

The Separation of Chlorophenols Using Inverse Emulsion with Carrier. II

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The paper aimed to highlight the influence of organic phase – receiving phase volume ratio, receiving phase nature and carrier nature on chlorophenols extraction efficiency using inverse emulsion with carrier. Based on results obtained the identification of chlorophenols transport mechanism in emulsion liquid membrane extraction was carried out. The experimental results revealed that the best extraction yields, over 90% are obtained with fatty amine as carrier, between 20-30 minutes, which represents a real advantage from technologically and economically point of view. It was also noted that the maximum values of chlorophenols extraction efficiency is obtained at relatively small (10 minutes), which shows a high rate of interphase transfer characteristic liquid membranes.

Keywords: carrier, chlorophenols, emulsion liquid membranes, separation

Phenol is a toxic substance which is normally present in wastewater generated from refineries, pharmaceutical and petrochemical operations [1, 2] and even in small quantities, it is toxic to living organisms.

The maximum phenol concentration for treated effluent is 1 ppm, while phenol concentration from the untreated industrial effluent can be in the range of 2.8–6900 ppm [3].

In this context, it is absolutely necessary to remove the phenol from industrial effluents before it is discharged into the water stream and a variety of treatment methods can be applied for phenol removal [4, 5].

The main treatment methods used are: biological treatment, adsorption on activated carbon, chemical oxidation and liquid membrane [6-8].

Liquid membranes have shown potential for chlorophenols removal from wastewaters. They are selective permeable materials which are capable to transport certain targeted solutes [9-19].

Compared to conventional processes, emulsion liquid membrane (ELM) method provides some attractive features, as: simple operation, high efficiency, extraction and stripping in one stage, larger interfacial area, scope of continuous operation and a non-dependence on equilibrium consideration [20].

In the application for wastewater treatment, ELM consists of water–oil–water system whereby the oil phase (membrane) acts as a selective barrier and encloses the aqueous stripping agent (internal phase). The emulsion will then be dispersed into the wastewater (external phase) for targeted solutes extraction [21, 22].

Emulsion liquid membrane (ELM) technique is an accessible and easy way for the removal of chemicals (pollutants) from wastewaters and transport them into desired phases, where the pollutants can be concentrated by 10-100 times. The decisive role for application of ELM technique is the establishment of chlorophenols transport

within three phases: external feed aqueous phase that contain pollutant, organic phase as permselective barrier, internal receiving and concentration aqueous phase. Therefore, the pollutant transport is influenced by the interfaces between the two immiscible phases [23].

Experimental part

Materials and methods

Kerosene (Merck), H₂SO₄ (Merck), HCl 25% (Merck), NaOH (Merck), NaHCO₃ (Merck), Na₂CO₃ (Merck), and distilled water were analytical grade. SPAN 80 (Sigma-Aldrich), nonylphenol ethoxylate with 4 moles of ethylene oxide and carriers (Aliquat 336, tri-octyl amine, fatty amines C₁₄-C₁₈) have a technical purity.

Chlorophenols removal from aqueous solution was carried out by contacting the inverse emulsion containing receiving phase, with source phase, under stirring, in order to make a contact area as large as possible. This way is produced a double emulsion A / U / A which exists as long as stirring is maintained.

The inverse emulsion dispersion into the source phase was performed using a multistage propeller-type stirrer, working at a stirring speed of 200 rpm which provides a good dispersion (the average particle size of the inverse emulsion was 0.25 mm).

After a certain contact time, when stirring was stopped, the inverse emulsion was rapidly separated on the source phase surface, due to the density difference.

The reverse emulsion will be destroyed in order to recover the receiving phase, which contains the extracted phenol ions [24].

The extraction experiments using inverse emulsion aimed to study the influence of the parameters:

- organic phase-receiving phase volume ratio;
- receiving phase nature;
- carrier nature.

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Results and discussions

Influence of organic phase-receiving phase volume ratio on the extraction yield

An important factor in the process of controlling chlorophenols removal from waters is the organic phase-receiving phase volume ratio.

In the case of Aliquat 336 0.1% carrier, extraction yields of 80% for an organic phase - receiving phase (NaHCO_3 1M aqueous solution) 1:1 volume ratio were obtained, and they decrease with volume ratio increase (fig. 1).

