The Transport of Nitrophenols Through Liquid Membranes

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The paper presents the experimental results obtained at the separation of some phenolic derivatives: phenol, p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol from aqueous medium through the technique of bulk liquid membranes. The influence of the solvent that forms the membrane on the efficiency of the transport of the studied phenolic compounds was investigated. The recuperation grade of the phenolic compounds varies in the receiving phase of the system from the point of view of the solvent used as membrane as follows: CHCl₃ > CH₂Cl₂ > CCl₄. Considering the partition equilibria at the interface of the transport system the optimum pH conditions (acid feed source, membrane-chloroform and alkaline receiving phase) were established. Transport efficiencies over 90% were obtained.

Keywords: phenolic derivatives, liquid membranes, phenols separation, transport through liquid membranes

Membrane separations have an important role in the domain of environmental remediation and treatment of water contaminated with toxic material. In industrial wastewaters phenols are frequently encountered pollutants with a high toxic potential. Thus the separation and recuperation of these compounds represents an activity of total utility.

For the separation of the phenolic compounds in membranary system the literature references regard mainly at the use of supported and emulsion liquid membranes. Both supported liquid membranes and emulsion liquid membranes were used with success in the separation of phenol from wastewater [1].

Emulsion liquid membranes were successfully used at the recuperation of phenol from the effluent that results at the production of phenolic resins [1]. In this case a study of the permeation of phenol derived from an installation of phenolic resins was realized. The membrane consisted of an aliphatic solvent and a non-ionic surfactant as an internal phase.

The experimental results that indicate the efficiency of the emulsion liquid membrane were obtained at the removal of nitrophenols from wastewater. In optimum operating conditions (surfactant concentration in oil phase 2%, NaOH concentration in internal water phase 2%, the ratio oil phase to internal phase 2, the pH of the external water phase 2 and the ratio external water phase to emulsion phase 3) the total nitrophenol content in the effluent can be reduced from 1050 mg/L at less than 1 mg/L [2].

An improved variant of the emulsion liquid membranes applied to the recuperation of phenol from wastewater is based on the use of a new polyamide type surfactant. This surfactant increases the stability of the emulsion (compared to SPAN 80). Therefore the breaking of the emulsion becomes difficult and decreases the efficiency of the process. In optimum conditions approximately 98% of the phenol can be removed in one stage and on the second stage the efficiency of removing the phenol increases up to 99, 8% [3].

Many other examples mentioned in literature confirm that emulsion liquid membranes represent a promising alternative for the treatment of wastewaters that contain a large range of contaminants such as: phenol, chlorophenol, nitrophenols [4-8].

In the case of supported liquid membranes a major concern was obtaining high transfer rates, high stability and high selectivity at transport so that it can be competitive with the methods applied in industry. Therefore supported liquid membranes have developed having a polymeric support [9-11]. These membranes have the disadvantage that the selectivity is reduced due to the uneven pores.

Most of the accomplishments in the field of supported liquid membranes applied to the separation of phenolic compounds are based on the use of membranes consisting of alumina foil coated with gold and then functionalized (for example with thiol groups). By this method self-assembled mono-layers, which permit the control of the hydrophobic properties of the membrane, are realized [12]. Better transport rate was obtained with this type of membrane for the transport of 2, 4, 6-trichlorphenol.

During the last years the technique of supported liquid membranes is based on fluid hydrophobic polymers, strongly permeable with a low viscosity. These polymers are functionalized with transporters capable of molecular recognition, thus increasing the selectivity of the process [13-16].

In this regard it is mentioned the use of the polysiloxane functionalized with amine groups at the separations of phenols. Liquid membranes from polypropylene impregnated with amine groups assure 100% permeation of phenol from a feed source with a concentration of 1000 mg/L.

Due to the well known pollutant character and the economic importance of the phenol derivatives in the present paper it was studied the possibility of recuperative separation of this compounds from aqueous solutions using the technique of bulk liquid membranes.

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The utilization of bulk liquid membranes was sustained by a series of very good results obtained at the separation of organic species as well as inorganic ones [17-21].

**Experimental part**

The transport experiments were realized in a wall in wall transport cell presented in a previous paper [22]. The feed source (FS) consisted of an aqueous or acid solution of phenol or phenol derivatives at a concentration between 10^{-4}-10^{-3} M. The volume of the feed source was 20 cm^3. The receiving phase (RP) was a NaOH solution 10^{-2} - 10^{-4} M with a volume of 7 cm^3. The two aqueous phases are separated with a membrane consisting from a chlorurated solvent (CHCl₃, CH₂Cl₂, CCl₄). The membrane has a volume of 50 cm^3. The work temperature was 25 ± 1°C, the transport time was 3 h.

