Research Paper

Extraction of Silver Ions from Aqueous Solutions by Emulsion Liquid Membrane

Saeed Laki[1], Ali Kargari[2,*]

[1] Department of Petrochemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Mahshahr Campus, Mahshahr, Iran
[2] Membrane Processes Research Laboratory (MPRL), Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran, Iran

ARTICLE INFO

KEYWORDS

GRAPHICAL ABSTRACT

HIGHLIGHTS

• An efficient liquid membrane was used for extraction of Ag^+ ions
• A novel industrial solvent (MIPS) was used as diluent
• An extraction efficiency of 99% within less than 15 minutes

ABSTRACT

A comprehensive study pertaining to the emulsion liquid membrane (ELM) extraction process to enrich dilute aqueous solutions of silver salt is presented. The study has highlighted the importance and influence of membrane composition for maximizing the extraction of Ag^+ ions. The liquid membrane was made up of Cyanex-302 as an extractant and the industrial solvent mainly consists of paraffinic and naphthenic hydrocarbons (C_{10}-C_{14}) as a diluent, Montane®-80 (sorbitan monooleate) as the surfactant and nitric acid solution as the stripping solution. The selection of the extractant (Cyanex-302) and the stripper (HNO_3) was based on conventional liquid–liquid extraction studies. The role of pH as an important parameter in the LEM process for extraction of Ag^+ was studied. Extraction of Ag^+ increased with an increase in strip phase and carrier concentration. The fundamental parameters (emulsion stability, pH of the feed aqueous solution, agitation speed, surfactant concentration, strip phase concentration, carrier concentration, surfactant concentrations and treatment ratio) affecting the separation of Ag^+ through the ELM were investigated to select the best combination of process parameters. The maximum extraction of Ag^+ (about 99%) was achieved at a Montane®-80 concentration of 5% (v/v), strip phase concentration of 0.4M nitric acid and a phase ratio of 1:1.

1. Introduction

The worldwide increase of industrialization and urbanization has caused serious pollution all around the world especially in the aquatic environment. Produced wastewaters are frequently laden with toxic heavy metals such as copper, mercury, silver, etc. that create very dangerous conditions due to easy transmission and their being more readily available to plants and animals. Poisoning by these metals can result in severe dysfunction of the kidney, reproduction system, liver, brain and central nervous systems of human beings [1]. Hence, many efforts have been made to remove the toxic heavy metals from wastewaters. Furthermore, precious recovery of the metals like silver, gold and platinum was not only for solving environmental problems, but also has profitable potential. The natural sources of silver are decreasing so there is a great deal of interest in silver recovery for both environmental and economic reasons [2]. Silver content in industrial effluents is very low

* Corresponding author at: Phone: +98 21 66499066, Fax: +98 21 66405847
E-mail address: ali_kargari@yahoo.com; kargari@aut.ac.ir (A. Kargari)

[3], therefore it is difficult to recover silver with simple physical and chemical methods.

Separation by liquid membrane (LM) constitutes an emerging separation technology with a wide variety of applications. Removal, recovery, and purification of many organic and inorganic compounds from industrial dilute solutions are interesting by this technique [4-6]. Recovery of precious metals [7-11], removal of organic pollutants from wastewaters especially phenolic compounds [12-17], heavy and radioactive metal ions [18-20], recovery of biological products [21-24] and even separation of gases from gas mixtures [25-32] are some of the examples for application of liquid membranes in different fields. However, separation of different compounds using a solvent has been widely used in the recovery of metal ions and organic compounds from aqueous solutions and even from gaseous streams [33-37], but this process is very difficult for the separation of trace amounts of metal ions because of a slight driving force, and hence a large amount of solvent is required which makes the extraction and stripping of desired species very expensive [11].

The idea of performing extraction in a three-phase system with ELM is relatively new and this technique is an improved solvent extraction that offers important advantages in comparison to common liquid–liquid extraction such as improvement of kinetics, selectivity of removable species and decreasing the necessary volume ratio of the organic phase to an aqueous feed solution [21, 38]. Further, it is characterized by simplicity and high efficiency [39]. Emulsion liquid membranes are typically first made by emulsification of the internal phase in an immiscible liquid and then dispersing this emulsion in a third phase (called the external phase). The internal and external phases are miscible, but both of them are immiscible with the membrane phase [7]. Depending on the nature of external and internal phases, the emulsion can be W/O or O/W type, so the three-phase extraction system is either O/W/O or W/O/W type. In general, the emulsion consists of encapsulated droplets about 1–10 µm in diameter, stabilized by surfactant added to the liquid membrane phase. The emulsion is dispersed in a continuous phase by agitation to yield globules of the order of 0.1–2 mm in diameter and the solute is selectively transported from the external continuous phase to the internal droplets [40].

Generally, there are two types of facilitated solute transport through ELMs, known as type I and type II. In type I, the diffusing species initially dissolves in the membrane phase, which is composed of some organic solvents, and then diffuses through the membrane layer and reacts with the internal phase. In this type of facilitation, the reaction in the internal phase effectively maintains a solute concentration equal to zero. The reaction of diffusing species with chemical reagent in the receiving phase forms a product that cannot diffuse back through the membrane. In type II, which is also called facilitated carrier transport, the diffusing species is carried across the membrane phase by incorporating a "carrier" compound (complexing agent or extractant) in the membrane phase. In this type of facilitation, the carrier compound carries the diffusing species and the reaction takes place at the external interface between the external and membrane phases, and at the internal interface between the membrane and internal phases. The used carrier can be regenerated after its reaction with the inner reagent at the interface between the membrane and the internal phase, so that it can be recycled between the outer and inner interfaces of the ELMs [8].

In this paper, the results of experimental studies on the ELM based separation of Ag^+ from aqueous solution have been reported. The external (continuous) phase of the emulsion is the source phase of Ag^+ ions in these experiments. Hence, the Ag^+ ion transport occurs from the external phase to the internal phase. The fundamental parameters, such as surfactant concentration, pH of the feed aqueous solution, strip phase concentration, carrier concentration and treatment ratio that affect the transport of Ag^+ ions through the ELM were studied to detect the optimum process conditions that would yield the best performance of the ELM.

