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Supported liquid membrane-based simultaneous separation of cadmium and lead from wastewater

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ABSTRACT

This work is aimed at the investigation of simultaneous extraction and recovery of heavy metals (cadmium and lead) from aqueous solutions through a coconut oil-based Flat Sheet Supported Liquid Membrane (FS-SLM). Environmentally benign nature of coconut oil is the prime advantage in this technique. *N*-Methyl-*N*,*N*-dioctyloctan-1-ammonium chloride (Aliquat 336) is an ideal carrier agent for the transportation of the said heavy metals. Ethylenediaminetetraacetic acid (EDTA) was selected as stripping agent keeping in view its metal chelating capacity. Initially, the performance of Supported Liquid Membrane (SLM) was investigated only for the transportation of cadmium, or precisely Cd(II). A porous polymeric solid membrane *viz*., polyvinylidene fluoride (PVDF) was used as a support in order to hold and contain the membrane liquid in the SLM structure. The size of the pores in the support is 0.2 μm. The effects of various operating conditions *viz*. concentration of the carrier in membrane phase, concentration of stripping agent, pH of feed phase *etc*. were studied. The optimum process conditions for the transportation of Cd(II) were: 0.5% (v/v) Aliquat 336 in coconut oil as membrane phase, 0.015 M EDTA as stripping agent, and pH of 6.5 in the feed phase. The initial feed concentration was 5 ppm and the total transportation time was 10 h. Transportation of another heavy metal *viz*., lead (Pb) was also carried out with the above optimum process conditions. Finally, simultaneous transportations of both metals (lead and cadmium) were studied with various molar ratios (Cd:Pb) in the feed. The optimum extraction and recovery of cadmium were found as 79% and 67%, respectively, and that of lead were found as 84% and 78%, respectively, in simultaneous transportation. Lead was observed to be preferentially transported through SLM due to its favorable electronic configuration.

1. Introduction

Contamination of highly toxic and non-biodegradable heavy metals into the environment through discharge of industrial effluents is a major problem [1–2]. Cadmium and lead are two such heavy metals released by some industries such as pulp and paper, chloro-alkali, battery, fertilizer, alloy and steel, paints and pigments, petrochemicals, and mining activities [3–4]. These heavy metals, once released into the environment, get accumulated in living organisms through the consumption of water. Toxicity of heavy metals, in general, causes severe damages to human health [3–6]. The World Health Organization (WHO) has reported allowable limits of these heavy metals in drinking water *viz*. 3 ppb and 10 ppb for cadmium and lead, respectively [7]. Hence, separation of these heavy metals from effluents is necessary before their discharge to the environment. SLM-based separation process is considered one of the most viable technologies for this purpose. The scope of simultaneous extraction and re-extraction (stripping) of the target species, the requirement of very less amount of extractant (carrier), and ability to recover trace amount of solute from dilute but bulky solutions are the major reasons for the viability of SLM process.

In SLM, a hydrophobic porous polymeric membrane holds the membrane liquid (*a.k.a* solvent or membrane phase) into its micro-pores by capillary action. The metal ions are transported from feed phase to strip phase through the membrane liquid [8]. Many research groups have studied the liquid membrane (LM) based separation of various heavy metals from aqueous solution. Altin et al. [9] employed SLM for facilitated transport of cadmium from aqueous feed solution. They used 0.06*M* EDTA stripping solution with 0.1 M Aliquat 336 as carrier and toluene as a solvent. The efficiency of transport of Cd(II) ions was reported as 82%. Ashraf et al. [10] studied the transport of Cd(II) through SLM and reported the role of concentration of proton in the feed solution as well as the carrier agent, *viz*. tri-ethanolamine (TEA). They observed the optimal concentrations of proton and carrier as

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2.0 M HCl in feed solution and 3.0 M in membrane phase, respectively. They achieved the maximum flux at 8.4×10^{-7} mol cm^{-2} s^{-1} using 0.1 M NaOH as strip solution. McDonald et al. [11] used 5% *n,n*-dioctyloctan-1-amine (alamine 336) or Aliquat 336 as carrier agent and EDTA as stripping agent to achieve 80% extraction of lead. Separation of Pb(II) ions was also reported by Gill et al. [12] who used SLM with TEA in cyclohexanone supported in microporous polypropylene films. A comparative study of transportation of Cd(II) and Pb(II) through the SLM and polymer inclusion membrane (PIM) was carried out using 7-(4-ethyl-1-methylocty)-8-hydroxyquinoline (Kelex 100) as carrier agent and kerosene as solvent [13]. A chemical model for the transportation of metals was proposed and a very high separation of metal ions was obtained in terms of flux and stability. On the other hand, Tripathy et al. [14] studied the performance of an acidic carrier, di-2-ethyl hexyl phosphoric acid (TOPS-99) for separation of Cd(II) with H_2SO_4 as a stripping agent. They obtained the maximum flux with pH 6.0 of feed solution and 0.1 M carrier. Anupama et al. [15] investigated the separation of Pb(II) in SLM process with neutral carrier, tributyl phosphate (TBP) as extractant and NaOH as stripping agent. The initial concentration of feed phase was 25 ppm and the transportation was successfully completed within 4 h. A permeability coefficient of 1.146×10^{-5} was obtained. Although, some studies on separation of cadmium and lead have been conducted with acidic carrier [14] as well as with neutral carrier [15] with corresponding and compatible stripping agents, majority of the researchers have reported the alkaline Aliquat 336 as the suitable carrier combined with EDTA as stripping agent for transportation of both lead (II) and cadmium (II). All these studies were reported for transportation of a single metal (either Cd or Pb) with a few exceptions as well *viz*., Aguilar et al. [13] and Rounaghi et al. [16]. The selective separation of lead (II) cation from aqueous solutions containing other interfering cations was carried out by Rounaghi et al. [16]. They used a bulk liquid membrane (BLM) composed of dicyclohexano-18-crown-6 (DC18C6) as the carrier agent in chloroform as a solvent.

