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Transport of Pb(II) by supported liquid membrane containing p-tert-butyl calix[4]amine derivative as carrier

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ABSTRACT

Facilitated transport of Pb(II) ions in acidic medium, across a supported liquid membrane (SLM) by using 5,11,17,23-tetra-tert-butyl, 25,27-bis(benzylamino etoxy)-26,28-dihydroxycalix [4]arene as carrier, dissolved in kerosene, has been investigated. The parameters studied are Pb(II) ions concentration in the feed phase, HCl concentration in the stripping phase, and solvent effect in the membrane phase. The Celgard 2500 membrane was used as the solid support. A Danesi mass transfer model was used to calculate the permeability coefficients for each parameter studied. Also, AFM technique and contact angle measurements were used to characterize the surface morphology of the prepared Celgard 2500-carrier **1** SLM.

Keywords: Facilitated transport; Supported liquid membrane; Pb(II) transport; Calixarene

1. Introduction

Membrane processes have been mainly developed as a potentially valuable technology for the separation and concentration of charged or neutral species [1]. Among the processes being developed, supported liquid membranes (SLMs), porous supports whose pores are impregnated with a solvent, have been showing tremendous potential in different applications [2–5]. The SLM technique is a combination of three simultaneously occurring processes: molecule extraction from the feed phase to the SLM, diffusion through SLM, and re-extraction to the received phase. Among their numerous advantages, the minimal amount of solvent needed and the fact that extraction and stripping steps which are combined into a single step are specific [2,6]. However, the instability of the liquid membrane in the pores of the inert membrane support (carrier lost) is the main disadvantage [7–10].

Lead (Pb) is one of the most ubiquitously spread toxic metals [11–13]. Lead is extensively used in many manufacturing processes, therefore without an appropriate treatment of pb-containing wastewaters it may contaminate the ecosystem through surface water, underground water, and soil. Due to its high toxicity, a lot of effort has been expended on developing techniques to effectively remove Pb from water [14–19].

Calixarenes and derivatives can be used as receptors to recognize a wide variety of ions and guest molecules, forming host-guest or supramolecular complexes [20,21]. This ability has been exploited in different fields and calixarenes and derivatives have been used extensively as selective ligands for a wide range

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of metal ions in liquid–liquid extraction, in selective transport, as ionophores in ion-selective electrodes and as cromophores in optical sensing [22,23]. Several studies have been published which make a case for calixarene derivatives as extractants for toxic metals [20,24–26]. There are a lot of SLM transport studies which are using calixarenes as a carrier [27–32]. Shamsipur et al. investigated that facilitated transport of silver ion across a SLM by calix[4]pyrroles, as selective ion carriers, dissolved in kerosene [31]. Fontas et al. studied a new macrocyclic compound based on thiacalix[4]arene bearing three amide substituents is investigated for the extraction of gold and palladium in chloride media [32]. However, in recent years there are not too much SLM studies for Pb(II) ions which are using calixarenes as carrier.

In this work, the co-transport of Pb(II) from aqueous solution through SLM has been investigated. 5,11,17,23-tetra-tert-butyl, 25,27-bis(benzylamino etoxy)-26,28-dihydroxycalix[4]arene **1** is the carrier ligand (as presented in Fig. 1), which was synthesized according to literature method [33]. Celgard 2500 membrane was used as the solid support.

2. Experimental

2.1. Reagents

The chemical reagents used in supported liquid membrane experiments were Pb(II) nitrate, xylene, toluene, HCl were obtained from Merck Co., 2-nitrophenyl octyl ether from Fluka, kerosene from Aldrich and used without further purification. The polymeric film Celgard 2500 (thickness: 25 μm, porosity 55%) was obtained from Celgard Inc. (Germany). The 5,11,17, 23-tetra-tert-butyl, 25,27-bis(benzylamino etoxy)-26, 28-dihydroxycalix[4]arene **1** compound was used as a carrier ligand in supported liquid membrane experiments.

2.2. Experimental apparatus

The flat-sheet SLM apparatus was used in this study. The membrane module was produced from Teflon material as two different cells (Fig. 2). The membrane was placed between two cell compartments which were tightly clamped. The total volume of the feeding and stripping solutions was 45 cm^3 for each. Digital magnetic stirrers (Yellow line MST basic, Germany) were used to homogenize feeding and stripping solutions.

