

# SYNTHESIS AND CHARACTERIZATION OF LOW-COST PLASTICIZED POLYMERIC MEMBRANES FOR SEPARATION OF BIVALENT CATIONS

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Recently, polymer inclusion membranes (PIMs) have surfaced as a viable solution for selective transport and metallic ions separation. The efficiency of such membranes is subject to a number of factors, including the preparation method and relevant physico-chemical characteristics. In this paper, an improvement of a novel category of PIMs for performing ions separation is reported. The membranes were prepared using a mixture of two polymers: cellulose triacetate (CTA) and poly(methyl methacrylate) (PMMA), three different carriers, Aliquat 336 (basic), di-(2-ethylhexyl) phosphoric acid (D2EHPA) (acid) and tributyl phosphate (TBP) (neutral) and plasticized by dioctyle phthalate (DOP). All synthesized membranes were characterized using Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). A study of the transport of Co(II), Cu(II), Ni(II) and Pb(II) species using the synthesized membranes was conducted. Our results indicate that facilitated transport through PIMs is an effective way of solving the permanent problem of membrane stability.

**Keywords:** polymeric membranes, carriers, plasticizer, metals, water purification

## INTRODUCTION

Water is an essential element for the life and functioning of any terrestrial ecosystem. Unfortunately, pure water is becoming increasingly scarce as human activities release increasing amounts of organic and mineral species that are not properly removed. One of the most serious forms of water pollution is that caused by heavy metals. Indeed, heavy metals, although natural elements of the earth, are among the most toxic pollutants because of their persistence, toxicity, and potential for bioaccumulation. Heavy metals are frequently found in industrial and agricultural wastewater, representing a serious concern for water quality and aquatic life. The presence of heavy metals in water poses significant health risks, as they are highly toxic pollutants in high concentrations in freshwater resources.<sup>1,2</sup>

Lead, copper, cobalt and nickel are classified by Cote<sup>3</sup> as strategic metals. These metals are the primary metals used in various industries. For example, copper is used in electrical engineering for the production of cables and wires; in the energy and chemical industries for the manufacture of radiators, chemical apparatus and heat exchangers; and in the automotive industry.<sup>4</sup> Nickel is a very good catalyst for reduction processes, commonly used in the hydrogenation of fats, and is also used as an additive in alloy steels, primarily stainless steel.<sup>4-6</sup> Lead, on the other hand, is still widely used for automotive batteries, pigments, ammunition, thermoplastic-sheathed cables, lifting weights, drive belts, lead crystal glass, radiation protection, and some solders. It is often used to store corrosive liquids.<sup>7</sup> Cobalt is an important metal in high-technology industries involving batteries, alloys, magnetic materials, and catalysts. Therefore, a stable supply of this metal is of considerable importance to these industries.<sup>8</sup>

The demand for metals such as cobalt (Co), nickel (Ni), copper (Cu), and lead (Pb), has steadily risen, leading to their presence in wastewater, sewage, and waste as a result of their extensive use in industrial production.<sup>9</sup> Insufficient treatment of wastes containing these heavy metals can result in their release into water bodies, causing severe harm to the environment and ecosystems.<sup>10</sup> These non-biodegradable metals pose a significant risk as they can accumulate within the ecosystem through the food chain, thereby polluting the aquatic environment. Even at low concentrations, the accumulation

of these metals in organisms and humans can induce various diseases in multiple organs and systems, and prolonged exposure can be life-threatening.<sup>11</sup> The protection of the environment from various types of pollution linked mainly to the rejection of toxic metals requires the use of new technologies expected to be clean, efficient, durable and less expensive.<sup>12</sup> The elimination of heavy metal ions from waste is carried out not only for environmental protection, but also to recover economically valuable metals.<sup>13-15</sup> Over the last few decades, membrane processes have emerged as a rapidly growing modern technology.<sup>16</sup> Researchers in the field of separation technology have shown great interest in this technology due to its superior efficiency compared to previous separation techniques.<sup>17</sup>

Liquid membrane processes (LMs) have become an interesting alternative to conventional solvent extraction for selective separation and concentration of compounds, such as metals and acids, from a dilute aqueous solution. This approach combines extraction and stripping operations into a single step. Facilitated transport through polymer membranes has been applied for ion separation.<sup>18-23</sup> Different types of LMs have been applied to the separation of metal ions, namely, emulsion liquid membranes, supported liquid membranes (SLMs),<sup>24</sup> hollow fibre LMs, and polymer inclusion membranes (PIMs).

