

Use of Polymer Inclusion Membrane for the Separation of Phenols Compounds Mixture from Dilute Aqueous Solutions

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Abstract: Separation of phenolic compounds mixture namely: phenol, resorcinol, Bisphenol A from dilute aqueous solutions by polymer inclusion membrane using Cellulose triacetate (CTA) as support was investigated as a means of recovering Bisphenol A from mixture of phenolic compounds. The effects of parameters influencing the separation performance were studied in terms of permeation flux and selectivity. For competitive transport of phenols across PIM with RC8 + NPOE, the selectivity order was Bisphenol > Phenol > Resorcinol. The high permselectivity of the membrane to Bisphenol A was primarily due to its high affinity towards calixresorcinarene macrocycle. This is of particular interest from an industrial point of view because the enriched phenol permeate can be easily recovered upon phase separation. The prepared PIM were characterized by using Raman spectroscopy, XPS and scanning electron microscopy (SEM) techniques.

Keywords: PIM, CTA, Membrane separation, Phenols mixture, Bisphenol A, Wastewater treatment.

1. INTRODUCTION

Phenolic compounds are chemicals that persist for a long time to accumulate in the environment, and thus exert toxic effects on humans and animals [1]. Phenolic compounds once found in water have the possibility of reacting with other components of the aquatic environment, namely inorganic compounds and microorganisms. Phenolic compounds belong to the class of organic compounds with one or more hydroxyl groups directly attached to one or more aromatic rings. Natural and anthropogenic activities are at the origin of the omnipresence of phenolic compounds in water. Natural springs engulf decaying dead plants and animals (organic matter) in the water. While industrial, domestic, agricultural and municipal activities are anthropogenic sources. Phenolic compounds abundant in nature constitute the colors of flowers and fruits [2]. Others are derived from synthesis. Similarly, the use of pesticides, insecticides and herbicides is the main source of water pollution by phenolic compounds of agricultural origin. The transfer of phenolic compounds

to the aquatic environment results from natural, industrial, domestic and agricultural activities. Their presence is due to runoff from agricultural land [3]. The elimination of phenolic compounds from the aquatic compartment is a necessity in order to protect the life of humans and aquatic organisms from possible contamination by these toxic chemicals, and then the separation and recovery of phenolic substances from industrial wastewater streams are of significant interest from an environmental perspective [4].

Applying appropriate technologies to effectively remove this class of compounds can both produce depolluted water and also recover value-added phenolic compounds as by-products. These methods include adsorption [5, 6], photocatalytic degradation, extraction [7, 8], biological methods, ion exchange and membrane separation techniques [4].

The membrane processes applied in the treatment of water loaded with phenols are considered as innovative technology, economically profitable and respectful of the environment. Membrane techniques such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are effectively applied to help address phenol removal problems by recovering phenol from water [9-11]. However, membrane fouling

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has long been known to be the major drawback to achieving high performance in membrane operations. Thus, the studies currently being conducted relate to polymer inclusion membrane (PIM) processes. The polymer inclusion membrane (PIMs) proposed by Sugiura [12] belonging to the family of liquid membranes, obtained by incorporating transporters within a plasticized polymer playing the role of a support, caught our attention as an alternative method for its selectivity and good stability.

These two points are important from the perspective of a membrane application. This study is a continuation of the studies already undertaken on the facilitated transport of phenol and bisphenol A [13-15], it aims to separate a mixture of phenolic compounds namely: phenol, resorcinol and bisphenol A, using an polymer inclusion membrane technology.

2. MATERIALS AND METHODS

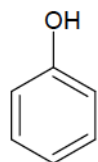
2.1. Chemicals

The transporter, (C-octyl)calyx[4] resorcinarene, abbreviated to RC8, is synthesized in our laboratory [16].

