

Efficient Facilitated Transport of Lead and Cadmium across a Plasticized Triacetate Membrane Mediated by D2EHPA and TOPO

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ABSTRACT

Cellulose triacetate membranes doped with organo-phosphoric carriers (2-ethylhexyl) phosphoric acid noted (D2EHPA) or trioctyl phosphine oxide noted (TOPO) as fixed carriers and 2-nitro phenyl octyl ether noted (NPOE) or tris ethylhexyl phosphate noted (TEHP) as a plasticizers have been prepared and applied for investigation to the facilitated transport of Pb(II) and Cd(II) ions from aqueous nitrate source phase. The membranes Polymer - Plasticizer - Carrier were characterised using chemical techniques as well as Fourier Transform Infra - Red (FTIR), X - ray Diffraction and Scanning electron microscopy (SEM). A study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using D2EHPA as carrier at pH 1-2.

Keywords: Cellulose Triacetate, NPOE, TEHP, D2EHPA, TOPO, Membrane

1. Introduction

Liquid membranes have received considerable attention by many researchers because of their high selectivity accomplished by carriers incorporated in the membranes. Many efforts have been done to investigate the use of liquid membranes for various separation and purification processes such as separation of isomers [1,2], gases [3-5], metal ions [6,7], etc.

The separation and removal of toxic metal cations and neutral chemicals from water has frequently been addressed in membrane separation systems. Environmentally damaging and toxic anions have received significantly less attention primarily due to the challenging nature of selectively binding anions. Recently, a novel type of liquid membrane called polymer inclusion membrane (PIM) has been developed which provides metal ion transport with high selectivity, as well as easy setup and operation [8]. Polymer inclusion membranes (PIM) show great potential for industrial separations over other membrane types. Bulk liquid membranes (BLM) are not economically scalable to industrial levels, while the more practical supported liquid membranes (SLM) tend to lose solvent to the water phases. PIM consist of a polymer support, which is commonly cellulose triacetate (CTA), a

plasticizer (solvent) and carrier molecules. The plasticizer is an integral part of the membrane, acting as the solvent in which the carrier diffuses. This makes the membrane easy to handle and promotes membrane durability. In fact, the common plasticizer *o*-nitrophenyl octyl ether (NPOE) suffers virtually no loss from the membrane into adjacent water phases [9]. Also, PIM demonstrate permeability of ionic and neutral species comparable to SLM [10]. Any loss of transport in PIM in comparison to SLM is due to slower diffusion across the membrane, however, the higher carrier capacity of CTA membranes helps increase transport to counteract this effect [11,12]. The PIM plasticizer can be changed to optimize transport. NPOE, TEHP are common plasticizers in CTA-based PIM. The durability and relatively high polarity of NPOE allow counter ions to be dissolved in the membrane as free ions. NPOE has the further advantages that it is non-volatile, high boiling and insoluble in water. CTA-based PIM using NPOE as the plasticizer retain macrocyclic carriers, such as calixarenes and provide a stable, durable membrane [13-17]. The fabrication and characterization of new membranes is reported recently [18,19].

Facilitated transport of metal ions through PIM carrier

equation $J = \frac{\Delta n}{S\Delta t}$ where Δn is the variation of the number of moles in the feed phase during the interval time Δt (s) and S is the membrane area (cm^2).

2.4. Analyses

The metal concentrations were determined by samplings at different time intervals aliquots of 0.5 ml each from the feed and strip solutions and analysed with an atomic absorption spectrophotometer (Perkin Elmer 2380). Mass flux $J(\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1})$ of the metal ions through the PIM transferred from the feed side of the membrane to the strip side was determined applying its definition: $J = \Delta n/S\Delta t$, where Δn represents the variation in mole number of metal ions in the receiving solution during the reference time Δt , and S is the membrane active area. IR spectra were recorded on with Perkin Elmer spectrophotometer (Spectrum one). X-ray analyses were recorded on a Bruker D8 Advance AXS diffractometer.

