Electrochemical reclamation of silver from silver-plating wastewater using static cylinder electrodes and a pulsed electric field

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ABSTRACT

Silver was reclaimed from silver-plating wastewater by using a pulsed electric field (PEF) combined with static cylinder electrodes (SCE). The conditions that produced the maximal silver recovery rate (RR_{Ag}) (99%) were as follows: average retention time of 10 min, interelectrode gap of 50 mm, solution pH of 9.0, temperature of 45 °C, initial Ag(I) concentration of 1000 mg L^{-1}, PEF pulse frequency of 1200 Hz, current density of 5.0 A m^{-2} and a pulse duty cycle of 60%. Compared with the conventional direct current (DC) technology, the PEF process exhibited improvements in the silver recovery rate (RR_{Ag}), total energy consumption (TEC) and physical properties of the silver deposits, especially for low Ag(I) concentrations, for example, from 500 to 1000 mg L^{-1}. For an initial Ag(I) concentration of 500 mg L^{-1}, the PEF process produced an RR_{Ag} of up to 99%, and the TEC was 4.56 kWh (kg Ag)$^{-1}$. In comparison, the RR_{Ag} and TEC were 90% and 5.66 kWh (kg Ag)$^{-1}$, respectively, in the DC process. The results of SEM observation and XRD analysis indicated that the silver deposits formed by the PEF process were smaller, denser, and of a higher purity than those produced by the DC process. Therefore, the presented method was effective for reclaiming silver from silver-plating wastewater.

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1. Introduction

Owing to its special properties such as the highest electrical and thermal conductivities and the lowest contact resistance of all metals, silver, a lustrous, soft, white metal, is extensively used in industry, especially in the electronics industry [1]. Silver electroplating is primarily used to deposit a layer of silver onto another metal to obtain a desired property such as abrasion and wear resistance, corrosion protection or aesthetic appeal. However, the electroplating process not only consumes a great deal of silver, but also produces a lot of wastewater containing silver and cyanide. The wastewater comes from metal surface cleaning, rinsing, silver stripping and spent electrolyte. Wastewater from the cleaning and rinsing process is a diluted solution, with Ag(I) concentrations between 1 and 3 g L^{-1}, but the spent electrolyte and silver stripping solution are much more concentrated, with Ag(I) concentrations from 20 to 60 g L^{-1}. As a pure metal or ore, silver cannot be dissolved

and is not harmful to the environment. However, high doses of some silver compounds have been found to be extremely toxic to aquatic life forms, such as fish [2–4]. Furthermore, supplies of silver raw materials are dwindling because of their scarcity while demands for silver in industries are still increasing. Therefore, recovery of silver from electroplating wastewater is of interest, for both water resource protection and silver reclamation.

To date, many methods have been developed to recover silver from industrial wastewater, including chemical reduction [5], membrane filtration [6], ion exchange [7], adsorption [8], and electrochemical methods [9–13]. Each of the methods has pros and cons in practical applications. The electrochemical approach to recover silver from wastewater is relatively simple and clean. Generally speaking, the equipment for electrochemical treatment is a cheap electrolyte bath with an insoluble anode and a proper cathode. Electrochemical treatment is also notable for requiring few extra chemical reagents, producing little sludge, exhibiting high selectivity and having low operating costs [14]. However, conventional electrochemical treatment using DC and static electrodes is undesirable, as the current is closely related to the Ag(I) concentration, and must be carefully tuned to avoid producing dendritic and spongy silver deposits. It is also possible for hydrogen evolution or oxygen reduction via DC to interfere with the electrochemical

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Nomenclature

C_i	initial Ag(I) concentration (mg L^{-1})
C_t	residual Ag(I) concentration at any time t (mg L^{-1})
d_e	interelectrode gap (mm)
D	diffusion coefficient (m^2 s^{-1})
DC	direct current
E	tank voltage (V)
EC	electrolyte circulation
f	pulse frequency (Hz)
i	limiting current density (mA cm^{-2})
I	current of the electrolysis process (mA)
J	current density (A m^{-2})
k	first order rate constant (min^{-1})
K_m	mass transfer coefficient (kg m^{-2} s^{-1})
PEF	pulsed electric field
Q	volumetric flow rate of electrolyte circulation (mL min^{-1})
RCE	rotating cylinder electrode
RR_{Ag}	recovery rate of Ag (%)
SCE	static cylinder electrodes
TEC	total energy consumption per kilogram silver deposits (kWh (kg Ag)$^{-1}$)
T	temperature of the solution (°C)
T_{on}	active time of pulsed electric field (ms)
T_{off}	inactive time of pulsed electric field (ms)
U_v	linear velocity at the surface of the cylinder (m s^{-1})
V	electrolysis reactor volume (mL)
V_T	solution volume (L)
W_1	energy consumption of the circulation pump (kWh)
W_2	energy consumption of electrolysis process (kWh)

Greek symbols

ρ	solution density (kg m^{-3})
r	pulse duty cycle (%)
μ	absolute viscosity of the solution (Pa s)
τ_T	average retention time of the electrolyte in the reactor (min)

recovery of silver. As a result, the recovery rate of DC electrochemical treatment is generally less than 85% [15]. In recent years, the rotating cylinder electrode (RCE) has been successfully applied in DC electrolysis metal removal processing of solutions with high concentrations of metal ions, resulting in high electric current efficiency [9,16–18]. Alejandro et al. have designed reactors with RCE for the recovery of silver from ammoniacal thiosulfate leaching solution. These reactors exhibit a recovery rate of 80% and produce deposits containing 90% silver [19]. Chatelut et al. designed a reactor with RCE for the recovery of silver from photographic wastewater with Ag(I) concentrations as high as 10 g L^{-1}, and achieved a recovery rate higher than 95% [20]. Robinson and Walsh have developed a method that uses RCE to reclaim silver from fixer solution with Ag(I) concentrations from 25 to 30 mg L^{-1} [21]. However, the results showed that the efficiency of the method was less than 15%. Therefore, RCE is unsuitable for the electrolysis of dilute Ag(I) solutions as the current efficiency is unsatisfactory and highly pure silver deposits cannot be obtained.

The PEF is firstly used as a novel means of controlling membrane ion-transport selectivity in electrodialysis of Na$^+$ and Ca^{2+} ions [22]. As opposed to the above DC method, the PEF technique applies a pulsed current, with a constant current density during the *pulse on* time (T_{on}), followed by a pause, the *pulse off* time (T_{off}). It is reported that desalination can be enhanced by employing PEF in electrodialysis [23–25]. In this work, an unexploited electroly-

sis process, combining PEF with SCE was developed to recover Ag from dilute silver-plating wastewater. Electrolyte circulation (EC), instead of RCE, was adopted to homogenize the electrolyte solution. EC stirs the solution better than rotating electrodes. To the best of our knowledge, electrolysis using PEF to recover silver from low silver-plating wastewater has not yet been reported. In this paper, the effects of EC flow rate, interelectrode gap, initial Ag(I) concentration (initial C_{Ag}), pH of the solution, temperature, pulse frequency, pulse duty cycle and current density on the RR_{Ag} and the TEC in the PEF process were investigated. In addition, the DC electrolysis process was carried out for comparison with the PEF process.

