Purification-Concentration Process of Zn(II), Ni(II) and Cd(II) Using Liquid Membrane with Different Carriers

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Abstract
Heavy metals are toxic to human beings and organisms. Industrial effluents drawn from different industries such as dyeing, mining, electroplating, nuclear power operations, aerospace and battery manufacturing processes are highly contaminated with heavy metals and create a major environmental problem to their discharge into land. Liquid membrane is considered as a low-cost method for treating wastes. Purification-concentration process using liquid membrane containing different extractants as carriers considered to be the most effective technique for the removal of heavy metals from wastewaters. This study primarily focuses on the extraction-reextraction in order to design a purification-concentration process using liquid membrane to remove different heavy metals (Zn, Ni, and Cd) and metal ions from aqueous solutions for industrial application. In order to design and optimize a transport process for industrial application, the effect of transport conditions has been studied. Moreover, it is important to study the influence of different parameters such as: the acidity, nature and concentration of the carriers, the time of transportation.

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1. Introduction
It only remained the setting of systems of treatment of leaching solutions suitable with solid-liquid extraction from the kinetic, technological and economic point of view. In this context we have developed a liquid-liquid extraction technique associating extraction to reextraction. The integration of the above preoccupations led to the examination of extraction procedures for Zinc, Nickel and Cadmium by using different extractants such as TOA, TBP, HDEHP and HDEHP/TOPO. The study of different chemical variables (acidity, pH, concentration of the extractant, concentration of metal, etc) allowed the determination of optimum outputs and the understanding of the reaction processes and the respective transfer phenomena.
2. Experimental

2.1 The purification-concentration reactor

We have designed and constructed [1] a purification-concentration reactor comprising two liquid-liquid extraction tubs. The two extraction tubs are made of Plexiglas, a material that is resistible to solvents, diluents and acids. The extraction compartment receives the feed which in our case is the leaching solution. It is separated from the reextraction compartment which contains the reextraction aqueous phase. The two compartments and the two solutions are put into contact thanks to the organic phase composed of an extractant and a diluent. A scheme of the extraction-reextraction reactor is depicted on figure 1.

![Scheme of extraction-reextraction reactor](image)

Fig. 1. Scheme of extraction-reextraction reactor.

The great interest is to avoid the regeneration of the solvent which remains intact at the end of operations. The organic phase (membrane) consists of the extractant (TOA), (TBP), (HDEHP) and the mixture (HDEHP-TOPO) dissolved in the kerosene. The stirring velocity is 280 rpm and the volume of the cells is 200 ml.

3. Results and discussion

We applied the process purification-concentration to three different systems:

\[ \text{Zn}^{2+}, \text{H}^+, \text{SO}_4^{2-}/\text{TOA/Na}_2\text{SO}_4 \ ; \text{Ni}^{2+}, \text{H}^+, \text{Cl}^-/\text{TBP/HCl} \text{ and } \text{Cd}^{2+}, \text{H}^+, \text{H}_2\text{PO}_4^-/\text{HDEHP/HCl} \]

The characterisation of the food phase and the liquid membrane has been made based on the time of transport.

3.1. Transport of the Zn(II) by tri-n-octylamine (TOA)

![Graph of Zn(II) concentration over time](image)

Extraction’s compartment: \([\text{Zn(II)}]_0 = 100 \text{ ppm}, \ [\text{H}_2\text{SO}_4] = 0.5\text{M}; \)
Membrane: \([\text{TOA}] = 0.01\text{M} / \text{kerosene}; \)
Reextraction’s compartment: \([\text{Na}_2\text{SO}_4] = 1\text{M} \)

