Mathematical Modeling of the Extraction of Uranium from Waste Solution Using Liquid Emulsion Membrane

[1]Abdelaziz Y.A., [2]Y.T.Mohamed, [3]N. Abdelmonem, and [1]A. Karamelden

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

Abstract: The extraction of uranium from aqueous waste solution using liquid emulsion membrane with synergistic mixture of Bis (2-etylhexyl) phosphate (HDEHP) and Tri-butyl phosphate (TBP) in an aromatic hydrocarbon as a diluent has been studied. Many extraction parameters have also been studied such as, concentration of extractant and uranium and pH of the feed solution. Various parameters affecting the transport of U (VI) through membrane layer have been optimized to remove U (VI) from liquid waste solution. More than 99% uranium was removed under certian conditions. The counter transport of uranium and hydrogen ions were facilitated by the carriers. The use of hydrochloric acid as an internal aqueous phase accelerates the uranium transport through LEM. Mathematical modeling of the permeation of uranium through LEM has been studied. Different parameters are calculated such as diffusion coefficients of uranium/carrier complex, carriers and mass transfer coefficients of uranium, carriers and uranium / carrier's complex besides calculating the membrane thickness.

1. Introduction

Treatment of radioactive liquid waste receiving considerable attention in most countries that have nuclear reactors [1], the management of radioactive wastes has become a major concern particularly with regard to the release of radioactive material into the environment and possible risk of contamination. The development of rational and acceptable options for radioactive waste disposal requires a clear understanding of radiators protection objectives and their application in planning, regulation and licensing. Considerable progress has been made over the past three decades within many countries utilizing nuclear reactors to develop strategies for management of nuclear wastes. All wastes should be managed in such a way that high standards of conditioning are maintained and that potential hazards originating from their disposal are reduced to levels that are as low as reasonable and well below permissible levels [2]. The nuclear fuel cycle consists of a great number of different mineral-chemical processes. Some of them produce liquid effluents with significant concentrations of uranium. For example, the precipitation process produces the uranyl ammonium tricarbonate (TCAU), a yellow solid. This yellow cake feeds the fluidized bed furnace and is converted into UO_2. The exhaust gases from the furnace, which contain uranium, ammonium and carbon dioxide, are reabsorbed in towers by the contact with water stream generating an alkaline uranium rich effluent (www.inb.gov.br). [3]

The aqueous solution contaminated by uranium is considered as a very serious environmental problem, which has been extensively discussed and presence of some uranium which display high and long term toxicity creates limitations on the recyclables of these solutions [4]. The amounts of uranium are especially high in industrial waste solutions and endanger public health and the environment if discharged without adequate treatment. In addition the presence of toxic heavy metals in waste solution has caused several health problems with animals, plants, and human being [5, 6].

Currently, the research and development work for the treatment of radioactive liquid wastes is concentrated by saving energy and raising efficiency. Several methods such as evaporation, ion exchange, precipitation, solvent extraction and liquid membrane (LM) have been widely used in the treatment of liquid wastes [7].

The strict regulation against the pollution of the environment together with the rising value of metals has resulted in an increasing the interest on the recovery of nuclear materials from waste solutions. The recovery of uranium by solvent extraction from uranium-containing ores has widely been applied industrially. However, several problems arise along with it, such as low extraction rate, a large amount of

extractant and solvent and quality of uranium produced. Different membrane process techniques have been considered for the removal of the uranium from waste solutions. These comprise liquid emulsion membrane (LEM), supported liquid membrane (SLM), hybrid liquid membrane (HLM) and bulk liquid membrane (BLM) [8].

The liquid emulsion membrane (LEM) technology, which is a simplified extraction process with no stripping stage and high extraction efficiency [9], will provide an attractive alternative to conventional extraction technique for the selective removal and concentration of valuable or toxic heavy metal from aqueous solutions. Liquid Emulsion Membrane (LEM) invented by **Li (1968) [10]** offers a promising technology for separation of heavy metal ions from aqueous solution. The potential advantages of LM techniques over traditional separation techniques and solid membrane techniques are lower capital and operational costs, lower energy and extractant consumption, and higher concentration factors and fluxes. In the present study, the batch extraction of uranium from liquid waste has been conducted using LEM under different conditions with some mathematical modeling to calculate important parameters such as diffusion coefficients for carriers and metal/carriers complex and mass transfer coefficients for carriers, uranium and uranium/carrier complex beside the membrane layer thickness.

2. Emulsification Method

The most widely applied method to produce emulsions is mechanical agitation including stirrer, mixer, homogenizer, etc. **[11-15]**.

