MEMBRANARY TECHNIQUES USED AT THE SEPARATION OF SOME PHENOLIC COMPOUNDS FROM AQUEOUS MEDIA

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Lucrarea prezintă un studiu de separare a unor derivați fenolici frecvent întâlniți în mediul înconjurător: m-nitrofenol, p-nitrofenol, m-crezol, p-crezol, prin tehnica membranelor lichide de volum. Folosind cloroform ca solvent organic pentru membrană, s-au studiat parametrii operaționali ai procesului de transport stabilind condițiile optime de separare ale derivaților fenolici (pH-ul fazei sursă, pH-ul fazei receptoare, durata transportului) Cele mai bune randamente de transport s-au obținut pentru m-nitrofenol şi p-nitrofenol. Randamentul de transport în cazul acestor derivați fenolici a fost de 92% pentru m-nitrofenol şi respectiv 98% pentru p-nitrofenol, în cazul în care transportul a avut loc dintr-o fază sursă cu pH=2 printr-o membrană de cloroform într-o fază receptoare alcalină (pH=12).

The paper presents a separation study of some phenolic compounds frequently encountered in the environment: m-nitrophenol, p-nitrophenol, m-cresol, p-cresol, using the bulk liquid membranes technique. Using chloroform as the organic solvent for the membrane, the operational parameters of the transport were studied and the optimum separation conditions have been established (the feed phase pH, the receiving phase pH, the time period of the transport). The best transport efficiencies were obtained for m-nitrophenol and p-nitrophenol. The transport efficiencies in the case of these phenolic derivatives were 92% for nitrophenol and 98% for p-nitrophenol, if the transport takes place from an acid feed phase with pH=2 through a chloroform membrane into an alkaline receiving phase (pH=12)

Keywords: nitrophenols, cresols, bulk liquid membranes, phenols separation, transport through bulk liquid membranes

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1. Introduction

The protection of the environment represents one of the main components of scientific research. Phenol and phenolic derivatives are important among the frequently encountered dangerous contaminants of waste waters. Due to their high toxic potential, the recuperation of these compounds from residual waste waters was intensively studied and has a great applicability [1].

Among the recuperation methods of phenol and phenolic derivatives we mention: solvent extraction [2-4], adsorption on active carbon or several polymers [5, 6] and membranary processes [7-10].

The main achievements in the field of membranary techniques used at the recuperation of phenols and phenolic derivatives from waste waters are based on the utilization of supported liquid membranes and emulsion liquid membranes. In comparison with other recuperation techniques, when applying these membranary processes the obtained results show an increased selectivity and an important concentration of the solute [11-15].

The applicability of these membranary techniques is still limited due to the low stability of the emulsion or to the fact that when the emulsion is stable it hardly breaks.

2. Experimental

The used reagents were analytical grade and were used without further purification. There were used m-nitrophenol, p-nitrophenol, m-cresol, p-cresol all from Merck. Chloroform (Merck) was saturated with distilled water. Distilled water was saturated with chloroform and used at the preparation of the feed phase and of the receiving phase.

Hydrochloric acid (Merck) and the sodium hydroxide (Merck) were used for the variation of pH between 2 and 12. The pH was measured with a combined glass/AgCl, Ag electrode, using a SevenMulti Metler Toledo pH-meter. The calibration of the pH-meter was realized using pH solution standards ranging between 4, 12±0, 02 and 9, 18±0, 02.

The transport experiments were realized in a “wall in wall” type transport cell presented in Fig. 1.

The feed phase (F.P.) consisted in an aqueous or acid phenolic compound solution with a concentration ranging between 10^{-4}-10^{-3} mol·L^{-1}. The volume of the feed phase is 20 cm^3. The receiving phase (R.P.) is a solution of NaOH with a concentration ranging between 10^{-2}-10^{-4} mol·L^{-1}. The volume of the receiving phase is 7 cm^3. The two aqueous phases are separated through a chloroform membrane having a volume of 50 cm^3. The work temperature was 25±1°C and the transport time was 3 hours.