2. Materials and methods

2.1. Reagents

Silver-plating wastewater containing silver cyanide was collected from a local plating company (Xiamen YongHong Technology Co. Ltd, China). The wastewater, with a pH value of 8.8 ± 0.1, was composed of many components, including potassium hydroxide (KOH), potassium cyanide (KCN) and some organic additives. In the experiments, the C_{Ag} of the electrolytic solutions ranged from 500 to 2500 mg L^{-1}, prepared by diluting the wastewater, which had a C_{Ag} of 4882 mg L^{-1}. AR grade KOH, sulfuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$) were obtained from Shanghai Reagent Co. Ltd, China. Deionized water was used for solution preparation.

2.2. Electrochemical apparatus

Fig. 1 shows the electrolysis setup used for silver reclamation. A 1.5 L batch electrolysis reactor was employed and a glass beaker was used as the electrolysis cell. In the reactor, a porous graphite column (with a diameter of 10 mm and a length of 100 mm) and a stainless steel cylinder (with diameters of 70 or 110 mm and a length of 100 mm), prepared by Xiamen Yonghong Technology Co. Ltd, China, were used as the anode and the cathode, respectively. A peristaltic pump (BT100-1L, Baoding Longer Precision Pump Co. Ltd, China) was used to circulate the electrolyte during the electrolysis process. An electrically heated thermostatic water bath (DK8-501A, Shanghai Precision & Scientific Instrument Co. Ltd, China) was used to regulate the solution temperature. An ammeter (DDS314, Zibo
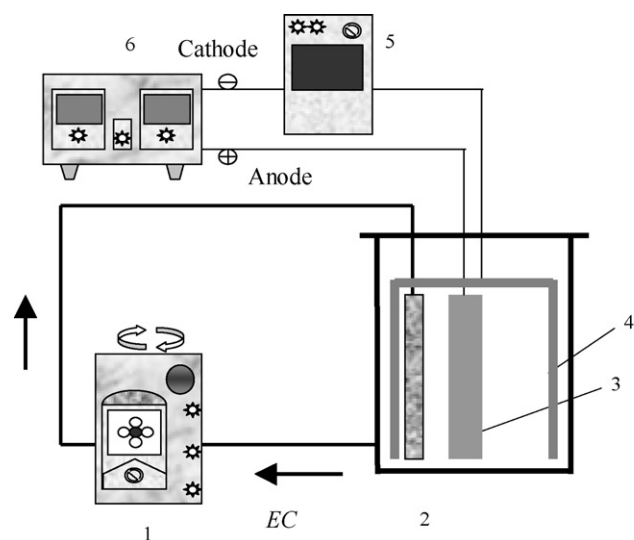

Fig. 1. Schematic experimental setup. (1) Peristaltic pump; (2) electrolysis reactor; (3) porous graphite anode; (4) stainless steel cathode; (5) ammeter; (6) pulse electrical source.

Billion Electron Co. Ltd, China) was employed to monitor the electrolytic current. The solution pH was monitored by a pH meter (PHS-3C, Xiamen Analysis Apparatus Co. Ltd, China). A digital electrical source (KYD-I, YuanShunDa Electronic Machinery Co. Ltd, China) with a voltage range of 0–50 V and a current range of 0–10 A was used to offer a regularly pulsed current or direct current to the cell.

2.3. Silver reclamation from wastewater via electrolysis process

Before the electrolysis process, the cathode and the anode were cleaned for 10 min with 0.5 and 1.0 mol L^{-1} H$_2$SO$_4$, respectively, and then rinsed for 10 min with deionized water. Then, 1.0 L of diluted wastewater was added to the cell. The PEF and the DC processes were carried out separately, for comparison. The pH of the solution was adjusted with either 30% HNO$_3$ or 30% NaOH, depending on the required pH of the solution. At 10-min intervals, 2-mL samples were taken from the cell for Ag(I) analysis, the electric current was monitored, and the electric work was measured, in order to calculate the energy consumption. The resulting deposits on the cathodes were washed with deionized water, dried in the air, and scraped from the cathodes. The electrolysis was stopped when the RR_{Ag} was 99% or the electrolysis time was 100 min.

2.4. Characterization

All experiments were carried out twice and each parameter was measured three times. The obtained variation coefficients were below 5% for the three measurements and for all the duplicate experiments.

The average retention time (τ_T, min) of the electrolyte in the reactor, which was used to describe the EC flow rate, was calculated using the following formula:

$$\tau_T = \frac{V}{Q} \tag{1}$$

where V (mL) is the volume of the reactor and Q (mL min^{-1}) is the volumetric flow rate of EC.

The Ag(I) concentration was determined by a flame atomic absorption spectrometer (FAAS Unicam 939, USA). The silver recovery rate (RR_{Ag}, %) was calculated as follows:

$$RR_{Ag} = \frac{C_i - C_t \times 100\%}{C_i} \tag{2}$$

where C_i (mg L^{-1}) is the initial Ag(I) concentration and C_t (mg L^{-1}) is the Ag(I) concentration at any time t.

The energy consumption for circulation (W_1), electrolysis (W_2) and heating (W_3) was measured by watt-hour meters (ZERA MT-3000, Germany). The total energy consumption per kilogram silver deposits (TEC, kWh (kg Ag)$^{-1}$) was calculated as follows:

$$TEC = \frac{(W_1 + W_2 + W_3) \times 10^6}{(C_i - C_t)V_T} \tag{3}$$

where W_1 (kWh) is the energy consumption for circulation, W_2 (kWh) is the energy consumption for electrolysis, W_3 (kWh) is the energy consumption for heating and V_T (L) is the volume of electrolyte.

