

Consideration of Polymer Inclusion Membranes Containing D2EHPA for Toxic Metallic Ion (Pb^{2+}) Extraction Recovery

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Abstract. CTA Polymer inclusion membranes (PIMs) containing an acidic carrier (D2EHPA) were prepared and characterized by Fourier transform infrared resonance spectroscopy (FT-IR). The surface and cross-section morphology of the membrane was inspected by scanning electron microscopy (SEM).

The transport through polymer inclusion membranes (PIMs) was found as an effective method of lead (II) cations removal from nitrate aqueous solutions. Transport of lead (II) through PIMs reduces the concentration of metallic cation in source aqueous phase from 12.4 to 0.86 ppm, which corresponds to an efficiency removal of 93%. The competitive transport of lead(II), cadmium(II) and zinc(II), from nitrate aqueous solution across the PIM was found efficient for the removal of all the metallic cations examined (lead(II) (89%), cadmium(II) (85%) and zinc(II) (84%)).

Keywords: Toxic Metal ions recovery; Facilitated transport; Polymer inclusion membrane (PIM); D2EHPA.

1. Introduction

Over the past few decades, membrane technology has found application in a variety of industries, ranging from water desalination to gas separations. At present, the demand of membrane technology in the field of gas separation, medicine, wastewater treatment, production of drinking water by desalination, and other methods is increasing day by day [1].

The big importance in membrane separation technology lies essentially in the fact that it is potentially energy-efficient. Separation systems have recently received much attention because of their lower costs and greater flexibility. Fundamentals properties required of such membranes are high permeability and high selectivity [2].

In recent years, separation methods based on polymeric inclusion membranes (PIMs) have received considerable attention due to the high stability of such membranes compared to that of supported liquid membranes [3]. These membranes are easy to prepare and have excellent mechanical properties [4]. It is envisaged that the development of metal selective PIMs will bring in a quantum jump in the field of separation science and technology [5]. These processes are of great importance because of the use of selective carrier species which would increase the mass transfer and improve the selectivity of the process [6].

PIMs appropriate for facilitated transport of organic and inorganic species consist of a polymer, a plasticizer, and a carrier. The polymer provides mechanical strength, while the plasticizer provides elasticity and constitutes the liquid phase in which the carrier molecule can diffuse. The carrier molecule acts as a guest-specific host that provides selective membrane permeability for target species [7].

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Mostly, polyvinylchloride (PVC) and cellulose triacetate (CTA) are used as polymer matrix for preparing PIMs, and 2-NPOE is the main compound employed as plasticizer. Other plasticizers have been evaluating to appreciate the role of the plasticizing effect on the transport efficiency of PIMs [8, 9].

The large number of reference devoted to PIMs during the last decades [10-13], reveals the great interest for these membranes. A general review concerning extraction and transport of metal ions and small organic molecules using polymer inclusion membranes (PIMs) has been published [14], pointing out their better mechanical properties and chemical resistance compared to the traditional SLMs. The transport mechanism in PIMs depends on factors like membrane composition, homogeneity of the membrane and surface morphology [15].

As a part of our continuing program of studying in the field of application of PIMs in separation methods, the purpose of this study was to synthesize PIMs based on cellulose triacetate polymer, incorporating D2EHPA as an acidic carrier, in order to study the facilitated transport of lead (II) from dilute aqueous solution. Lead is a heavy metal of concern for its role in environmental pollution, as it has toxic effects for humans via inhalation, oral ingestion and/or skin contact [16].

D2EHPA is a commercial carrier specially suited for metal cations recovery like Pb(II), Cd(II), Zn(II), Co(II) and Cr(III) [17-20]. It is also used in complexation reactions for several organics such as amino acids, polyamines and cationic dyes [21-23].

