



Recovery of high-purity silver directly from dilute effluents by an emulsion liquid membrane-crystallization process

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ABSTRACT

An emulsion liquid membrane (ELM)-crystallization process, using hypophosphorous acid as a reducing agent in the internal aqueous phase, has been developed for the purpose of recovering high-purity silver directly from dilute industrial effluents (waste rinse water). After pretreatment with HNO₃, silver in waste rinse water can be reliably recovered with high efficiency through the established process. The main parameters in the process of ELM-crystallization include the concentration of carrier in the membrane phase, the concentration of reducing agent in the internal aqueous phase, and the treatment ratio, which influence the recovery efficiency to various extents and must be controlled carefully. The results indicated that more than 99.5% (wt.) of the silver ions in the external aqueous phase were extracted by the ELM-crystallization process, with an average efficiency of recovery of 99.24% (wt.) and a purity of 99.92% (wt.). The membrane phase can be used repeatedly without loss of the efficiency of recovery.

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1. Introduction

Silver has been mined and used to make ornaments, and later, coins for a long time. In the modern world, silver is an important raw material in many industrial fields, such as electronics, catalysts and photography, and its antimicrobial and anti-inflammatory properties have found use in burn, surgical and wound dressings, and other antibiotic roles. Generally, silver is obtained from natural sources and as a by-product from copper or antimony metallurgical processes, but in recent years the silver content of industrial wastes has led to environmental pollution and represents a major loss of resources; in Europe, about 38% silver-containing wastes were sent to landfill [1]. The natural sources of silver are decreasing, but the content and concentration of silver in industrial effluent is very low [2], and silver is difficult to recover with simple physical and chemical methods. There is a great deal of interest in recovering silver for both environmental and economic reasons.

In the photographic industry, silver-containing wastes are generated in several categories, including spent development and fixing solutions, and waste rinse water. The concentration of silver in these effluents varies widely, in spent developing and fixing solutions, the concentration of silver may be as high as several g/L, but in waste rinse water it may be as low as a few mg/L. Methods such

as solvent extraction, adsorption, electrochemical deposition, and chemical precipitation have been investigated for recovering silver from developing and fixing solutions [3–6]. Waste rinse water from the photographic industry is often discharged after being treated to reach the national emission standard (<0.5 mg/L) and seldom considered the recovery of silver, which inevitably results in loss of silver. From an economic point of view, electrochemical deposition and chemical precipitation are not cost-effective in terms of energy or chemicals when the concentration of silver is less than 0.1 g/L. Ion-exchange [7] was once used to treat dilute effluents (fixing rinse water) to achieve the required discharge standard, but it was very difficult to obtain the desired silver product without further treatment.

The liquid membrane (LM) process is one of the techniques that are suitable for hydrometallurgical recovery of metal ions. In most cases, the selectivity of a LM process for the target metal ion is mainly determined by carriers in the membrane phase of the emulsion liquid membrane (ELM) and the supported liquid membrane (SLM). Identifying the appropriate carrier is of paramount importance for increasing the selectivity of a LM process, but is often time-consuming and costly. Studies have focused mainly on searching for a high-selectivity carrier(s) to improve the efficiency of separating silver from other metals [8–15]. Compared with SLM, the mass transfer velocity (mol/s) is higher in an ELM process because of the larger area of the interface. As a result, ELM has found many investigations recently in hydrometallurgy [16], wastewater treatment [17] and metal recovery [18] by virtue of its advantages in

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separating and concentrating a solute from very dilute solutions [19–21].

In earlier studies, the function of the internal aqueous phase in an ELM system was to strip the target metal ion from the membrane phase and convert it into a new kind of compound that cannot penetrate reversibly. These studies did not usually consider the selectivity of the internal agent within the ELM system, although the internal aqueous phase acted as a kind of separation process in most cases. In previous work [22], we proposed the use of a reactive ELM system, in which a suitable precipitating agent was introduced into the internal aqueous phase to precipitate cadmium, and the selectivity for cadmium versus zinc was improved significantly by the selective precipitating reaction in the internal aqueous phase. A low concentration of cadmium was separated successfully from zinc in a hydrometallurgical leachate. It has been determined that the selectivity of an ELM system may be enhanced greatly by the integrative effect of a carrier and an internal agent, which provides more opportunities to achieve a higher level of selectivity with a cheaper carrier. In an earlier study [19], chloride ions were introduced into the internal phase to capture silver ions in an ELM system, in which silver ions transported into the internal aqueous phase were converted to insoluble AgCl and enriched in the internal aqueous phase. The results of these studies indicated that converting the target metal ion into a solid state was very convenient for separation from the liquid phase afterwards.