The phenolic derivatives content in the aqueous phase was measured by molecular absorption spectrometry in the UV region using a Camspec M501 spectrometer. The phenolic compounds present absorption bands in the UV region at the next wave lengths:m-nitrophenol at λ= 274 nm (acid , neutral medium) and λ = 293 nm (alkaline medium), p-nitrophenol at λ = 317 nm (acid, neutral medium) and λ = 404 nm (alkaline medium), m-cresol at λ = 272 nm (acid, neutral medium) and λ = 289 nm (alkaline medium), p-cresol at λ = 278 nm (acid, neutral medium) and λ = 295 nm (alkaline medium).

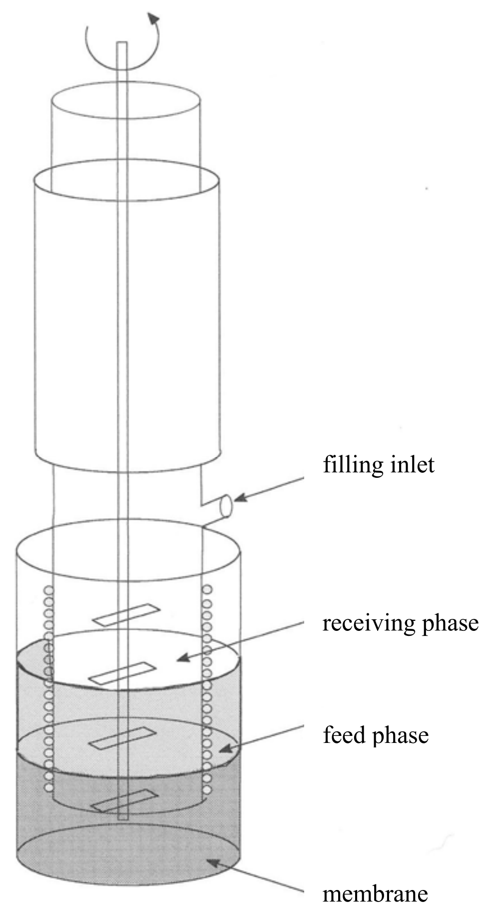

Fig 1. Experimental transport device

3. Results and discussions

The transport experiments of the studied phenolic derivatives (m-nitrophenol, p-nitrophenol, m-cresol and p-cresol) were performed by establishing the optimum operational parameters in membranary system.

Generally, neutral molecules can be transported through organic liquid membranes by a series of diffusion-extraction equilibriums that take place at the two interfaces of the membrane. Thus the studied phenolic derivatives being weak acids in aqueous solution are a predominant molecular form being able to cross over a chloroform membrane in order to concentrate itself in a receiving alkaline phase. The results are presented in Fig. 2.

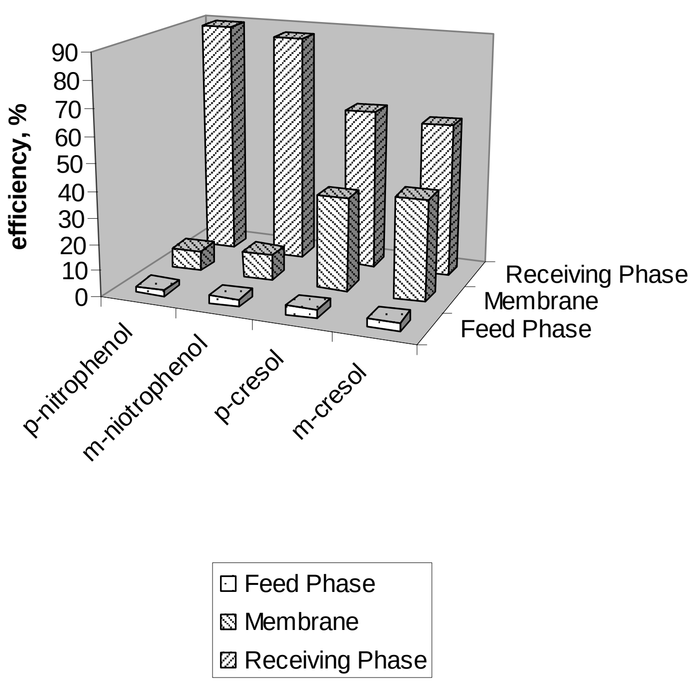

Fig 2. Distribution of the phenolic compounds in the phases of the membranary system at the end of the transport experiment
Feed Source = Phenolic compound with concentration ranging between 10^{-4}-10^{-3} mol·L^{-1}
Membrane = Chloroform
Receiving phase = NaOH solution 10^{-2} mol·L^{-1}

The obtained experimental data show that the phenolic nitroderivatives transport takes place with higher efficiencies (m-nitrophenol, transport efficiency:

87, 28-96, 17%; p-nitrophenol, transport efficiency: 90-97, 76%) than for o-cresols (m-cresol, transport efficiency: 58,5% - 28,14 %; p-cresol, transport efficiency: 61, 12% - 31, 21%).

