# Studies on Membrane Stability for Recovery of Uranium from Waste Solution by Liquid Emulsion Membrane (LEM)

[1]Abdelaziz Y.; [2]Y. Mohamed; [3]N. Abdelmonem and [1]A. Karameldin

[1]Nuclear Research Center - Atomic Energy Authority, Inshas- Cairo-Egypt
[2]Hot Laboratories and Waste Management Center- Egyptian Atomic Energy Authority
[2]Chemical Engineering Department-Faculty of Engineering-Cairo University – Egypt
ytselim@yahoo.com, **Yossryaly9@yahoo.com**

**Abstract:** Extraction process using liquid emulsion membrane (LEM) has received significant attention due to their potential as an effective technique for treatment of radioactive wastes. However, the need to obtain desired level of stability is very important in order to overcome the obstacles of the application of emulsion at large scale. The study has highlighted the importance of emulsion stability for maximizing uranium recovery from radioactive waste solution. The emulsion constitutes di-ethylhexyle phosphoric acid with tri n-butyl phosphate as carriers, benzene as organic solvent, an emulsifying agent and stripping phase. The residence time required for adequate permeation of uranium has been evaluated. The important variables affecting the LEM stability such as surfactant type, surfactant concentration, speed of agitation, aqueous feed solution, pH, and stripping phase solution are investigated. It was found that emulsifying agent span 80 with concentration 4%, (25%HDEHP, 0.005M+75%TBP, 0.01M) as a carrier and Hcl, 1M as stripping agent gives the maximum membrane stability.

[Abdelaziz Y.; Y. Mohamed; N. Abdelmonem and A. Karameldin. **Studies on Membrane Stability for Recovery of Uranium from Waste Solution by Liquid Emulsion Membrane (LEM).** *J Am Sci* 2012;8(12):1292-1297]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 174

**Keywords:** Uranium Extraction, Liquid Emulsion Membrane, Stability of LEM

## 1. Introduction

Effective separation, concentration, purification and removal of uranium (VI) from its secondary sources and wastewater are one of the challenging tasks faced by nuclear industries. It is always desirable to recover all the uranium even as traces from dilute solutions not only for its strategic value as fuel for nuclear reactor but also to meet stringent discharge standards.

The various techniques available for recovery and removal of uranium from aqueous solutions include biological treatment, liquid –liquid extraction ion exchange, precipitation etc [1- 3]. The Liquid emulsion membrane (LEM) technology which was invented by **Li (1968) [4]** has been investigated as an advanced extraction technology to combat disadvantage of other separation techniques. The advantages of LEM technology over conventional liquid- liquid extraction have been previously studied [5]. The LEM technology refers to simultaneous extraction and stripping, where metal ions present in feed solution form a complex with the extractant. The complex formed then defuses through a membrane phase to a stripping phase interface from where it is stripped into the bulk of encapsulated stripping phase. The volume of the stripping zone liquid is very small compared to aqueous feed phase thereby resulting in pre-concentration of uranium. The concentrated uranium from the stripping phase can be recovered by breaking the emulsion [6].

Despite much work done on the LEM extraction of uranium [7- 10], published literature doesn't provide much data on emulsion stability. The present study aims to give a scope on the parameters affecting the emulsification and stability of the prepared LEM for recovery of uranium from water solution. The most important parameters include selection of the types and concentration of; feed solution, carrier, diluents, surfactant and stripping solution.

The stability of LEM is related to the droplet diameter of the prepared emulsion. Small droplets diameters tend to have better breaking and producing membrane of greater surface area. On the other hand, large droplet diameters result poor stability and extraction efficiency because of a low surface/volume ratio, suggested that emulsions with droplets in the range of 0.3 -10 mm (preferably 0.8 – 3 mm), therefore, it combine rapid extraction rates, good stability and are readily broken by electrostatic means [11- 14].

In emulsion preparation, energy must be supplied to produce such meta-stable mixtures. Energy may be provided through various means. The most widely applied method to produce emulsions is mechanical agitation. Ultrasound generation is an alternative method to dissipate mechanical energy required for droplet rupture in the liquid [15].

