

SELECTIVE SEPARATION AND REMOVAL OF LEAD(II) ION FROM MULTICOMPONENT SYSTEM THROUGH BLMs SUPPORTED BY FATTY ACIDS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

Selective separation and removal of a metal species from complex matrices of other species is of critical importance in separation sciences and especially in industrial processes. The selectivity and efficiency of Pb(II) ion removal from an aqueous solution in the presence of Ni(II), Zn(II), Co(II), Cu(II), and Cd(II) ions as competing ions in a multi-component aqueous source phase through bulk liquid membrane system were investigated. The influence of the palmitic and oleic acid as supporting surfactants in the membrane phase on the removal of Pb(II) ions was also analyzed. Dicyclohexano-18-crown-6 dissolved in chloroform, proved to be a selective and efficient carrier for Pb(II) ions. In the optimized procedure, 3 hours of equilibrium time was required to achieve the maximum removal efficiency. It was found, that removal of Pb(II) ions was achieved without significant reduction in the efficiency compared to the liquid membrane transport of a single-component system. None of these cations interfered with Pb(II) removal. The presence of the oleic and palmitic acid in the membrane phase increase the content of Pb(II) removed to the receiving phase. In optimal transport conditions, more than 97% efficiencies for the removal of Pb(II) were obtained for a system supported by oleic acid. The excellent efficiency and high degree of selectivity for the Pb(II) ion removal by the proposed BLM system, reveals its potential application for the selective removal, concentration, and purification of lead ions from its different mixtures.

KEYWORDS: liquid membrane transport; Pb(II) ion removal; dicyclohexano-18-crown-6; oleic acid; palmitic acid

INTRODUCTION

Lead, Pb(II) is a toxic metal that is mainly introduced into the environment through various industrial applications such as batteries, fuels, paints, constructions, and foundries. Because of its toxicity and non-biodegradable nature, controlling lead in the environmental samples is of major importance [1]. Due to the increasing industrial use of lead and its serious hazardous effect on human health, the investigation of new methods for selective removal, concentration, and purification of Pb(II) ion from its mixtures is of special interest. A variety of separation methods such as chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation-flocculation, flotation, solvent extraction, and liquid membrane transport have been utilized to remove toxic heavy metal ions from the environmental and biological systems [2]. New technologies in wastewater treatment are precisely membrane processes. Liquid membrane is known as a green technology because of its green characteristics such as being eco-friendly and its low consumption of organic

solvent [3]. A liquid membrane system involves an organic liquid membrane that serves as a semipermeable barrier between two aqueous phases, the source phase (SP) and receiving phase (RP). Macrocycles as extractants were successfully used for metal ions separation in solvent extraction and as ion carriers in transport through liquid membranes. Along with cryptands, crown ethers are an important class of ion carriers [4,5]. With regard to molecular recognition and selective binding, macrocyclic and chelating ligands are extensively studied in the transport of alkali and alkaline earth metal cations across liquid membranes [6,7]. The interaction of the ligand and metal cation depends on the nature of the metal cation but also depends on the number, distance, and orientation of the donor atoms of the ligand that are structurally accessible to the complexed cation [8]. The Pb(II) ions are removed from the source phase (SP) to the receiving phase (RP) via a membrane phase (MP). The movement of charged species (carrier-metal complex) through the hydrophobic liquid membrane is accomplished by the presence of a large

lipophilic anion, such as picrate, in the source phase [9]. In this technique, the extraction and stripping steps are combined into a one-step process and, due to its simplicity, low cost, and efficiency, it plays an important role in biology, chemistry, and separation sciences [10,11,12].

Surfactant systems have been recognized as very useful alternatives for improving analytical methodologies and development of new concepts in analytical chemistry [13]. The addition of a long chain fatty acid, reduces the degree of carrier loss and also could have a cooperative effect in the uphill transport of the metal cation through the ligand membrane. A possible reason for this cooperative behavior would be the existence of some proton donor–acceptor interaction between the lipophilic fatty acid (as proton donor) and the donor atoms of the ligand (as proton acceptor), which can impart a greater degree of lipophilicity to the ligand–metal ion complex, in order to facilitate the cation transport through the liquid membrane [14]. It has been shown that the addition of long chain fatty acids to the membrane phase could not only overcome the carrier loss but also provide a cooperative effect in the uphill transport of metal ions through the liquid membrane via imparting a greater lipophilicity to the carrier species [15]. It is well-known that the transport selectivity of mixture ions are significantly dependent on the nature of the macrocyclic ligand and fatty acids.