There were few reports about generating silver metal in the internal aqueous phase from the industrial effluents. Dai et al. [23] reported the preparation and the morphology of a fine silver powder with pure reagents as the feed solutions. Othman et al. [24] described an ELM system to separate silver from photographic wastes in the form of silver salts in the internal aqueous phase. In most cases, there is a direct relation between the purity of silver and its price and applications, so it is of great importance to obtain high-purity silver metal directly in an economic way for guaranteeing the feasibility of a recovery process. The primary objective of this study is to recover high-purity silver from dilute effluents (waste rinse water from a photographic factory), and two related aspects are considered: (1) develop and validate an ELM-crystallization system with a selective internal agent that is suitable for recovering high-purity metallic silver directly in the internal phase from effluents with low concentration of silver ions (Ag^+) and (2) investigate the main parameters that influence the efficiency of the ELM-crystallization process for the recovery of silver.

2. Transport and recovery mechanism

2.1. Mobile carrier

The most important factor that influences the selectivity of an ELM system is the choice of a suitable mobile carrier, which can often be made on the basis of a conventional liquid–liquid extraction process. In several studies [14,19,23], di-2-ethylhexyl phosphoric acid (D2EHPA) has been shown to be an appropriate carrier for extraction Ag^+ , in the organic phase, it often exists as a dimer [25], and reacts with Ag^+ to form a complex of $\text{Ag}\cdot\text{D2EHPA}$ [$\text{AgR}(\text{HR})$] at the external interface of the membrane phase, and carries Ag^+ through the membrane phase. At the internal interface of the membrane phase, Ag^+ is stripped by the internal agent and transformed into a new species that cannot penetrate the membrane reversibly. The following reversible reaction occurs at both interfaces of the membrane phase with D2EHPA as carrier in an ELM system:

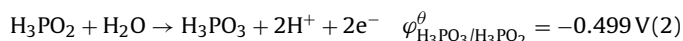


2.2. Stripping agent

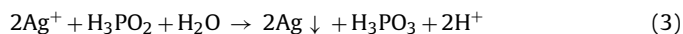
The choice of stripping agent in the internal aqueous phase is another important factor that influences the selectivity of an ELM system. A suitable agent will convert the target metal ion to the desired product directly, and thus shortens the recovery process.

Ag^+ is a reducible substance with high electrode potential ($\varphi_{\text{Ag}^+/\text{Ag}}^\theta = 0.0800 \text{ V}$), if a suitable reducing agent is introduced into the internal aqueous phase, it may strip Ag^+ from the membrane phase and reduce it to metallic silver. There are several reports of methods designed to prepare silver powder by chemical reduction [23,26–28] and reducing agents such as hydrazine hydrate, formaldehyde, glucose, ascorbic acid, sodium formaldehydesulfoxylate (SFS) and potassium borohydride (KBH_4) have been investigated in some practical cases. In this study, hypophosphorous acid (H_3PO_2) was selected as the reducing agent in the internal phase for the first time in an ELM process. Compared with the reducing agents mentioned above, H_3PO_2 has several advantages: it is cheaper, requires less dosage, has a rapid reaction, and can be used in ambient conditions.

H_3PO_2 is a moderately strong acid with low standard electrode potential; in acid solutions, the half-reaction and its standard electrode potential can be expressed as follows:



It can be seen that H_3PO_2 is a strong reducing agent that can reduce Ag^+ to silver metal. The reducing capacity of H_3PO_2 is increased with increased pH, but Ag^+ generally forms the hydroxide in alkaline conditions. For the purpose of totally reducing Ag^+ to silver metal and avoiding precipitation of the hydroxide, the original pH value in the internal aqueous phase should be controlled at 2–4 (adjusted pure H_3PO_2 solutions with sodium hydroxide). Considering the half-reactions of Eq. (2) and the reduction of Ag^+ , the redox reaction in the internal aqueous phase can be expressed as follows:



According to Eq. (2) and the standard electrode potential of Ag^+ , the cell potential of Eq. (3) can be calculated as:

$$E^\theta = \varphi_{\text{Ag}^+/\text{Ag}}^\theta - \varphi_{\text{H}_3\text{PO}_3/\text{H}_3\text{PO}_2}^\theta = 0.800 - (-0.499) = 1.299 \approx 1.30 \text{ V} \quad (4)$$

