J. Applied Membrane Science & Technology, Vol. 3, June 2006, 1–14

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UNIVERSITI TEKNOLOGI MALAYSIA

Emulsion Liquid Membrane Extraction of Silver from Photographic Waste using Tetramethylthiuram Disulfide (TMTDS) as a Mobile Carrier

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ABSTRACT

The recovery of precious metals such as silver from photographic wastes is required in order to save raw materials and to protect the environment from dispersed compound, especially heavy metals. For that matter, several technologies have been used such as precipitation, electrolytic, and ion exchange processes which offer some advantages as well as drawbacks over others. Recently, emulsion liquid membrane extraction has been recognized to be a potential process for industrial wastes treatment and recovery of heavy metals. This process has the ability to selectively separate and rapidly concentrate metals through its very thin layer liquid membrane which has a large interfacial area. An attempt was made to recover silver from liquid photographic wastes using tetramethylthiuram disulfide as a mobile carrier. The important variables affecting the emulsion liquid membrane (ELM) process including residence time, surfactant concentration, carrier concentration, level of agitation and phase ratio between emulsion and feed phase were investigated. The results showed that tetramethylthiuram disulfide is selective towards silver (>80%) compared to other metals in the photographic waste. The highest silver extraction is obtained using 0.05 M tetramethylthiuram disulfide, 3% (w/v) Span 80, 300 rpm stirring speed, 1.0 M thiourea in 0.1 M HCl stripping agent, 1:3 of treat ratio, and toluene as the diluent.

Keywords : Emulsion liquid membrane, silver extraction, photographic wastes, tetramethylthiuram disulfide

1.0 INTRODUCTION

Liquid membrane permeation is a well-known process for the separation of metals from industrial wastewaters and it also has been utilized in the separation of organic acids from aqueous waste [1]. Recently, it has become a promising technique in treating industrial wastes because of its capability to separate and concentrate precious metals even at very low concentration like silver, gold and platinum from industrial waste. Recovering precious metals would be an attractive approach due to the price of these metals and increasing pressure concerning environmental and economic aspects.

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In photographic industry, recycling silver was done for development and fixing waste solutions, spent rinse water and scrap films. These solutions are particularly interesting, from economical point of view, due to the amount of contained silver and compliance to waste water discharge standards. There are many methods, which have been established commercially to recover silver existed in photographic wastes such as precipitation, electrolysis, solvent extraction, ion-exchange, and reductive exchange. For instance, electrolysis is a commonly method used to recover silver from photographic wastes but it is not suitable for dilute silver concentration due to low plating efficiencies. This process requires also high initial capital investment and high operating cost, and critical operating conditions that need to constantly be supervised.

The oldest and conventional method of silver recovery, precipitation, would not achieve the required discharge level although it has provided an effective technique for silver recovery. It also faced several other problems such as formation of silver complexes in the effluent. This silver complex is sometimes very stable and difficult to be precipitated by the precipitation process. Ion exchange process is generally used for effective recovery of silver from dilute solutions. It involves the exchange of ions in the solution with ions of the similar charge on the resin. This method are considered uneconomical for silver recovery from photographic waste but are feasible for low silver concentration in separating waste streams where the total ionic strength is not much greater than the silver salt concentration [2]. To overcome the problem many researchers found that emulsion liquid membrane extraction has a great potential for separating and concentrating metal ions compared to solvent extraction. This separation technique has been tested in hydrometallurgy and waste water treatment. Several pilot plants for recovery of zinc, copper, chromium, and nickel have proved the technical feasibility of the emulsion liquid membrane process [3]. However, there is lack of research paper published on the application of ELM technique for silver extraction from liquid photographic wastes. The ELM process has already been applied to an industrial pilot plant in Austria and it has reached the stage of practical application [3]. An emulsion liquid membrane process (ELM) has enough ability to solve the above problems and capable to separate and concentrate metals very rapidly through its very thin liquid film and large interfacial area. Hayworth *et al.* [4] economically compared an emulsion liquid membrane process to conventional solvent extraction process for the recovery of uranium ions from wet process of phosphoric acid and concluded that the ELM is superior compared to conventional solvent extraction from the viewpoints of both capital and operating costs. Despite of much research on the extraction of various metals using ELM, only Lee *et al.* [5] attempted to use ELM for silver extraction. On the other hand, demulsification is one of the key processes for emulsion liquid membrane application. Demulsification is mainly used for the recovering of the membrane phase including organic solvent, surfactant, extractant, and valuable solute ions in waste treatment processes. The common methods of demulsification are centrifugation, sedimentation, thermal breaking, and the electrostatic method. The electrostatic method in a high voltage field is one of the most effective and simplest demulsification methods.