2. Experimental

2.1. Reagents

The liquid membrane phase is composed of four main components: surfactant, carrier, stripping agent, and diluent. Montane®-80 (sorbitan monooleate) was used as a non-ionic surfactant for stabilizing the emulsion and was supplied from Seppic Co., France. Fig. 1 shows the chemical structure of sorbitan monooleate. Bis (2,4,4-trimethylpentyl) mono thiophosphonic acid (Cyanex®-302) was purchased from Sigma–Aldrich Co. and was used as a mobile carrier without further purification. MIPS, an industrial solvent mainly consisting of paraffinic and naphthenic hydrocarbons in the range of C_{10}-C_{14} were supplied from Marun Petrochemical Co. (Iran) and were used as the inert diluent for the membrane phase. The chemical composition of MIPS is shown in Table 1. Silver nitrate, nitric acid, sodium hydroxide and all other used chemicals had analytical

grade and were bought from Merck, Germany. Demineralized water (conductivity < 0.5 µS/cm and pH=5.5-6.0) was used for preparation of the desired solutions.

Table 1
The specifications of the industrial paraffinic solvent.

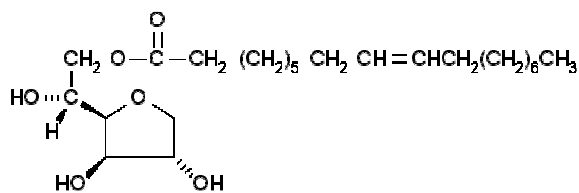| Specification	Value	Unit
< n-C10	max 0.5%	mole %
n-C10+ to n-C11	min 40% max 50%	mole %
n-C12+ to n-C13	min 43% max 56%	mole %
> n-C13	max 1.5%	mole %
Aromatic and Water	max 100	mg/kg
Total Sulfur content	max 1	mg/kg
Kinematic viscosity	1.96 @ 20°C	cSt

Fig. 1. The chemical structure of sorbitan monooleate [18].

2.2. Apparatus

The ELM experiment was carried out in a cylindrical glass container with 105 mm diameter and 145 mm height equipped with four round glass baffles having 8 mm diameter. They have four baffles, 90° apart, that extend one-tenth (1.04 cm) of the way into the tank. The stirrer for the extraction experiments was made of Teflon® with a 95 mm diameter and had three pitched blades with a 45° angle (Fig. 2). The agitating equipment was an electrically driven, model Heidolph RZR-2020, Germany, with variable speed from 40–2000 rpm (Fig. 3). The primary emulsions were prepared using an ULTRA-TURRAX® T-25 digital homogenizer (IKA, Germany) with a speed range of 3400-24000 rpm, equipped with a high-speed dispersing element (S25N-18G). Sampling was done at pre-determined time intervals by disposable sanitary syringes and centrifuged by a laboratory centrifuge (model Denley BS400) in order to separate the emulsion phase from the external phase. An atomic absorption spectrometer (Perkin Elmer model AA700) with a deuterium background corrector equipped with a 10 cm long slot-burner head, a lamp and an air–acetylene flame was used for determination of Ag^+ ion concentration in the aqueous samples. The pH values of the aqueous solutions were set by a digital pH meter (Metrohm-700).

Fig. 2. Dimensions of the preparation and processing tanks.

2.3. Membrane preparation

Internal aqueous phase was prepared by taking the required amount of HNO_3 in demineralized water. The organic membrane phase was prepared by dissolving the appropriate amount of Montane-80 and Cyanex-302 in MIPS under a gentle mixing by a magnetic stirrer. The emulsion was prepared by mixing the internal aqueous solution with the organic membrane phase using

a high-speed homogenizer for a fixed mixing time. The volume ratio of the organic phase to the internal strip phase was kept as 1:1.
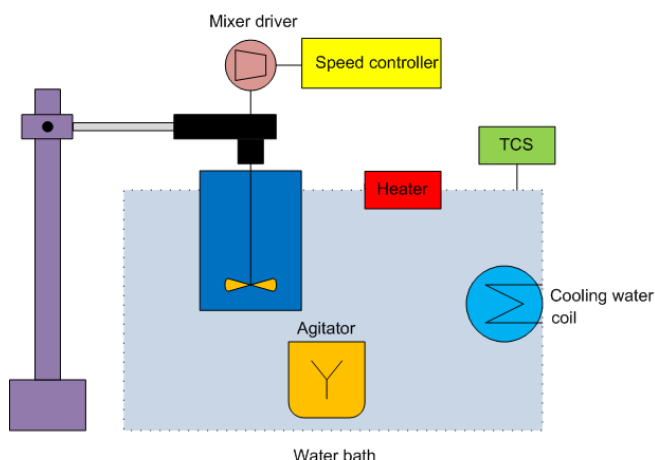

Fig. 3. A scheme of the experimental set-up.

2.4. Membrane stability

In the cylindrical glass vessel that was equipped with an overhead mechanical stirrer, a certain volume of the prepared W/O emulsion was added to 500 mL of external aqueous solution (demineralized water). The content of the vessel was stirred in order to disperse the emulsion in the external phase for different contact times to make the W/O/W double emulsion. The pH of the external phase was continuously measured in order to follow its evolution against time. The leakage of H ions in the external phase decreases the pH of the aqueous solution (demineralized water) and indicates rupture of the W/O emulsion. Each experiment was performed at least twice and the average value was reported.

2.5. ELM experiments

The prepared ELM was added to 500 mL of the feed solution in a beaker. The contents were stirred by a variable speed mixer for an extraction time of 15 min. To determine the effect of important governing variables on permeation and separation of Ag^+, surfactant and carrier concentrations, internal phase concentration, agitation speed, volume ratio of emulsion to

external phase, effect of Ag^+ ions concentration and pH of the feed solutions were changed.
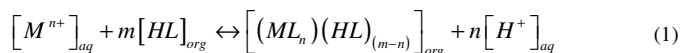
2.6. Analytical method

The uptake of Ag^+ ions was monitored by removing samples of the feed solution periodically for analysis. After the phase separation (about 10-20 sec.), an aqueous phase was carefully separated from the organic phase and the pH equilibrium was measured. The concentration of Ag^+ ions in the organic phase was calculated from the difference between the aqueous phase concentration before and after extraction. From the concentrations results, the distribution coefficient and the percentage of extraction (% E) were determined. All experiments were performed at a constant temperature of 28 ± 0.1 °C using a water bath that was equipped with a temperature control system with accuracy of ± 0.1 °C (Julabo, SW-20C).
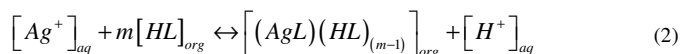
3. Result and discussion

