Study of Co(II) Transfer through a Ceramic Supported Liquid Membrane Impregnated with Di-(2-ethylhexyl)phosphoric Acid (D2HEPA)

A.T. Kassem
Atomic Energy Authority, Hot Labs. Center, P.Code 13759, Cairo, Egypt.

Introduction
Wastewaters from metal industries contain various toxic heavy metals. These heavy metals present a high health risk when they enter the human food chain[1,2]. Cobalt is a very toxic element affecting the environment. Cobalt is present in the wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments and electronic industries. High levels of cobalt may affect several health problems[3-10].

Whereas membrane technologies are one of the most important topics in today’s research and practical use, liquid membrane processes have been proposed as clean ones owing to their characteristics of high specificity, low energy utilisation, the extraction and stripping steps are combined in a single operation etc.; thus, the use of liquid membranes has gained a general interest in the treatment of effluents were solute concentrations are low and large volume of solutions must be processed, and if possible, without generating any secondary waste[11-18]. Recommended in the report which applied to different equations of permeation behavior since before and after treating membrane, calculations of $\beta$ (separation factor) Co(II)/Pb(II), porosity calculation in an aqua ceramic membrane system and the $\Delta p$ (difference pressure) in an aqua membrane drop for these experiments was in the range of 10–354 kPa found the concentration of [D2HEPA] is stable and the layer not affected temperature, so that and It has also been used as a protective layer for ceramic disc and it can be used in ceramic painting. In previous works, the extraction of cobalt (II) from aqueous solutions using different mixtures of acidic reagents were

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studied[19]. The performance of these extractants mixtures on cobalt extraction, i.e. allowing the metal extraction at more acidic values than each separate reagent, had led to implement one of these extraction systems in a ceramic supported liquid membrane design in order to investigate the cobalt transport using the mixture of different extractants such as D_{2}HEPA and DP-8R extraction reagents in Exxsol D100 as mobile carrier phase.

Ceramic Membrane Materials supported disc was used different composition and impregnated in extractant di-(2-ethylhexyl) phosphoric acid (D_{2}EHPA soluble in 15% kerosene in used in this work.

For this extraction system, the extraction reaction of cobalt or lead ions can be given by Eq. (1):

\[ \text{Co}(II)_{aq} + (2 + n)\text{NO}_{3}^{-} + n\text{H}^{+} + n\text{R} \rightleftharpoons [(LR)_{n}\text{CoNO}_{3}^{2-}]_{2\text{aq}} \]  

Ceramic disc supported liquid membrane used in separation processes in two metals. Figure 1. The system consists of two aqueous phases and an organic phase[20-24], which contains [D_{2}HEPA] as a carrier dissolved in 15% kerosene as diluent. The ceramic disc renders for both a supported membrane for the organic and bulkhead from ceramic between the two aqueous phases. Theoretically the following different steps depends on the permeability of two metals from feed bulk solution into ceramic pores of cobalt and lead ions with D_{2}HEPA or permeation of the complex in the organic membrane phase. To the other side of the ceramic disc membrane and another suggested the dissociation of two ions after the advent in contact with EDTA stripping phase. Equation (1); show the react between the metal ion and the carrier of membrane interface is predominated by the equilibrium, the extraction distribution coefficient D and equilibrium constant \( K_{\text{ext}} \) are given by

\[ D = \frac{([LR]_{n}\text{CoNO}_{3}^{2-})_{2\text{org}}}{[\text{M}]^{+2}} \]  

\[ K_{\text{ext}} = \frac{D}{[\text{H}^{+}]^{n}[\text{R}]^{3n-1}} \]  

Where \([\text{H}^{+}]\), [M] and [R]^{n-1} are activities of Co and Pb ions species.

