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# Emulsion Liquid Membrane Extraction of Silver from Photographic Waste Using Cyanex 302 As A Mobile Carrier

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## Abstract

*The recovery of precious metals such as silver from photographic wastes is absolute necessity in order to save raw materials and to protect environment from hazardous compounds especially heavy metals. Several technologies have been used such as precipitation, electrolytsis, and ion exchange processes offering some advantages as well as drawbacks over others. Recently, emulsion liquid membrane extraction has been recognized to be potential process for industrial wastes treatment and recovery of heavy metals. This process has enough ability to separate selectively and concentrating rapidly of the metals through its very thin layer liquid membrane having large interfacial area. An attempt was made to recover silver from liquid photographic wastes using with Cyanex 302 as a mobile carrier. The important variables affecting the emulsion liquid membrane (ELM) extraction process including extraction time, surfactant concentration, carrier concentration, stripping agent solution, level of agitation and phase treatment ratio between emulsion and feed phase were investigated. The results showed that the Cyanex 302 is selective towards silver more than 80% compared to other metals existed in the photographic waste. The highest silver extraction was obtained by using 0.05 M Cyanex 302, 3 % (w/v) Span 80, 250 rpm stirring speed, 1.0 M thiourea in 1.0 M $H_2SO_4$ as stipping agent, 1:5 of treat ratio, and kerosene as a diluent.*

**Keywords:** Emulsion liquid membrane extraction; silver extraction; photographic waste; Cyanex 302.

## Introduction

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 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.

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

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 having large interfacial area. An emulsion liquid membrane process reported more economic and also superior process compared to conventional solvent extraction from the viewpoints of both capital and operating costs [2]. The ELM operation has already been applied in an industrial pilot plant in Austria and has reached the stage of practical application [3]. Despite of much research on the extraction of various metals using ELM, only [4], was 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 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 most established method is a high voltage demulsifier which offered the most effective and simplest method and being used in this study.

Extraction of silver from photographic waste by 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 ELM process and this choice can be made on the basis of conventional liquid–liquid extraction studies. The efficiency of extraction system is measured in terms extraction percentage, E. The result shows that Cyanex 302 in kerosene was found to be one of the most effective carrier by virtue of its highest extraction percentage and very selective to silver [5].

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 volume ratio of the emulsion phase to aqueous feed phase. The nature of carrier which depicts ability to form complex 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 Cyanex 302 as a mobile carrier, which was conducted in a batch ELM extraction process. Various parameters influencing the transport of silver across the membrane such as concentration of carrier and strip agent, treat ratio, surfactant concentration, and agitation speed will be discussed in this paper.

## Experimental Procedures

*Reagents and Solutions*

Cyanex 302 was obtained from Sigma. This extractant was dissolved in kerosene obtained from Fluka Chemica Company. An acidic thiourea solution was used as a stripping agent. Thiourea was obtained from Riedel-de Haen and hydrochloric acid (37 %) and sulfuric acid were obtained from Merck (M) Sdn. Bhd. All chemicals used were analytical grade and used as received. The photographic waste sample used was obtained from photographic shops. Table 1 shows the chemical and physical properties of photographic waste which shows that some metals concentration is high while the anion content are in the following order: sulphate > nitrate > chloride [5]. 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 [6].

*Table 1- Physical and Chemical Properties Waste of photographic waste* [5].

| Cations | [cation], ppm | Anions | [anion], ppm | Physical properties | |
|---|---|---|---|---|---|
| Ag | 2490 | $Cl^-$ | 249 | pH | 8.02 |
| Na | 3630 | $NO_3^-$ | 2202 | Density | 1.04 g/ml |
| K | 6240 | $SO_4^{2-}$ | 3712 | Viscosity | 0.77 cP |
| Fe | 1480 | $F^-$ | 62 | | |

*Emulsion Liquid Membrane Extraction*

The emulsion was prepared by emulsifying aqueous solutions (stripping phase) with formulated organic phase. Equal volume (10 ml) organic and aqueous solutions were stirred continuously at 13500 rpm using homogenizer for 5 minutes to obtain a white stable emulsion liquid membrane. The emulsion must have freshly prepared each time before the permeation experiment to avoid any destruction occurred.