## 2. Experimental

All solutions were prepared from analytical grade chemical reagents and were used without further purification. All solutions were freshly prepared using doubly distilled water. The chemicals used for obtaining primary emulsion were the following:

- Internal, receiving phase consisted of hydrochloric acid, sulfuric acid and sodium hydroxide solutions with various concentrations.
- Carrier agents, Bis(2-etylhexyl)phosphate (HDEHP) ($C_{16}H_{35}O_4P$), Tri-butyl phosphate (TBP) ($C_{12}H_{27}O_4P$) with different concentrations and benzene as diluents.
- Surfactant agent, Span 80 (Sorbitan monooleate), span 20 (Sorbitan monolaurate) and Span 85 (Sorbitan trioleate) with different concentrations. All experiments were carried out at ambient temperature (25 ±1 $^oC$) and pH was measured by pH meter model pH 211.

The concentration of uranium in the aqueous feed solution and stripping phase were spectrophotometrically determined using Arzanaso III method. Type 1601PC Shimadzu Corporation, the detection limit of UV-Visible for uranium is 0.1 ppm. The concentration of uranium in the organic phase was calculated by mass balance. The extraction percentage (%E) was calculated by the relation:

$$\%E = [(C_o - C_t)/C_o] \times 100 \quad (1)$$

Where: $C_o$: is the initial concentration of metal ion in the aqueous solution.

$C_t$: is the metal ion concentration in the aqueous solution at time, t.

The liquid emulsion membrane was prepared by mixing 25 ml of the organic extractant (carrier) in the selected diluents with suitable surfactant. Then 25 ml of the stripping aqueous phase solution was added drop-wise to enhance the stability of LEM. The solution was then emulsified with an ultra-high speed homogenizer. A stirring speed of 8000 rpm was used for three minutes to form the LEM, Figure (1).

The prepared LEM was then poured into the external aqueous phase containing the uranium ions. The system was stirred with a magnetic stirrer at 500 rpm, unless otherwise stated. Samples were taken at different time intervals from the external aqueous phase for uranium determination.

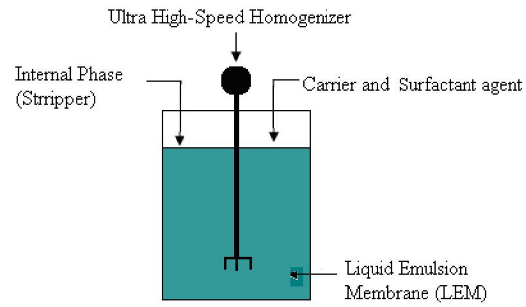


**Figure (1)** Preparation of liquid emulsion membrane (LEM)

## 3. Results and Discussion.

### 3.1 Liquid - Liquid Extraction investigation

Extraction equilibrium was first examined to identify the extraction behavior and suitable conditions for uranium extraction from aqueous waste solution using (TBP) as an extractant, (HDEHP) as stability modifier and benzene as a diluent.

3.1.1 Effect of pH on the extraction percent of uranium, with different ratios of carrier (HDEHP+TBP).

It is clear from figure (2) that, the maximum extraction percent of uranium occurs at pH= 5, for all ratios, except at (0%HDEHP+100%TBP) ratio. At higher pH, the extraction percent of uranium decreases, but at pH 9 the extraction of uranium starts to increase again, this may be due to the precipitation of uranium in alkaline medium.

### 3.1.2 Effect of carrier concentration.

#### 3.1.2.1 At constant concentration of (HDEHP) 0.1M.

Figure (3) illustrates the effect of TBP concentration on the extraction percent of uranium at constant concentration of HDEHP 0.1M, and pH 5. It is clear from this figure that the extraction percent of uranium slightly increases with increasing the TBP concentration, and the maximum extraction percent of uranium (99.6%) occurs at TBP concentration equal to 0.01M.

#### 3.1.2.2 At constant concentration of (TBP).

Figure (4) shows the effect of HDEHP concentration on the extraction percent of uranium at constant concentration of TBP which equal 0.01M. It is clear from this figure that the extraction percent of uranium increases with increasing the HDEHP concentration and the maximum extraction percent of uranium is (99.7%) occur at HDEHP concentration equal to 0.005M.