The partition process of the phenolic derivatives in membranary system is a complex process. Besides the partition-diffusion equilibria, the competitive chemical equilibria take place. Thus, in the feed, phase the phenolic derivative (Ar-OH) is involved in a protolytic equilibrium:

$$(ArOH)_{F.P.} + HOH \leftrightarrow (ArO^{-})_{F.P.} + H_3O^{+} \qquad (1)$$

This equilibrium is controlled by pH. At $pH<pK_{a,\ Ar\text{-}OH}$ predominates the un-dissociated form of the phenolic derivative, which is partitioned between the feed phase and the membrane in agreement with the partition equilibrium:

$$(ArOH)_{F.P.} \leftrightarrow (ArOH)_{M} \qquad (2)$$

in a proportion depending on the partition constant expressed through the relationship:

$$R_{ArOH} = \frac{[ArOH]_M}{[ArOH]_{F.P}} \qquad (3)$$

The molecular form of the phenolic derivative compound crosses over the membrane and the chemical equilibrium takes place at the interface with the receiving phase:

$$(ArOH)_{M} + (HO^{-})_{R.P.} \leftrightarrow (ArO^{-})_{R.\ P.} + (HOH)_{R.P.} \qquad (4)$$

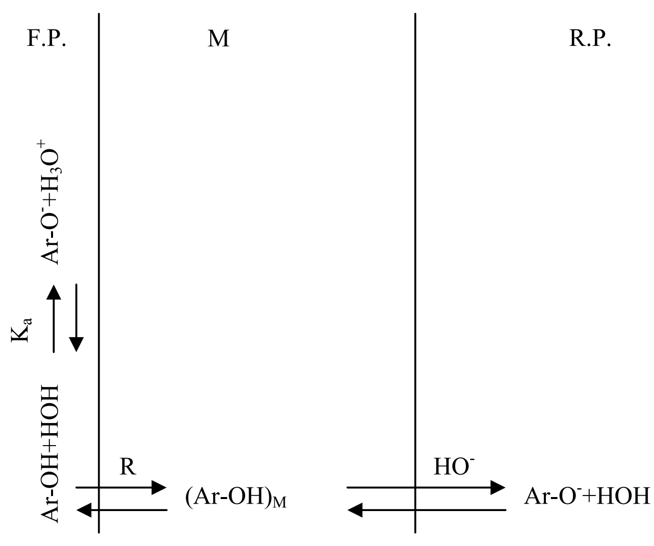

Fig. 3. Functional scheme of the nitroderivatives phenolic compounds in the membranary system process of partition

Analyzing these equilibria we can conclude that the pH represents an operational parameter that can play a significant role in the optimization of the studied phenolic derivatives transport process. Therefore, we studied the influence of the pH of feed phase and of the receiving phase on transport efficiency.

Influence of the feed phase pH

The pH of the feed phase ranged in the 2-6 domain, corresponding to an acidic media, which can assure a shift of the equilibrium from the feed phase to the transformation in majority of Ar-OH un-dissociated compound. Maintaining the pH of the receiving phase at the value 12, for the four studied compounds we determine the transport efficiencies depending on the feed phase pH (fig. 4).