From Eq. (3), it is known that Ag^+ transported into the internal aqueous phase is reduced to the metallic form. Obviously, this redox reaction is spontaneous and is generally very rapid and complete, which efficiently prevents Ag^+ from penetrating reversibly. The reduced product H_3PO_3 in Eq. (3) is also a reducing agent, but its reducing capacity and reaction rate with Ag^+ are far less than that of H_3PO_2 , and the reduction reaction in the internal aqueous phase is mainly between H_3PO_2 and Ag^+ . Other cations, such as Na^+ , K^+ and Al^{3+} , might be partially transported into the internal aqueous phase, but they have rather negative electrode potentials ($\varphi_{\text{Na}^+/\text{Na}}^\theta = -2.71 \text{ V}$, $\varphi_{\text{K}^+/\text{K}}^\theta = -2.92 \text{ V}$, $\varphi_{\text{Al}^{3+}/\text{Al}}^\theta = -1.66 \text{ V}$). Thus, based on the difference of their electrode potentials, the selectivity of the ELM-crystallization process is further improved by the internal reducing agent.

2.3. Transfer process

The process that combines ELM transport, redox, and metal crystallization in one step is called an ELM-crystallization process, which includes the followed stages and is illustrated in Fig. 1.

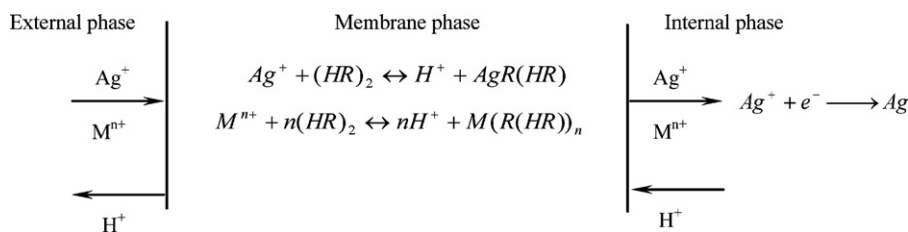


Fig. 1. A schematic description of silver ion transport and recovery by an ELM-crystallization process.

- (1) Metal ions move from the bulk solutions to the outer surface of membrane phase.
- (2) Metal ions react with the carrier D2EHPA at the outer surface of membrane phase to form M–D2EHPA complexes and hydrogen ions.
- (3) Metal complexes M–D2EHPA diffuse from the outer surface to the internal surface of the membrane phase.
- (4) At the internal surface of the membrane phase, metal ions are stripped by H⁺, D2EHPA is recovered and diffuses back to the external surface of membrane phase.
- (5) In the internal phase, only silver ions can be reduced to silver metal, whereas other metal ions cannot.

After Ag⁺ is extracted by the carrier (a dimer of D2EHPA) at the outer interface of the membrane phase, a complex of Ag–D2EHPA [AgR(HR)] is formed and transferred from the outer to the internal interface. In the internal aqueous phase, H₃PO₂ reduces Ag⁺ to metallic silver immediately once Ag⁺ is stripped from the membrane phase. Among the mentioned five stages, the diffusing stage in the membrane phase is very slow and determines the velocity of the whole transfer process from the bulk solutions of the external phase to the internal phase [19]. In the reported literatures [16,17,19,21], the diffusing process was confirmed to be dependent on the characteristic and the thickness of the membrane phase. The characteristic is determined by the composition of the membrane phase including the concentrations of kerosene, surfactant and carrier. The thickness of membrane phase is mainly controlled by the mixing speed and the phase ratio, which influence the diffusing process of an ELM system in a complicated way. Higher mixing speed is in favor of improving the dispersion of emulsion in the treated feed solutions and then decreases the thickness of membrane phase, which promotes the diffusing process, but excessively high mixing speed may also result in breaking the emulsion droplets, and decreasing the separation efficiency. Othman et al. [24] observed that increasing the mixing speed from 200 to 250 rpm would increase the rate of extraction, but after 400 rpm, the degree of extraction decreased from 95% to 50%. Phase ratio is defined as the volumetric ratio of the membrane phase to the internal phase (R_{oi}), which determines greatly the stability and the thickness of the membrane phase. It is obvious that higher R_{oi} leads to a more thick and stable membrane phase, which impedes the diffusing process and increases the consumption of membrane phase, lower R_{oi} decreases the thickness and stability of the membrane phase, and thus improves the diffusing process. R_{oi} has been investigated as an important factor in the range of 0.8–1.4 for separating different metal ions, it turns out the optimal value is related to the target metal ion [16,17]. For the silver ion, the value of $R_{oi} = 1:1$ has already been employed by Othman et al. [24] for separating silver from photographic wastes, and has also been used in our experiments.

