TRANSPORT OF Cr(III), Cd(II), Pb(II), AND Ag(I) IONS THROUGH BULK LIQUID MEMBRANE CONTAINING *p-tert*-BUTYLCALIX[4]ARENE – TETRAETHYLESTER AS ION CARRIER

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ABSTRACT

The study on transport of Cr(III), Cd(II), Pb(II), and Ag(I) through bulk liquid membrane using p-tert-butylcalix[4]arene-tetraethylester as ions carrier has been conducted. The aims of this work are to determine the optimum condition, efficiency, and selectivity of transport of the carriers for those ions. Both optimum condition and efficiency of transport were obtained by determination of the concentration of transported ions with variation of source phase pH, ion carrier concentration, the nature of stripping agent in the target phase, and transport time. The ion transport selectivity of ion carrier was obtained from the ions transport competition experiments using equimolar mixtures. The amount of Cr(III), Pb(II), Cd(II), and Ag(I) that was transported across liquid membrane was about 0, 10, 10 and 50 % respectively after 24 hours, except for Pb(II) (32 hours). The ion carrier is selective for Ag(I) where separation factor to Cd(II) was 16.0, that to Pb(II) was 42.8, and that to Cr(III) was infinite.

Keywords: transport, calix[4]arene, efficiency, selectivity, bulk liquid membrane, heavy metals

INTRODUCTION

Separation techniques for removing, decreasing, and recovering heavy metals from industrial liquid waste are very important because of the growing environmental protection problem. The most common treatment of industrial liquid waste that involves the precipitation of metal as hydroxide, basic-salt or sulfide, is not effective for metal recovery and for dilute waste waters treatment [1]. In this respect, liquid membrane transport method has shown great potential, especially in cases where solute concentrations in waste are relatively low.

Liquid membrane transport is a relative new separation method where ion transported from source phase to receiving phase through membrane that contain ion carriers where processes separation involves extraction, stripping and regeneration in single unit operation. It can be developed for treatment liquid waste especially that contain solute in low concentration [2]. This method has been proposed as a clean technology for their characteristic, such as high selectivity, low energy requirement, continuous processes, the ability to transport species from high concentration to low concentration, low inventory of solvents, etc.[3]. Efficiency and selectivity of transport of ion in this separation processes is very affected by the nature of the system and ion carrier [4,5].

Molecules of *p-tert*-buthylcalix[n]arene with ethyl-ester groups derivatives of calix[n]arene where in synthetic aspect and structure are potential as ion carrier for separation metal ions with liquid membrane transport. A calix[n]arene with ethylester group can be synthesized by reaction of *p-t*-buthylcalix[n]arene and ethyl-2-chloroacetate [4]. Oxygen atoms in this group acts as electron donors for the metals ions in complexation. The compound is soluble in organic solvent such as chloroform, dichloromethane, dichloroethane, etc. [6,7]. Several authors have described the use of *p-t*-calix[n]arene-n-alkylester (n = 4, 6, dan 8) as an *extractant* or ion carrier in extraction or transport of alkali metals [6,7,8,9]. Compound of *p-t*-buthylcalix[4]-arene-tetraethylester is a calix[4]arene derivative that is selective for Na$^+$ and *p-tetramethyl*-butylcalix[4]arene-tetramethylester which is identical of this compound is selective for Ag(I) over Pd(II) in HNO$_3$ 1 mol L^{-1} solution in liquid-liquid extraction [10]. Those report described that this calix[4]arene has been used as *extractant* in separation of metals ion but the use of this compound as ion carrier for heavy metal ions in liquid membrane transport has not been reported yet.

Therefore, the aim of this work was to investigate the transport behavior of Cr(III), Cd(II), Pb(II), and Ag(I) ions through bulk liquid membrane containing *p-tert*-butyl-calix[4]arene-tetraethylester as ions carriers, including the effects of pH, ion carrier concentration, the nature of decomplexant, and transport time on transport efficiency and selectivity. Structure of the ion carrier employed in present work is shown in Fig 1.