The reagents used were analytically grade and were used without further purification. The reagents that were used: phenol, p-nitrophenol, o-nitrophenol, 2,4-dinitrophenol were supplied from Merck. The organic solvents: chloroform (Merck), dichloromethane (Carlo Erba), carbon tetrachloride (Chimopar) were previously saturated with distilled water. The distilled water was saturated with organic solvent and used for the preparation of the feed source and of the receiving phase.

The hydrochloric acid (Merck) and the sodium hydroxide (Merck) were used for the variation of the pH between 2 and 12. The pH was measured with a glass/AgCl, Ag combined electrode using SevenMulti Meller 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 phenol and phenol derivatives content from the aqueous phase was measured through molecular absorption spectrometry in the UV region using a Camspec MS01 spectrometer. The phenolic compounds present absorption bands in the UV region at the next wave lengths: phenol at λ = 270 nm (acid, neutral medium) and λ = 288 nm (alkaline medium), p-nitrophenol at λ = 317 nm (acid, neutral medium) and λ = 404 nm (alkaline medium), o-nitrophenol at λ = 363nm (acid, neutral medium) and λ = 417nm (alkaline medium), 2,4 dinitrophenol at λ = 358 nm (acid, neutral medium) and λ = 361nm (alkaline medium).

The phenol content in the membrane was determined from the mass balance of the three phases of the membrane system.

**Results and discussions**

The transport experiments of the phenolic compounds had as objective establishing the optimum conditions of the process taking in account the influence of the membranary solvent and the association of the process

<table>
<thead>
<tr>
<th>Phenolic Compound</th>
<th>The Composition of the Phases, % molar</th>
<th>Transport efficiency, %</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Feed Source pH&lt;7</td>
<td>Membrane</td>
</tr>
<tr>
<td>Phenol</td>
<td>4,34</td>
<td>16,12</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>3,11</td>
<td>7,63</td>
</tr>
<tr>
<td>o-Nitrophenol</td>
<td>3,04</td>
<td>13,02</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>1,11</td>
<td>14,35</td>
</tr>
</tbody>
</table>

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</thead>
<tbody>
<tr>
<td></td>
<td>Feed Source pH&lt;7</td>
<td>Membrane</td>
</tr>
<tr>
<td>Phenol</td>
<td>5,14</td>
<td>26,74</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>5,51</td>
<td>14,34</td>
</tr>
<tr>
<td>o-Nitrophenol</td>
<td>6,62</td>
<td>16,37</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>3,84</td>
<td>15,93</td>
</tr>
</tbody>
</table>
with proton transfer reactions capable to assure an active transport.

**The influence of the membranary solvent**

In order to choose the right membranary solvent to realize the transport of the phenolic compounds three of the most mentioned in the literature solvents were investigated, namely: CHCl₃, CH₂Cl₂, CCl₄. The efficiency of the separation, expressed in percents of the phenolic compound transported in the receiving phase, depending on the membranary solvent is presented in tables 1-3.

From the tables it is observed that the best results are obtained in the case of the chloroform membrane. The other solvents offer a low permeability towards the phenolic compounds transported which is reflected in the percent of phenol remained in the feed source.

Based on these results for the studied solvents we can establish the following order regarding the efficiency at the transport: CHCl₃ > CH₂Cl₂ > CCl₄.

Due to the fact that the best transport efficiencies was obtained when using chloroform as membranary solvent, the influence of the other operational parameters were studied under the condition of using chloroform as liquid membrane.

**The influence of the pH of the feed source**

In the experiments realized the transport efficiencies of phenol and phenolic derivatives studied were determined at different values of the pH of the feed source (pH=2-6). The results obtained prove that the transport efficiencies of phenol and phenol derivatives in the receiving phase depend largely with the pH.

In the case of all the studied compounds their recovery grade in a receiving alkaline phase (pH=12) increases at the same time with the decrease of the pH of the feed source.