In order to get a better understanding of selective metal cation separation using PIM, the membranes have been characterized to obtain information regarding the composition and the interactions between the components. The physical structure of PIMs is subject to investigations using different techniques devoted to bring knowledge on the manner by which the selective extractant (carrier) is immobilized into a plasticized polymer matrix and interacts with it.

2. Experimental

2.1. Reagents

Organophosphorus extractant, D2EHPA was kindly supplied by Albright and Wilson (USA) and used as received. CTA (cellulose triacetate), 2-NPOE (2-nitrophenyloctylether) were obtained from Aldrich and were used without purification. Chloroform (CHCl_3) was acquired from Prolabo. Other inorganic chemicals: $\text{Zn}(\text{NO}_3)_2$, NaNO_3 , (Labosi), HNO_3 (Prolabo), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka), $\text{Pb}(\text{NO}_3)_2$ (Riedel-de Haën) were analytical reagent grade and were used for the preparation of the different solutions. Redistilled water was used in all experiments.

2.2. Preparation of Polymeric Membrane

The membranes were prepared using a procedure similar to that reported by Hayashita *et al.* [24]. CTA (200 mg) was dissolved in 20 ml of CHCl_3 at room temperature. 0.3 ml of 2-NPOE in 5 ml of CHCl_3 was then added. After vigorous stirring, the carrier (D2EHPA) was added and the solution was stirred for 30 min to obtain a homogenous solution. The solvent of this mixed solution was allowed to slowly evaporate in a 9.0 cm diameter Petri Dish, which was covered loosely, overnight evaporation. A small quantity of water was deposited on the film to help its unsticking of the glass support.

2.3. Membrane Characterizations

To illustrate membrane morphology of the PIMs, a 5 KV scanning electron microscope (SEM) (Hitachi S4500) was used. Membrane samples were prepared by freezing under liquid nitrogen (70 K) and rapid fracturing, resulting in a clean break fracture image to view the cross-section. The samples were mounted with conductive glue to metal stubs with the fractured edge up and then coated with gold by sputtering. These samples were then viewed in the SEM.

FTIR spectra were acquired using IR Affnity-1 (Shimadzu) spectrometer. Measures were taken in wave number range from 500 to 4000 cm^{-1} .

2.4. Membrane Transport Experiments

The membrane cell consisted of two Plexiglas compartment (250 cm³). The chambers were separated by the PIMs and clamped together (the area of each side of the PIMs in contact with the solution was 10.74 cm²). The source phase was an aqueous lead (II) solution in NaNO₃ 0.1M. Aqueous receiving phase was 0.1M HNO₃. Transport experiments were conducted at room temperature (23-25 °C) and both source and receiving aqueous phases were stirred at 900 rpm with two mechanic stirrers (Heidolp RZR 2101).

The metal concentration was evaluated by sampling at different time intervals aliquots of 0.2 ml each from the feed and strip solutions and analyzed with an atomic absorption spectrophotometer (SCHIMADZU AA6500).

The kinetics of the transport across PIMs was described as a first-order reaction in metal-ion concentration:

$$\ln(C/C_i) = -kt \quad (1)$$

Where C is the metal ion concentration at a given time in the feed phase, C_i is the initial concentration of metal ion in the feed phase, k is the rate constant (s⁻¹), and t is the time transport (s).

The k values were calculated from the plots of ln(C_i/C) vs time. The relationship of ln(C_i/C) vs time used to plot the data obtained in this work was linear as expected from Equation 1.