The morphology of the deposits was investigated using a scanning electron microscope (SEM) (LEO-1530, Germany) equipped with energy-dispersive X-ray spectroscopy (EDX). The crystalline structure of the deposits was determined with an X'Pert Pro X-ray Diffractometer (XRD) (40 kV, 30 mA, Cu Kα PANalytical BV, Netherlands).
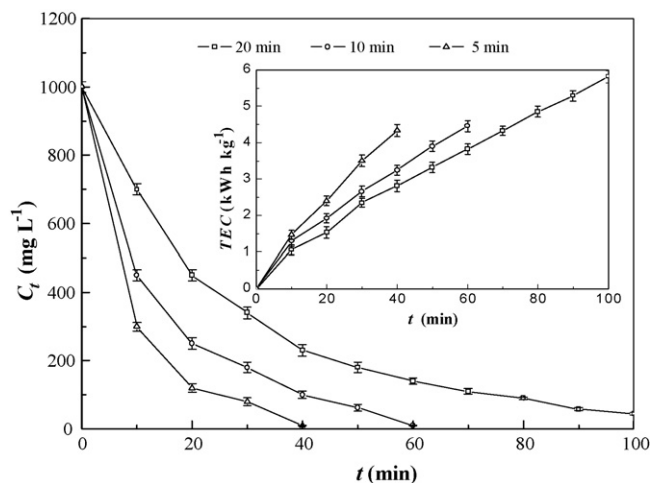

Fig. 2. Effect of average retention time on residual Ag(I) concentration; the inset shows the effect of average retention time on TEC (f = 1200 Hz; r = 60%; J = 5.0 A m^{-2}; C_i = 1000 mg L^{-1}; pH = 9.0; T = 45 °C; d_e = 50 mm).

3. Results and discussion

3.1. Operating conditions of the PEF process

3.1.1. Effect of average retention time

The effect of the average retention time (τ_T) on the RR_{Ag} is shown in Fig. 2. It could be seen that the residual Ag(I) concentration (C_t) decreased with electrolysis time, and the reclamation of Ag(I) and RR_{Ag} increased with decreasing retention time (τ_T). The inset in Fig. 2 indicates that the TEC increases with electrolysis time. For a constant electrolysis time, the TEC decreased with increasing retention time (τ_T). When the retention time was 5 min, the RR_{Ag} was 99% with a TEC of 4.35 kWh (kg Ag)$^{-1}$ and an electrolysis time of 40 min. As the retention time increased to 10 min, the TEC increased to 4.46 kWh (kg Ag)$^{-1}$ and the electrolysis time was prolonged to 60 min for an RR_{Ag} of 99%. For a retention time of 20 min, the RR_{Ag} only reached 95%, even for a TEC as high as 5.81 kWh (kg Ag)$^{-1}$ and an electrolysis time of 100 min. Therefore, the optimum retention time of the electrolyte in the reactor was 10 min for the PEF process. With a lower retention times (e.g., 5 min), the energy consumption of the circulation pump was so high that it approached TEC. These results could be clarified by understanding the characteristics of mass transfer around the electrode surface.

The electrodepositing of silver on the cathode surface from silver-plating wastewater with low C_{Ag} is diffusion-controlled [26]. In the PEF process, the electrolyte is circulated by pumps, to increase mass transfer around the electrode surface [1]. K_m (kg m^{-2} s^{-1}) is the mass transfer coefficient of a cylindrical electrode, which can be described by the following equation [1,9,17]:

$$K_m = 0.0791 d^{-0.3} \left(\frac{\mu}{\rho}\right)^{-0.344} D^{+0.644} U_v^{+0.7} \tag{4}$$

where D (m^2 s^{-1}) is the silver diffusion constant, d (m) is the diameter of the cylindrical cathode, ρ (kg m^{-3}) is the solution density, μ (Pa s) is the absolute viscosity of the solution and U_v (m s^{-1}) is the linear velocity at the surface of the cylinder.

Obviously, K_m varied as the EC flow rate to the power 0.7. Increasing of the EC flow rate enhanced the mass transfer rate, and thus improved the RR_{Ag}, especially in the case of low C_{Ag}, for example, below 1000 mg L^{-1} [27,28]. Furthermore, the limiting current density for silver deposition increased with increasing of mass transfer rate. As a result, the current efficiency could be improved, thereby reducing the TEC for electrolysis.
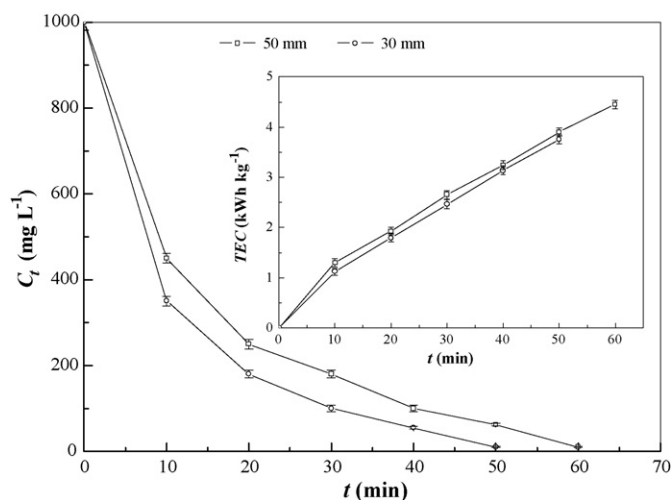
Fig. 3. Effect of interelectrode gap on residual Ag(I) concentration; the inset shows the effect of interelectrode gap on TEC (f = 1200 Hz; r = 60%; J = 5.0 A m^{-2}; τ_T = 10 min; C_i = 1000 mg L^{-1}; pH = 9.0; T = 45 °C).

3.1.2. Effect of interelectrode gap

In general, interelectrode gap (d_e) affects the quality of the deposits, the required energy, and the recovery efficiency [1]. However, it has been reported that interelectrode gap (d_e) of less than 220 mm has little effect on the electrolysis performance of copper electroplating with 69.9% nitric acid (pH of the solution 1.4) [12]. In this work, two different cylindrical cathodes (one with d_e 30 mm, and the other with d_e 50 mm) were used to investigate its effects on the RR_{Ag} and the TEC in the PEF process. The results from both cathodes are presented in Fig. 3.

As shown in Fig. 3, the rate of silver reclamation increases, and the energy consumption decreases when the interelectrode gap (d_e) is decreased from 50 to 30 mm. However, the changes in the RR_{Ag} and TEC were slight. After 50 min of electrolysis, the RR_{Ag} and TEC were 99% and 3.78 kWh (kg Ag)$^{-1}$, respectively, for the cell with an interelectrode gap (d_e) of 30 mm. For the cell with an interelectrode gap (d_e) of 50 mm, the RR_{Ag} and TEC were 93.8% and 3.90 kWh (kg Ag)$^{-1}$, respectively, for the same electrolysis time. Because of the smaller diameter, the cathode with an interelectrode gap (d_e) of 30 mm provided a smaller surface area and produced a higher current density, which increased the silver electrodepositing rate on the cathode. These results could also be explained by Eq. (4). K_m varied as the cathode diameter to the power −0.3. The mass transfer rate increased with the decreasing cathode diameter, and thus the RR_{Ag} improved. However, processing the cathode with 30 mm of interelectrode gap (d_e) was much more complex and expensive than processing the 50-mm cathode. Thus, the cathode with 50 mm of interelectrode gap (d_e) was chosen and used in this work.