3. 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 is hydrochloric acid 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 with different concentrations. All experiments were carried out at ambient temperature (25 ±1 °C) and pH was measured by pH meter model pH 211**[16].**

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[**17**].. The concentration of uranium in the organic phase was calculated by mass balance. The extraction percentage (%E) was calculated by the relation:

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

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.

All LEM experiments were 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 [18], shown figure (1).
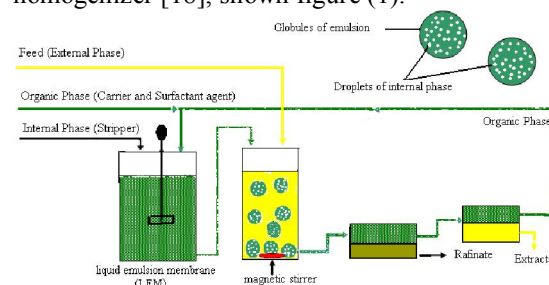

Figure (1) Preparation of liquid emulsion membrane (LEM)

4. Extraction Mechanism of Uranium.

Extraction mechanism of uranium with XY (assuming XY = (25%HDEHP, 0.005M+75%TBP, 0.01M)) had been investigated. This mechanism was built on assumptions of an immobilized hollow spherical emulsion globule model that assumed a coupled counter current transport. A transport of a uranyl nitrate ion across the emulsion globule during LEM extraction is shown in figure 2. The transportation process can give as the following:

i. The uranyl nitrate ion diffuses from the external aqueous phase to the boundary of the membrane phase;

ii. Uranyl nitrate ion forms a complex with carrier (XY) on the external aqueous interface;

iii. the complex diffuses to the peripheral oil layer of the emulsion globule;

iv. A stripping reaction occurs between the complex compound and the stripping agent (HCl) when the complex diffuses toward the internal aqueous phase. The uranyl nitrate ion is released from the complex to the internal aqueous phase;

v.   Carrier (XY) diffuses from the internal interface to the external interface and forms a complex again with the metal ion.
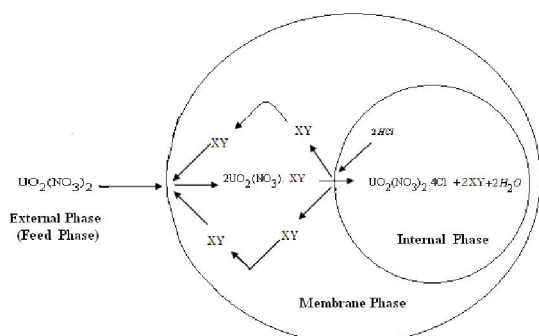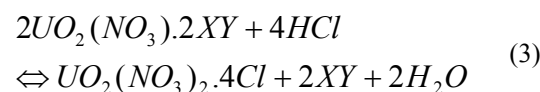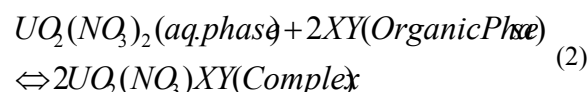

Figure (2) Transport of a uranyl nitrate ion across the emulsion globule

The equations exhibiting the extraction process, (2) and the stripping equation process, (3) of uranium occurring in liquid emulsion membrane is given below. [13]

$$UO_2(NO_3)_2(aq.phase) + 2XY(Organic Phase)$$
$$\Leftrightarrow 2UO_2(NO_3)XY(Complex) \quad (2)$$

$$2UO_2(NO_3).2XY + 4HCl$$
$$\Leftrightarrow UO_2(NO_3)_2.4Cl + 2XY + 2H_2O \quad (3)$$

5. Results and Discussion.
5.1. Effect of Carrier Concentration on the Extraction Percent of Uranium.
5.1. 1. Effect of TBP Concentration

Figure (3) illustrates the effect of different concentrations of TBP on the extraction percent of uranium, at constant concentration of HDEHP. It is clear from the figure that the extraction percent of uranium through LEM decreases with increasing TBP concentrations, from 0.01 to 1M. The maximum extraction percent of uranium (99.95%) occurs at TBP concentration equal 0.01M.

5.1.2. Effect of HDEHP Concentration.

Figure (4) illustrates the effect of HDEHP concentrations on the extraction percent of uranium through LEM, at constant concentration of TBP. It is clear from the figure that the extraction percent of uranium through LEM decreases with increasing of HDEHP concentrations from 0.005 to 0.1M. The maximum extraction percent of uranium (99.95%) occur at HDEHP concentration of 0.005M.
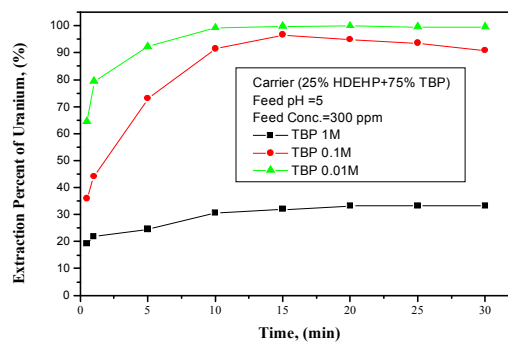