From the analysis above, it is concluded that the concentration of the carrier in the membrane phase, the concentration of the reducing agent in the internal aqueous phase and the treatment ratio may have some influence on the recovery efficiency.

3. Experimental details

3.1. Reagents

The membrane solvent was prepared with distilled commercial kerosene from Guangzhou Petrochemical Complex and sulfonated with oleum in our laboratory by the procedure: acid-washing, water washing and then washed with saturated sodium bicarbonate solution, dried with anhydrous sodium sulfate. Sorbitan monooleate (Span-80) was used as a surfactant for stabilizing the emulsion and was purchased from Longyou County Chemical Co., D2EHPA was from Shanghai Institute of Organic Chemistry, NaOH from Guangzhou Chemical Reagent Co. Ltd., and all of these chemicals were analytical-grade reagents. Pharmaceutical grade H₃PO₂ was from Wuhan Ruiji Chemical Co. Ltd., H₃PO₄, HNO₃ and other used chemicals were all of reagent grade and from Guangzhou Chemical Reagent Co. Ltd.

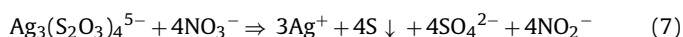
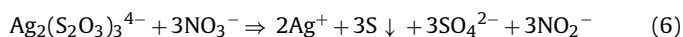
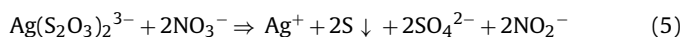
3.2. Methods for measurement

Measurement of the silver content of the aqueous phase was done with a PerkinElmer flame atomic absorption spectrometer (Model 2380) at a wavelength of 328.1 nm. The total phosphate (TP) content was determined by measuring the concentration of phosphate in the aqueous phase with a Jasco V-550UV/vis spectrophotometer at a wavelength of 710 nm. Contents of other ions were measured with an ion chromatograph (Model IC1010 from Shanghai Techcomp Ltd.), pH was measured with a pH meter (Model pHS-25 from Shanghai LIDA).

3.3. Feed solutions and pretreatment

The feed solutions were waste rinse water from a photographic factory, which contained Ag⁺, some other soluble ions and insoluble substances. The soluble ions included Na⁺, K⁺, Al³⁺, S₂O₃²⁻, SO₄²⁻, and some silver complexes, the insoluble substances included scrap film. The composition of the waste rinse water was quite similar to that of fixing solutions, but the concentration of ions were very low. Silver in the waste rinse water was mainly in the form of Ag(S₂O₃)₂³⁻, Ag₂(S₂O₃)₃⁴⁻, and Ag₃(S₂O₃)₄⁵⁻. It was not easy to release Ag⁺ from these complex anions only by an ELM process; so, a pretreatment step was necessary.

At the mixing speed of 250 rpm, a beaker with 1000 mL raw waste rinse water was added drop wise with 1 mol/L HNO₃ solution till the pH value to 2–4. The reactions to release Ag⁺ from complexes anions such as Ag(S₂O₃)₂³⁻, Ag₂(S₂O₃)₃⁴⁻, and Ag₃(S₂O₃)₄⁵⁻ with HNO₃ can be expressed by the followed equations:



After reactions, silver complexes were converted to silver nitrate, and elemental sulfur was formed. Al³⁺ in the feed solutions may act as a flocculating agent and agglomerate the sulfur

Table 1
Chemical composition of the feed solutions (pH 3.14).

Ions	Concentration (mg/L)
Ag ⁺	51.32
Na ⁺	102.60
K ⁺	175.42
Al ³⁺	154.50
NO ₃ ⁻	379.20
NO ₂ ⁻	76.54
SO ₄ ²⁻	315.81

particles, under a mixing condition, the produced sulfur particles agglomerated to micron-sized or more larger particles, then the solutions were filtered to remove the agglomerated sulfur particles and other insoluble substances with a quantitative filter paper (1–3 μm, purchased from Hangzhou Xinhua Paper Mill) under normal conditions. The AgNO₃ electrolyte was chosen for the ease of subsequent handling [29]. The composition of the waste rinse water after this treatment is given in Table 1 and this was the composition of the feed solutions (external aqueous phase) in all experiments.