Among them, supported liquid membranes (SLMs) were introduced as a novel and promising method of separation. They have some advantages, such as facility of use, low cost of exploitation, good selectivity and simultaneous nature of the process (extraction and back extraction can be performed simultaneously). However, LM techniques have not been adopted for large-scale industrial processes, principally because of the lack of long-term stability, difficulty in operation of emulsification and de-emulsification.<sup>25</sup> Sugiura *et al.*<sup>26</sup> proposed an alternative approach, which encountered a true success. It consists of the preparation of membranes in which an extractant (*i.e.*, carrier) is incorporated in a plasticized thermoplastic polymer. These membranes called plasticized polymeric membranes (PPM) or polymer inclusion membranes (PIMs) or fixed sites membranes (FSM) have been involved in separation processes like SLM.<sup>17,22,27,28</sup> Recently, polymer inclusion membranes (PIMs) have become a very important alternative to conventional processes used for wastewater treatment, separation and pre-concentration of various constituents, such as metal ions, anions, metallic complexes and organic compounds.<sup>29,30</sup>

Owing to their higher stability, PIMs can be reused multiple times in batch separation processes,<sup>31</sup> or can be used for prolonged periods of time in continuous separation processes (*e.g.*, several months<sup>32</sup>), with no significant loss in performance, thus making them of potential interest to industrial separation. In addition, it has been demonstrated that most of the extractants used in conventional solvent extraction systems can be incorporated in PIMs, thus providing a wide range of applications involving the selective separation of numerous both metallic and non-metallic inorganic and organic species.<sup>33-36</sup> This simple technique allows easy modification of the composition of the membrane, which is very important since it enables affecting the efficiency and selectivity of the metal ion separation process.<sup>37</sup> The transport rate across PIMs is affected by a variety of parameters, such as the type of polymer matrix, the concentration of the carrier, the amount of the plasticizer, the thickness of the membrane, and membrane surface morphology.<sup>38</sup>

The polymer plays a key role in the synthesis of different kinds of membranes.<sup>39</sup> Several polymers are available, but the selection of membrane polymer is not a trivial task. A polymer has to have appropriate characteristics for the intended application. The polymer has to be a suitable membrane former in terms of chain rigidity, chain interactions, stereo-regularity, and polarity of its functional groups. The most commonly used as polymer base for PIMs preparation is cellulose triacetate (CTA), which has thin film forming ability with good properties. CTA is a polar polymer containing a number of acetyl and hydroxyl groups that are able to develop hydrogen bonding, giving this polymer a crystalline structure.<sup>22</sup> Polymeric membranes using CTA have been successfully used for the extraction of metals using solvating-type extractants, such as crown ethers, trioctyle phosphine oxide (TOPO), Aliquat-336, tributyl phosphate (TBP), and di-(2-ethylhexyl) phosphoric acid (D2EHPA).<sup>25,40-43</sup> However, CTA decomposes when used in strongly acidic or basic solutions. The concern of the long-term stability caused by CTA hydrolysis limits the practical application of PIMs with CTA as the base polymer.<sup>44</sup> To resolve this problem, a typical approach is to use other base polymers for PIMs.<sup>45</sup> Polymethyl methacrylate (PMMA) is an economical alternative to other polymers, when flexural strength, transparency and polishability are more important than chemical and heat resistance. It is often preferred due to its moderate properties, easy handling, and processing and low cost.<sup>46</sup>

Plasticizer is also generally added to the formulation of PIMs. The role of the plasticizer/modifier is to make the PIMs less rigid, thus increasing the diffusion coefficients of species in the membrane and improving the compatibility of the membrane components.<sup>47</sup> Nowadays, it is important to note that the addition of the plasticizer to PIMs affects both the physical and chemical properties of the membranes. Initially, plasticizers were added to the formulation of PIMs to separate the chains of the polymer, thus improving the flexibility of the membrane.<sup>41</sup> Plasticizers used in the preparation of the polymeric membrane must be compatible with the polymer and also miscible with the solvent used in the membrane preparation. The plasticizers with high lipophilicity are preferred.<sup>48</sup> Di-octyl phthalate (DOP) is frequently employed in plastic films and coatings to augment their flexibility and heat resistance. Additionally, DOP can serve as a carrier in polymer inclusion membranes (PIM), where it facilitates the transport of metal ions in aqueous solutions.<sup>2,49,50</sup>

Complexing agents (carriers) are used to enhance the transport of solutes across the membrane.<sup>47</sup> Furthermore, a good carrier should be stable, inexpensive, non-toxic, and soluble in the membrane.<sup>22,28,51</sup> The carrier's principal role is to facilitate the transport of ions across the membrane.<sup>39</sup> Depending on the nature of the carrier, different extraction mechanisms are possible, such as ion exchange or chelation. Therefore, the analyte and the carrier form a hydrophobic ion-pair or a complex that is able to diffuse through the membrane. Using an appropriate receiving solution, the analyte will be released, and the carrier will again be able to repeat the transport process.<sup>41</sup>

In this paper, novel polymeric membranes were synthesized using cellulose triacetate (CTA) and polymethyl methacrylate (PMMA) as polymers, plasticized by di-octyl phthalate (DOP) and modified by carrier incorporation that are selectively permeable to copper, lead, nickel and cobalt cations. All synthesized membranes were characterized using several techniques, namely, Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and contact angle. A comparative study was conducted to evaluate the transport efficiency of the synthesized membranes in the selective separation of Pb(II), Cu(II), Co(II), and Ni(II) ions.