Figure (3) Effect of TBP concentrations on the extraction percent of uranium at constant concentration of HDEHP, 0.005M
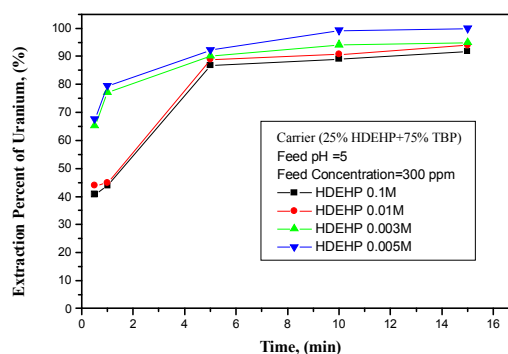

Figure (4) Effect of HDEHP concentrations on the extraction percent of uranium at constant concentration of TBP, 0.01M

5.2. Effect of pH of the external aqueous phase on Extraction Percent of Uranium.

Figure (5) illustrates the effect of different pH of the external aqueous phase on the extraction percent of uranium through LEM. It is clear from the Figure that the extraction percent of uranium increases with increasing the pH from 1 to 7.5. The maximum extraction percent of uranium (99.95%) occurs at pH equal 5.0. It is worth mentioned that, the extraction percent of uranium at pH 1 is very low due to the competition between uranium ions and hydrogen ions on the membrane feed interface.

5.3. Effect of Stripping phase Concentration on the Extraction Percent of Uranium through LEM.

Figure (6) illustrates the effect of different concentration of hydrochloric acid on stripping efficiency of uranium in the internal aqueous phase, at constant pH 5.0 of the external aqueous phase. It is clear from the figure that, the stripping efficiency of uranium increases with increasing of stripping agent concentration from (0.1 to 1.0M). The results of experimental work showed that the maximum

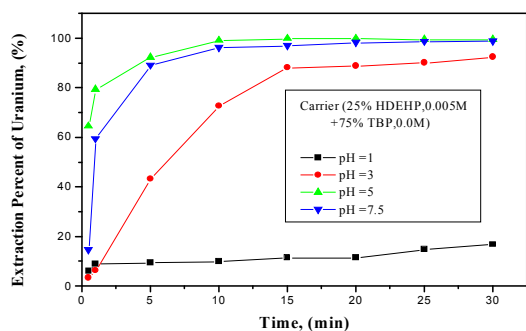stripping efficiency of uranium (99.9%) occurred at stripping agent concentration equals 1.0M or higher.

Figure (5) Effect of pH different values on extraction percent of uranium at constant concentration of carrier
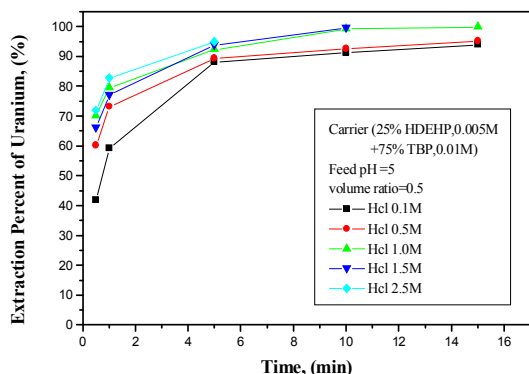

Figure 6: Effect of Hcl concentration on the stripping efficiency of uranium at constant concentration of carrier.

5.4. Effect of Volume Ratio of Organic Phase on Extraction percent of Uranium.

The volume ratio is the ratio between the volumes of organic phase to the total volume of liquid emulsion membrane. Figure (7) illustrates the effect of different volume ratio of organic phase on the extraction percent of uranium, at constant pH =5. It clears from the figure that the increasing of extraction percent of uranium with increasing of volume ratio from 0.37 to 0.5. Above volume ratio 0.50 the extraction percent of uranium will be decrease because coagulation of membrane occurs who led to the decreasing of total membrane surface area and hence decreasing the permeation percent of uranium through LEM. The maximum extraction percent of uranium (99.95%) occur at volume ratio of organic phase equal to 0.5.

5.5. Effect of LEM Ratio on Extraction Percent of Uranium.

The liquid emulsion membrane ratio is the percent between the volumes of liquid emulsion membrane to the volume of the external aqueous phase. Figure (8) depicted the effect of different LEM ratios on the extraction percent of uranium, at constant pH 5. It is clear from this figure that, the extraction percent of uranium increases with increasing of LEM ratio from 0.1 to 0.2. Above LEM ratio 0.2, the extraction percent of uranium decreasing and the maximum extraction percent of uranium (99.95%) occurred at LEM ratio equal to 0.2.