Extraction of silver from photographic waste by the ELM process is governed by several parameters and poses a challenging problem in the field of metal recovery from industrial wastes. The choice of carrier and strip agents is vital for the success of the ELM process and this choice can be made on the basis of conventional liquid-liquid extraction studies. The efficiency of the extraction system is measured in terms of extraction percentage, E. The results show that TMTDS in toulene was found to be one of the most effective carriers by virtue of its high extraction percentage and high selectivity for silver [6].

The major parameters influencing the extraction efficiency in ELM systems is the types and concentration of carrier, stripping agent for the target metal ion, the level of agitation, and the change in the viscosity of the membrane phase. The other important parameters affecting the rate and the extent of extraction are concentration of surfactant used in the membrane phase and the volume ratio of the emulsion phase to the aqueous feed phase. The nature of the carrier which determines its ability to form a complex with the silver ion is also important along with its concentration.

This paper presents the selective extraction of silver from photographic waste using emulsion liquid membrane containing tetramethylthiuram disulfide as the mobile carrier, which was conducted in a batch extraction process. Various parameters influencing the transport of silver across the membrane such as concentration of carrier and strip agent, surfactant concentration, agitation speed, and emulsion stability will be discussed in this paper.

2.0 EXPERIMENTAL PROCEDURES

2.1 Reagents and Solutions

Tetramethylthiuram disulfide (97% purity) was obtained from Acros Organics. The chemical structure of tetramethylthiuram disulfide is shown in Figure 1. Toluene was used as organic diluents obtained from Merck(M) Sdn. Bhd. Surfactant, Span 80 was obtained from Fluka Chemika while the stripping agent, thiourea was supplied by Riedel-de Haën. The stripping solutions were prepared by using hydrochloric acid (37%), which was obtained from Merck (M) Sdn. Bhd. All chemicals used are analytical grade and used as received. The photographic waste sample used was obtained from photographic shops. Table 1 shows that the silver, sodium, potassium, and iron exist in high concentration in the photographic wastes while the anion content are in the following order: sulphate > nitrate > chloride [5]. However, during the photo processing, particularly in the fixing or bleach-fix, silver is removed from the film or paper usually in the form of thiosulfate complex [7].

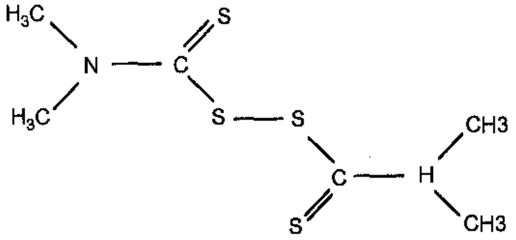

Figure 1 Chemical structure of tetramethylthiuram disulfide

Table 1 Physical and chemical properties of photographic waste

Cations	Concentration (ppm)	Anions	Concentration (ppm)	Physical properties	
Ag	2490.5	Cl^-	249	pH	8.02
Na	3628.6	NO_3^-	2202	Density	1.04 g/ml
K	6238.1	SO_4^{2-}	3712	Viscosity	0.77cP
Fe	1478.9	F^-	62		

2.2 Emulsion Liquid Membrane Extraction

The emulsion was prepared by emulsifying aqueous solutions (stripping phase) with the formulated organic phase. Equal volumes of 10 ml portions of organic solutions and aqueous solution were stirred continuously at 13 500 rpm using a motor driven homogenizer for 5 minutes to obtain a stable white emulsion liquid membrane. The emulsion is then cooled down to room temperature and is ready for the extraction study. The emulsion must be freshly prepared each time before the permeation experiment to avoid any destruction occurring.

The prepared emulsion was then dispersed in the agitated vessel containing the external solution (photographic waste) with a treat ratio of 1 to 5. The mixture was stirred at 200 rpm for 20 minutes. After that, the samples are quickly poured into a separation funnel and left for phase separation. The aqueous phase was filtered in order to remove entrainment and this raffinate phases are analyzed by an Atomic Absorption Spectrophotometer (AAS) for metal concentration.

3.0 ELM MECHANISM OF SILVER EXTRACTION

ELM process involves simultaneous extraction and stripping in one step. Silver in the form of thiosulfate anionic complex Ag $(S_2O_3)_2^{3-}$ can be removed from the photographic processing solution or photographic waste [8]. In the presence of thiosulfate, the reduction of TMTDS in the membrane phase and formation of the silver (I) *N*, *N*-dimethyldithiocarbamate complex occurs according to the reaction below [9]:

$$\begin{aligned}&(CH_3)_2NCS_2S_2CN(CH_3)_2 + Ag(S_2O_3)_2^{3-} \leftrightarrow \\ &\qquad \left[(CH_3)_2NCS_2 - Ag - S_2CN(CH_3)_2\right]^- + S_4O_6^{2-}\end{aligned} \tag{1}$$