3.1.3. Effect of initial C_{Ag}

Silver reclamation from wastewater with initial values of C_{Ag} (C_i) equal to 500, 1000 and 2000 mg L^{-1} was also studied with the PEF. The effect of the initial C_{Ag} (C_i) on RR_{Ag} is given in Fig. 4. The results indicated that RR_{Ag} increased with initial C_{Ag} (C_i). After 30 min of electrolysis, C_{Ag} was reduced from the initial 1000 to 70 mg L^{-1}, giving an RR_{Ag} of 93%. For comparison, the concentration reductions from the other solutions were from 500 to 45 mg L^{-1}, with an RR_{Ag} of 91%, and from 2000 to 200 mg L^{-1}, giving an RR_{Ag} of 90%. It can be seen in Fig. 4 that the apparent rate constant (k) evidently increases from 0.085 to 0.095 min^{-1} as the initial C_{Ag} (C_i) increases from 500 to 1000 mg L^{-1}. However, the rate constant value (k) decreased to 0.083 min^{-1} at an initial C_{Ag} of 2000 mg L^{-1}. This indicated that the
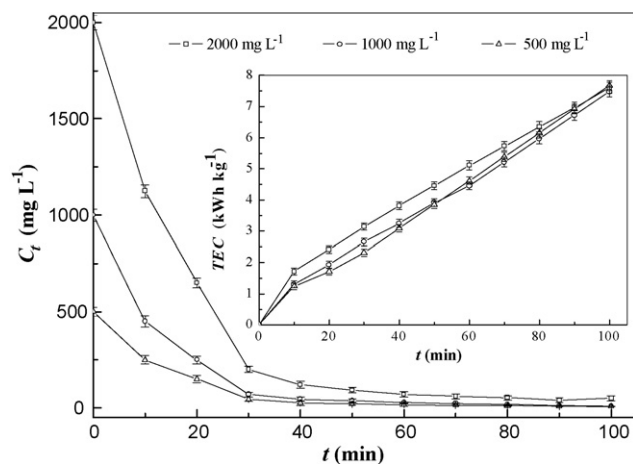

Fig. 4. Effect of initial C_{Ag} on residual Ag(I) concentration; the inset shows the effect of initial C_{Ag} on TEC (f = 1200 Hz; r = 60%; J = 5.0 A m^{-2}; τ_T = 10 min; pH = 9.0; T = 45 °C; d_e = 50 mm).

electrolysis reaction rate decreased significantly at high initial C_{Ag} (e.g., C_i = 2000 mg L^{-1}), probably because of the different morphology of the silver deposits formed on the electrode surface, and its subsequent influence on further silver deposition [29].

The inset in Fig. 4 shows that the TEC for an initial C_{Ag} of 2000 mg L^{-1} is higher than that for initial C_{Ag} values of 1000 or 500 mg L^{-1}. However, the TEC with 1000 mg L^{-1} was higher than that of 500 mg L^{-1} before 55 min, and thereafter slightly lower. This indicated that the energy consumption of electrolysis (W_2) played an important role in determining the TEC at high initial C_{Ag} (e.g., C_i = 2000 mg L^{-1}), while, at lower initial concentrations (e.g., C_i = 1000 or 500 mg L^{-1}), the energy consumption of the circulation pump (W_1) was dominant. The above results showed that solutions with high initial C_{Ag} (C_i = 2000 mg L^{-1}) led to high TEC and low RR_{Ag}, as reported by Hwang et al. [30,31]. Thus, an initial C_{Ag} of around 1000 mg L^{-1} should be used in practical applications.

3.1.4. Effect of pH of the solution

The cyanide oxidation process is very sensitive to the pH of the solution. The pH has an effect not only on the cyanide characteristics but also on the reaction rate constant of the pulse electrolysis process [1]. The change of the solution pH during the pulse electrolysis process was studied. The results showed the pH of the solution decreased with the electrolyte time according to the following equation:

$$y = 1.845 \times \exp(-0.0366t) + 7.138 \tag{5}$$

where y is the pH value of the solution and t is the electrolyte time. The R^2 of the Eq. (5) is 0.99987.

The decreasing in the pH value is caused by gradual consumption of hydroxyl anions, as well as production of hydrogen cations [32]. Thus, the pH of the solution had to be regularly adjusted with 30% NaOH, to maintain a necessary constant value.

Three pH values were selected to investigate the effect of the pH on the RR_{Ag} and the TEC in this work. Fig. 5 shows that the residual Ag(I) concentration (C_t) decreases at different rates for different pH values. This indicated that the reaction rate of silver reclamation varied with the pH of the solution. The rate constant value (k) was 0.0765 min^{-1} at a pH of 9, which was higher than that at a pH of 7 (0.0681 min^{-1}) and at a pH of 11 (0.0553 min^{-1}). The rate of the pulse electrolysis reaction at a pH of 9 was higher than it was at the other pH values because of the different oxidation rates of cyanide at these pH values. Varying the pH value subsequently influenced the silver reclamation process. After 60 min of electrolysis at a pH of 9, an RR_{Ag} of 99% and a TEC of 4.46 kWh (kg Ag)$^{-1}$ were obtained. At
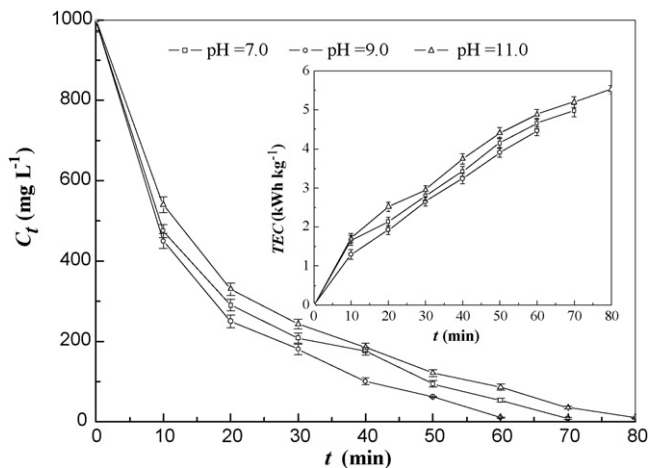
Fig. 5. Effect of solution pH on residual Ag(I) concentration; the inset shows the effect of solution pH on TEC ($f = 1200\,Hz$; $r = 60\%$; $J = 5.0\,A\,m^{-2}$; $\tau_T = 10\,min$; $C_i = 1000\,mg\,L^{-1}$; $T = 45\,°C$; $d_e = 50\,mm$).

a pH of 7, an RR_{Ag} of 99% could be obtained after 70 min of electrolysis, with a TEC of 4.98 kWh (kg Ag)$^{-1}$. At a pH of 11, an RR_{Ag} of 99% could not be obtained until 80 min of electrolysis time, with a TEC of 5.52 kWh (kg Ag)$^{-1}$. These results showed that the current efficiency in the PEF electrolysis process was higher at a pH of 9 was higher than at other pH values; i.e., it took less time and electric energy to obtain the same RR_{Ag}. Therefore, a pH of 9 is appropriate in the PEF process.