3.1. Transport mechanism of Ag^+

Carrier-facilitated transport of Ag^+ through the liquid membrane is schematically represented in Fig. 4. In order to determine the formation mechanism of the metal–extractant complex during Ag^+ ion extraction, an ideal extraction system was assumed (liquid phase activity=1). Arroyo et al., proposed equation (1) for the metal–extractant complex formation [41]:

$$\left[M^{n+}\right]_{aq} + m\left[HL\right]_{org} \leftrightarrow \left[\left(ML_n\right)\left(HL\right)_{(m-n)}\right]_{org} + n\left[H^+\right]_{aq} \qquad (1)$$

where $[M^{n+}]_{aq}$ is the metal ion concentration in aqueous phase, $[HL]_{org}$ is the extractant concentration in the organic phase, $[(ML_n)(HL)_{(m-n)}]_{org}$ is the metal–extractant complex, $[H^+]_{aq}$ is the released hydrogen ion during metal complex formation, n is the valence of the metal or metal complex ion and m is the number of molecules of extractant engaged in the reaction (coordination number). The extraction reaction for Ag^+ ions can be written as:

$$\left[Ag^+\right]_{aq} + m\left[HL\right]_{org} \leftrightarrow \left[\left(AgL\right)\left(HL\right)_{(m-1)}\right]_{org} + \left[H^+\right]_{aq} \qquad (2)$$

As soon as the complex is formed, it diffuses through the membrane phase to the internal interface between the membrane and the aqueous stripping phase, where the undissociated Ag^+ is released into the stripping phase by the stripping reaction and the uncharged carrier diffuses back. (Fig. 4)
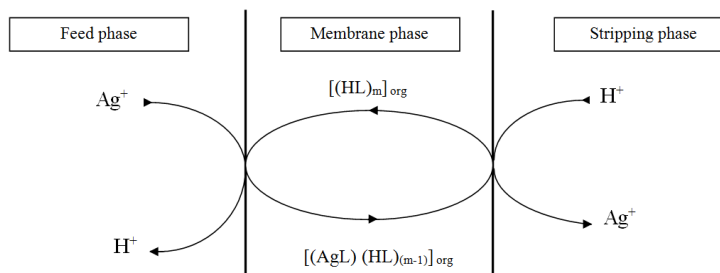

Fig. 4. Extraction and stripping of Ag^+ from the acidic leach solutions by ELM process using Cyanex-302 as extractant or carrier.

3.2. Membrane stability

The stability of ELM is one of the most important parameters that affect the permeation process. Membrane break-up causes a decrease in the separation efficiency due to the leakage of the separated ions from the internal aqueous phase to the external aqueous phase [42]. A tracer method was used to determine the stability of the liquid membrane. To determine the stability of ELM in the demineralized water, experiments were done with different concentrations of Montane-80 and emulsification time. The concentration of H^+ ions was used as a tracer in the internal aqueous phase in all stability experiments for controlling the effect of mass transfer. Breakage recognition would result in the transfer of the tracer from the internal to the external aqueous phase and the stability of ELM was quantified as the percentage of transferred H^+ ions concentration from the internal to the external phase. The break-up percent is defined as follows [2]:

$$\% \ B = \frac{V_e \times \left\{[H^+]_e - [H^+]_i\right\}}{V_i \times [H^+]_0} \times 100 \qquad (3)$$

where B is the break-up percent of the emulsion which represents the stability of the ELM system, $[H^+]_o$ is the initial concentration of total H ions in the internal aqueous phase, $[H^+]_e$ is the concentration of H ions in the external aqueous phase at contact time, $[H^+]_i$ is the initial concentration of total H ions in the external aqueous phase and V_e and V_i are the volume of the external and the internal aqueous phase, respectively. By measuring the concentration of H ions in the external phase at various durations of time, the stability of ELM with time can be determined by Eq. (3).

3.2.1. Effect of emulsification time

In order to determine the influence of emulsification time on the stability of the ELM system, the studies were conducted with various emulsification times in the range of 4–20 min. Experiments were conducted for a surfactant concentration of 5% (w/w), agitation speed of 130 rpm, concentration of internal phase (HNO₃ 0.3M), distilled water as the external phase, emulsion to external phase volume of 1:10, membrane phase to internal phase volume of

1:1 (R_{oi} =1:1) and emulsification speed of 7000 rpm. Fig. 5 shows the effect of emulsification times on the stability of the ELM system. The effect of emulsification time on the emulsion stability showed that a lower breakage was obtained for an emulsification time of 8 and 15 min and a further increase in emulsifying time decreased the stability (Fig. 5). For insufficient emulsification time (< 4 min), the breakage was great because the droplets had a large size, which led to their coalescence. In contrast, for a long emulsification time, the breakage was important because of the high internal shearing conducive to a very high number of small droplets by volume unit. Thus, 10 min emulsification was selected as the best emulsification time.
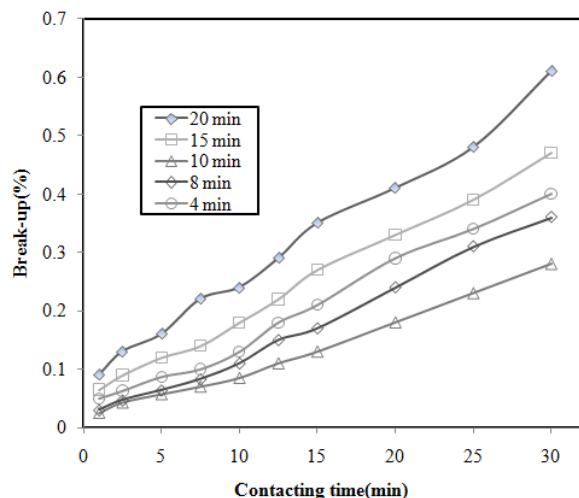

Fig. 5. Effect of emulsification time on the stability of the ELM system (Cyanex-302: 0.05M; Montane-80: 5%; stripping solution: 0.3M HNO₃; agitation speed: 130 rpm; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:10).

3.2.2. Effect of surfactant concentration

Surfactant concentration is an important factor as it directly affects the ELM stability, the extraction rate and the emulsion swelling. Fig. 6 represents the variation of emulsion stability for various surfactant concentrations. The operating parameters were selected identical to those used previously and the internal phase concentration was of 0.3N HNO₃. The results indicates that the break-up of emulsion or emulsion stability strongly depends on the surfactant concentration. From Fig. 6, it was observed that the emulsion stability increases by increasing the surfactant concentration up to 7% (w/w). At lower surfactant concentrations (less than 3%), emulsions broke easily because this amount is insufficient for surrounding all the internal aqueous phases. Consequently, the amount of surfactant in the membrane phase must be optimum and enough to stabilize the emulsion. Fig. 6 shows that increasing the concentration of the surfactant Montane-80 leads to a more stable ELM system. When the concentration of Montane-80 in the membrane phase was 3% (v/v) or 4% (v/v), the break-up percent increased remarkably after 10 min, which indicated the limitation of the stabilization period, but it had a linear relationship with the contact time during the time period (30 minutes) when the concentration of Montane-80 was 5% (v/v) or 7% (v/v). The stability of the emulsion was determined by the molecular layer formed by the surfactant between the oil and the aqueous phase. Increasing the concentration of the surfactant resulted in more surfactant molecules arrayed between the surface of the oil and the aqueous phase, but excessive surfactant increased the resistance of the interface, which decreased the rate of mass transfer [43]. According to Fig. 6, the concentration of surfactant was set at 5% (v/v) in all the subsequent experiments since the break-up percent at 5% (v/v) was rather close to that at 7% (v/v).