## EXPERIMENTAL

### Chemicals

Cellulose triacetate (CTA pellets), di-(2-ethylhexyl) phosphoric acid (D2EHPA), and Pb(NO<sub>3</sub>)<sub>2</sub> (99%) were purchased from Fluka (Buchs, Switzerland). Polymethyl methacrylate (PMMA pellets), Aliquat 336, and tributyl phosphate (97%) were received from Sigma Aldrich. Cu(NO<sub>3</sub>)<sub>2</sub> (99.99%), Co(NO<sub>3</sub>)<sub>2</sub> (99%), and Chloroform (99%) were received from VWR Chemicals. DOP (99.5%) was a product of CARLO ERBA (Val de Reuil, France). Ni(NO<sub>3</sub>)<sub>2</sub> (98%) was purchased from Biochem (Georgia, USA). All reagents were used as received without any supplementary treatment. Deionized water was used to prepare all the aqueous solutions.

### Preparation of membranes

PIMs were prepared using the procedure reported previously.<sup>26,52-54</sup> Briefly, a mass of 0.15 g of CTA was dissolved in 15 mL of chloroform (CHCl<sub>3</sub>), and the heterogeneous mixture was stirred moderately for 4 hours. Then, a mass of 0.15 g of PMMA was added and maintained for 2 h under vigorous stirring. After that, an adequate quantity of a specific carrier was introduced into the solution. Furthermore, a given volume of plasticizer (DOP) was added, and the solution was left under magnetic stirring for 2 hours to ensure homogenization. The solution was transferred to a circular glass container and allowed to undergo a gradual evaporation process over a period of 24 hours. Subsequently, the resulting membrane was detached by adding distilled water and then subjected to drying at a temperature of 40 °C.

### Characterization of membranes

FTIR spectra of different membranes were obtained using an Alpha Bruker (single reflection diamond ATR) spectrometer in the region of 4000–400 cm<sup>-1</sup>. The contact angles were measured using a Lauda TD3 Tensiometer with a glass buoyancy probe, which was calibrated using deionised water. Thermogravimetric analysis (TGA) was carried out on a TA Instruments Q500 (TA Instruments Co., USA) under nitrogen atmosphere, with a heating rate of 10 °C/min. The surface morphologies of the synthesized membranes were observed using SEM imaging via a scanning electron microscope type JSM-7610F Plus.

### Transport experiments

The transport experiments were carried out with a cell (500 mL) composed of two plexiglass compartments separated by the the membrane film. The feed compartment was filled with a 25 mg/L solution of Co(II), Cu(II), Ni(II), or Pb(II), and the other compartment was filled with distilled water. The experiments were performed at 25 °C and both compartments were mechanically stirred at the speed of 800 rpm. The metal concentrations were

determined by sampling 10 mL from the feed solution at different time intervals and analyzed using the atomic absorption spectroscopy technique (AAS) with an Analytik Jena novAA 350.

## RESULTS AND DISCUSSION

### Contact angle measurement

The determination of contact angles of the various elaborated membranes provides valuable insights into the surface state and surface tensions of the materials. This characterization helps to ascertain the hydrophobic/hydrophilic nature of the different polymeric membranes. Table 1 summarizes the values of contact angles and densities of the various elaborated cellulose membranes.

Based on the results, the pure TAC-based membrane presented a water contact angle ( $\theta$ ) value of  $58.1 \pm 0.01^\circ$ . This value is comparable to the recently published results,<sup>46</sup> suggesting the CTA membrane has a hydrophilic nature ( $\theta < 90^\circ$ ).

The addition of PMMA increased the contact angle of the CTA membrane from  $58.10^\circ$  to  $70.22^\circ$ . This is due, on the one hand, to the less hydrophilic nature of PMMA (polymethyl methacrylate) with a contact angle equal to  $70.9^\circ$ . On the other hand, it may be explained by the interaction between the polar functional groups of the CTA membrane (such as acetyl and hydroxyl groups) and the methacrylate groups of PMMA, forming intermolecular bonds between the two materials. These interactions reduce the free energy surface of the CTA membrane and modify its wettability, resulting in a change in the contact angle with water. The addition of the plasticizer DOP, which is a hydrophobic, apolar organic plasticizer, further increased the contact angle of the PMMA surface on the CTA membrane from  $70.22^\circ$  to  $72.52^\circ$ . This could be due to the presence of carbonyl groups (C=O) in DOP, which interact with the methacrylate groups of PMMA and the acetate and hydroxyl groups of TAC. These interactions may slightly reduce the affinity of both TAC and PMMA for water, thus increasing the contact angle.

Incorporating various carrier molecules (extractants) into the membranes leads to a decrease in the water contact angle, which shows that the addition of Aliquat-336, D2EHPA, and TBP enhances the wettability of the membrane surface. Previous research suggests that a more hydrophilic surface can lead to increased transport efficiency and permeability.<sup>55</sup> However, it is important to note that the extent to which the wettability of PIMs is altered depends heavily on the nature of the carrier being used.<sup>25</sup>

Indeed, the inclusion of Aliquat-336 in the membrane matrix (TAC+PMMA+DOP) significantly modified its surface properties, shifting from a slightly hydrophilic character ( $72.52^\circ$ ) for the TAC+PMMA+DOP membrane to a highly hydrophilic one ( $34.7^\circ$ ) for the TAC+PMMA+DOP+Aliquat-336 containing membrane. In fact, the functional group (quaternary ammonium of Aliquat-336) is known for its hydrophilic nature induced by positively charged quaternary amine. Also, the polarity of this functional group, exposed on the surface, makes the membrane more hydrophilic. This result is in agreement with the findings of other researchers.<sup>56,57</sup>

For the CTA+PMMA+DOP+D2EHPA and CTA+PMMA+DOP+TBP membranes, the addition of D2EHPA and TBP decreases the contact angle with surface water. In fact, the contact angle is  $52^\circ$  and  $54^\circ$ , respectively, indicating an increase in their hydrophilic character compared to the CTA+PMMA+DOP membrane. This may be explained by the fact that D2EHPA and TBP contain polar groups, and exposing these groups to the membrane surface makes the membrane more hydrophilic.