We examined the transport of \(\text{Zn}^{2+}\) through the TOA liquid membrane. The transferred quantity of Zn(II) is higher than the receiving phase meaning that a quantity of 33 ppm reextracts (~33%) after around 6 hours.
The extraction of Zinc (II) by the tertio-amine (TOA) in the presence of sulphuric acid is based on an anions-exchange mechanism [2]:

\[ R_3N + H_2SO_4 \Leftrightarrow [R_3NH^+ \cdot HSO_4^-] \]  
(a) Protonation of the amine:

\[ 2[R_3NH^+ \cdot HSO_4^-] + Zn(SO_4)^{2-} \Leftrightarrow [(R_3NH)^{2+}Zn(SO_4)^{2-}] + 2H SO_4^- \]  
(b) Extraction by exchange of anions:

\[ [(R_3NH)^{2+}Zn(SO_4)^{2-}] + H SO_4^- \Leftrightarrow 2 [R_3NH^+ \cdot HSO_4^-] + Zn(SO_4)^{2-} \]  
(c) Competition of the extraction of the sulphuric acid:

3.2. Transport of the Ni(II) by tri-n-buthylphosphate (TBP)

Extraction’s compartment: [Ni (II)]_0 = 100 ppm, [HCl] = 0.1M
Membrane: [TBP] = 0.1M / kerosene
Reextraction’s compartment: [HCl] = 1M

We note that the quantity of the Nickel in the phase of reextraction grows with time. A quantity of around 40 ppm is reextracted (an output of 40%) after 7 hours.
The transport mechanism of Nickel ions is depicted in Fig. 5.

The transfer of Ni\(^{2+}\) from the extraction’s compartment toward the reextraction’s compartment through the membrane, takes place by active transportation. The ions (H\(^{+}\), Cl\(^{-}\)) activate the “carrier” to the interface I while in the interface II the “carrier” is disactivated by the Cl\(^{-}\).

The extraction of Ni(II) by tri-n-butylphosphate (TBP) in the presence of chlorhydric acid is done by the following mechanisms

**Extraction’s compartment:**

We propose the mechanism by solvatation [3-5] as follows:

- For the weak acidities:

\[
\text{Ni}^{2+} + \text{H}^{+}, \text{Cl}^{-} + 2\text{TBP} \rightleftharpoons \text{NiCl}_2 .2\text{TBP} \quad (4)
\]

- For the strong acidities the following mechanism is in competition:

\[
\text{H}_2\text{O}^{+}, \text{Cl}^{-} + \text{TBP} \rightleftharpoons \text{H}_2\text{O}^{+}, \text{Cl}^{-},\text{TBP} \quad (5)
\]

The Nickel is extracted by the extractant oxide tri-n-butylphosphate and subsequently transferred in the aqueous phase by means of the hydrochloric acid solution. The reextraction of Ni\(^{2+}\) takes place according to the reaction:

**Reextraction’s compartment:**

\[
\text{NiCl}_2.2\text{TBP} + \text{H}^{+} + \text{Cl}^{-} \rightleftharpoons \text{NiCl}_2 + 2\text{TBP} + \text{H}^{+} + \text{Cl}^{-} \quad (6)
\]

### 3.3. Transport of the Cd(II) by acid di (2-éthyl hexyl) phosphoric (HDEHP)

The experimental results are described in Fig. 6.

![Fig. 6. Transport of Cadmium by HDEHP](image)
Extraction’s compartment: $[\text{Cd (II)}]_0 = 100 \text{ ppm, } [\text{H}_3\text{PO}_4] = 2\text{M}$; 
Membrane: $[\text{HDEHP}] = 0.1\text{M} / \text{kerosene}$; 
Reextraction’s compartment: $[\text{HCl}] = 1\text{M}$

According to Fig. 6 the quantity of the cadmium in the reextraction’s compartment increases considerably with time, and an output of the order of 80% is established after 8h.

The respective transport mechanisms [6, 7] are schematically presented in Fig. 7.

**Extraction’s compartment:**

We propose the ion-exchange mechanism as follows:

*To the weak acidities*

Extraction of Cadmium by HDEHP (HX):

\[
\text{Cd}^{2+} + \frac{3}{2} (\text{HX})_2 \Leftrightarrow \text{X}_2\text{Cd, HX} + 2 \text{H}^+ \quad (7)
\]

*To the strong acidities,* while taking into account the predominance of the $\text{H}_3\text{PO}_4$ species [9], an exchange like mechanism takes place as follows:

\[
\text{CdHPO}_4 + \sqrt{2} (\text{HX})_2 \Leftrightarrow \text{CdHPO}_4\cdot\text{HX} \quad (8)
\]

An elevation of the acidity increases the extracted quantities, with the latter ones being limited however by the capacity solvate of the HDEHP.