3.3. Permeation

3.3.1. Effect of the external phase pH

The experimental conditions are those conducted by stable W/O emulsion and are summarized as below:

Emulsion volume: 50 mL; external feed phase (silver nitrate solution) volume: 500 mL; volume ratio of internal phase to organic phase: 1:1; emulsification time: 10 min; agitation speed 130 rpm; concentration of Montane-80: 5% (w/w); volume ratio of emulsion to external phase: 50/500; internal phase concentration (HNO₃): 0.3N; diluent: MIPS.
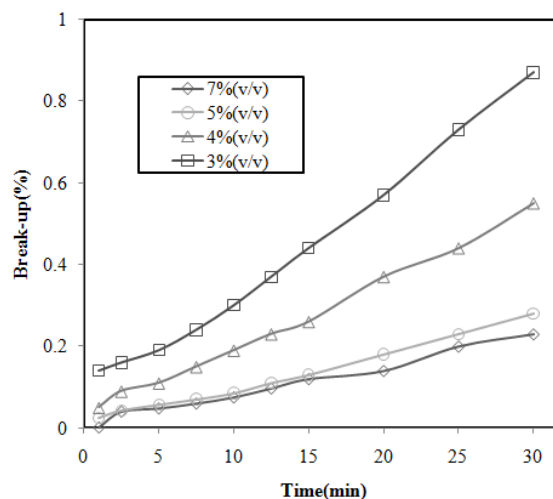

Fig. 6. Effect of surfactant concentration on stability of the ELM system (Cyanex-302: 0.05M; Montane-80: 3-7%; stripping solution: 0.3M HNO3; agitation speed: 130 rpm; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:10).
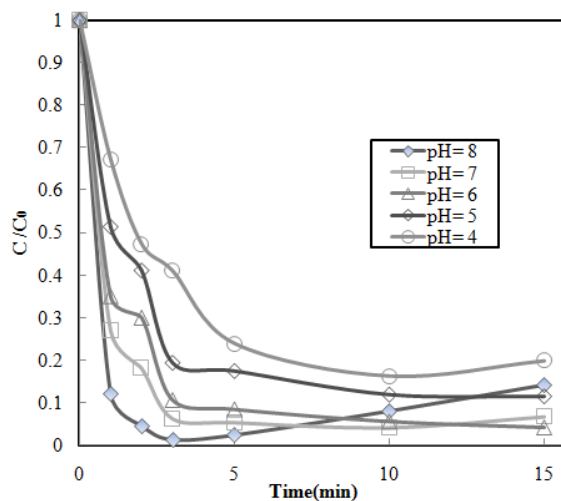

Fig. 7. Effect of feed solution pH on the extraction rate (Montane-80: 5%; Cyanex-302: 0.05M; stripping solution: 0.3M HNO3; agitation speed: 130 rpm; Co C_o: 3500 mg/L; feed solution pH: 4.5–6.5; R_{oi} =1:1; treatment ratio: 1:10.

It is known that the acidity of the feed phase plays an evitable role in the extraction of the solute from the external phase to the internal phase. In this study, the effect of the acidic feed solution pH was changed in the range of 4.0–8.0, using NaOH solution, water and nitric acid. Fig. 7 shows the effect of feed phase pH (H⁺ ions concentration) on the kinetics of Ag⁺ ions extraction and on the final Ag⁺ ions concentration. It is quite clear from Eq. (2) that the transport of Ag⁺ ions through ELM is dependent on the H ions concentration in the feed solution. As seen from Fig. 7, Ag⁺ extraction increased by increasing the pH between 4.0 and 6.0, but between 6.0 and 7.0, the extraction efficiency of Ag⁺ hardly changed by increasing the pH. This is probably due to the emulsion instability, but when pH of the feed phase is increased up to 7.0, the extraction and enrichment of Ag⁺ decreases due to swelling of the emulsion. The osmotic pressure difference resulting in the increase of the feed phase pH drives water into the internal phase, and thereby swelling occurs. It is interesting to note that the defined LEM system is an excellent potential to enrich Ag⁺ from acidic feed phase. The poor performance at low pH could be explained by the competition of H⁺ ions with the solute due to the release of H ions from the extractant to the acidic leach solution. As a result, maximum extraction was achieved at a pH of 6.0 and at this pH value, the swelling of the emulsion was not observed. Thus, a pH of 6.0 was found as the optimal pH and chosen for subsequent studies.

3.3.2. Effect of internal phase concentration

As the extraction step in the interface occurs between the feed solution and the liquid membrane, the extraction of metal necessarily requires a simultaneous back-extraction step at the opposite side of the membrane. In the back-extraction stage, the extractant is regenerated and the metal is

stripped [44]. The influence of nitric acid concentrations (0.1–0.5 M) on the extraction efficiency was investigated. It can be noted from Fig. 8 that when nitric acid concentration increases from 0.1 to 0.4 M, extraction efficiency increases, but decreases when nitric acid concentration is increased from 0.4 to 0. 5 M. Furthermore, the extraction efficiency of Ag$^+$ increased by increasing the acidity in the stripping phase. The differences of hydrogen ion chemical potentials between the two aqueous phases are the main driving force in the emulsion liquid membrane process. Thus, the extraction efficiency increases by increasing the concentration of HNO$_3$ in the stripping solution from 0.1 to 0.4 M. However, for a concentration of 0.5 M nitric acid, the emulsion swells up due to osmosis, which leads to dilution of the internal phase causing a less effective stripping. Othman et al. [43] have supported this phenomenon. The highest efficiency during the extraction process was obtained with a HNO$_3$ concentration of 0.4 M, and therefore it was accepted as the most suitable concentration.
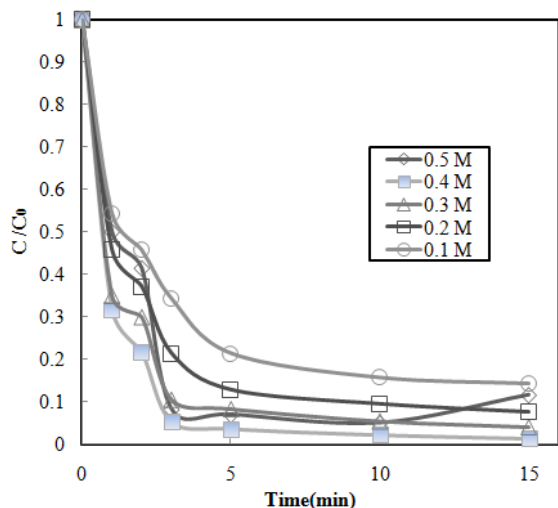

