

Extraction of phenol from aqueous solutions by means of supported liquid membrane (MLS) containing tri-*n*-octyl phosphine oxide (TOPO)

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ABSTRACT

This paper deals with the liquid–liquid extraction and the facilitated transport through a supported liquid membrane (SLM) system of aqueous phenol using tri-*n*-octyl phosphine oxide (TOPO) dissolved in an appropriate organic solvent. Phenol has been quantitatively extracted from aqueous acidic solutions using TOPO dissolved in kerosene as organic phase. The effect of TOPO concentration dissolved in kerosene on the extraction efficiency reveals that TOPO combined with phenol in the ratio of 1:1.

Using a flat-sheet SLM (FSSLM) system, more than 65% of the initial phenol content in the feed phase was extracted and stripped in a NaOH aqueous receiving phase. The important operational variables affecting the facilitated transport of phenol through the FSSLM system studied are concentration of TOPO, membrane viscosity, feed phase pH, initial phenol concentration, polymeric support type and membrane stability. Regardless of its comparatively low extraction efficiency of phenol, the SLM based on TOPO exhibits higher long-term stability as compared to tributyl phosphate (TBP). Elaborated SLM system retained its stability and initial performance during the 5 days long experiment contrary to the TBP-SLM system where a time dependent negative tendency (transport efficiency decline) was observed.

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1. Introduction

The development of new low cost techniques able to substitute existing separation and purification technologies is a challenging task. Membrane technologies are increasingly employed in many industrial sectors as important alternative to the classical processes of separation and purification. Well-known examples are pressure driven different types of filtration and reverse osmosis, electrical field driven electro dialysis, and finally gas and vapor separation processes where the driving factor often is a combination of pressure, concentration difference and also temperature [1]. Among liquid membranes, supported liquid membrane (SLM) is a promising technology for recovering organic compounds or metals because it combines extraction and stripping process in one unit [2,3]. A SLM; using a porous membrane support impregnated with complexing carriers to separate the feed and strip phases; presents one of the feasible type of liquid membrane. Besides that it is possible to dissolve some hydrophobic chemicals in the organic liquid, so that they will be able to interact with the transported hydrophilic species. This process would remind extraction, can be based on fine chemical interactions and can be highly specific. Then the complex could easily diffuse through the organic liquid. Bloch was probably

the first who has proposed to use extraction reagents dissolved in an organic solution and immobilized on microporous inert supports for removal of metal ions from a mixture [4]. In SLM, usually organic liquid is imbedded in small pores of a polymer support and is kept there by capillary forces. If the organic liquid is immiscible with the aqueous feed and strip streams, SLM can be used to separate the two aqueous phases. It may also contain an extractant, a diluent which is generally an inert organic solvent to adjust viscosity and sometimes also a modifier to avoid so-called third phase formation. Relatively small volume of organic components in the membrane and simultaneous extraction and stripping in one technological step offers the advantages of possible usage of expensive carriers, high separation factors, easy scale-up, low energy requirements, low capital, operating costs, etc. [5].

Phenol and substituted phenols are used widely in many industrial processes, such as coking plants, paper, cosmetic and dyes industries. They are released in industrial wastewater and domestic water, and may directly or indirectly cause serious health and odor problems [6,7]. They can, in fact, inhibit growth of or exert lethal effects on aquatic organisms even at relatively low concentrations (5–25 mg L⁻¹, depending on the temperature and the organism state of maturity), and impart off flavors in drinking water and food processing water [8]. As a consequence, they are listed in the US Environmental Protection Agency priority list of pollutants and in the 76/464/EEC Directive of the European Union, related to dangerous substances discarded into the aquatic environment. Most of

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the overall world production of phenol, which was 7.78×10^6 tons in 2001, is related to the production of bisphenol A (39%), phenolic resins (27%), caprolactam (16%), alkylphenols (5%), 2,6-xyleneol (3%), and anilines (2%) among others (8%) [9].