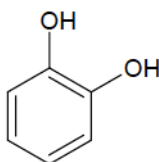
Phenol, resorcinol, bisphenol A (Figure 1), hydrochloric acid, potassium hydroxide, salts, dichloromethane, cellulose triacetate (CTA, molecular weight $M_w = 72,000 - 74,000$, with an acetyl content of approximately 43.6 %), 2-nitrophenyl-octylether (2-NPOE) are analytical grade reagents purchased from Sigma-Aldrich. Aqueous solutions have a resistivity of at least $18.2 \text{ M}\Omega \text{ cm}$ obtained with a Milli-Q Plus system. The pH adjustment is carried out by adding dilute hydrochloric acid (0.01 M) or sodium hydroxide (0.25 M) in order to prepare the solution with the desired pH.

2.2. Membrane Preparation

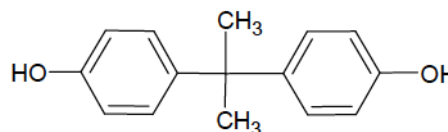
PIMs are prepared according to the procedure reported by Sigiura [12], the amount of each



Phenol



Resorcinol



Bisphenol A

Figure 1: Chemical structure of Phenols used in this study.

constituent depends on the desired membrane. Thus, for PIM, 10 ml of a solution of polymer (0.1 g of CTA in dichloromethane), calix[4] resorcinarene (0-0.06 g/g CTA) and plasticizer (0-3 g plasticizer/g CTA) are transferred to a 9.0 cm diameter Petri dish. The solution is left to evaporate overnight at ambient temperature ($25 \pm 1^\circ\text{C}$). The film formed is carefully peeled off from the bottom of the Petri dish and kept in demineralised water for 24 hours.

2.3. Membrane Characterizations

In order to characterize the PIM, we used SEM, Raman and XPS techniques,

- The observation of the various membranes by scanning electron microscopy was carried out using a microscope of the JEOL-JSM-7200F type, operating at 15 kV.

- Raman spectra were acquired using the HORIBA Scientific Raman spectrophotometer. The measurements were taken in the wavenumber range from 400 to 3500 cm^{-1} .

- XPS analysis of CTA membranes and CTA PIM membrane supports was evaluated using Kratos Axis Ultra (XPS).

2.4. Transport Experiments

A laboratory-scale micro-reactor is used to carry out the experiments for the separation of mixtures of phenols via the PIM. The PIM cell consists of two Teflon compartments with a maximum capacity of 230 ml separated by the PIM (Figure 2). The surface of PIM exposed to the aqueous phase is of the order of 07.08 cm^2 . The source and extraction compartments are equipped with a mechanical stirrer set at 600 rpm (based on previous research on the removal of organic pollutants from an aqueous solution [13-15]). One of them contained an equimolar content of a mixture of three phenols: phenol, resorcinol and bisphenol A as



Figure 2: Membrane reactor used in separation/recovery of phenols mixture.

the feed phase, and the other, constituting the extraction phase, contained water deionized. Transport can occur by diffusion. All transport experiments are performed in duplicate at $25 \pm 1^\circ\text{C}$.

The performance of the system was studied in terms of its phenols removal (%), defined by Eq. (1) and its initial flux (J_0), calculated by Eq. (2)

$$\text{Phenol removal (\%)} = \frac{[\text{Phenols}]_{s,t}}{[\text{Phenols}]_{f,o}} 100 \quad (1)$$

Where $[\mathbf{Phenols}]_{s,t}$ refers to the Phenols concentration in the stripping phase at time t and $[\mathbf{Phenols}]_{f,o}$ refers to the initial concentration of Phenols: phenol, resorcinol, bisphenol A in the feed phase

$$J_0 = \left(\frac{V}{S}\right) \left(\frac{\Delta[\text{Phenols}]_f}{\Delta t}\right) \quad (2)$$

Where V is the volume of feed phase, S the exposed surface area of the PIM.