5.6. Effect of LEM Preloading of Uranium on Extraction Percent of Uranium.

Figure (9) depicted the effect of LEM preloaded by different uranium ions on the extraction percent of uranium, at constant pH =5. It is clearly observed from figure (9) that the extraction percent of uranium decreases with increasing of uranium preloaded inside the internal aqueous phase to show the maximum uranium could be permeated before membrane recycled. The obtained results from the experimental work showed that the maximum extraction percent of uranium (87%) occur at LEM preloaded with 700 ppm.
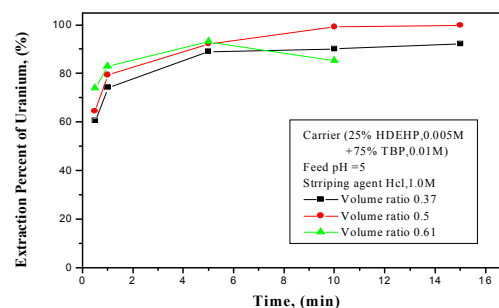

Figure (7) Effect of different volume ratio of organic phase on extraction percent of uranium, at constant concentration of carrier
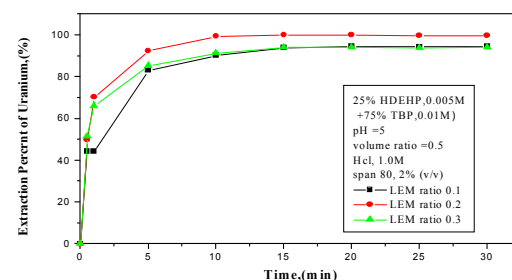

Figure (8) Effect of different LEM ratio on extraction percent of uranium, at constant concentration of carrier
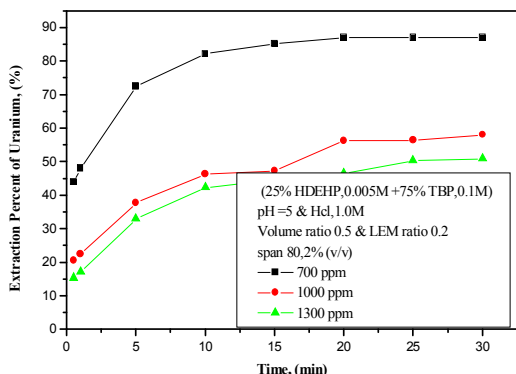
Figure (9) Effect of LEM preloading of uranium on extraction percent of uranium, at constant concentration of carrier

6. Modeling of Uranium Permeation through liquid emulsion membrane and volumetric rate of leakage.

6.1. Volumetric Rate of Leakage v_b

The volumetric rate of leakage v_b of the internal aqueous phase to the external aqueous phase due to membrane break-up was obtained by plotting F (fraction of leakage) against time t for the different parameters under investigation. The value of v_b was calculated as a product of the slope obtained from the fraction of leakage- time curve and the volume of the internal aqueous phase.

Leakage % = [C_{ex}] x100/ [C_{in}]$_{max.}$ (4)

Where **[C_{ex}]** denotes the concentration of tracer in the external phase and **[C_{in}]$_{max}$** stands for the maximum possible tracer concentration in the internal phase and fraction of leakage, F can be calculated by the following equation:

F = 1-Φ [C_{ex}] / Φ   [$C_{in,o}$]   (5)

Where   is the volume fraction of W/O emulsion in W/O/W multiphase = V_{org} + V_{in}/V_T, **[$C_{in,o}$]** is the initial concentration of tracer in the internal aqueous phase and **Φ** is the volume fraction of the internal aqueous phase in W/O emulsion drop = $V_{in}/(V_{in}+V_{org})$ where V_{in} is the volume the internal phase, V_{org} is the volume of membrane phase and V_T is the total volumes.

Figure.10 shows the effect of surfactant types on the fraction of leakage. Considerable leakage was observed in the feed solution when the emulsion was dispersed at the start of the extraction, and F increased linearly with time. The volumetric rates of leakage v_b for the surfactants, Span20, Span80, Span85, were calculated and given in table (1). It is clear that, span 80 give the lowest volumetric rate of leakage while span85 gives the highest v_b. This result confirms that span80 gives the most stable emulsion globules.