The various techniques available for the treatment of phenolic effluents can be subdivided into two main categories, the destruction and the recovery methods [10]. Among the destruction methods, there are biological treatments [11,12], incineration, ozonization in the presence of UV radiation, and oxidation with wet air [10]. On the other hand, the recovery methods include liquid–liquid extraction [13,14], ionic exchange with resins [15], and membrane processes, such as pervaporation [16], and extraction with SLM [13,17]. Current official analytical methods for phenolic compounds extraction are liquid–liquid extraction for liquid samples, and Soxhlet extraction for solid samples (US EPA Methods 604, 605, 8041 and 3540 B, respectively). Solvent extraction is the most often used technique to recover phenol ($pK_a = 9.98$) in its neutral form [18]. This method requires expensive and hazardous organic solvents, which are undesirable for health and disposal reasons. Actually, the use of simple organic solvents, such as benzene, heptane, toluene, methylisobutyl ketone, isopropyl ether, isopropyl acetate, etc., is now limited due to the high hydrophilicity and solubility of these solvents in aqueous streams and/or their toxicity. In contrast, the use of various basic and solvating reagents, including different alkylamines (e.g. Amberlite® LA-2, Alamine® 336 [19], tributyl phosphate (TBP) [13] and trialkylphosphine oxides [20] is now preferred. Tri-*n*-octyl phosphine oxide (TOPO) is a stable solid reagent (must be dissolved in an appropriate solvent) which, in contrast to TBP, will not undergo hydrolysis either in contact with aqueous acid or alkaline solutions. Moreover, TOPO shows lower solubility in water than TBP. Owing to all of these factors, the extraction of phenol from aqueous solution using TOPO as extractant by liquid–liquid extraction experiments and across a SLM system is investigated in this paper. Obtained results were compared to our previous experiments carried out using TBP as extractant [13], especially the stability concern of the designed SLM system.

2. Theoretical

The theoretical part of phenol extraction using tributyl phosphate (TBP) has been widely described in our previous work [13]. The reaction of phenol (PhOH) with tri-*n*-octyl phosphine oxide (TOPO, solvating reagent) can be illustrated by the following reaction:



and the equilibrium constant, K_{ex} by:

$$K_{\text{ex}} = \frac{[\text{PhOH} \cdot \text{TOPO}]_{\text{org}}}{[\text{PhOH}]_{\text{aq}} [\text{TOPO}]_{\text{org}}} \quad (2)$$

The above equilibrium can also be expressed using the distribution coefficient, D , for the phenol, as shown in Eq. (2):

$$D = \frac{[\text{PhOH}]_{\text{org}}}{[\text{PhOH}]_{\text{aq}}} = \frac{[\text{PhOH} \cdot \text{TOPO}]_{\text{org}}}{[\text{PhOH}]_{\text{aq}}} = K_{\text{ex}} [\text{TOPO}]_{\text{org}} \quad (3)$$

The stripping of phenol from the organic phase $(\text{PhOH} \cdot \text{TOPO})_{\text{org}}$ can be effectively ensured using aqueous NaOH solution via its conversion into aqueous sodium phenolate as follows:



The phenol concentration in the receiving solution is not constant but increases as a function of time. From the slope of the straight line (at time tending to zero, negligible diffusion lag time) obtained when plotting the phenol concentration in the receiving phase as

Table 1

Physical characteristics, experimental and normalized initial phenol fluxes and percentage of phenol transported of used polymeric supports. Source phase: 200 mg L^{-1} phenol at pH 2. Support: Accurel® PP or Durapore® PVDF. Organic phase: $5 \times 10^{-3} \text{ M}$ TOPO dissolved in kerosene. Stripping phase: 0.2 M NaOH.

Polymeric support	Accurel® PP 2E-HF; Membrana, Germany	Durapore®; Millipore, USA
Material	Polypropylene	Polyvinylidene difluoride
Thickness (d_0 ; μm)	160	120
Pore diameter (d ; μm)	0.2	0.2
Porosity (ϵ ; %)	75	65
Tortuosity ($\tau = 1 - \ln \epsilon$) [23]	1.29	1.43
$\epsilon/d_0 \tau$ ($\times 10^{-3} \mu\text{m}^{-1}$)	3.63	3.79
J_{exp} ($\times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$)	4.1	2.7
J_{N} ($\times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1}$)	4.1	2.6
%Phenol transported (24 h)	66.6	51.6

a function of time, the initial flux (J) can be calculated according to the following equation [13,21,22]:

$$J = \left(\frac{V}{S} \right) \left(\frac{d[\text{PhOH}]_r}{dt} \right) \quad (5)$$

where V is the volume of the aqueous receiving solution (L), S is the effective exposed surface area of the membrane (m^2), and $[\text{PhOH}]_r$ is the phenol concentration in the receiving phase (mol L^{-1}) at elapsed time (s).

3. Experimental

3.1. Reagents and materials

Phenol, tri-*n*-octyl phosphine oxide (TOPO) with purity above 97%, 2-nitrophenyl octyl ether (NPOE), decane, 2-octanol and kerosene were purchased from Fluka (Switzerland). Whereas, hexane is a Fisher Scientific (USA) product. NaOH was procured from Carlo Erba (Italy). All used chemicals were of analytical reagent grade.