Conventional hazardous solvents have been employed in most of the separation studies based on the SLM technique. Very few researchers have explored the scope of environmentally benign vegetable oils as solvent in SLM-based solute transportation. Some researchers reported the separation of textile dyes and phenol using various vegetable oils as solvent in SLM for wastewater treatment [17–19]. Chakraborty et al. [8] separated Hg(II) using coconut oil as the membrane liquid and reported 93.2% extraction. The SLM comprising coconut oil as solvent was quite stable (up to 98 h) with regard to flux. This is because coconut oil has high viscosity, high boiling point, high chemical stability and its physical compatibility with support material PVDF is also high. In our previous work, we used 1.0% (v/v) *N-N*-dimethyloctylamine (DMOA) in coconut oil and obtained 92% extraction of the cadmium, but recovery was only 14%. Although the extraction was very high, recovery was very difficult due to the formation of highly stable cadmium-carrier complex that could not be decomplexed even in the presence of metal chelating agent, EDTA.

Suren et al. [20] studied the simultaneous removal of lead and mercury via a hollow fiber supported liquid membrane (HF-SLM) and demonstrated the role of extractants in the selective removal of individual metals present in the effluents. They found an acidic extractant, *viz*. di-2-ethylhexyl phosphoric acid (D2EHPA), as the best extractant for lead cation (Pb^{2+}) whereas Aliquat 336 was the best for $HgCl_4^{2-}$ using single module hollow fiber membrane (HFM). They required two HFMs in sequence for selective separation of lead (Pb^{2+}) and $HgCl_4^{2-}$. The first module contained D2EHPA followed by the second containing Aliquat 336.

In the present work single FS-SLM containing Aliquat 336 was employed to investigate the selective transport of one metal over the other, present as a mixture in the same feed. Various industries, such as battery, paint and chloro-alkali, release lead and cadmium in a varied range of 0.11–4.0 ppm (see Table 1) [4,21]. We have selected 0.5 vol% Aliquat 336 in coconut oil for the transportation of Cd(II) and optimized various operating parameters. Finally, simultaneous transportation of both Cd(II) and Pb(II) was accomplished with the same set of LM and at the said optimized parameters. The selectivity of individual metals was investigated by varying their molar ratios in the feed solution.

Table 1
Various industries releasing Cd and Pb in their effluents.

Name of the industry	Cd (ppm)	Pb (ppm)	Reference
Chloro alkali	1.1	2.2	[4]
Battery	4.01	0.12	[21]
Paint	0.23	0.11	[21]

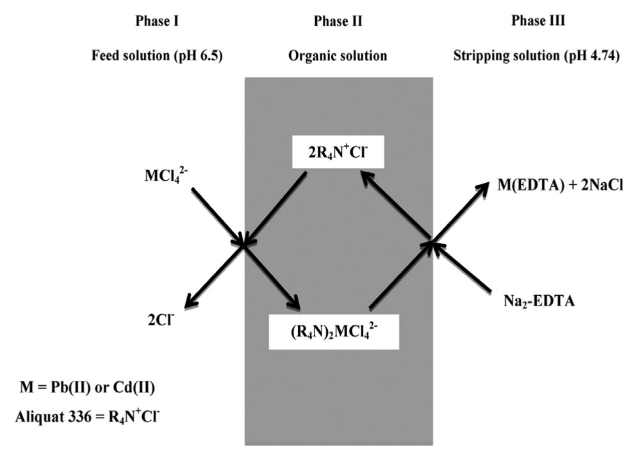

Fig. 1. Schematic diagram of co-transport mode for metals (Cd and Pb) transportation.

2. Theoretical background

Three phase studies were performed using FS-SLM configuration. Na_2-EDTA was selected as the stripping agent for re-extraction of Cd(II) or Pb(II) from the membrane phase [3]. Concentration of stripping phase was identified for efficient stripping. Subsequently, the effects of other parameters such as pH of feed and stripping phases, carrier concentration and initial feed concentration were optimized for maximum possible yield.

In the presence of HCl in the feed solution, metal chloride (MCl_2) transforms into anion (MCl_4^{2-}) where M is either Cd or Pb. The carrier agent (Aliquat 336, expressed as $R_4N^+Cl^-$) itself is a stable material and it forms a solute-carrier complex $(R_4N^+)_2\, MCl_4^{2-}$ at the feed–membrane interface. The solute-carrier complex diffuses through the membrane phase. The solute is re-extracted by the stripping agent (Na_2-EDTA) at the strip side interface and diffuses to the bulk strip phase. The schematic diagram of co-transport mode for transportation of two metals (Cd and Pb) is reported in Fig. 1. Reaction mechanism for the separation of heavy metals is as follows:

Complexation of metal (M) by chloride ions in the feed solution:

$$MCl_2 + 2Cl^- \rightleftharpoons MCl_4^{2-} \quad (1)$$

In the feed, MCl_4^{2-} is exchanged with Cl^- of Aliquat 336 ($R_4N^+Cl^-$) in the membrane phase:

$$2R_4N^+Cl^-(org) + MCl_4^{2-}(aq) \rightleftharpoons (R_4N^+)_2\, MCl_4^{2-}(org) + 2Cl^-(aq) \quad (2)$$