Removal of Bisphenol A from synthetic wastewater solutions using a polymer inclusion membrane

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ABSTRACT

The purpose of this study was to assess the feasibility of polymer inclusion membrane (PIM) to eliminate xenoestrogens (EDCs) bisphenol A (BPA) from synthetic wastewater as well as identify the major variables playing a significant role in the process. To achieve this goal, prepared PIM containing derivatives of calix[4]resorcinarene as the carrier, cellulose triacetate (CTA) as the base polymer, and 2-nitrophenyloctylether (2-NPOE) as a plasticizer has been used. The capability of PIM to remove contaminants was assessed using BPA as a model contaminant. The transport flux of BPA through the prepared PIMs was found to be dependent on various external factors such as; concentration of the carrier and the plasticizer in the membrane phase, pH of the aqueous feed phase, and thickness of the membrane. The corresponding stirring speed, pH of feed phase, the initial concentration of BPA in feed phase, carrier content, and plasticizer were: 600 rpm, pH 4, 100 mg dm^{-3}, 400 mg g^{-1} of support, and 3 mL g^{-1} CTA, respectively. Up of 90% of BPA was transported from the feed phase to the stripping phase in 5 d, when the initial concentration of target was 100 mg L^{-1}, and initial flux was found to be 5×10^{-7} (mol m^{-2} s^{-1}). BPA can be transported through PIM when it is present in an undissociated state in aqueous solution. PIM stability after three cycles of transport processes was examined. The separation by using PIM has been identified as a promising technology for removing organic contaminants entering the water cycle.

Keywords: Bisphenol A; Xenoestrogens (EDCs); Polymer Inclusion Membrane; Calix[4]resorcinarene; Cellulose triacetate; Wastewater treatment, Membrane technology

1. Introduction

For some decades, synthetics endocrine-disrupting chemicals (EDCs) have been intensively rejected into the environment, which caused the exposure of animals and humans to their action. EDCs or xenoestrogens are natural or synthetic compounds that are capable of disrupted function of various hormones including sex hormones, leptin, insulin, and thyroxin and causes hepatotoxic, immunotoxic, mutagenic, and carcinogenic effects [1]. There is some concern that BPA may act as an endocrine-disrupting compound [1,2], because it binds to the estrogen receptors α (ERα) and β (ERβ), although with an affinity four orders of magnitude lower than that of estradiol [3]. Bisphenol A (BPA) is one of the most produced chemicals, with a

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worldwide production capacity of approximately 7.7 million tons in 2015 and can reach 10.7 million tons in 2020 [4]. It is primarily used as the monomeric building block of polycarbonate plastics and epoxy resins [5], and thermal paper, but it can also be used as additive in other polymers (PE, PP, and PVC). BPA is also used in food contact materials including packaging, bottles, and lacquers coatings for tins leading to exposure of consumers to BPA through food and drinking water. Leaching of BPA in the aquatic environment can occur from food and drink packaging debris [6] or via untreated wastewater entering the environment [7]. Several techniques have been applied to remove the bisphenol A and its derivatives from wastewater, including adsorption [8,9], photoelectrochemical degradation [10], biodegradation [11], sorption [12], and membrane process [13]. Of these methods, membrane separation appears to be suitable process based on overall separation performance. Alternative separation technology is transport across liquid membranes which offers a potentially attractive alternative to the solvent extraction process and combines the process of extraction and stripping in single unit operation. Today a remarkable increase of the applications of the liquid membrane in the separation of small organic molecules from dilute aqueous solution observed. These membranes include bulk liquid membrane (BLMs) [14,15], emulsion liquid membranes (ELMs) [16], liquid surfactant membranes (LSMs), and supported liquid membranes (SLMs) [17,18]. Another type of liquid membrane system called polymer inclusion membranes (PIMs) has been developed [19–22]. PIMs are usually composed of a base polymer (support) commonly cellulose triacetate (CTA) or polyvinylchloride (PVC), the plasticizer commonly 2-nitrophenyloctyl ether (2-NPOE) provide elasticity/flexibility to the system, the plasticizer decreases the glass transition temperature of the membrane and improves the solubility of the extracted species in the membrane liquid phase [23,24]. The transporter act as a complexing agent, by binding to target and transporting it through the PIM to the stripping phase. Macrocyclic and macromolecular type carrier has outstanding selectivity by means of extraction and also form stable complexes with the different types of molecules (cations, anions, and neutral). Crown ethers, calix crowns, calixarenes, and cyclodextrins are the few examples of macrocyclic and macromolecular extractant [25].

Benosmane et al. [22] used derivatives of calixresorcinarene in PIMs and performed experiments for transportation of Zn, Pb, and Cd ions from their aqueous solution. Zulkefel et al. [25] have developed PIMs using calixresorcinarene as extracting agent, with the base polymer CTA. They used it for removal of Pb(II). PIMs were applied successfully in the chemical analysis [26–28] and for removal of organic compounds such as lactic acid, antibiotic, and dyes [29–31]. An attempt was made to study the applicability of PIM for the removal and transfer of bisphenol A from an aqueous solution. This study was done to evaluate the removal efficiency of Bisphenol A (BPA) from synthetic wastewater by using the synthesized PIM based on the CTA as support, calix[4]resorcinarene as carrier, and 2-NPOE as plasticizer. Many factors that influence the flux of molecule target, such as BPA initial concentration, pH of an aqueous solution, carrier and plasticizer content, membrane thickness and

concentration of NaOH in stripping phase, among others, are discussed.

2. Materials and methods

2.1. Chemicals

The structure and abbreviation of the carrier (RC8) and plasticizer used in the present study are shown in Fig. 1. The carrier, (C-octyl) calix[4]resorcinarene, abbreviated as RC8, and the carrier were synthesized in our laboratory [32].