The prepared emulsion was then dispersed into the agitated vessel having the external solution (photographic waste) with treat ratio of 1 to 5. The mixture was stirred at 250 rpm for 20 minutes. Then, 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 aqueous phase was analyzed by an Atomic Absorption Spectrophotometer (AAS) for metal concentration.

## Results and Discussions

*Metal Selectivity*

Metal selectivity is a key consideration in any separation processes. As photographic wastes usually contain many compounds of anion and cation, the ability of the membrane to transport only the target metal ion becomes important. Selectivity in ELM processes is governed primarily by the carrier used in the liquid membrane formulation.

Figure 1 shows the ELM process using Cyanex 302 is very selective toword silver which is almost completely extract silver in 3 minutes process over the others metals. This trend is agreement with the result of using Cyanex 302 as an extractant in a solvent extraction process [7]. However in longer extraction time it was found that the percentage of the others metal increases especially at 10 to 20 minutes. It is due to the reaction of carrier with sodium, potassium and ferum whiles the silver was completely extracted in earlier process.

Figure 1 also shows that at 15 to 20 minutes extraction time, the percentage of silver extraction slightly decreased; means that the present of silver in the feed phase after a few minutes of absence. It is due to the instability of emulsion in longer extraction time. Increasing the extraction time makes up emulsion to swell and tends to

break down at certain time. The swelling will decrease the efficiency of metal recovery and when breakage occurred, the stripped metal will leak from the receiving phase to the feed phase and the amount of silver in the feed phase increased. If the extraction process continued to longer extraction time the emulsion liquid membrane performance will collapse.

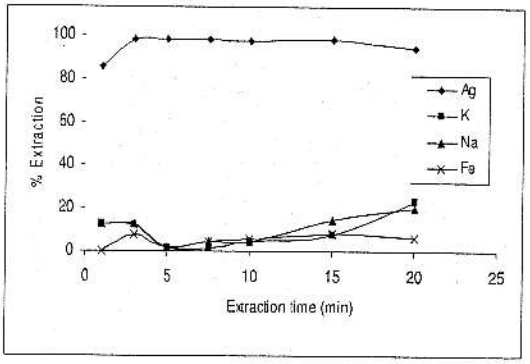


*Figure 1- Metal selectivity in ELM extraction process (Experimental condition: TR: 1:5, surfactant: 5% (w/v), extractant: 0.05M Cyanex 302, speed: 250 rpm, feed phase: real liquid photographic waste, and diluent: kerosene).*

*Effect of Extraction Time*

The extraction time is defined as the mixing time of three phases process of W/O/W emulsion. It becomes one of important parameters in emulsion liquid membrane system. The longer extraction time resulted in more transfer of water inside the internal phase, which caused the membrane to swell and subsequently might have initiated breakage of the emulsion phase and causes leakage of solute from the internal phase to the external phase [8]. Besides, appropriate exxtraction time is needed to increase the mass transfer of metal ions from the external phase to the organic phase. Figure 2 exhibits the percentage of extraction of silver from external phase as a function of extraction time.

The extraction performance increased when the extraction time increased and reached its maximum extraction at 3 minutes process. After 15 minutes, the degree of extraction decreased adversely which maybe resulted from 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 15 minute. Figure 2 also shows that the percentage of emulsion breakage increased up to 18 % during the extraction process. It is due to many factors such as type of stripping agent, agitation speed, method of emulsion making and many others that will discuss later in this thesis. However at initial 15 minutes operation no emulsion breakage was recorded but the emulsion was swollen up to 12 %. However at minutes 20, neither emulsion swelling nor breaking was observed, indicated the rate of swelling and emulsion breaking were in the same degrees. Then, further extraction will cause emulsion break-up.