Two different flat-sheet polymeric supports were evaluated. Their physical characteristics are collected in Table 1.

3.2. Liquid–liquid extraction experiments procedure

2 mL of aqueous solution containing almost 200 mg L^{-1} of phenol adjusted to pH 2 with few drops of H_2SO_4 and 2 mL of $5 \times 10^{-3} \text{ M}$ TOPO dissolved in an organic solvent were mixed in stoppered glass tubes and shaken at 50 rpm during 24 h (time suggested as sufficient to reach equilibrium) and at $25 \pm 1 \text{ }^\circ\text{C}$. The mixture was then centrifuged and the two phases were separated. Concentrations of phenol were determined by UV–vis spectrophotometry (Jenway UV–vis spectrophotometer type 6705) at 270 nm.

The percentage of extraction (% E) was calculated from the concentration of phenol before ($[\text{Phenol}]_{\text{aq},i}$) and after ($[\text{Phenol}]_{\text{aq}}$) extraction:

$$\%E = \frac{[\text{PhOH}]_{\text{aq},i} - [\text{PhOH}]_{\text{aq}}}{[\text{PhOH}]_{\text{aq},i}} \times 100 \quad (6)$$

The recovery of the extracted phenol in the separated organic phase (2 mL) was investigated by using 2 mL of 0.2 mol L^{-1} NaOH solution. The percentage of recovery (% R) was calculated from the concentration of recovered (stripped) phenol ($[\text{Phenol}]_{\text{aq},r}$) and the initial concentration of phenol in the aqueous phase ($[\text{Phenol}]_{\text{aq},i}$):

$$\%R = \frac{[\text{PhOH}]_{\text{aq},r}}{[\text{Phenol}]_{\text{aq},i}} \times 100 \quad (7)$$

Table 2

Extraction and recovery efficiencies and distribution ratios of phenol using 5×10^{-3} M TOPO dissolved in some organic solvents. Experimental details are given in the text.

Organic phase: 5×10^{-3} M TOPO dissolved in an organic solvent	%E	log D	%R
Decane	91.2	1.02	85.9
Hexane	95.6	1.34	54.1
2-Octanol	98.3	1.76	80.8
Kerosene	88.7	0.89	83.1
2-Nitrophenyl octyl ether (NPOE)	93.9	1.19	9.2

Used water was deionised through a MilliQ plus column (Millipore, USA).

3.3. Transport experiments procedure

The flat-sheet SLM (FSSLM) was prepared by soaking for at least 24 h the polymeric inert support in a TOPO-kerosene solution and then wiping it with filter paper. Obtained SLM was placed in a circular window (diameter of 2 cm) of a two-compartment permeation cell described elsewhere [13,21,24].

The feed solution (100 mL) was a 200 mg L^{-1} phenol aqueous solution adjusted at pH 2. The stripping solution (100 mL) was a 0.2 mol L^{-1} NaOH aqueous solution. Both aqueous feed and stripping solutions were magnetically stirred at 600 rpm at $25 \pm 1^\circ \text{C}$ to avoid concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. 1 mL sample of each feed and stripping solutions was periodically taken to determine phenol concentration. The flow times of different concentrations of TOPO solutions dissolved in kerosene were measured by a capillary viscosimeter from Schott thermostated in a water bath and equipped with an electronic timer (ViscoClock, Schott). All experiments were carried out in duplicate and standard deviations were less than $\pm 5\%$.

4. Results and discussion

4.1. Liquid–liquid extraction experiments

4.1.1. Extraction and recovery efficiencies

TOPO (5×10^{-3} M) was dissolved in some organic solvents *viz.* decane, hexane, 2-octanol, kerosene and NPOE. Extraction efficiencies (%E) as well as the distribution coefficients (log D) are given in Table 2. It can be noted that all tested solvents provided an extraction efficiency of phenol higher than 88%. The best extraction efficiency was obtained using 2-octanol as organic solvent to dissolve TOPO. In the same way, Jiang et al. [14] demonstrated that alcohols are more effective for phenol extraction than amines and carboxylic acids. On the other hand, Kujawski et al. [17] revealed that methyl-*tert*-butyl ether (MTBE) was found to be the best extraction solvent for phenol in a membrane-based solvent extraction system as compared to a mixture of hydrocarbons and cumene.