The separation factor (S) was calculated by the formula (3)

$$S = \frac{[\text{Phenols}]_{\text{source}} [\text{Bisphenol}]_{\text{receiving}}}{[\text{Phenols}]_{\text{receiving}} [\text{Bisphenol}]_{\text{source}}} \quad (3)$$

2.5. Phenols Mixture Analyses

The influence of the studied parameters on the transport of mixture of Phenols was analyzed during 5 days. Samples of 4 ml were manually extracted with a pipette from both half-cells each day, and the mixture of phenols quantification in the transport experiments was carried out using a chromatograph Perkin Elmer-

Flexar with an UV detector at 275 nm, based on the absorption UV spectra of each constituent separately.

HPLC Conditions: Column: Discovery HS C_{18} Supelco Analytical 25 cm \times 4.6 mm, 5 μm Mobile phase: ACN/ H_2O : 45/55, UV detector λ at 275nm, flow rate: 1 mL/min

3. RESULTS AND DISCUSSION

3.1. PIMs Characterizations

3.1.1. SEM Observation of the Developed PIMs

The SEM micrographs of the membrane based on the CTA alone (a) and prepared polymer inclusion membrane containing calix[4] resorcinarene (RC 8) as carrier and plasticizer 2-NPOE (b) are presented in Figure 3. The membrane of the CTA has a homogeneous dense surface with a uniform structure. Hence, the membranes containing the calix[4] resorcinarene (RC8) and plasticizer are a smoother and firmer surface with dense structures suggesting pores filled by transporters solubilized in the liquid phase constitute by plasticizer NPOE when occupied the pores of PIM by capillarity.

3.1.2. Raman Characterization of PIMs

The peak around 1052 cm^{-1} characteristic of the aromatic existing in the carrier RC8 and the plasticizer NPOE is observed on the Raman spectrum of the PIM (Figure 4) thus confirming the presence of the two constituents the carrier and the plasticizer, in the same way we observe the two bands around 1279 cm^{-1} and 3081 cm^{-1} characteristic of the H-C= group in RC8 and NPOE. Indeed a new band which appears on the Raman spectrum of PIM around 1586 cm^{-1} is characteristic of the two CH_3/CH_2 groups existing in transporter RC8 and the plasticizer NPOE.

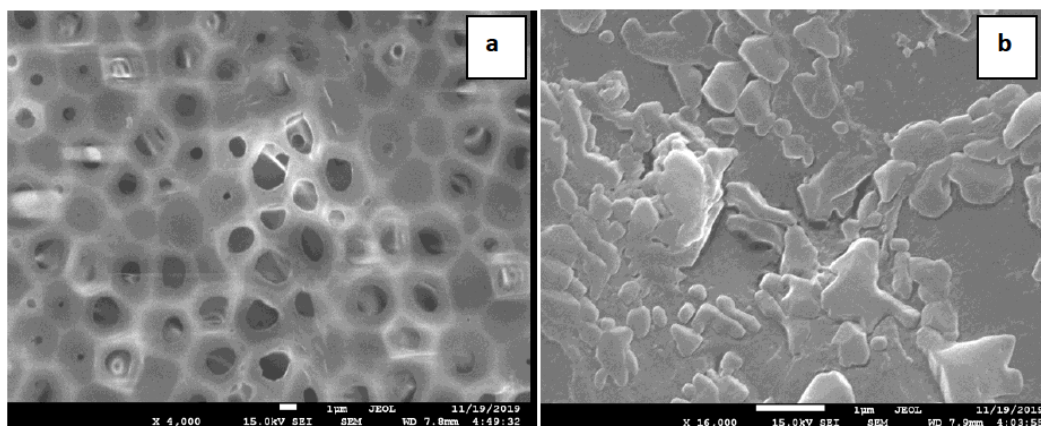


Figure 3: SEM micrographs of CTA membrane alone (a) and PIM CTA with RC8 and 2-NPOE (b)