Figure.11 shows the plot of the fraction of leakage F against time using different span80 concentrations, 2.0, 4.0 and 6.0 % v/v. It is clear that, 4.0% v/v of span80 gives the lowest v_b while the 6.0 % v/v gives the highest v_b. From the data obtained, 4.0 % v/v shows the highest stability of the emulsion globules.
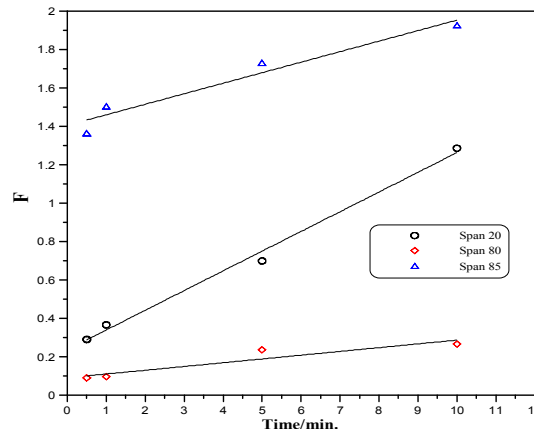

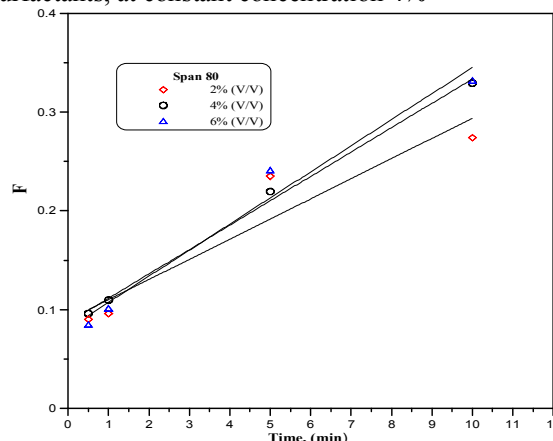**Figure (10)** Determination of v_b with different surfactants, at constant concentration 4%

Figure (11) Determination of v_b with different span 80 concentration

Table (1) the values of v_b different surfactants types and different concentration of surfactant (span 80)

Surfactant type- (4%)	v_b ml/sec
Span20	1.7113×10^{-2}
Span80	3.2×10^{-3}
Span85	0.914×10^{-2}
Span 80 Concentration	v_b ml/sec
2.0 %	0.55×10^{-2}
4 .0%	4.5×10^{-3}
6 .0%	6.3×10^{-2}

6.2 Modeling permeation of uranium through liquid emulsion membrane.

A general permeation model for the permeation of uranium by liquid emulsion membrane using TBP and HDEHP as carriers is presented. The external mass transfer around the drop k_A, the rate of

formation and decomposition of complex at the aqueous /organic interface k_f and the internal mass transfer of carrier and complex in the W/O emulsion drop k_B and k_C respectively were calculated.

To better understand the transfer mechanism, the transfer sequence needs to be examined in more detail. There are actually five steps involved, and each step has a specific mass transfer coefficient. If the transfer is from the external phase to the internal phase as shown in figure (12), the first step is the mass transfer from the external phase to the interface between the external and membrane phase. This is represented by the mass transfer coefficient k_A. The second step is the transfer across this interface, which can be represented by km. The third step is diffusion through the membrane phase represented by the mass transfer coefficient k_C or k_B. The fourth step is the transfer across the interface between the membrane and the internal phase represented by the mass transfer coefficient k_{me}. The last step is the diffusion into the internal phase represented by k_i[20]
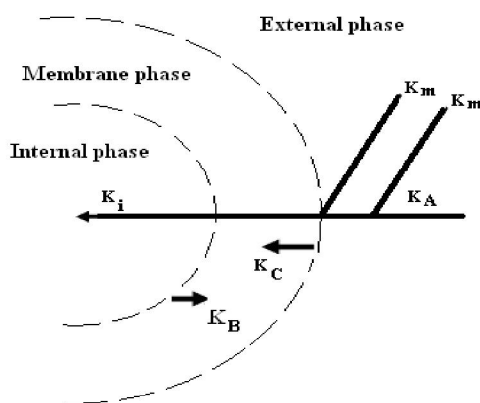

Figure (12) Permeation model based on Teramoto et al.

