleaning

Figure 13. Electrorefining of silver cathode obtained after electrowinning of transparent electroplating waste solution.

Table 2. Chemical composition of silver cathode after electrowinning (by ICP-OES).

Waste solution	Electrowinning time (h)	Element (wt%)					
		Ag	Cu	Zn	Al	Na	Other
Transparent	4	96.07	1.04	0.53	1.03	1.31	0.02
	6	98.22	0.69	-	0.55	0.53	0.01
	8	99.11	0.56	-	0.22	0.10	0.01
	10	98.60	0.75	-	0.28	0.30	0.07
	12	99.00	0.44	-	0.26	0.27	0.03
	24	98.55	0.46	-	0.51	0.43	0.05
Dark	6	99.95	-	0.037	-	-	0.012
	8	99.73	-	0.235	0.003	-	0.010
	10	99.78	-	0.205	0.004	-	0.014
	12	99.73	-	0.235	0.030	-	0.010
	24	99.82	-	-	-	-	0.020

Table 3. Electrorefining results of silver cathode obtained from electrowinning.

Type of waste solutions	Weight loss at anode (g)	Ag crystal deposited at cathode (g) [1]	Ag in electrolyte after filtering (g) [2]	Ag loss from electrolyte (g) [3]	% Ag recovery based on [1]	% Ag recovery based on [1] + [2] - [3]	% purity
Transparent	0.9194	0.7836	0.1589	0.0313	85.23	99.11	>99.99
Dark (ER 1)	0.6624	0.5502	-	-	83.06	-	>99.99
Dark (ER 2)	0.2738	0.1595	-	-	58.14	-	-

Table 4. Chemical composition of electro-refined silver cathode (by ICP-OES).

Spent solution	Element ($g \cdot L^{-1}$)					% Purity
	Cu	Zn	Al	Na	P	
Transparent	0.002	0.002	0.002	0.001	0.003	99.990
Dark	0.001	0.001	-	-	-	99.998

Table 5. Chemical composition of electrolytes before and after electrorefining (by ICP-OES).

Electrolyte		Composition ($g \cdot L^{-1}$)					
		Ag	Cu	Zn	Al	P	Na
Before electrorefining		118.20	0.0074	0.0035	0.0069	0.0003	0.0310
After electrorefining	Transparent	111.94	0.0775	0.0043	0.0076	0.0026	0.0395
	Dark	98.105	0.0776	0.0044	0.0050	0.0020	0.0305

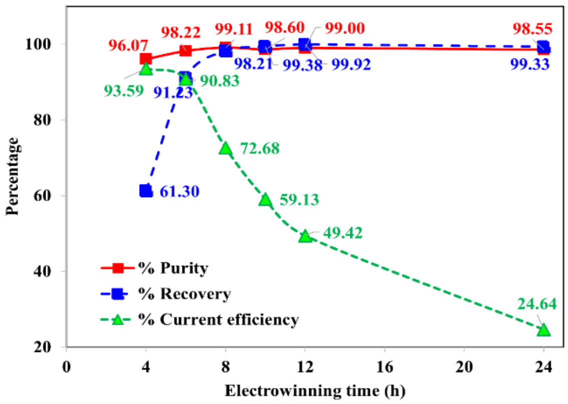


Figure 14. % Current efficiency, % purity, and % recovery for electrowinning of spent silver electroplating solution (transparent) over 4 h to 24 h.

According to experimental results, silver recovery from spent electroplating solutions of the two types could be achieved via electrowinning and followed by electrorefining. Electrowinning offered effective recovery of silver at higher than 99.33% and 97.54% while its purities were 98.55% and 99.82%, for transparent and dark solutions respectively. The main impurities were copper and aluminium for the transparent type and other elements such as tin in trace amount for dark type solution. Subsequent electrorefining could purify the electrowon silver cathode to give around 85.23% (silver precipitate excluded) and 99.11% (silver precipitate included) recovery at the purity of higher than 99.99% for transparent solution. The amount of copper in the silver cathode obtained after electrowinning reduced from 0.46 wt% to a trace amount after electrorefining. Moreover, ICP-OES result of electrolyte as listed in Table 5, indicated that copper might be dissolved and stayed in electrolyte, giving the values of 0.0074 $g.L^{-1}$ and 0.0775 $g.L^{-1}$ of copper before and after electrowinning. It is plausibly that the amount of silver in the electrolyte might be high enough (118.2 $g \cdot L^{-1}$) to facilitate deposition of pure silver, while less noble metal such as copper stayed dissolved in the electrolyte. Further, the difference between silver and copper potentials is large at 0.5 V. Therefore, co-deposition of copper on the cathode might be inhibited [9]. In comparison to zinc cementation route, the recovery was lower, which was at 86.16%, and the purity was greater than 94% prior to melting. The significant loss was due to silver precipitate on the zinc metal surface.