2.3. Surface characterization

In order to characterize the SLM, AFM techniques and contact angle measurements were used. AFM images were obtained by using Veeco diCaliber instrument. The speed of scanning was 2 kHz. Contact mode of AFM in air was used to investigate the membrane surface morphology.

The sessile drop method was used to measure the contact angle of the Celgard 2500-carrier ligand **(1)** membrane [34,35]. A 3.5 μL droplet of distilled water was placed on the membrane surface by means of a

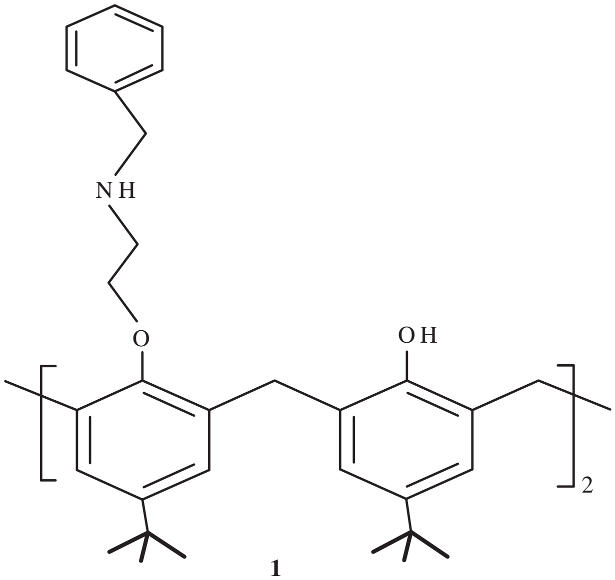

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Fig. 1. Chemical structure of carrier 1.

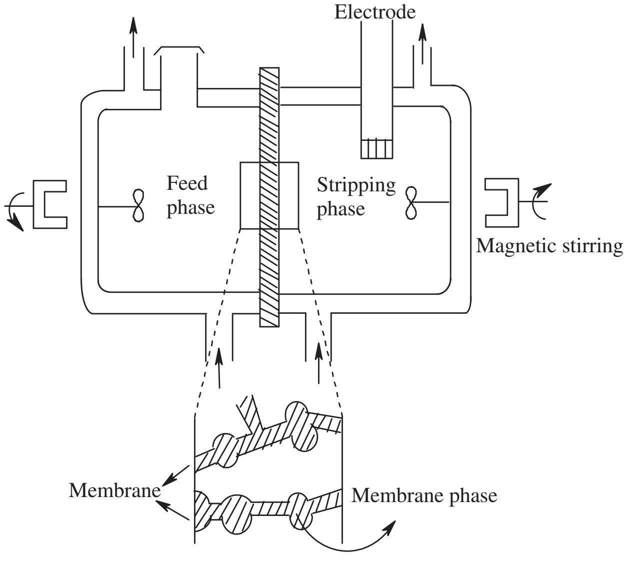

Fig. 2. Supported liquid membrane apparatus.

0.10 cm^3 syringe and contact angle was measured by a horizontal beam comparator (KSV CAM 200).

2.4. Experimental procedure

The transport experiments were carried out in a permeation cell consisting of two identical cylindrical compartments (half-cell volume: 45 cm^3) (Fig. 2), previously described [36]. The supported liquid membrane consisted of a thin, microporous polypropylene film (Celgard 2500; thickness: 25 μm, porosity 55%) immobilizing the solution of carrier **1** in organic solvents. Aqueous 1.0×10^{-3} M $Pb(NO_3)_2$ solution was used as the feed phase and 1 M HCl was used as the stripping phase. The soaking time of the Celgard 2500 membrane is 24 h and the stirring speed is chosen as 600 rpm in the all transport experiments. The measurements were performed at a constant temperature of 25˚C at least twice and effective membrane area was 9.08 cm^2. Samples (1.0 cm^3) were taken at regular time intervals from the tanks of both the sides, and Pb(II) concentrations in the feed and stripping phases were analyzed by using an atomic absorption spectrophotometer (Perkin Elmer AAnalyst 200 model). In the SLM experiments, transport duration was 5 days.

In this study, the influences of the feed and stripping phase concentrations, the solvent, and the carrier concentration parameters are examined on the transport efficiency.