BPA (purity 99%), resorcinol, aldehydes, ethanol, hydrochloric acid, potassium hydroxide, salts, dichloromethane, cellulose triacetate (CTA), 2-nitrophenyloctylether (2-NPOE), were analytical grade reagents purchased from Sigma-Aldrich (Burghausen, Germany). Aqueous solutions were prepared by dissolving the respective analytical grade reagent in deionized water with a resistivity no less than 18.2 MΩ cm obtained with a Milli-Q Plus system. The pH adjustment was done by the addition of dilute hydrochloric acid (0.01 mol dm^{-3}) or sodium hydroxide (0.25 mol dm^{-3}) to prepare the desired pH solution.

2.2. Membrane preparation

PIMs were prepared according to the procedure reported by Sugiura [19], the amount of each constituent was a function of the series of experiments to be performed. Thus, CTA (100 mg) was dissolved in 10 cm^3 of CHCl$_3$ at room temperature, calix[4]resorcinarene (RC8) (0–500 mg g^{-1} CTA), and plasticizer (0–4 cm^3 of plasticizer g^{-1} CTA) was then added and vigorously stirred, then placed into a Petri dish of 9.0 cm diameter. This solution was allowed to evaporate overnight at room temperature (25°C ± 1°C). The film was then carefully peeled out of the bottom of the Petri dish and stored in deionized water for 24 h.

2.3. BPA analyses

The influence of the studied parameters on the transport of BPA was analyzed for 5 d. Samples of 4 cm^3 were manually extracted with a pipette from both half-cells each day, and the bisphenol A quantification in the transport experiments was carried out using a UV/visible Junway-6800 at the wavelength ($\lambda = 278$ nm).

2.4. PIMs characterization

Membranes were characterized by their infrared spectra using FTIR spectrometer Perkin-Elmer (Waltham, USA); the spectra were obtained directly inserting the membrane sample in the spectrophotometer. The morphology of the PIMs was analyzed using Jeol/scanning microscopy; model JSM-7200F under low vacuum, and at 20 kV. The thickness of PIMs was determined manually using micrometer (Thickness Gauge). Each point was averaged from six measurements (±1 μm). The water contact angles of the surface PIMs were measured with a contact angle Goniometer (ramé-hart Instrument Co., Succasunna, USA). A piece of 0.01 m × 0.01 m membrane was stick on a glass slide and

R=C$_8$H$_{17}$(RC8), R=C$_4$H$_9$ (RC4)
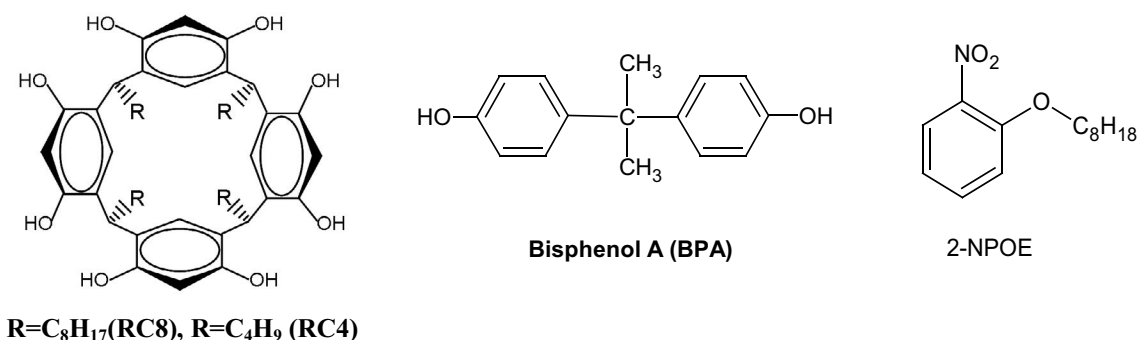
Bisphenol A (BPA)   **2-NPOE**

Fig. 1. Chemical structure of calix[4]resorcinarenes (RC4,8), 2-nitrophenyloctylether (2-NPOE), and bisphenol A (BPA).

mounted on the goniometer. The drop size was 0.01 cm^3. Each point was averaged from six measurements (±1°).

2.5. Transport experiments

A typical laboratory scale device was used for bisphenol A transport experiments through the PIM. The PIM cell consists of two compartments made of teflon with a maximum capacity of 400 cm^3 separated by the PIM [22]. The PIM area exposed to the aqueous phase is 0.1256 × 10^{-2} m^2. In order to minimize the boundary layer thickness, both the source and stripping compartments were provided with a mechanical stirrer adjusted to 600 rpm (based on previous research work on the removal of organic contaminants such as citric acid [33] and phenol [35] using the same membranes composition and cell for transport, the optimal stirring rate was 600 rpm. thus we have chosen 600 rpm). One of them contained 100 mg dm^{-3} of BPA as the feed phase, and the other, the stripping phase, contained deionized water. All transport experiments were carried out in duplicate at room temperature 25°C ± 1°C. The reported error bars in all figures represent the standard deviation of the data.

The performance of the system was studied in order to bisphenol A removal (%), defined by Eq. (1) and its initial flux (J_0), calculated by Eq. (2):

$$BPA\,removal\;(\%) = \frac{(BPA)_{s,t}}{(BPA)_{f,0}}\,100 \qquad (1)$$

where $(BPA)_{s,t}$ refers to the BPA concentration in the stripping phase at time t and $(BPA)_{f,0}$ refers to the initial concentration of BPA in the feed phase at time $t = 0$ s.

$$J_0 = \left(\frac{V}{S}\right)\left(\frac{\Delta(BPA)_f}{\Delta t}\right) \qquad (2)$$

where V is the volume of the feed phase and S the exposed surface area of the PIM.