Table 1  
Contact angle and density of elaborated membranes

Membrane	Contact angle (average $\pm$ sd) ( $^\circ$ )	Density (mg/cm <sup>2</sup> )
CTA	$58.10 \pm 0.01$	2.225
CTA+PMMA	$70.22 \pm 0.02$	4.1875
CTA+PMMA+DOP	$72.52 \pm 0.01$	6.2125
CTA+PMMA+DOP+Aliquat-336	$38.19 \pm 0.01$	6.35
CTA+PMMA+DOP+D2EHPA	$52.65 \pm 0.01$	6.6
CTA+PMMA+DOP+TBP	$58.48 \pm 0.06$	10.0375

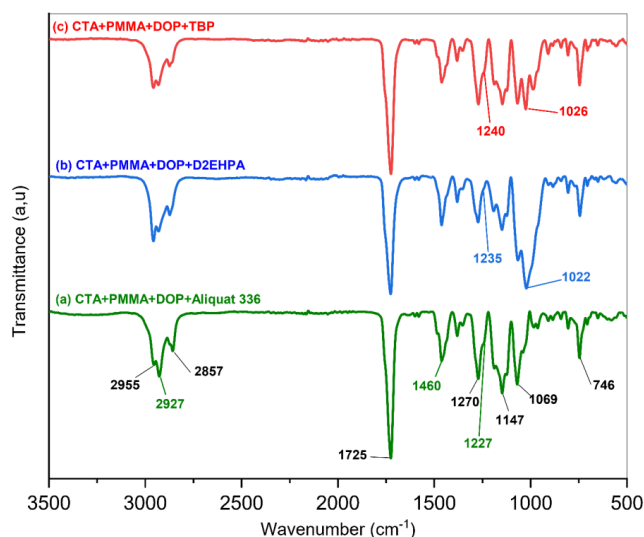


Figure 1: FTIR spectra of the different membranes

### Characterization of membranes by FTIR spectroscopy

Several experimental methods are used to characterize and study polymers and membranes, both in solution and in the solid state. Fourier transform infrared spectroscopy (FTIR) remains the most suitable technique for such investigations, as it allows the identification of different functional groups within each compound. Its high sensitivity enables the study of molecular behavior and movements of polymer chains on a microscopic scale. This advanced technique also allows the identification and quantification of various interactions that may occur between the different constituents of a membrane (polymer, plasticizer, and extractant).

Figure 1 presents the FTIR spectra of the three synthesized membranes, which differ in the nature of the carrier (TBP, D2EHPA, or Aliquat-336).

We observed that the FTIR spectra of the membranes grouped in Figure 1 (a, b and c) exhibit distinct bands that can be attributed to specific functional groups of both TAC and PMMA polymers, the DOP plasticizer, and the complexing agent. The main absorption band is detected at  $1725\text{ cm}^{-1}$ , corresponding to the stretching vibration of the carbonyl group  $\text{C}=\text{O}$  in both DOP and TAC/PMMA polymers. Additionally, the presence of bands at  $2955\text{ cm}^{-1}$ ,  $2927\text{ cm}^{-1}$ , and  $2857\text{ cm}^{-1}$  is, respectively, attributed to the asymmetric and symmetric stretching vibrations of  $-\text{C}-\text{H}$  and  $-\text{CH}_2-$  bonds.

The peaks at  $1270\text{ cm}^{-1}$  and  $1069\text{ cm}^{-1}$  are attributed to the asymmetric and symmetric stretching vibrations of the  $\text{C}-\text{O}-\text{C}$  group, respectively. Two bands at  $1460\text{ cm}^{-1}$  and  $746\text{ cm}^{-1}$  were also observed, corresponding to the angular deformation of the  $-\text{CH}_2$  and  $-\text{CH}$  groups of the DOP plasticizer.<sup>58</sup> Finally, a band at  $1140\text{ cm}^{-1}$  corresponds to the characteristic stretching vibration of the  $\text{C}-\text{O}-\text{C}$  group in PMMA.<sup>59</sup>

Regarding the confirmation of the presence of carriers, characteristic bands of Aliquat-336 are observed in Figure 1 (a). Thus, the band at  $1227\text{ cm}^{-1}$  is assigned to the quaternary ammonium group in Aliquat 336,<sup>60</sup> and another band was observed at  $1460\text{ cm}^{-1}$ , which is related to the stretching vibration of the functional group  $-\text{N}-\text{C}$ .<sup>61</sup>