By comparing the distribution ratios of phenol given in Table 2 to the distribution ratios of phenol given in the literature using some common organic solvents without TOPO addition [13,25,26], it can be concluded that TOPO addition improves the extraction efficiency (synergistic effect). In fact, log D shifts from 1.44 using pure octanol [25] to 1.76 when TOPO dissolved in 2-octanol is used as organic phase. In all cases, the use of TBP provides higher phenol distribution coefficients than TOPO [13]. Additionally, Cichy and Szymanowski [26] showed that Cyanex 923 (contained various trialkyl (C_6 , C_8) phosphine oxides as the active substance with their content above 92%, operating at pH 2–8) has a much higher distribution ratio than Amberlite LA-2 (contained *N*-dodecyl-*N*-(1,1,3,3,5,5-hexamethylhexylamine) as

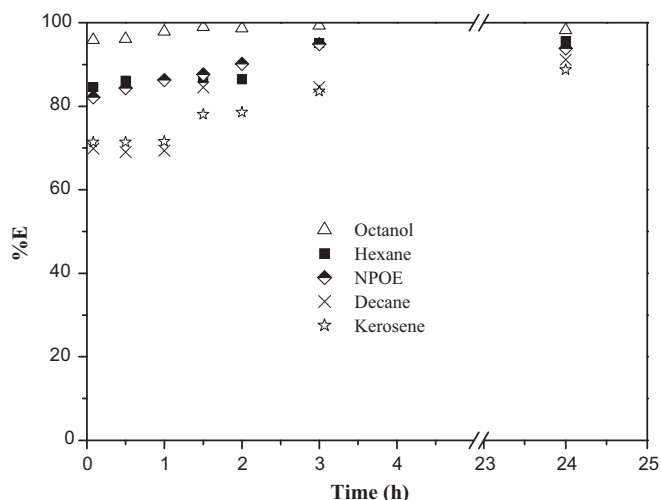


Fig. 1. Variation of the extraction efficiency as a function of time (0–24 h). Aqueous phase: 2 mL of 200 mg L^{-1} phenol at pH 2. Organic phase: 2 mL of 5×10^{-3} M TOPO dissolved in an organic solvent.

the active substance, operating at pH 6–8), which, in turn, has a higher distribution ratio than trioctylamine (TOA, at pH 4–8), which, in turn, has a much higher distribution ratio than kerosene alone. Cyanex 923, a commercial mixture of trialkylphosphine oxides analogous to TOPO structure, forms relatively strong and reversible hydrogen bonds with phenol, showing the highest capacity for phenol extraction [27].

The stripping of phenol from organic phases has been studied using 0.2 M NaOH solution and recovery efficiencies (%R) are also presented in Table 2. The results show that the NaOH solution provided a 54–86% recovery of phenol for all tested solvents except for NPOE. The small detection of phenol in the stripping aqueous phase (9.2%) in the case of NPOE can be explained by the fact that the formed complex is steady enough to be dissociated in the contact of NaOH solution towards sodium phenolate formation [13]. Contrary to the hypothesis of the irreversible and instantaneous reaction formulated by Zha et al. [28], a residual phenol amount in the organic phase was obtained as using the solvating reagent TBP [13]. This result is in accordance with the mathematical model proposed by Palma et al. [29] to describe phenol extraction with methyl isobutyl ketone (MIBK) as well as with the observations of Bizek et al. [30].

4.1.2. Extraction kinetics

Kinetics of phenol extraction using TOPO as extractant dissolved in different organic solvents has been studied following the experimental protocol described above. Aqueous and organic phases were mixed at different contact times (0–24 h). The variation of the extraction efficiency as a function of time is given in Fig. 1. From this variation, it was observed that the percentage of extraction was more or less constant after 3 h of phase contact. In all cases and after only 3 h of phase equilibrium, the extraction of phenol reached more than 82%. The prolongation of the phase contact time to over 3 h had only a very slight effect on the yield of phenol extraction. These results show that the time suggested as sufficient to reach apparent equilibrium is almost 3 h. The equilibrium time was not accurately determined in this case, in contrast to TBP case where 3 min was considered as necessary and sufficient to reach the equilibrium [13].