3. Results and discussions

3.1. Effect of pH on UV absorption of BPA in an aqueous medium

This section aims to note a possible effect of pH on UV absorption of BPA in an aqueous medium, for this, the solutions of BPA in aqueous solution at a fixed concentration of BPA (100 mg dm^{-3}) with varying pH of 2–12 has been prepared. Fig. 2 shows the UV spectrum of BPA shows two bands at 228 and 278 nm, assigned to the π–π* and n–π* transitions, respectively. We do notice that the pH of the medium greatly influences the absorption band shape and position. A bathochromic effect in the acid medium has been observed, the absorption band is observed at 225 nm while in basic medium this band increases to 245 of 20 nm. This shift is due to the dissociated form of BPA. pK$_a$ of BPA is in the range 9.73–10.6, and this modification of position band absorption in UV, were observed when the pH value of the medium is greater than 9. During the analysis of BPA, it is necessary to take into account the effect of pH on the absorption shape, for that, we choose the wavelength of absorption of BPA during the analysis as a function of medium pH.

3.2. Effect of contact time

The contact time is an important operational factor that affects removal efficiency. Fig. 3 depicts BPA removal as a function of contact time. In Fig. 3, it is shown that an increase in contact time increased removal efficiency. As shown, the BPA transport by PIM was very slow within the first day. After 2 d, the uptake of BPA progressively increased with time and reaches the maximum at 5 d. It was found that, under the optimum conditions, the transport of BPA from the aqueous source phase into the stripping phase is almost quantitative after 5 d. As is obvious the results show that >90% transport of BPA (with R.S.D of 7%) with an initial flux $J_0 = 5 × 10^{-7}$ (mol m^{-2} s^{-1}) can be transported at a time interval of 5 d. As the treatment time proceeded.

3.3. Effect of membrane thickness on the BPA flux

The effect of membrane thickness on the transport flux of BPA is presented in Fig. 4. Percent transport of BPA from the feed phase decreases with increasing membrane thickness from 30 to 70 μm, the occurrence of a milky layer was observed on the membrane surface. This observation was likely one of the reasons of the flux limit. However, other reasons could be related to the kinetics of the BPA complexation, which could have reached its maximum value, or to a complex of different stoichiometries formed at the concentration less soluble in the PIM core.
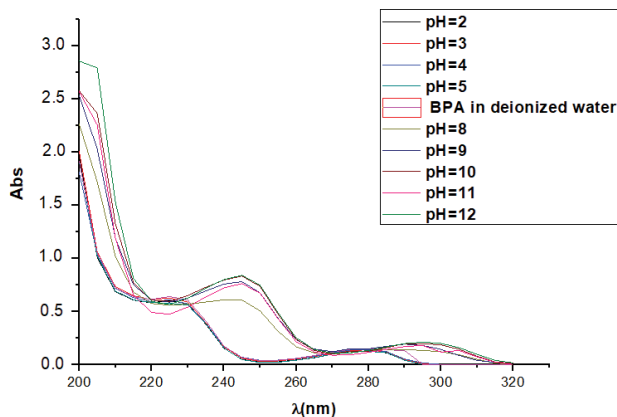
Fig. 2. UV spectrum of BPA (100 mg dm^{-3}) in aqueous solution at different pH.
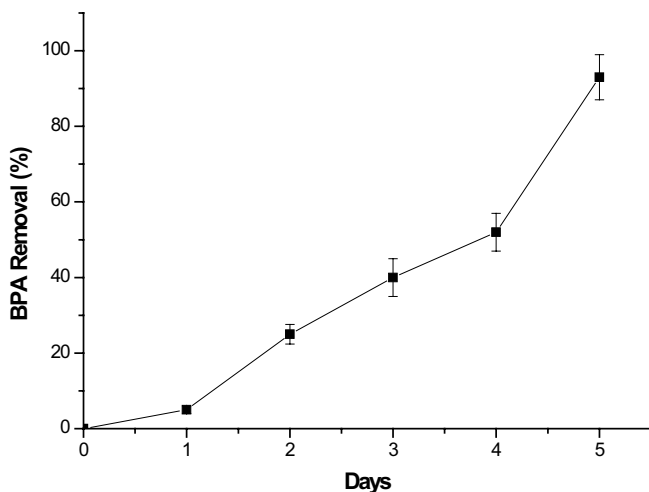

Fig. 3. Effect of contact time on removal of BPA. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260 × 10^{-2} m^2 of surface area, 68% 2-NPOE, 22% CTA, and 10% carrier: RC8 (3 cm^3 2-NPOE/1 g CTA). Membrane thickness: 50 μm. Values obtained after 5 d of transport, $RT = 25°C$.
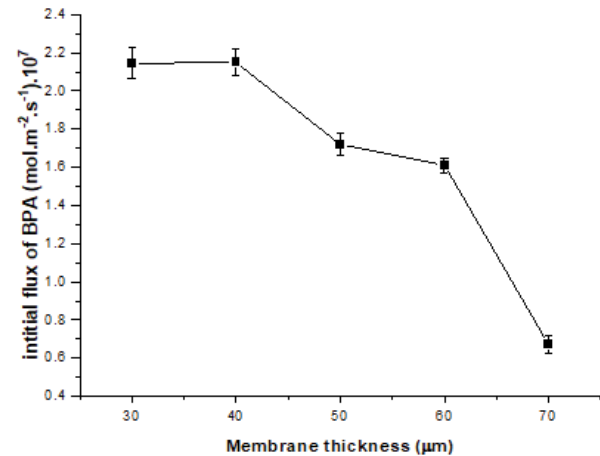

Fig. 4. Effect of membrane thickness on initial flux of BPA. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260 × 10^{-2} m^2 of surface area, 68% 2-NPOE, 22% CTA, and 10% carrier: RC8 (3 cm^3 2-NPOE/g CTA). Values obtained after 3 d of transport, $RT = 25°C$.

