Studying of the effect of many parameters on a bulk liquid membrane and its opposition in Cd(II) removal from wastewater

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Abstract. Because of their tendency to accumulate in the body and their highly toxic potential, heavy metal pollution is becoming one of the main problems globally. The presented study examined the likelihood of eliminating heavy metals by means of the Bulk Liquid Membrane (BLM) method, which is a tool of high importance in various applications of such type. BLM is a simple type of liquid membrane which is showing excellent membrane stability yet insignificant solute fluxes. Therefore, this study outlines the BLM's membrane resistance in removing heavy metals and recovery from the waste-waters. The cadmium (Cd) ions are fully prepared from the acidic aqueous solutions in this study with the use of the BLM. With regard to stirred transfer cell type, an experimental research has examined the recovery and extraction of Cd ions from synthetic wastewater solution via carrier Tri-butyl-phosphate TBP [C12H27O4P] with the use of BLM as an approach of separation. The impact of some parameters such as feed and stripping stirring speed, carrier concentration, membrane stirring speed, initial feed concentration, temperature, feed, and stripping phase pH is assessed for Cd removal. At pH 4 for feed, pH 10 for strip, 10 % (v/v) carrier concentration, 2 ppm initial concentration, 150 rpm, (S:F) = (1:1) in toluene, and the room temperature the maximal efficiency of extraction and stripping of cadmium (II) metal ions was 82 % and 93 %.

Keywords: heavy metals, bulk liquid membrane, recovery, membrane resistance, removal.

INTRODUCTION

Pollution of water by toxic pollutants is a critical problem in industrial wastewater treatment; the increasing global environmental concerns are requiring the chemical industries to reduce the discharges regarding effluents (wastewater) containing many pollutants, particularly heavy metals [1, 2]. Being exposed to heavy metals shows serious and direct toxicity to the environment and human health [3]. Industrial wastewater always contains heavy metals like lead, nickel, cadmium, etc., from anthropogenic industries, such as Petrochemicals, mining activities, batteries, pulp, paper, alloys, steel, pigment paint, and fertilizer [4][5]. Heavy metals can be removed using several separation processes, such as membrane techniques, ion exchange, organic solvent extraction, electrochemical processes, reverse osmosis, adsorption processes, precipitation processes, bio-sorption, biological processes, evaporation [5], ion-exchange, adsorption [6], Electrolysis [7], membrane filtration [8], adsorption [9, 10], etc. These
techniques have various disadvantages, for example, sensitive operating conditions, high capital, and operating costs, low selectivity, less efficiency, provide a considerable amount of sludge, and further, the disposal is a costly affair [11, 12]. Therefore, better techniques for treatment are needed for overcoming such problems. Besides, the liquid membrane can be defined as a liquid which is behaving as a semipermeable liquid that is creating a barrier between 2 phases; the stripping phase and feed phase; also, the chosen solute transfers selectively between phases. The stripping and extraction processes will be combined in a single phase in the presented method; thus, providing low supplied capital and operating costs, practical effortlessness, and without limiting the transfer equilibrium [13].

A small number of the advantages of Liquid membrane are high purification, high selectivity, ease of operation, high throughput, clean-up efficiency, and the requirement of just small organic solvent quantities [14] [15] [16]. Among the liquid membrane types, BLM is the most well-known and simplest design for performing liquid membrane processes [17]. BLM includes the stripping and feed phases being separated via membrane organic, water immiscible liquid phase [16]. Also, the technique of solute's transport in BLM was the transportation mediated or facilitated via the carrier and specified via subdiffusion. Besides, the solute dissolves on a feed membrane as well as reacting with a carrier chemically complex in liquid membrane. The complex reaction on the membrane stripping partitions strips into the stripping phase accelerates the transport [17]. Many studies examined some parameters influencing the efficiency of separation, like the effect of pH on the feed and stripping phases, organic to aqueous phase ratio, mixing time, initial concentrations, carrier concentration, feed concentration, etc. [18, 19]. As far as the author of this work is concerned, there are no works on using the statistical techniques to optimize the procedure parameters of Cd (II) extraction through natural solvents such as toluene. In this work, the major aim is optimizing the process parameters: pH receiving phase, initial feed concentration, pH-feed phase, and carrier concentration for Cd ions removal efficiency via BLM.