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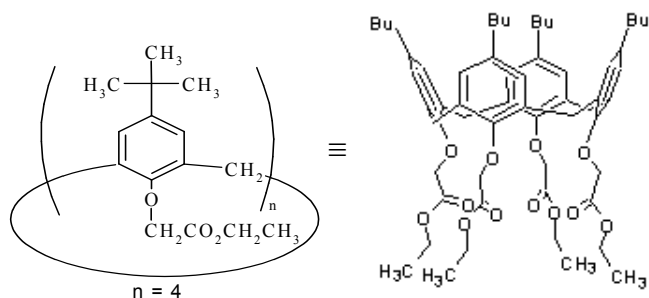Email address : maming_gfr @yahoo.com

Fig 1. Structure of the ion carrier *p-tert*-butylcalix[4]-arene-tetraethylester or 5,11,17,23-tetrakis-(*tert*-butyl)-25,26,27,28-tetrakis(ethoxycarbonilmethoxy)calix[4]-arene

EXPERIMENTAL SECTION

Material

Formaldehyde, *p-tert*-Butylphenol, ethychloro-acetate, chloroform, $Cr(NO_3)_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $AgNO_3$, HNO_3, HCl, H_2SO_4, $Na_2S_2O_3$ and other chemicals were used in synthesis of *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[4]arene-tetra-ethylester. All chemicals used in this study were the highest purity available from Merck or Aldrich chemical companies and were used without further purification. Compound of *p-tert*-butylcalix[4]arene-tetraethylester as ion carrier was synthesized according to a procedure described in a previous paper [4].

Instruments

IR spectrometer (Shimadzu FTIR-8201PC), ^{1}H and ^{13}C-NMR (Jeol JNM-MY500), atomic absorption spectrophotometer (Perkin Elmer 3110), Orion-pH-meter, transport cell (U glass pipe, ϕ_d = 1.25 cm) 30 mL in volume, stirrer bar (1 cm), analytical ballance, and reflux apparatus.

Procedure

Preparation of solution

Chloroform was used as liquid membrane. A stock solution of ions carrier was prepared by dissolving an appropriate amount of *p-tert*-butylcalix[4]arene-tetra-ethylester in chloroform (membrane) and was diluted by this solvent for making solution with different concentration, i.e. $1.0 \times 10^{-4} - 4.0 \times 10^{-4}$ mol L^{-1}. The stock of 100 ppm solutions of each metals ions were made by dissolving an appropriate amount of nitrite of metals compound in 1000 mL of distilled water. A metal ion solution of 1.0×10^{-4} mol L^{-1} was prepared by dilution an appropriate amount of a stock solution in distilled water, used as source phase. The pH of source phase (1.0 − 5.5) were adjusted by addition of HNO_3 solution. Receiving phase were acid solutions with concentrations of 0.1 − 3.0 mol L^{-1} which were prepared by dilution of

concentrated HNO_3, HCl and H_2SO_4 in distilled water. Another receiving phase were solutions of 0.005 – 0.100 mol L^{-1} $Na_2S_2O_3$ which were prepared by dissolving an appropriate amount of $Na_2S_2O_3$ distilled water.

Transport experiment

All transport experiments were done in 29 ± 1 °C. For transporting cations across liquid membrane, a U bulk-type liquid membrane cell was used in this study. The membrane phase (6 mL) in which the carrier was dissolved, was separating two aqueous phase (source and receiving phase, 5 mL). The membrane was stirred at 150 rpm by teflon-coated magnetic bar (1 cm in length). The cell covered with an aluminium foil or plastic sheet to minimize solvent evaporation. After allowing a periodic of time, the metal ion concentration of both *aquous* phase were sampled and measured by atomic-absorption spectroscopy. This procedure was conducted for the experiments of obtaining the optimum pH at source phase, concentration ion carrier in membrane, the nature of the receiving phase, transport time. Selectivity of transport metals ions was done by equimolar experiment transport (concentration each metal ion was 1.0×10^{-4} mol L^{-1}) in optimum condition of single metal ion transport experiments.

RESULT AND DISCUSSION

Percentage of metal ion in both source and receiving phase (%M) was calculated using equation 1, where V, [M] and $[M]_o$ are volume, metal ion concentration (source and receiving phase after transport processes), and initial concentration of metal ion in source phase, respectively [11,12].

$$\%M = \frac{V[M]}{V[M]_o} \times 100 \qquad (1)$$

Transport selectivity of metal ion 1 on metal ion 2 ($\beta_{M1/M2}$) was calculated using equation 2, where $\%M_1$ and $\%M_2$ are percentage metal ion 1 and 2 transported [13].

$$\beta_{M_1/M_2} = \frac{\%M_1}{\%M_2} \qquad (2)$$

Effect of the pH of the Source Phase

The effects of the source phase pH on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I) ions were investigated (Fig. 2). Percentages of the metal ions in source phase decreased with an increasing of pH of source phase up to optimum pH. The results revealed that the optimum transports of those metals ion occur at pH 4.5 − 5.5. It is clear that no transport of both Cr(III) and Pb(II) ion occur, which was different from both Cd(II) and Ag(I) where was transported with low

efficiency. It is probably due to the different in their complex stabilities.