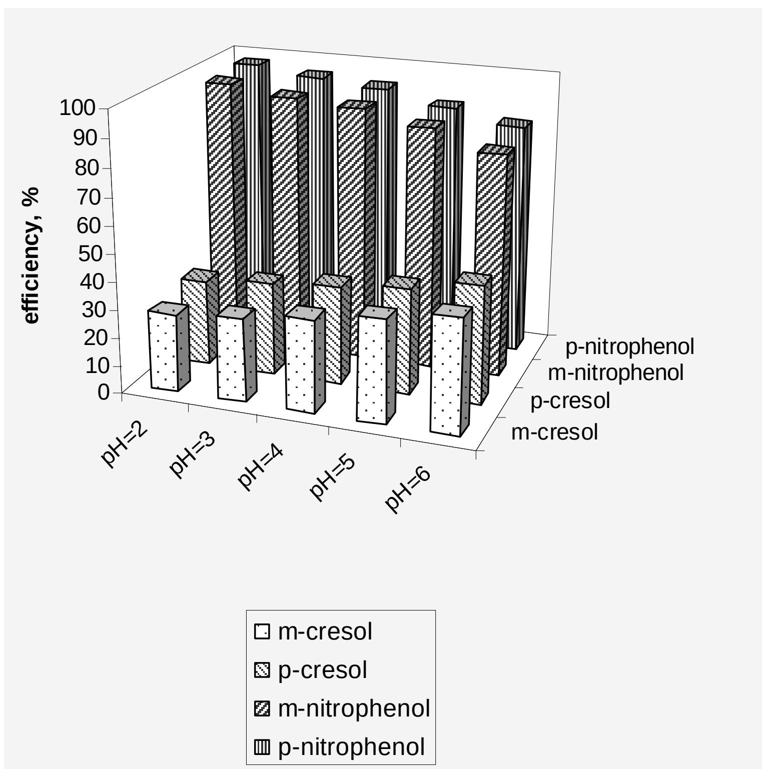

Fig. 4. Transport efficiencies variation depending on the feed phase pH
Feed phase-phenolic compound, 10^{-4}-10^{-3} mol·L^{-1}, at pH=2-6
Membrane-chloroform
Receiving phase-NaOH, 10^{-2} mol·L^{-1}

While for studied nitroderivatives the decrease of the feed phase pH implies the increase of the transport efficiencies, for the case of cresols, the transport efficiencies significantly decreases with the decrease of the pH of the feed phase. In the case of the cresols at the decrease of the feed phase pH leads to an accumulation of these in the membrane takes place. This results in the decrease of the transport efficiencies from 58 % to 28 % for m-cresols and from 61,12% to 31,21% for p-cresol, respectively.

Influence of the receiving phase pH

Due to the transport with reaction in the receiving phase, the receiving phase pH is expected to have an important role on the process efficiency. This hypothesis was confirmed by the experimental data presented in Fig. 5.

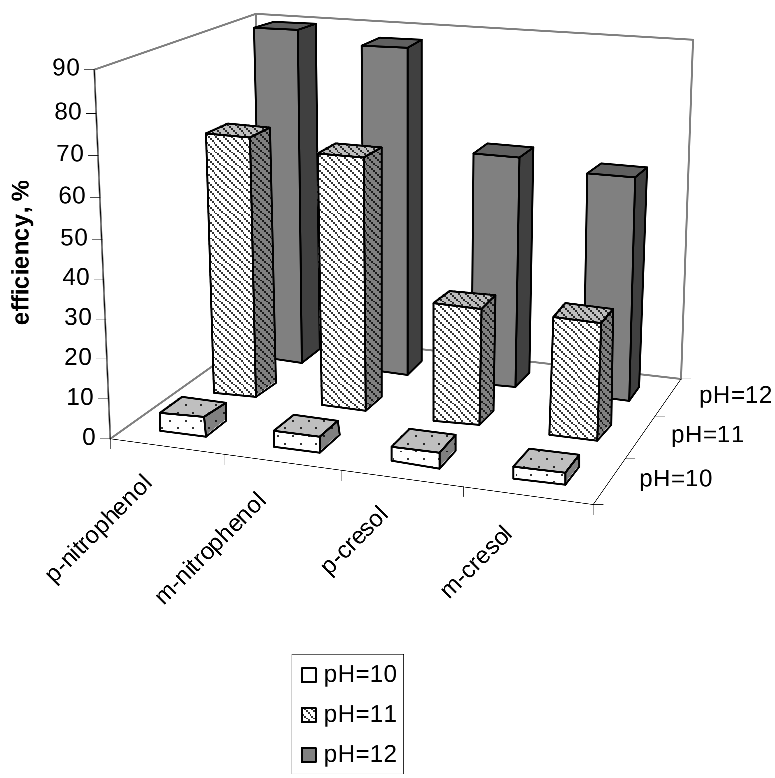

Fig. 5. Transport efficiencies variation depending on the receiving phase
Feed phase- phenolic compounds, 10^{-4}-10^{-3} mol·L^{-1}
Membrane-chloroform
Receiving phase-NaOH, 10^{-2}-10^{-4} mol·L^{-1}

It can be observed that for all the studied phenolic derivatives the decrease of the receiving phase pH decreases dramatically the transport efficiencies.

