SEPARATION OF Co (II) AND Ni (II) IONS FROM WASTEWATER BY EMULSION LIQUID MEMBRANE TECHNIQUE

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Abstract
Emulsion liquid membrane (ELM) technique has been used to the extraction of metals pollutants from simulated wastewater and recovery and concentration of them. The transfer of Co (II) and Ni (II) ions from aqueous solution containing single component and dual components systems across emulsion liquid membrane has been investigated. Ammonia buffer solution was used as mobile carrier and stripping phase. The effects of important parameters that affect cation flux into the liquid membrane have been evaluated: external feed pH value, ion concentration, carrier concentration and hydrodynamic conditions. Ni (II) ion was not transported under single component system conditions, while from dual components system Ni ion accompanied Co ion. Under these conditions, at pH=5.3 the separation factor ($\alpha_{Co/Ni}$) was 4. Therefore, by using of this ELM type, a good concentration of Co(II) ion was obtained in order to recover it (the concentration factor was 4.08).

Introduction
Emulsion liquid membrane technique is a process used for the recovery of metal ions and the separation of carboxylic acids and aminoacids (1-11). The one specie separation from a mixture is an important step in industrial, analytical and environmental chemistry (1).

An immiscible organic liquid phase separating two aqueous phases (feed and stripping) may be considered as a liquid membrane. For liquid membrane technique the extraction and stripping operations are combined in a single process. Liquid membranes may contained only liquid phases (bulk liquid membranes and emulsion liquid membranes) or in addition a polymeric membrane to support the organic phase (supported liquid membranes) (2).

The liquid membrane transport can be facilitated transport when the carrier agent is added. The carrier agent presence allows the highly selective ion separation and a good concentration of ion.

The transport and separation of Co(II) and Ni(II) ions by liquid membrane technique have been investigated by many authors. For separation of Co and Ni ions from sulphate solutions by emulsion liquid membrane (ELM) technique as carrier agent phosphonic acid derivates was used (3). Also, for the separation of these ions from chloride solutions by supported liquid membrane, the carrier agent was amine reagent (tertiary and quaternary amine).

This paper has been studied the transport of Co(II) and Ni(II) ions from chloride solutions by type single component system and the transport and the separation of these ions each other from dual component system, following the concentration and the recovery of ions too, by ELM technique. The ELM applied contain ammonium buffer (NH_4Cl/NH_4OH) both as carrier and stripping agent.

Methods
The generation of the primary emulsion WI/OII and of the double one WI/OII/WIII was carried out by a variable speed - stirring device having two steps of speed (first step: 500-1300 rpm and the second step: 25-500 rpm). The device was a Sartorius stirrer RW47 type, helicoidally shape (W-water; O-organic phase).

The concentrations of Co and Ni ions were controlled by atomic absorption spectroscopy, Varian Spectra AA 110.

The hydrodynamic conditions for generating the primary emulsion WI/OII were as follows: stirring intensity: 1200 rotations/min.(fast stirring); duration: 15 minutes. The working volumes (ml) of phases were: WIII/OII/WI= 120/20/20.

The process was operated with control parameters: the removal efficiencies for Co(II) and Ni(II)(η); the separation factor ($\alpha_{Co/Ni}$); the recovery efficiency (R); the concentration factor (f); final concentration for Co(II) and Ni(II) in the treated water (C_f). It was defined the following parameters:
The removal efficiency (η) was expressed as:

$$\eta = \frac{C_i - C_f}{C_i} \times 100 \ (\%) \qquad (1)$$

where: C_i-initial concentration of Me^{2+} ion in feed phase
C_f- final concentration after treatment by ELM technique
The recovery efficiency (R) was expressed as:

$$R = \frac{C_{int,f} \cdot V_{int}}{C_i \cdot V_{ext}} \times 100 \ (\%) \qquad (2)$$

where: $C_{int,\,f}$ - final internal concentration after treatment by ELM technique
V_{int} – volume of receiving phase
V_{ext} – volume of external phase
The separation factor ($\alpha_{Co/Ni}$):

$$\alpha_{Co/Ni} = \frac{\frac{C_{Co,f}}{C_{Co,i}}}{\frac{C_{Ni,f}}{C_{Ni,i}}} \qquad (3)$$

where: $C_{Co,f}$ - final external concentration of Co^{2+}after treatment by ELM technique
$C_{Co,i}$- initial concentration of Co^{2+} ion in feed phase
$C_{Ni,f}$ - final external concentration of Ni^{2+}after treatment by ELM technique
$C_{Ni,\,i}$- initial concentration of Co^{2+} ion in feed phase
The concentration factor:

$$f = \frac{C_{int,f}(mg/L)}{C_i(mg/L)} \qquad (4)$$

The main characteristics of ELM used in the process were as follows: the organic phase: Romanian kerosene; receiving phase: NH_4Cl(1M)/NH_4OH(20M); organic phase: receiving phase ratio =1:1; tensioactive agent: Span 80(0.1 % wt., versus organic phase).