In order to suggest a mechanism of the metals ions transport, the pH value of the source and receiving phase were measured before and after metals ion transport. The change of the pH at source and receiving phase were not significant after transport processes, showing that the mechanism is *symport* transport which

are transported by ion carrier *p-tert*-butylcalix[4]arene-tetraethylester ($L(CO_2Et)_4$) in metal salt form.

Effect of the Concentration of Ion Carrier in Membrane Phase

Fig 3 shows the influence of the concentration of $L(CO_2Et)_4$ in membrane phase on transport efficiency of Cr(III), Cd(II),Pb(II) and Ag(I) ions under the optimum
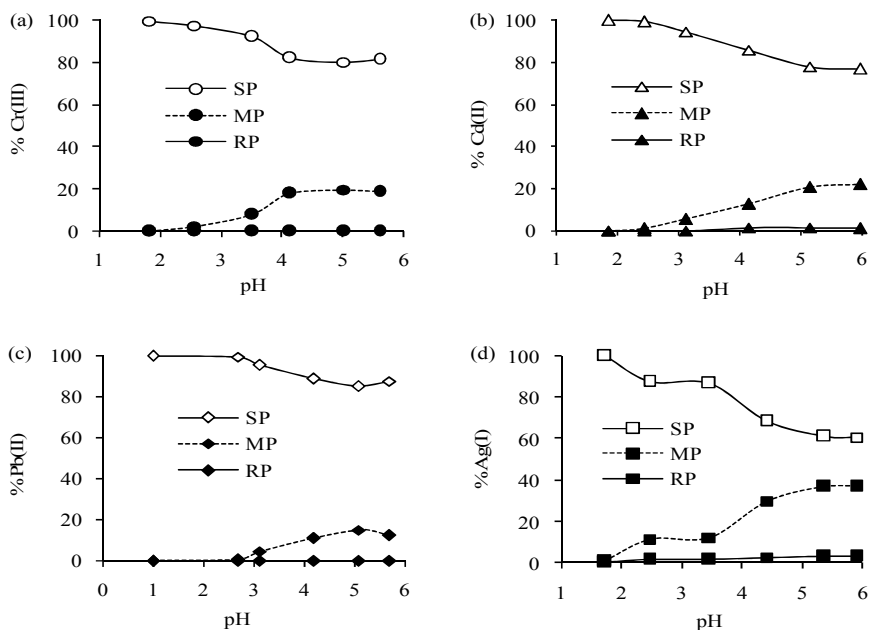

Fig 2. The pH effects of source phase on transport efficiency of metals ions Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) (d) by *p-tert*-butylcalix[4]arene-tetraethylester ($L(CO_2Et)_4$) (SP, source phase; MP, membrane phase; RP, receiving phase).
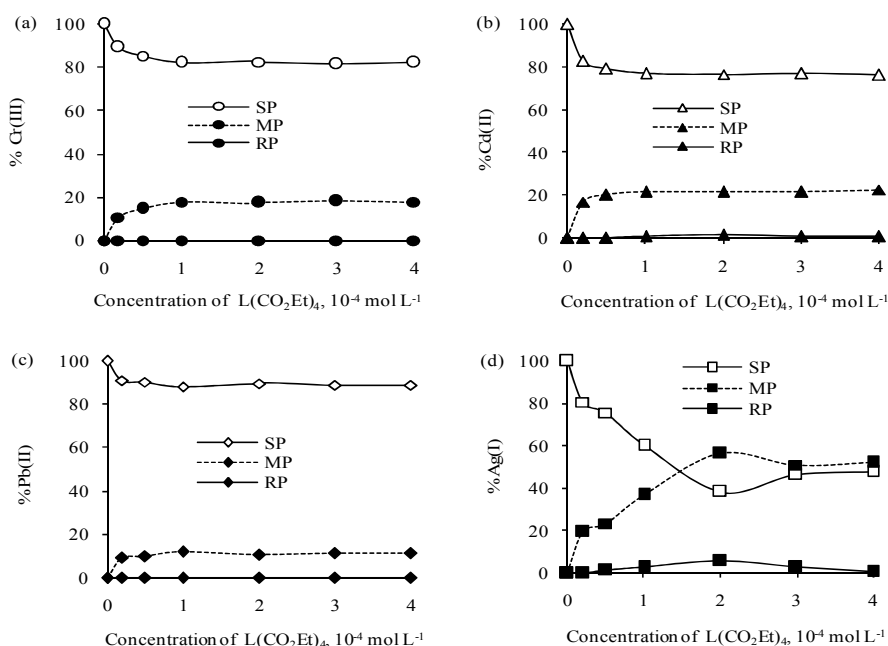

Fig 3. Concentration effects of $L(CO_2Et)_4$ in membrane chloroform on transport of   Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) (d) ions (SP, source phase; MP, membrane phase; RP, receiving phase).

