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Recovery of Cu (II) from Model Water using Emulsion Liquid Membrane (ELM) Technique

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ABSTRACT

The proper condition of the emulsion liquid membrane (ELM) technique for the recovery and concentration of copper (II) from model water is investigated. The ELM is a solution of di (2-ethylhexyl) phosphoric acid in kerosene and sorbitan monooleate Span 80 as surfactant. The extraction efficiency of the metallic ion in the ELM in batch tests is determined. The results show good extraction percentage in relatively period of time (15 minutes) under the following conditions: pH of the feed is 8; feed concentration of 500 ppm, carrier concentration of di (2-ethyl-hexyl) phosphoric acid (D2EHPA) 4% and treatment ratio (volume of external phase to volume of emulsion phase) of 2.

Key words: Emulsion, Membrane Technique, Metallic Efficiency.

الخلاصة

الظروف المثلى لتقنية الغشاء النفاذي السائل لازالة وتركيز النحاس الثنائي التكافؤ قد اختبرت في هذه الدراسة. يتكون الغشاء النفاذي السائل من محلول داي(٢- ايثايل هكسايل) حامض الفوسفوريك في النفط الابيض والمادة السطحية سوربيتون مونولييت (سبان ٨٠). كفاءة الاستخلاص للمعدن النحاس الثنائي التكافؤ في تقنية الغشاء النفاذي السائل باستخدام نظام دفعي قد استخدمت. اوضحت النتائج نسبة استخلاص جيدة في وقت قصير يقدر بـ(١٥) دقيقة بالظروف التالية: الدالة الحامضية (٨) ، تركيز الداخل (٥٠٠ ملغم /لتر)، تركيز الحامل (٤%) ونسبة المعاملة (٢).

INTRODUCTION

In the near future, the exhaustion of heavy metals from industry will become a more serious problem all over the world. In order to overcome the problem towards creating favorable environment, recovering the valuable metals from industrial waste effluents offers a good alternative approach. This is important in order to save precious raw materials and to protect the environment from heavy metal contamination (1).

There are many methods, which have been established commercially to recover metals from industrial wastes such as solvent extraction, precipitation, ion exchange, electrolysis, cementation, and membrane separation. Current technology shows that the electrochemical method for metal recovery is promising technique, but it has low plate efficiency due to waste streams are often dilute in metals. As a result, solvent extraction of metals has been extensively used in hydrometallurgical process, however because of metal salts usually is not soluble in organic solvents, the process requires the introduction of an extract ant that will combine with the metal ion to form an organic soluble species. However, the capital outlay for such equipment can be expensive, large volumes of organic extract ants are required and the performance is often limited by hydrodynamic constraints such as flooding and entrainment. There is also the potential for cross-contamination of the aqueous stream with the organic solution and it is not suitable for dilute metal concentration of wastes in term of cost and equipment's (2).

Problems associated with polymeric membranes such as: low selectivity, low mechanical strength, low flux rates due to high diffusional resistance and short life span have restricted the use of supported liquid membrane as a potential industrial separation process. Thus, mass transfer area, efficiency and economic viability have become necessary requirements in the application of liquid membranes in any large-scale operation. Emulsion liquid membrane (ELM) developed by Li (3), overcome the problem encountered in achieving large mass transfer area at low cost.

The basic principle of the liquid membrane process lies basically on solute partitioning between three liquid phases as shown in figure (1); feed, membrane and receiving phases. The emulsion liquid membrane process has three phases dispersion system, which is also known as double emulsion system. This system consists of organic solution (membrane phase), stripping solution (internal phase) and dispersed phase (external phase), which is the feed or effluent to be treated (4).

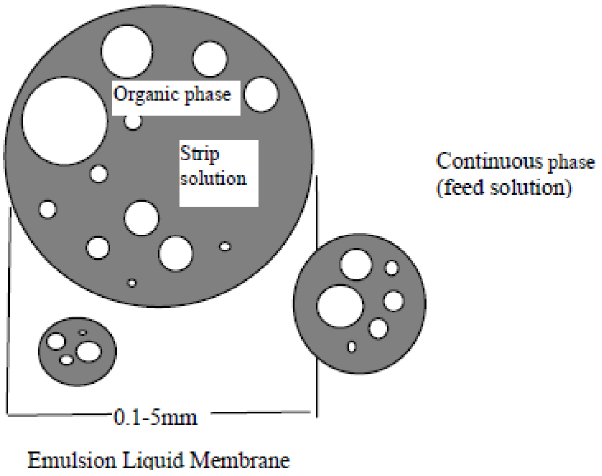

Figure (1) A Schematic Diagram of Liquid Membrane.