The permeability coefficient (P) was calculated as follows:

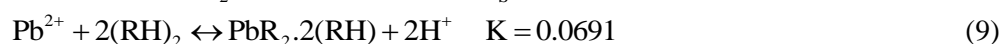
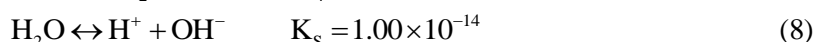
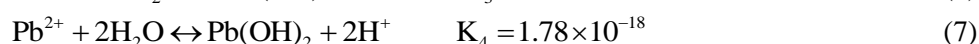
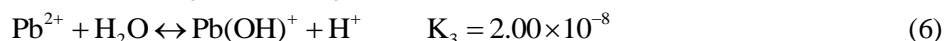
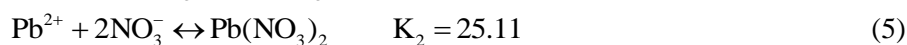
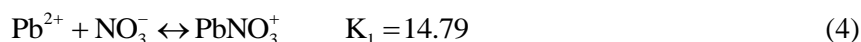
$$P = - (V/A).k \quad (2)$$

Where V is the volume of aqueous feed phase, and A is the area of the effective membrane. The initial flux (J_i) was determined as:

$$J_i = P.C_i \quad (3)$$

3. Mechanism of the Complexation

The Pb²⁺ ion in the aqueous solution takes part to the following complexation reactions [25].



The various species formed by Pb²⁺ in an aqueous acid medium were studied in a previous work [26] by using an equilibrium calculation computer programme. The results shows that the molar fraction species diagram for the speciation of Pb(II) as a function of pH indicated that under the experimental conditions used for the Pb(II) extraction, 0.1M NaNO₃ and pH between 1 and 5, lead ion is present as Pb(II) (65%), PbNO₃⁺ (31%) and Pb(NO₃)₂ (4%)

As shown in Eq. (9), the transport of Pb²⁺ is coupled to that of the released protons since the forward and backward reactions imply the substitution of bivalent metal ion in the feed solution for two protons and the substitution of two protons in the receiving solution for one metal ion. This imposes that the difference between the sum of the chemical potentials for the transported ions in the receiving and the feed phases has to lie below zero (Δμ < 0).

4. Results and Discussion

4.1. Membrane Characterization

SEM and FTIR are the techniques investigated to characterize the different membranes elaborated in this work.

4.1.1. SEM investigation

Homogeneous dense membranes were obtained without macro-voids in the cross section (Fig. 1) due to delayed demixing in the phase separation by evaporation of the solvent. A smooth surface was observed in the case of the pure CTA but the presence of additives (2-NPOE and DEHPA) make the surface quite rough

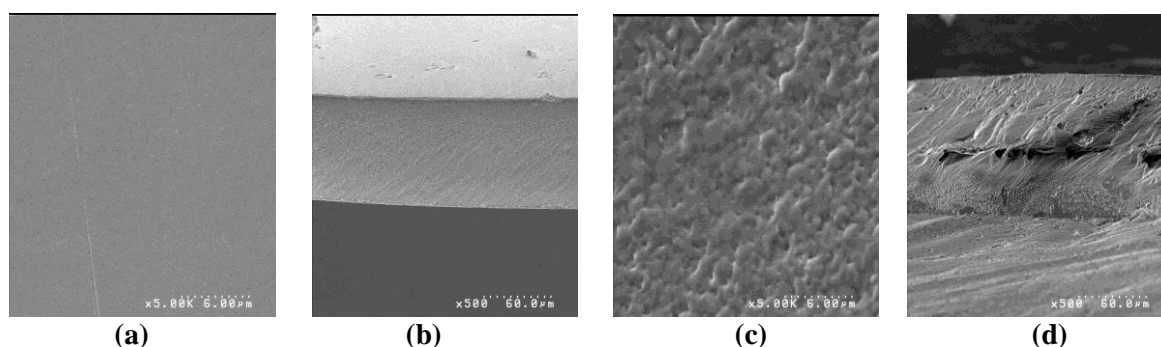


Fig. 1: SEM views of blank membrane (CTA) (a and b) and PIM containing DEHPA at 53% (w_{DEHPA}/w_t) (c and d) (surface morphology and cross-section morphology).