Current efficiency was investigated in the case of spent silver electroplating (transparent) solution. The current was recorded and read at 1 h interval for the calculation of % current efficiency as expressed in Equation (9) and Equation (10) as follows:

$$m = (M \times i \times t)/(n \times F) \qquad (9)$$

$$\% \text{ Current efficiency} = (W_{\text{Ag loss at anode}}) / m) \times 100 \qquad (10)$$

where m is theoretical yield (current efficiency) in gram, M is atomic mass of silver in gram, i is current in ampere, t is time in seconds, n is oxidation state of silver (n = 1), F is Faraday's constant (96487 Coulombs), and $W_{\text{Ag at cathode}}$ is weight of silver at cathode. It is shown in Figure 14 that current efficiency is high when electrowinning for 4 h, giving 93.59% current efficiency. The value reduced to 90.83% and 72.68% when electrowinning for 6 h and 8 h respectively and reached the lowest value of 24.64% at 24 h. If % current efficiency is considered, electrowinning for 8 h might be preferred. However, for electrorefining, current efficiency was obtained at 64.69%.

Material flow and mass balance of spent silver electroplating (transparent) solution recycling via electrowinning and electrorefining is demonstrated in Figure 15. To start with 20 L of the transparent waste solution having 354.2 g of silver remaining in the solution, electrowinning controlled at current density of 0.015 $A \cdot cm^{-2}$ (for 8 h to 24 h) when consider % recovery will give silver deposited at cathode of 351.82 g (99.33% recovery) after DI water rinsing. This requires 15 L of DI water, which can be reused after water treatment.

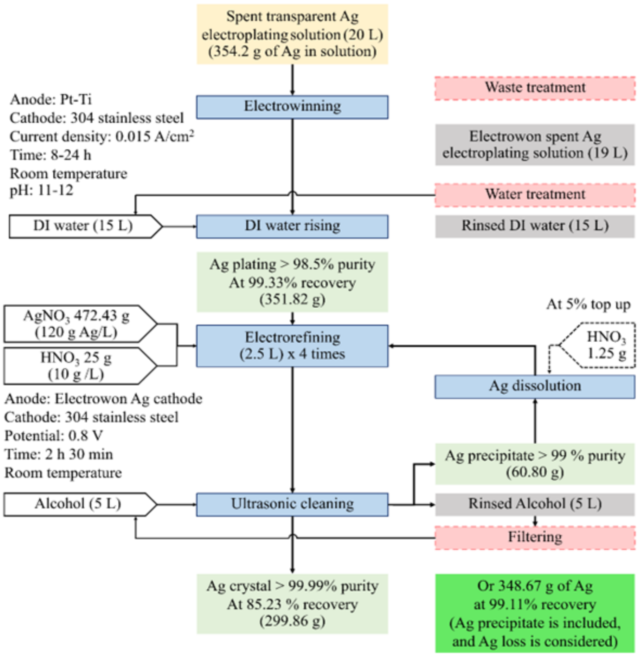


Figure 15. Materials flow and mass balance of spent silver electroplating (transparent) solution recycling via electrowinning and electrorefining.

The silver plate is subsequently set as the anode for electrorefining at potential of 0.8 V, and HNO_3 (10 g·L^{-1}) + $AgNO_3$ (120 g Ag/L) is used as the electrolyte. Finally, pure silver crystal of 299.86 g is obtained at 85.23% recovery and > 99.99% purity. Ultrasonic cleaning requires 5 L of alcohol and can be reused. If silver precipitate is included and the silver loss in the electrolyte is considered, silver of 348.67 g at 99.11% recovery is obtained. In this case, reuse of the electrolyte in the electrorefining process is considered. Silver precipitate of 60.8 g is dissolved back to the electrolyte, plus 5% top up of silver to assure silver ion saturation.

4. Conclusions

According to experimental results, it can be deduced that electrowinning of spent silver electroplating solutions, followed by electrorefining were found effective for the two different wastes, irrespective of silver contents (17.17 g·L^{-1} to 33.36 g·L^{-1}). The key parameter for electrowinning was the low current density at 0.015 A·cm^{-2}, to obtain high recovery (> 97.5%) and purity of silver (> 98.55%) at cathode. For electrorefining, it required high silver content in the electrolyte, using nitric acid (HNO_3) at 10 g·L^{-1} and silver nitrate ($AgNO_3$) at 120 g Ag/L to obtain high purity silver of greater than 99.99%. Recycling via zinc cementation route yielded comparatively lower recovery at only 86.16% due to silver loss in precipitate forms.

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