<table>
<thead>
<tr>
<th>Phenolic Compound</th>
<th>The Composition of the Phases, %</th>
<th>Transport efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed Source</td>
<td>Membrane</td>
</tr>
<tr>
<td></td>
<td>pH&lt;7</td>
<td>pH=12</td>
</tr>
<tr>
<td>Phenol</td>
<td>12,23</td>
<td>27,54</td>
</tr>
<tr>
<td>p-Nitrophenol</td>
<td>8,97</td>
<td>19,78</td>
</tr>
<tr>
<td>α-Nitrophenol</td>
<td>8,18</td>
<td>22,37</td>
</tr>
<tr>
<td>2,4 Dinitrophenol</td>
<td>7,73</td>
<td>20,15</td>
</tr>
</tbody>
</table>

**Table 3**

RESULTS OF THE TRANSPORT OF THE PHENOLIC COMPOUNDS THROUGH A CARBON TETRACHLORIDE LIQUID MEMBRANE UNDER pH GRADIENT (FEED SOURCE: PHENOLIC COMPOUND: 10⁻¹⁻⁻⁻¹⁰ MOL/L, V=20cm³, MEMBRANE PHASE: CHLOROFORM, V=50cm³, RECEIVING PHASE: NaOH 10⁻² MOL/L, V=7cm³)

To exemplify we represented in figure 1 the distribution of p-nitrophenol in membranary system at the end of the transport experiment depending on the pH of the feed source. The transport was realized from a feed source with the pH=2-6 through a chloroform membrane into a receiving phase with pH=12.

The transport efficiency in the receiving phase in the case of almost all of the studied nitroderivatives exceeds 90% when the transport process takes place with a chloroform membrane at a pH of the feed source of 2 and the pH of the receiving phase equal with 12 (fig. 2).

These results can be correlated with the chemical and partition equilibria which take place at the interfaces of the membranary system.

In the receiving phase the phenolic compound with an acid character is involved in equilibria like this one:

\[
(Ar-OH)_{F.S.} + (H_{3}O^{+})_{F.S.} \leftrightarrow (Ar - O^{-})_{F.S.} + (H_{2}O)_{F.S.}^{+} (1)
\]

This equilibrium is controlled by the pH. In acid pH (pH<\(pK_{a}\_\text{phenol}\)) predominates the undissociated form of the phenolic compound. This is distributed between the feed source and the membrane according to the following partition equilibrium:

\[
(Ar - OH)_{F.S.} \leftrightarrow (Ar - OH)_{M} (2)
\]

After the molecules of the phenolic compounds go through the membrane, at the interface between the membrane and the receiving phase the next partition equilibrium takes place:

![Fig. 1. Distribution of p-nitrophenol in membranary system depending on the pH of the feed source at the end of the transport (Feed Source -solution of p-nitrophenol 2x10⁻⁴ mol/L and HCl at different concentrations, Membrane phase-Chloroform, Receiving Phase- solution of NaOH 10⁻² M)](image)

![Fig. 2. Distribution of the phenolic compounds in the phases of the membranary system at the end of the transport (Feed Source -solution of phenolic compounds, Membrane phase-Chloroform, Receiving Phase- solution of NaOH 10⁻² M)](image)
This mechanism that totalizes the equilibria above is validated with the increase of the transport efficiency depending on the pH of the feed source and justifies the transport mechanism presented in figure 3.

\[
(Ar-\text{OH})_{M.} + (\text{HO}^+)_{R.P.} \leftrightarrow (Ar-\text{O}^-)_{R.P.} + (\text{HOH})_{R.P.}
\]

We observe that the transport efficiency decreases with the decrease of the pH of the receiving phase. These results can be construed bearing in mind equilibrium 3. Thus we can observe that when the pH of the receiving phase decreases equilibrium 3 shifts to the left contributing to a proportional decreasing of the concentration of the phenolate in the receiving phase of the membranary system.

Conclusions
The paper presents a recuperative separation study of some phenolic derivatives using the technique of bulk liquid membrane.

The influence of the solvent that forms the membrane on the transport efficiency of the studied phenol compounds, the influence of the pH on the feed source and receiving phase were studied.

From the point of view of the solvents used as membrane the recuperation grades of the phenolic compounds in the receiving phase of the system varied in this order: CHCl₃ > CH₂Cl₂ > CCl₄.

The experimental results demonstrated that the pH gradient between the terminal phases of the membranary system is the driving force that assures in the case of nitrophenols transport efficiencies of over 90% (for example: in the case of p-nitrophenol the transport efficiency is of 98.7%).

We can appreciate that bulk liquid membranes as well as emulsion liquid membranes and supported liquid membranes may consist in an appropriate technological line for the recuperative separation of some phenolic compounds (especially nitrophenols) with various advantages: low energetic costs, low waste quantities, the elimination of some disadvantages related to the breaking of the emulsions.

References

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