Table 1. Concentration effects of HNO_3 in receiving phase on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I)

Concentrations of HNO_3, mol L^{-1}	Percentages of metals ions in receiving phase after transport				Percentages of metals ions in source phase after transport			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	78.4	93.7	94.5	70.4	0.0	0.0	0.0	1.9
1.0	80.9	92.9	92.4	69.4	0.0	0.2	0.0	7.0
2.0	71.0	89.5	96.6	66.4	0.0	1.0	0.0	10.7
3.0	72.0	91.3	96.5	69.3	0.0	0.8	0.0	7.3

Table 2. Concentration effects of HCl in receiving phase on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I)

Concentrations Of HCl, mol L^{-1}	Percentages of metals ions in receiving phase after transport				Percentages of metals ions in source phase after transport			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	79.7	70.8	93.1	55.0	0.0	8.2	4.2	7.2
1.0	80.5	73.7	93.8	54.2	0.0	3.0	1.4	19.2
2.0	79.8	80.3	96.6	46.4	0.0	1.7	0.0	30.6
3.0	80.8	82.5	97.9	56.4	0.0	0.2	0.0	9.6

Table 3. Concentration effects of H_2SO_4 in receiving phase on transport efficiency of Cr(III), Cd(II), Pb(II), and Ag(I)

Concentrations of H_2SO_4, mol L^{-1}	Percentages of metals ions in receiving phase after transport				Percentages of metals ions in source phase after transport			
	Cr(III)	Cd(II)	Pb(II)	Ag(I)	Cr(III)	Cd(II)	Pb(II)	Ag(I)
0.1	81.7	83.3	95.9	70.5	0.0	1.5	0.0	1.7
1.0	82.9	81.4	96.5	66.7	0.0	6.1	0.0	4.9
2.0	82.5	79.5	95.2	68.1	0.0	8.0	0.9	4.1
3.0	82.0	83.0	96.6	69.0	0.0	1.1	0.1	3.7

Table 4. Concentration effects of $Na_2S_2O_3$ in receiving phase on transport efficiency of Ag(I)

Concentration of $Na_2S_2O_3$, mol L^{-1}	Percentages of Ag(I) in receiving phase after transport	Percentages of Ag(I) in source phase after transport
0.00	68.7	14.2
0.01	62.7	23.1
0.05	32.9	54.9
0.10	65.9	22.8

Experimental conditions (Table 1, Table 2, Table 3, and Table 4): metals ions, 5 mL of 1.0×10^{-4} mol L^{-1}, ; ion carrier, 6 mL of 1.0×10^{-4} mol L^{-1} (for Cr(III), Cd(II) and Pb(II) transport) and 2.0×10^{-4} mol L^{-1} (for Ag(I) transport); source phase pH: 4.0 (Cr(III)), 5.0 (Cd(II) and Pb(II)), 5.5 (Ag(I)); time transport, 24 hours; stirring 150 rpm in speed; receiving phase volume, 5 mL; temperature, 29 ± 1 ^oC.

pH experiment condition. Concentrations of $L(CO_2Et)_4$ in the range of $1.0 - 4.0 \times 10^{-4}$ mol L^{-1} in chloroform were used. It is obvious that, the percent transport of metals raise with an increase in carrier concentration in membrane phase and becomes constant after the optimum concentration. The optimum transport occurred at a concentration of 1.0×10^{-4} mol L^{-1} of $L(CO_2Et)_4$, except for Ag(I) where concentration optimum of ion carrier occurred at 2.0×10^{-4} mol L^{-1}. Thus, these concentrations were chosen as concentration of $L(CO_2Et)_4$ for further study.