Fig. 8. Effect of stripping solution acid concentration on the extraction rate (Montane-80: 5%; Cyanex-302: 0.05M; stripping solution: 25mL 0.1- 0.5M HNO$_3$; agitation speed: 130 rpm; C$_o$: 3500 mg/L; feed solution pH: 6.0; R$_{oi}$ =1:1; treatment ratio: 1:10).

3.3.3. Effect of carrier concentration

Ag$^+$ ions are 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$^+$ ions between the external and the internal 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 [44-50] have confirmed the feasibility of using Cyanex-302 for the recovery of metal ions, and the effect of different concentrations of Cyanex-302 were investigated in this study. Experiments were carried out in which the concentration of the carrier in the membrane phase was changed from 0.02 M to 0.06 M while the other parameters were kept constant. Fig. 9 indicates that the transfer rate of Ag$^+$ ions in the external phase increases with increasing the concentration of the carrier in the membrane phase. It can be clearly seen that the extent of transferred Ag$^+$ ions through ELM is enhanced as the content of extractant in the membrane solution is increased. It is also clear that metal extraction is favored at the beginning of the experiment. According to Fig. 9, an increase from 0.02 M to 0.05 M in extractant concentration leads to an increase in initial rates between the first 3 and 5 min. Also, the results indicate that further increase of the concentration of the carrier had little effect on the transfer rate of Ag$^+$ ions above a concentration of Cyanex-302 in the range of 0.03-0.05 M in the membrane phase. However, in the extractant concentration of 0.06 M, a decrease in the extraction efficiency of Ag$^+$ occurs due to lowering the emulsion stability. Reduction of the extraction efficiency can also be attributable to the decrease of the membrane phase viscosity as the carrier concentration increases. Furthermore, in the ELM process, the presence of an acidic or basic agent in the membrane solution can cause the hydrolysis of surfactant and/or the extractant. This hydrolysis causes the decrease of both emulsion stability and Ag$^+$ transport. A similar effect was reported by Othman et al. [44], 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 highlighted in this study, where no Ag$^+$ ions were transferred from the internal to the external phase in the ELMs process, even though breakage of the emulsion sometimes occurred. It is reasonable to conclude that there is a slight effect on the

transfer rate above a certain concentration of the carrier in the membrane phase. Under the used conditions in this study, a carrier concentration of 0.03M is sufficient for the extraction of Ag$^+$ ions.
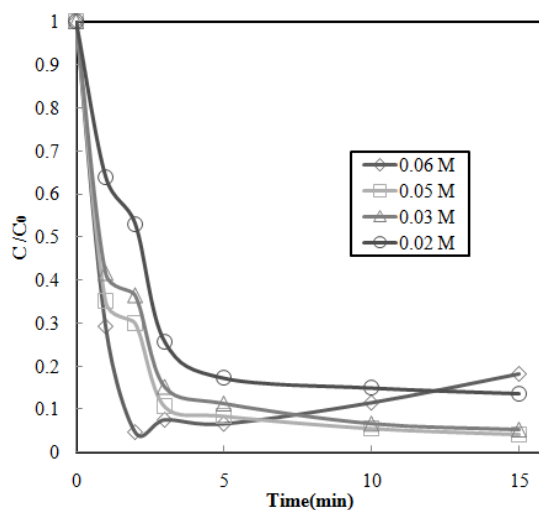

Fig. 9. Effect of extractant concentration on the extraction rate (Montane-80: 5%; Cyanex-302: 0.02–0.06M; stripping solution: 25mL 0.3M HNO$_3$; agitation speed: 130 rpm; C$_o$: 3500 mg/L; feed solution pH: 6.0; R$_{oi}$ =1:1; treatment ratio: 1:10).

3.3.4. Effect of surfactant concentration

Surfactant concentration is an important factor because it directly affects the stability, swelling and break up of ELM. An insufficient amount of surfactant renders the membrane weak, while an increase in surfactant concentration leads to larger diffusional resistance. Experiments were performed at various concentration levels from 4% to 7% (v/v) and the obtained results were exhibited in Fig. 10. At low surfactant concentrations (less than 3%), instantaneous emulsions breakage was observed without any measurement therefore, the results for the emulsions containing 3% surfactant and less are not presented in this figure. As it was shown in Fig. 10, decreasing the surfactant concentration from 7 to 4%, resulted in a sharp increase in the amount of extracted Ag$^+$ ions, except for 4%. At surfactant concentration of 4%, although the extraction efficiency increases up to 2 min, after that the efficiency of extraction sharply decreased. This could be attributed to the insufficient amount of the surfactant for surrounding all the internal aqueous phase droplets. As the concentration of the surfactant is increased from 5% to 7%, the ELM stability increases but the extraction efficiency drops from 95% to 87%. Excessive surfactant tends to increase the resistance at the interface and this can be attributed to a number of possible factors caused by high interfacial occupancy of the surfactant that includes a increase in interfacial viscosity and decrease in movement of inner droplets within the emulsion globule [45]. At surfactant concentration of 5%, however, the membrane stability increases but the extraction slightly decreases. Hence, 5% (v/v) Montane-80 was selected as the best extractant concentration.