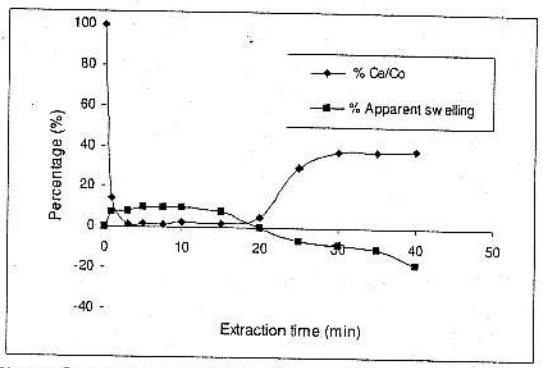


*Figure 2- Effect of residence time on the extraction of silver (Experimental conditions: TR: 1:5, surfactant: 5% (w/v), extractant: 0.05M Cyanex 302, speed: 250 rpm, feed phase: real liquid photographic waste, internal phase: 1 M Thiourea in 1 M $H_2SO_4$, and diluent: kerosene).*

*Effect of Carrier Concentration*

Figure 3 shows the effect of carrier concentration on the extraction of silver from photographic waste. Increasing concentration of Cyanex 302 from 0.01 to 0.07 M, the extraction of silver increased and almost completely extracted at 0.05 M at three minutes process. Further increase in the concentration, results in no significant effect on extraction performance. This is because of the two reasons; maximum percentage of silver remains in the complex form (in the membrane phase) without getting stripped which in its turn affected the final recovery by the ELM process. The other reason is increase in carrier concentration; swelling of the emulsion was also increased, thereby diluting the stripping phase. High concentrations in the membrane phase have been observed to lead to high osmotic swelling and high rates of membrane breakdown. Therefore, Cyanex 302 in the liquid membrane is not to be saturated with silver, but merely should act as a shuttle to carry silver ions from one side of the membrane to the other side.

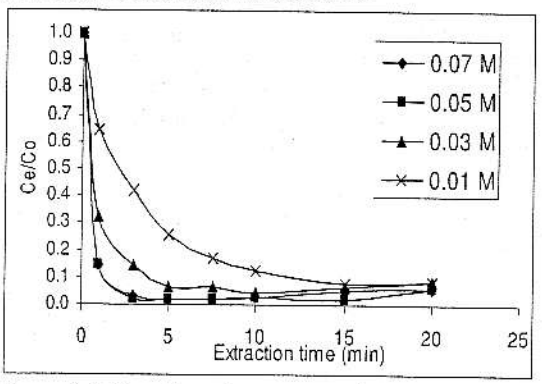


*Figure 3- Effect of carrier concentration on silver extraction (Experimental conditions: speed of agitation: 250 rpm, TR: 1:5, surfactant: 5% (w/v), feed phase: real*

*photographic waste, strip phase: 1 M Tu in 1M $H_2SO_4$, and diluent: kerosene).*

*Effect of Surfactant Concentration*

Since liquid membranes are thin, mobile and subject to shear, they tend to rupture during the extraction process. The stability of an ELM depends on the shear produced by agitation [9,10], internal droplet size [11,12] and composition of the membrane [10,11]. The composition of liquid membrane is crucial in determining good extraction.

Both the stability of the emulsion and the viscosity of the liquid membrane are altered by the proportion of surfactant in the organic phase [13]. Figure 4 shows the effect of surfactant concentration on the silver extraction from photographic wastes. As expected, as a concentration of surfactant increases, the stability of the liquid membrane was increased. It is due to an increasing adsorption of the surfactant in the interface by an increase in the interface film force of surfactant molecules. If there is no surfactant used, the net interaction energy between two interfaces is attractive when they get closer, and there is no energy barrier to coalescence.

