Iono-molecular Separation with Composite Membranes

VI. Nitro-phenol separation through sulfonated polyether ether ketone on capillary polypropylene membranes

ION SPIRIDON DIN[1], ANCA MARIA CIMBRU[1], ABBAS ABDUL KADHIM KLAIF RIKABI[1,2], SZIDONIA KATALIN TANCZOS[3]*, SIMONA TICU (COTORCEA) [1], GHEORGHE NECHIFOR[1]*

[1]Politehnica University of Bucharest, Faculty of Applied Chemistry and Material Science, Analytical Chemistry and Environmental Engineering Department, 1-7 Gheorghe Polizu, 011061, Bucharest, Romania

[2]Technical college of Al-Mussaib (TCM), Al-Furat Al-Awsat Technical University, Foundation of Technical Education, Baghdad, Iraq

[3] Sapientia University, Str. Libertatii., 500104, Mircurea Ciuc, Romania

The importance of removing and / or separating nitro phenols from aqueous solutions through membranes is substantiated by the multitude of recent research in the field, which broadly justifies both the economic and ecological reasons of such an approach. The present paper outlines the results of the transfer of nitro phenols through a membrane system made up of PPET impregnated polypropylene capillaries (PP) impregnated with sulfonate polyetheretherketone (SPEEK). The experiments were carried out in a PP-SPEEK capillary membrane module, with a useful size of 1 m^2. Determinations made by using a 4 L / min flow rate source at a 5 mg / l nitrophenol concentration and pH 5 or pH 7, and the pH 12 receiving phase and a flow rate of 0.3 L / min, revealed that o- and p-nitrophenol were transferred much faster than m-nitrophenol (the flux is nearly double); the source phase of the system is concentrated in m-nitrophenol, and the receptor phase in o- and p-nitro phenols; the transfer data correlates with the higher water solubility of m-nitrophenol; mono nitro phenols transfer much faster than di nitrophenol, but both the mono and di nitrophenol streams decrease over time; after 4-5 hours of work, the mono nitrophenol concentration triples in the receiving phase, while the 2,4-dinitrophenol concentration doubles in the source phase.

Keywords: nitro-phenols transport, nitro-phenols separation, sulfonated-polyethereterketonee, polypropylene membranes, composite membranes

The results recently obtained in the separation of nitro phenols by colloidal ultrafiltration and pervaporation through flat composite polymeric membranes [1-3], but also by liquid and carrier membranes [4-6] constitute a major breakthrough in the direction of switching to pilot mode of this type process.

The importance of removing and / or separating nitro phenols from aqueous solutions is substantiated by the multitude of recent research in the field, which broadly justifies both the economic and ecological reasons of such an approach [5-10].

Of course, it can also be noted that nitro phenols are a predilection substance in membrane studies because they can be analyzed effectively both optically and electrochemically after extraction or in situ [11-14].

Another remarkable aspect of the separation of nitro phenols is related to the operational and process parameters that are significantly influenced by the *p*H of the working medium (scheme 1) [15-17], so that there is the possibility of discrimination between the mono-, di- and tri - substituted, but also among isomers of mono nitrophenol [18, 19].

$$O_2N\text{-}Ar-OH_{SP} \longrightarrow O_2N\text{-}Ar-OH_{M} \longrightarrow O_2N\text{-}Ar-OH_{RP}$$

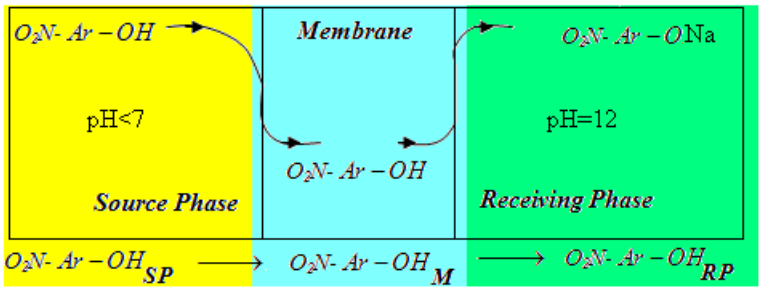
The distribution of chemical species between immiscible liquid phases is characterized by a series of fundamental sizes in solvent extraction, whose knowledge and use is the basis for the elaboration of separation methods for solvent extraction, including dynamic membrane systems [15-19].

Nitrophenols (Ar-OH) are organic acid compounds [16, 17]. Thus, when nitrophenols come into contact with two liquid phases: water and a water-immiscible organic solvent will be distributed between the two phases according to equilibrium:

$$(O_2N\text{-}Ar\text{-}OH)_w \rightleftharpoons (O_2N\text{-}Ar\text{-}OH)_s \quad (1)$$

where w represents the aqueous phase, and s is the organic solvent.