Emulsion liquid membrane in different formulations renders it an extremely versatile process useful for different applications. This includes waste water treatment, minerals recovery, hydrocarbon separation and a number of biochemical and biomedical applications. Due to the advantages of these membranes, several recent studies employed this technique (4). Chakravarti et al. (5) showed the results of Cr (VI) and Cu (II) separation with ELM from simulated wastewater solutions. They studied the effect of variation of oil membrane constituents, different concentrations of sulfuric acid as stripping in the internal phase, pH and the ion concentration in the refine, and the Cu (II) content in the wastewater. They found that the main cause of Cr (VI) transport was the ion-exchange behavior of carriers in the membrane and the coupled counter-transport resembling a “chemical pump”. They, also, found that the application of the reaction site model and involvement of a pseudo-first-order process reasonably justified the transport method of Cu (II) separation. Bourenane and El-Hadi (6) presented the applicability of the Liquid Surfactant Membrane (LSM) process for the removal and the concentration of lead and cobalt. The aim of their work is to find a process for the purification of wastewater, which contains cobalt and lead. A complete study of the metal extraction by the liquid membrane process using HDEHP as extract ant and SPAN 80 as surfactant is performed in terms of extraction and stripping efficiencies, emulsion breaking and swelling. The results show that it is possible to recover 98.83% of cobalt and 94.21% of lead in the inner phase after 2 minutes of contacting time with a concentration factor of 50 for lead and 50 for cobalt. . Reis and Bart (7) investigated the liquid membrane permeation of zinc in a continuous counter current column. The permeation of zinc with emulsion liquid membranes was carried out in a stirred countercurrent column. The carrier used in the membrane phase was bis (*2*-ethylhexyl) monothiophosphoric acid. The composition of the aqueous feed was zinc sulphate (4.59´ 10^{-3} kmol m^{-3}) and sulphuric acid. The influence of the stirring speed on zinc extraction was tested in the range of 200-320 rpm. The experimental concentration profiles of the external aqueous phase were compared with the ones predicted by numerical simulation. The mathematical model used takes into account the diffusion and reaction of solutes within the membrane and connects the hydrodynamics with mass transfer.

The goal of this paper is to study the effect of different parameters (pH of the feed, Contact Time, Feed Concentration, Carrier Concentration and Treat Ratio) on the performance of liquid membrane for recovering the copper ion from modeled water.

EXPERIMENTAL

Material Used

The mobile carrier di (2-ethyl-hexyl) phosphoric acid (D2EHPA) (Molecular Weight=322g/mole, density=1.06 g/cm^3 is purchased from Fluka company. Sorbitan monooleate (Span 80) acts as non-ionic surfactant and is a product of Fluka Company. Commercial kerosene was used as diluent. Other chemical reactants such as sulfuric acid (H_2SO_4), ammonia (NH_3), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were analytically graded.

Experimental Procedure

The emulsification of the organic phase and the internal phase was prepared by mixing (200 ml) of kerosene containing surfactant concentration (5% v/v) and mobile carrier concentration (1-8% v/v) with aqueous solution of internal phase(H_2SO_4, pH=1) ratio(2/1) for 15 minutes. The emulsion phase being formed was transferred to a vessel containing a known concentration of copper (500-1000 ppm) in feed solution (external phase) with treat ratio (external volume to emulsion volume) with range of (2-10) ratio . The mixture was stirred in a vessel equipped with a four bladed agitator for a given contact time. The stirrer was then, stopped and the mixture was left to settle for 5 minutes. The emulsion droplets floated to the top and the external aqueous phase and the emulsion were recovered from the extractor. Then the de-emulsification process was done by placing the emulsion between two parallel plate electrodes 16 mm part and applying an AC voltage. A schematic diagram of the equipment is as shown in Figure 2.

Samples were analyzed using atomic absorption spectrophotometer. The extraction efficiency was calculated by:

$$\%Ex = \frac{[Cu]_i - [Cu]_f}{[Cu]_i} \times 100 \qquad (1)$$

Where $[Cu]_i$ and $[Cu]_f$ are initial and final concentration of copper in the aqueous phase, respectively.