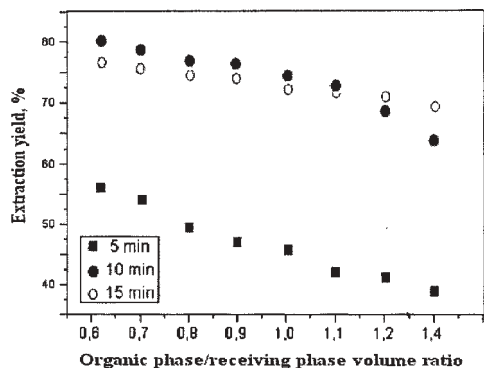


Fig.1. Influence of organic phase-receiving phase volume ratio on extraction yield (Span 80 1.5%; source phase $\text{pH} = 5$)

For fatty amines 1-3% carrier, extraction yields in the first 5 min increase starting from organic phase/receiving phase (NaHCO_3 1M aqueous solution) volume ratio = 0.6, reaching a maximum at a value of 0.9 of this ratio; then a decrease is observed, reaching minimum yield values at an organic phase/receiving phase volume ratio = 1.4 (fig. 2).

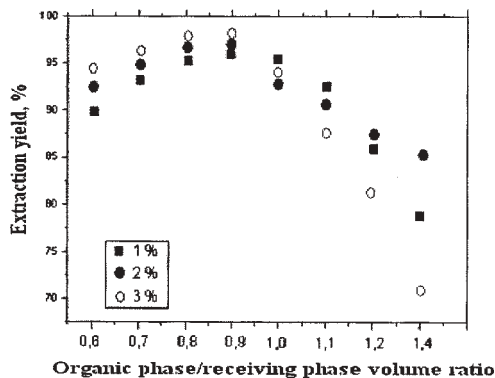


Fig.2. Influence of organic phase-receiving phase volume ratio on extraction yield (stirring time: 5 min, source phase $\text{pH} = 5$)

In alkaline medium ($\text{pH} = 8$), the chlorophenols extraction yields increase with the increase of the organic phase - receiving phase volume ratio (fig. 3).

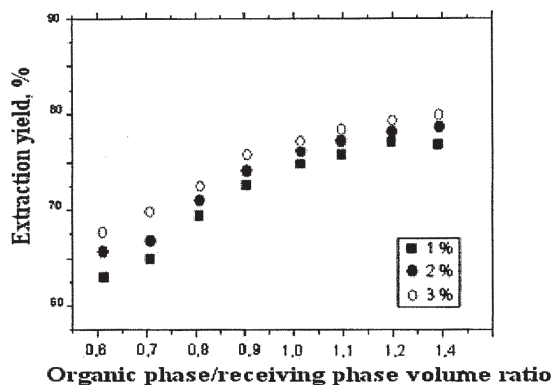


Fig.3. Influence of organic phase-receiving phase volume ratio on extraction yield (stirring time: 10 min, source phase $\text{pH} = 5$)

The best yield values (about 80%) are obtained for a 1.5% concentration of fatty amines, at a volume ratio greater than 1: 1. Unlike the yields obtained in acidic medium, the one obtained in alkaline medium are lower, the maximum yield being 80% for a 3% concentration of fatty amines at a volume ratio of 1: 1.2-1.4.

Receiving phase nature influence on the extraction yield

Receiving phase nature has a great influence on chlorophenols extraction yield.

Three solutions with 1M concentration were tested: sodium bicarbonate, sodium carbonate and sodium hydroxide (fig.4).

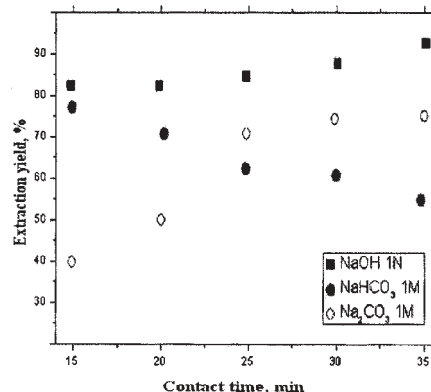


Fig. 4. Receiving phase nature influence on extraction yield (carrier: Aliquat 336 0.1%; surfactant: Span 80 1.5%; source phase $\text{pH} = 5$)

The differences of extraction yields values are related both to the pH established by the substances used in the receiving phase, and to the ability to stabilize organic phase / receiving phase emulsion.

Sodium hydroxide use results in a slightly increase of the yield in the time range 15-35 min, the maximum value (93%) being obtained after 35 min.

Sodium carbonate has a predictable behavior with a lower initial yield, but with an increase of the values approaching to the ones obtained with sodium hydroxide at the end of the time interval.

After an increase in the first 25 min, the extraction yield is maintained almost constant during the next 10 minutes at about 75%.

In the case of using 1M *sodium bicarbonate* solution as receiving phase the best extraction yields are obtained in the first 15 min, when the extraction yield is about 80%, and then decreases over time, due to, most probably emulsion break. It is not insignificant the amphoteric character of bicarbonate ion.