4.1.2. FTIR results

The FTIR spectra of CTA membrane, 2NPOE, D2EHPA, (CTA + 2NPOE) and (CTA + 2NPOE + D2EHPA) membranes have been recorded and IR absorption frequencies assignments to the polymeric matrix (CTA), the plasticizer (2NPOE) and the extractant HL (D2EHPA) have been reported.

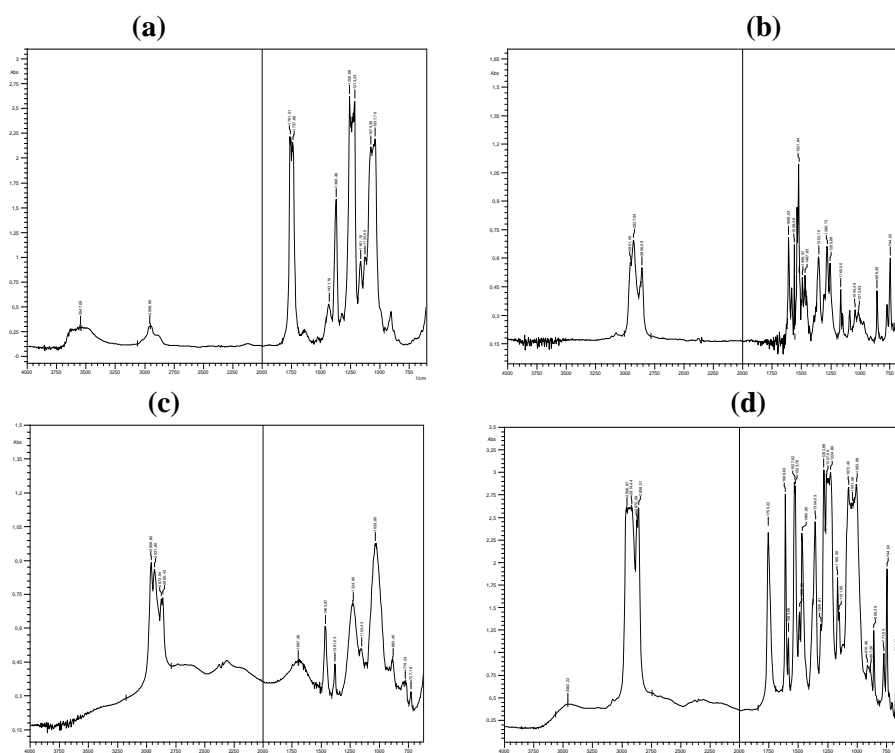


Fig. 2: FTIR spectra of CTA membrane (a), 2-NPOE (b), D2EHPA (c), and CTA-2NPOE-D2EHPA membrane (d).

The IR spectra of the CTA (Fig. 2a) exhibit essentially two absorption bands at 1738 cm^{-1} and 1761 cm^{-1} assigned to asymmetric and symmetric C=O (acetate) stretching, the absorption band at 1370 cm^{-1} is due to CH deformation of CH_3 . Other absorption bands at 1037 , 1074 , 1213 and 1255 cm^{-1} attributed to stretching mode of C–O bonds in the cellulose ring and the acetate groups are also observed.

The spectra of the plasticizer (2NPOE) (Fig. 3b) shows mainly the bands at 1522 and 1352 cm^{-1} correspond respectively to the stretching asymmetric and symmetric modes of N=O (in NO_2) bonds and the band at 1608 cm^{-1} is due to the stretching mode of C=C bonds of the aromatic ring. The band at 856 cm^{-1} is attributed to the C–N bond.

The IR assignment of the PIM (CTA + 2NPOE + D2EHPA) shows some modifications of the characteristic normal modes compared with the spectrum of the pure CTA, 2NPOE and D2EHPA. Shift in the phosphoryl stretching bands may be observed. The P–O absorption band in the PIM shifts to a lower frequency (1002 cm^{-1}) comparatively to that in the free reagent (1033 cm^{-1}). On the other hand, the

absorption stretching band (1738 cm^{-1}) assigned to asymmetric vibration of the C=O bond in the acetate of CTA became undetectable in the IR PIM spectra and the stretching band (1761 cm^{-1}) assigned to symmetric vibration of the same bond shift slightly at 1755 cm^{-1} .