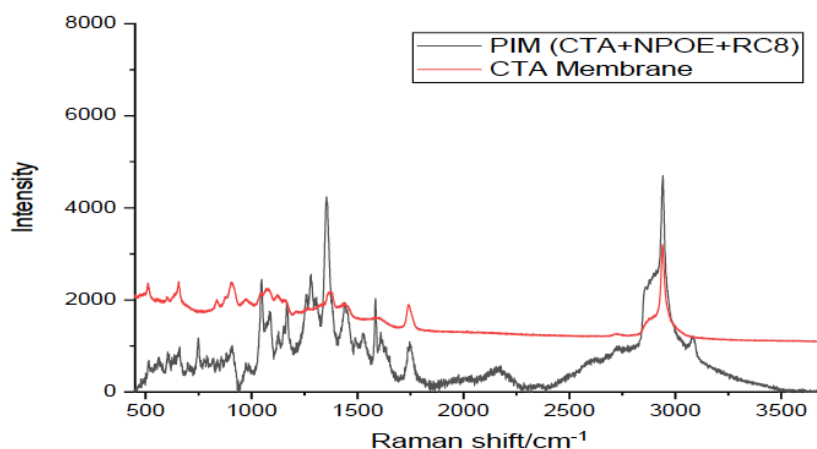


Figure 4: Raman spectrum of CTA alone and PIM (CTA+RC8+2-NPOE).

3.1.3. XPS Spectroscopy Characterization of PIM

The XPS spectrum of carbon C 1S in Figure 5, confirms the presence of transporter RC8 in matrix membrane through the increase in the intensity of the band towards 284 eV characteristic of the C-H bond in the CTA polymer and the transporter. Similarly, we observe the disappearance of the band characteristic of the C-O bond of the CTA polymer around 286 eV because of the commitment of this type of groups in specific interactions with the RC8 transporter, thus confirming the incorporation of the RC8 transporter within the polymer chains.

3.2. Transport of Bisphenol A, Alone Through the PIM

We have studied the facilitated transport of bisphenol A alone through the PIM (Figure 6). Indeed we notice a basal elimination rate in the first two days

but after the third day the rate exceeds 50% to reach 95% in the fifth day. The optimal parameters for the

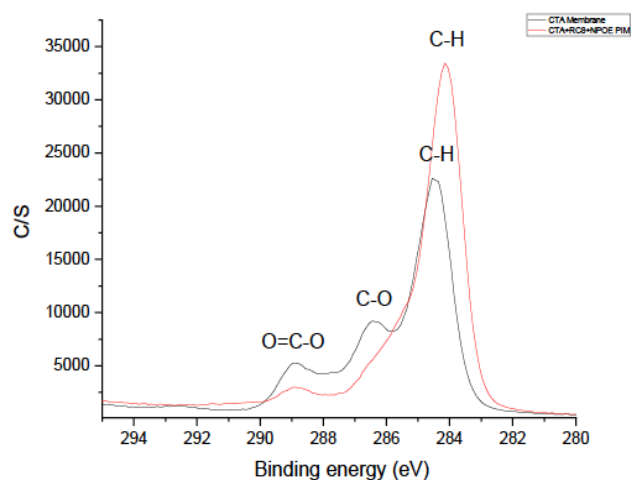


Figure 5: XPS carbon (C 1S) spectra of CTA membrane alone and (CTA+RC8+NPOE) PIM.

transport of bisphenol A through the PIM are: feed phase pH 4, reception phase pH 9. 68% of the plasticizer, 22% of the CTA support and 10% of the carrier.