The working conditions for the ELM application are presented in table 1.

Table 1. Experimental working conditions.

System type	Feed aqueous phase (WIII)	Receiving (stripping) aqueous phase (WI)	Organic phase (O II)	External feed pH
Single component	Co(II) 23.8; 42.7; 120 mg/L Ni (II) 17.05 mg/L	Ammonium buffer; pH=9.3	Romanian kerosene	2; 2.5; 3.5; 5.5
Dual components	Co(II) 24.87 mg/l and Ni (II) 18.5 mg/L	Ammonium buffer; pH=9.3	Romanian kerosene	2; 2.5; 3.5; 5.5

Results

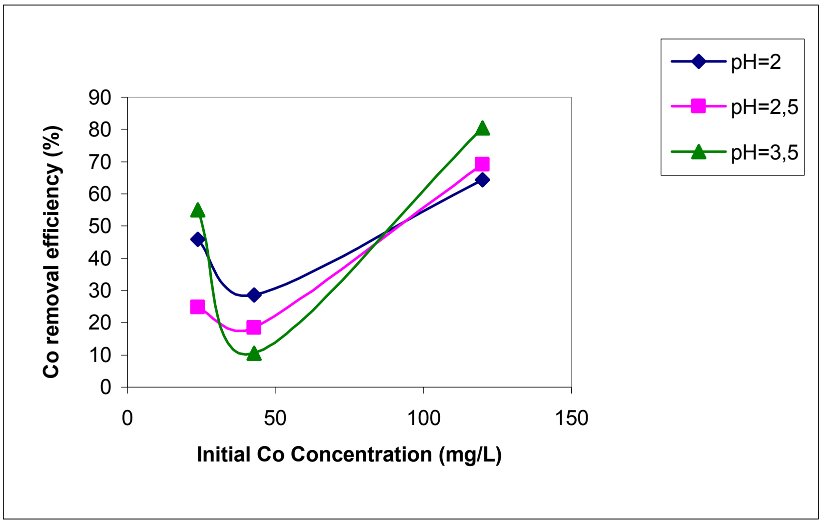
Table 2 presents the results obtained after the application of ELM on aqueous phase by type single component system (both Co and Ni ions).

Table 2.The removal efficiencies of Co and Ni ions from aqueous solution by type single component system; $C_{Ni,i}$=17 mg/L and $C_{Co,i}$=23.8 mg/L

Me^{2+} type	Exterior feed pH	η(%)
Co	2 2.5 3.5	47 26 54
Ni	2 2.5 3.5	- - -

Figure 1 shows the influence of initial Co ion concentration from feed phase on the removal efficiency

Figure 1. The removal efficiency of Co ion versus the exterior feed Co concentration



In order to separate the both ions (Co and Ni) each other the ELM technique was applied on aqueous solution by type dual components system. The results are presented in figure 2.

Figure 2.Influence of the external feed pH on the removal efficiency of Co and Ni ions

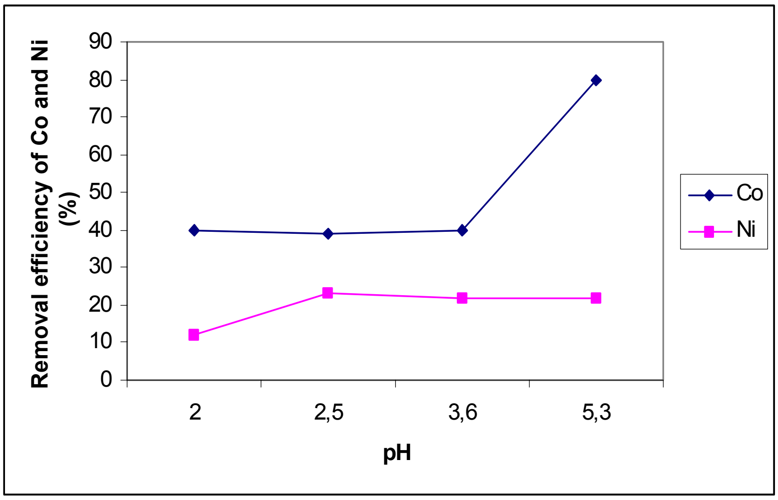
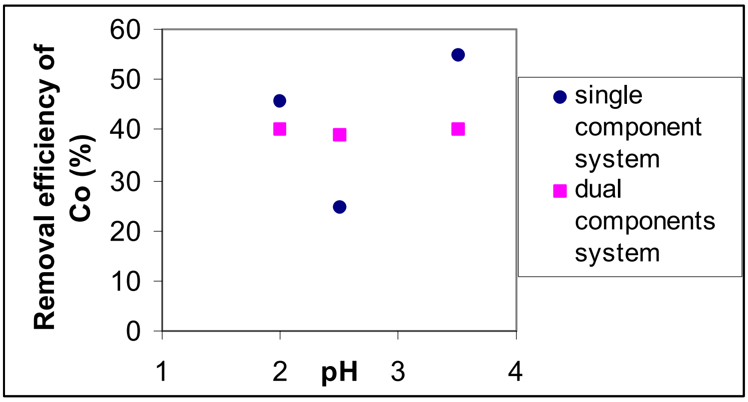