In our previous work, kerosene was used to study the facilitated transport of phenol across a flat-sheet SLM system containing TBP as extractant [13]. Moreover, kerosene is commonly and widely used for the elaboration of SLM systems. Therefore, kerosene was

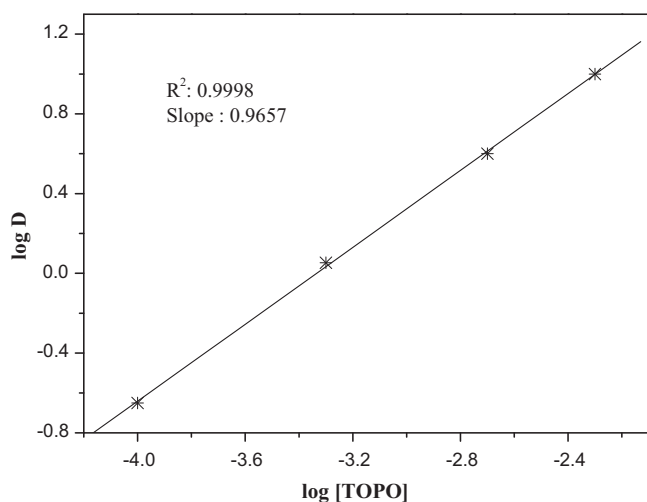


Fig. 2. Plot of $\log D$ versus $\log [\text{TOPO}]$. Aqueous phase: 2 mL of 200 mg L^{-1} phenol at pH 2. Organic phase: 2 mL of different concentrations of TOPO dissolved in kerosene. Contact time: 3 h.

used throughout the study as organic solvent to dissolve TOPO to compare results with previous TBP-kerosene mixture results.

4.1.3. Effect of TOPO concentration in the organic phase

Aqueous phenol solutions were mixed with different concentrations TOPO solutions dissolved in kerosene and shaken for 3 h. The plot of $\log D$ versus $\log [\text{TOPO}]$ is given in Fig. 2. It can be noted that the distribution coefficient values increase with increasing TOPO concentration. The addition of TOPO improves the efficiency of liquid–liquid extraction system used to extract phenol from an aqueous phase at pH 2. The log–log plot of D against TOPO concentration in the organic phase permits an estimation of the number of TOPO molecules involved in the extraction scheme (see Eq. (3)) [31,32]. This drawn plot was found to be a straight line with slope of approximately 1. This implied that TOPO (extractant) combined with phenol in the ratio of 1:1.

4.2. SLM transport experiments

4.2.1. Transport kinetics

The concentration time profile of the phenol transport was studied over a period of 24 h. Fig. 3 shows the time dependence of the

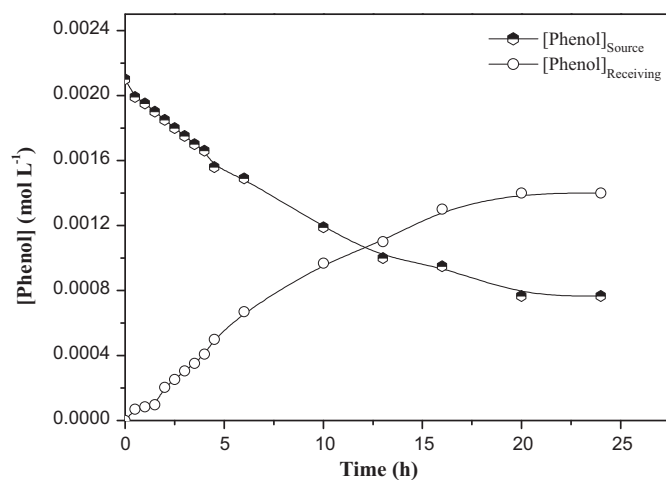


Fig. 3. Time courses of phenol concentration in both source and receiving phases. Source phase: 200 mg L^{-1} phenol at pH 2. Support: Accurel® PP. Organic phase: $5 \times 10^{-3} \text{ M}$ TOPO dissolved in kerosene. Stripping phase: 0.2 M NaOH.

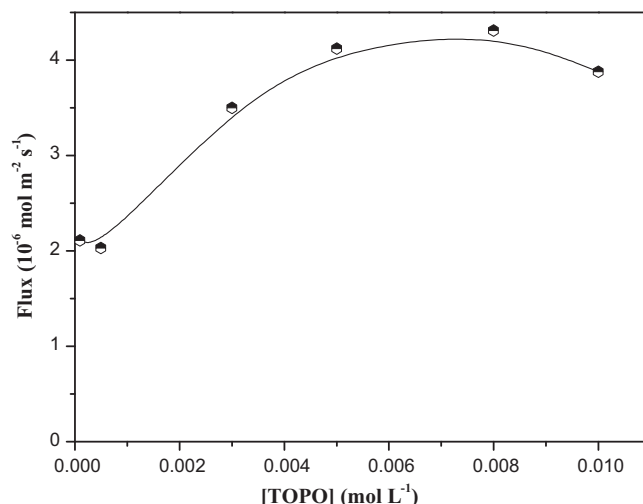


Fig. 4. Effect of the TOPO concentration on the initial flux of phenol. Source phase: 200 mg L^{-1} phenol at pH 2. Support: Accurel® PP. Organic phase: different TOPO concentrations dissolved in kerosene. Stripping phase: 0.2 M NaOH.