If the nitrophenols are absent from chemical reactions in the two phases of equilibrium (1) it is characterized by the distribution constant R:



Scheme 1. influence of *p*H on transport of nitrophenol through liquid membranes

* email: tczszidonia@yahoo.com; doru.nechifor@yahoo.com

$$R_{Ar-OH} = \frac{[O_2N-Ar-OH]_o}{[O_2N-Ar-OH]_w} \quad (2)$$

Nitrophenols are acidic compounds. Thus in the aqueous phase it reacts with water and equilibrates (2.3), balance with proton transfer:

$$O_2N\text{-}Ar\text{-}OH + HOH \rightleftharpoons O_2N\text{-}Ar\text{-}O^- + H_3O^+ \quad (3)$$

The equilibrium (2.3) is characterized by the acidity constant Ka:

$$K_a = \frac{[O_2N-Ar-O^-]\cdot[H_3O^+]}{[O_2N-Ar-OH]} \quad (4)$$

The global distribution balance must take into account the existence of the heterogeneous system in the aqueous phase. Thus, the global heterogeneous equilibrium is established:

$$(O_2N\text{-}Ar\text{-}O^-)_w + (H_3O^+)_w \rightleftharpoons \quad (5)$$

$$\rightleftharpoons (O_2N\text{-}Ar\text{-}OH)_w + (O_2N\text{-}Ar\text{-}OH)_s$$

$$(O_2N\text{-}Ar\text{-}O^-)_w + (H_3O^+)_w \rightleftharpoons (O_2N\text{-}Ar\text{-}OH)_s \quad (6)$$

The distribution of nitrophenols between the two phases is characterized by the distribution coefficient r:

$$r_{Ar-OH} = \frac{[O_2N-Ar-OH]_{membr.}}{[O_2N-Ar-OH]_{solut.}} =$$

$$= \frac{[O_2N-Ar-OH]_o}{[O_2N-Ar-OH]_o + [O_2N-Ar-O^-]_w} \quad (7)$$

Taking into account relationship 2 and 4, relation 7 becomes:

$$r_{O_2N-Ar-OH} = \frac{R_{O_2N-Ar-OH}}{1+10^{pH-pK_a}} \quad (8)$$

Practically, the theoretical exploitation of the relationship (8) allows the establishment of working conditions favorable to the passage of nitrophenol from the source phase into the membrane, and from there in the receiving phase.

Taking into account all these considerations, the transition to the laboratory pilot scale was predictable and expected with interest, especially for liquid membrane support (SLM) modules and systems [20-27].

The solid support provides certain rigidity to the liquid membrane [20, 21]. Due to the porosity of the support on which the organic phase (or, as the case may be, the aqueous phase) is physically immobilized, a much larger contact surface is obtained compared to the cell-type liquid membranes, while a small membrane thickness [22-24] is achieved. The variety of materials used as supports is limited, being conditioned by the stability of the materials [25]. The interphase contact surface is much larger and the thickness of the membrane much smaller than the case of cell-type membranes, giving a flow of the chemical species transferred depending on the solid support structure [26, 27].

SLMs can be manufactured in different geometries. Types of SLM modules are commonly found on thin, tubular or spiral-shaped capillaries or spindles [28-30].

Among the advantages of using immobilized liquid membranes on capillary fiber supports are: the large surface area of the membrane and the reduced thickness allowing fast transport, the source phase and receivers are readily recovered compared to other systems, or the source and receiver phases are not no contact with the membrane [31, 32].

Disadvantages of using this type of system would be: the need for the use of membrane solvents with a high hydrophobicity to maintain the integrity of the membrane; these systems must be cleaned between uses and thus may result in contamination and additional technical and economic costs [32-34].

In the present paper, the separation of nitrophenols is studied in a laboratory plant with polypropylene (PP) capillary membranes with a usable area of 1 m2, which is deposited as selective polyether-ether sulfonate membrane material (SPEEK).

Experimental part

Materials

Hydrochloric acid (37%), phosphoric acid (70%), acetic acid, sodium hydroxide and sodium acetate) Merck, and *o-, m-, p*-nitrophenols (NP), 2, 4 dinitrophenols (DNP) were purchased from Sigma Aldrich.

The water used in all experiments was purified by a Millipore System (RO).

The laboratory installation

The pertraction device (fig.1) consists of a polypropylene (PP) capillary fiber module (1 m^2) impregnated with sulfonated polyetheetherketone (SPEEK) working and two tanks with aqueous solutions: nitrophenol (source phase) and constant *p*H (receiver phase). The source phases and receivers are transported in the installation with variable flow peristaltic pumps (1-4 L / min) [35].