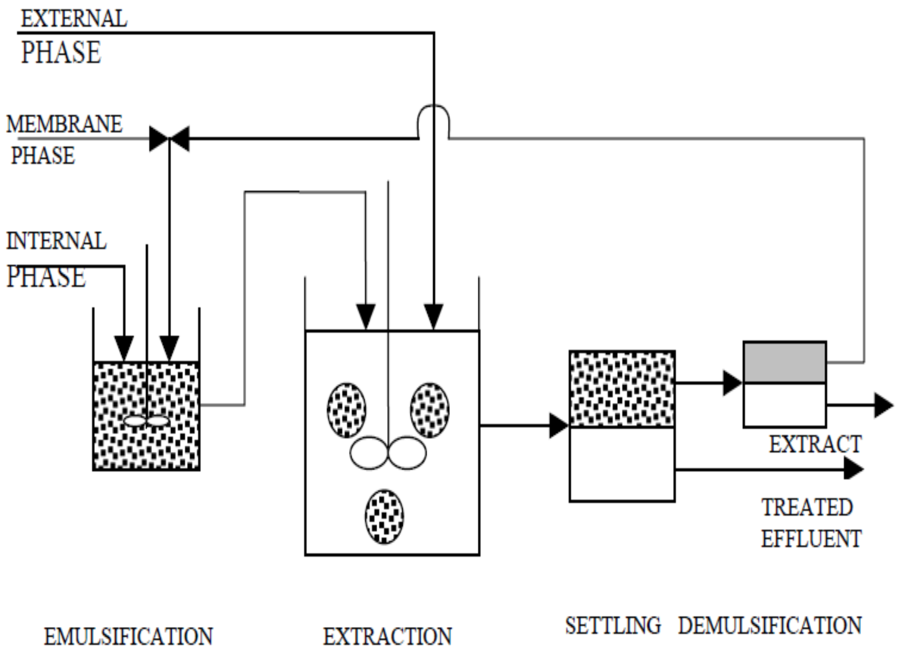

Figure (2) Schematic diagram of apparatus

RESULTS and DISCUSSIONS

2. Effect of Contact Time

Figure (3) shows the effect of contact times on extraction efficiency. As the contact time increases, the mass transfer rate of Cu increases and hence the extraction efficiency increases. With increasing contact time, the mass transfer of copper through the membrane phase increases and increasing the extraction percentage.

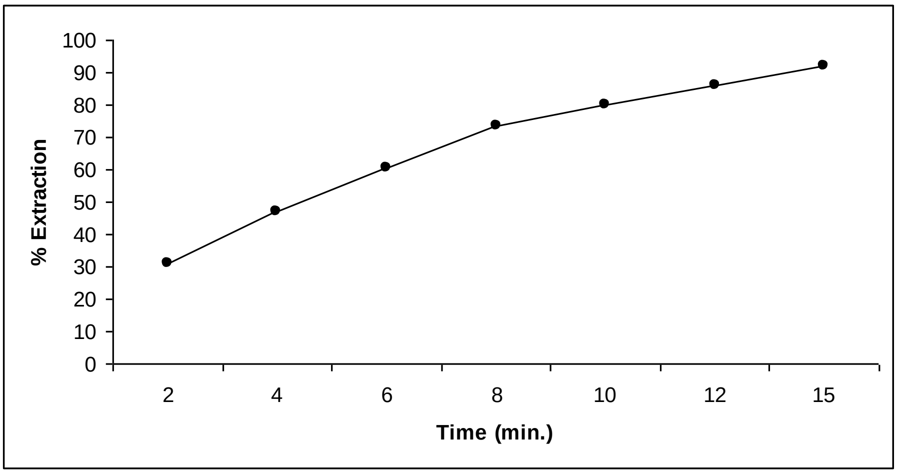

Figure (3) Effect of contact time on percent extraction operating conditions (pH = 8, feed conc. = 500ppm, carr. Conc. = 4%, treatment ratio = 2)

3. Effect of Feed Concentration

Figure (4) shows the effect of the initial copper concentration in the external aqueous phase. As can be seen that the extraction percentage decrease with increasing the concentration of copper in the feed solution. An increase in the concentration of copper the transfer resistant of the membrane increased. Also this is may be due to the emulsion breakup.