The bands at  $1235\text{ cm}^{-1}$  and  $1022\text{ cm}^{-1}$  correspond to the stretching vibration modes of  $\text{P}=\text{O}$  and  $\text{P}-\text{O}$  bond of D2EHPA, respectively,<sup>62</sup> which appear in Figure 1 (b). However, the bands at  $1240\text{ cm}^{-1}$  and  $1026\text{ cm}^{-1}$ , as shown in Figure 1 (c), correspond to the stretching vibration of the  $\text{P}=\text{O}$  and  $\text{P}-\text{O}-\text{C}$  functional groups, respectively. These groups are characteristic of the carrier TBP.<sup>63</sup>

### Characterization of membranes by TGA

During this study, we aimed to investigate the thermal stability of the prepared membranes using thermogravimetric analysis (TGA). This technique allowed examining the behavior of the various constituents within the mixtures and their impact on the thermal stability of the polymeric membranes. Figures 2, 3 and 4 show the TGA weight loss thermograms and the corresponding derivatives DTG curves of the synthesized membranes (CTA+PMMA+DOP+Aliquat-336, CTA+PMMA+DOP+TBP and CTA+PMMA+DOP+D2EHPA).

From Figure 2, it can be observed that the membrane composed of both TAC and PMMA polymers, as well as the complexing agent Aliquat-336 and the plasticizer DOP, remains relatively stable over a temperature range up to 182 °C, and it undergoes degradation in three main steps. During the first degradation step, which spans over a temperature range from 180 °C to 280 °C, this membrane loses 29% of its initial mass. The  $T_{\text{onset}}$  is located at 182 °C, while  $T_{\text{max}}$  is at 216 °C. This degradation step is primarily attributed to the evaporation of the Aliquat-336 complexing agent, which has a boiling point of 225 °C. The second degradation step, on the other hand, extends over a temperature range from 280 °C to 340 °C, during which membrane M1 loses approximately 22% of its initial mass. The  $T_{\text{max}}$  for this step is around 311 °C.

Due to the significant mass loss observed during this degradation step, it can be attributed to the degradation of the DOP plasticizer linked to the TAC polymer. It is worth mentioning that the boiling point of the DOP plasticizer is 384 °C. The final degradation step of this membrane, occurring between 350 °C and 440 °C, is associated with the degradation of the PMMA polymer.

Based on Figure 3, we observe that the membrane composed of both TAC and PMMA polymers, the TBP complexing agent, and the DOP plasticizer, remains relatively stable over a temperature range up to 140 °C, and it also undergoes degradation in three steps, despite being composed of four components. During the first degradation step, spanning over a temperature range from 140 °C to 320 °C, this membrane loses 23% of its initial mass. The  $T_{\text{onset}}$  is located at 138 °C, while  $T_{\text{max}}$  is at 311 °C. This degradation step is attributed to the degradation of TBP. The second degradation step, on the other hand, extends over a temperature range from 315 °C to 380 °C, during which the membrane loses approximately 48% of its initial mass. The  $T_{\text{max}}$  for this step is around 340 °C.

Due to the significant mass loss observed during this second degradation step (a high mass loss of 48%), it can be attributed to the degradation of the DOP plasticizer linked to a large portion of the TAC polymer. The final degradation step of this membrane, occurring between 360 °C and 430 °C, is related to the degradation of the TAC/PMMA blend, with a  $T_{\text{max}}$  located at 397 °C.

Finally, for the membrane TAC+PMMA+DOP+D2EHPA, the TGA thermogram revealed three degradation steps (Fig. 4). The first step occurred from 140 °C to 260 °C, during which the membrane lost 43% of its initial mass. The  $T_{\text{onset}}$  is located at 142 °C, while  $T_{\text{max}}$  is at 249 °C. This degradation step is mainly attributed to the degradation of the extractant D2EHPA. The second step is recorded between 260 °C and 375 °C, during which the membrane lost 20% of its initial mass. This degradation step is attributed to the degradation of the DOP plasticizer. The last mass loss of this membrane occurs between 380 °C and 420 °C, and is related to the degradation of the TAC/PMMA blend, with a  $T_{\text{max}}$  located at 389 °C.