EXPERIMENTAL

Material and Equipment

Cadmium (Cd (NO₃)₂) (99%, purity) (CDH Chemicals Ltd company, INDIA) was used in the feed phase. Toluene C₇H₈ (99.9% purity) and TBP (99% purity) were used in the membrane phase. NaOH (98% purity), hydrochloric acid (HCl) (98% purity) was used to adjust pH in feed and stripping phases. A hotplate magnetic stirrer (Ika, Germany) (30-120 rpm) has been utilized to combine the carrier and solvent organic, whereas pH meters (WTW, Germany) are utilized for pH measurement in stripping and feed phases. Furthermore, the concentration of Cd (II) in stripping and feed was once decided with flame atomic absorption spectrophotometer, AAS: (GBC, Germany)

Experimental

The transport experiments are conducted at room temperature (Temp.=21±1ºC or 30±1ºC), with 100 rpm as stirring speed and 7 hours as transport time. The experiments are carried out utilizing 6 cm width, 12 cm length, and 6 cm high glass cell. There are 2 equal compartments in cells; at the cell's center, there has been a partition wall that is 0.2 cm thick, this will be increased by 8 mm from the surface of the feed and stripe to allow Cd (II) from one portion to another to be transferred. (0.4 and 2) ppm concentration Cd ions solution representing the feed phase, whereas NaCl (0.50M) has been a stripping phase. In addition, the volumes of stripping and feed phases are 150ml; the same volume of toluene is assessed and transferred to the cell above. Figure (1) shows the utilized cell's schematic diagram. The mechanical stirrer (OS20-S) with stainless steel propeller (4-bladed with a diameter of 3.5 cm) is utilized for agitating the membrane phase, whereas the magnetic stirrer (VELP-SCIENTIFICA) with magnetic bar is utilized for agitating the stripping and feed phases. A sample of (1ml) is taken each hour from stripping and feed
phase and scanned via flame atomic absorption spectrophotometer to obtain Cd (II) extraction and recovery efficiency.

FIGURE 1. Bulk liquid membrane system used in this work.

Figure 1 represents a schematic diagram related to the BLM system utilized in the presented work. It consists of three phases, namely, membrane phase, feed phase, and stripping phase. Both of the stripping and feed phases have been separated with a strong, impermeable wall and layered on top by way of the membrane phase. An aqueous feed phase of various initial cadmium ions concentrations was prepared in distilled water. While an aqueous strip phase is containing distilled water. Finally, the organic membrane phases are prepared via loading TBP as a carrier dissolved in toluene. The pH regarding the stripping and feed phases has been altered to the required value via adding drops of NaOH or HCl. Extraction Percentage (% E) of heavy metals was calculated according to eq (1):

\[
% \, E = \frac{(C_{F_0} - C_F)}{C_{F_0}} \times 100 \quad (1)
\]

Where: \( C_F \) and \( C_{F_0} \) are representing the final and initial concentrations in the feed phase, respectively. At the same time, the recovery percentage (% S) of Cd (II) was calculated by eq. (2):

\[
% \, S = \frac{C_S}{C_{F_0} - C_F} \times 100 \quad (2)
\]

Where: \( C_S \) represents the final concentricity in stripping phase. Throughout the analyses, the preliminary concentration values regarding Cd (II) in each of the stripping and membrane phases have been considered to be zero.

Mechanism of Transport of Solute in Bulk Liquid Membrane
According to the film model of mass transfer through BLM, the solute transport mechanism might be divided into the next steps: 1- The carrier X dissolved in the membrane phase is reacting with solute Cd$^{+2}$ related to feed phase at membrane/feed interface and creates a complex Cd$^{+2}$ -X. 2- The component Cd$^{+2}$-X diffuses through membrane, dissociating at interface of strip/membrane and releasing solute A in stripping phase. 3- The carrier X will be diffused back to feed phase, and it will be ready to create a different complex. 4- Transporting of as many A molecules is likely in such a way till the feed phase has been depleted and/or stripping phase has been saturated with the solute. Figure 2 schematically represents the mechanism.