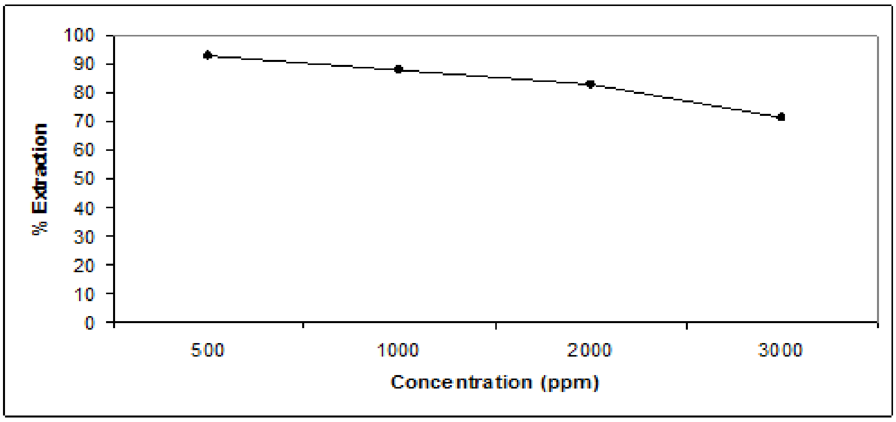

Figure (4) Effect of copper concentration in Feed on percent extraction, operating conditions (pH = 8, time = 15 min., carr. Conc. = 4%, treatment ratio = 2)

4. Effect of pH on Feed

The extraction curve obtained for copper ion solution in pH range of 3-10 is shown in figure (5); the range of pH values was adjusted with sulfuric acid. Extraction of copper metal from external phase and concentrate it in the internal phase depend on the strength of the acid/base of these phases, as can be seen that the extraction increase with decrease in acidity and it is maximum at pH=8 (base range).

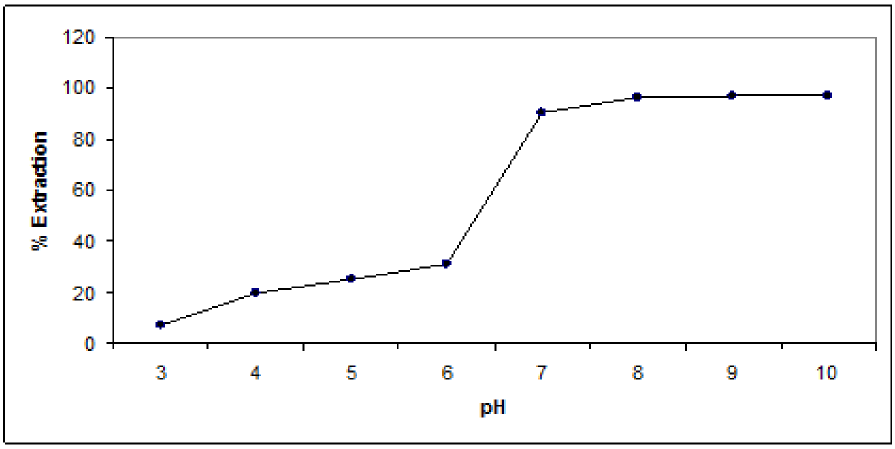

Figure (5) Effect of pH on Feed on percent extraction, operating conditions (time = 15min., feed conc. = 500ppm, carr. Conc. = 4%, treatment ratio = 2)

5. Effect of Carrier Concentration

Figure (6) shows the effect of carrier concentration in the membrane phase on extraction, it can be seen that the extraction increases until carrier concentration reaches 4%, then it decreases with increasing the concentration. This decreasing may be, due to the increase in the viscosity of the liquid membrane phase. The interfacial tension sharply decreased with increasing D2EHPA concentration. Increasing the D2EHPA concentration would not result in an improvement in the extraction of copper because the viscosities of both the membrane and emulsion have a tendency to increase for higher carrier concentrations. Larger globules would then be produced and the diffusivity of the complex would be lowered under such conditions, as is noted by A. Elsayed. From this data, it is concluded that the copper extraction is controlled by the interfacial interaction.