3.1.5. Effect of temperature

Fig. 6 displays the effect of temperature on the RR_{Ag} and the TEC. The temperatures used were 25, 35, 45 and 55 °C. The results showed that the RR_{Ag} increased rapidly as the temperature increased from 25 to 45 °C. Further increases in temperature did not have much influence on the RR_{Ag}, but could lead to large increases in the TEC. After 40 min of electrolysis at 25 °C, an RR_{Ag} of 90% and a TEC of 3.24 kWh (kg Ag)$^{-1}$ were obtained. At 35 °C, the RR_{Ag} increased to 94.4%, with a TEC of 3.65 kWh (kg Ag)$^{-1}$. When the temperature was raised to 45 °C, the RR_{Ag} could reach 99% at a TEC 3.65 kWh (kg Ag)$^{-1}$. Finally, at 55 °C, the RR_{Ag} only increased to 99.2%, with an increased TEC (4.24 kWh (kg Ag)$^{-1}$), 16% higher than the TEC at 45 °C. Moreover, temperatures higher than 45 °C
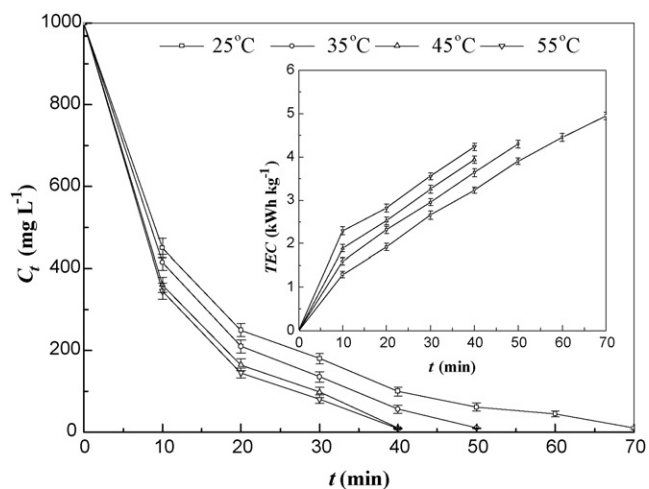

Fig. 6. Effect of temperature on residual Ag(I) concentration; the inset shows the effect of temperature on TEC ($f = 1200\,Hz$; $r = 60\%$; $J = 5.0\,A\,m^{-2}$; $\tau_T = 10\,min$; $C_i = 1000\,mg\,L^{-1}$; pH = 9.0; $d_e = 50\,mm$).

Fig. 7. Effect of pulse frequency on residual Ag(I) concentration; the inset shows the effect of pulse frequency on TEC ($r = 60\%$; $J = 5.0\,A\,m^{-2}$; $\tau_T = 10\,min$; $C_i = 1000\,mg\,L^{-1}$; pH = 9.0; $T = 45\,°C$; $d_e = 50\,mm$).

should be avoided, to prevent water being lost through evaporation. Consequently, a temperature of 45 °C was preferred in this work.

The deposition of the silver onto the cathode surface from silver-plating wastewater with low C_{Ag} is diffusion-controlled. An increase in temperature increases the diffusion of Ag(I), i.e., the diffusion constant (D) is increased. At the same time, the conductivity decreases as a result of silver deposition from the electrolyte, and so the energy consumption will increase. Additionally, a great deal of added energy would be consumed by the heating system to maintain higher temperatures.

3.2. Parameters of pulse current

3.2.1. Effect of pulse frequency

The effect of the pulse frequency (f) on the RR_{Ag} and the TEC is shown in Fig. 7. As can be seen in Fig. 7, the Ag(I) concentration (C_t) decreases rapidly with electrolysis time, and the RR_{Ag} and the TEC are heavily affected by the pulse frequency (f). The rate constant (k) obviously increased with increasing frequency (f) when the pulse frequency (f) was less than 1200 Hz. However, when the frequency (f) was increased to 1600 Hz, the effect was reversed, i.e., the rate constant (k) decreased rapidly with the frequency (f). For example, after 60 min of electrolysis, when the frequency (f) increased from 400 to 800 Hz, the rate constant (k) changed from 0.029 to 0.053 min^{-1} and the RR_{Ag} increased from 92.6% to 95.2%, with the TEC decreasing from 5.07 to 4.76 kWh (kg Ag)$^{-1}$. When the pulse frequency (f) was 1200 Hz, the rate constant (k) reached 0.076 min^{-1} after 60 min of electrolysis, and an RR_{Ag} of 99% was achieved with a low TEC of 4.46 kWh (kg Ag)$^{-1}$. However, when the frequency was increased to 1600 Hz, a contrary result was obtained, i.e., the rate constant (k) dropped to 0.023 min^{-1}, and the RR_{Ag} was reduced to 89.3%, with a high TEC (5.26 kWh (kg Ag)$^{-1}$) after 60 min. This can be explained by the mechanism of silver electrodepositing at low Ag(I) concentration, where diffusion is catalyzed by the pulsed current. Increasing the pulse frequency accelerates the formation of nuclei, and thus the silver deposition is enhanced. However, at high frequencies, the capacitance effect of the double layer and the inability of the double layer to fully charge during the *pulse on* time or fully discharge during the *pulse off* time combine to produce conditions where the metal deposition current only slightly fluctuates around the average current density, i.e., the PEF process is similar to the DC process. Thus, at high pulse frequencies, for example 1600 Hz, the pulsing had little effect on the silver deposi-
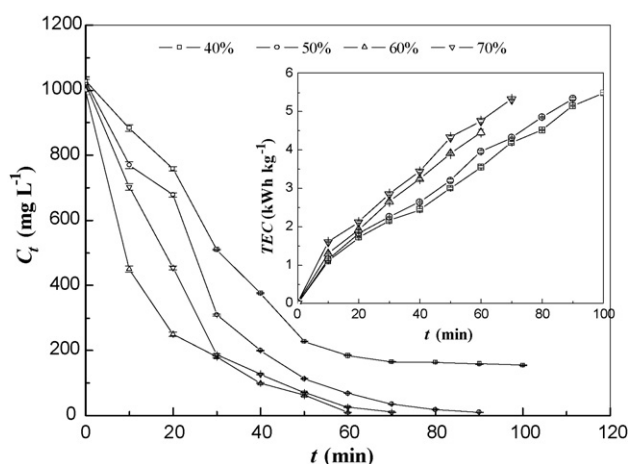
Fig. 8. Effect of pulse duty cycle on residual Ag(I) concentration; the inset shows the effect of pulse duty cycle on TEC (f = 1200 Hz; J = 5.0 A m^{-2}; τ_T = 10 min; C_i = 1000 mg L^{-1}; pH = 9.0; T = 45 °C; d_e = 50 mm).