**Experimental**

Di-(2-ethylhexyl) phosphoric acid (D_{2}EHPA) was purchased from Merck (German) and was used as received. HNO\(_3\) (0.5M) was used as kerosene from Misr Petroleum Co. (Egypt Oil&Gas) a diluent for the organic phase. The Co (NO\(_3\))\(_2\) was used in this study EDTA as stripping agents was supplied by analytical grade. Stock solutions were prepared by dissolving the required amount of cations in HNO\(_3\) (0.5-3) mol/L. Another chemicals used in the work were of analytical reagent grade. The \(\alpha\)-Al\(_2\)O\(_3\) with SiO\(_2\) and TiO\(_2\) was obtained as nature, sources of feldspar, Aswan clay and Abu-Eldarag clay to fabricated disc ceramic supported liquid membrane previously manufactured [19] with a pore size of 0.1µm, thickness of 100µm and a porosity of 80%; surface area 6.25 cm\(^2\), was also employed in the study and was obtained from after polishing in one side. The concentration of two metals solutions was determined using Atomic absorption/Emission Spectrophotometer/210/VGP, Buck Scientific, USA, was used for determination of cobalt and lead ions concentration and determination of particle size by Quanta chrome instruments model Nova 1000e. An apparatus used for membrane extraction.

![Fig. 1. Schematic diagram in supported liquid membrane.](image-url)
Ceramic disc membrane supported preparation

The Ceramic disc membrane was prepared from nature clays containing SiO₂ and α-Al₂O₃ (high quality) impregnated the 100-μm membrane support disc with D2EHPA for 8 h before use. The supported CDM was then taken out from the SLM and the excess liquid attached to the surface of the membrane by polishing process in one side Ra < 0.1 μm. The CDM prepared was fixed into the SLM cell in Figure (2). Thickness 100μm, pore diameter 0.1μm, surface area 6.25 cm² and porosity 80%. Circular pieces in pertraction apparatus of ceramic microporous as nature materials [20-22].

Figure 2 S. Scheme for pertraction apparatus. (1) Double shield glass outer vessel; (2) Teflon cross-stirring blade; (3) supported membrane (cellulose nitrate); (4) feed compartment; (5) strip compartment. The SLM cell consisted of two square deal of a cylindrical chamber (65 mm internal diameter, 75 mm length) separated from the CD supported membrane. A magnetic stirrer agitated the HNO₃ (0.5-3M) aqueous solution in each chamber. The effective volume of each chamber was 100 ml. With the central part in contact with the aqueous solution having a 40 mm diameter. Transport of Co(II) ion experiments were carried out in a pertraction CDs membrane supported cell in which the membrane disc was clamped tightly[22].

Determination of permeation coefficient

The flux (Jₘₐₓ Co(II) & Pb(II)) was obtained using equation [22]

\[ J_m = \frac{-V_d C_{Co,Pb}}{A dt} \ldots 4 \]

Where V is the volume of the feed solution, A is the membrane area in contact with the aqueous solution, C is the concentration of Cobalt and Lead ions and t is the neglected time. The permeability coefficient (P) was then calculated using equation[20]:

\[ \ln \frac{C_t}{C_0} = -\frac{AP}{V} \ldots 5 \]

Where Cₜ and C₀ are concentration of Cobalt and Lead ions in the acidic medium at a given time and t₀, respectively, A is the effective ceramic membrane area and V is the volume of the feed phase and the t = 0.
Results and Discussion

A study of diffusion experiments was perfected to investigate the effect of Co(II) ion concentration, carrier concentration, acid concentration and stripping solution (EDTA) on metals transport.

Effect of divalent ion concentration

Figures 3-6 show the plot of cobalt (II) ions concentration vs time. It is clear that the transports of metal ions are affected by the Co ions concentration existent in the feed phase of the CDs membrane. The stripping solution used is (0.1-2) mol/L EDTA. As the concentration of cobalt ions of feed solution is increased and the extraction of metal ions. It can also be seen that Co (II) ions are transported via the CDs membrane, although the concentration of cobalt ions and lead ions in the feed phase are less than that in the stripping phase.