phenol transport through the SLM containing TOPO dissolved in kerosene under mentioned conditions. As is evident, a rapid rise in phenol concentration in the receiving phase, as well as a sharp decrease in phenol concentration during the first 12 h of transport experiments. Phenol extracted from the feed solution into the membrane organic phase was almost completely stripped from the former phase into the receiving solution. Residual phenol in the membrane organic phase was not detected and 0.2 M NaOH solution can be considered as a suitable stripping aqueous solution. After 24 h of transport through our SLM system, about 67% of phenol initially present in the source phase was removed to the receiving phase. Besides, the increase of the effective exposed surface area of the membrane could increase the transport efficiency of the system. The driving force of the transport is a concentration gradient of the phenolic complex species formed in the membrane organic phase with TOPO dissolved in kerosene $(\text{PhOH} \cdot \text{TOPO})_{\text{org}}$. In fact, the phenolic complex species formed at the interface feed-membrane, will diffuse across the membrane to the interface membrane-stripping where they are dissociated in contact with NaOH stripping solution (formation of sodium phenolate insoluble in the organic phase). As a result, sodium phenolate will not diffuse back to the membrane and a concentration driving force of transport would be maintained [13,33,34].

4.2.2. Effect of TOPO concentration in the membrane phase

The results concerning the transport of phenol from the feed phase containing 200 mg L^{-1} phenol at pH 2.0 and the receiving phase 0.2 M NaOH, and a varying concentration of TOPO dissolved in kerosene in the range of 10^{-4} to 10^{-2} M are presented in Fig. 4. It can be perceived that the initial flux is dependent on the TOPO concentration in the membrane organic phase. The maximum phenol initial flux was achieved at the range of TOPO concentration from 10^{-4} to $8 \times 10^{-3} \text{ M}$. At the TOPO concentration higher than $8 \times 10^{-3} \text{ M}$, the rate of transfer of phenol across the liquid membrane is lower. The flux increase can be explained on the basis of equilibrium reaction (1) where the formation of the phenolic complex species is favored with increasing TOPO concentration. Actually, an increase of the TOPO concentration in the membrane phase is expected to increase the extraction of phenol and hence to transport the phenolic complex species with a greater speed. Above $8 \times 10^{-3} \text{ M}$ TOPO, the phenol transport flux decreases probably due to the increase of the viscosity of the organic resultant solution at TOPO concentrations higher than $8 \times 10^{-3} \text{ M}$ as revealed in Table 3.

Table 3

Effect of TOPO concentration, dissolved in kerosene, on the viscosity (η) of the liquid membrane phase ($\theta = 25^\circ\text{C}$).

[TOPO] (mol L^{-1})	η (cP)
$\times 10^{-4}$	1.85
5×10^{-4}	1.87
5×10^{-3}	1.88
8×10^{-3}	1.88
$\times 10^{-2}$	1.92

The viscosity of the liquid membrane increases with increase in concentration of carrier (TOPO) in the membrane organic solution [35]. As diffusivity is inversely proportional to viscosity; an increase of liquid membrane viscosity causes reduction of the phenolic complex species diffusivity which eventually decreases initial flux of phenol [13,22]. This means that the effective diffusivity of these species decreases significantly while the reaction rate of their formation increases rather slowly as the TOPO concentration increases above 8×10^{-3} M. In this case, the increase of the TOPO concentration at this point does not compensate for the increase in the solution viscosity. On the basis of the observations made in the present study, a solution of 5×10^{-3} M TOPO dissolved in kerosene was selected as the optimum carrier concentration for all the subsequent studies to evaluate different parameters.

4.2.3. Effect of source phase pH

The effect of the pH of the source phase on the efficiency of phenol transported in the pH range 1–9 was studied and the results are depicted in Table 4. It can be observed that percentage of phenol extraction decreases with increasing source pH above pH 2.0. In fact, after 24 h of transport process, the extraction percentage decreases from 66.6% (pH=2.0) to 21.5% (pH=9.0). It is trivial that the molecular (un-dissociated) form of phenol is extracted. Thereby, subsequent experiments were performed at a feed phase pH of 2.0 to ensure the existence of phenol in its molecular state which is indispensable for its transport [13]. An aqueous source pH of 2.0 was also suggested by Venkateswaran and Palanivelu [36] as optimal pH for the transport of phenol through a SLM system using vegetable oils as liquid membrane. Trivunac et al. [37], subsequent to their study about the amount of molecular and dissociated phenol at different pH values, recommended to adjust the initial pH to less than 4.0 with the intention to keep the phenol in its molecular state to obtain an efficient phenol removal.