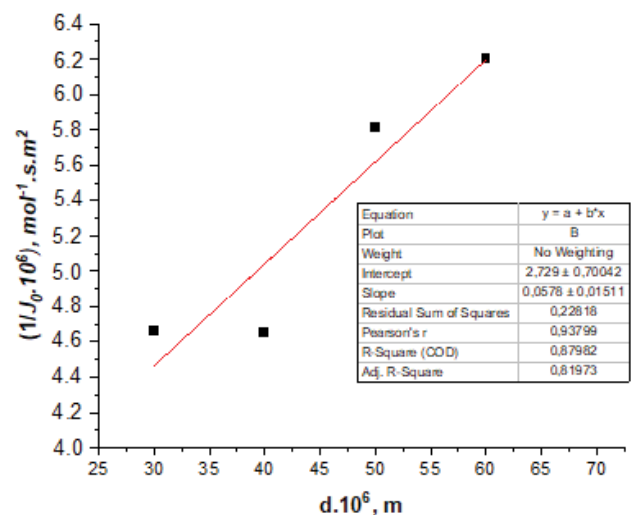Fig. 5. Influence of membrane thickness on the initial flux of BPA across the CTA-based PIMs containing 10% and 68% 2-NPOE.

The inverse relationship between the initial flux of BPA and membrane thickness (Fig. 5) is found to be a straight line with the good correlation coefficients equal to 0.88. The linear relationship confirms the existence of a rate-limiting transport due to the diffusion of a complex (RC8-BPA) across the PIM. Additional argument supporting rather carrier-diffusion are observations of Fontas et al. [34] that in PIMs the carriers are not bound chemically and as a consequence, no typical fixed-site jumping transport occurred in such membranes.

3.4. Effect of the initial concentration of BPA in the feed phase

The effect of concentration of BPA in the feed phase solution on the percent BPA removal by PIMs with a thickness of 40 μm was studied at various initial concentrations varying from 20 to 100 mg dm^{-3}, as shown in Fig. 6. It can be observed that removal was significant at higher concentrations of BPA and vice versa. Percent transport increases with increasing BPA concentrations from 20 to 100 mg dm^{-3}. At the concentration of 100 mg dm^{-3}, the rate of complexation with the carrier is not affected and the saturation is not reached.

3.5. Effect of carrier content in PIMs

Fig. 7 depicts BPA removal efficiency as a function of carrier dosage in the membrane phase. The carrier calix[4] resorcinarene RC8 percentage composition in PIMs were varied between 2.43% and 11.11%, as shown in Fig. 7. As expected, at high carrier dose the removal increased because the number of available complexation sites
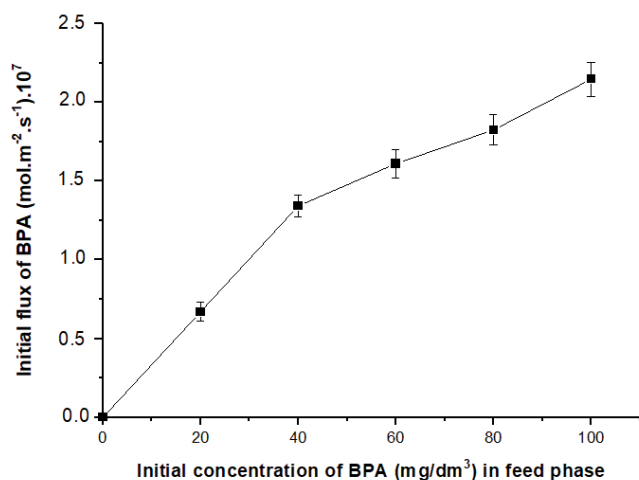
Fig. 6. Effect of initial concentration of BPA. Transport conditions: feed phase: pH 4, BPA = 20–100 mg dm^{-3}. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260 × 10^{-2} m^2 of surface area, thickness: 40–50 μm, 68% 2-NPOE, 22% CTA, and 10% carrier: RC8 (3 cm^3 2-NPOE/g CTA). Values obtained after 3 d of transport, *RT* = 25°C.
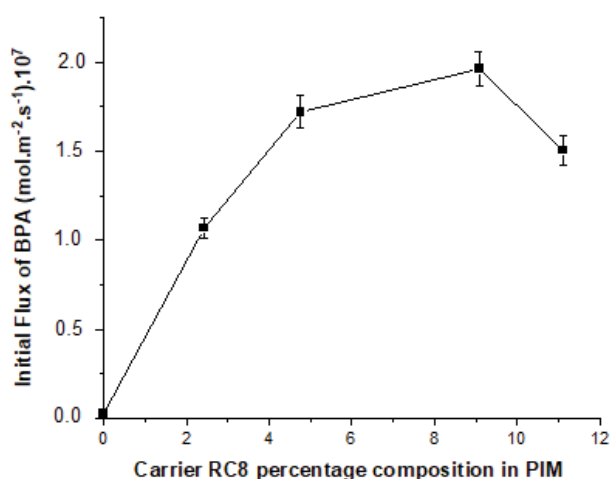

Fig. 7. Effect of carrier contents on the transport of BPA. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260 × 10^{-2} m^2 of surface area, Calix[4]resorcinarene: RC8 (0%–11.11%), 3 cm^3 2-NPOE/g CTA. Values obtained after 3 d of transport, *RT* = 25°C.

increased. Calixarene can react with BPA by developing a specific interaction such as hydrogen bond, dipole–dipole, ion–ion, ion–dipole, cation–π, π–π, and Van der Waals forces. The flux increases with increasing concentration of RC8 in the membrane phase up to a 9.09% level, while a further increase in the carrier concentration results in a slight decrease in extraction efficiency is observed a similar behavior for the carrier concentration in the PIM has already been reported in the literature [35,36]. This could be due probably to the most difficult release of a BPA into the receiving phase, as a result of its firm bonding to the carrier

and/or the increased viscosity of membrane phase with increasing carrier quantity. The optimum carrier percentage for BPA removal was 9.09%, as shown in Fig. 7.