The influence of the studied parameters on the transport of Pb(II) was evaluated by means of permeability coefficient (P). P which can be defined according to Eq. (1) [34].

$$P = \frac{\varepsilon}{100}\frac{dC}{C}\frac{1_V}{dt^A} \tag{1}$$

By integration of the Eq. (1), the following Eq. (2) is obtained:

$$\ln\frac{C_i}{C} = \frac{\varepsilon}{100}\frac{A}{V}Pt \tag{2}$$

where P is the permeability coefficient (cm/s), C_i is the initial concentration of Pb(II) in the feed phase, and C is the concentration of Pb(II) in the feed phase at time t (s). ε is the porosity of supported liquid membrane (55%), A is the effective membrane area (9.08 cm^2), V is the volume of the feed phase (cm^3).

The knowledge of P values allows establishing the initial membrane flux (J_i) according to Eq. (3).

$$J_i = PC_i \tag{3}$$

3. Results and discussion

3.1. Effect of Pb(II) concentration of feed phase

In order to assess the influence of the Pb(II) concentration on its transport through the SLM, the transport experiments were carried out at four different concentrations in the range of 1×10^{-4}–1×10^{-3} M. Results are shown in Figs. 3, 4 and also in Table 1. It is observed in Fig. 3 that during 5 days of transfer duration, upon increasing the concentration of Pb(II) from 1×10^{-4} to 1×10^{-3} M in the feed phase, the permeability coefficient (P) increased from 0.5×10^{-6} to 8.02×10^{-6} cm/s.

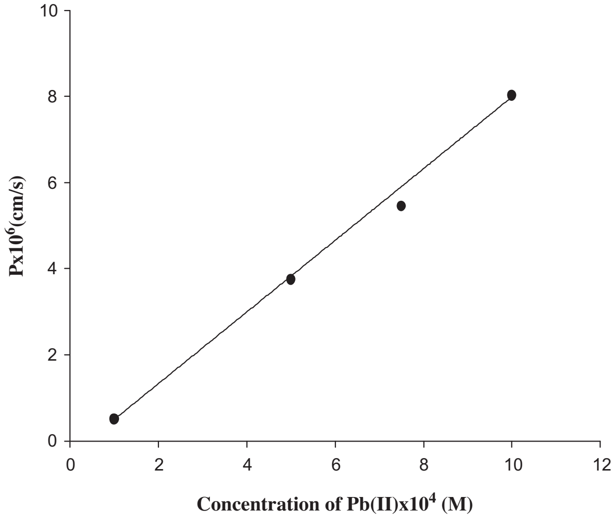

Fig. 3. Effect of feed phase concentration on the transport of Pb(II). (Stripping phase: 1 M HCl, membrane support: Celgard 2500, membrane liquid: 1×10^{-4} M carrier 1 in kerosene, Stirring rate: 600 rpm).

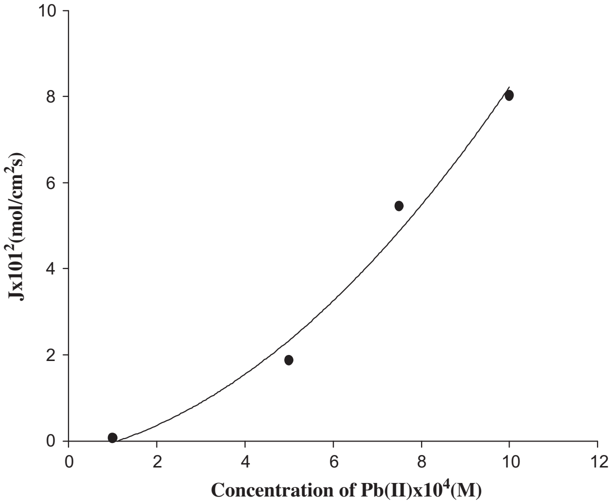

Fig. 4. Effect of feed phase concentration on the transport of Pb(II) by using flux values. (Stripping phase: 1 M HCl, membrane support: Celgard 2500, membrane liquid: 1×10^{-4} M carrier 1 in kerosene, Stirring rate: 600 rpm).

Table 1
P and *J* values for the transport of Pb(II) ion through SLM by using different feed phase concentrations

Concentration (mol/L)	$P \times 10^6$ (cm/s)	$J \times 10^{12}$ (mol/cm^{2}s)
1.0×10^{-4}	0.5	0.05
5.0×10^{-4}	3.74	1.87
7.5×10^{-4}	5.45	4.09
10.0×10^{-4}	8.02	8.02

The influence of the Pb(II) concentration on the transport is evaluated by using flux values, which are defined according to Eq. (3). The flux values were in the range of 0.06×10^{-12}–8.02×10^{-12} mol/cm^2 s for different concentration of Pb(II) from 1×10^{-4} to 1×10^{-3} M (Fig. 4). In transport studies, flux values are so low, so the donor phase medium is diluted. This phenomenon conforms to the other manuscripts [31,37]. The obtained result is in accordance with the expected trend because according to the Eq. (3) higher concentration results in a higher flux. In other words, as the Pb(II) concentration increases, the complexation rate in feed phase-SLM interface increases too, and related with this, the decomplexation rate in the SLM-stripping phase interface increases.