3.3.5. Effect of agitation speed

The agitation speed plays a major role in the rate of extraction through the emulsion liquid membrane. The effect of agitation speed was studied in the range of 100–200 rpm and the obtained results were shown in Fig. 11. From Fig. 11, it was observed that increasing the agitation speed from 100 to 160 rpm increased the rate of extraction, but a further increase from 160 to 200 rpm resulted in reduction in the extraction efficiency. While an increase in the level of agitation would increase the interfacial area for the mass transfer, increase of agitation speed beyond a certain level, causes the breakage of the emulsion globules and consequently reduces the overall extraction efficiency. The shear as an induced breakage of the emulsion droplet near the tip of the impeller or impact on the wall of a contactor imposes an upper limit on the speed of mixing [46]. According to Hirato et al. [47], by increasing the agitation speed, the size of the dispersed emulsion globules in the external phase decreases, and as a result, the extraction rate increases and at the same time, the breakdown rate of the emulsion increases, too. Therefore, at the speeds above 160 rpm, leakage of the internal phase reagent might be initiated due to rupture of emulsion globules, which ultimately resulted in a gradual depletion in extraction and stripping. Thus, 160 rpm was recommended as the most appropriate agitation speed.
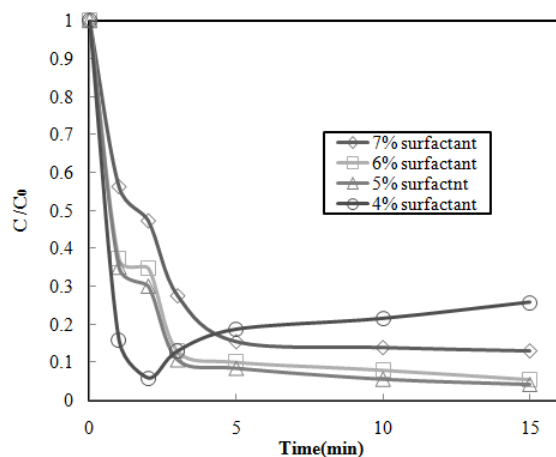
Fig. 10. Effect of surfactant concentration on the extraction rate (Montane-80: 4- 7%; Cyanex-302: 0.05M; stripping solution: 25 mL 0.3M HNO_3; agitation speed: 130 rpm; C_o: 3500 mg/L; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:10).
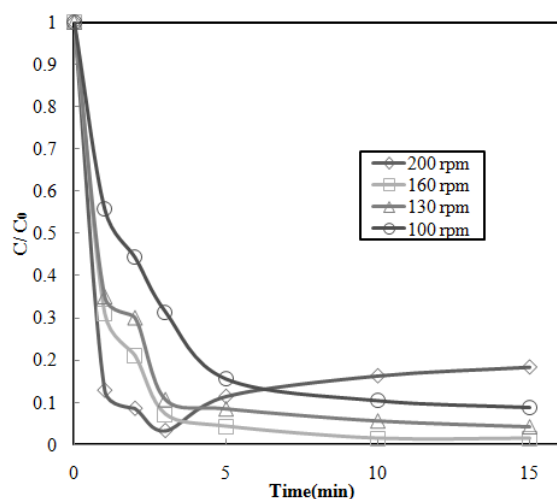

Fig. 11. Effect of agitation speed on the extraction rate (Montane-80: 5%; Cyanex-302: 0.05M; stripping solution: 0.3M HNO_3; agitation speed: 100- 200 rpm; C_o: 3500 mg/L; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:10).

3.3.6. Effect of volume ratio of emulsion to external phase

It is known that the rate of mass transfer in ELM systems are directly related to the specific mass transfer area (m^2/m^3). The volume ratio of the emulsion to the external solution (treatment ratio: V_E/V_F) controls the specific interfacial mass transfer area. It is identical with the solvent to feed ratio in the conventional liquid extraction. It is a measure of the emulsion hold-up in the system. An increase in treatment ratio results in an increase of the emulsion phase holdup and simultaneously an increase in the extraction capacity of the emulsion. It also results in an increase in the amount of extractant and overall surface area for mass transfer in the system. An increase in treatment ratio is expected to increase the extraction efficiency. The treatment ratio was varied by changing the amount of emulsion added to the feed phase and keeping the volume of the later constant [48]. The effect of the volume ratio of emulsion to external phase on the extraction efficiency was studied in the range of 0.07 (V_E: V_F = 1:15) to 0.33 (V_E: V_F = 1:3), and the obtained results were shown in Fig. 12. It was found that at a treatment ratio of 1:10, the extraction performance of the solute from external phase was high and a further increase in treatment ratio slightly increased the extraction efficiency. It is evident that the decrease of volume ratio of emulsion to feed solution leads to a decrease in the extraction efficiency. In general, a larger treatment ratio value translates to a larger contact area of ELM with the solution to be treated, resulting in a greater mass transfer area, but at the expense of higher emulsion volume. Additionally, the influence of the volume ratio of emulsion to the external feed solution on the stability was not significant because the breakage increases very slightly with an increase in the volume ratio [49, 50]. The lower treatment ratio means less emulsion is required to extract the solute, which is desirable from a processing point of view to ensure maximum enrichment with respect to the feed phase. Increasing emulsion holdup from 1:10 to 1:3 slightly increased the extraction efficiency. Consequently, in order to ensure a good dispersion of emulsion in

the feed solution and to enhance the concentration of the solute in the internal aqueous phase, the volume ratio of emulsion to external feed solution of 1:10 was selected as the best treatment ratio.

3.3.7. Effect of feed concentration

In order to investigate the influence of initial feed concentration, different experiments were performed with Ag^+ concentrations from 1500 to 5500 mg/L. The obtained results are shown in Fig. 13. The removal efficiency increased with the increase of Ag^+ concentration from 1500 to 3500 mg/L. This may be attributed to an increase in the driving force, the concentration gradient, with an increase in the initial Ag^+ concentration. For Ag^+ concentrations higher than 3500 mg/L (3500–5500 mg/L), the extraction percentage decreased. The saturation of the internal droplets in the peripheral region of the emulsion is attained more rapidly for high concentrations of Ag^+ in the external phase. When the solute concentration is high, the Ag^+-ligand complex must diffuse through the membrane phase towards the outer surface of the internal phase droplets. This suggests that the mass transfer resistance in the emulsion globule is important [51]. Additionally, the required time for attaining a certain extraction efficiency increases by increasing the external phase concentration.

Fig. 12. Effect of volume ratio of emulsion to external phase on the extraction rate (Montane-80: 5%; Cyanex-302: 0.05M; stripping solution: 25 mL 0.3M HNO_3; agitation speed: 130 rpm; C_o: 3500 mg/L; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:15- 1:3).