Influence of the transport time

The necessary time for the transport process to take place is an important parameter that needs to be taken into account in order to define the optimum conditions of deploying the process. In Fig. 6 it is represented the variation of the transport efficiencies in time.

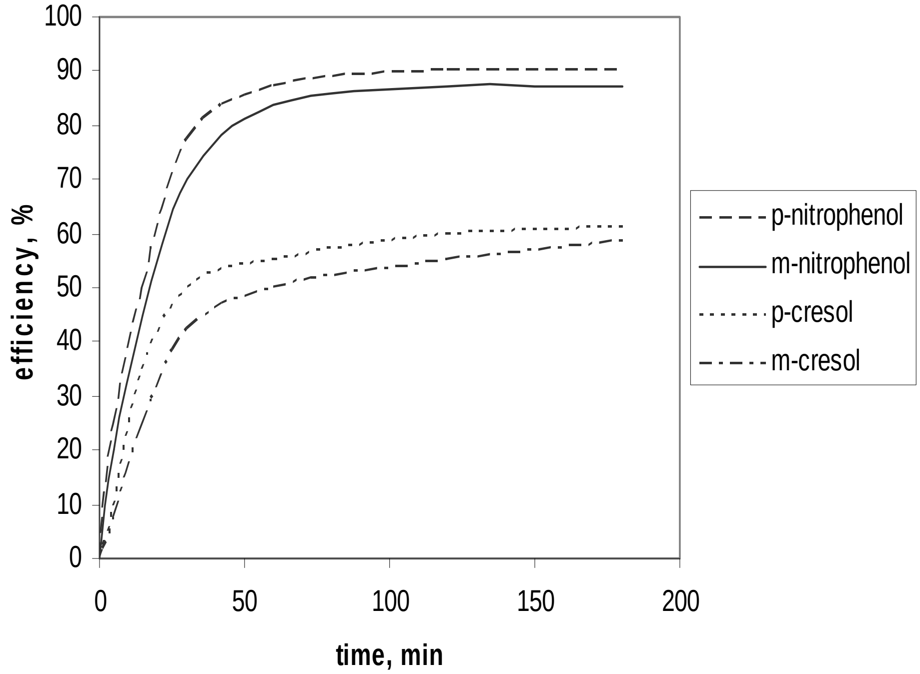

Fig 6. Variation of the transport efficiencies in time
Feed phase- phenolic compound solution10^{-4}-10^{-3} mol·L^{-1}
Membrane-chloroform
Receiving phase-NaOH, 10^{-2} mol·L^{-1}

The study of the phenolic compound content in the receiving phase in time, led us to the conclusion that the transfer is practically produced for all the studied compounds, mainly, in the first 30 minutes from the beginning of the experiment.

4. Conclusions

The paper presents the experimental data obtained at the transport through bulk liquid membranes of some phenolic derivatives: m-nitrophenol, p-nitrophenol, m-cresol, p-cresol.

Operational parameters that can influence significantly the efficiencies transport have been studied, as for instance: the feed phase pH, the receiving phase pH and the transport time. The results were correlated with the equilibria that take place in the phases at the interfaces of the membranary system. The best results were obtained in the case of phenolic nitroderivatives. When using optimum operational conditions (feed phase pH=2, membrane= chloroform, receiving phase pH=12) the nitrophenols were transferred in to the receiving phase with transport efficiencies of 93% for m-nitrophenol and 98% for p-nitrophenol, respectively.

These results are similar to those obtained through the technique of supported liquid membrane or by the technique of emulsion liquid membrane. Unlike these membranary techniques the bulk liquid membranes technique eliminates the disadvantages related to the stability and breaking of the emulsion. Therefore, the bulk liquid membranes technique can be considered a good way to separate some phenolic compounds from waste waters.

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