3.2. Effect of HCl concentration on Pb(II) ion transport

In order to determine the effect of the concentration of HCl solution as the stripping phase on Pb(II) ion transport, 0.1, 0.5, 0.8, 1.0, 1.2 M HCl were used. Fig. 5 shows the permeability values calculated according to Eq. (2). In addition J and P values are shown in Table 2.

As it can be seen in Fig. 5, the maximum permeability value was obtained for 1.0 M HCl. However, the permeability values showed a tendency to decrease at lower or higher concentrations of HCl. In literature, it was reported that increasing stripping phase concentration facilitates to achieving an optimum permeability value [7,38,39]. The reason for this may be explained that as the concentration of the solute increases, the solution reaches saturation value and therefore solubility decreases.

3.3. Effect of solvents on Pb(II) ion transport

When the different solvents were used carrier **1**, the values of permeabilities obtained were also different. It has been previously pointed out that the nature of solvent has a great influence on the transport efficiency through bulk liquid membranes [40–43]. The calculated permeability values are given in Fig. 6. In addition J and P values are shown in Table 3.

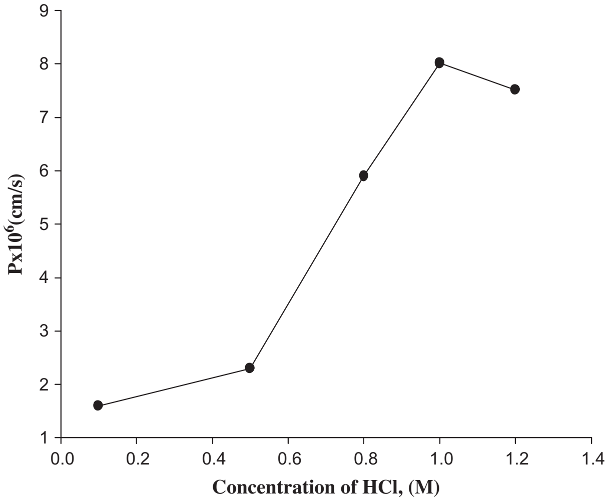

Fig. 5. Effect of stripping phase concentration on the transport of Pb(II). (Feed phase: 1×10^{-3} M Pb(NO$_3$)$_2$, membrane support: Celgard 2500, membrane liquid: 1×10^{-4} M carrier 1 in kerosene, Stirring rate: 600 rpm).

It is apparent from the results that the permeability values are remarkably different in different solvents and found in the order of 2-NPOE > kerosene > xylene > toluene. In the case of xylene and toluene, the values of permeabilities are smaller than that of 2-NPOE and kerosene. Nitrophenyl alkyl ethers (NPHE-hexyl; NPOE-octyl) were used because they

Table 2
P and *J* values for the transport of Pb(II) ion through SLM by using different stripping phase concentrations

Concentration (mol/L)	$P \times 10^6$ (cm/s)	$J \times 10^{12}$ (mol/cm^{2}s)
0.1	1.60	1.60
0.5	2.30	2.30
0.8	5.90	5.90
1.0	8.02	8.02
1.2	7.52	7.52

Table 3
P and *J* values for the transport of Pb(II) ion through SLM by using different organic solvents

Solvent	$P \times 10^6$ (cm/s)	$J \times 10^{12}$ (mol/cm^{2}s)
2-NPOE	16.30	16.30
Kerosene	8.02	8.02
Xylene	2.07	2.07
Toluene	1.45	1.45