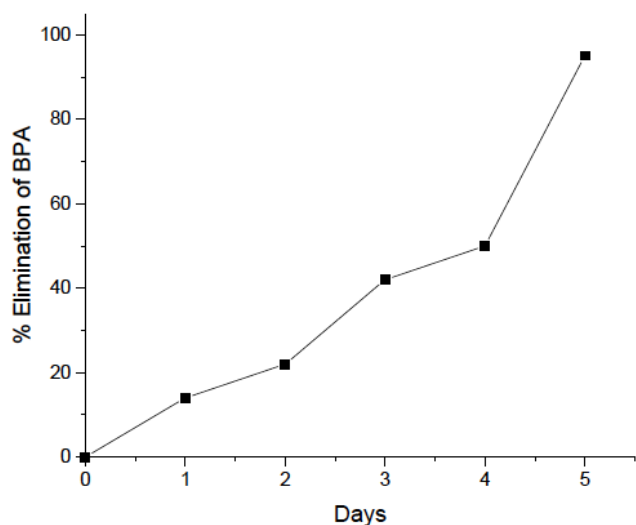


Figure 6: Transport of Bisphenol A through the PIM.

Transport conditions: feed phase: BPA 100 ppm, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 68% 2-NPOE, 22% CTA, and 10% carrier: RC8. Values obtained after 5 d of transport, R.Temperature = 25°C.

3.3. Competitive Transport Experiments of Phenols Mixture Through the PIM

The competitive transport of Bisphenol A, phenol and resorcinol (initial concentration of each molecule: 4.38×10^{-4} M, at pH 4) through the PIM with calix[4] resorcinarenes as carriers and 2-NPOE, as plasticizers was studied (Figure 7). It should be noted that the parameters used in this study are those obtained in the subsequent study carried out on the transport of Bisphenol [14].

The transport kinetics of target molecules is shown in Figure 7. Initial fluxes, selectivity orders and selectivity ratios calculated by Eq. (3) for PIM transport with calyx[4] resorcinarene (RC8) are shown in Table 1.

For the competitive transport of phenols through the PIM with RC8 + NPOE, the order of selectivity obtained is: Bisphenol > Phenol > Resorcinol. The high selectivity towards Bisphenol A molecules observed could be explained by the size complementarity between the cavity of the calyx [4] resorcinarenes formed by the phenol oxygen atoms at the upper edge and the Bisphenol A skeleton. The low transport observed for resorcinol can be explained by the high affinity due to Van der Waals type π - π interactions between resorcinol and the aromatic ring of the calixresorcinarene macrocycle thus preventing its transport across the membrane.

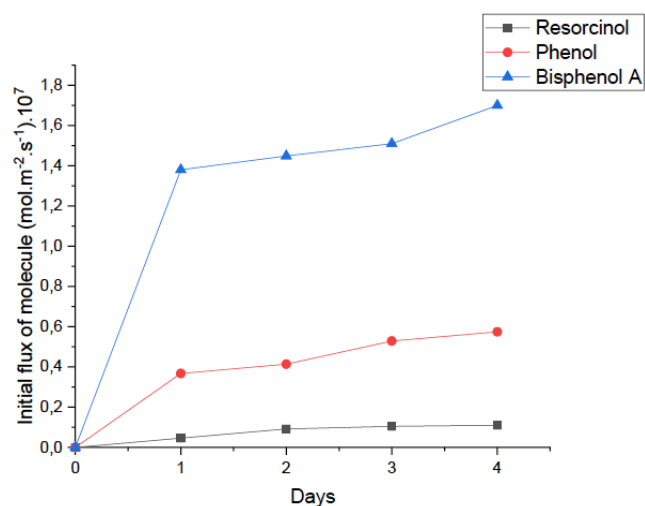


Figure 7: competitive transport of phenols mixture through the PIM.

Transport conditions: feed phase: mixture of phenols, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 68% 2-NPOE, 22% CTA, and 10% carrier: RC8. Values obtained after 4d of transport, R.Temperature = 25°C.

