ASSESSMENT OF LIQUID EMULSION MEMBRANE FOR CLEAN UP OF AQUEOUS WASTE EFFLUENTS FROM HAZARDOUS ELEMENTS

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ABSTRACT

Four liquid emulsion membrane (LEM) systems are given to remove different hazardous elements such as uranium, thorium, cobalt, copper, lead, and cadmium from different aqueous waste effluents. The optimum conditions for use of these systems are deduced. The potentiality of LEM for removal of hazardous pollutants from aqueous waste solutions is given.

INTRODUCTION

Over the last decades , there are increasing concern about hazardous waste disposal due to the problem of environmental pollution. One of the challenging problems in the waste management is the clean up of aqueous waste effluents from hazardous elements before reuse or discharge to the environment.
Liquid emulsion membranes (LEMs) are improved solvent extraction technique that found application in liquid waste treatment and hydrometallurgy(1-5) . This technique offers some advantages in comparison to common liquid – liquid extraction such as improvement of kinetics, selectively of species to be removed and decreasing the necessary volume ratio of organic phase to aqueous feed solution. Further, it is characterized by simplicity and high efficiency.
The present work is directed to assess LEM technique for removal and recovery of certain pollutants to clean up waste effluents produced from nuclear activities as well as other industrial processes. In this concern, different LEM systems were developed based on using specific extractants (carriers) that make the removal process viable.
The carriers employed were: di-2-ethylhexyl phosphoric acid (DEHPA)and triaryl phosphine oxide (Cyanex-921) for removal of U(VI) , bis,2,2,4 trimethyl dithio-phosphininc acid (Cyanex-301) for removal of Co(II), thenoyltrifluoroacetone (HTTA) for removal and recovery of U(VI), Th(IV) and Co(II) and finally, the carrier 2- hydroxy –5-nonyl-acetophenone oxime (Lix-84) for removal of Cu. Optimum conditions for preparation of LEMs containing the aforementioned carriers were elaborated to obtain suitable efficient and stable LEM system.

EXPERIMENTAL

Chemicals and reagents used were of analytical grade

LEM preparation

In general the LEM was prepared by mixing 25 cm^3 of the organic extractant in the chosen diluent with the proper surfactant . To this mixture, 25 cm3 of the stripping aqueous phase solution was added . The emulsification of the membrane was performed by vigorous mixing using an ultra high-speed homogenizer (~6000 rpm).
The preparation of the different LEMs used are given in details in Refs.(6,7).
It is to be mentioned that Span-80 was found to be the suitable surfactant for emulsifying the prepared LEMs.

Permeation procedure

The permeation procedure was carried out by pouring a known volume of the prepared LEM into a thermostated vessel containing a known volume of the feed solution which contains the elements under investigation.
The system was mixed with a magnetic stirrer. Samples were withdrawn from the mixture at known time intervals and filtered. The concentration of the elements was determined in the filtrate.

Analysis of elements

The concentration of the elements in the filtrate was determined as follows:

- U(VI) , Th(IV), Fe(III) were determined spectrophotometrically(8),
- Co(II) , Cu(II), Cd and Pb(II) were determined by atomic spectrometry, while radioactive Co^{60} was determined radiometrically.

The different LEM systems employed are summarized in Table 1.

Table 1. Different LEM Systems Employed

Pollutants	Feed Solution	Carrier	Pollutant Removed	Stripping solution
System I U(VI) ^{60}Co	$10^{-3}MHNO_3$	DEHPA in kerosene Cyanex-301 in toluene	U(VI) ^{60}Co(II)	1.0M H_2SO_4 2.0M HNO_3
System II Th(IV) U(VI) Co(II)	$0.01MHNO_3$	HTTA in toluene Cyanex-921 in cyclohexene	Th(IV) U(VI) Co(II) in feed solution	0.5M HNO_3 0.2M Na citrate
SystemIII U(VI) Fe(III)	$0.1MH_3PO_4$	DEHPA in cyclohexane	U(VI) Fe(III)	1.0M HNO_3
System IV U(VI) Cu(II) Co(II) Pb(II) Cd(II)	0.01M HNO_3	DEHPA+Lix-84 in kerosene Cyanex-301 in toluene	U(VI)+ Cu(II) Co (in strip. Sol.) Pb,Cd (in LEM phase)	1M H_2SO_4 2M HNO_3

RESULTS AND DISCUSSION

In general ,before applying the permeation process ,liquid –liquid extraction and stripping of the pollutant elements in the different systems used were studied. The suitable conditions to be applied in the composition of the LEMs and in the permeation processes were deduced from the data obtained. The degree of stability of the prepared LEMs that depends on the choice of the suitable surfactants was measured in terms of the degree of leakage of a tracer that leaks from the internal aqueous phase to the feed solution (6,7). The parameters affecting the permeation process were studied and the optimum conditions used for the removal of the pollutants in each system were applied.