3.4. Experimental procedures

The membrane phase was composed of a surfactant (Span-80), a mobile carrier (D2EHPA) and a solvent (sulfonated kerosene). Concentration of surfactant determines the stability of membrane phase, which was tested from 0.1% (v/v) to 5.0% (v/v) in the membrane phase. The internal solutions were freshly prepared with H₃PO₂ dissolved in deoxygenated, double-distilled water and adjusted pH value to 2–4 by adding saturated NaOH solutions directly before experiments, and mixed 1:1 (v/v) ($R_{oi} = 1:1$) with the membrane phase to prepare water-in-oil (W/O) emulsion under mechanical agitation at 3000 rpm. For total recovery of Ag⁺ from the external aqueous phase, the amount of H₃PO₂ in the internal aqueous phase was at least 1.5-fold greater than the stoichiometric amount based on Eq. (3). The freshly prepared emulsion was mixed in a baffled glass beaker with feed solutions at volumetric ratios (R_{ew}) between 1:1 and 1:100. All experiments, unless stated otherwise, were done in a beaker with a 250 mL volume of feed solution. The mixing speed was controlled at 250 rpm according to the results of Othman et al. [24], during which the W/O emulsion was dispersed to form a water-in-oil-in-water (W/O/W) ELM. Once mixed with the feed solutions, the emulsion quickly became black, and after contacted for a period of time between 1 min and 30 min, it was separated from the feed solutions and demulsified with an electrostatic coalescer. Silver powder was separated from the membrane and internal aqueous phase by centrifugation at 3000 rpm in a desktop centrifuge (TDL-50B rotor, Shanghai Anting Scientific Instrument Company). The silver powders were washed twice with ethanol and deionized water alternately (20 mL each time), then dried to constant weight in a desiccator containing silica gel. Each experiment was done in duplicate. The efficiency of silver recovery can be calculated as:

$$R_e \text{ (wt.)} = \frac{Q_r}{Q_t} \times 100\% \quad (8)$$

where R_e is the efficiency of silver recovery, Q_r is the quantity of silver metal obtained by the ELM-crystallization process, and Q_t is the total amount of silver in the feed solutions.

4. Results and discussion

4.1. Stability of ELM

The stability of an ELM system determines the success of the separation process, which is influenced mainly by the concentration of the surfactant (Span-80 is frequently used as the surfactant in ELM systems). To determine the stability of ELM in the feed solutions (Table 1), experiments were done with different concentrations of Span-80. H₃PO₄ was used as a tracer in the internal aqueous phase in all stability experiments as a control for the effect of mass transfer. Recognizing that breakage of the emulsion would result in the transfer of the tracer from the internal to the external aqueous phase, the stability of ELM is quantified as the percentage of phosphate transferred from the internal to the external phase. The breakage ratio is defined as follows:

$$B = \frac{C_{TP}V_e}{C_{i0}V_i} \times 100\% \quad (9)$$

where B is the breakage ratio of the emulsion, which represents the stability of the ELM system, C_{i0} is the initial concentration of total phosphate (TP) in the internal aqueous phase, C_{TP} is the concentration of TP in the external aqueous phase at contact time t , and V_e and V_i are the volume of the external and the internal aqueous phase, respectively. By measuring the concentration of TP in the external phase at various time points, the stability of ELM with time can be determined by Eq. (9).

Fig. 2 shows that increasing the concentration of the surfactant Span-80 leads to a more stable ELM system. When the concentration of Span-80 in the membrane phase is 0.5% (v/v) or 1.0% (v/v), the breakage ratio increases markedly after 45 min, which indicates the limitation of stabilization period, but it keeps a linear relationship with the contact time during the time period (60 mins) when the concentration of Span-80 is 2.5% (v/v) or 5.0% (v/v). The stability of the emulsion is determined by the molecular layer formed by the surfactant between the oil and the aqueous phase, increasing the concentration of the surfactant results in more surfactant molecules arrayed between the surface of the oil and the aqueous phase, but excessive surfactant increases the resistance of the interface, which decreases the rate of mass transfer [24]. On the basis of the results shown in Fig. 2, the concentration of surfactant is set on 2.5% (v/v) in all the subsequent experiments since the breakage ratio on 2.5% (v/v) is rather close to that on 5.0% (v/v).