4. CONCLUSION

Polymeric membranes with plasticized inclusion based on cellulose triacetate as support and calixresorcinarene as transporter have been elaborated and characterized by means of Raman spectroscopy, XPS and SEM. All the analysis techniques confirm the inclusion of transporter in the liquid membrane organic

Table 1: Selectivity Order and Selectivity Ratios (S) of Molecules Target Transported Through the PIM

PIM	Molecule	Flux (mol.m ⁻² .s ⁻¹).10 ⁷	Selectivity Order and Selectivity Ratios (S)
CTA+RC8+NPOE	Bisphenol A	1.70	Bisphenol A > Phenol > Resorcinol S: 2.92 5.21
	Phenol	0.57	
	Resorcinol	0.11	

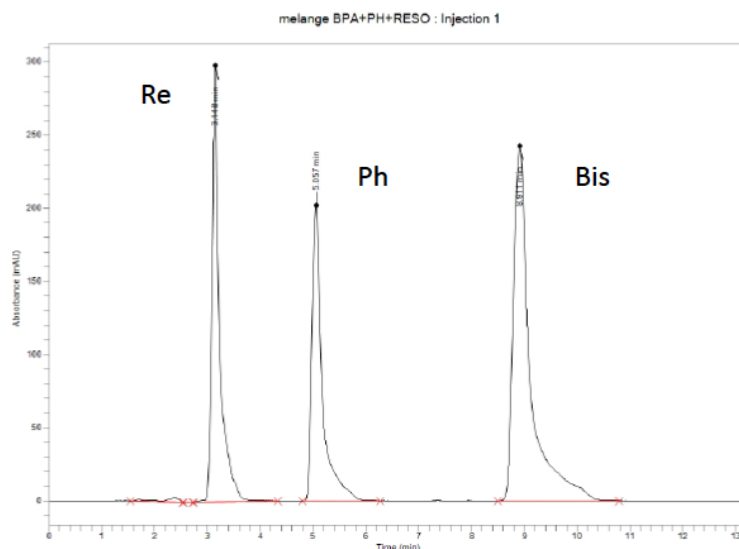


Figure 8: Chromatogram of equimolar mixture: Resorcinol (Re), Phenol (ph), and Bisphenol (Bis) in feed phase at t=0 min.

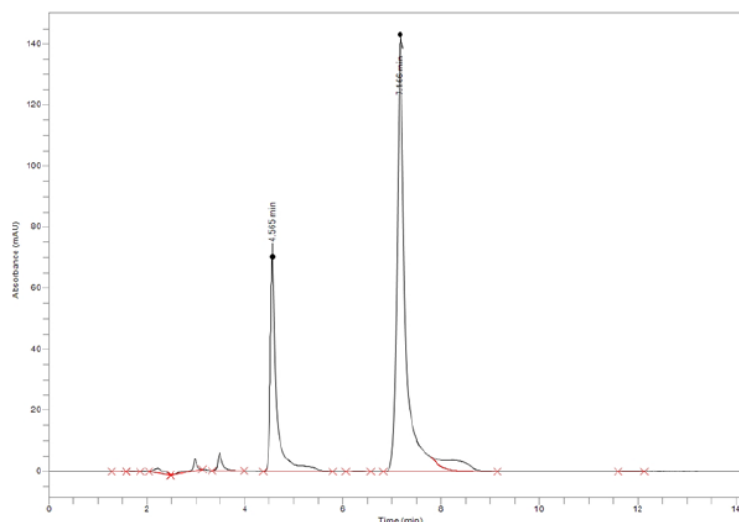


Figure 9: Chromatogram of receiving phase after 4 days of transport through the PIM.

matrix formed by the plasticizer 2-NPOE occupying the pores by capillarity. The competitive transport of three phenols namely: Bisphenol A, Phenol and resorcinol through the PIM shows that the membrane is selective with respect to Bisphenol A and phenol, the order of selectivity being Bisphenol > phenol > resorcinol. This study shows the effectiveness of such a membrane in the separation and recovery of target species such as phenols. In the same way this membrane can be applied to other mixtures of the phenol type.

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