Fig. 9. Effect of current density on residual Ag(I) concentration; the inset shows the effect of current density on TEC (f = 1200 Hz; r = 60%; τ_T = 10 min; C_i = 1000 mg L^{-1}; pH = 9.0; T = 45 °C; d_e = 50 mm).

tion. Therefore, the optimized frequency for this pulse electrolysis was 1200 Hz.

3.2.2. Effect of pulse duty cycle

Given a constant electrolysis time, the pulse duty cycle (r) directly affects the energy consumed by the PEF process. The effect of pulse duty cycle (r) on the RR_{Ag} and the TEC is shown in Fig. 8. As can be seen from Fig. 8, at low pulse duty cycle (r < 60%), the RR_{Ag} increases with an increasing pulse duty cycle (r), with a slight increase of TEC. However, when the pulse duty cycle (r) was increased to larger than 60%, the current efficiency and RR_{Ag} dropped significantly, and a large increase in the TEC was observed. For example, after 60 min of electrolysis, when the pulse duty cycle (r) increased from 40% to 50%, the RR_{Ag} increased from 81.5% to 93.2%, with the TEC increasing from 3.56 to 3.96 kWh (kg Ag)$^{-1}$. At a pulse duty cycle (r) was 60%, the RR_{Ag} was raised to 99% with a TEC of 4.46 kWh (kg Ag)$^{-1}$. However, when the pulse duty cycle (r) was increased to 70%, the RR_{Ag} dropped to 97.5%, with a TEC of 4.75 kWh (kg Ag)$^{-1}$.

It was mentioned above that there were two diffusion layers in the PEF process, one near the electrode surface and the other farther away. Their thicknesses remained stable when steady state was reached. These thicknesses were proportional to $(DT_{on})^{1/2}$, where T_{on} is the *pulse on* time and D is the diffusion coefficient [33]. The thicknesses of these diffusion layers, which controlled the pulse electrolysis reaction on the electrodes, appeared to be small at low pulse duty cycles ($r \leq 60\%$). With a higher pulse duty cycle (r > 60%), the thicknesses were large enough to affect the reaction rate. Therefore, the optimum duty cycle was 60%.

3.2.3. Effect of current density

Experiments were carried out to investigate the effect of current density (J) on the RR_{Ag} and the TEC. The results are given in Fig. 9. It can be seen in Fig. 9, as the current is increased from 2.0 to 6.5 A m^{-2}, the apparent rate constant (k) initially increases, and then decreases at higher current densities (J). This was due to the different reaction dynamics in the two regimes. When the current density was 2.0 A m^{-2}, the constant (k) was 0.030 min^{-1}, and an RR_{Ag} of 73.7% was attained, with a TEC of 3.17 kWh (kg Ag)$^{-1}$ after 40 min. At a current density of 3.5 A m^{-2}, after 40 min of electrolysis, the constant (k) had increased to 0.076 min^{-1}, and an RR_{Ag} of 90% was obtained, with a TEC of 3.24 kWh (kg Ag)$^{-1}$. At a current density of 5.0 A m^{-2}, the constant (k) reached 0.095 min^{-1} after 40 min of electrolysis, and the RR_{Ag} increased to 99.4% with a TEC of 3.64 kWh (kg Ag)$^{-1}$. However, when the current density increased to 6.5 A m^{-2}, the con-
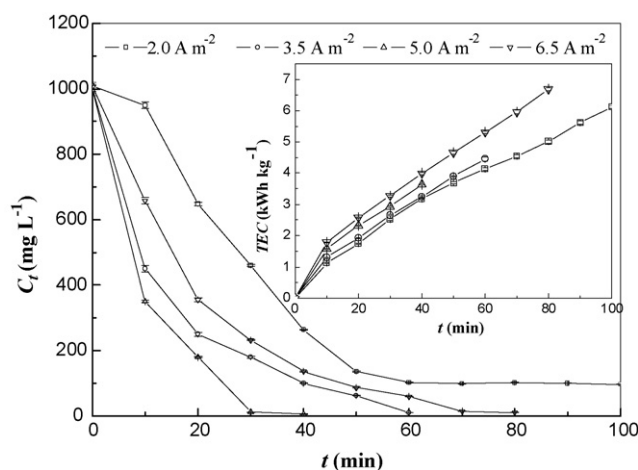
stant (k) dropped to 0.054 min^{-1}, and the RR_{Ag} was reduced to 86.4%, lower than the RR_{Ag} of any other tested current, with a TEC of 3.99 kWh (kg Ag)$^{-1}$ after 40 min of electrolysis. In the pulse electrolysis process, the efficiency of the electrode and the symmetry of the current distribution were improved at higher current densities (J), so the silver reclamation was increased and the energy consumption was decreased. However, when the current density was increased beyond 5.0 A m^{-2}, other reactions involving oxidation of hydroxyl ions and passivation of electrodes were enhanced, which resulted in lower current efficiencies and RR_{Ag} values, with higher TEC values. Furthermore, the silver deposits became rough and dendritic. Therefore, the optimized current density was 5.0 A m^{-2}.

3.3. Comparison between the PEF and DC processes

The DC reclamation process is commonly used for wastewater with high Ag(I) concentrations (C_i > 2500 mg L^{-1}), rather than low Ag(I) concentrations (C_i < 2500 mg L^{-1}) [1]. For wastewater with low Ag(I) concentrations, the PEF process achieved a higher RR_{Ag} and higher purity of silver deposits, as well as a lower TEC, than the DC process. To compare the PEF and DC processes, the RR_{Ag}, current efficiency, TEC and the morphology of the deposits were evaluated under similar conditions in this work. Comparison of the RR_{Ag} values of the PEF and DC processes was carried out for initial C_{Ag} values of 500 and 2500 mg L^{-1}. The results are shown in Fig. 10. From Fig. 10, the relationship between residual Ag(I) concentration (C_t) and electrolysis time (t) can be extracted as follows:

$$-\frac{dC_t}{dt} = kC_t \tag{6}$$

This revealed that both PEF and DC processes follow the first-order reaction kinetics. The apparent rate constants (k) from the PEF and DC processes are listed in Table 1. The results showed that the PEF process had a higher rate constant (k) than the DC process, and that the rate constant (k) at an initial C_{Ag} of 500 mg L^{-1} was higher than at an initial C_{Ag} of 2500 mg L^{-1}. This indicated that

Table 1
Apparent rate constant (k) of PEF and DC process.