According to Equation (1), it is assumed that only 1 mole of TMTDS is required to form the silver (I) complex, since the actual stoichiometry will not be covered in this research, this assumption will be used in the following discussion. The silver-TMTDS complex transfers across the membrane phase and reacts with the acidic thiourea in the internal phase at the internal interface according to Equation (2):

$$\begin{aligned}&\left[(CH_3)_2NCS_2 - Ag - S_2CN(CH_3)_2\right]^- + 2CS(NH_2)_2H^+ \leftrightarrow \\ &\qquad 2(CH_3)_2NCS_2^- + 2NH_4^+ + Ag(SCN)_2^- + 2H^+\end{aligned} \tag{2}$$

Possible scheme for silver transport from feed solution to internal phase through TMTDS-Span 80-toluene liquid membrane can be shown in Figure 2. During the extraction process, the carrier molecules first react with the metal ions on external/membrane interphase to form metal complexes (Equation (1)). For every mole of metal ion extracted into the membrane phase, two moles of proton are produced. Therefore, one of parameters controlling the extraction is acid content of the aqueous phase. In a similar manner, the acid content in the stripping side is also an important parameter for the extraction due to the stripping reaction requiring the help of protons present in the receiving solution like acidic thiourea in this study.

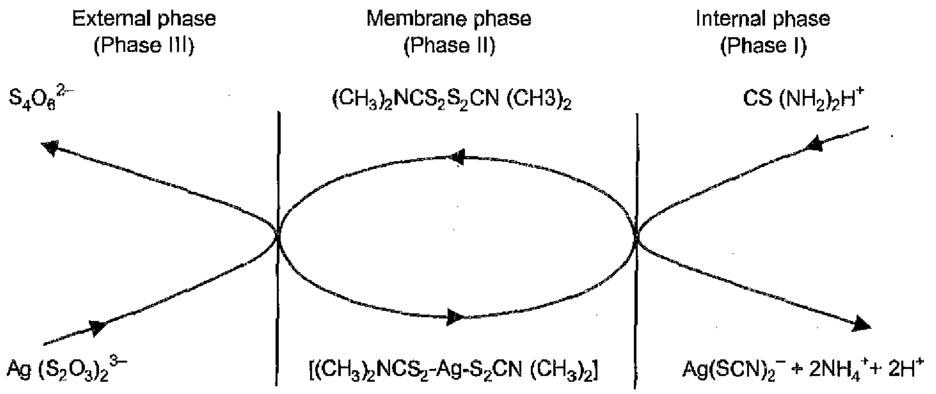

Figure 2 A simultaneous extraction and stripping mechanism of silver extraction using ELM

4.0 RESULTS AND DISCUSSIONS

4.1 ELM Formulation

As reported in the literature, emulsion liquid membrane is a versatile reagent that can be used to perform separations by a variety of mechanisms [10]. In this research, silver is extracted from the photographic waste by using carrier-facilitated transport mechanism. Tetramethylthiuram disulfides (TMTDS) is used as the mobile carrier because it is an efficient extractant reagent and selectively extracted silver in thiosulfate media from real liquid photographic wastes based on screening by solvent extraction technique. The effect of equilibrium pH is shown in Figure 3. Therefore, the pH equilibrium selected for this system is 8.02. TMTDS, as a chelating extractant is incorporated in the

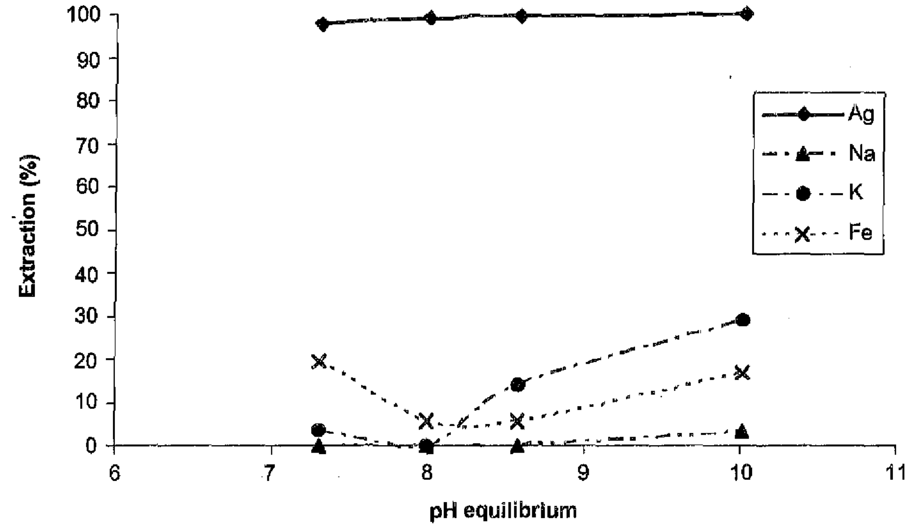

Figure 3 Percentage of metals extraction at various pH_{eq} for TMTDS. (Experimental conditions: [thiuram]:0.03M; temperature: 25°C; 250 rpm; shaking period: 18 hours; volume ratio: 1:1)

membrane phase to increase the mass transfer rates due to large interfacial area. Span 80, a nonionic surfactant is added to form a stabilized liquid membrane. After the formulation of liquid membrane, thiourea in HCl solution, which acts as the stripping agent at the receiving phase will be added into the liquid membrane to form two phases. Membrane phase will be the upper phase whereas the treat phase will be the bottom phase. Emulsification will be carried out using a homogenizer and a stable milky ELM is formed and ready to be used in the separation process.