3. Results and Discussion

3.1. Physical and Chemical Characteristics of Cellulose Triacetate Membranes

In **Table 1**, some of the characteristics of the membrane made with the carriers have been listed in comparison with those of the reference CTA membrane. As the carrier

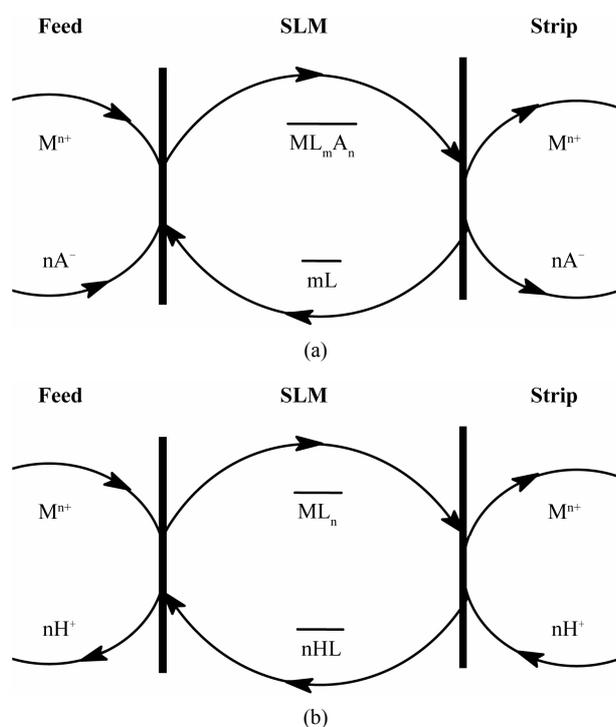


Figure 4. (a) Facilitated co-transport; (b) Facilitated counter-transport mechanisms.

Table 1. Chemical and physical characteristics of cellulose triacetate membranes.

membrane	thickness (μm)	density (mg/cm^2)	contact angle ($^\circ$)
CTA	10	4.88	46.4
CTA-NPOE	15	6.12	80.5
CTA-TEHP	12	5.84	75.8
CTA-NPOE-TOPO	32	7.42	79.2
CTA-TEHP-TOPO	28	6.91	76.3
CTA-NPOE-D2EHPA	27	6.87	78.8
CTA-TEHP-D2EHPA	25	6.33	76.1

molecules (TOPO and D2EHPA) and plasticizers (NPOE and TEHP) are hydrophobic, the location of carrier molecules at the surface of the CTA modified membranes should modify the contact angle which is a parameter indicative of the wetting character of a material.

3.2. X. Ray Diffraction

Figures 5 (a-d) show the X - ray curves for cellulose triacetate (CTA) + plasticizers + carriers membranes.

Based on this figure, we can observe the following:

- The CTA membrane presents a single maximum located at approximately 20° found in all polymers and corresponds to the Van der Waals halo [36,37]. Thus, this material presents basically amorphous characteristics.
- The systems constituted by the mixture of CTA + NPOE + carrier and CTA + TEHP + carrier do not give any diffraction. It can be due to the absence of crystallisation within the membrane which permits us to eliminate the mechanism of transfer of the ions by successive jumps between carrier complexing sites in a 3D assembled state.

3.3. Characterization by FTIR

The membranes CTA + Plasticizer + Carrier were characterised using chemical techniques as well as Fourier Transform Infra - Red (FTIR). IR spectra were recorded on with Perkin - Elmer (Spectrum One) spectrophotometer.

Figures 6 and **7** show the spectrums of the different membranes synthesised.

Table 2 collects the peak values and the corresponding radical of the reference CTA, TEHP, NPOE, CTA + TEHP and CTA + NPOE membranes.