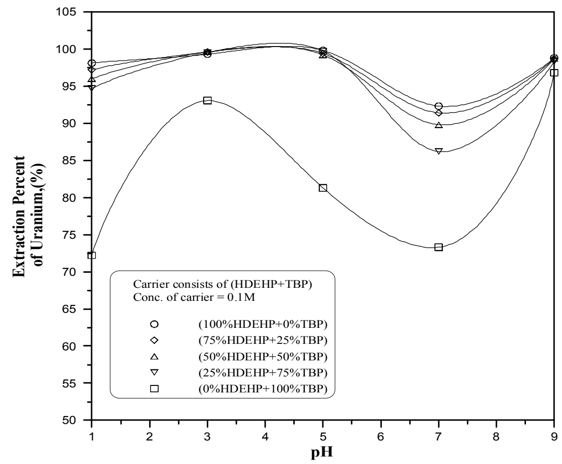


**Figure (2)** Effect of pH value on extraction percent of uranium

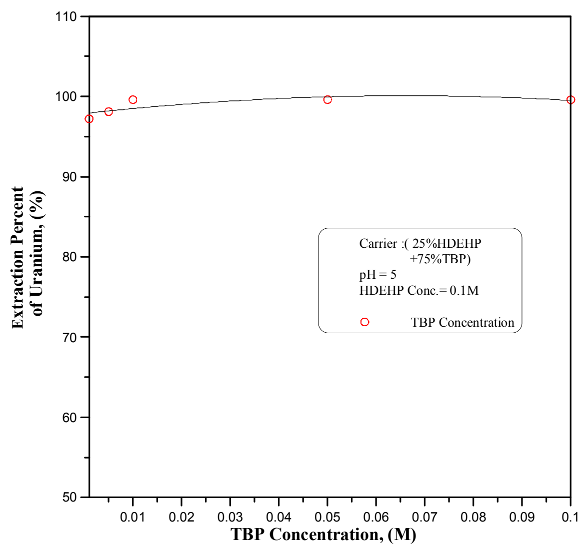


**Figure (3)** Effect of TBP concentration on the extraction percent of uranium

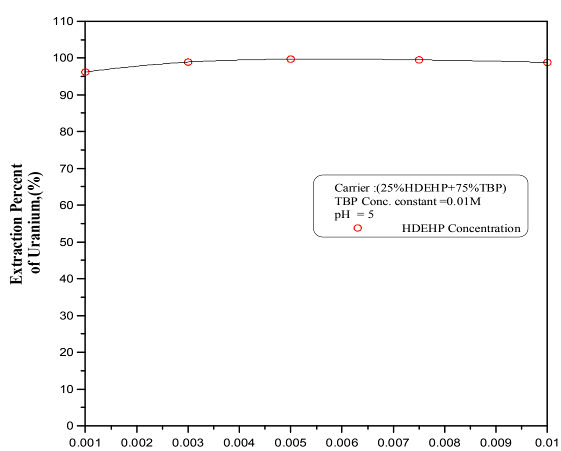


**Figure (4)** Effect of HDEHP concentration on extraction percent of uranium

### 3. 1. 3 Effect of stripping agents.

Stripping of the extracted uranium from their organic phase was investigated using different stripping agents. Aqueous solutions of hydrochloric acid, sulfuric acid, and sodium hydroxide were tested as stripping agents. Table (1) and Figure (5) illustrate the effect of stripping agent concentration on the % of stripping efficiency of uranium, using different stripping agents. It is clear from the table and the figure, that the hydrochloric acid (HCl), [1M] is the best stripping agents for uranium, (69.4%).

**Table (1)** Effect of different stripping agents on the stripping efficiency, % of uranium

| Different stripping agents and concentration | Stripping efficiency of uranium,% |
|---|---|
| Hydrochloric Acid (HCl), 1M | 69.4 |
| Sulfuric Acid ($H_2SO_4$), 0.5M | 68.3 |
| Sodium Hydroxide (NaOH), 0.5M | 60.4 |

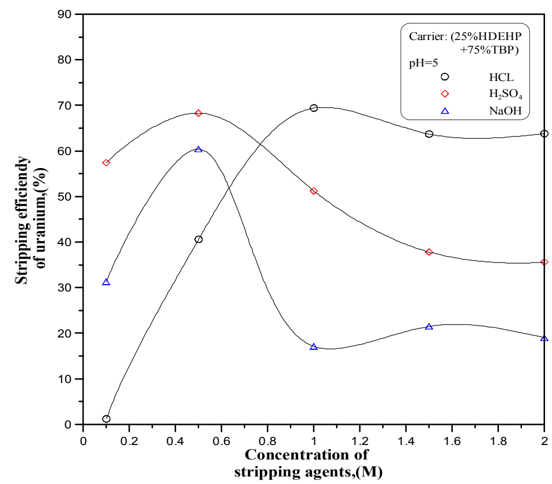


**Figure (5)** Effect of stripping agent's concentration on the stripping efficiency of uranium, with different stripping agents