4.2 Effect of Extraction Time

The extraction time of emulsion plays an important role for the ELM extraction process. The longer extraction time will result in more transfer of water inside the internal phase, which cause the membrane to swell and subsequently might have initiated breakage of the emulsion phase [11]. Figure 4 shows the extraction rate increasing when the extraction time increased and reached its optimum time at 6 minutes. After 6 minutes, the degree of extraction decreased probably as result of the breakage of the emulsion phase. This emulsion breakage will cause the leakage of silver from the internal phase to the external phase and therefore, the metal remaining in the external phase increased after 6 minutes. In order to get a better overall mass transfer, it was decided to carry out all the remaining experiments using a contact time of 6 minutes.

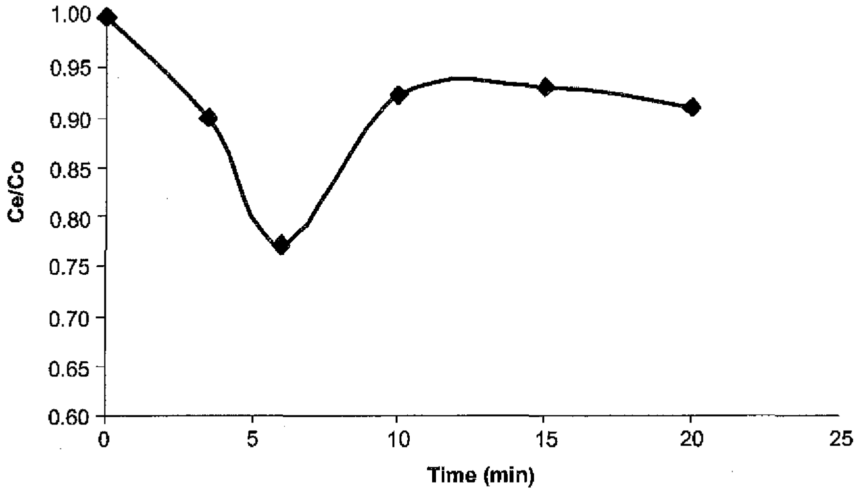

Figure 4 Extraction time in silver extraction (Experimental conditions: [TMTDS]=0.03M in toluene; [thiourea] = 0.5 M in 0.5 M H_2SO_4; Span 80 = 5% w/v; stirring speed = 250 rpm; treat ratio = 1:5)

4.3 Level of Agitation

The speed of agitation plays a major role in the rate of transfer through emulsion liquid membrane process. Teramoto *et al.* [12] and Martin and Davies [13] have reported that the extraction rate generally increases with an increase in agitator speed up to a critical point. When it exceeds the critical speed, membrane breakage occurs. Theoretically, increase in agitation speed will increase the extraction rate due to reduction of the emulsion globule size thereby providing high interfacial contact area between external and membrane phases and increase of the external phase mass transfer

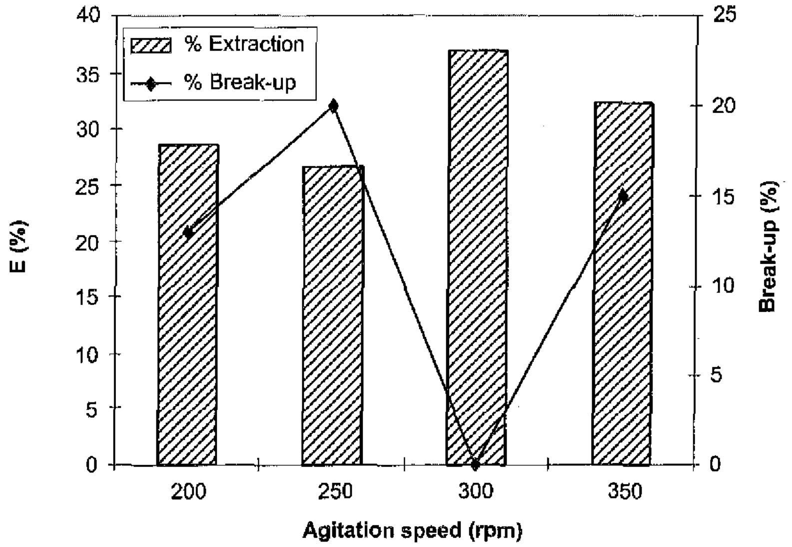

Figure 5 Effect of agitation speed on the extraction and break-up of emulsion droplets (Experimental conditions: [TMTDS]=0.03M in toluene; [thiourea] = 1M in 0.1 M HCl; extraction time = 6 min; Span 80 = 5% w/v; treat ratio=1:5)

coefficient. However, increasing the agitation speed above a critical level not only does not increase the extraction rate considerably, but rather breaking down the emulsion globule and thereby reducing overall extraction. Figure 5 shows the performance of silver extraction at a few level of agitation speed in a range of 200-350 rpm. The rate of emulsion breakage is high at 250 and 350 rpm.