Figures 5 and 6 show the effect of feed concentration solution of the transport of cobalt (II) ions through the membrane using 2M EDTA as a stripping agent. It is obvious in Fig. 7 that there is a slight increase in flux with an increase in cobalt concentration and maximum flux is found when 20.54×10⁻⁴ mol/L for cobalt ion concentration is used. According reaction (6) and Eq. (7). The amounts of stripping (EDTA) concentration lightly influences the flux. About 2 M EDTA concentrations are adequate to strip cobalt ion.

\[ Co(II)aq + (2+n)\text{HNO}_3 + n\text{H}^+ + n\text{H} = [(LR)_n\text{Co(NO}_3^2\text{)}_3]_{2n} \ldots -6 \]

\[ J_m = \frac{D_c}{\kappa C_1} = \frac{D_c}{\kappa} \frac{\Delta C_1}{t} \ldots \ldots 7 \]

Effect of HNO₃ concentration

Figures 7 and 8. The explicates the effect of HNO₃ concentration of metal ions in the feed solution on the transport of cobalt ions through the existing of CDs membrane. It is clear that the flux of metal ions increases up to a 2 mol/L HNO₃ concentration and then decreases. The concentration, extent studied for HNO₃ is from 0.1 to 2.0 mol/L. According to equations Eq. (8), the cobalt ions obtain to convert into [Co(NO₃)₃][, in the presence of 2mol/L HNO₃. So the cobalt or lead anions associates with D₄HEPA ions in the presence of protons to form a [(D₄HEPA)₂]CoNO₃,₃+ type complex, which permeate towards the other side of the CDs membrane, resulting in Co(II) transport.

\[ R + n\text{H}^+ \rightleftharpoons [\text{RH}_n]^n^+ \ldots \ldots 8 \]

\[ \log n = \log A^+ + n \log[\text{R}] + n \log[\text{H}^+] + [(3-n) \log[\text{NO}_3^-]] + \log c_0^\text{m} - \ldots \ldots 9 \]

An increase in HNO₃ concentration as the concentration of the cobalt(II) ions in carrier complex at the feed –ceramic disc membrane interface increases, according to the equilibrium relationship seen the reaction in equation. 9.
From the Figure 9. Showed that the before treated membrane flux increased by [HNO₃] increase from 1.0 to 1.5 mol/L after 1.5 mol/L concentration of [HNO₃] before treated of membrane decreased. The second curve showed that after treating membrane increased in flux from 1.5-2 mol/L [HNO₃] and the permeation behavior science before and after treating membrane in the Table (1). The separation factors were calculated inequation (10) and are given in Table (1) when solution containing Pb(II) with Co (II).

\[
\beta = \frac{P_1}{P_2} = \frac{J_{mb}}{J_{mA}} \cdot \frac{[M_{Co,Pb}]_{feed}}{[M_{Co,Pb}]_{feed}}
\]

Where \( J_{mb} \) = flux before and after treating

### Fig. 5. [Co] decrease in feed phase against time, min at different C0 in feed phase of solution against 2 mol/L EDTA as stripping phase. [EDTA] 2 mol/L, [HNO₃] 0.5-3 mol/L, [D₂HEPA] 2.5 mol/L, [Co] (7.98-20.54) \( \times 10^{-4} \) mol/L, at pH 6.03±0.03.

### Fig. 6. [Co] strip increase against Time, min at Cc feed, 2 mol/L [EDTA] stripping phase. [HNO₃] 2 mol/L, [D₂HEPA] 2 mol/L, [Co] (7.98-20.54) \( \times 10^{-4} \) mol/L at pH 6.03±0.03.

### Fig. 7. Effect of [Co] permeation rate, [HNO₃] =2 mol/L, [D₂HEPA] =1.5 mol/L, [EDTA] 0.1-2.5 mol/L at pH 6.03±0.03.

### Fig. 8. Effect of [Co] in feed when decrease against time, min at different [HNO₃] fed 0.2-3 mol/L, [D₂HEPA] 1.5 mol/L, [EDTA] =2 mol/L, [Co] 12.33 \( \times 10^{-4} \) mol/L, pH 6.03±0.03

\[ \text{Egypt. J. Chem. 63, No. 6 (2020)} \]
membrane, respectively, show the maximum separation factor at [HNO$_3$] higher separation factor in 2 mol/L and less a separation factor at 0.19 mol/L.