### 3.2 Stability of Liquid Emulsion Membrane.

When LEM is dispersed in the external aqueous phase (feed solution), the emulsion must be sufficiently stable in order to extract the metal ions into the internal aqueous phase, and the LEM breakdown will result of operation failure, lower extraction efficiency and loss of the extracted species. The degree of extracted metal species into the internal aqueous phase is highly affected by the degree of LEM stability. The LEM globules are stabilized by adding suitable surfactant and suitable surfactant concentration. The stability of LEM was investigated by tracing the yellow dye which loaded in the internal aqueous phase during the LEM preparation and detected in the external aqueous phase [17- 19]. The percentage of leakage (%) was determined using the following equation:

Leakage (%) = $(C_{ext.} / C_{in,maxt}) * 100$ --------------- (2)

Where: $C_{ext}$: is the concentration of yellow dye leaked from the internal phase to the external phase.

$C_{in,maxt}$: is the max concentration of yellow dye in the external aqueous phase, when all yellow dye leaked to external aqueous phase from internal aqueous phase.

The emulsion composition used during studying the stability of membrane under investigation was the following unless otherwise stated, concentration of extractant (25%HDEHP, 0.005M+75%TBP, 0.01M), different surfactants and different surfactant concentrations were used. The internal aqueous phase was 1M HCl, while the ratio of membrane phase to internal phase is 1, with a stirring speed of 500 rpm; meanwhile the yellow dye was used as a tracer, at room temperature. The used ratio of the liquid emulsion membranes to aqueous feed is 20: 100 ml.

### 3.2.1 Effect of surfactant types on the stability of LEM.

Surfactants play very important role in the formation and stability of liquid emulsion membrane. The effect of surfactant type on the amount of yellow dye leaked from the internal aqueous phase to the external aqueous phase was studied. The surfactants used with constant concentration were span 20, span 80, and span 85. Figure (6) showed the leakage percent of LEM against time with different surfactants under investigation. It is clear from the figure that, the span 80 shows the best stability results than span 20 and span 85, this finding is the same as there published [20-22].

### 3.2.2 Effect of surfactant concentrations on the stability of LEM.

The effect of span 80 concentration on the stability of LEM was studied. Different span 80 concentrations were used in the preparation of LEM, 2%, 4% and 6% (v/v). It is clear from Figure (7); that the leakage percent of liquid emulsion membrane sharply increases with decreasing the surfactant concentration and that there is no big difference between 4% and 6% in the stability results. The 4% span 80 is chosen as a best concentration because high concentration of span80 is undesirable in the stirring tank to avoid the emulsion swelling [23-25].

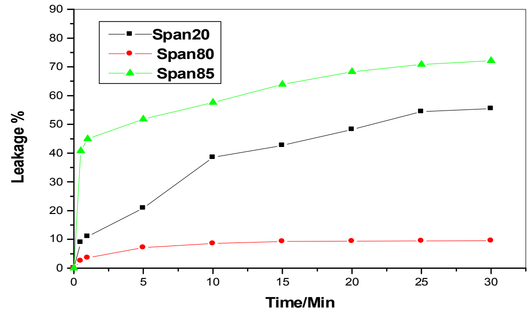


**Figure (6)** Effect of surfactant types on the stability of LEM

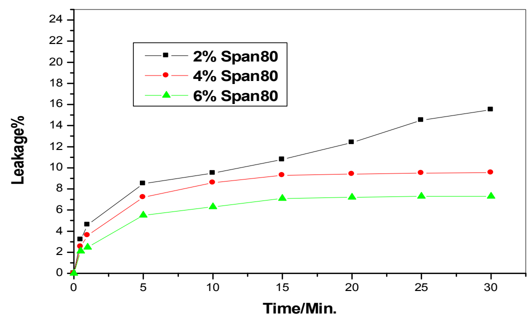


**Figure (7)** Effect of surfactant concentrations on the stability of LEM

### 3.3.1 Effect of surfactant types on the permeation percent of uranium.

Figure (8) shows the effect of different surfactants on the on the extraction percent of uranium by LEM, at constant concentration of surfactant. It is clear from the figure that the span 80 shows the best permeation results on the extraction of uranium through LEM in spite of span 20 shows the high permeation percent of uranium in the beginning but due to the stability problem, span 80 shows the best results. The obtained results from the experimental work showed that, the maximum extraction percent of uranium (99.95%) occurred at using surfactant agents (span 80) after 15 minute.