The obtained results showed that all the maximum values extracted from the spectrum of the CTA reference membrane, *i.e.* without plasticizer and carrier, are present

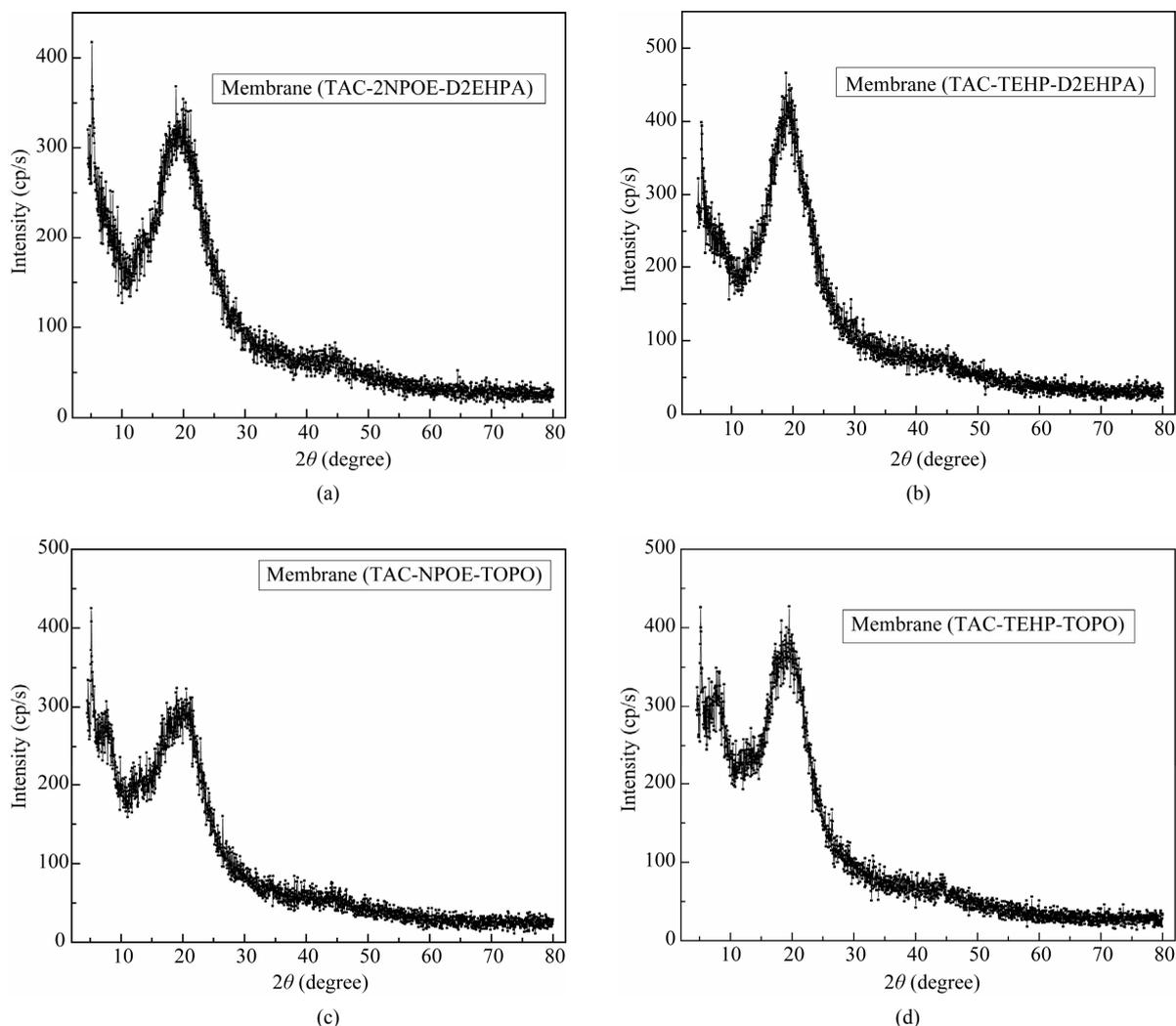


Figure 5. X-ray curves for (CTA + NPOE + D2EHPA), (CTA + TEHP + D2EHPA), (CTA + NPOE + TOPO) and (CTA + NPOE + TOPO) membranes.

in the modified membranes spectra in addition to those of the carrier molecules. This result confirms the presence of plasticizer and carrier in the polymer matrix.