It was observed (Figure 5) that there were two zones of speed range; (1) 200-250 rpm and (ii) 300-350 rpm that manifested the same trend in which the extraction rate decreased with an increase in emulsion breakage rate. In zone (1), the extraction rate does not increase with the agitation speed because the emulsion break-up rate dominated in the extraction process and its effect overtook the influence of agitation speed in the ELM process. It was inline with the agreement by Kulkarni and Kumar [14], which is increasing the agitation speed from 200 to 400 rpm resulted in reduction of extraction. The same phenomenon occurred in zone (2). It seems that there is a transition zone between 250 and 300 rpm in which the emulsion globules may undergo some size adjustment caused by hydrodynamic shear and also the shear induced by the magnetic stirrer in the beaker. At 300 rpm, the extraction rate was at its optimum point where there was no emulsion break-up observed. Further studies on the effect of hydrodynamic instability towards emulsion breakage will be carried out in future work.

4.4 Surfactant Concentration

Both the stability of the emulsion and the viscosity of the liquid membrane were altered by the proportion of surfactant in the organic phase [15]. Figure 6 shows the effect of surfactant concentration on silver extraction from photographic waste.

Emulsion stability generally increased when increasing the concentration of surfactant due to the increase in viscosity of the organic phase [16]. The surfactant layer adsorbed on the interfaces of the globules is modeled as having an effective thickness δ, the magnitude of which represents the amount

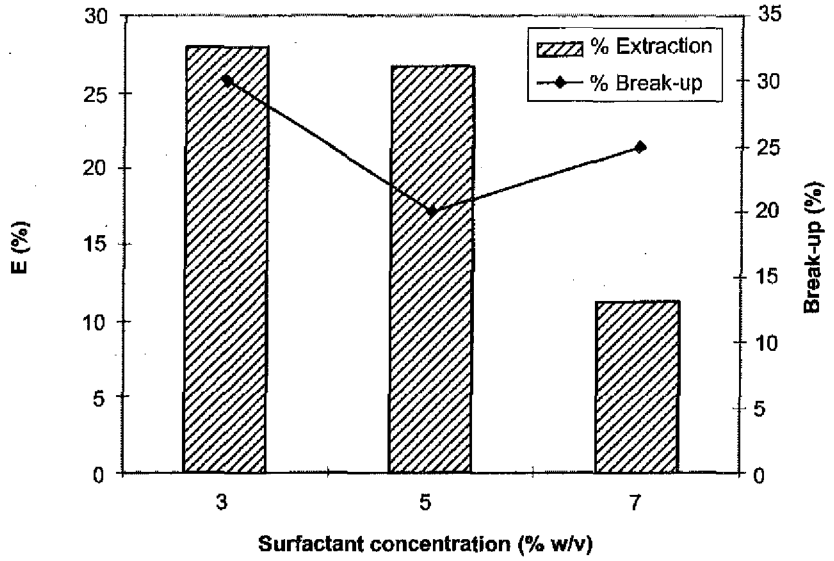

Figure 6 Effect of surfactant concentration on the silver extraction and break-up (Experimental conditions:[TMTDS] = 0.03M in toluene; [thiourea] = 1M in 0.1 M HCl; stirring speed = 250 rpm; treat ratio =1:5; extraction time = 6 min)

of surfactant present [17]. If there is no surfactant used (δ=0), the net interaction energy between two interfaces is attractive when they get closer and there is no energy barrier to coalescence. The structure is thus expected to be inherently unstable, which will show an instant emulsion breakdown. Therefore, when 3% w/v of Span 80 is used in this experiment, the breakage is the highest because the surfactant layer is thin. These thin layers do not have a strong influence on the interaction energy and produce no obstacle on oil film rupture. Therefore, when the surfactant concentration increased to 5% (w/v), the breakage rate will decrease. It may be because the internal water droplet starts experiencing a net repulsive van der waals interaction with the external aqueous phase, which will produce a stable globule. However, when the surfactant continues to increase until 7%, the breakage rate starts to increase which may be assisted by the swelling that cannot be observed through this experiment [18]. Increasing surfactant concentrations from 3 to 7% (w/v) decrease the degree of extraction (Figure 5). An increase in membrane phase viscosity decreases the diffusion coefficient and mass transfer coefficient according to Equation (3), which is basically the Wilke-Chang diffusion coefficient;

$$D = 1.17 \times 10^{-16} \frac{T(\psi M)^{0.5}}{\mu V_A^{0.6}} \tag{3}$$

where, the solvent association factors, ψ, for the aqueous and oil phases are 2.6 and 1.0, respectively; V_A is the solute molar volume (m^3/kg mol); μ is the viscosity of solvent (kg/m. s) and M is the molecular weight of solvent (kg/kg mol) [19, 20]. When the viscosity of membrane increase from 3 to 7% (w/v), the solute diffusivity increased but the extraction rate will decrease due to membrane interface resistance. Since there is a trade-off between membrane stability and mass transfer rate, it was decided to take 3% w/v of surfactant concentration as the optimum condition based on its highest extraction rate and economic aspect.

