TRANSPORT OF CADMIUM IONS THROUGH A BULK LIQUID MEMBRANE WITH D2EHPA AS CARRIER

Mariana MATEESCU1, Liliana PACURARIU2, Gheorghe NECHIFOR3, Irina FIERASCU4

The transport of cadmium ions from an aqueous solution feed into an aqueous stripping solution through a bulk liquid membrane containing D2EHPA as a carrier was examined. The influences of the carrier concentration in the organic membrane phase and of the time of transport on the mass transfer process was studied. Results showed that using 0.2M di-(2-ethyl-hexyl)phosphoric acid in the organic phase, concentration of cadmium cations transported across the liquid membrane after 20 h was of 69.82%.

Keywords: bulk liquid membranes, di-(2-ethyl-hexyl)phosphoric acid (D2EHPA), cadmium transport, carrier

1. Introduction

The presence of cadmium ions in many industrial aqueous waste solutions presents harmful effects on aquatic life and human life.

In spite of its toxicity, cadmium is used in different industries such as hydrometallurgy, electroplating, and other industries. Thus, removal and recovery from the various effluents which contained cadmium is very valuable for environment protection [1].

In order to remove these toxic metals from liquid effluents, many technologies have been investigated, including precipitation, solvent extraction, ion exchange, etc. Among these, liquid membrane technique has gained importance for its use in separation and concentration of metal cations from aqueous solutions [2, 3, 4].

In comparison with other separation methods the liquid membrane technique had gained particular interest, because it has many advantages as

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operational simplicity, low organic phase inventory, low energy consumption and high selectivity [5, 6].

Transport of metal cation through a membrane plays an essential role in many chemical or biochemical processes [7, 8] and has many useful practical applications in separation science [9]. Liquid membrane systems consist in a liquid barrier between a feed and stripping phase [10]. In this process the selection of a suitable carrier plays a crucial role in order to selectively extract a desired substance at the feed/membrane interface and to release it on the second interface (i.e. membrane/stripping phase interface) [11].

In the recent years, the use of liquid membrane for removing metal cations from aqueous solutions had been reported in literature [12, 13, 14].

The selective transport with a mobile carrier across a liquid membrane represents a promising technology for cadmium cations separation and enrichment. Extensive research has been achieved for separation, concentration, and recovery of cadmium ions using liquid membrane processes. For example, S. Jafari and M.R. Yaftian have studied the transport of cadmium ions from iodide solutions across a bulk liquid membrane by using hexade-cyltrimethylammonium bromide (HDTBr) as carrier dissolved in dichloromethane [11].

Dingsheng He and others have investigated the separation of Cd(II) from an aqueous feed chloride solution to an ammonium acetate receiving solution through a bulk liquid membrane (BLM) consisting in tri-n-octylamine (TNOA) or tricapryl amine (N235) as carriers in carbon tetrachloride solution [15]. The facilitated transport of cadmium (II) using Cyanex 923 as ionophore was researched by Manuel Alonso and others [4]. The removal of cadmium cations from aqueous solutions using liquid membrane technique was studied by other a few researchers [16, 17, 18].

In this paper, the D2EHPA was used as carrier in a bulk liquid membrane for removing Cd$^{2+}$ cations from aqueous solutions. The aim of this study was to find the optimum carrier concentration in membrane phase to achieve maximum transport of cadmium cations from feed phase through organic membrane in the stripping phase.

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical grade and were used without further purification. Cadmium nitrate Cd(NO$_3$)$_2$ * 4H$_2$O (E. Merck, Germany) was used dissolved in double distilled water as the feed phase. The pH for the feed solution was adjusted at pH 2 with 1M HNO$_3$ (Chim Reactiv).

Di(2-ethylhexyl)phosphoric acid (D2EHPA) was obtained from E. Merck, Germany and used as carrier. Toluene were purchased from Chimopar and it was
used as an organic membrane solvent. The stripping phase was prepared from H₂SO₄ 97% (Chim Reactiv).

### 2.2. Procedure

Bulk liquid membrane transport studies were carried out using experimental transport device shown in Fig. 1. The membrane phase was 30 mL of 0.1M, 0.2M and respectively 0.25 M D2EHPA dissolved in toluene. The feed phase contained 105 mL of 0.0005 M metal ion solution, and the receiving phase consisted in 27.5 mL of 1M H₂SO₄ as stripping agent. The system was stirred with 250 rpm at room temperature for 20 h. The concentration of metal ions in the samples was determined using ICP Emission Spectrometer Varian Liberty 110. The pH adjustments were made using Seven Multi Mettler TOLEDO pH Meter.