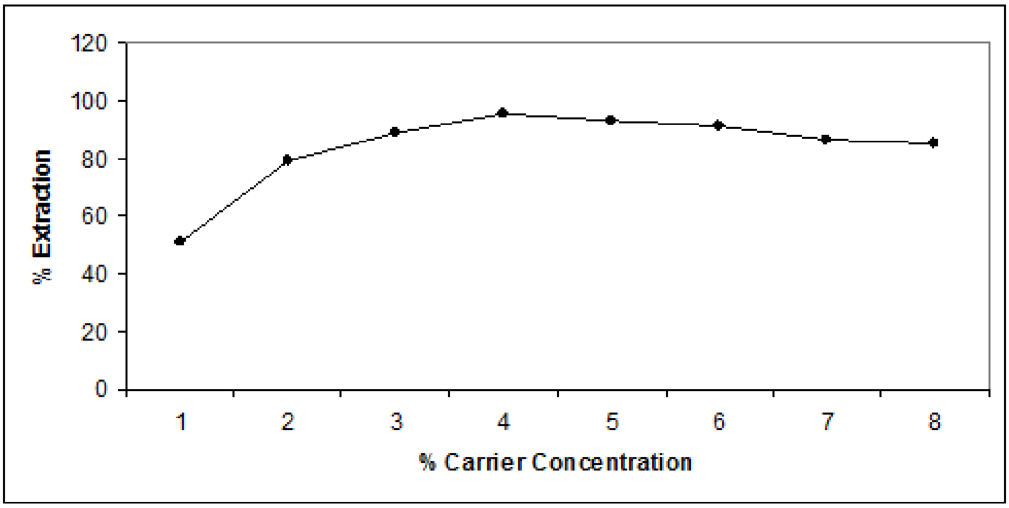

Figure (6) Effect of Carrier Concentration on percent extraction, operating conditions (pH = 8, feed conc. = 500ppm, time = 15min., treatment ratio = 2)

6. **Effect of Treat Ratio**

Figure (7) shows the effect of treat ratio of external volume to the emulsion volume. It can be seen that the extraction decreases slightly with increasing the ratio. This parameter controls the equipment size and chemicals used, i.e. minimize the economical cost of the process. With a decrease in the treatment ratio, the volumes of both the carrier and the stripping agent, i.e., the volume of emulsion as a whole, increased towards the external aqueous phase. Therefore, the surface area for mass transfer increased due to the formation of a larger number of emulsion globules. As a result, a higher degree of extraction was obtained. The higher treatment ratio means less emulsion is required to extract the metal ions, which is desirable from a processing point of view to ensure maximum enrichment with respect to the feed phase.

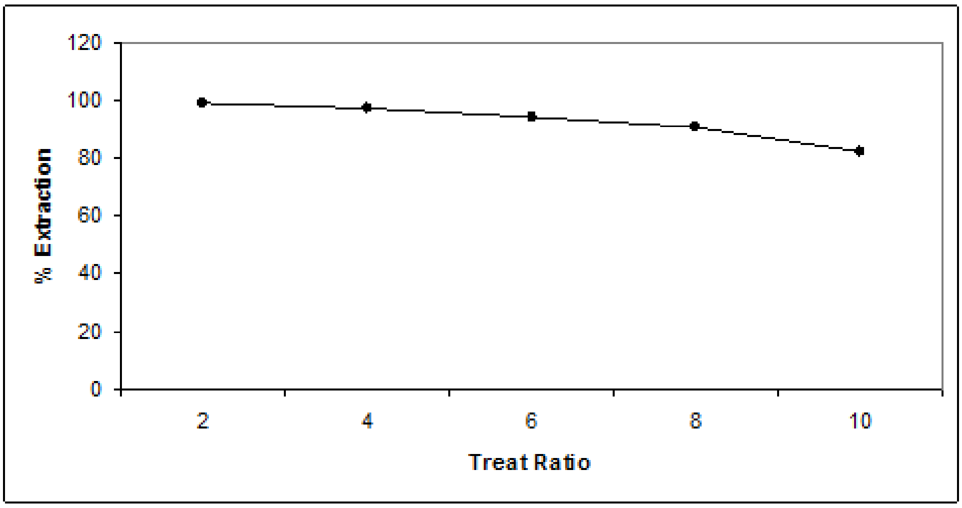

Figure (7) Effect of Treat Ratio ($V_{external}/V_{emulsion}$) on percent extraction, operating conditions (pH = 8, feed conc. = 500ppm, carr. Conc. = 4%, time = 15min.)

CONCLUSION

In this research application of emulsion liquid membrane to copper separation is studied. It was concluded that the best conditions for metal extraction are carried at pH equals (8) with contact time (15 min.), the best carrier concentration is (4%) and (2) for external to emulsion volumes ratio.

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