4.5 Carrier Concentration

The effect of the concentration of TMTDS (mobile carrier) in the organic phase on the extraction of silver is shown in Figure 7. By increasing the concentration of TMTDS from 0.01 to 0.07 M, the degrees of extraction increases and almost plateau at 0.05 M. This is because with an increase in TMTDS concentration, the diffusion of solute-carrier complex across the membrane also increases. The concentration of carrier in the membrane phase should phenomenally increase the interfacial silver concentration and increase the extraction rate. However, it should be noted that as a result of the equilibrium of the stripping reaction, there is a limit to the carrier concentration that will give significant increase in the extraction rate. When the percentage of silver remains in the complex form (in membrane phase) reaches its maximum without getting stripped due to excess carrier concentration, it will reduce the extraction efficiency since in ELM process, extraction and stripping occur simultaneously.

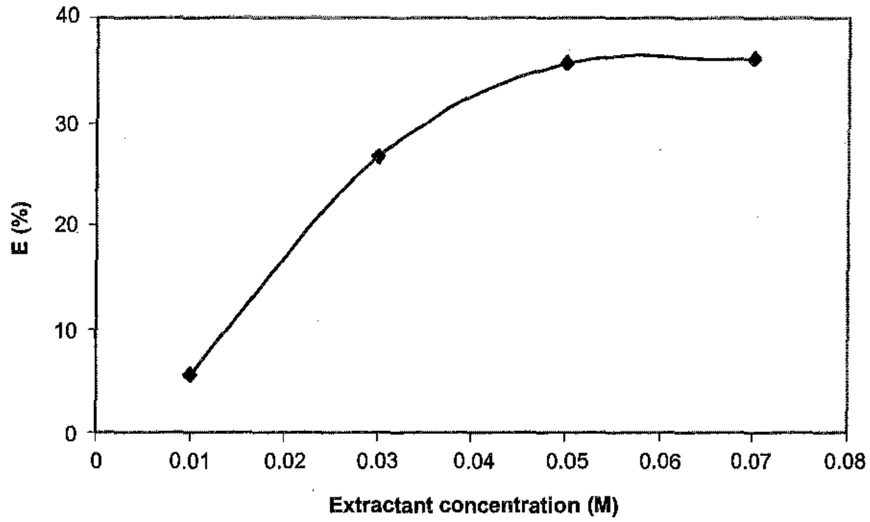

Figure 7 Effect of extractant concentration on the extraction of silver (Experimental conditions: [thiourea] = 1M in 0.1 M HCl; Span 80 = 5% w/v; extraction time = 6 min; stirring speed = 250 rpm; treat ratio = 1:5)

4.6 Stripping Solution

Gherrou *et al.* [21] has pointed out that thiourea has been demonstrated to be an excellent leaching reagent for metals due to is high ability to complex, especially precious metal ions. Besides, Mendoza and Kamata [9] also found out that thiourea is an effective stripping agent for silver, but with certain limitation. Since thiourea has both basic and acidic groups, a dependence of the extraction efficiency on the pH in the internal phase is important. Based on stripping reaction of metal loaded TMTDS with acidic thiourea by Othman *et al.* [22], the highest stripping performance is by using 1 M thiourea solution. Therefore, 1 M thiourea solutions of different acidity have been prepared by adding HCl with different concentration before mixing with the organic phase to form emulsion. Figure 8 shows the effect of HCl concentration on silver extraction. From the results, it can be concluded that the