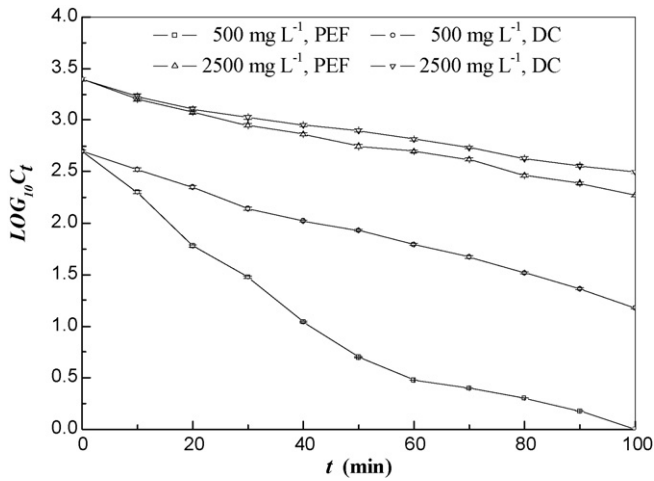| C_i (mg L^{-1})	Electrical sources	k (min^{-1})
500	PEF	0.0365
500	DC	0.0146
2500	PEF	0.0101
2500	DC	0.0083

Fig. 10. Comparison of the PEF and DC process for the logarithm of residual Ag(I) concentration at initial C_{Ag} 500 and 2500 mg L^{-1} ($f = 1200$ Hz; $r = 60\%$; $J = 5.0$ A m^{-2}; $\tau_T = 10$ min; pH = 9.0; $T = 45$ °C; $d_e = 50$ mm).

Fig. 12. Comparison of the PEF and DC process for total energy consumption at different initial C_{Ag}; the inset shows the close-up of the relation of TEC and C_t from 1500 to 2500 mg L^{-1} ($f = 1200$ Hz; $r = 60\%$; $J = 5.0$ A m^{-2}; $\tau_T = 10$ min; pH = 9.0; $T = 45$ °C; $d_e = 50$ mm).

the electrolysis rate of the PEF process was higher than that of the DC process. Hence, PEF electrolysis effectively improved the RR_{Ag}, especially for low Ag(I) concentration solutions ($C_i = 500$ mg L^{-1}).

The relationship between the current efficiency and the residual Ag(I) concentration (C_t) in the PEF and DC process is shown in Fig. 11. The results revealed that the current efficiency of the PEF process was higher than that of the DC process, and that the difference was remarkable at low Ag(I) concentrations. For example, the current efficiency of the PEF was 15% higher than that of the DC process when the Ag(I) concentration was 500 mg L^{-1}. However, the current efficiency of the PEF process was only 8% higher than that of the DC process when the Ag(I) concentration was 2500 mg L^{-1}. Fig. 12 shows that the TEC of the PEF process is lower than that of the DC process, and that the difference is larger at lower concentrations ($C_i \leq 1000$ mg L^{-1}). As the Ag(I) concentration increased from 500 to 1000 mg L^{-1}, the difference in TEC between the DC and PEF processes decreased from 1.97 to 0.21 kWh (kg Ag)$^{-1}$. The inset of Fig. 12 shows that the difference in TEC between the DC and PEF processes is not significant for Ag(I) concentrations from 1000 to 2500 mg L^{-1}.

The PEF process effectively improved the RR_{Ag} and reduced the TEC of processing wastewater with low Ag(I) concentrations
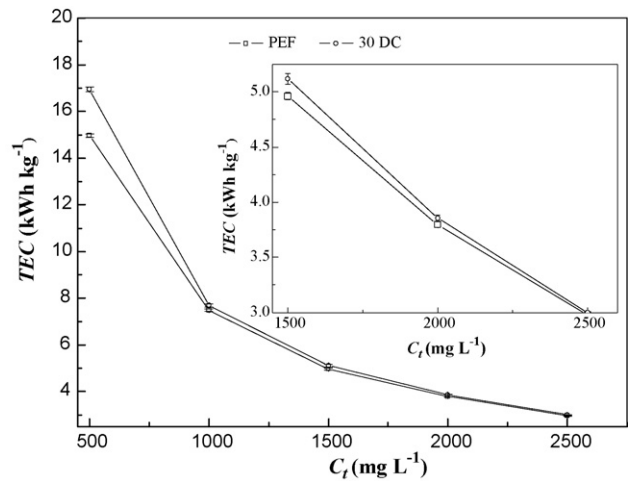
($C_i < 1000$ mg L^{-1}). At the same average current density, the PEF process had a much higher peak current density than the DC process. Silver recovery and cyanide decomposition were accelerated, and the side reactions, hydroxyl oxidation and hydrogen reduction, were suppressed. Thus, the current efficiency and the RR_{Ag} were increased while the TEC was decreased, especially at low Ag(I) concentrations ($C_i < 1000$ mg L^{-1}).

Fig. 13 shows the XRD patterns from the silver deposits from the PEF and DC processes. These patterns revealed that the purity of sliver deposits was higher for the PEF process than the DC process. The average diameter of the silver deposits from the PEF process and the DC process were calculated, according to the Scherrer equation [15,34], to be ~40 and 90 nm, respectively. The results could be validated by SEM observation of the silver deposits. The SEM images in Figs. 14 and 15 show that the silver crystals from the PEF process are smaller and denser than those from the DC process are. As a consequence, the PEF process gave rise to smoother surface than the DC process. The alternating action of the PEF was mainly responsible for the high pure silver deposits. When the pulse was inactive, the concentration polarization in the solution was decreased. When the pulse was active, the deposition of impurities or hydrogen over the cathode surface could be suppressed. Consequently, the purity of
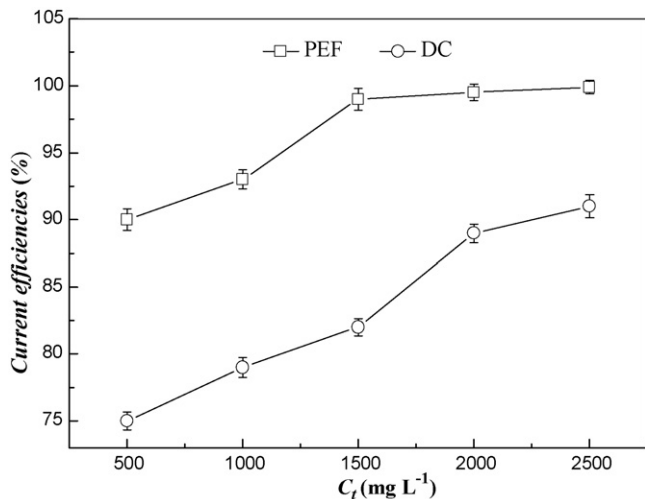