*Table 2-Viscosity of liquid membrane (Cyanex 302 in kerosene) and Span 80*

| [Cyanex 302], M | [Span80], w/v | Viscosity, cP |
|---|---|---|
| 0.05 | 1 | 2.02 |
| 0.05 | 3 | 2.36 |
| 0.05 | 5 | 2.42 |
| 0.05 | 7 | 2.50 |

As a result, the structure is thus expected to be inherently unstable, which will show an instant emulsion breakdown. Therefore, when 1% (w/v) of Span 80 is used in this experiment, the breakage is the highest because the surfactant layer is thin. This thin layer does not have a strong influence on the interaction energy and produces no obstacle on oil film rupture. As surfactant increases to 5% (w/v), the breakage rate decreases. 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% (w/v), the breakage rate starts to increase which may be caused by the swelling.

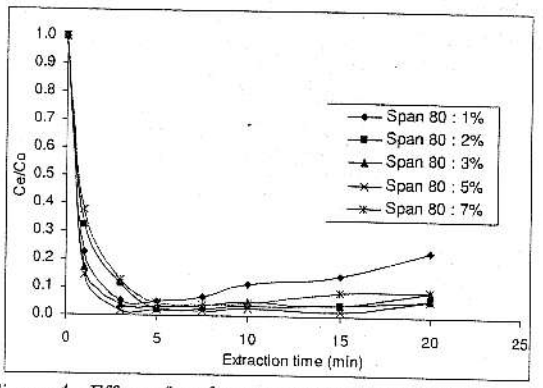


*Figure 4 - Effect of surfactant concentration on the extraction of silver (Experimental conditions: speed of agitation: 250 rpm, TR: 1:5, carrier conc.: 0.05 M Cyanex 302, feed phase: real photographic waste, strip phase: 1 M Tu in 1M $H_2SO_4$, and diluent: kerosene).*

*Effect of Agitation Speed*

Figure 5 shows the effect of agitation speed in the silver extraction process from photographic wastes. It was observed that increasing agitation speed from 200 to 250 rpm, the rate of extraction increased. It was due to an increase in volumetric mass transfer coefficient in the external phase (between the emulsion globules and aqueous solution), but further increase in agitation speed from 250 to 350 rpm resulted in reduction in the extent of extraction. At microscopic levels, some particles are getting broken because of shear after reaching larger size. At the same time swelling is also increasing. There exists a trade-off between these two effects. The swollen particles can breakdown on their own or breaking induced by shear. At 300 rpm, despite of high swelling the breakage indicated less extraction and enrichment Therefore, the speed of agitation plays an important role in a mechanically agitated contactor.

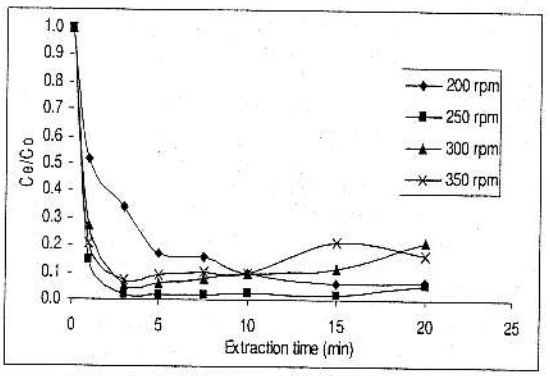


*Figure 5-Effect of agitation speed on the extraction of silver (Experimental conditions: TR: 1:5, surfactant: 5% (w/v), extractant: 0.05M, feed phase: real liquid photographic waste, strip phase: 1.0 M Tu in 1.0 M $H_2SO_4$, and diluent: kerosene)*

*Effect of treat ratio (TR)*

The treat ratio defined as the volume ratio of emulsion phase ($V_m$) to the aqueous feed phase ($V_{III}$ ). It plays an important role in determining the effectiveness of ELM. The treat ratio was varied from 0.143 ($V_m$:$V_{III}$=1:7) to 0.33 ($V_m$:$V_{III}$ =1:3). As shown in Figure 6, there is a steady increase in the extraction of silver with increasing values of treat ratio. Increasing the treat ratio, the volume of emulsion as a whole increased. Therefore, the surface area for mass transfer owing to the formation of a larger number of emulsion globules increased. As a result, a higher degree of extraction was obtained. The lower treat ratio means less amount of emulsion is used to extract silver, which is desired from the process point of view to have maximum enrichment with respect to the feed phase of silver.