Fig. 13. Effect of Ag^+ concentration on the extraction efficiency (Montane-80: 5%; Cyanex-302:0.05M; stripping solution: 25 mL 0.3M HNO_3; agitation speed: 130 rpm; C_o: 1500-5500 mg/L; feed solution pH: 6.0; R_{oi} =1:1; treatment ratio: 1:10).
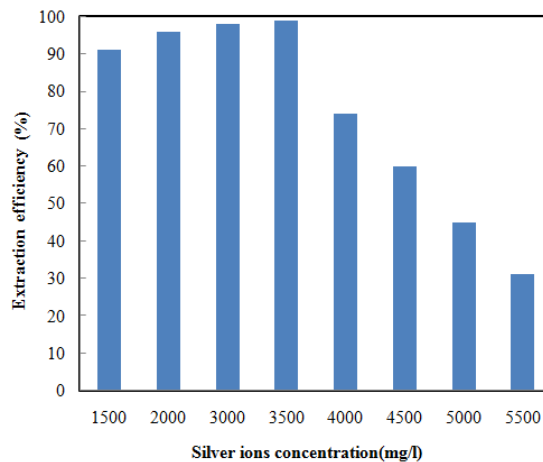
4. Conclusion

An emulsion liquid membrane was developed to extract and concentrate Ag^+ ions from aqueous solutions, effectively. The following results were obtained:

- The operational conditions conducting an excellent stability of the W/O emulsion were: 130 rpm for agitation speed, 7000 rpm for emulsification speed, 10 min emulsification time; concentration of surfactant of 5% (w/w); volume ratio of internal phase to organic phase: 1:1; internal phase concentration (HNO_3): 0.3M; volume ratio of W/O emulsion to external phase: 1:10.
- The extraction of Ag^+ ions was influenced by a number of variables like emulsion stability, pH of the feed aqueous solution, agitation speed, surfactant concentration, strip phase concentration, carrier concentration, surfactant concentrations and treatment ratio.
- At the optimum conditions, the extraction of Ag^+ ions was achieved with an efficiency of 95–99% from aqueous solutions within 15 min.
- Extraction efficiency increased with increase of feed pH and Cyanex-302 concentration.
- It was found that the increase of the extractant concentration up to a certain value (0.02- 0.05M) in the membrane solution had a positive influence on the extent of metal extraction and on initial extraction rate.
- Although the higher concentration of HNO_3 in the internal phase increased the concentration driving force and hence extraction efficiency, it had a reverse effect at high concentrations, which caused swelling and/or hydrolyzing of the surfactant and led to rendering the extraction efficiency.

- Extraction efficiency increased with an increase in surfactant concentration up to a certain quantity (4- 6% (v/v)), and then decreased due to inhibiting the effect of surfactant on the mass transfer rate.
- Extraction efficiency increased by increasing the agitation speed up to a certain agitation speed (100- 160rpm), then decreased due to a break in the emulsion droplets thereby reducing overall extraction.
- Decreasing the concentration of solute in the external phase declined extraction efficiency of the system.
- The experimental results showed the ability of the ELM system for Ag^+ recovery from aqueous solutions.

5. Acknowledgements

References

[1] J.P. Chen, L.L. Lim, Key factors in chemical reduction by hydrazine for recovery of precious metals, Chemosphere 49 (2002) 363–370.
[2] B. Tang, G. Yu, J. Fang, T. Shi, Recovery of high-purity silver directly from dilute effluents by an emulsion liquid membrane-crystallization process, J. Hazard. Mater.177 (2010) 377–383.
[3] Y.J. Park, D.J. Fray, Recovery of high purity precious metals from printed circuit boards, J. Hazard. Mater. 164 (2009) 1152–1158.
[4] J. Yan, R. Pal, Osmotic swelling behavior of globules of W/O/W emulsion liquid membranes, J. Membr. Sci. 190 (2001) 79–91.
[5] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: A review, Desalination 235 (2009) 199–244.
[6] T. Kaghazchi, M. Takht Ravanchi, A. Heydari, A. Kargari, Application of liquid membrane in separation processes, J. Sep. Sci. Eng. 1 (2009) 81-89.
[7] A. Kargari, T. Kaghazchi, M. Sohrabi, M. Soleimani, Batch extraction of gold (III) ions from aqueous solutions using emulsion liquid membrane via facilitated carrier transport, J. Membr. Sci. 233 (2004) 1-10.
[8] A. Kargari, T. Kaghazchi, B. Mardangahi, M. Soleimani, Experimental and modeling of selective separation of gold (III) ions from aqueous solutions by emulsion liquid membrane system, J. Membr. Sci. 279 (2006) 389-393.
[9] A. Kargari, T. Kaghazchi, M. Sohrabi, M. Soleimani, Application of experimental design to emulsion liquid membrane pertraction of gold (III) Ions from aqueous solutions, Iranian J. Chem. Eng. 3 (2006) 76-90.
[10] A. Kargari, T. Kaghazchi, M. Soleimani, Extraction of gold (III) ions from aqueous solutions using polyamine type surfactant liquid membrane, Canadian J. Chem. Eng. 82 (2004) 1301-1306.
[11] A. Kargari, T. Kaghazchi, M. Soleimani, Role of emulsifier in the extraction of gold (III) ions from aqueous solutions using emulsion liquid membrane technique, Desalination 162 (2004) 237-247.
[12] A. Kargari, K. Abbassian, Study of phenol removal from aqueous solutions by a double emulsion (W/O/W) system stabilized with a polymer, Sep. Sci. Technol. 50 (2015) 1083–1092.
[13] K. Abbassian, A. Kargari, Effect of polymer addition to membrane phase to improve the stability of emulsion liquid membrane for phenol pertraction, Desal. Water Treat. *accepted for publication*, doi: 10.1080/19443994.2014.983981.
[14] K. Abbassian, A. Kargari, T. Kaghazchi, Investigation of stabilized emulsion by polymer and its effect on the extraction of phenol from aqueous solution by emulsion liquid membrane, Iranian J. Chem. Chem. Eng. 32 (2013) 57-67.
[15] A. Kargari, Simultaneous extraction and stripping of 4-chlorophenol from aqueous solutions by emulsion liquid membrane, Desal. Water Treat. 51 (2013) 2275-2279.
[16] B. Nabieyan, T. Kaghazchi, A. Kargari, A. Mahmoudian, M. Soleimani, Bench-scale simultaneous extraction and stripping of iodine using bulk liquid membrane system, Desalination 214 (2007) 167-176.
[17] Sh. Mohammadi, A. Kargari, H. Sanaeepur, K. Abbassian, A. Najafi, E. Mofarrah, Phenol removal from industrial wastewaters: A short review, Desal. Water Treat. 53 (2015) 2215–2234.
[18] M. Nabavi Nia, M. Soleimani, A. Kargari, Vanadium recovery from oil refinery sludge using emulsion liquid membrane technique, Int. J. Chem. Environ. Eng. 3 (2012) 149-152.
[19] S. Mohammadi, T. Kaghazchi, A. Kargari, A model for metal ion pertraction through supported liquid membrane, Desalination 219 (2008) 324-334.
[20] N.S. Rathore, A.M. Sastre, A.K. Pabby, Membrane assisted liquid extraction of actinides and remediation of nuclear waste: A review, J. Membr. Sci. Res. 2 (2016) 2-13.
[21] T. Kaghazchi, A. Kargari, R. Yegani, A. Zare, Emulsion liquid membrane pertraction of L-lysine from dilute aqueous solutions by D2EHPA mobile carrier, Desalination 190 (2006) 161-171.
[22] S.A.M. Fathi, M.R. Yaftian, A. Kargari, Water-in-oil emulsion liquid membrane transport of L-Cysteine, Sep. Sci. Technol. 48 (2013)105-112.