In this paper, we studied the efficiency of Pb(II) removal from an aqueous solution in the presence of Ni(II), Zn(II), Co(II), Cu(II), and Cd(II) ions as competing ions in a multi-component aqueous source phase through the bulk liquid membrane system. We propose an environmental removal technique for heavy metal ions based on selective and spontaneous transfer supported by fatty acids. In the presence of picrate ion as a hydrophobic counter ion in the source phase and disodium-EDTA ion as a selective stripping agent and Triton X-100 as a suitable synergistic co-stripping agent in the receiving phase, the Pb(II) ion found to transport selectively and quantitatively across the chloroform bulk liquid membrane in 3 h. The addition of fatty acids to the membrane phase leads to better transport efficiency.

MATERIALS AND METHODS

For every transport experiment, two aqueous solutions and one non-aqueous solution (membrane), were prepared, as follows.

Source solutions were prepared from:

- Standard Pb(II), Ni(II), Zn(II), Co(II), Cu(II) and Cd(II) solution (1000 mg/L), Merck

- Picric acid ($C_6H_3N_3O_7$), $c = 1 \cdot 10^{-3}$ mol/L, 99%, Kemika
- Formic acid buffer solution (pH=3), prepared from HCOOH and NaOH (g.r., Merck)

Membrane solution were prepared from:

- Organic solvents: chloroform ($CHCl_3$)
- Macrocyclic ligands: dicyclohexano-18-crown-6 (DCH18C6), 18-crown-6 (18C6)
- Fatty acids: oleic, palmitic, stearic acids

Receiving solution were prepared from:

- Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L)
- Disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)
- Acetate buffer solution (pH=5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck)

TRANSPORT PROCEDURE

Cylindric glass container, i.e. "transport cell", with inner diameter of 5 cm and central glass tube (2 cm in diameter), have been used for this study.

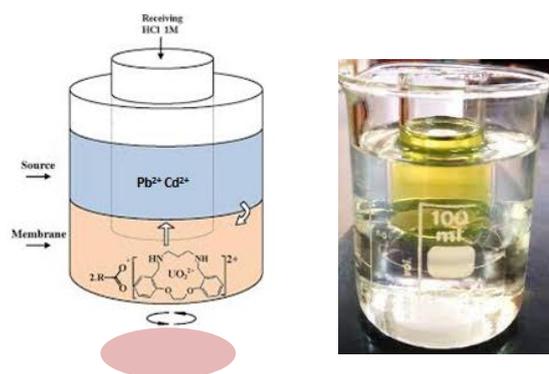


Figure 1. a) Scheme of a cylindrical glass vessel, "Transport Cell"; b) Homemade transport cell used in experiments [16]

Central tube provides physical separation of two aqueous phases: source phase (SP), and receiving phase (RP). Membrane phase (MP) lies under the aqueous phases and connects them. The source phase (SP) contained 10 mL of a mixture of tested Pb(II) ions ($1 \cdot 10^{-3}$ mol/L, $1 \cdot 10^{-4}$ mol/L) and metal cations Ni(II), Zn(II), Co(II), Cu(II), Cd(II) ($1 \cdot 10^{-3}$ mol/L, $1 \cdot 10^{-4}$ mol/L). The receiving phase (RP), which is outside the central tube, contained a stripping agent. The membrane phase (MP) contained a suitable ligand ($1 \cdot 10^{-3}$ mol/L) dissolved in organic solvent; the membrane layer lies beneath the aqueous phases and connects them. The membrane phase is mixed with a magnetic stirrer so that under these conditions the contact surfaces between the aqueous phases are

straight and precisely defined [17]. pH measurements of aqueous solutions were performed using the pH meter (GLP31 Crison Instruments). Quantification of metal ions removed during the transport experiments was obtained by Flame Atomic Absorption Spectrometry technique, using the instrument Perkin Elmer AAnalyst 200.

RESULTS AND DISCUSSION

The results of the measured content of removed Pb(II) ions in the final phase, for the among different mixture, was tested by performing the transport of Ni(II), Zn(II), Co(II), Cu(II), Cd(II) metal cations containing Pb(II) ions in their mixtures. From the results shown in Figure 1. there is no serious interference and a significant reduction in the efficiency compared in the transport process of Pb(II) ions, from different mixtures with the liquid membrane transport of a single-component system. The highest efficiency removed Pb(II) ions was achieved for a single-component system, approximately 60 % removed Pb(II) ions compared to other mixtures of metal ions. Dicyclohexano-18-crown-6 (DC18C6) due to its very lipophilic character and its corresponding cavity size for selective complexation with Pb(II) ion proved to be a selective and efficient carrier for Pb(II) removal via BLM.