Fig. 11. Comparison of the PEF and DC process for current efficiency at different initial C_{Ag} ($f = 1200$ Hz; $r = 60\%$; $J = 5.0$ A m^{-2}; $\tau_T = 10$ min; pH = 9.0; $T = 45$ °C; $d_e = 50$ mm).
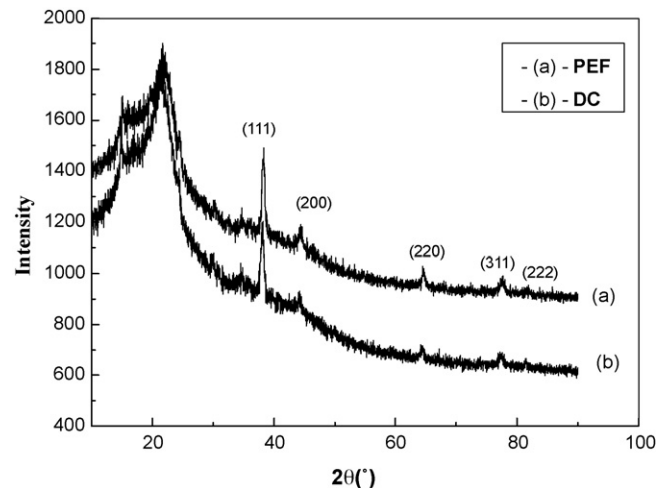

Fig. 13. Comparison of the PEF and DC process for XRD of silver deposits ($f = 1200$ Hz; $r = 60\%$; $J = 5.0$ A m^{-2}; $\tau_T = 10$ min; pH = 9.0; $C_i = 1000$ mg L^{-1}; $T = 45$ °C; $d_e = 50$ mm).
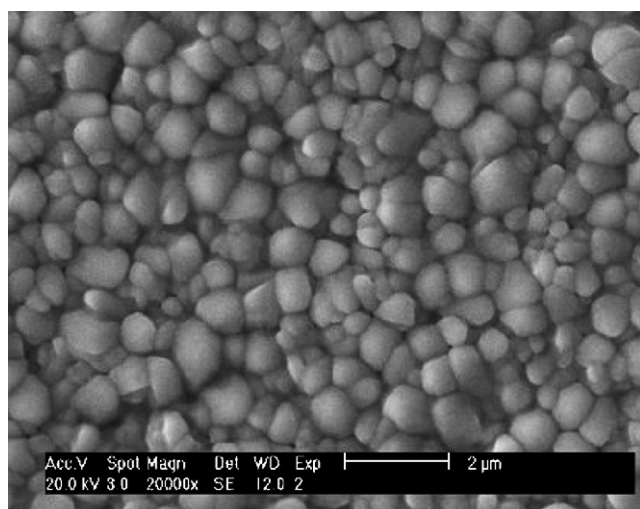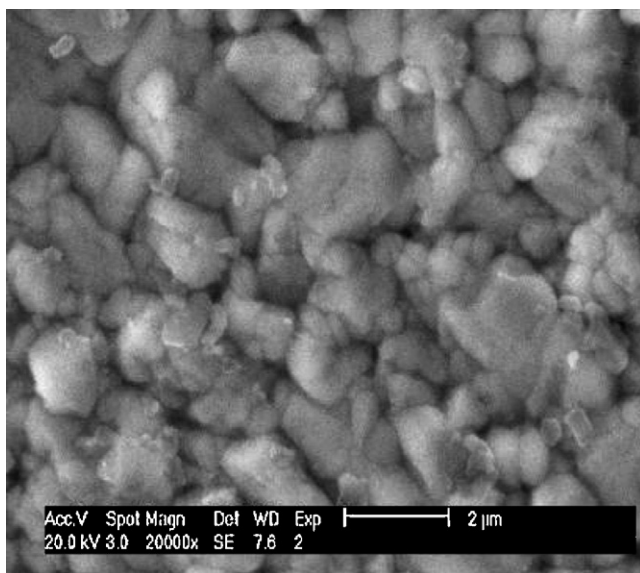
Fig. 14. SEM of silver deposits for PEF (f = 1200 Hz; r = 60%; J = 5.0 A m^{-2}; τ_T = 10 min; pH = 9.0; C_i = 1000 mg L^{-1}; T = 45 °C; d_e = 50 mm).

Fig. 15. SEM image of silver deposits for DC (f = 1200 Hz; r = 60%; J = 5.0 A m^{-2}; τ_T = 10 min; pH = 9.0; C_i = 1000 mg L^{-1}; T = 45 °C; d_e = 50 mm).

silver deposits was increased in the PEF process. In addition, the peak pulse current, which was much higher than the average current, accelerated the formation of fresh nuclei. As a result, the PEF process promoted the production of fine grain crystallites with high purity and low resistance.

4. Conclusions

In summary, the reclamation of silver from silver-plating wastewater with Ag(I) concentrations below 1000 mg L^{-1} by combining a pulsed electric field with static cylindrical electrodes was investigated. The effects of the operating parameters (including average retention time of electrolyte in the reactor, interelectrode gap, initial silver concentration, pH of the solution, temperature, pulse frequency, pulse duty cycle and current density) on the silver recovery rate and total energy consumption were determined and the optimum conditions were as follows: an initial Ag(I) concentration of 1000 mg L^{-1}, interelectrode gap of 50 mm, average retention time of 10 min, solution pH of 9.0, temperature of 45 °C, pulse frequency of 1200 Hz, pulse duty cycle of 60% and a cur-

rent density of 5.0 A m^{-2}. After 40 min of electrolysis, 99% of silver was recovered from silver-plating wastewater with an initial Ag(I) concentration of 1000 mg L^{-1}, with a total energy consumption of 4.45 kWh (kg Ag)$^{-1}$.

The results showed that electrolysis with a pulsed electric field was more suitable for wastewater with low silver concentrations (below 1000 mg L^{-1}) than the conventional DC technology. Compared with the conventional electrolysis method using direct currents, the presented process with a pulsed electric field could significantly improve the current efficiency and recovery rate, minimize the energy consumption and obtained thinner, more compact silver deposits. This study demonstrated that using a pulsed electric field and static cylindrical electrodes was a viable alternative to the conventional techniques.

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