### 3.3.2 Effect of surfactant concentrations on the permeation percent of uranium.

Figure (9) shows the effect of span 80 concentrations on the extraction percent of uranium using hydrochloric acid, 1M as stripping agents. The permeation results support the stability results which show that, 4% of span 80 is the best choice for preparing LEM. The high surfactant concentration not only increases the stability of emulsion but also decreases the permeation percent of uranium due to emulsion swelling. The results of emulsion swelling decrease the diffusion rate of uranium in the peripheral oil layer. In spite of the high surfactant concentration shows the high stable emulsion but it is clear from the Figure that the 4% span 80 shows the highest extraction percent of uranium.

### 5.3.3 Effect of stirring speed on the permeation percent of uranium.

Figure (10) shows the effect of stirring speed on the extraction percent of uranium, Hcl, 1M as stripping agent and surfactant agent (span 80, 4% v/v) were used. Different stirring speeds from 500 to 1200 rpm also were used. It is clear from the figure that the extraction percent of uranium increases with increasing the stirring speed. The stability of prepared LEM plays an important role on the extraction behaviors of uranium at high stirring speed. It is clear from the figure that the extraction percent of uranium increases with increasing of stirring speed from 500 to 600 rpm and there is no big difference for the results. It is worth to mentioned, above stirring speed 600 rpm the extraction percent of uranium decreases with increasing of stirring speed, due to the membrane resistance to high shear force and the membrane stability failed.

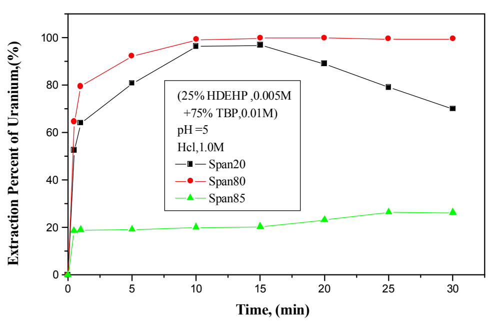


**Figure (8)** Effect of surfactant Types on the extraction percent of uranium.

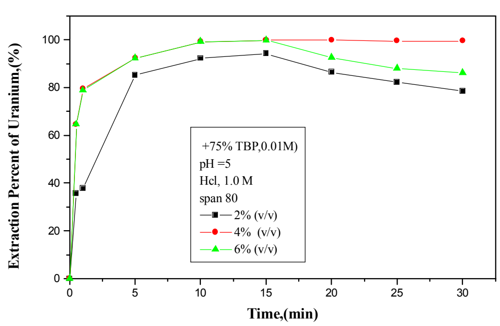


**Figure (9)** Effect of surfactant concentration on the extraction percent of uranium

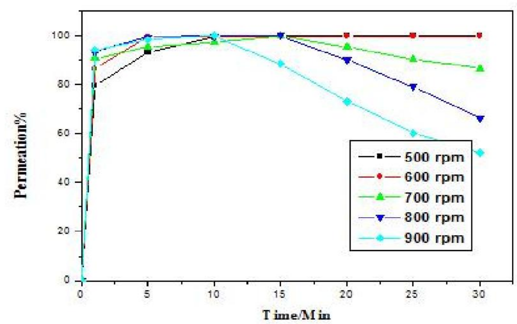


**Figure (10)** Effect of stirring speed on the extraction percent of uranium

### Conclusions

Liquid emulsion membrane is a promising method for radioactive waste treatment and recovery of nuclear materials of interest. The successful application is not only depend on the selection of suitable emulsification method but also on the emulsion formulation in accordance with the solute which is to be recovered. This is related to the emulsion stability that is still remains a great challenge in the application of the LEM in industrial scale. Emulsion instability occurs through various physical mechanisms such as coalescence, swelling and leakage. The two mechanisms were found to be the main problem in practical use of LEM which can decrease the extraction efficiency and cause emulsion breakdown. Swelling is caused by surfactant, carrier difference in ionic strength, residence time, pH, diluents viscosity, acidity of aqueous phase and agitation speed. While membrane leakage is significantly affected by properties of surfactant, diluents, internal phase, and its volume fraction, membrane preparation procedure and stirring speed of extraction. It is clear from the results that span 20 followed by span 80 as surfactants used in the preparation of liquid emulsion membrane, but span 80, 6% (v/v) gives the highest stability of LEM and span 80, 4% (v/v) gives the maximum extraction percent of uranium, (99.95%). The maximum extraction percent of uranium and good stability of LEM occurred at stirring speed from 500 to 600 rpm, above 600 rpm of stirring speed the extraction percent of uranium decreases. The results showed that the stirring speed of extraction and type and concentration of surfactant are very important parameters for stability of liquid emulsion membrane.