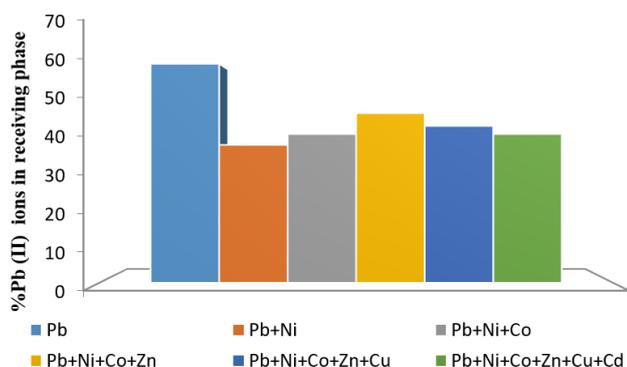


Figure 2. Amount of Pb(II) ions removed from various mixtures through BLMs; SP: $1 \cdot 10^{-3}$ mol/L mixture of metal ions and $1 \cdot 10^{-3}$ mol/L picrates; MP: organic solvent chloroform contained $1 \cdot 10^{-3}$ mol/L of DCH18C6; RP: Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L) disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)

It was found that a major role of the fatty acids is to contribute to the transport process by increasing in lipophilicity of crown-cation complex through some proton-donor and proton-acceptor interactions between surfactant (as proton donor) and oxygen atoms of ligand (as proton acceptor) which can facilitate the cation transport through liquid membrane and also serve to inhibit any bleeding of partially

species from the organic membrane phase into either of the aqueous phases. To evaluate the influence of adding a fatty acids on Pb(II) ion removal; stearic, palmitic and oleic acid were added into the membrane phase.

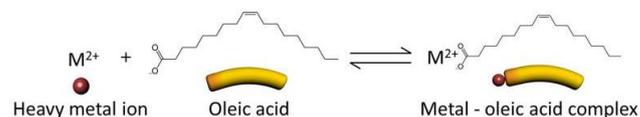


Figure 3. Schematic illustration of the spontaneous phase transfer-mediated selective removal of heavy metal ions using oleic acid

The influence of the palmitic and oleic acid as surfactant ($1 \cdot 10^{-3}$ mol/L) in the membrane phase containing a known concentration of the carriers; 18C6 and DCH18C6 ($1 \cdot 10^{-3}$ mol/L) and organic solvents (chloroform) on the removal of Pb(II) ions was also investigated. The results are summarized in Figure 4. As it is evident, the efficiency of Pb(II) ion transport increases in the presence of the surfactants with 18-crown-6 ether as a ligand for metal ions in chloroform as liquid membrane. But, in the case with DCH18C6 as a ligand for metal ions, the transport decreases in the presence of the surfactants, therefore, the cooperative behavior in the presence of these long-chain hydrocarboxylic acids is decreased. This may be due to the formation of hydrogen bonds between the donor atoms of the ligand and the acidic proton of the carboxylic acids in these solvent systems which results in formation of a weaker complex between the Pb(II) ion and the ligand in the presence of these fatty acids. Another possibility is the formation of micelles of the fatty acids in the membrane phase which trap the ligand-cation complex and, therefore, the transport rate of Pb(II) decreases.

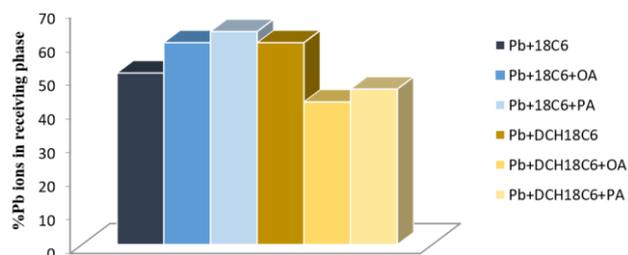


Figure 4. Comparison of the Pb(II) removal efficiencies in presence of oleic acid (OA) and palmitic acid (PA) (source phase: $1 \cdot 10^{-3}$ mol/L mixture of metal ions and $1 \cdot 10^{-3}$ mol/L picrates; organic solvent chloroform contained 18C6 and DCH18C6 ($1 \cdot 10^{-3}$ mol/L); receiving phase: Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L) disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)

The efficiency of Pb(II) removal from an aqueous solution in the presence of Ni(II), Zn(II), Co(II), Cu(II) ions as competing ions in a multi-component aqueous source phase through the bulk liquid membrane system in the presence of oleic acid were investigated. The effect of Pb(II) ions concentration in the source phase on Pb(II) ions removal under optimal experimental conditions was investigated and the results are shown in Figure 5. As seen, the removal efficiency is increased with decreasing concentration of Pb(II) ions in the source phase. It may be due to the carrier loading effect in the membrane [18]. Optimal transport conditions were obtained for a system with decreasing concentration supported by oleic acid. The excellent efficiency and high degree of selectivity for the Pb(II) ions showed a system with lowest concentration of Pb(II) ions in source phase with more than 97% removed Pb(II) ions (Figure 5).