\[ m \text{ Cd}^{+2} + n \text{ X (org)} \rightarrow \text{ Cd}^{+2} - \text{ Xn (org)} \] (3)

**FIGURE 2.** Schematic illustration for the transport mechanism of Cd$^{+2}$ through BLM

**RESULTS AND DISCUSSIONS**

**Carrier Concentration**

One of BLM’s important elements, the carrier, is reacting with the feed's active component through making a complex by it and following a consecutive diffusion to the organic phase; the component will be discharged to phase of stripping. For examining carrier concentration effects on Cd (II) transportation, the experimentations are carried out at two carrier concentration values: 5, 10, and 15 vol. %. Figure 3 shows that there is a rise in the Cd (II) stripping and extraction efficiencies with time, indicating the fact that the system has the ability of extracting significant amounts of Cd (II) from the dilute solution. Also, it was identified that the Cd (II) transport is enhanced with the increase in TBP concentration up to a specific concentration. Besides that, the maximal transport occurs at a carrier concentration of 10 vol.%. This might be explained as the increase in the concentration in the TBP causes an increase in the complex formation probability. Experiments are conducted more with 15 vol.% TBP, and it has been identified that there is a decrease in the efficiency of extraction, specifying that more increase in the concentration of TBP won't be significant in this process; which might be because of a slow release regarding TBP from Cd(II)-TBP complex, also because of the increase associated with the resistance to the mass transfer, since the increases in the viscosity of the membrane phase leads to decreased Cd(II)-TBP complex diffusivity over the membrane phase. It is always desirable to have small amounts of TBP for making
BLM less costly as long as there was a suitable carrier for extracting Cd (II) from an aqueous solution; thus, TBP of 10 vol.% has been selected for all the experiments.

![Graph showing carrier concentration effect on the Cd (II) extraction efficiency](image)

**FIGURE 3.** The carrier concentration effect on the Cd (II) extraction efficiency (Feed phase pH=4; Feed concentration= 2 ppm; Aqueous phase agitation speed= 100 rpm; Stripping phase pH= 10; Temp. =25°C; speed of membrane agitation = 50 rpm).

**Effect of Feed Concentration**

The concentration of the feed phase effects on the extraction have been put to the test at different initial Cd (II) concentrations (0.4 - 2) ppm. Figure. 4 is showing the concentration effects of Cd (II) on the efficiency of the extraction. The final efficiency of the extraction for Cd (II) will be increased due to the increase in feed concentration from 0.4 to 2 ppm; this might occur due to the increase in driving force. Besides, such quick improvement might be clarified via the fact that in the case when there is an increase in the concentration, there will also be an increase in the contact between TBP and Cd (II), and a concentration up to 2 ppm, TBP will be saturated and attain maximal efficiency of the extraction, while at high concentration, carrier has been saturated entirely with no ability for effectively transferring the transfer the Cd (II) from aqueous to the organic phase.
FIGURE 4. Feed concentration effect on extraction efficiency of TBP via BLM (Cd (II) = 0.4 -2 pmm; Stripping phase pH= 10; Feed phase pH=4; speed of membrane agitation = 50 rpm; Aqueous phase agitation speed= 100 rpm; Temperature =25ºC).

Effect of Strip Phase pH

The effects of pH regarding strip phase on the effectiveness of Cd ion transport have been examined. In the case when the metal complex isn't stripped completely, the membrane phase will be saturated with the complex, and a transport rate might be decreased. Fig.5 is showing that there is a significant increase in the Cd removal efficiency in the case when the pH related to stripping phase is increased up to 10, where the efficiency of extraction reaches 82%, and the efficiency of stripping is approximately 89%, this might be because of the fact that the driving force saturation for diffusion via BLM because of the increase in the concentration of the metal complex at the interface of the membrane strip. Thus, the strip phase pH must be long compared to that of the feed phase for effective transportation of the Cd ion. There was a trivial increase in the efficiency of the removal, which has been identified at high levels of pH. These effects might be explained via the fact that at neutral pH, the carrier's de-complexing ability in membrane strip interfaces was reduced.
FIGURE 5. Extraction efficiency for Cd (II) at different pH of stripping phase; Feed concentration= 0.4 ppm; Feed phase pH=4; speed of membrane agitation = 50 rpm; speed of the aqueous phase agitation = 100 rpm; Temperature =25ºC).