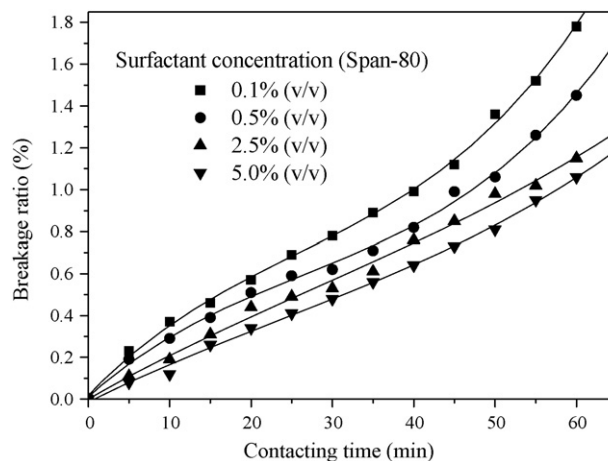


Fig. 2. Stability of ELM (concentration of internal solutions: H₃PO₄ = 0.5 mol/L; $R_{ew} = 1:20$; $R_{oi} = 1:1$; mixing speed: 250 rpm).

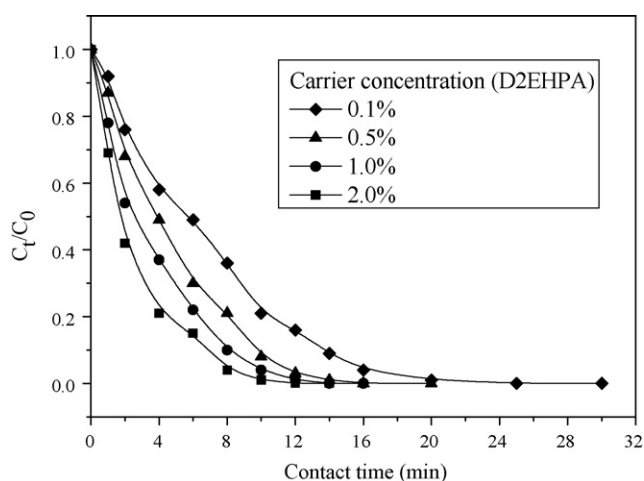


Fig. 3. Effect of carrier concentration on silver recovery (concentration of internal solutions: $\text{H}_3\text{PO}_2 = 0.02 \text{ mol/L}$; $R_{ew} = 1:10$, $R_{oi} = 1:1$; mixing speed: 250 rpm).

4.2. Effect of carrier concentration

Ag^+ is insoluble in organic solvents without the assistance of a mobile carrier. The carrier in the membrane phase has two important roles: one is to transport Ag^+ between the internal and the external interface of the membrane phase, and the other is to improve the selectivity of ELM. The efficiency and separation velocity of an ELM system are determined by both the type and the concentration of the carrier. Several studies [14,19,23] have confirmed the feasibility of using D2EHPA for the recovery of silver, and the effect of different concentrations of D2EHPA was investigated in this study.

Experiments were carried out, in which the concentration of the carrier in the membrane phase was changed from 0.1% (v/v) to 2.0% (v/v) while the other parameters were kept constant. The results shown in Fig. 3 indicate that the transfer rate of Ag^+ in the external phase increases with increasing concentration of the carrier in the membrane phase. The results indicate also that further increase of the concentration of the carrier had little effect on the transfer rate of Ag^+ above a concentration of D2EHPA of 0.5–1.0% (v/v) in the membrane phase. A similar effect was reported by Othman et al. [24], who found that an excessive concentration of carrier led to a high degree of osmotic swelling and a high frequency of membrane breakage. These phenomena were not so marked in this study, where no Ag^+ was transferred from the internal to the external phase in the ELM-crystallization process, even though breakage of the emulsion sometimes occurred. It is reasonable to conclude that there is little effect on the transfer rate above a certain concentration of the carrier in the membrane phase. Under the conditions used in this study, a carrier concentration of 1.0% (v/v) is sufficient for the extraction of Ag^+ .

4.3. Effect of reducing agent concentration

In the ELM-crystallization system described here, H_3PO_2 in the internal phase acted as a stripping agent, and provided the ability to distinguish Ag^+ from other metal ions through a selective reduction reaction. For total recovery of Ag^+ from the external phase, the amount of H_3PO_2 in the internal phase should exceed the stoichiometric amount of Ag^+ based on Eq. (3). Under the present conditions, the volume of the external phase in each experiment was 250 mL and contained 12.83 mg of Ag^+ , which needed at least 3.92 mg of H_3PO_2 to capture all Ag^+ . This corresponded to a concentration of $4.76 \times 10^{-3} \text{ mol/L}$ in the internal aqueous phase.