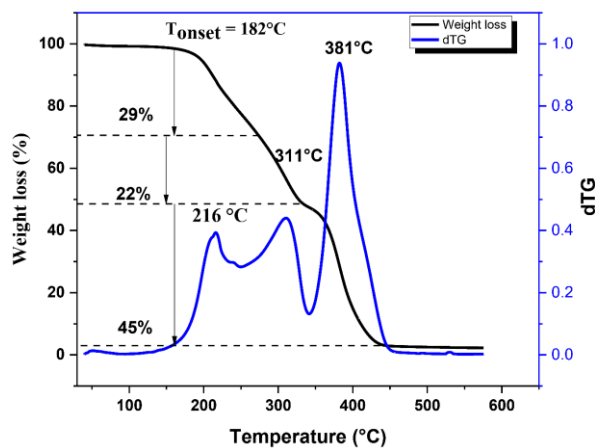


Figure 2: TGA and DTG curves of CTA+PMMA+DOP+Aliquat-336 membrane

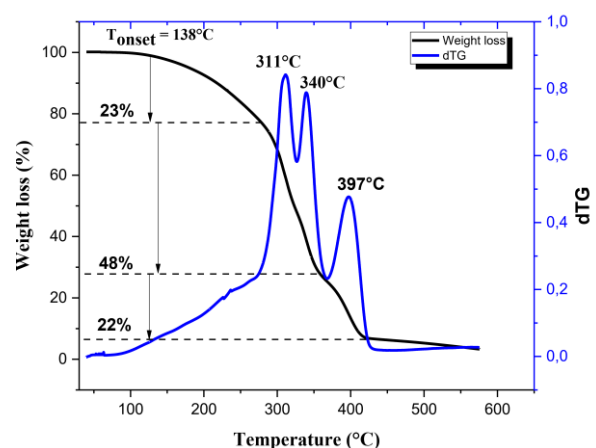


Figure 3: TGA and DTG curves of CTA+PMMA++DOP+TBP membrane

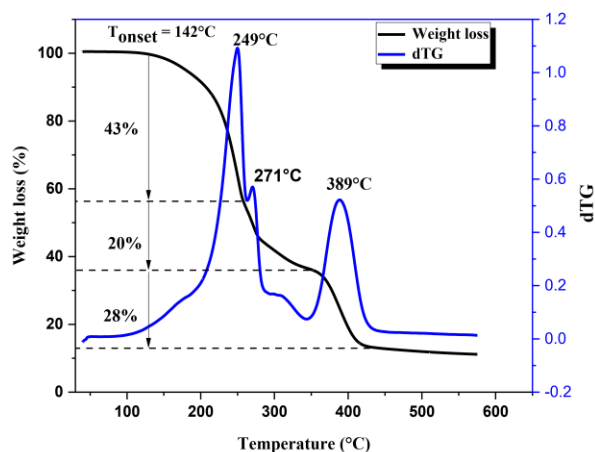


Figure 4: TGA and DTG curves of CTA+PMMA++DOP+D2EHPA membrane

### SEM analysis

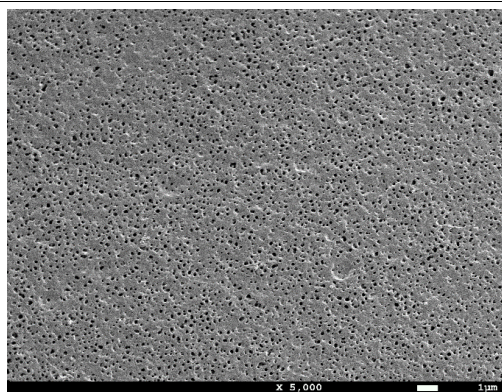
The efficiency of metal ion transport through a polymer inclusion membrane (PIM) is highly dependent on its microstructure, which directly affects the distribution of the carrier within the polymer matrix. To assess the membrane's performance, scanning electron microscopy (SEM) is essential for determining both the surface characteristics (homogeneity and density) and the textural properties (porosity and thickness). Figure 5 displays the SEM images of the membranes before and after transport.

The morphology of the membranes CTA+PMMA+DOP+D2EHPA and CTA+PMMA+DOP+TBP (Fig. 5 (b and c)) before transport shows that the membranes present a uniform and dense surface, with no apparent porosity, as the pores of the membrane have been filled by the DOP, PMMA, TBP and D2EHPA molecules, yielding a thicker and less porous membrane.

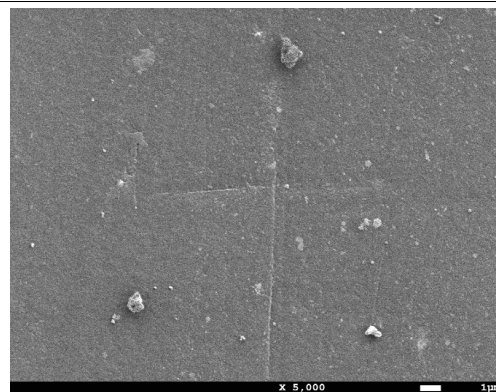
On the other hand, the membrane CTA+PMMA+DOP+Aliquat 336 (Fig. 5 (a)) displays a porous structure, with a relatively uniform pore distribution. This is probably due to the fact that the Aliquat-336 increases the spaces or pores, which may be generated after the interactions developed between the two polymers and the plasticizer.

Furthermore, the three elaborated membranes exhibit a non-textured surface, confirming the compatibility between the two polymers TAC and PMMA, the DOP plasticizer, and the carriers.

It is important to note the radical change in the morphology of all synthesized membranes after metal ion transport. Crystalline structures with deposits are observed on the surfaces of the membranes after the metal ion transport process. This confirms the formation of metal-carrier complexes inside the membranes. The SEM images also clearly indicate the disappearance of porosity in the case of the membrane based on Aliquat-336, where the pores have been filled by the deposition of the Aliquat-336/metal complex.<sup>64</sup>