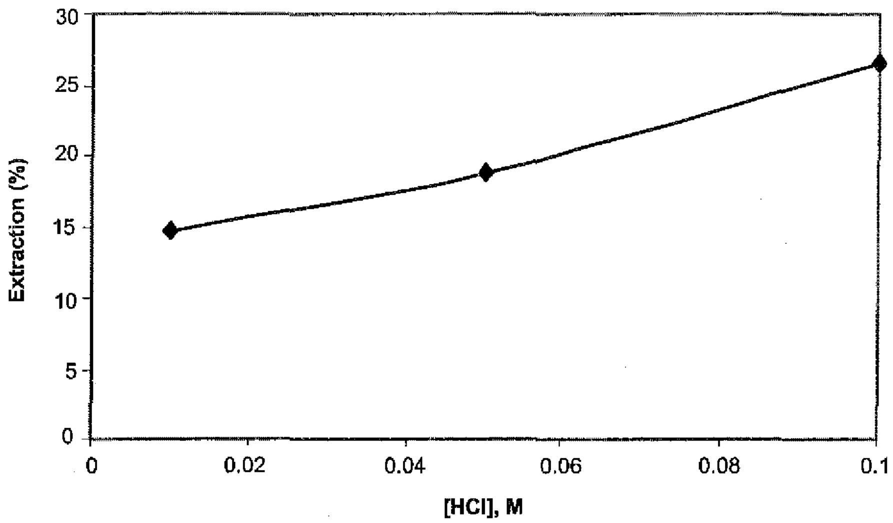

Figure 8 Effect of HCl concentration in the stripping agent on the extraction of silver (Experimental conditions: [TMTDS] = 0.03 M in toluene; extraction time = 6 min; Span 80 = 5% w/v; stirring speed = 250 rpm; treat ratio = 1:5)

extraction efficiency increased with an increase in the acidity of thiourea solution from 0.01 to 0.1 M HCl. Therefore, 0.1 M HCl will be selected as the favorable acidity for thiourea solution in this study.

4.7 Treat Ratio

Figure 9 shows the effect of treat ratio on the silver extraction. The extraction performance increased with the ratio because the total interfacial area between the external phase and emulsion dropped and the capacity of internal phase for trapping silver increased simultaneously. This agrees with the

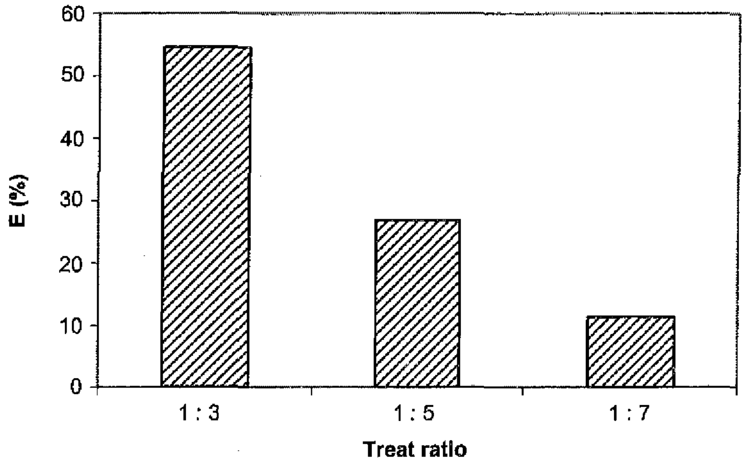

Figure 9 Effect of treat ratios on the extraction of silver (Experimental conditions: [TMTDS] = 0.03 M in toluene; [thiourea] = 1 M in 0.1 M HCl; residence time = 6 min; Span 80 = 5% w/v; stirring speed = 250 rpm)

literature and has been attributed to shorter diffusion lengths as the packing of the droplets becomes tighter. However, further increase in the treat ratio is not feasible because of the increase in water transport to the interior phase which strongly influences the emulsion swelling. This similar effect were reported by [23] and [24] in mercury and zinc separation respectively.

4.8 Diluents

The selection of diluents is important in the ELM process because it determines the thickness of the membrane and permeability of the membrane for the solute. Different diluent produces different effect in emulsion stability and percentage of extraction. In this experiment, toluene and chloroform were selected as the diluents to prepare the organic phase. It has been found that toluene system has some advantages over chloroform system that makes it a better system for silver extraction by using ELM process. Figure 10 exhibits the extraction performance between toluene system and chloroform system.