3.4. Characterisation by Scanning Electron Microscopy (SEM)

The morphologies of the CTA + Plasticizer + carrier membranes (cross section) (**Figure 8**) show that the CTA-plasticizer (NPOE or TEHP) and carrier (TOPO or D2EHPA) membranes present a dense structure where the pores of membrane have been filled by the NPOE, TEHP TOPO and D2EHPA molecules yielding a thick and less porous membrane.

3.5. Influence of the Plasticizer Nature

We examined the effect of a plasticizer nature. We used

two plasticizers (NPOE and TEHP).

Figure 9 shows the concentrations of lead in a strip phase using TOPO as carrier and two plasticizers. It can be perceived that tris (2-ethylhexyl) phosphate (TEHP, viscosity, $\eta = 10.2$ cP, dielectric constant, $\epsilon_r = 4.8$) and 2-nitrophenyl octyl ether (NPOE, $\eta = 12.8$ cP, $\epsilon_r = 23.1$) produces the highest PIM transport of ions.

3.6. Influence of the Carrier Nature

The transport has been achieved with two carriers (TOPO and D2EHPA) using a same polymer and a same plasticizer (NPOE).

Figure 10 represents the variation of the concentration of lead ions in the strip phase versus time using TOPO and D₂EHPA carriers. The results show that the concentration of lead in the strip phase obtained with D₂EHPA