This mass transfer analysis is built on an immobilized hollow spherical emulsion globule model **(Chan and Lee, 1986)** that assumed a couple countercurrent transport mechanisms. The basic steps of metal permeation through the liquid membrane including the following (i) metal ion diffuses from the external aqueous phase to boundary of membrane phase; (ii) metal ion forms a complex with carrier on the external interface; (iii) the complex diffuses to the center of the emulsion globule; (iv) a stripping reaction occurs when the complex diffuses toward the internal aqueous phase and metal ion is release to the internal aqueous phase; (v) carrier diffuses from the internal interface to the external interface and forms a complex again with metal ion, as shown in figure (13).
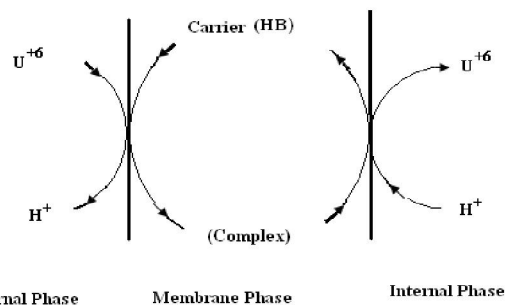

Figure (13) Mechanism of facilitated transport of uranium ion

In order to simplify the mathematics of model development the following assumptions are made: (i) an ideal batch system is under complete mixing and constant temperature operation (ii) carrier and solvent are insoluble in water (iii) physical and transport properties are constant during the permeation process (iv) the droplets dispersed in the external phase as the emulsion globules are immobile and are uniformly distributed.

The values of k_A (the mass transfer around the drop) and k_f (the rate of formation of complex at the aqueous/organic interface) were obtained as follows, the rate determining step of thorium extraction changes depending on the experimental conditions that, $A_{I,o}$ (initial metal ion concentration in the outer phase) is low compared with B_o (initial concentration of carrier), the rate is limited by diffusion of thorium through the external aqueous stagnant film if H_I (hydrogen ion concentration in the outer phase) is sufficiently low and by the reaction at the interface of the emulsion drop if H_I is high, when the reverse reaction is ignored. The extraction rate is expressed as follows:

$$V_I \, dA_I/dt = k_A \, S \, (A_I - A_{I,i}) = k_f \, S \, A_{I,i} \, B_i / H_I$$
$$= A_I \, S / 1/k_A + H_I/k_f \, B_o = K_A \, S \, A_I \quad (6)$$

Integration of equation (6) gives

$$\ln A_I/A_{I,o} = \ln y = -\{K_A \, a_o/(1- \Phi)\}t = -\{3K_A \, \Phi /(1-\Phi)R\}t \quad (7)$$

Where:

$$1/K_A = 1/k_A + H_I/k_f \, B_o \quad (8)$$

Experiments were carried out at various hydrogen ion concentrations with other conditions kept constant. As shown in figure (14), the plot of ln y vs t gives straight lines and K_A's are calculated from their slopes. Figure (15) indicates that the plot of $1/ K_A$ against H_I also give straight lines in accordance with equation (8). The values of k_A and k_f can be calculated from their intercept and slope, respectively.

It was impossible to determine k_B or k_C in the W/O/W multiphase system however; a rough

estimate was made by the extraction experiment using an agitation vessel 7 cm and 14 cm height equipped with magnetic stirrer. 100 ml of the aqueous uranium solution was first introduced into the vessel. Then 20 ml of the W/O emulsion phase was carefully poured over the aqueous phase so as not to disturb the interface. Stirring in the emulsion phase was started at 500 rpm and samples were taken from the aqueous phase for analysis. Under the condition that $A_{I,o}$ was sufficiently high and $H_{I,o}$ was considerably low, the resistance of the aqueous stagnant film diffusion and the interfacial reaction could be neglected. It was anticipated that, the diffusion rate of the complex in the emulsion phase would be fast due to the convection caused by agitation. The experimental results are shown in figure (16)

Uranium concentration in the aqueous phase decreased linearly with time, suggesting that, the rate of the extraction was independent of thorium concentration. This means that, on the aqueous side of the oil layer almost the entire carrier was consumed by complexation with uranium. Thus the extraction rate is expressed by:

$-V_I \, dA_I/dt = k_B \, S \, (B_o-B_i)/2 = k_B \, S \, (B_o-0)/2$ (9)

From Eq.(9) and the data shown in Fig.17 the value of k_B was calculated and also the values of k_C was estimated using the relation,

$k_C = k_B \, (D_C/D_B)$ (10)

The diffusion coefficient of carrier (B) and complex (C) estimated by Wilke-Chang is given in eqs 11 and 12 and shows in Fig. (17).