**Reextraction’s compartment:** it operates in a more complex manner. The mechanisms is described by the following 3 reactions:

\[
\text{CdX}_2, \text{HX} + 2 \text{HCl} \Leftrightarrow \text{CdCl}^+ + 3(\text{HX}) + \text{Cl}^- \quad (9)
\]

\[
3\text{HX} \Leftrightarrow \text{CdCl}^+ + \sqrt{2} (\text{HX})_2 \quad \text{(dimerisation)} \quad (10)
\]

\[
\text{CdCl}^+ + \frac{3}{2}(\text{HX})_2 \Leftrightarrow \text{CdClX} + 2\text{HX} + \text{H}^+ \quad (11)
\]

The two compartments function in the same way but the outputs are distinctly different because of the dimerisation of the HDEHP.

**3.3. Transport of Cd(II) by synergism**

We achieved the transport of cadmium (II) through the membrane by using a mixture of extractants, HDEHP –TOPO diluted in kerosene [8]. The respective experimental results are depicted in Fig. 8.
Fig. 8. Concentration of extracted and reextracted cadmium (II) as function of time.

Extraction’s compartment: \([\text{Cd (II)}]_o = 100 \text{ ppm}, [\text{H}_3\text{PO}_4] = 0.5\text{M} \);  
Membrane: \([\text{HDEHP}] / [\text{TOPO}] = 6 \text{ M in kerosene} \);  
Reextraction’s compartment: \([\text{HCl}] = 1\text{M} \)

We observe that the quantity of the cadmium in the reextraction’s compartment increases considerably with the time, ending up to an output of around 91.71% after 9h.

The cadmium ion is reextracted according to the reaction:

\[
(CdHPO_4)_x(HX)_{1-x}(TOPO)_{1-x} + 2HCl \rightarrow CdCl_2 + x\text{TOPO} + (1-x)\text{HX} + H_3\text{PO}_4 \quad (12)
\]

4- Conclusions

The present work aims to develop a process treatment of diluted solutions. An extraction-reextraction process through liquid-liquid membranes has been established, where the two extraction-reextraction compartments are coupled thanks to a membrane constituted of an extractant + diluent. The transport of divalent ions Zn(II), Ni(II) and Cd(II) has been examined by testing liquid membranes made of TOA, TBP and HDEHP. The Zn (II) extracted by tri-n-octyl amine (TOA) in sulfuric acid medium (0.5M H$_2$SO$_4$ in kerosene), showed a significant extraction in the order of 80%. The transferred quantity of Zn(II) is higher than the one when the receiving phase consists of HCl since the reextracted quantity ranges in the order of 33ppm, equals to an output of 33% after a 6 hours of the process experiment. The quantity of Nickel in the reextraction’s phase grows considerably with the time. A quantity of around 40 ppm is reextracted, representing an output of 40% at the end of 7 hours. The transferred quantity of Cd(II) is higher with time than the receiving phase of the HCl medium leading to a reextracted quantity of around 40 ppm which equals to an output of 40% at the end of 7 hours. The extraction by the di (2-ethyl hexyl) phosphoric acid (HDEHP) in the kerosene, showed that for the weak concentrations in orthophosphoric acid, the outputs of extraction are important, of the order of 82% for H$_3$PO$_4$ 2M. The synergistic extraction leads to an output of 91.71% at the end of 9h. The symmetrical behavior of the two compartments, extraction and reextraction, shows that we have a significant transfer through the membrane while the coupling makes it possible to carry out transport, an against-transport. The results obtained highlight the feasibility of the process purification-concentration and the performance of the coupling. This lets the prediction of an industrial application of the studied process and opens the door for broad applications both for industrial wastes (more economic feasible) as well in the field of metalliferous processing liquid wastes (less feasible). This also allows an effective protection of the environment while being profitable.

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