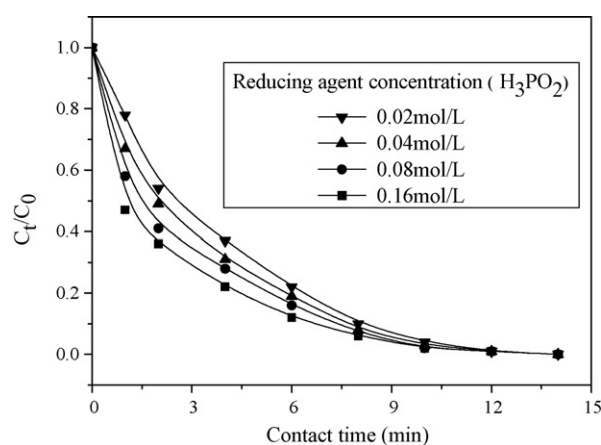


Fig. 4. Effect of reducing agent concentration on silver recovery (concentration of carrier in membrane phase: 1.0% (v/v); $R_{ew} = 1:10$; $R_{oi} = 1:1$; mixing speed: 250 rpm).

Fig. 4 shows the effect of the concentration of the reducing agent on the transfer rate of Ag^+ , indicating that increasing the concentration of the reducing agent shortens the contact time, but the effect is only small. The data shown in Fig. 4 are all rather similar, as the reduction reaction in the internal phase is rapid, and the velocity of the stripping reaction is independent of the concentration of reducing agent.

4.4. Effect of the treatment ratio (R_{ew})

It is known that the process of diffusion through the membrane phase and the interfacial reaction are related directly to the rate of mass transfer and the recovery efficiency of the ELM process. The treatment ratio (R_{ew}), which is defined as the volumetric ratio of the membrane phase to the external aqueous phase, controls the contact area between the emulsion phase and the external aqueous phase, and is a crucial factor in determining the enrichment of Ag^+ and the economic feasibility of the whole recovery process. In general, larger R_{ew} may provide a greater volume of emulsion to make contact with the external aqueous phase, but the emulsion is not dispersed very well in the external aqueous phase with excessively high R_{ew} , which is associated with a marked decrease of the contact area between the emulsion phase and the external aqueous phase, as well as the transfer rate of Ag^+ . A low R_{ew} might provide more space for the emulsion to disperse, which increases the contact area between the emulsion and the external aqueous phase; however, it might result in the loss of silver when the quantity of the internal agent is inadequate to capture all of the Ag^+ in the external phase. The experimental data shown in Table 2 reveal the effect of the treatment ratio on the efficiency of recovery.

From a practical point of view, higher R_{ew} increases emulsion consumption and operating costs, leading to low enrichment of silver and decreasing the cost-effectiveness of the ELM process. The

Table 2

Effect of treatment ratio (R_{ew}) (carrier concentration: 1.0% (v/v); concentration of internal reagent: 0.04 mol/L; $R_{oi} = 1:1$; contact time: 5 min; mixing speed: 250 rpm).

R_{ew} (v/v)	R_e (%) (wt.)
1:1	38.06
1:2	52.16
1:5	63.25
1:10	88.74
1:20	92.11
1:50	90.26
1:100	58.63

Table 3

Recovery efficiency and purity of the obtained silver metal (carrier: 1.0% (v/v); surfactant: 2.5% (v/v); reducing agent in the internal phase: 0.08 mol/L; treatment ratio (R_{ew}): 1:20; phase ratio (R_{oi}): 1:1; contact time: 10 min; mixing speed: 250 rpm).