[23] S.A.M. Fathi, M. Yaftian, A. Kargari, D. Matt, Emulsion liquid membrane pertraction of L-Cysteine from sodium chloride aqueous solutions mediated by a narrow rim phosphorylated cone-shaped calix[4]arene, J. Iranian Chem. Soc. 9 (2012) 783-789.
[24] S.A.M. Fathi, M. Nasiri, M.R. Yaftian, A. Kargari, Highly selective extraction and transport through a bulk liquid membrane of L-Cysteine using [K•DC18C6]$^+$ complexes, Sep. Sci. Technol. 46 (2011) 2473-2480.
[25] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Effect of complexation reaction constant on the separation of propylene/propane by supported liquid membrane, J. Membr. Sci. Res. 1 (2015) 85-89.
[26] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Selective transport of propylene by silver ion complex through an immobilized liquid membrane, Iranian J. Chem. Eng. 7 (2010) 28-41.
[27] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Supported liquid membrane separation of propylene-propane mixtures using a metal ion carrier, Desalination 250 (2010) 130-135.
[28] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Separation of propylene-propane mixture using immobilized liquid membrane via facilitated transport mechanism, Sep. Sci. Technol. 44 (2009) 1198–1217.
[29] A. Heydari Gorji, T. Kaghazchi, A. Kargari, Selective removal of carbon dioxide from wet CO_2/H_2 mixtures via facilitated transport membranes containing Amine blends as carriers, Chem. Eng. Technol. 32 (2009) 120-128.
[30] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, Immobilized liquid membrane for propylene-propane separation, Int. Scholarly Sci. Res. Innov. 2 (2008) 74-76.
[31] M. Takht Ravanchi, T. Kaghazchi, A. Kargari, New approach in separation of olefin-paraffin gas mixtures by a membrane system, Amirkabir 68-D (2008) 47-55.
[32] S. Azizi, T. Kaghazchi, A. Kargari, Propylene/propane separation using N-methyl pyrrolidone/AgNO3 supported liquid membrane, J Taiwan Inst. Chem. Eng. 57 (2015) 1-8.
[33] K. Abbassian, A. Kargari, T. Kaghazchi, Phenol removal from aqueous solutions by a novel industrial solvent, Chem. Eng. Commun. 202 (2015) 408-413.
[34] A. Kargari, T. Kaghazchi, M. Soleimani, Mass transfer investigation of liquid membrane transport of gold (III) by methyl iso-butyl ketone mobile carrier, J. Chem. Eng. Technol. 27 (2004) 1014-1018.
[35] A. Najafi, A. Kargari, M. Soleimani, Extraction of palladium from aqueous wastewaters using Alamine 300 as extractant, Desal. Water Treat. 53 (2015) 2177–2183.
[36] S. Azizi, A. Kargari, T. Kaghazchi, Experimental and theoretical investigation of molecular diffusion coefficient of propylene in NMP, Chem. Eng. Res. Des. 92 (2014) 1201-1209.
[37] S. Azizi, H. Tahmasebi Dezfuli, A. Kargari, S.M. Peyghambarzadeh, Experimental measurement and thermodynamic modeling of propylene and propane solubility in N-methyl pyrrolidone (NMP), Fluid Phase Equilib. 387 (2015)190-197.
[38] C.C. Wang, A.L. Bunge, Multisolute extraction of organic acids by emulsion liquid membranes– batch experiments and models, J. Membr. Sci. 53 (1990) 71–103.
[39] M. Rajasimman, R. Sangeeth, Optimization of process parameters for the extraction of chromium (VI) by emulsion liquid membrane using response surface methodology, J. Hazard. Mater. 168 (2009) 291–297
[40] A. Kargari, T. Kaghazchi, M. Soleimani, Mathematical modeling of emulsion liquid membrane pertraction of gold (III) from aqueous solutions, J. Membr. Sci. 279 (2006) 380–388.
[41] Z.G. Arroyo, M. Stambouli, D. Pareau, A. Buch, G. Durand, M.A. Rodriguez, Thiosubstituted organo-phosphorus acids as selective extractants for Ag(I) from acidic thiourea solutions, Solvent Extr. Ion Exch. 26 (2008) 128–144.
[42] A. Dâas, O. Hamdaoui, Extraction of anionic dye from aqueous solutions by emulsion liquid membrane, J. Hazard. Mater.178 (2010) 973–981.
[43] N. Othman, H. Mat, M. Goto, Separation of silver from photographic wastes by emulsion liquid membrane system, J. Membr. Sci. 282 (2006) 171–177.

[44] J. Marchese, F. Valenzuela, C. Basualto, A. Acosta, Transport of molybdenum with Alamine 336 using supported liquid membrane, Hydrometallurgy 72 (2004) 309–317.

[45] L. Yang, Z. Zhang, Y. Guo, X. Gao, H. Takeuchi, Uranium(VI) extraction by liquid surfactant membrane with N-alkylcaprolactams as a carrier, Sep. Purif. Technol. 47 (2005) 88–94.

[46] P.S. Kulkarni, V.V. Mahajani, Application of liquid emulsion membrane (LEM) process for enrichment of molybdenum from aqueous solutions, J. Membr. Sci. 201 (2002) 123–135.

[47] T. Hirato, I. Kishigami, Y. Awakura, H. Majima, Concentration of uranyl sulfate solution by an emulsion-type liquid membrane process, Hydrometallurgy 26 (1991) 19–33.

[48] P.S. Kulkarni, V.V. Mahajani, Application of liquid emulsion membrane (LEM) process for enrichment of molybdenum from aqueous solutions, J. Membr. Sci. 201 (2002) 123–135.

[49] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane, Part 1. Membrane stability, Sep. Purif. Technol. 62 (2008) 636–641.

[50] M. Djenouhat, O. Hamdaoui, M. Chiha, M.H. Samar, Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane. Part 2. Permeation and stripping, Sep. Purif. Technol. 63 (2008) 231–238.

[51] S.C. Lee, J.H. Chang, B.S. Ahn, W.K. Lee, Mathematical modeling of silver extraction by an emulsion liquid membrane process, J. Membr. Sci. 114 (1996) 171–185.