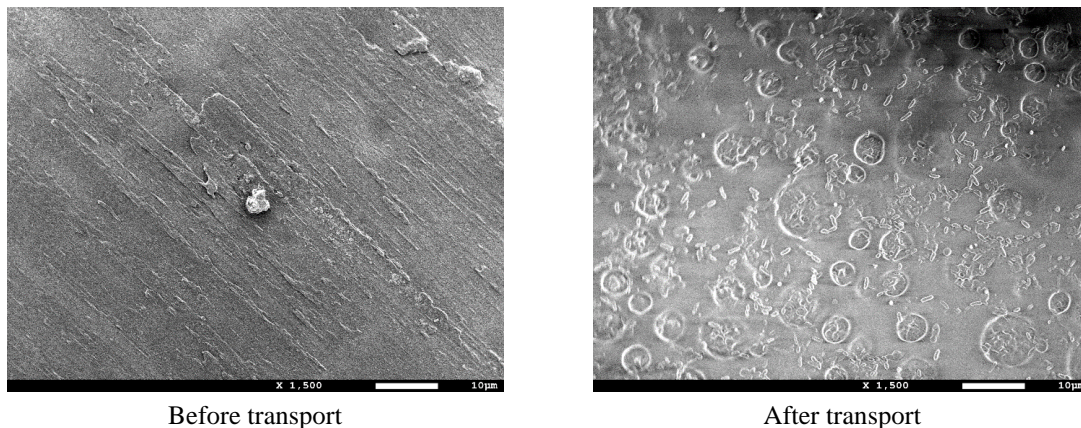


Before transport



After transport

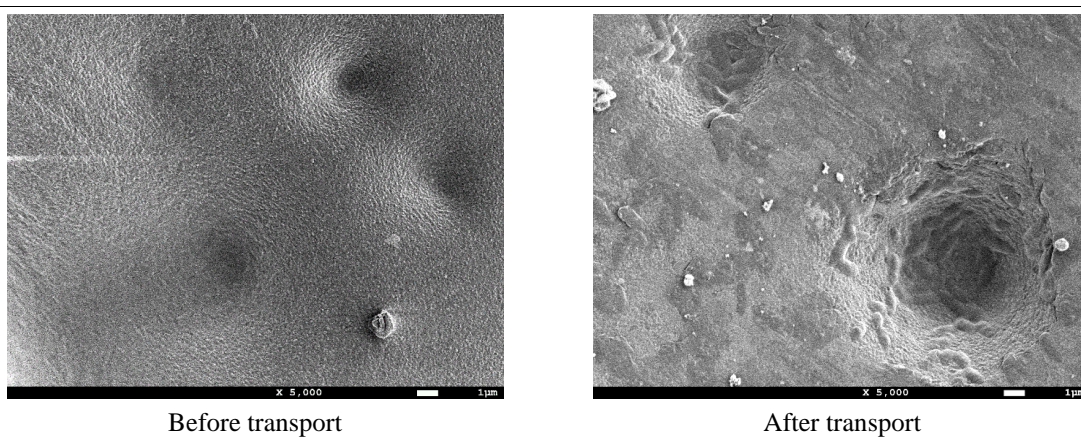
a) CTA+PMMA+DOP+Aliquat-336 membrane



Before transport

After transport

b) CTA+PMMA+DOP+D2EHFA membrane



Before transport

After transport

c) (CTA+PMMA+DOP+TBP) membrane

Figure 5: Scanning electron microscopy images of the synthesized membranes before and after metal ion transport

**Ni(II), Cu(II), Co(II) and Pb(II) transport experiments**

Figure 6 illustrates the evolution of Pb(II), Cu(II), Co(II), and Ni(II) ion concentrations in the feed compartment over time using the three membranes differing in the nature of the complexing agent (Aliquat-336, D2EHFA, and TBP). The initial concentration of each metal was set to 25 mg/L. The obtained results show that the membranes used exhibit different performances for the transport of the four metals over time.

**Nickel (II) transfer**

The membrane TAC+PMMA+DOP+Aliquat-336 exhibited the highest efficiency for nickel transport, achieving a maximum transfer percentage of 100% after 6 hours of transport. However, the other two membranes TAC+PMMA+DOP+D2EHFA and TAC+PMMA+DOP+TBP showed a decline in performance, with transfer percentages of 31.12% and 4.48%, respectively. These results indicate that the membrane containing Aliquat-336 forms the most stable complex with nickel.

**Cobalt (II) transfer**

The results obtained for Co(II) transport through the three membranes showed very similar performances. The membrane CTA+PMMA+DOP+D2EHFA demonstrated the highest selectivity for Co(II) transport, with an acceptable transfer percentage of 32.7%. The membranes CTA+PMMA+DOP+Aliquat-336 and CTA+PMMA+DOP+TBP showed slightly lower transfer percentages of 23.5% and 29.5%, respectively.