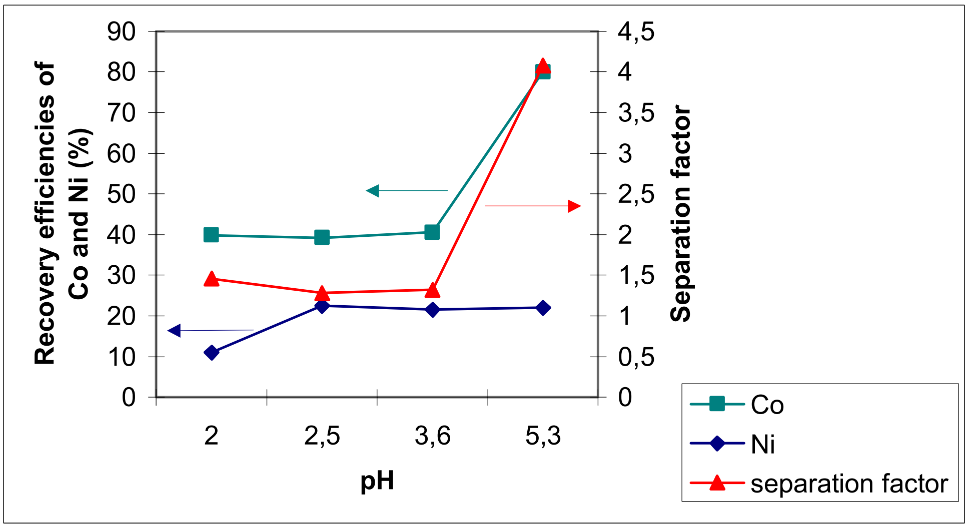
Figure 3 shows the Co ion transport results obtained by the application of ELM on the both Co (II) systems types (single and dual components)

Figure 3. Influence of the system type (single and dual components) on the Co ion removal efficiency



The separation and the recovery data after the application of ELM on aqueous phase containing the dual components system (Co and Ni) are presented in figure 4.

Figure 4. Comparative results regarding the separation factor and recovery efficiency of the both ions (Co^{2+} and Ni^{2+})



After the emulsion breaking by centrifugation the stripping phase was analysed by AAS. It was obtained the following factor concentration: f_{Co}=4.08 and f_{Ni}=2.52.

Discussion

In order to obtain a selective transport of Co ions from a mixture of two ions (Co and Ni) the ELM technique was applied on the aqueous phase containing single component system for each ion. NH_4^+ concentration of ammonium buffer was NH_4Cl (1M) /NH_4OH (20M). For low quantity of ammonium buffer (NH_4Cl (0.05M) /NH_4OH (1M), the emulsion was broken. Table 2 gives Co II and Ni II ions removal data that show the possibility to transport Co II ion across the membrane while Ni II ions stay into the external feed phase, using ammonia buffer solution as mobile carrier and stripping phase, too. The effect of the external feed Co ion concentration and pH on the removal efficiency of the Co II ion is shown in the figure 1. pH value presents a lightly influence on the removal efficiency, while for the high concentration the removal efficiency is very good.

Under the same conditions, the application of ELM on the aqueous phase containing the dual components system (both Co and Ni ions) led to the results presented in figures 2and 4. In this case, it can be noticed that the Co ion transport was accompanied by Ni ion transport. Under these conditions, the both ions were transported into the stripping phase but the Co transport was better than the Ni one, permitting a separation of Co ion (figure 4 presents both the separation factor and the recovery efficiencies for Co and Ni ions). Co transport across the membrane is lightly influenced by system type (figure3).

Conclusion

ELM technique allows removal, recovery and concentration of metal ions (Co II and Ni II) from aqueous solution. Also, this technique may be applied for separation of a metal (Co II ion) from a mixture of two metal ions (Co II and Ni II).

The transport of Me^{2+} ion is influenced by external phase pH, the type of system (single or dual components) and ELM type. The ELM type appropriate to transport Co ion in various conditions consists of ammonium buffer as carrier agent and stripping phase too. The emulsion stability is influenced by ammonium buffer quantity.

For single component system, this ELM type allowed only Co ion transport and for dual components system the both ions (Co and Ni) were transported. The ions separation and the recovery processes depended by external feed pH value, the high separation was obtained at pH=5.3

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