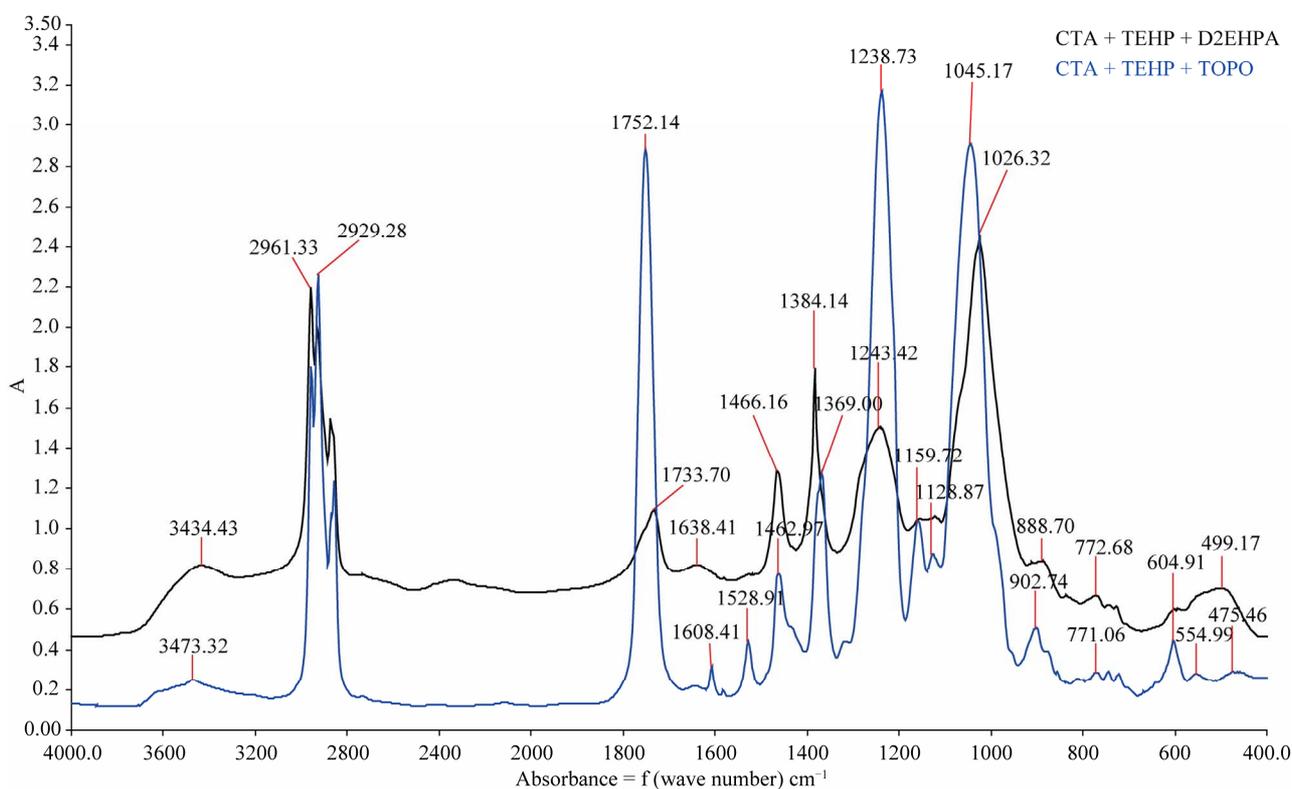


Figure 6. FTIR spectra of the CTA + TEHP + carriers membranes.