**Effect of permeation Rate**

The determination of the permeation rate is known to be due to the carrier concentration reaches at saturation at the feed membrane interface. According to Eq. (9), if $C_p$ and [D$_2$HEPA] are preserved constant, i.e. at the same divalent ions like cobalt and lead ion concentration in feed solution and at the stable concentration of [D$_2$HEPA] in the CDs liquid membrane, a plot of log $J_m$ versus log[H$^+$] can be obtain base a straight line and the value of ‘$n$’ from its slope. It can be shown that up to about 2 mol/L HNO$_3$, it is a straight line (Fig. 10). Having a slope of 0.66. The fact that $n$ is found to be 0.66 suggests the extraction mechanism which is based on the complexation of cobalt ions with a [H$^+$]$^1$ proton. To study the transport of H$^+$ ions with time, pH of feed phase was determined at regular duration’s time. It can be shown that pH of feed phase increases with time, due to the transport of [H]$^+$ from the feed phase (Fig. 11). The effect of D$_2$HEPA concentration on the extraction of cobalt (7.98-20.54).10$^{-4}$ mol/L, and lead (5.66-12.68).10$^{-4}$ mol/L was studied in the range 1.0–4mol/L. It was shown that the percentage extraction of Co (II) increased with an increase of D$_2$HEPA concentration. The D$_2$HEPA concentration in the membrane phase varied from1 to 4 mol/L. The Co (II) and Pb (II) concentrations in the feed solution were kept constant at $C_p$ mol/L for the two metals. Fig.12. Show the extraction of Co (II) 98.7%, while Pb (II) 66.4% respectively. Table 2. It was shown that the separation factor increased from 2.27 to 16.39 with an increase of [D$_2$HEPA] concentration from 0.25 to 1.5 mol/L and then decreased from 1.39 to 1.34 of [D$_2$HEPA] 2-3mol/L.

<table>
<thead>
<tr>
<th>[HNO$_3$], mol/L</th>
<th>$J_{c}$, mol/m$^2$.sec</th>
<th>$J_{m}$, mol/m$^2$.sec</th>
<th>$P_{c}$, m/sec.10$^{-4}$</th>
<th>$P_{m}$, m/sec.10$^{-4}$</th>
<th>$P_{Co/Pb}$</th>
</tr>
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<tr>
<td>0.25</td>
<td>1.596</td>
<td>0.33</td>
<td>0.528</td>
<td>1.19</td>
<td>0.277</td>
</tr>
<tr>
<td>0.5</td>
<td>2.87</td>
<td>0.25</td>
<td>0.708</td>
<td>1.26</td>
<td>0.198</td>
</tr>
<tr>
<td>1</td>
<td>2.752</td>
<td>0.36</td>
<td>0.684</td>
<td>1.06</td>
<td>0.34</td>
</tr>
<tr>
<td>2</td>
<td>3.058</td>
<td>0.37</td>
<td>0.57</td>
<td>0.7</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**Fig.9.** Effect of [HNO$_3$] permeation rate [HNO$_3$] = 2 mol/L, [D$_2$HEPA] 1.5 mol/L, [EDTA] 2 mol/L.