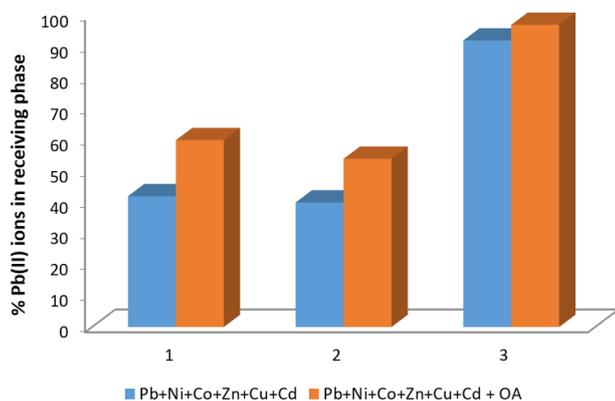


Figure 5. Efficiencies of the Pb(II) removal in presence of oleic acid (OA) for varying concentration of metal mixtures source phase: (1) $1 \cdot 10^{-3}$ mol/L, (2) $2,5 \cdot 10^{-4}$ mol/L and (3) $1 \cdot 10^{-4}$ mol/L M^{2+} ; organic solvent chloroform contained $1 \cdot 10^{-3}$ mol/L DC18C6 with oleic acid $1 \cdot 10^{-3}$ mol/L, receiving phase; Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L) disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)

Considering that the system with the lowest concentration of Pb (II) ions, achieved the highest level of removal of these metal ions, with DCH18C6 supported by oleic acid, (Figure 5), these results were compared with the same competitive transport systems in the presence of stearic and palmitic acid. Selective separation and removal of Pb (II) ions were efficient in BLM systems supported by this fatty acids. The efficiency of removed Pb (II) ions increases in the presence of fatty acids following the order: palmitic < stearic < oleic acid (65 < 77.4 < 97%).

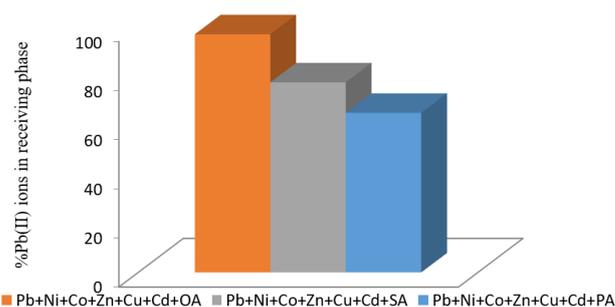


Figure 6. Efficiencies of the Pb(II) removal in presence of oleic acid (OA), palmitic acid (PA), stearic acid (SA) source phase, M^{2+} conc. ($1 \cdot 10^{-4}$ mol/L),

50 mL organic solvent chloroform contained $1 \cdot 10^{-3}$ mol/L DC18C6 with oleic, palmitic and stearic acid ($1 \cdot 10^{-3}$ mol/L); receiving phase: Triton X-100 surfactant ($1,4 \cdot 10^{-3}$ mol/L) disodium-EDTA ($1 \cdot 10^{-3}$ mol/L)

CONCLUSIONS

The BLMs experiments of Pb(II), Zn(II), Cu(II), Co(II), and Cd(II), metal cations using 18C6 and DCH18C6 as a carrier in organic membranes, supported by fatty acids, showed that it is possible to separate and removed Pb(II) ions from the different mixtures of metal ions. The transport rate of the Pb(II) cation is influenced by the nature and also the composition of the membrane solvents. Removal of Pb(II) ions from different mixtures were achieved without significant reduction in the efficiency compared to the liquid membrane transport of a single-component system. The results show that the transport rate of the Pb(II) ion increases in the presence of stearic acid, palmitic acid, and oleic acid as supported surfactants in the membrane phase. The simplicity, efficiency, and selectivity for Pb(II) ions demonstrate its potential applicability to selective removal, concentration, or purification of the Pb(II) ions from its different mixtures.

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