$A_I/A_{I,o} = S(2\Phi \, D_C)^{0.5} \, (B_o \, H_{III,o} \, t)^{0.5}/3A_{I,o} \, V_I$ (11)

$D_B = 7.4 \times 10^{-8} \, (\O M)^{0.5} \, Tk/ \mu \, V_B^{0.6}$ (12)

Then the oil layer thickness calculated from **$\delta = D_B/k_B$**   (13)

From equation (6) to equation (13) we can calculate the values of various physical parameters and the oil layer thickness with TBP and with HDEHP, as shown in tables (2) and (3).
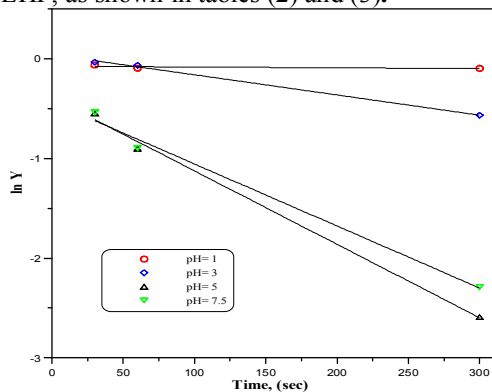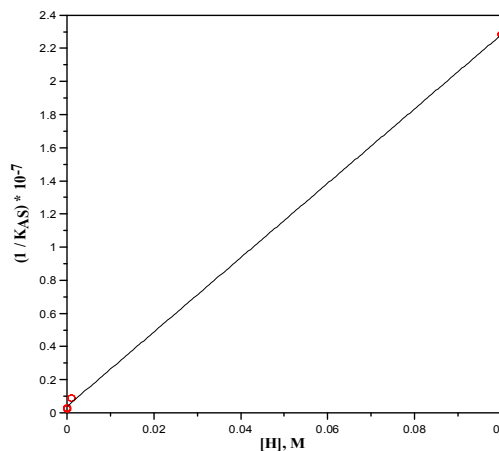

Figure (14) Determination of K_{As}

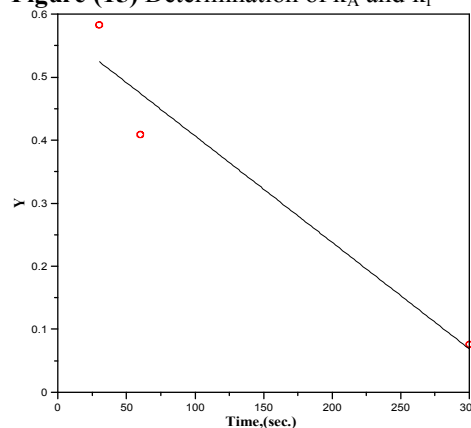**Figure (15)** Determination of k_A and k_f

Figure (16) Determination of k_B
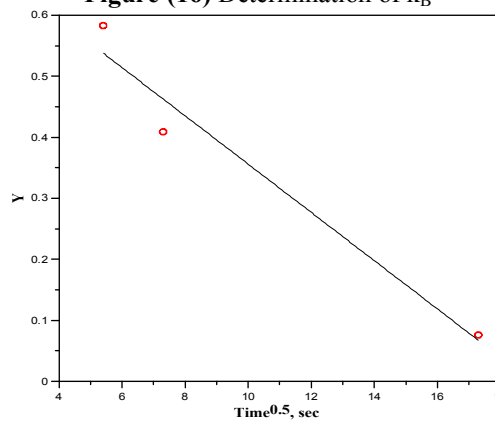
Figure (17) Determination of D_c

Table (2) the values of various physical parameters, with TBP.

Parameters(TBP)	Uranium
k_A	$2.5 * 10^{-6}$ cm/sec
k_{B1}	4.2×10^{-4} cm/sec
k_{C1}	4.6×10^{-10} cm/sec
D_{C1}	8.1×10^{-9} cm²/sec
D_{B1}	$7.3 * 10^{-3}$ cm²/sec
k_{f1}	$4.4 * 10^{-7}$ cm/sec
δ_1	17.3 μm

Table (3) the values of various physical parameters, with HDEHP

Parameters (HDEHP)	Uranium.
K_A	$2.5 * 10^{-6}$ cm/sec
K_{B2}	8.4×10^{-5} cm/sec
K_{C2}	2.9×10^{-9} cm/sec
K_{f2}	$8.9 * 10^{-7}$ cm/sec
D_{C2}	$1.6 * 10^{-8}$ cm^2/sec
D_{B2}	$4.6 * 10^{-4}$ cm^2/sec
δ_2	5.4 µm

7. Conclusion

The present study concerned with uranium extraction from waste solution using LEM techniques. The experimental work showed that: The liquid emulsion membrane consists of (25%HDEHP, 0.005M+75%TBP, 0.01M) as extractant (carrier), Span 80, 4% (v/v) (Sorbitan monooleate) as surfactant agent, Hydrochloric acid (HCl), [1M] as stripping agent. The maximum extraction percent of uranium is about (99.95%) occurred at the selecting operating conditions: pH =5, magnetic stirrer = 500 rpm, the ratio between LEM and external aqueous phase = 20ml: 100 ml, the ratio between organic phase to membrane phase = 0.5 and hydrophilic – lipophilic numbers (HLB) = 4.3.