3.6. Effect of plasticizer content

The plasticizer plays an important role in the transport of the target, it thus constitutes the solvent liquid medium in which the complexed target molecule can circulate, and it gives the PIM softness and flexibility. The influence of the content of plasticizer 2-NPOE in the PIM on the transport of BPA was studied by preparing PIM with a fixed dose of calix[4]resorcinarene RC8 (400 mg g^{-1} CTA) and of the plasticizer percentage composition in PIM (41.66%–74.07%). The PIMs obtained with the different amounts of plasticizer were transparent with a uniform thickness. In addition, PIM with RC8 carrier but without plasticizer shows no transport efficiency transport of BPA, an additional variation in the amount of 2-NPOE results in higher transport efficiency up to 68.18% of NPOE, which could be due to the favorable plasticizing effect, but an excessive plasticizer concentration makes plasticizer to exclude to the membrane/aqueous interface and form a film on the surface of the membrane so that it becomes a barrier to the transport across the PIM. Beyond this quantity, a decrease in the transport flow is observed as seen in Fig. 8. Nghiem et al. [23] have indicated that the excess of plasticizer could migrate to the membrane surface and form a film there, which would form a barrier to the transport of metal ions across the membrane. However, Gyves et al. [37] have demonstrated that the decrease in permeability with increasing plasticizer content in membranes was related to an increment in the viscosity of the membrane that limited the plasticization effect and also carrier movement. On the one hand, presence of the plasticizer is necessary, as Fontas et al. [34] emphasized, for formation of liquid micro-domains of the carrier solvated by the plasticizer which facilitates the transport of metal ions. Indeed, the increase in plasticizer content could enhance interactions between the plasticizer and the polymer chains reducing the occurrence of the liquid domains.

3.7. Effect of pH of feed phase

The dependence of the BPA extraction with pH of feed phase solution in the range of 2–8, adjusted with NaOH and HCl in the feed phase, was studied. The NaOH solution in the present study was used as a stripping solution at pH 9. When water was used as the stripping phase, it did not result in a significant transfer of BPA. Whereas, the use of NaOH solution as a stripping agent at pH 9, resulting in an increase in BPA transfer. The initial flux of BPA was found to increase from 0.72 × 10^{-7} to 1.32 × 10^{-7} (mol m^{-2} s^{-1}) with an increase in pH of feed phase from 2 to 4. Further, an increase in pH from 4 to 8 resulted in a decrease in the initial flux of BPA from 1.32 × 10^{-7} to 0.05 × 10^{-7} (mol m^{-2} s^{-1}) (Fig. 9). Bisphenol A can be transported through PIM when it is present in a molecular or undissociated state in aqueous solution. Since a pK$_a$ value of BPA is 9.73–10.6, the BPA will be present in undissociated form when the pH of the feed phase was 4.0, which resulted in the highest membrane transfer. The BPA is dissolved in the PIM organic phase and
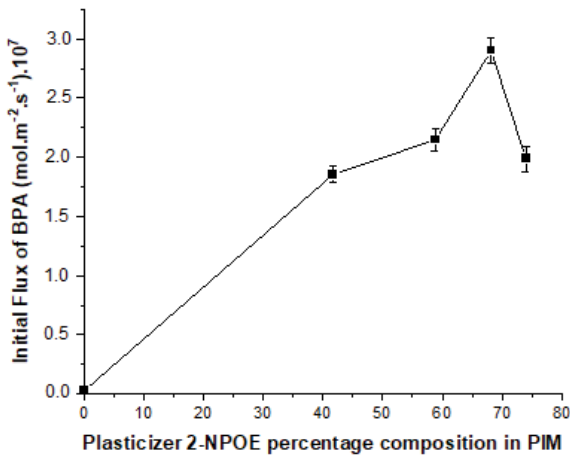
Fig. 8. Effect of plasticizer (2-NPOE) content on the transport of BPA. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH 4. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260×10^{-2} m^2 of surface area, Calix[4]resorcinarene: RC8 (400 mg g^{-1} CTA), (1–4 cm^3) 2-NPOE/g CTA. Values obtained after 3 d of transport, *RT* = 25°C.

Fig. 10. Fluxes of BPA in consecutive transport experiments performed on the PIM with RC8 and 2-NPOE. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH 4. Stripping phase: deionized water adjusted with NaOH, pH = 9. Membrane: 0.1260×10^{-2} m^2 of surface area, 68% 2-NPOE, 22% CTA, and 10% carrier (3 cm^3 2-NPOE/g CTA). Membrane thickness: 50 μm. Values obtained after 3 d of transport, *RT* = 25°C.
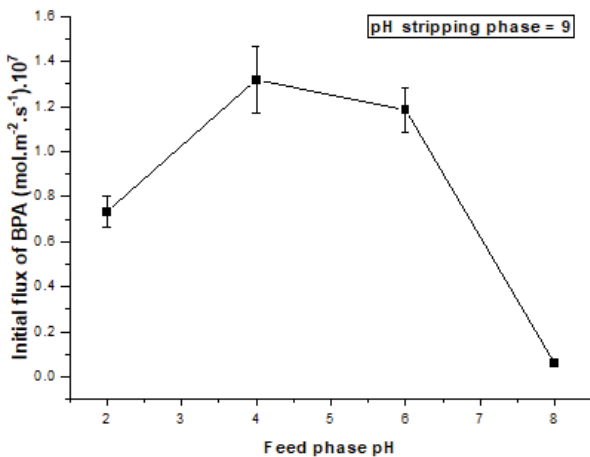

Fig. 9. Effect of pH solution of feed phase on the removal efficiency of BPA. Transport conditions: feed phase: BPA 100 mg dm^{-3}, pH varying 2–8. Stripping phase: deionized water adjusted with NaOH, pH 9. Membrane: 0.1260×10^{-2} m^2 of surface area, 68% 2-NPOE, 22% CTA, and 10% RC8, (3 cm^3 2-NPOE/g CTA). Values obtained after 3 d of transport, *RT* = 25°C.

passes through the porous membrane support, while the concentration gradient acts as a driving force. As the BPA probe reaches the interface of the membrane on the side of the stripping phase, it reacts with sodium hydroxide and converts into BPA, which cannot diffuse back through PIM.