Preparation of membranes on capillary support (CLM)

The commercially available suppository capillary fibers are made from surface-modified polypropylene (PP) to provide optimal porosity) [36]. For impregnation of the capillary bundle they are placed in the *U* shape, after crevices are immersed in a 2 L cylindrical vessel containing

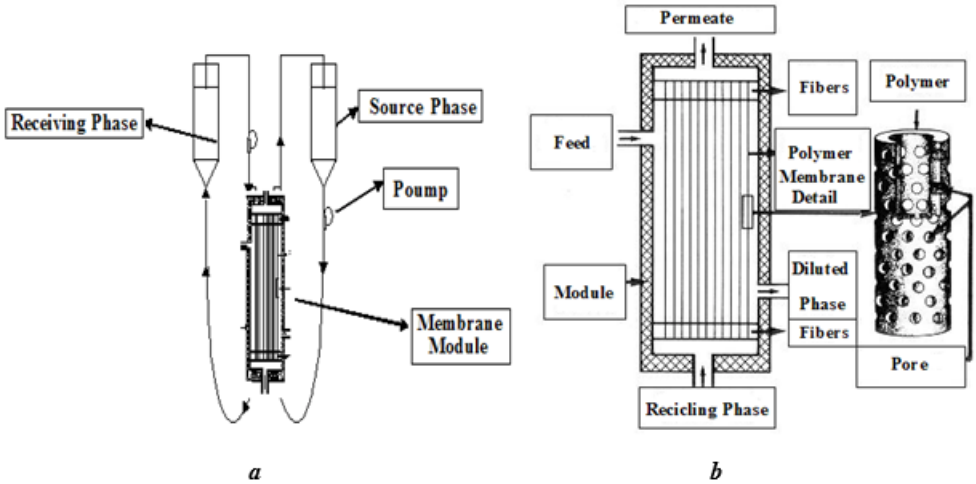


Fig. 1. Laboratory installation [35]: a) the assembly of the installation; b) the fluid circulation details and the configuration of a capillary

the 1.5 L selected SPEEK [37, 39]. After 24 h, the membranes are removed and coupled to a preliminary vacuum pump (100 mm Hg) so that the capillary becomes empty inside and the porous walls of the cave membranes will remain soaked with the chosen SPEEK. The volume or amount of SPEEK in the membrane walls can be readily determined by the gravimetric method, after weighing the initial membrane and the impregnated membrane.

Analytical methods

The determination retention or effective efficiency (***R***) of nitro phenol is accomplished through the spectrophotometric method with Spectrometer CAMSPEC [21, 22].

$$R = (c_o - c_f)/c_o \quad (9)$$

where: c_f is the final concentration of the solute (nitrophenol),

c_o - initial concentration of solute (nitrophenol)

$$R = (A_o - A_{sample})/A_o \quad (10)$$

where: A_0 - initial nitrophenol sample solutions absorbance

A_{sample} - current nitrophenol sample absorbance

The molar flow (J) of the chemical species through the membrane is given by the relation (10):

$$J = \frac{M}{S \cdot t} \quad (\text{mol/m}^2\text{xh}) \quad (11)$$

where: M = permeate moles (L)

S = effective membrane area (m^2)

t = time to collect permeate volume (h)

Morphological analysis of samples was performed by scanning electron microscopy (SEM). It used a higher solution microscope, Quanta 3D EGF model with dual beam and equipped with X-ray (EDX) Apollo X energy dispersive detector.

Results and discussions

Capsule liquid membranes (PP-SPEEK) obtained by impregnation of polypropylene (PP) fiber with sulfonated polyetherether (SPEEK) were characterized by SEM electronic microscopy (fig. 2), high HRSEM reuptake electron microscopy fig. 3) and X-EDAX rays analysis (fig. 4). The porosity of the capillary (PP) fiber over 40% was highlighted (SEM-PP, fig. 2), and the average pore size of approx. 0.15μm was determined (HRSEM-PP, fig. 3). The EDAX spectrum clearly shows the appearance of the sulfonated polymer (fig. 4b) in the composition of the PP-SPEEK membrane.

The PP-SPEEK membrane integrated in the pertraction mode (fig. 1) has a usable mass transfer area of 1 m^2 which has allowed accurate determination of the molar flow of nitrophenols (fig. 5). The determinations were performed using a 4 L / min flow rate source at a concentration of 5 mg / L of nitrophenol and *p*H 5 (a) or *p*H 7 (b), and the *p*H-receiving phase 12 and the rate of Flow rate of 0.3 L / min.