At the same time characteristic absorption bands of the 2NPOE remained unaltered. This become visible that the Intermolecular interactions are essentially related to those that exist between the base polymer and the extractant. This can mainly be attributed to the strong interactions between the P=O D2EHPA group and the C=O (acetate) CTA group.

4.2. Transport Experiment

Blank experiments, in the absence of a carrier, yielded no significant flux across PIM with only support and plasticizer. From this result it can be established that the PIM without carrier served as an effective barrier to ion permeation.

A membrane contained 21 wt% CTA, 50 wt% D2EHPA and 29 wt% 2-NPOE is used here. This membrane composition was already optimised in our previous work [27] for the facilitated transport on cadmium (II).

4.2.1. Concentration profiles versus time

The concentration profiles is shown at the Fig. 3 for Pb(II) concentration of 12 mg/L in the feed solution. The maximal recovery factors of Pb(II) is 92 % after 24 hours. As can be seen from the curves, the exponential variation of Pb(II) concentration values with the time of process was observed. No retention was noticed in transport of Pb(II) by D2EHPA/CTA based membrane, that denote the good facilitated transport of this cation.

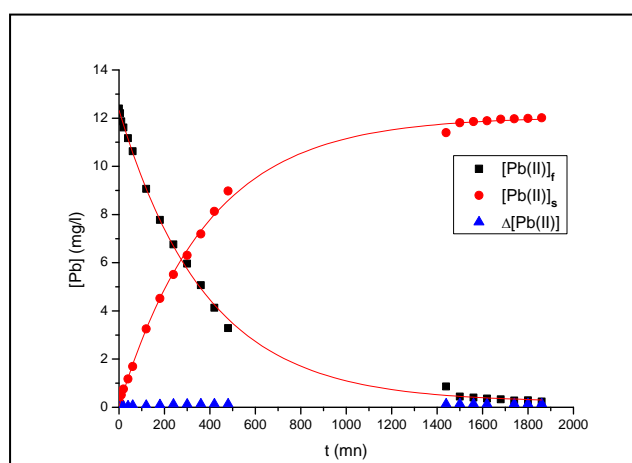


Fig. 3: Concentration profile versus time for Pb(II) cross PIM
 Feed solution: Pb(II) : 12 mg/L in NaNO₃ 0.1M; Receiving solution: HNO₃ 0.1M
 PIM: 200 mg CTA, 312 mg 2-NPOE and 578 mg D2EHPA

4.3. Selectivity Study (Efficiency of Metal Recovery)

Selectivity is an important issue in the implementation of PIMs for many reasons. For instance, in environmental applications, the concentration of the target metal ions can be quite low and reasonably high selectivity is essential for an effective treatment. The selectivity of the PIMs was investigated by determining the selectivity coefficient, S, defined as the ratio between the initial flux of a given ion (Pb(II)) and the flux of another ion existing in the same solution (Cd(II) or Zn(II)).

The linear relation of $\ln(c/c_i)$ versus time of transport (Figs 4 and 5) shows a facilitated mechanism of the metal ions transport across PIMs in individual and competitive transport.

The results of the individual transport and competitive transport cations mixture fluxes are assembled in Table 1.

The selectivity coefficients or Pb(II)/Cd(II) and Pb(II)/Zn(II) for transport have been found equal to 1.063 and 1.055, respectively.