3.8. Stability of PIMs

From Fig. 10, it appears that the percentage of transported BPA found in the stripping phase generally decreases with the increase in the repeated use of membrane from once, twice, and three times. This is possibly due to the leaching of membrane components, in
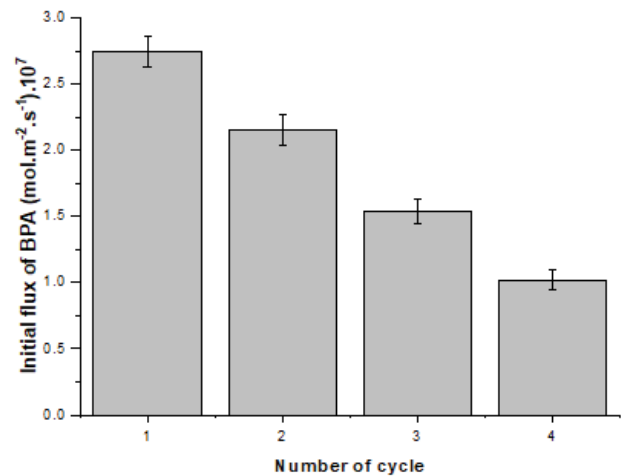
particular, calix[4]resorcinarene as a carrier and plasticizer 2-NPOE compounds into the solution at the first application, second, and so on [35]. This loss of compounds results in the reduced number of active sites of the membrane so that the π–π interactions and hydrogen bonds that can be formed between BPA and membrane carrier compound also decrease. As a result, the percentage of BPA transport for the second and third applications decreases. The initial flux is 2.748×10^{-7} mol m^{-2} s^{-1} in the first cycle and reaches 1.538×10^{-7} mol m^{-2} s^{-1}, in cycle three, the PIM used in this study was found to be quite stable for at least 9 d. However, when the same membrane was used up the fourth time, the system reveals some 45% decrease in the membrane efficiency for the transport of BPA.

To confirm a possible loss of membrane components, in particular, plasticizer 2-NPOE compound into the solution at the application of PIM in transport, we have analyzed the same PIM before and after transport with FTIR and SEM, Fig. 11. We constate with FTIR as a quantitive technique for analyzing, that the intensity of bond at 1,364 cm^{-1} characterizing the group Ar-NO$_2$ in 2-NPOE has been decreased after three cycles of transport of BPA. In addition, SEM analysis corroborates with FTIR, Indeed the pictures (b, b') in Fig. 12. Shows that the surface composition of PIM after the transport has been modified confirming that the possible loss of plasticizer 2-NPOE outside the membrane matrices, which is in perfect agreement with the results of Baczynska et al. [26].

3.9. Suggested mechanism

Transport of BPA by using the calix[4]resorcinarene RC8 obeys a facilitated counter-transport. As it is shown in Fig. 13, the BPA forms a double charge complex at the interface feed phase/membrane and after forming a pair
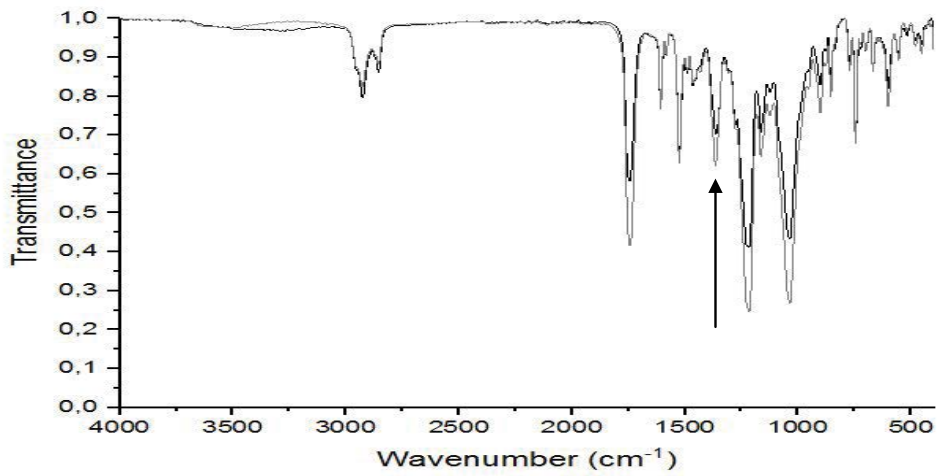
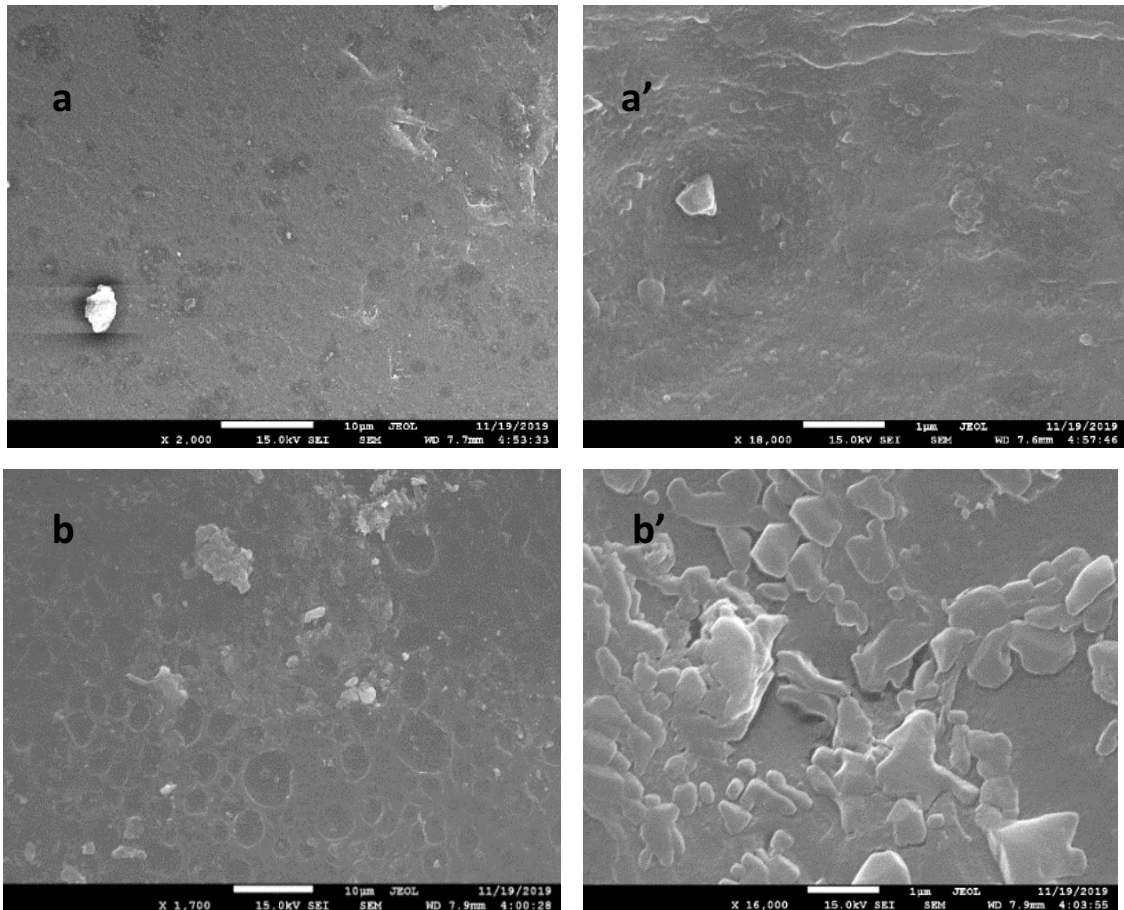Fig. 11. FTIR spectrums of PIM before (gray) and after (black) transport of BPA.