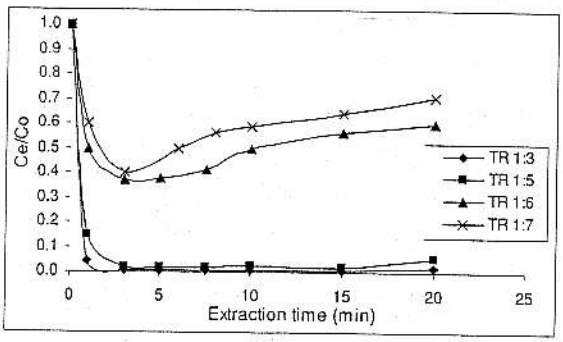


*Figure 6-Effect of treat ratios on the silver extraction (Experimental conditions: speed of agitation: 250 rpm, surfactant: 5% (w/v), extractant: 0.05M Cyanex 302, feed phase: real photographic waste, strip phase: 1M Tu in 1M $H_2SO_4$, and diluent: kerosene ).*

The result also shows that, at lower treat ratio the silver extraction also decreased. It is because the amount of droplet did not contain enough internal reagents to react with the solute transported through the liquid membrane. As a result, extracted silver (carrier-silver complex) accumulated in the membrane phase and cause no carrier diffuse back to react with silver in external phase. Besides, water transportation by surfactant still carries on.

*Effect of Stripping Agent Concentration*

The type of stripping agent plays an important role in the emulsion liquid membrane extraction process. The results show that at fixed thiourea concentration (1.0 M), decreasing solution acidity will decrease the extraction performance (Figure 7). It indicates that the thiourea acidity is one of the factors influencing the silver extraction in the emulsion liquid membrane system. The result shows that at 1.0 M $H_2SO_4$ solution, it is enough acidity for 1.0 M thiourea. Increasing to 1.5 M does not make any difference in the silver extraction performance but it was concerned about the excess acidity will lead to destroy emulsion for long extraction process. However, at 0.5 M $H_2SO_4$, the emulsion globules were in unstable after 3 minutes. Then the extractions drastically drop. As a result, emulsion break down and leakage occurred which cause the extraction efficiency was gradually losing. It is due to not enough protons to form acidic thiourea as a stripping agent.

On the other hand, increasing thiourea concentration from 0.5 M to 1.5 M in the 1.0 M $H_2SO_4$ solution will increase the extraction performance but at 1.5 M concentration the extraction exceeds the limiting value which is no significant increment was observed as shown in Figure 8.

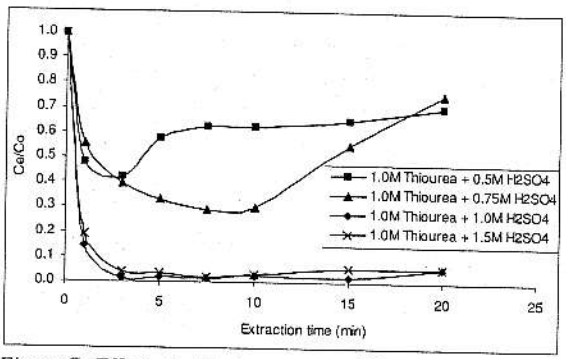


*Figure 7- Effect of stripping agent acidity on the extraction of silver (Experimental conditions: TR: 1:5, surfactant: 5% (w/v), carrier: 0.05M Cyanex 302, speed: 250 rpm, feed phase: real liquid photographic waste, and diluent: kerosene)*