Effect of Feed Phase pH

Figure 6 is showing that Cd (II) extraction efficiency associated with toluene BLM is fairly constant in the case when the feed phase pH is not more than the pH value (4.5). Yet, in the case when the feed solution pH approaches the value of pH value or becoming more than the value of pH, the efficiency of extraction has been drastically decreased. Fig. 6 shows that the Cd (II) extraction efficiency remains constant at 82% in the case when the feed phase pH is not more than 4 and becomes 63 % at pH values 8.

FIGURE 6. The effects of feed phase pH on removal efficiency of Cd (II) via BLM (carrier = 10 %; Feed concentration= 2 ppm; speed of the membrane agitation = 50 rpm; Aqueous phase agitation speed= 100 rpm; Temperature =25 ºC).

Effect of Temperature on Extraction Efficiency
The extraction efficiency experiments are conducted at temperatures of 15, 25, and 35 °C for examining the temperature effects upon the extraction efficiency of Cd (II). Fig. 7 is showing that the extraction efficiency of Cd (II) depends on temperature, which the efficiency is improved with the temperature increase. The enhancement might be explained via enhancing the species diffusion, which is transferred via liquid membrane regarding the toluene because of the membrane viscosity reduction. In addition, the diffusion coefficient (D) was associated with viscosity $\eta$ through Einstein-Stokes Eq4, in which it was proportional (inversely) to viscosity of the liquid and; thus, the temperature increase results in the increase in the extraction efficiency, which is majorly depending on the process of diffusion [20].

$$D = \frac{kT}{\eta \pi c}$$ (4)

In which D represents the coefficient of diffusion (m$^2$/s), T represents absolute temperature (k), k represents Boltzmann's constant (J/K), $\eta$ represents the liquid viscosity (Pa s), c represents the constant (4-6), and $r$ represents Stokes radius or effective hydrodynamic (m).

**FIGURE 7.** Extraction Efficiency of Cd(II) at different temperature. [Feed concentration= 2 ppm, feed with pH=4; stripping with pH=10; carrier = 10 %; agitation speed of aqueous phase = 100 rpm and speed of membrane agitation = 50 rpm].

**Effect of Feed and Stripping Phases Agitation Speed**

Fig. 8 indicates that the increase in the speed of the agitation has been associated with the stripping and aqueous phases between (50 and 150 rpm) results in a considerable increases in the efficiency of extraction. Also, high aqueous agitation speed causes an increase in the extraction rate via offering good mixing; therefore, reducing the boundary layer thickness between aqueous phase and membrane phase with no alteration in its hydrodynamic stability. Besides, it has been indicated that additional increases regarding the agitation speed reduced the efficiency since the interfaces between phases are deformed at high speeds of agitation, while the stripping phase drops are mechanically transferred to donor phase.
FIGURE 8. The effects of stripping phase and feed phase speed of agitation on Cd (II) efficiency of the extraction (Feed phase concentration=2ppm; pH of Feed phase =4; concentration of NaCl = 0.5 M; TBP = 10%; Temperature =25°C; speed of membrane agitation = 50 rpm).

CONCLUSIONS

A The results of the experiments showed the liquid membrane technology (BLM that consists of TBP as a carrier) for cadmium removal and aquatic solutions contaminated ions. The presence of the carrier was found to be very important for transporting metal ion. The optimal carrier concentration of Cd^{2+} (v/v) was 10%. The test results reveal that when the pH of feed and strip phases are adjusted to a value of 4 and 10 the highest Cd^{2+} transmission occurs. The increased concentration of heavy metal reduced the transport by the membrane phase of the metal ions. The transportation rate was also reduced at very low concentrations. Following 7 hours, Cd^{2+} transfer of about (82%) to the stripping phase is achieved. This technique might be of high importance in treating the waste-water as secondary process.

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