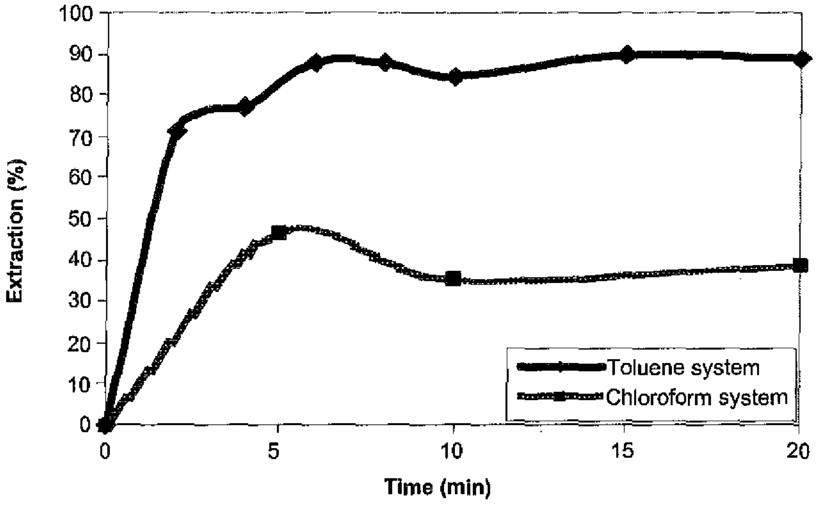

Figure 10 Extraction performance of toluene and chloroform system

Toluene system can extract the silver up to 89.69% by optimizing the parameters such as extraction time, level of agitation, surfactant concentration, carrier concentration, thiourea acidity and treat ratio. Meanwhile, chloroform system can only perform 46.45% at its optimum condition. Besides, the polar nature of these two diluents have attributed to the selection because chloroform has higher polar nature than toluene and it tends to interact with the carrier that can result in lower extraction efficiency of metal ions. By the formation of a carrier-diluent species in the organic phase, it will produce a lower concentration of the free carrier with a consequent decrease in the extraction efficiency. Furthermore, its polar nature will lead to emulsion instability by enhancing the permeation of water into the internal phase. During the separation process, the ELM phase of the chloroform system will settle at the bottom of the separation funnel which is impractical for industrial application. Therefore, toluene system will be the better choice for the silver extraction from the photographic waste.

4.9 Membrane Selectivity

After varying a few parameters, the most favorable conditions obtained were used to check the feasibility of silver extraction from photographic waste with emulsion liquid membrane using tetramethylthiuram disulfides as the mobile carrier. The selected carrier is 0.05 M in toluene, 3% (w/v) Span 80 as surfactant concentration, agitation speed 300 rpm and treating ratio is 1:3. Meanwhile, after a few screening process, the applicable stripping agent is 1.0 M thiourea in 0.1 M HCl.

Figure 11 shows the extraction performance of metals extraction during 20 minutes process times. The extraction performance increases with longer extraction time. There was a slight decrease from 8 to 10 minutes that may be caused by the emulsion break-up, but the effect is marginal. By using the optimum conditions, silver extraction can reach its best extraction percentage until 90% at 15 minutes. The emulsion break-up measured is less than 10%, and therefore, its effects on ELM process can be neglected.

Table 2 shows the separation factor of silver over the other metals. The results show that silver is selectively separated from iron, sodium and potassium especially after 6 minutes process time.

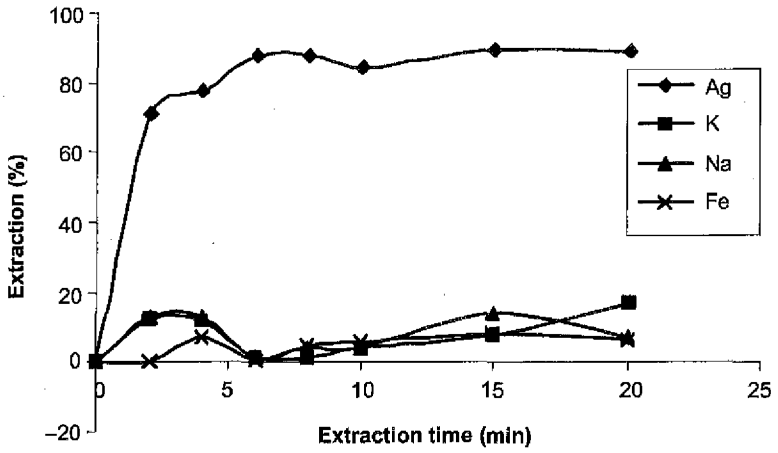

Figure 11 Extraction of silver from photographic waste (Experimental conditions: [TMTDS] = 0.05 M in toluene; [thiourea] = 1M in 0.1 M HCl; Span 80 = 3% w/v; treat ratio = 1:3; stirring speed = 300 rpm)

Table 2 Separation factor (S) of silver toward other metals in ELM system

Time (min)	S (Ag/K)	S (Ag/Na)	S (Ag/Fe)	S (Ag/(K,Na,Fe))
2	17.3	17.2	1854.0	8.58
4	25.6	23.5	42.9	9.54
6	545.0	431.5	775.2	183.80
8	597.0	169.9	150.2	70.26
10	117.0	116.1	88.0	35.10
15	107.0	52.7	95.0	25.80
20	27.0	32.4	119.6	13.10

However, the value of separation factor of silver decreases for longer extraction process due to emulsion breakage and swelling phenomena.

5.0 CONCLUSION

The recovery of silver from liquid photographic waste solution using liquid surfactant membranes was studied with respect to various parameters for silver extraction from liquid photographic waste. Tetramethylthiuram disulfide, Span 80 and acidic thiourea were used as a carrier, surfactant and stripping agent, respectively. It was found that the extraction performance was very encouraging and further study should be carried out to model and optimize the extraction parameters.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support from the Ministry of Science, Technology and Environment, Malaysia (IRPA grant no. 74032) and Universiti Teknologi Malaysia for the scholarship awarded to Norasikin Othman to make this study possible.

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