Effect of the Nature of Decomplexant Agent in Receiving Phase

The transport of Cr(III), Cd(II), Pb(II), and Ag(I) ions in the presence of different compounds in receiving phase was studied, the results are given in Table 1, 2, 3 and 4. It was observed that the nature and composition of receiving phase were found to have a significant influence on the transport of those ions. The complex of Cr(III) ion can not be decomplexed by HNO_3, HCl or H_2SO_4 in receiving phase. Both 0.1 mol L^{-1} and 2.0 mol L^{-1} are optimum concentration for decomplexation of Cd(II) compounds in receiving phase by using hydrochloric and sulfuric acid, respectively with the transport percentage of 8 %. Optimum condition for decomplexation of complex of Pb(II) in receiving phase is in hydrochloric acid 0.10 mol L^{-1} with 4.2 % in efficiency. Ag(I) ion was the most efficient to be transported where 0.05 mol L^{-1} $Na_2S_2O_3$ was used as decomplexant, its efficiency was about 55 %. In addition, Ag(I) ion was transported with efficiency of 31 % using 2.0 mol L^{-1} hydrochloric as decomplexant. The difference in the transport efficiency
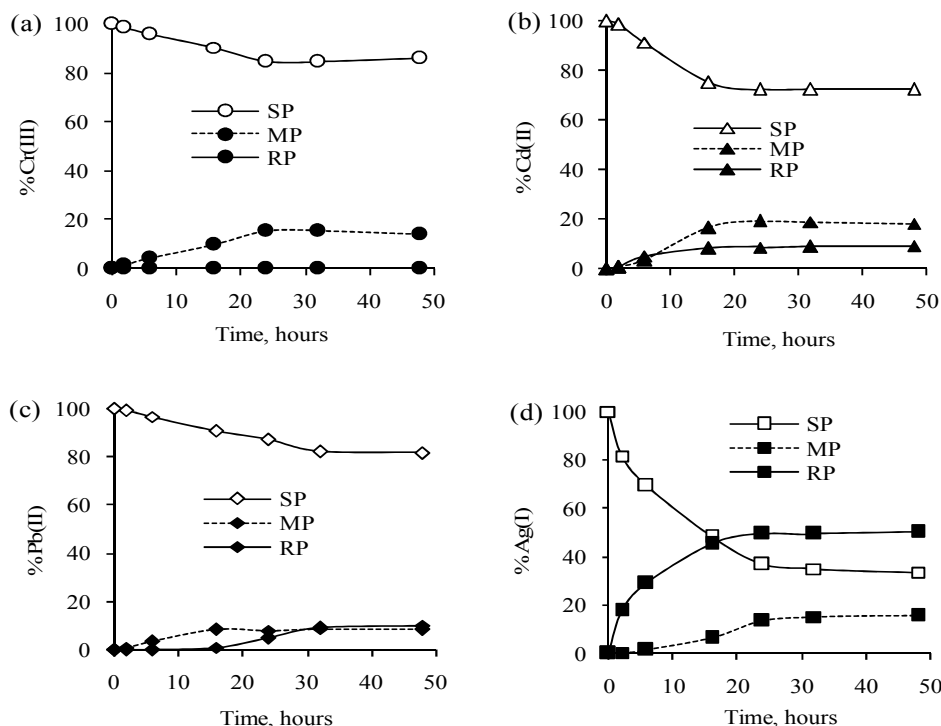
Fig 4. The time effects on transport efficiency of metals ions Cr(III) (a), Cd(II) (b), Pb(II) (c), and Ag(I) (d) by L(CO$_2$Et)$_4$ (SP, source phase; MP, membrane phase; RP, receiving phase).

of Cr(III), Cd(II), Pb(II), and Ag(I) was probably due to the effects of competition in stability of their complex, solubility of their salt in acid decomplexant, anion affinity in receiving phase, and ability of acid-base interaction [3,4,14].

Effect of Time

Fig 4 shows the time dependence of Cr(III), Cd(II), Pb(II), and Ag(I) transport through the liquid membrane under optimum experimental condition. It is obvious that, an increase in time increased the percentage transport metals ion to the receiving phase and decreased the percentage remaining of metals in source phase, except for Cr(III) is detained in membrane for 48 hour transporting. The amount of Cr(III), Cd(II), Pb(II), and Ag(I) transported across liquid membrane was about 0, 10, 10 and 50 % respectively after 24 hour transporting, except for Pb(II) (48 h). After these time, the concentration of the metal ions in aquous phases was relatively constant. The differences of rate transport of the metals ions were probably due to the difference of both lability of cations and diffusity of their complexes.