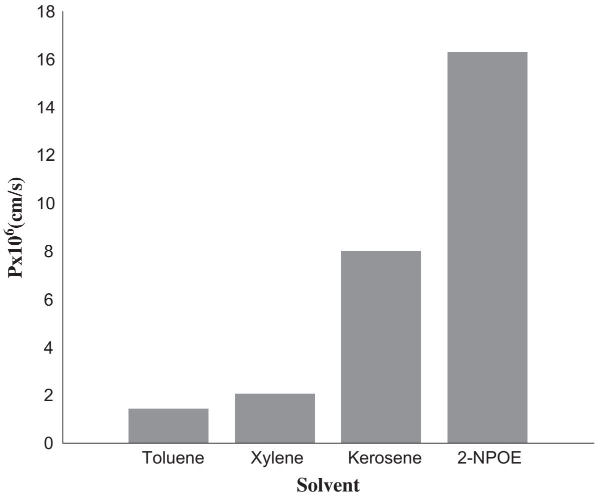

Fig. 6. Effect of different solvents on the transport of Pb (II). (Feed phase: 1×10^{-3} M $Pb(NO_3)_2$, Stripping phase: 1 M HCl, membrane support: Celgard 2500, membrane liquid: 1×10^{-4} M carrier 1 in different solvents, Stirring rate: 600 rpm).

lead to a stable membrane due to their very low solubility in water [44–46,28]. But their disadvantage is only their high-cost. Therefore, we used kerosene as a membrane solvent in our SLM studies.

Also, the polymeric support materials used are very important in the stability of the membrane. The requirement for a good polymeric support are high porosity, small pore size, good mechanical strength, chemical resistance, thinness, hydrophobicity, and low cost.

3.4. Characterization of the SLM

AFM technique and contact angle measurements were used to characterize the surface morphology of the prepared Celgard 2500-carrier **1** SLM. The AFM pictures of SLM formed with Celgard 2500 and Celgard 2500 + carrier **1** are shown in Fig. 7. As can be seen in Fig. 7a and b, prepared Celgard 2500 + carrier **1** SLM is more porous than Celgard 2500 membrane. This difference between the Celgard 2500 membrane and prepared Celgard 2500 + carrier **1** SLM was due to the inclusion of the carrier **1**.

Contact angle measurement is used to investigate the hydrophilicity of the material surfaces [34]. In the present study, contact angle measurement taken at room temperature for SLM containing Celgard 2500 + carrier **1** in 2-NPOE was found to be 86.3°. If the solid surface is hydrophilic, the contact angle will be less than 90° [47]. Therefore, prepared Celgard 2500-carrier **1** SLM is hydrophilic.

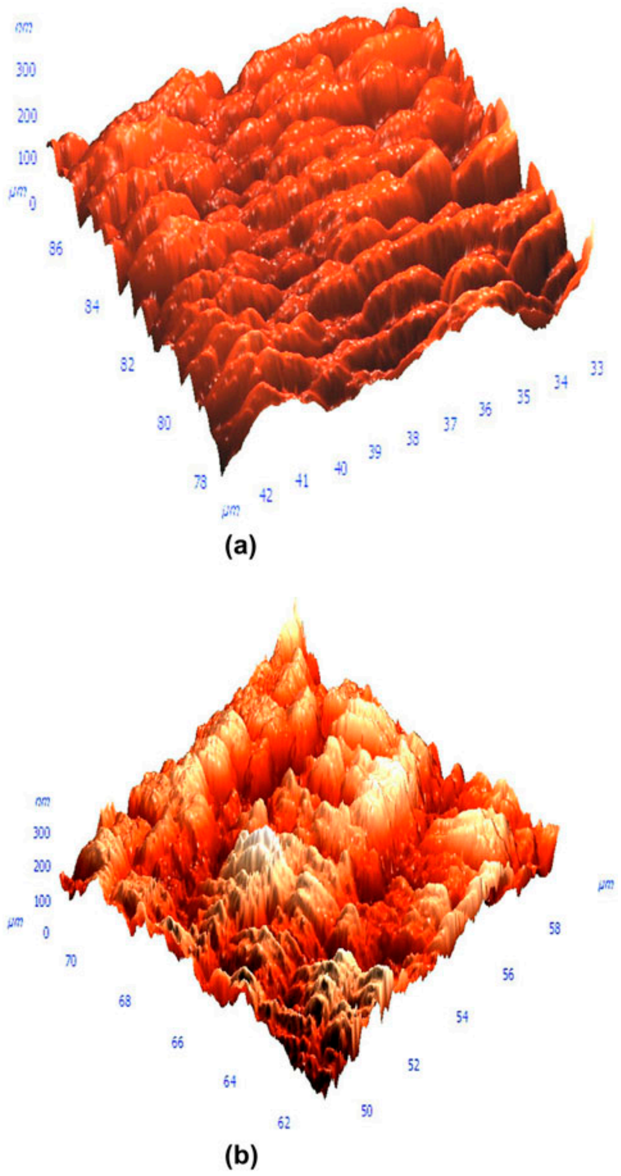

Fig. 7. AFM images of Celgard 2500 membrane (a) and SLM containing Celgard 2500 + carrier 1 in 2-NPOE (b).