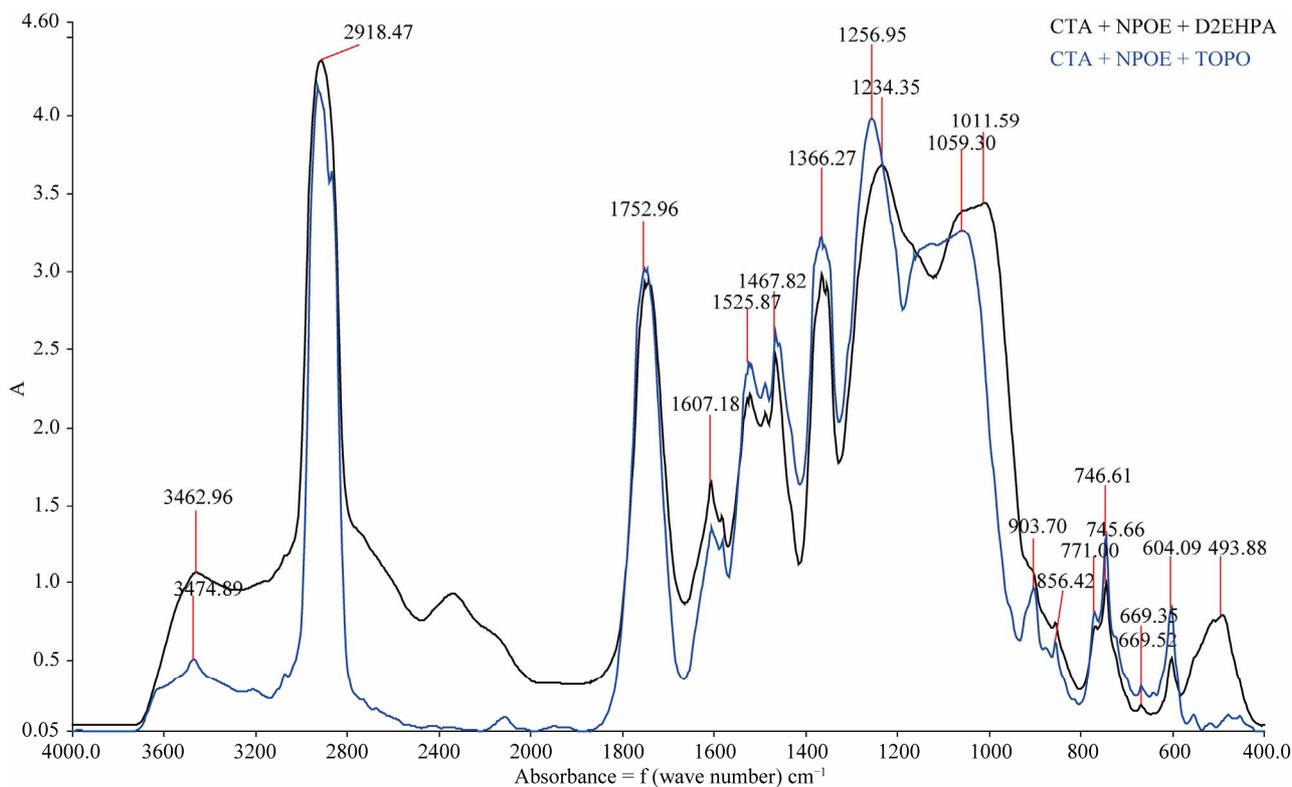


Figure 7. FTIR spectra of the CTA + NPOE + carriers membranes.