Transport Selectivity

In order to investigate the transport selectivity of ion carrier to the metals ions, equimolar mixture of the metals ions (4.0 x 10^{-5} mol L^{-1}) were placed in source phase. Then the transport of the mixture was investi-

Table 5. Transport selectivity of Pb(II) and Ag(I) ions by L(CO$_2$Et)$_4$

Metals Ions	Percentages transported and selectivity (β)	
	Optimum condition of Pb(II)	Optimum condition of Ag(I)
Cr(III)	0.0 (~)	0.0 (~)
Cd(II)	0.1 (11.0)	2.9 (16.0)
Pb(II)	1.1	1.1 (42.8)
Ag(I)	0.0 (~)	46.7

Experimental conditions : metals ions, 5 mL of 0.4 x 10^{-4} mol L^{-5}; transport experiments were done in their condition optimum transport each metals ion ; stirring 150 rpm in speed; temperature experiment, 29 ± 1 ^{o}C. The values of β were calculated using equation 2.

gated under optimum condition of each ion. A comparison of the results in Table 5 depicts that the ion carrier of L(CO$_2$Et)$_4$ was selective for Ag(I) where the separation factor of Ag(I) to Cd(II) was 16,0 and that of Ag(I) to Pb(II) was 42,8 and that of Ag(I) to Cr(III) was infinite. The highest transport selectivity of Ag(I) is probably due to the Ag(I) cation size which is match with the cavity of ion carrier, the nature of decomplexant S$_2$O$_3$$^{2-}$ which is soft base prefer to soft acid like Ag(I), and the polarity of Ag(I) complex which is relatively low. Thus, the results suggested the fact that the selectivity of the transport system depends on the nature of decomplexant agent and stability of metal ion complexes.

CONCLUSION

Transport systems for Cr(III) , Cd(II), Pb(II) and Ag(I) ions through a bulk-liquid membrane containing *p-tert*-butylcalix[4]arene-tetraethylester as ion carrier was studied. Transport efficiency of the metals depends on source phase pH, concentration of ions carrier in membrane, nature and concentration of the decomplexant agent in receiving phase, and transport time. Transport selectivity of ion carrier depends on nature of decomplexant agent. The ion carrier   is selective for Ag(I) where separation factor to Cd(II) was 16.0, that to Pb(II) was 42.8, and that to Cr(III) was infinite.

REFFERENCES

1. Harrison, R. M., 1997, *Pollution, Causes, Efects, and Control*, 3rd Ed., 139 – 143, Springer, Berlin.
2. Leon, G. and Guzman, M. A., 2004, *Desalination* 162, 211 – 215.
3. Mulder, M., 1996, *Basic Principles of Membrane Technology*, 2nd ed, Kluwer Academic Publisher, Netherlands, 1 - 6.
4. Maming, Jumina, Siswanta, D., and Sastrohamidjojo, 2007, *Indo. J. Chem.*, 7(2), 172 – 179.
5. Tayeb, R., Zaghbani, A., Tingri, S., Seta, P., and Dahbi, M., 2007, *Desalination*, 204, 234-240.
6. Bohmer, V., 1995, *Angew Chem. Int. Ed. Engl*, 31, 713 – 745.
7. Gutsche, C. D., 1998, *Calixarenes Revised,* The Royal Society of Chemistry (Series Editor : J. Fraser Stoddart, FRS), USA.
8. Fanni, S., Armaud, N. F., McKervey, M. A., Sehwing, A. J., and Ziat, K., 1996, *Tetrahedron Lett.*, 37, 7975 – 7978.
9. Ye, Z. F., Wang, Y. P., Liu, Y. S., Jiang, Z. L., She, X., Zhu, L. G., and Shi, X. F., 1999, *J. Memb. Sci.*, 163, 367 – 372.
10. Ohto, K., Murakami. E., Shinohara, T., Shiratsuchi, K., Inoue, K., and Iwasaki, M., 1997, *Analitica Chimica Acta*, 341, 275 – 283.
11. Akhond, M. and Tashkhourian, J., 2003, *Bull. Corean Chem. Soc.*, 24, 489 –493.
12. Abbaspour, A. and Tavakol, F., 1999, *Anal. Sci.,*, 15, 1005 – 1008.
13. Bartsch, R. A. and Way, J. D., 1996*, Chemical Separation with Liquid Membranes,   ACS Symposium Series 642*, American Chemical Society, New York.
14. Huheey, J. E., 1978, *Inorganic Chemistry, Principles Structure and Reactivity*, 2nd Ed., 278-288, 348-390, 489-498, Harper International Edition, New York.