4.2.4. Effect of initial phenol concentration in the source phase

The influence of the initial phenol source concentration on the SLM extraction efficiency was also investigated. This study was carried out using source solutions containing different phenol concentrations ranging from 3.5 to 1000 mg L^{-1} , and results are shown in Fig. 5 as the phenol initial flux against the phenol concentration in the source solution. This shows that under the experimental conditions, the flux is influenced by the initial phenol concentration, being enhanced when the phenol concentration in the feed solution increases. Moreover, in the studied concentration range, we did

Table 4

Effect of aqueous source pH on the percentage of phenol transported. Source phase: 200 mg L^{-1} phenol at different pHs. Support: Accurel® PP; organic phase: 5×10^{-3} M TOPO dissolved in kerosene. Stripping phase: 0.2 M NaOH.

Source phase pH	%Phenol transported (24 h)
1	66.1
2	66.6
4.3	58.5
5.7	41.7
7.6	33.4
9	21.5

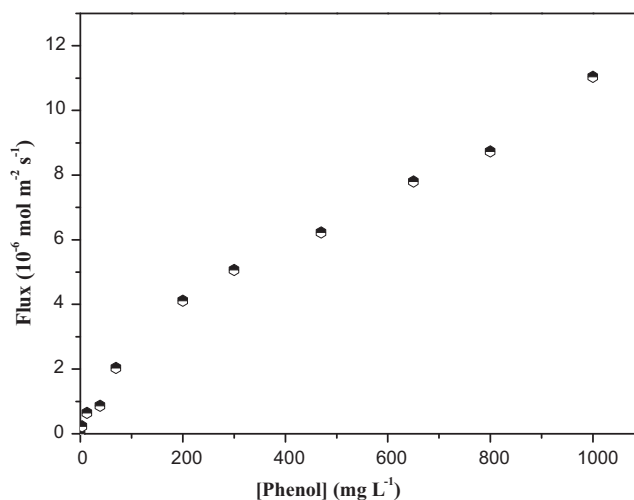


Fig. 5. Effect of the initial phenol concentration on the initial flux. Source phase: different phenol concentrations at pH 2. Support: Accurel® PP. Organic phase: 5×10^{-3} M TOPO dissolved in kerosene. Stripping phase: 0.2 M NaOH.

not observe the typical “plateau” of the flux. The initial flux increase was also observed in our previous works [13,38]. An increase in flux at low feed concentrations is expected, followed by an approach to a plateau value at high feed concentration when the carrier is fully loaded [39]. As the flux increases almost linearly throughout the studied concentration range in this particular investigation, the liquid membranes have probably not reached saturation. This phenomenon can be attributed to the permeation process being controlled by diffusion of solute species in the range of concentration studied [40].

Taking into account the flux increase in the concentration studied range; the elaborated SLM system can be promisingly applied to extract phenol from diluted or concentrated aqueous samples. In addition, this system recommends low capital investment and operating cost and low energy consumption compared to some other processes. The electrocoagulation process, for example, is not proper to phenol removal from concentrated aqueous samples as demonstrated by Abdelwahab et al. [41]. These authors report that by increasing the concentration of phenol from 30 to 250 mg L^{-1} , the percentage removal of phenol was gradually decreased from 99 to 34%. Nevertheless, the energy consumption was decreased from 0.52 to 0.18 kWh g^{-1} phenol, while electrode consumption slightly increased from 0.02 to 0.07 g Al g^{-1} phenol.

4.2.5. Effect of polymeric support type

In this study, two supports with different chemical composition and physical properties were tested under the same experimental conditions.