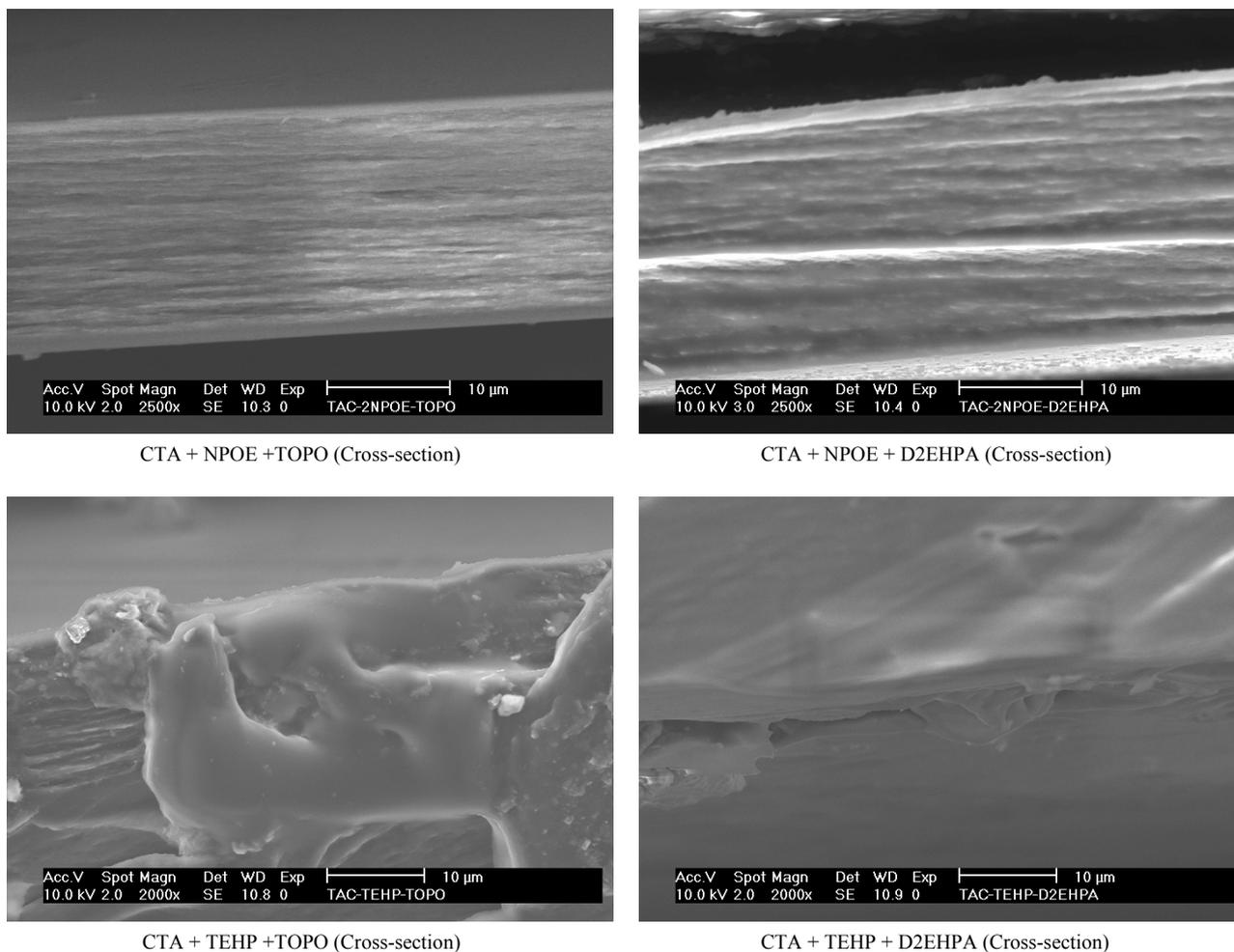


Figure 8. Scanning electron microscopy of various membranes.

is slightly lower than that of TOPO. This can be also related to the difference in viscosity between the two organic phases of D₂EHPA and TOPO, and probably, to the formation of emulsions in the organic phase of TOPO that would block the active surface of the membrane and prevent the metallic ions to react with TOPO molecules present in the membrane.

3.7. Influence of the pH of the Strip Phase

Extraction and transport of a metal cation by an acidic carrier is governed by the exchange of the metal ion for protons of the carrier. Consequently, counter-transport of protons is the driving force and is achieved by maintaining a suitable pH difference between the strip and feed solutions. In addition, careful pH control in the source solution can result in good selectivity as in the case of solvent extraction systems using acidic reagents.

Figure 11 represents the variation of the concentration of lead and cadmium ions in the strip phase versus pH

using D₂EHPA carrier. We demonstrate that a maximum permeability for Pb(II) and Cd(II) across a CTA + TEHP + D2EHPA membrane from a source phase to a receiving phase was obtained at pH 1 - 2.

4. Conclusions

A cellulose triacetate (CTA) membrane containing organo-phosphoric carriers (2-ethylhexyl) phosphoric acid noted (D2EHPA) or trioctyl phosphine oxide noted (TOPO) and 2 - nitrophenyloctyl ether noted (NPOE) or Tris ethylhexyl phosphate (TEHP) noted (TEHP) as a plasticizer has been synthesized. These CTA - plasticizer - Carrier membranes were characterised using chemical techniques as well as Fourier Transform Infra-Red (FTIR), X-ray diffraction (DRX) and SEM analysis. The systems constituted by the mixture of CTA + plasticizers + carriers do not give any diffraction. The morphologies of the CTA + Plasticizer + Carrier membranes (view of Cross-section) show that these membranes present a dense structure. A

Table 2. peak values and the corresponding radicals in different membranes. m (CTA) = 0.2 g, v (TEHP) = v (NPOE) = 0.2 mL.

Membrane	Peak value (cm ⁻¹)	Corresponding radical
CTA	3480 - 3550	O-H
	2935	C-H
	1755	C=O
	1526	COO ⁻
	1246	C-O-C asym
	1054	C-O-C sym
	TEHP	2960
1464		CH ₂
1381		CH ₃
1285		P=O
1020		P-O-C
NPOE	1534	NO ₂ (NPOE)
	1488	-CH ₃ (NPOE)
	1325	C-N (NPOE)
	TAC + TEHP	3477
2913		C-H
1767		C=O (TAC)
1370		-CH ₃ (TAC)
1241		C-O-C asym
1054		C-O-C sym
1034		P-O-C
TAC + NPOE	3481	O-H (TAC)
	1755	C=O (TAC)
	1534	NO ₂ (NPOE)
	1488	-CH ₃ (NPOE)
	1325	C-N (NPOE)
	1169	C-O-C (NPOE)
	1096	C-O-C (TAC)