Fig. 12. SEM pictures of PIM before (a and a′) and after (b and b′) transport of BPA.

complex by several types of interaction such as hydrogen bonds between the hydroxyl group of calix and hydroxyl group of BPA, cation–π, and π–π interactions; the resulting complex diffuses through the membrane phase to the membrane/strip phase interface. Then the free carrier diffuses back across the PIM and the cycle starts again [22,34]. The source and receiving phase showed a significant difference in pH. The results suggest that BPA transport occurs where the driving force is generated by the complexation of BPA at the source phase/membrane interface and by the

difference in proton concentration in both aqueous solutions. The net result is the mass transfer of BPA from the source phase to the receiving phase through a PIM system.

4. Characterization of synthesized PIMs

4.1. Scanning electron microscopy

Fig. 14 shows the micrographs of the different PIMs, the CTA film shows a very porous surface. This porous surface has a highly cross-linked specific morphology, the look of a woven network with a pore size of the order of a micrometer which is in agreement with the data given by other authors [22,34]. With the incorporation of carrier RC8 and plasticizer 2-NPOE the surface morphology changes. The PIM surface has a rather smooth, dense, homogenous, and featureless surface. The immediate explanation is that this morphology is due to the presence of plasticizer in pores acting as liquid media dissolving
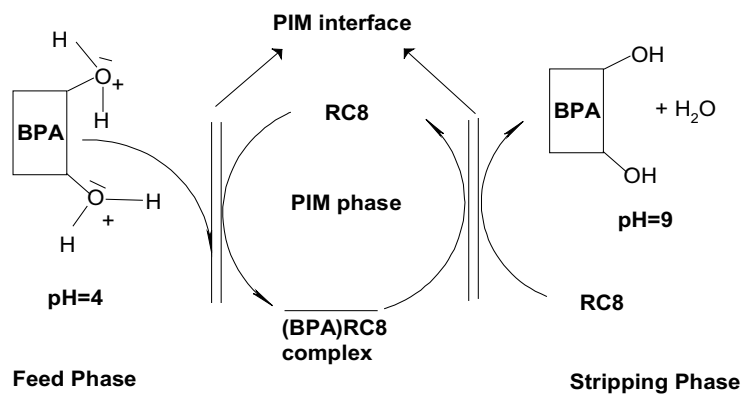

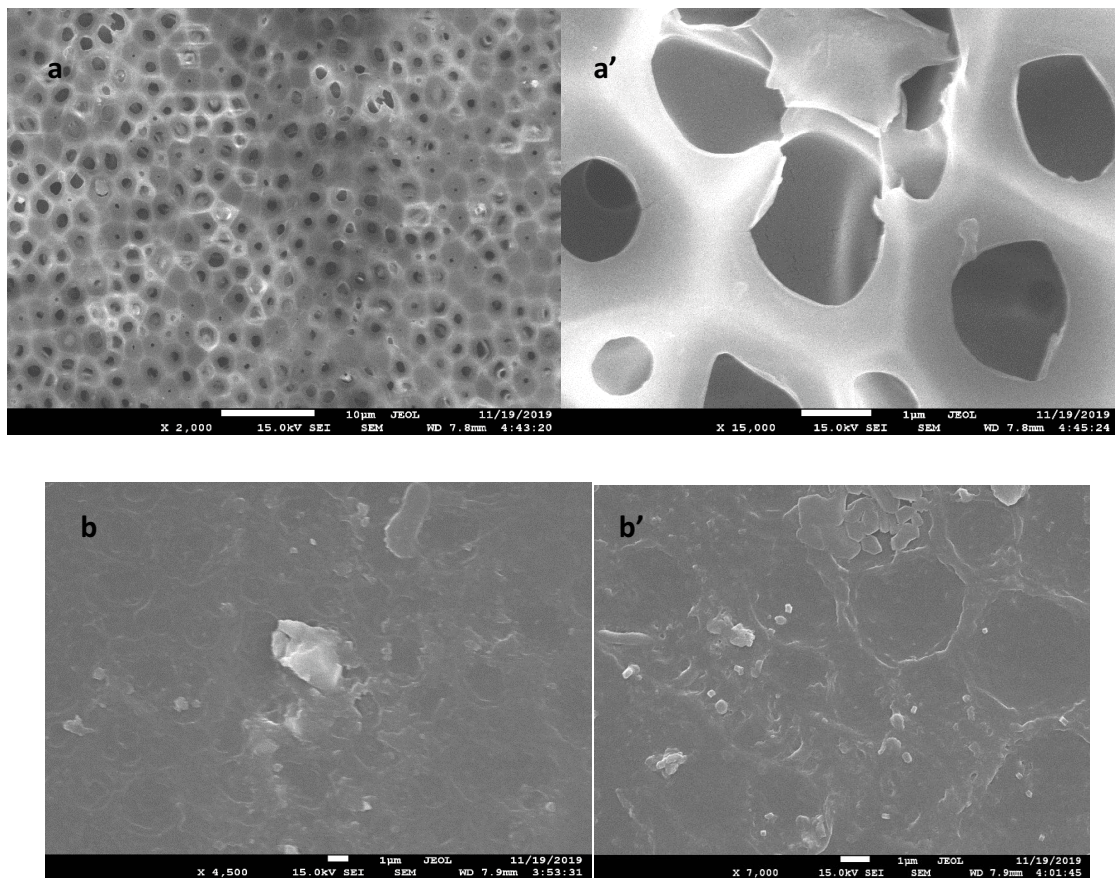Fig. 13. Representation scheme of the transport mechanism of BPA by carrier through PIMs system.