System I

This system deals with the removal of uranium and radioactive cobalt from medium level active waste solutions. In this concern , the two extractants DEHPA and CYANEX-301 are used as mobile carriers in preparing the LEM. Uranium was first removed by DEHPA carrier. The optimum conditions used for such removal were as follows:

- A feed solution of 100 cm^3 of 10^{-3}M HNO_3 containing 120 ppm of U(VI) and 150 ppm of cobalt (II) spiked with 0.03mCi of ^{60}Co.
- An emulsion membrane of 10 cm^3 prepared from 25 cm^3 of 0.02M DEHPA (carrier) +3% Span –80 (surfactant) in kerosene +25 cm^3 of 1.0M H_2SO_4 solution(stripping solution)
- A stirring speed of 400 rpm.

After the removal of uranium,Cyanex-301 was used as a carrier for removal of cobalt. The optimum conditions used for such removal were as follows:

- A feed solution of 100 cm^3 of 10^{-3}M HNO_3 containing cobalt (II).
- An emulsion membrane of 10 cm^3 prepared from 25 cm^3 of 0.2M CYANEX-30 +4% Span 80 in toluene +25 cm^3 of 2.0M HNO_3 solution.
- A stirring speed of 400 rpm.

The results obtained showed a quantitative separation of both elements. The prepared LEMs were found stable towards the radiation emitted from radioactive cobalt for 3 hours.

System II

This system is directed to the removal and recovery of Th(IV) ,U(VI) and Co(II) from nitrate medium. In this concern, two different types of LEM s were prepared based on using HTTA as a carrier for removal of Th and Cyanex-921 for removal of U from Co.

The conditions used for the removal of Th(IV) were as follows:

- A feed solution of 100 cm^3 of 0.01M HNO_3 containing 100ppm of Th and 50ppm of each of U and Co.
- An emulsion membrane of 10 cm^3 prepared from 25 cm^3 of 0.1M HTTA +4% Span-80 in toluene + 25 cm^3 of 0.5M of HNO_3 solution.
- A stirring speed of 450 rpm.

The data obtained showed the removal and quantitative separation of Th(IV) from dilute HNO_3 solution containing a mixture of Th, U and Co.

The conditions used for removal and separation of U from Co after the removal of Th were as follows:

- A feed solution of 100 cm^3 of 0.01M HNO_3 containing 50ppm of each of U and Co.
- An emulsion membrane prepared from 25cm^3 of 0.1M Cyanex-921 +6%Span-80 in cyclohexane + 25cm^3 0f 0.2M Na citrate.
- A stirring speed of 700rpm.

The data obtained showed the removal and separation of U(VI) from dilute nitric acid solution containing both U(VI) and Co(II).

System III

In this system, a LEM was prepared based on using DEHPA as a carrier for the removal of U(VI) and Fe(III) from simulated waste water effluents obtained from wet process phosphoric acid industry.

The conditions used in this process was as follows:

- A feed solution of 100 cm^3 of 0.1 M H_3PO_4 containing 50ppm of U(VI) and 100ppm of Fe(III).
- An emulsion membrane prepared from 25cm^3 of 0.1M HDEHP +1% Span-80 in cyclohexane +25cm^3 of 1.0M HNO_3 solution.
- A stirring speed of 550 rpm.

The results obtained showed the possible removal of ~98% of both U(VI) and Fe(III) from dilute phosphoric acid.

System IV

This system deals with the removal and recovery of U(VI),Co(II),Cu(II),Pb(II) and Cd(II) of concentrations simulated to their presence in industrials waste solutions. Different types of LEMs were prepared based on using selective carriers for successive removal of most of the aforementioned pollutants. The suitable conditions found to be applicable for the removal process were as follows:

-Removal of U(VI) and Cu(II)

- A feed solution of 100cm^3 of 0.01M HNO_3 containing 120ppm U(VI)+ 200ppm Cu(II) +150ppm Co(II) +50ppm Pb(II) +50ppm Cd(II)
- An emulsion membrane prepared from 25cm^3 of 0.02 M DEHPA +0.04M Lix-84 +2.4% Span-80 in kerosene +25cm^3 of 2M H_2SO_4 solution.
- A stirring speed of 450 rpm.

The data obtained showed a quantitative removal of U and Cu from dilute HNO_3 solution containing a mixture of the five elements under investigation.

- Removal of Co(II),Pb(II) and Cd(II)
- A feed solution of 100cm^3 of 0.01M HNO_3 containing 150ppm Co(II),50ppm Pb(II) and 50ppm Cd(II).
- An emulsion membrane of 10cm^3 prepared from 25cm^3 of 0.2M Cyanex-301 +4% Span-80 in toluene +25cm^3 of 2.0M HNO_3 solution.
- A stirring speed of 400rpm.

The data obtained showed that Co, Pb and Cd are removed from the feed solution. Breaking the emulsion to aqueous stripping phase and organic phase, it was found that the stripping phase contained only Co ,while the organic phase contained Pb and Cd.

Conclusion

The above mentioned systems showed the potentiality of LEM for removal of some hazardous pollutants from aqueous waste effluents. The variety of carriers in LEM systems offered a broad range to remove many hazardous elements from different waste effluents. One of the main advantages of LEM is the high preconcentration factor. The LEM system could be a continuous one based on breaking the LEM to separate the pollutant from the stripping phase followed by recycling the organic phase for preparing

a new LEM for reuse. More efforts are needed to develop specific LEM system for specific industrial aqueous waste solutions.

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