4. Conclusions

The Pb(II) ions can be effectively transported through supported liquid membranes containing calix[4]arene derivative **1**. The efficiency of the methods depends on various parameters, i.e. concentration of feed phase, concentration of stripping phase, and the type of solvent. A Danesi mass transfer model was used to calculate the permeability coefficients for each parameter studied. As the Pb(II) concentration increases, the complexation rate in donor/membrane interface increase, and depending on this, the decomplexation rate in the membrane/acceptor interface increase. It is apparent from the results that the permeability values are remarkably different in different solvents and found in the order of 2-NPOE > kerosene > xylene > toluene. Also, AFM technique and contact angle measurements were used to characterize the surface morphology of the prepared Celgard 2500-carrier **1** SLM. As a result of the characterization studies, the difference between the surface at Celgard 2500 membrane was due to the inclusion of the carrier **1** and the prepared Celgard 2500-carrier **1** SLM is hydrophilic.

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References

[1] O.K. Senhadji, S. Tingry, P. Seta, M. Benamor, Selective extraction of Cr(VI) over metallic species by polymer inclusion membrane (PIM) using anion (Aliquat 336) as carrier, Desalination 258 (2010) 59–65.

[2] L.J. Lozano, C. Godínez, A.P. de los Ríos, F.J. Hernández-Fernández, S. Sánchez-Segado, F.J. Alguacil, Recent advances in supported ionic liquid membrane technology, J. Membr. Sci. 376 (2011) 1–14.

[3] G. Muthuraman, K. Palanivelu, Transport of textile dye in vegetable oils based supported liquid membrane, Dyes Pigm. 70 (2006) 99–104.

[4] S. Happel, R. Streng, P. Vater, W. Ensinger, Sr/Y separation by supported liquid membranes based on nuclear track micro filters, Radiat. Meas. 36 (2003) 761–766.

[5] L.J. Lazano, C. Godinez, F.J. Alguacil, Facilitated transport of vanadium by supported liquid membranes, Hydrometallurgy 80 (2005) 196–202.

[6] X.J. Yand, A.G. Fane, K. Soldenhoff, Comparison of liquid membrane processes for metal separations: permability, stability and selectivity, Ind. Eng. Chem. Res. 42 (2003) 392–403.

[7] S. Altin, Y. Yildirim, A. Altin, Transport of silver ions through a flat-sheet supported membrane, Hydrometallurgy 103 (2010) 144–149.

[8] R.M. Izatt, G.A. Clark, J.D. Bradshaw, J.D. Lamb, J.J. Christensen, Macrocycle facilitated transport of ion in liquid membrane system, J. Sep. Pur. Rev. 15 (1986) 21–72.

[9] L. Boyadzhiev, Z. Lazarova, Liquid membranes (liquid pertraction) in membrane separations technology, principles and applications, Membr. Sci. Technol. 2 (1995) 283–352.

[10] J.A. Calzado, C. Palet, M. Valiente, Metal affinity liquid membrane. Part III: Characterization of transport selectivity, J. Sep. Sci. 24 (2001) 533–543.

[11] W.J. Liu, F.X. Zeng, H. Jiang, X.S. Zhang, Adsorption of lead (Pb) from aqueous solution with Typha angustifolia biomass modified by SOCl$_2$ activated EDTA, Chem. Eng. J. 170 (2011) 21–28.

[12] I. Fisher, D.J. Pain, V.A. Thomas, Review of lead poisoning from ammunition sources in terrestrial birds, Biol. Conserv. 131 (2006) 421–432.

[13] H. Cheng, Y. Hu, Lead (Pb) isotopic finger printing and its applications in lead pollution studies in China: A review, Environ. Pollut. 58 (2010) 1134–1146.

[14] M.Z. Barciszewska, M. Szymanski, E. Wyszko, J. Pas, L. Rychlewski, J. Barciszewski, Lead toxicity through the leadzyme, Mutat. Res. Rev. Mutat. Res. 589 (2005) 103–110.