Fig. 14. SEM micrographs surface of synthesized PIMs without (a and a′) and with carrier (RC8)/plasticizer (2-NPOE) (b and b′).

extractant calix[4]resorcinarene. This observation proves higher compatibility between the components of the PIM (calix[4]resorcinarene/2-NPOE) and CTA support.

4.2. FTIR of PIMs and hydrophobicity evaluation

The FTIR spectra of PIMs are shown in Fig. 15. In addition to the absorption of cellulose triacetate (3,344; 2,961; 1,714; 1,303; and 1,049 cm⁻¹), new bands were observed in PIM with RC8 and 2-NPOE; in particular at around 2,854 characteristics of alkyl chains in RC8 and 2-NPOE, at 1,748, and at 1,527 cm⁻¹ characteristic of nitro groups in 2-NPOE and 1,463 cm⁻¹. From comparison with IR spectra reported in the literature [22,26], these are consistent with the incorporation of carrier RC8 in the support CTA matrix. In addition, certain differences and collapse were observed in relative band intensities as well as the shift of some bands characteristic of carbonyl groups C=O in CTA between 1,714 and 1,748 due to the interactions developed between RC8/NPOE and support CTA. These are most probably due to the inclusion of calix[4]resorcinarene and plasticizer 2-NPOE in the membrane, this result corroborates with the difference in surface morphology observed by SEM analysis. Table 1 lists the surface characteristics of the membranes. The hydrophobicity was improved after the addition of carrier RC8 and plasticizer 2-NPOE, as indicated by the increase of water contact angle from 60.60° to 78.51°.

Table 1
Contact angle of different PIMs measured by drop method

PIM composition	Water contact angle (°) (±0.1)
CTA without (RC8/2-NPOE)	60.60
68% 2-NPOE, 22% CTA, and 10% carrier RC8	70.96
67% 2-NPOE, 23% CTA, and 10% carrier RC8	73.46
74% 2-NPOE, 18% CTA, and 8% carrier RC8	78.51

5. Conclusion

This study concerning the applicability of PIM for the removal of bisphenol A from an aqueous solution. According to these results, elimination of BPA from synthetic wastewater, reaching up 90% of the initial amount of the molecule target in a single-stage process. The extraction efficiency was found to be strongly dependent on the membrane composition, calix[4]resorcinarene present in PIM matrix acting as extracting agent, which form a stable complex by hydrogen bonding and/or intermolecular interactions with BPA leading to higher extraction efficiency. The processing conditions such as stirring speed (600 rpm), pH of feed phase (4.0), concentration of stripping (NaOH) phase (0.2 mol dm⁻³) resulted in higher initial flux (5 × 10⁻⁷ mol m⁻² s⁻¹), which resulted in 90% removal of BPA from feed solution (100 mg dm⁻³) in 5 d. The study proves that synthesized PIM with calix[4]resorcianrene as a carrier can be successfully used for the removal of BPA from the aqueous feed.

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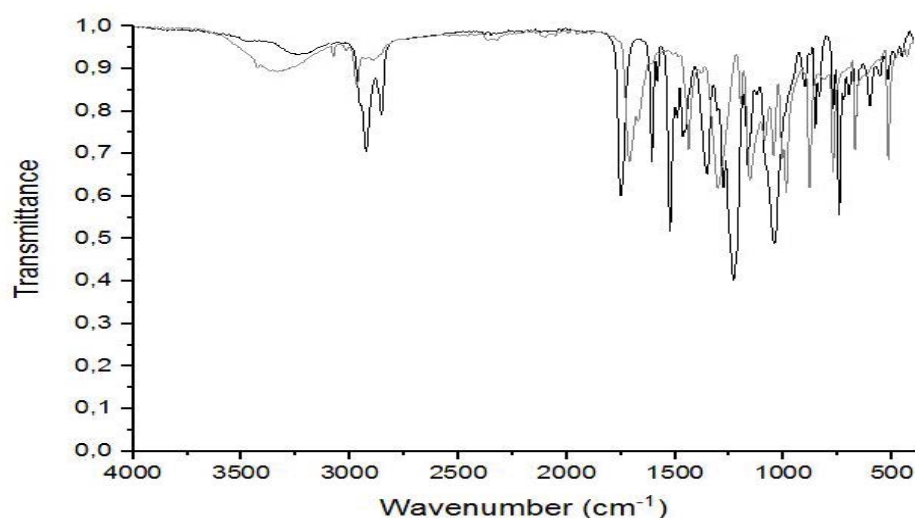[6] J. Sajiki, J. Yonekubo, Leaching of bisphenol A (BPA) to seawater, Chemosphere, 51 (2003) 55–62.

Fig. 15. FTIR spectra of CTA film without carrier and plasticizer (in blue) and PIM: CTA with RC8 and 2-NPOE (in red).

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