**Fig.10.** plot log $J_m$ vs. log [HNO$_3$], slope= 0.7.

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Conclusions

Transport of cobalt and lead divalent ions was carried out by a ceramic disc supported liquid membrane technique by using nature of clays impregnated in D_2HEPA/ kerosene 15% as carrier. Study of various parameters explained in this work. Studies the slope analysis studies of \( \log J \) vs. [HNO_3] indicate that 0.7 or approach \( \sim 1 \) mol/L of the hydronium ion in nitrate media and extractants were contributed to extracted metal ion species of both cobalt and lead. The cobalt and lead ions flux increased with an increase of [HNO_3] 0.25-3 mol/L, flux increased from \( 1.2 \times 10^{-4} \) mol/m^2.s for [Co] and \( 4.3 \times 10^{-6} \) mol/m^2.s for [Pb], the effect of pH of [Co]^extractation and [Pb]^extractation 6.03-3.5±0.03 respectively. \( J_{Co/Pb} \) increased with the increase of the [D_2HEPA] as carrier concentration at 2 mol/L and then decreased. It was seen that the maximum separation factor of \( J_m \) (membrane treated before and after) for [Co]^feed and [Pb]^feed at different [HNO_3] increased at 2 mol/L and less than 0.5 mol/L, for study separation factor for [Co]^feed with [Pb]^feed at [D_2HEPA] extractant at 1.5 mol/L where separation factor for divalent metal ions in feed phase increased from [7.98-17.39] \times 10^{-4} \) mol/L for [Co] and [5.66-11.23] \times 10^{-4} \) mol/L for [Pb] ions respectively. And the best separation of cobalt and lead ions in wastewater or (feed solution) is obtained pH 3.5±0.03, 1.5 mol/L of [D_2HEPA] and 2mol/L[EDTA]_strip in aqueous solution. The divalent ions are transported via [D_2HEPA]/kerosene ceramic supported membrane and hydronium ion will be decreased from feed solution. Nearly all cobalt and lead ions, were extracted from feed phase and were transported to strip side via [D_2HEPA]/kerosene ceramic supported membrane.

TABLE 2. Separation factor for cobalt and lead ions at different [D_2HEPA].

<table>
<thead>
<tr>
<th>[D_2HEPA]</th>
<th>( J_{Co} ) mol/m^2.sec</th>
<th>( J_{Pb} ) mol/m^2.sec</th>
<th>( P_{Co}, \text{m/sec.} \times 10^{-4} )</th>
<th>( P_{Pb}, \text{m/sec.} \times 10^{-4} )</th>
<th>( \beta_{Co/Pb} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>( 4 \times 10^{-6} )</td>
<td>( 2.9 \times 10^{-9} )</td>
<td>0.5</td>
<td>0.22</td>
<td>2.27</td>
</tr>
<tr>
<td>0.5</td>
<td>( 6 \times 10^{-9} )</td>
<td>( 3.1 \times 10^{-9} )</td>
<td>0.68</td>
<td>0.277</td>
<td>2.15</td>
</tr>
<tr>
<td>1</td>
<td>( 8.2 \times 10^{-9} )</td>
<td>( 3.4 \times 10^{-9} )</td>
<td>0.83</td>
<td>0.269</td>
<td>3.08</td>
</tr>
<tr>
<td>1.5</td>
<td>( 9.8 \times 10^{-9} )</td>
<td>( 3.6 \times 10^{-9} )</td>
<td>1.05</td>
<td>0.062</td>
<td>16.93</td>
</tr>
<tr>
<td>2</td>
<td>( 10.2 \times 10^{-9} )</td>
<td>( 3.8 \times 10^{-9} )</td>
<td>1.07</td>
<td>0.769</td>
<td>1.39</td>
</tr>
<tr>
<td>2.5</td>
<td>( 11.2 \times 10^{-9} )</td>
<td>( 3.9 \times 10^{-9} )</td>
<td>1.07</td>
<td>0.83</td>
<td>1.21</td>
</tr>
<tr>
<td>3</td>
<td>( 12 \times 10^{-9} )</td>
<td>( 4 \times 10^{-9} )</td>
<td>1.12</td>
<td>0.832</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Fig. 11. Effect of pH of feed phase vs time, min. [HNO_3] 3 mol/L,[D_2HEPA]2mol/L,[EDTA]=2mol/L, [Co]12.33x10^{-4} at pH 6.03±0.03,[Pb]6.33x10^{-4} at pH 3.5±0.03 respectively.

Fig. 12. Effect of D_2HEPA concentration on percentage extraction of Co 98.7% and Pb 66.4%.
ions have been found to be removed when ceramic supported membrane system is used for removal of this ion from waste solutions into feed. Ceramic membrane is on the promising technology in removing heavy metals from wastewater such as cobalt ions by 98.7% and lead ions by 66.4% respectively.

References


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