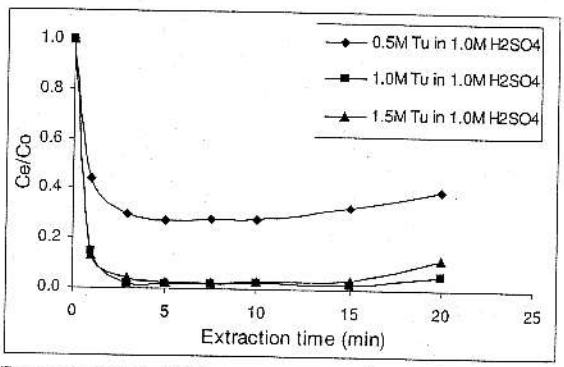


*Figure 8- Effect of thiourea concentration on the extraction of silver (Experimental conditions: TR: 1:5, surfactant: 5% (w/v), carrier: 0.05 M Cyanex 302, speed: 250 rpm, feed phase: real liquid photographic waste, and diluent: kerosene)*

## Conclusion

The separation and recovery of silver from a liquid photographic waste solution through an emulsion liquid membrane was studied by changing various parameters to find the most favorable conditions. Cyanex 302 in kerosene, Span 80 and acidic thiourea were used as a carrier, surfactant and stripping agent, respectively. Optimum concentrations existed for the carrier and the

surfactant were 0.05M and 3% (w/v), respectively. Aliphatic solvents provided the good result for silver recovery based on the lower swelling ration and high stability of emulsions. Almost complete recovery of silver was achieved from the real photographic waste under these conditions. It was found that the extraction performance was very encouraging and further study should be carried out to model and optimize the extraction parameters.

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## References

[1] O'Brien D. J. and Senske D. E. 1989. Separation and recovery of low molecular weight organic acids by emulsion liquid membrane. *Sep. Sci. Technol.* 24:617.

[2] Hayworth H C., Ho W. S., Burns Jr. W. A., and Li N. N. 1983. Extraction of uranium from wet process phosphoric acid by liquid membranes. *Sep. Sci. Technol.* 18(6): 493-521.

[3] Ho W. S. and Sirkar K. K. 1992. Membrane Handbook Editions. Van Nostrand Reinhold, New York: 701-717.

[4] Sang C. L., Byoung S. A., and Won K. L. 1996. Mathematical Modeling of Silver Extraction by an Emulsion Liquid Membrane Process. *Journal of Membrane Science*, 114: 171-185.

[5] Othman, N., Goto, M. and Mat, H. 2004. Precious metal extraction from liquid photographic wastes. Proceeding of 10th Asian Pacific Chemical Engineering Congress, Japan.

[6] DEHNR 2003. Silver recovery system and waste reduction in photo processing.

[7] Othman N., Goto M., and Mat H. 2003. Extractant Selectivity of Metal Extraction From Liquid Photographic Waste. 17th Symposium of Malaysian Chemical Engineers Proceeding, Penang, Malaysia.

[8] Kulkarni P.S., Tiwari K.K., and Mahajani V.V. 2000. Membrane stability and enrichment of nickel in liquid emulsion membrane process. J. Chem. Technol. Biotechnol. 75 (7): 553.

[9] Volkel, Halwachs W, and K. Schugerl 1980. Copper extraction by means of a liquid surfactant membrane process. Journal of Membrane Science 6: 19-31.

[10] Stroeve P. and Varanasi P. P.1984. An experimental study on double emulsion drop breakup in uniform shear flow. J. Colloid Interface Sci. 99: 360-373.

[11]Cahn, R. P., Frankenfeld, J. W., Norman N. Li, Naden, D., and Subramanian, K. N. 1981. Extraction of Copper By Liquid Membranes. In. Norman N. Li. ed. *Recent Developments In Separation Science*. Volume VI. Boca Raton, Florida: CRC Press, Inc.: 51-64.

[12]Frankenfeld J.W., Chan R.P., and Li N.N. 1981. Extraction of copper by liquid membranes. Sep. Sci. and Technol. 16(4): 385-402.

[13] Quan-Min Li, Qi Liu, Qing-Fen Z., Xian-Jun W., and Jin-Zhi G. 1998. Separation study of cadmium through an emulsion liquid membrane using triisooctylamine as mobile carrier. Talanta, 46: 927-932.