Experimental data on the batch extraction of uranium by liquid emulsion membrane using TBP and HDEHP as carriers were analyzed on the basis of general permeation model in which the diffusion in the W/O emulsion drop, the external mass transfer around the drop, the rate of the formation, as well as the decomposition of the complex at the aqueous – organic interface, membrane thickness and the leakage of the internal phase to the external phase due to the membrane breakup were taken into account. The verification of the results by using anionic surfactant revealed that the reaction at the organic – aqueous interface is the rate-determining step at slightly high hydrogen ion concentration in the external aqueous phase and also the present model used in this study gives a better understanding and conforming to the experimental results

8. Reference.

1. Karameldin A.," Innovation in radioactive wastewater-stream management: Part one", Int. J. Nuclear Energy Science and Technology, Vol. 1, No. 4, 2005.
2. Merz. E.P, 'Multibarrier effectiveness as the expedient measure for selecting the appropriate stabilization and immobilization procedure for the various waste categories', NATO, Advanced Workshop on Defense Nuclear Waste Disposal in Russia, Implications for the Environment Krasnoyarsk (Russia Federation), June 24–27, (1996) , pp.17–31.
3. Ladeira A.C.Q., C.A. Morais, "Uranium recovery from industrial effluent by ion exchange—column experiments." Minerals Engineering 18 (2005) 1337–1340.
4. Polat H, D. Erdogan, "Heavy metal removal from waste waters by ion flotation", Journal of Hazardous Materials 148 (2007) 267–273, February 2007.
5 Todorovic. M., S. k. Milonjic and J.J.Comor. "A sorption of radioactive ions $^{137}Cs^{2+}$, $^{85}Sr^{2+}$, and $^{60}Co^{2+}$ on natural magnetite and hematite", Scientific Fund of Serbia and the International Atomic Energy Agency, Vienna, Austrian (Contract RB-YU-4933).
6. IAEA, Safety of Uranium and Plutonium Mixed Oxide Fuel Fabrication Facilities, in IAEA Safety Standards for protecting people and the environment. 2010, IAEA: Vienna.
7. Wang-Xiande and Sun-Mingsheng (1990) 'Research and development on the technology for the treatment of low- and intermediate-level liquid radioactive wastes in the last ten years', Journal of Nuclear and Radiochemistry, March, Vol. 12, No. 2, pp.65–71, 84.
8. The web sits of www. Google.com "Liquid Membrane Types".
9. Sznejer G. and A. Marmur "Cadmium removal from aqueous solutions by an emulsion liquid membrane the effect of resistance to mass transfer at the outer oil–water interface" Physicochemical and Engineering Aspects 151 (1999).
10. Li N.N., Separation hydrocarbons with liquid membrane, U.S. Patent 3,410,794 (1968).
11. Mohamd Y. T. "Removal of Hazardous Pollutants from Industrial Waste Solutions Using Membrane Techniques", Ph.D. Thesis, Ain Shams University, 2001.
12. Kulkarni P. S.." Recovery of uranium (VI) from acidic wastes using tri-n-octylphosphine oxide and sodium carbonate based liquid membranes." Chemical Engineering Journal 92 (2003) 209–214.
13. Li Yang , Z. Zhang , Y. Guoa, X. Gaoa, and H. Takeuchi," Uranium(VI) extraction by liquid surfactant membrane with N-alkylcaprolactams as a carrier.", Separation and Purification Technology 47 (2005) 88–94.
14. The web sits of "www.Chemical elements.com".
15. IL PATNAIK P., "Liquid emulsion membranes: Principles, Problems and Application in Fermentation Process", Biotechnelosy Advaaom, Vol. 13, No. 2, pp. 175-208, 1995.
16. Hanna Instruments, "Instruction Manual" 17. Heidolph Instruments Gmbh &Co. "Technical Manual".
18 Liang. P., Y. Bing-hua, FU Xing-long, and W. Li-ming (La(III) Transport in Dispersion Supported Liquid Membrane Including PC-88A as the Carrier and HCl Solution as the Stripping Solution), The Chinese Journal of Process Engineering, Vol.8 No.6, Dec. 2008.
19. von Bergen R.), E. Rogel," A lattice fluid approach to the concept of hydrophile lipophile balance: alkylethoxylated surfactants." Departamento de Quı́mica, Uniĺersidad Simoń Bolı́Íar, Apartado 89000, Caracas, Venezuela Received 22 December 1997; accepted 6 August 1998
20. Chakraborty M.; C. Bhattacharya; S. Datta, " Mathematical Modeling of Simultaneous Copper (II) and Nickel (II) Extraction from Wastewater by Emulsion Liquid Membranes ", " Separation Sciences and Technology Vol. 38, No. 9, pp. 2081–2106, 2003.

12-20-2012