[15] Q. Chen, Z. Luo, C. Hills, G. Xue, M. Tyrer, Precipitation of heavy metals from wastewater using simulated flue gas: Sequent additions of fly ash, lime and carbon dioxide, Water Res. 43 (2009) 2605–2614.

[16] N.V. Medvidovic, J. Peric, M. Trgo, M.N. Muzek, Removal of lead ions by fixed bed of clinoptilolite – the effect of flow rate, Micoporous Mesoporous Mater. 105 (2007) 298–304.

[17] Y. Maeda, Y. Morinaga, Y. Tomita, K. Kobayashi, Photoanodic response of iron oxide electrode in aqueous solution and its application to Pb^{2+} removal under visible light irradiation, Electrochim. Acta 54 (2009) 1757–1761.

[18] A. Nagendran, A. Vijayalakshmi, D.L. Arockiasamy, K.H. Shobana, D. Mohan, Toxic metal ion separation by cellulose acetate/sulfonated poly (etherimide) blend membranes: effect of polymer composition and additive, J. Hazard. Mater. 155 (2008) 477–485.

[19] O.F. Agunbiade, B.I. Olu-Owolabi, K.O. Adebowale, Phytoremediation potential of Eichornia crassipes in metal-contaminated coastal water, Bioresour. Technol. 100 (2009) 4521–4526.

[20] N. Benosmane, B. Guedioura, S.M. Hamdi, M. Hamdi, B. Boutemeur, Preparation, characterization and thermal studies of polmer inclusion cellulose acetate membrane with calix[4] resorcinarenes as carriers, Mat. Sci. Eng. C 30 (2010) 860–867.

[21] F. Arnaud-Neu, M.J. Schwing-Weill, Calixarenes, new selective molecular receptors, J. Synth. Met. 90 (1997) 157–164.

[22] D.N. Reinhoudt, Durable chemical sensors based on field-effect transistors, Sensor. Actuat. B-Chem. 24 (1995) 197–200.

[23] S. Kunsagi-Mate, L. Nagy, G. Nagy, I. Bitter, L. Kollar, Complex Formation of Fe(II) and Fe(III) Ions with Octafunctionalized *C*-Methyl-calix[4]resorcinarene Possessing $-\mathrm{OCH_2COOH}$ (K) Moieties, J. Phys. Chem. B 107 (2003) 4727–4731.

[24] N. Benosmane, S.M. Hamdi, M. Hamdi, B. Boutemeur, Selective transport of metal ions across polmer inclusion membranes (PIMs) containing calix(4)resorcinarenes, Sep. Purif. Technol. 65 (2009) 211–219.

[25] I.H. Gubbuk, O. Gungor, H.K. Alpoguz, M. Ersoz, M. Yılmaz, Kinetic study of mercury (II) transport through a liquid membrane containing calix[4]arene nitrile derivatives as a carrier in chloroform, Desalination 261 (2010) 157–161.

[26] A. Yilmaz, A. Kaya, H.K. Alpoguz, M. Ersoz, M. Yilmaz, Kinetic analysis of chromium(VI) ions transport through a bulk liquid membrane containing *p-tert*-butylcalix[4]arene dioxaoctylamide derivative, Sep. Purif. Technol. 59 (2008) 1–8.

[27] D.R. Raut, P.K. Mohapatra, S.A. Ansari, A. Sarkar, V.K. Manchanda, Selective transport of radio-cesium by supported liquid membranes containing calix[4]crown-6 ligands as the mobile carrier, Desalination 232 (2008) 262–271.

[28] J.K. Kim, J.S. Kim, Y.G. Shul, K.W. Lee, W.Z. Oh, Selective extraction of cesium ion with calix[4]arene crown ether through thin sheet supported liquid membranes, J. Membr. Sci. 187 (2001) 3–11.

[29] D.R. Raut, P.K. Mohapatra, S.A. Ansari, V.K. Manchanda, Evaluation of a calix[4] bis-crown-6 ionophore-based supported liquid membrane system for selective 137Cs transport from acidic solutions, J. Membr. Sci. 310 (2008) 229–236.

[30] T. Oshima, K. Inoue, S. Furusaki, M. Goto, Liquid membrane transport of amino acids by a calix[6]arene carboxylic acid derivative, J. Membr. Sci. 217 (2003) 87–97.

[31] A.A. Amiri, A. Safavi, A.R. Hasaninejad, H. Shrghi, M. Shamsipur, Highly selective transport of silver ion through a supported liquid membrane using calix[4]pyrroles as suitable ion carriers, J. Membr. Sci. 325 (2008) 295–300.