Carrier nature influence on extraction yield

Ideally, in industrial separation processes is to use minimal amounts of chemical substances, and therefore, emulsion liquid membrane technique is suitable for practical solving of this goal, by using low carrier amounts and operational parameters regulating substances from aqueous, source and receiving phase.

Figure 5 presents chlorophenols extraction yields using emulsions having volume ratios between emulsion and source phase of 1: 5, and the receiving phase-organic phase ratio of 1: 1, using as carriers: trioctyl-amine 0.1%, Aliquat 336 0.1%, fatty amines 1.5%. The data presented in figure 5 reveal considerable differences between the three carriers. It is also noted that the maximum chlorophenol extraction yields are obtained at relatively small times (10 min), which shows a high interphase transfer speed, characteristic to liquid membranes.

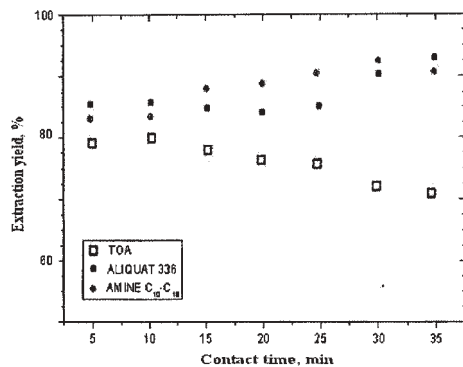


Fig. 5. Carrier nature influence on extraction yield (Span 80 1.5%; receiving phase: NaOH 1M; source phase pH = 5)

Increasing the contact time leads to a decrease in the extraction yield, for TOA (tri-octyl amine), probably as a result of partial emulsified phase (receiving phase) destruction, which is transferred in the source phase.

A different behavior presents the emulsions stabilized with Alquat 336 and fatty amines, case in which, the extraction yields are lower at the beginning time range (the maximum being 80%) and are slowly increasing with operation time.

A possible explanation for this particular behavior could be attributed to the synergistic stabilizing effect of the membrane / receiving phase emulsion.

In the case of trioctylamine carrier low yields (70%) are observed, probably due to very low solubility of the carrier at membrane / source phase interface.

The best results (yields over 90%) are obtained with fatty amines as carrier, between 20 and 30 min, which is a real economic and technological advantage.

Chlorophenols transport mechanism in liquid membranes extraction

In addition to the aspects related with extraction yields depending on surfactant, carrier nature and other emulsion characteristics, an important aspect is represented by the transport mechanism, which allows permeate flow optimization.

Chlorophenols transport mechanism through membranes is shown in figure 6.

Chlorophenols transfer by means of the mechanism described above, imagined for experimental conditions in which the separation yield was maximum, involves:

- acid source phase pH (< 5);
- alkaline receiving phase pH (> 10);
- membrane phase: kerosene;
- carrier: tri-octylamine (TOA).

The transport scheme is valid also in the case of fatty amines use as carrier and stages are:

- I. chlorophenol transition from source phase into acid form;
- II. chlorophenol diffusion towards source phase / membrane interface;
- III. chlorophenol solubilization in membrane phase and ion pair formation;
- IV. ion pair diffusion from phase source / membrane interface towards membrane / receiving phase interface;
- V. Phenolate solubilization in the receiving phase, assisted by alkaline pH (NaOH);
- VI. difuzia clorfenolatului in faza receptoare (imobilizarea in aceasta faza datorita pH-ului).

Conclusions

The paper aimed to highlight the influence of organic phase - receiving phase volume ratio, receiving phase

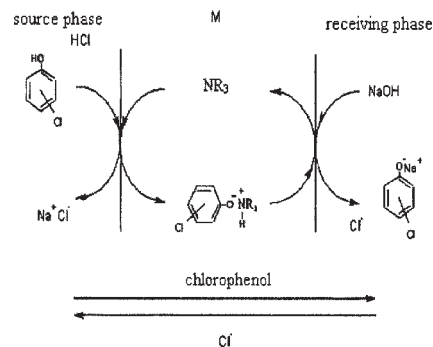


Fig.6. Chlorophenols transport mechanism through membranes

nature and carrier nature on chlorophenols extraction efficiency using inverse emulsion with carrier.

The experimental results revealed that the best extraction yields, over 90% are obtained with fatty amine as carrier, between 20-30 min, which represents a real advantage from technological and economic point of view.

It was also noted that the maximum values of chlorophenols extraction efficiency is obtained at relatively small (10 minutes), which shows a high rate of interphase transfer characteristic liquid membranes.

In addition to the aspects related with extraction yields depending on surfactant, carrier nature and other emulsion characteristics, an important aspect is represented by the transport mechanism, which allows permeate flow optimization.

In this context, based on the results obtained, chlorophenols transport mechanism in emulsion liquid membrane extraction identification was carried out.

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