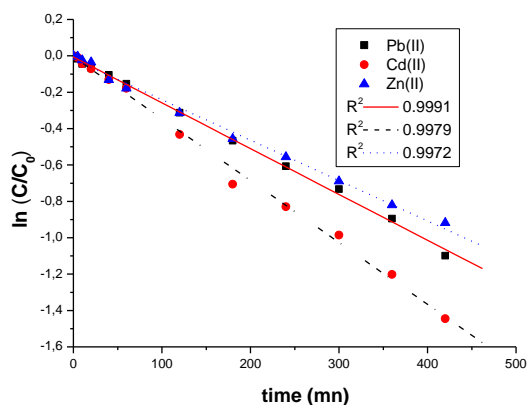


Fig. 4: $\ln(c/c_i)$ versus time of transport ($M(II) = Pb(II)$, $Cd(II)$ or $Zn(II)$) across a PIM in individual cation transport.

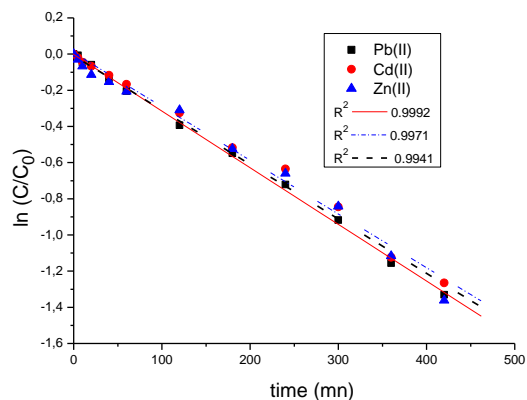


Fig. 5: $\ln(c/c_0)$ versus time of transport $M(II) = Pb(II)$, $Cd(II)$ or $Zn(II)$) across a PIM in competitive cation transport.

Kozłowska et al. [28] have obtained $S (J_i(Pb)/J_i(Cd)) = 9.090$ and $S (J_i(Pb)/J_i(Zn)) = 0.575$, with D2EHPA/CTA PIM, the difference with our results is presumably due to differences in the membrane constituents (membrane: 72% ONPPE, 17% CTA, and 11% carrier (4.0 cm^3 ONPOE/1.0 g CTA, 0.50M carrier based on plasticizer volume).

The observed selectivity coefficients led us to conclude that D2EHPA is able to extract all the studied cations without any marked selectivity.

Table 1: Fluxes (J_i) of cations transported as individual metal species or cations mixture and selectivity coefficient (S) in the competitive metal transport

Feed solution: $[M(II)] : 12 \text{ mg/L}$ in NaNO_3 0.1M, Receiving solution: HNO_3 0.1M.

$M(II) = Pb(II)$, $Cd(II)$ or $Zn(II)$.

Metallic cation	$J_i (\mu\text{mol.m}^2.\text{s}^{-1})$ (Single metal cations)	$J_i (\mu\text{mol.m}^2.\text{s}^{-1})$ (competitive transport)	$S=J_i(Pb)/J_i(M)$
Pb(II)	1.08	1.34	
Cd(II)	1.45	1.26	1.063
Zn(II)	0.94	1.27	1.055

5. Conclusion

PIM systems containing D2EHPA as carrier and 2-NPOE as plasticizer membranes were prepared and employed in transport experiments to extract Pb(II) using the commercial reagent (D2EHPA).

Surface characterization analyses of the sample surfaces with SEM showed the existence of a nodular structure consisting of smooth ridges and valleys in the PIM containing D2EHPA. The FTIR results lead us to conclude that the Intermolecular interactions are essentially related to those that exist between the base polymer and the extractant. Transport experiments demonstrated the ability of the fabricated membranes to extract highly (up to 92%) Pb(II), in diluted aqueous solutions. However, the selectivity depends on the relative composition of the membranes.

This work shows that in this field, the preliminary physico-chemical studies are indispensable to decide relevance of a process with membrane and that general laws of behavior are very difficult to obtain, each case of application seeming to have to be regarded as a case in oneself whose performances for a type of separation given must be evaluated.

6. Acknowledgement

We are very indebted to DEF and CNRS, respectively for financial support and travel assistance in the frame of an exchange programme no. 18429.

7. References

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