Thickness, porosity, and tortuosity of the support are fundamental parameters that act on the mass fluxes of the solute. Table 1 collects both experimental (J_{exp}) and normalized phenol fluxes (J_N) obtained with Durapore® related to the thickness $d_{0,A}$, porosity ε_A and tortuosity τ_A of Accurel® PP support, as described in the following equation [42,43]:

$$J_N = J_{\text{exp}} \frac{d_0 \tau}{\varepsilon} \frac{\varepsilon_A}{d_{0,A} \tau_A} \quad (8)$$

Durapore® would normally provide higher fluxes than Accurel® due to its higher ratio $\varepsilon/d_0 \tau$, whereas in our case, the latter showed the best flux value as well as the best phenol transport efficiency. Similar results were obtained in previous works [13,44,45] where it was reported that not only the physical parameters but also both

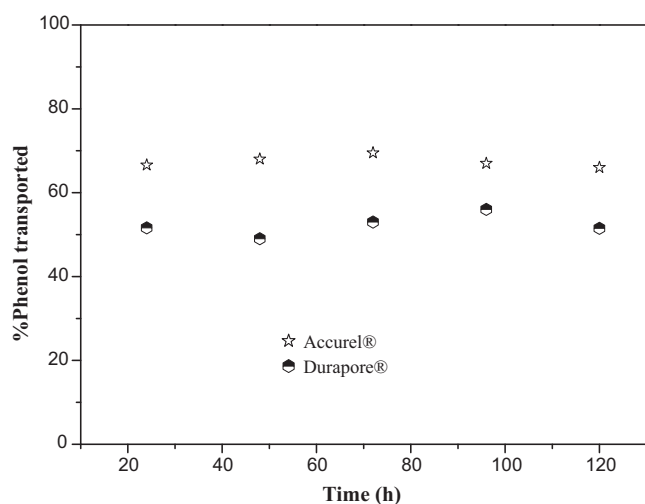


Fig. 6. Stability behaviour of the SLM system: percentage of phenol transported as a function of time. Source phase: 200 mg L⁻¹ phenol at pH 2. Support: Accurel® PP or Durapore® PVDF. Organic phase: 5 × 10⁻³ M TOPO dissolved in kerosene. Stripping phase: 0.2 M NaOH.

chemical composition and physical parameters of the support affect the chemical species transport efficiency through a SLM system.

Both supports show higher initial phenol flux when phenol is transported across a SLM system containing TBP as carrier instead of TOPO [13]. Moreover, Accurel® PP support embedding TBP seems to be slight more efficient (transport efficiency of 74.3% in 24 h) than TOPO – Accurel® system (transport efficiency of 66.6% in 24 h).

4.2.6. Stability of the SLM

The stability of both used membrane supports was tested following the phenol transport efficiency for a period of 5 days on continuous run mode under the optimum conditions without re-impregnation of the membrane (experimental details are given in Fig. 6). The percentage of transported phenol was calculated each 24 h, and after this period of time, depleted source and enriched strip solutions were replaced with fresh ones. A plot of percentage of transported phenol versus time is given in Fig. 6. From the observations made in this figure, it can be stated that both polymeric supports (Accurel® and Durapore®) proven only marginal transport efficiency differences and do not exhibit a time dependent negative tendency. It can be concluded that after 5 days of permanent operation the membrane retained its initial performance.

Contrary to TBP, TOPO offers a 5-day stable phenol transport SLM system. Indeed, once TBP is used as carrier and after 3 days of continuous run, a transport efficiency decline of 17% and 52% was observed using Durapore® and Accurel® as polymeric supports, respectively [13]. Obtained results suggest a good expectancy for the lifetime of SLM with TOPO, in relation with its solid state and its lower solubility in water than TBP, which is usually a critical weakness of SLM systems [46,47]. TOPO can be successfully used to design stable SLM system allowing the extraction of phenol from aqueous acidic solutions.

5. Conclusions

In this paper we have described the results of an experimental study on a SLM system. SLM based on TOPO effectively transport phenol from aqueous acidic solutions. Obtained results are compared to previous results when TBP is used as carrier (solvent reagent). Under optimum operating conditions, a transport efficiency of 66.6 and 74.3% (24 h) and an initial phenol flux of 4.1 × 10⁻⁶ and 14.0 × 10⁻⁶ mol m⁻² s⁻¹ using TOPO and TBP are

achieved, respectively. Regardless of its rather low extraction efficiency of phenol, the main feature of SLM based on TOPO is its higher stability compared to TBP-SLM system. Constant extraction efficiency around 65% through TOPO-SLM system was found during the 5 days long experiment, which is promising.

The present study permit us to predict an auspicious industrial application of the described system, especially when the effective exposed surface area of the membrane could be considerably increased using a hollow-fiber SLM (HFSLM) system. The former system could be a useful tool to remove phenol from industrial effluents even at high concentrations. Nevertheless, the use of this system may perhaps require a pre-treatment of the effluent depending on its quality characteristics.

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