### References


1. Huang C.T., T.C. Huang, The equilibrium reaction of the extraction of uranium(VI) with

di-(2-ethylhexyl) phosphoric acid from nitric acid solutions, Solvent Extraction. Ion Exchanger. 5 (4) (1987)

2. Huang T.C., C.T. Huang, The mechanism of transport of uranyl nitrate across a solid supported liquid membrane using tributyl phosphate as mobile carrier, J. Membrane. Science. 29 (3) (1986)
3. Sifniades S., T. Largman, A.A. Tunick, F.W. Koff, Recovery of uranium from phosphoric acid by means of supported liquid membranes, Hydrometallurgy 7 (3) (1981)
4. Li US Patent N.N. (1968)
5. Hayworth H.C., H.S. Ho, W.A. Burns Jr., N.N. Li, Extraction of uranium from wet process phosphoric acid by liquid membranes, Separation. Science. Technology. 18 (6) (1983)
6. .Gu Z, W.S.Ho and N.N.Li, Emulsion Liquid Membrane: Design Considerations, in W.S.Ho, K.K.Sirkar (Eds.) Membrane Handbook, Chapman&Hall, NewYork,1992,
7. EI-Reefy S.A., Y.T. Selim, H.F. Aly, Equilibrium and kinetic studies on the separation of uranium and thorium from nitric acid medium by liquid emulsion membrane based on trioctylphosphine oxide extractant, Analytical . Science. 13 (3) (1997)
8. EI-Reefy S.A., Y.T. Selim, H.F. Aly, Recovery of uranium from thorium in hydrochloric acid medium by liquid emulsion membranes containing trioctylphosphine oxide, J. Radio analytical. Nuclear. Chemistry. 228 (1–2) (1998).
9. Mohamd Y.T.,"Removal of Hazardous Pollutants from Industrial Waste Solutions Using Membrane Techniques", Ph.D. Thesis, Ain Shams University, 2001.
10. Mohanty, S. Emulsion liquid membranes: Applications in separation processes. Chemical. Engneering. World 39 (2004).
11. Yang Li, Zhengxi Zhang, Yaju Guo, Xuhui Gao and Hiroshi Takeuchi Separation and Purification Technology Volume 47, Issues 1-2(2005)
12. . Joshi J.M, P.N.Pathak, A.K.Pandy and V.K.Manchanda, Hydrometallurgy 96(2009).
13. Mishra S.L, R.Vijayalakshmi and H.Singh, Indian Journal of Chemical Technology Vol.12 (2005).
14. .Wan Y, X.Zhang , Journal of Membrane Science 196 (2002)185-201
15. .Yan J, R.Pal, Journal of Membrane Science 244 (2004).
16. Matsuoka H., M. Aizawa, S. Suzuki, Uphill transport of uranium across a liquid membrane, J. Membrane. Science. 7 (1) (1980).
17. Kulkarni P.S., S. Mukhopadhyay, M.P. Bellary, S.K. Ghosh, Studies on membrane stability and recovery of uranium(VI) from aqueous solutions using a liquid emulsion membrane process, Hydrometallurgy 64 (2002).
18. Kulkarni P.S., Recovery of uranium (VI) from acidic wastes using tri-*n*-octylphosphine oxide and sodium carbonate based liquid membranes, Chemical. Engneering. J. 92 (2003).
19. Kulkarni P. S., S. Mukhopadhyay and S. K. Ghosh, Industrial. Engineering. Chemical. Research, 2009, 48 (6).
20. .Pfeiffer R.M, A.L.Bunge, W.Navidi Separation Science and Technology 38(2003).
21. Ahmad A.L., A.Kusumastuti, C.J.C.Derek and B.S. Ooi, Chemical Engineering Journal 171(2011).
22. Liang P., Y. Bing-hua, FU Xing-long, and W. Li-ming (The Chinese Journal of Process Engineering), Vol.8 No.6, 2008
23. Ohtak T., T.Hano, K.Takagi and F.Nakashio, Journal of Chemical Engineering of Japan 21(1988).
24. .Ding X.C, F.Q.Xie, Journal of Membrane Science 59 (1991)183-188.
25. Yan J., R.Pal, Journal of Membrane Science 213 (2003).

12-20-2012