![Fig 1. Experimental transport device](image)

### 3. Results and discussions

In this study the influence of the concentration of D2EHPA in the organic phase on the transport efficiency of cadmium was studied. In order to establish the optimum transport of Cd²⁺ through the liquid membrane, the experiments were carried out using different concentrations of D2EHPA as carrier in organic membrane. The experimental results presented in Fig. 2, 3 and 4 shows that the
carrier concentration in the membrane phase plays an important role on the removing of cadmium in the liquid membrane.

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**Fig. 2.** Concentration of cadmium in feed phase (Cf), membrane phase (CM) and stripping phase (Cs) vs. time with 0.1 M D2EHPA as carrier in organic membrane.

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**Fig. 3.** Concentration of cadmium in feed phase (Cf), membrane phase (CM) and stripping phase (Cs) vs. time with 0.2 M D2EHPA as carrier in organic membrane.
As it is seen from Figs. 2, 3 and 4 the transport efficiency of cadmium was found to be dependent on the concentration of D2EHPA in the organic phase. Maximum transport of 69.82% Cd\(^{2+}\) occurs at 0.2 M D2EHPA. Fig. 4 shows that further excess of the carrier over 0.2 M D2EHPA in the organic membrane produces a considerable decrease of Cd\(^{2+}\) transport efficiency in stripping phase up to 34.78%.

Table 1 shows the values of the concentration factors (CF). The concentration factors (CF) defined as the ratio of metal concentration in the stripping solution after the time \(t\) (\(C_{s,t}\)) to the initial feed concentration (\(C_{f,t=0}\)) (Wódzki & Szczepański, 2001). They were calculated using Eq. (1) from [19]:

\[
CF = \frac{C_{s,t}}{C_{f,t=0}}
\]  

(1)

The concentration factors CF were calculated to demonstrate the transfer of cadmium cations from the feed phase to the stripping solution, when CF > 1.

<table>
<thead>
<tr>
<th>Time [h]</th>
<th>CF for 0.1 M D2EHPA</th>
<th>CF for 0.2 M D2EHPA</th>
<th>CF for 0.25 M D2EHPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2.000</td>
<td>0.327</td>
<td>0.324</td>
<td>0.386</td>
</tr>
<tr>
<td>4.000</td>
<td>0.526</td>
<td>0.641</td>
<td>0.410</td>
</tr>
</tbody>
</table>
The experimental results presented also in Table 1 show that the CF values after 20 hours of the transport is influenced on the concentration of D2EHPA in organic membrane, i.e. this value reach from 1.788 to 2.666 when the concentration of the carrier in organic phase increase from 0.1 to 0.2 M D2EHPA. In the systems with 0.25 M D2EHPA, lower CF values were obtained. In this case the results demostrated that the transfer of cadmium cations from the feed phase to the stripping solution is less effective. In order to show the amount of cadmium transferred through the stripping solution/membrane interface, the transport $Q(s)$ of cadmium cations versus time was determined as it is shown in Fig. 5, in which: $Q_s$ is the amount (in moles) of metal species transported into the stripping solution (s) after the time $t$, through 1 cm$^2$ of the working membrane area [20].

![Graph showing the transport $Q(s)$ of cadmium cations versus time.](image)

**Fig. 5.** Transport $Q(s)$ of cadmium cations in stripping solution versus time.

The results from Fig. 5 reveal that the transport $Q_s$ for Cd$^{2+}$ in stripping solution was also found to be dependent on the concentration of the carrier in membrane phase. The experimental data show that, in liquid membranes with 0.2 M D2EHPA as carriers in the organic membrane, the transport $Q_s$ for cadmium cations is more efficient than at 0.1 M and 0.25M D2EHPA in the liquid membrane.
4. Conclusions

A transport system for cadmium through a bulk liquid membrane system containing di-(2-ethyl-hexyl)phosphoric acid as carrier was studied and it was found that D2EHPA is a good carrier for removing cadmium cations from aqueous solutions. This study demonstrates that the transport efficiency of cadmium is dependent on the concentration of carrier in the membrane phase. The highest transport rate was found of about 70% by using 0.2 M carrier in the toluene membrane. Cadmium cations contamination of industrial effluents and waste waters is a very important environmental problem. So, this search demonstrated the potential for application of the liquid membrane system studied to the selective removal and purification of cadmium ion from aqueous solutions.

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