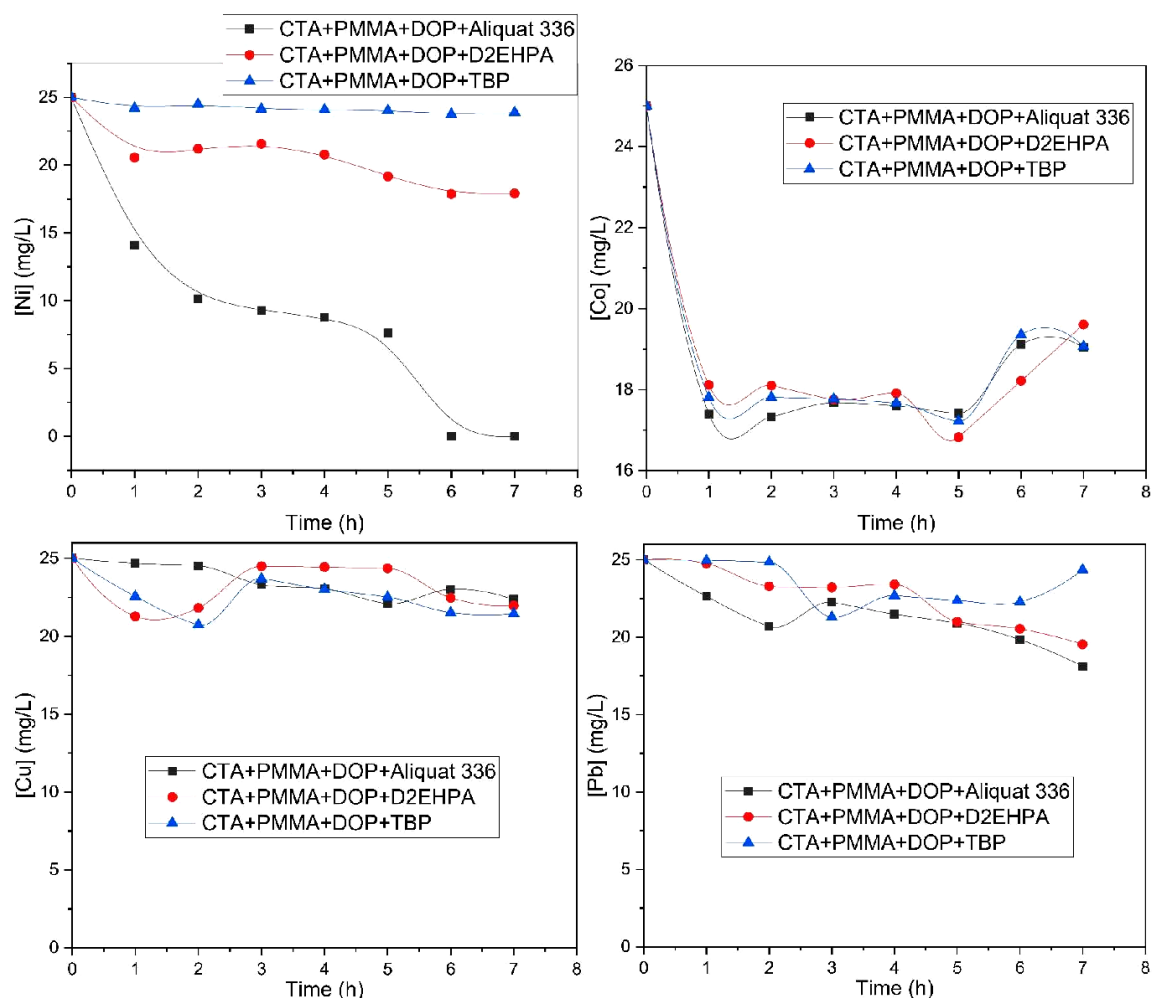


Figure 6: Evolution of the concentration of Pb(II), Cu(II), Co(II), and Ni(II) in the feed compartment over time

### ***Copper (II) transfer***

Experiments for Cu(II) transport were conducted using the three developed membranes. The obtained results showed that the membranes CTA+PMMA+DOP+D2EHPA, CTA+PMMA+DOP+TBP and CTA+PMMA+DOP+Aliquat-336 demonstrated low copper removal with transfer performances of 17.1%, 14.9%, and 11.6%, respectively.

### ***Lead (II) transfer***

According to the results, the membrane CTA+PMMA+DOP+Aliquat-336 exhibited the best performance for lead (II) ion transport, with a transfer percentage of up to 27.55%. The membrane CTA+PMMA+DOP+D2EHPA showed a lower performance, with a transfer percentage of up to 21.85%. On the other hand, the membrane CTA+PMMA+DOP+TBP exhibited the lowest performance for lead (II) ions, with only 14.57% elimination.

## **CONCLUSION**

In this work, we have successfully synthesized a novel type of polymeric membranes by utilizing a blend of two polymers, CTA and PMMA. The membranes were prepared by solution casting, followed by solvent evaporation. To enhance their performance, we incorporated the selective mobile carriers Aliquat-336, D2EHPA, and TBP, along with the plasticizer DOP.

We employed various physical and chemical characterization techniques, including Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and contact angle measurements. The FTIR analysis confirmed the presence of characteristic bands corresponding to specific functional groups of both polymers, as well as the three

carriers and the DOP plasticizer. Our findings indicate that the inclusion of Aliquat-336, D2EHPA, and TBP into the membranes resulted in homogeneous and hydrophilic membranes.

The thermal stability of the synthesized membranes was investigated through TGA, revealing a three-step degradation process. The main weight loss was observed at 135 °C, which can be attributed to the thermal degradation of the plasticizer and of the carriers. This finding indicates that all the synthesized membranes exhibited satisfactory thermal stability. Moreover, SEM observation of the membranes revealed a structure that was either dense or porous with uniform distribution. Additionally, we conducted a study on the transport of metal ions across the polymer inclusion membranes. The results showed that the retention efficiency for nickel, copper, cobalt, and cadmium ions increased when Aliquat-336, DEHPA, and TBP were used as carriers.

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