No. of experiments	R_e (%) (wt.)	Purity (%) (wt.)	Residual Ag^+ in the external aqueous phase after treatment (mg/L)
1	99.62	99.97	0.10
2	98.83	99.85	0.28
3	99.56	99.95	0.12
4	98.65	99.94	0.31
5	98.98	99.96	0.26
6	99.82	99.86	0.07
Average	99.24	99.92	0.19

results given in Table 2 show that the efficiency of Ag^+ recovery increases markedly with decreasing R_{ew} down to 1:20, but after 1:20, it decreases only gradually. In this study, it was observed that the emulsion was dispersed poorly in the feed solutions when R_{ew} was >1:5, but the emulsion was dispersed completely when R_{ew} was <1:10, which increased the contact area between the emulsion and the feed solutions, and improved the rate of transfer of Ag^+ . However, when R_{ew} reached 1:100, the recovery efficiency decreased significantly, because there were insufficient reducing agents in the internal phase to capture all Ag^+ in the external phase. These results indicate that low R_{ew} is preferable both for achieving a high transfer rate and the cost-effectiveness of the process, as long as there are sufficient internal agents to capture all the Ag^+ from the external phase. The results indicate also that the dispersion state of the emulsion is a key factor in determining the efficiency of mass transfer.

4.5. Recovery efficiency and purity of the silver

The above results indicated that the transfer rate and the efficiency of recovery were affected by several parameters, including the concentration of carrier in the membrane phase, the concentration of reducing agent in the internal phase, and R_{ew} . Considering both the efficiency of recovery and cost-effectiveness, parallel experiments were done to examine the feasibility of the ELM-crystallization system. The experimental conditions were determined as follows: 1.0% (v/v) carrier; 2.5% (v/v) surfactant; 0.08 mol/L reducing agent in the internal phase; treatment ratio (R_{ew}) 1:20; 10 min contact time.

The results obtained using these conditions are given in Table 3, which show that >99.5% (wt.) of Ag^+ in the external aqueous phase are extracted by the ELM-crystallization process, and the silver obtained in the internal phase is of high purity. Comparing the data of R_e with the residual concentration of Ag^+ in the external aqueous

Table 4

Results of silver recovery efficiency using the recycled membrane phase (carrier: 1.0% (v/v); surfactant: 2.5% (v/v); reducing agent in the internal phase: 0.08 mol/L; treatment ratio (R_{ew}): 1:20; phase ratio (R_{oi}): 1:1; contact time: 10 min; mixing speed: 250 rpm).

No. of recycles	R_e (%) (wt.)
0	99.19
1	98.93
2	99.83
3	98.96
4	98.47
5	99.53
6	98.89
7	99.83
8	98.64
9	99.26
10	98.56

phase after treatment, the amount of Ag^+ captured by the emulsion is a little greater than that recovered in the internal aqueous phase in the form of metallic silver, indicating that trace amounts of Ag^+ are retained in the membrane phase.

4.6. Reuse of the membrane phase

The ability to reuse the membrane phase is another important factor in determining the cost-effectiveness of the recovery process. In this investigation, recovery efficiency was chosen as the parameter to evaluate the applicability of the recycled membrane phase.

Experiments using the conditions described in Section 4.5 were carried out to determine the feasibility of re-using the recycled membrane phase. The results given in Table 4 indicate that the recovery efficiency is not affected adversely when using the recycled membrane phase.

5. Conclusions

Silver in dilute waste rinse water can be recovered by an ELM-crystallization process after pretreatment with HNO_3 . The ELM-crystallization process described here combines separation, purification, redox reaction, and crystallization in one step, which is suitable for recovering high-purity silver metal directly. The main parameters including R_{ew} , concentration of carrier and reducing agent, influence the efficiency of recovery with different degree and are investigated in order to determine the suitable conditions. The average efficiency of recovery and the purity of the silver recovered are 99.24% (wt.) and 99.92% (wt.), respectively. The remnant solutions containing less than 0.5 mg/L Ag^+ after treatment, have reached the national emission standard. It is shown that the membrane phase can be used repeatedly without affecting the efficiency of recovery, which greatly decreases the operating costs. The use of this ELM-crystallization process to recover Ag^+ in the metallic state directly from dilute effluents is a relatively simple and clean method.

List of symbols

C_{Ag^+}	concentration of Ag^+ at the outer interface of the membrane phase (mol/L)
C_{H^+}	concentration of H^+ at the interface of the membrane phase (mol/L)
$C_{(HR)_2}$	concentration of $(HR)_2$ in the membrane phase (mol/L)
$C_{AgR(HR)}$	concentration of $AgR(HR)$ in the membrane phase (mol/L)
C_o	concentration of Ag^+ in the feed solutions (mol/L)
C_t	concentration of Ag^+ in the feed solutions after contacting for t min (mol/L)
R_e	recovery efficiency
R_{ew}	volumetric ratio of the emulsion to the external phase (treatment ratio)
R_{oi}	volumetric ratio of the membrane phase to the internal phase (phase ratio)

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