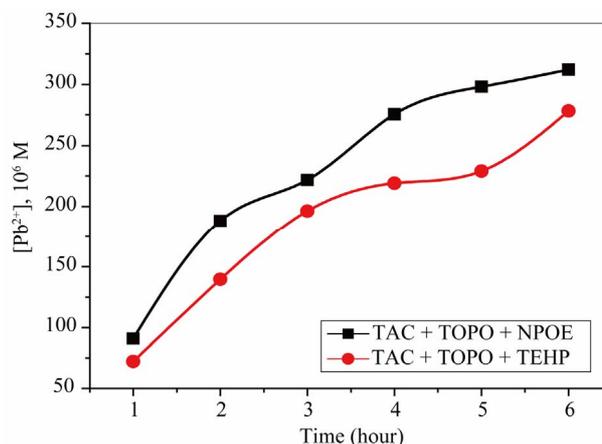


Figure 9. Evolution of the concentration of lead in a strip phase versus time using two plasticizer (NPOE) and (TEHP).

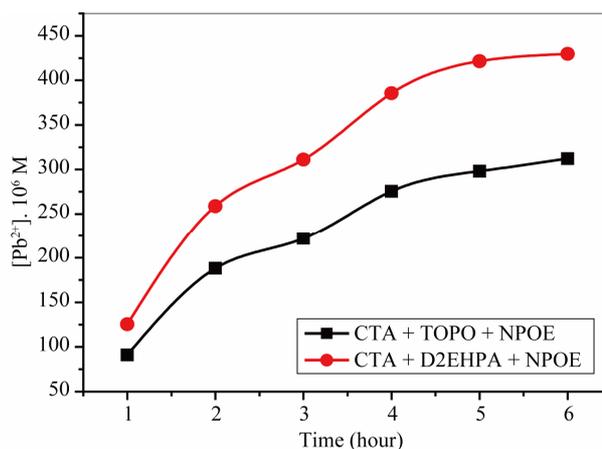


Figure 10. Evolution of the concentration of lead in a strip phase versus time using (CTA + TOPO + NPOE) and (CTA + D2EHPA + NPOE) membranes.

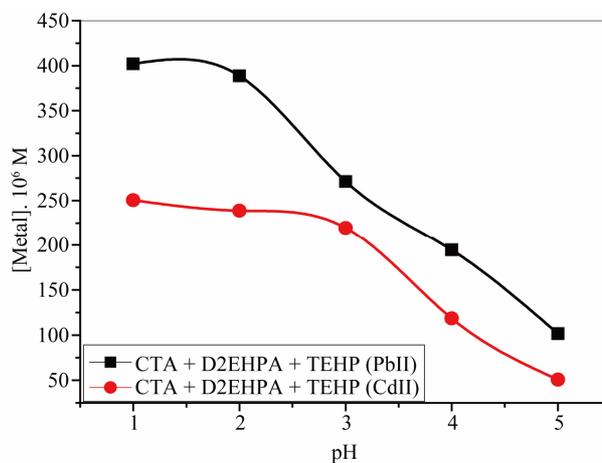


Figure 11. Evolution of the concentration of lead and cadmium in a strip phase versus the pH of a strip phase using (CTA + D2EHPA + TEHP) membrane.

study of the transport across a polymer inclusion membrane has shown that the lead or cadmium transport efficiency was increased using D2EHPA as carrier at pH 1 - 2.

The inclusion of a selective TOPO or D2EHPA in the matrix of a polymer CTA gives rise to stable membranes able to transport ions and to work for a long time. Our results indicate that facilitated transport through plasticized membranes is an attractive and effective way to solve the enduring problem of membrane stability whilst improving the permeability to metal ions.

Further efforts will be directed to the determination of the nature of interactions between polymer and carrier by use of other materials and analysis as well.

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