[32] A. Zaghbani, R. Tayeb, M. Dhahbi, M. Hidalgo, F. Vocanson, I. Bonnamour, P. Seta, C. Fontas, Selective thiacalix[4]arene bearing three amide groups as ionophore of binary Pd(II) and Au(III) extraction by a supported liquid membrane system, Sep. Purif. Technol. 57 (2007) 374–379.

[33] A. Yilmaz, B. Tabakci, M. Tabakci, New diamino derivatives of p-tert-butylcalix[4]arene for oxyanion recognition: Synthesis and complexation studies, Supramol. Chem. 21 (2009) 435–441.

[34] A. Yilmaz, G. Arslan, A. Tor, I. Akin, Selectively facilitated transport of Zn(II) through a novel polymer inclusion membrane containing Cyanex 272 as a carrier reagent, Desalination 277 (2011) 301–307.

[35] F. Garbassi, M. Morra, E. Occhiello, Polymer Surfaces. From Physics to Technology, Wiley, New York, 1994.

[36] H.C. Visser, D.N. Reinhoudt, F. Dejong, Carrier-mediated transport through liquid membranes, Chem. Soc. Rev. 23 (1994) 75–81.

[37] F.J. Alguacil, H. Tayibi, Carrier-facilitated transport of Cd(II) from a high-salinity chloride medium across a supported liquid membrane containing Cyanex 923 in Solvesso 100, Desalination 180 (2005) 181–187.

[38] H.G. Nowier, N. El-Said, H.F. Aly, Carrier-mediated transport of toxic elements through liquid membranes: Transport of Cd (II) from high salinity chloride medium through supported liquid membrane containing TBP/cyclohexane, J. Membr. Sci. 177 (2000) 41–47.

[39] G.H. Rounaghi, M.S. Kazemi, H. Sadeghian, Transport of silver ion through bulk liquid membrane using macrocyclic and acylicligands as carriers in organic solvents, J. Inclusion Phenom. Macrocyclic Chem. 60 (2008) 79–83.

[40] H.K. Alpoguz, A. Kaya, I. Sener, Carrier-mediated transport of Hg(II) through bulk and supported liquid membranes, J. Macromol. Sci. Part A: Pure Appl. Chem. 44 (2007) 1061–1068.

[41] H.K. Alpoguz, A. Kaya, H. Deligoz, Liquid membrane transport of Hg(II) by an azocalix[4]arene derivative, Sep. Sci. Technol. 41 (2006) 1155–1167.

[42] H.K. Alpoguz, A. Kaya, A. Yilmaz, M. Yilmaz, Study on the transport kinetics of Hg^{2+} through calix-oligomer bulk liquid membrane, J. Macromol. Sci. Part A: Pure Appl. Chem. 44 (2005) 577–586.

[43] H.K. Alpoguz, S. Memon, M. Ersoz, M. Yilmaz, Transport of Hg^{2+} through bulk liquid membrane using a bis-calix[4]arene nitrile derivative as carrier: Kinetic analysis, New J. Chem. 26 (2002) 477–480.

[44] F. Arnaud-Neu, V. Böhmer, J.F. Dozol, C. Grüttner, R.A. Kraft, D.O. Mauprivez, H. Rouquette, M.J. Schwing-Weill, N. Simon, W. Vogt, Calixarenes with diphenylphosphorly acetamide functions at the upper rim. A new class of highly efficient extractants for lanthanides and actinides, J. Chem. Soc. Perkin Trans. 2(6) (1995) 1175–1182.

[45] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud-Neu, S. Fanni, M.J. Schwing, R.J.M. Egbering, F. Jong, D.N. Reinhoudt, Synthesis, complexation, and membrane transport studies of 1,3-alternate calix[4]arene-crown-6 conformers: A new class of cesium selective ionopheres, J. Am. Chem. Soc. 117 (1995) 2767–2777.

[46] J.F. Dozol, N. Simon, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, D.D. Marc DCC/DESD/SEP, R. M. Macias DIST/UDC, A solution for cesium removal from high-salinity acidic or alkaline liquid waste: The crown calix[4]arenes, Sep. Sci. Technol. 34 (1999) 877–909.

[47] R. Förch, H. Schönherr, A. Tobias, A. Jenkins, Surface Design: Applications in Bioscience and Nanotechnology, Wiley-VCH, Weinheim, 2009, p. 471.