The data show that at the lower *p*H of the source phase, the nitrophenol streams are higher, and that the three isomers of mononitrophenol have significantly different behaviors, especially with respect to m-nitrophenol, which exhibits the smallest fluxes (fig. 5 a and b). The flux results correlate with the higher water solubility of m-nitrophenol and consequently a more difficult transfer in the membrane and hence in the receiving phase. However, it can be appreciated that the liquid membrane has sulfonic ionic groups participating both through hydrophobic and ionic interactions with the chemical species to be separated. The ensemble of specific equilibria (r) and constants (Ka, R) (SCHEME II) indicates the complexity of transport by such type of membranes.

Analysis of the obtained results suggests that PP-SPEEK membranes can be used to discriminate m-nitrophenol o-p-nitrophenol isomers. Thus, it can be appreciated that after a period of 5 to 6 h of operation the source phase will be

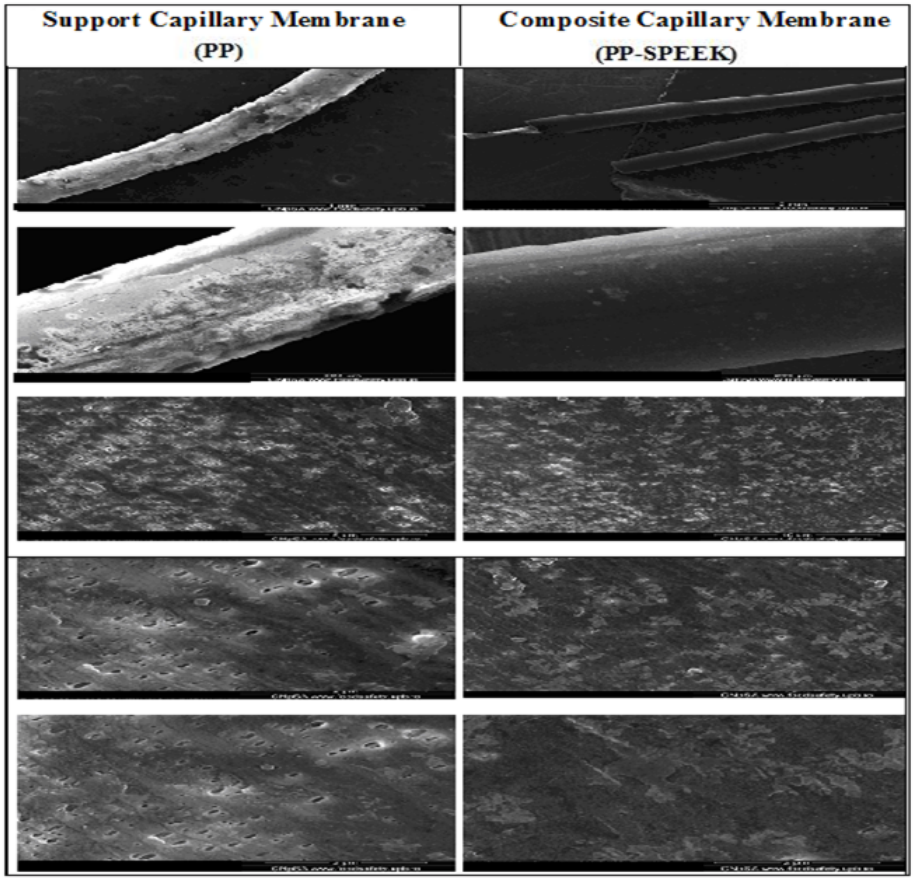


Fig. 2. The morpho-structural characteristics of polypropylene (PP) support fibers and sulfonated polyetheretherketone base (PP-SPEEK)

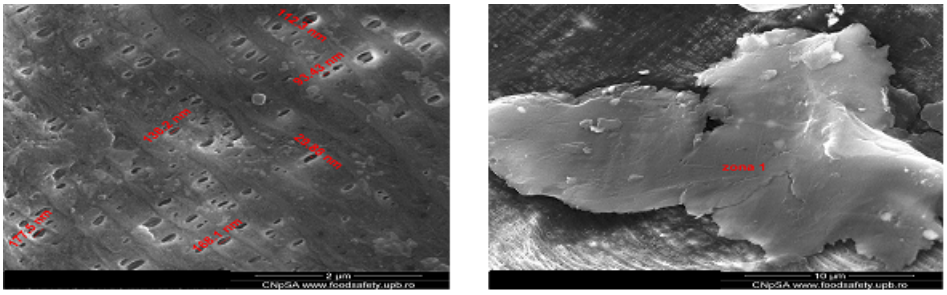


Fig. 3. Electronic particle microscopy of capillary (PP) fiber (a) and detailed electronic microscopy of impregnated capillary fiber (PP-SPEEK) (b)

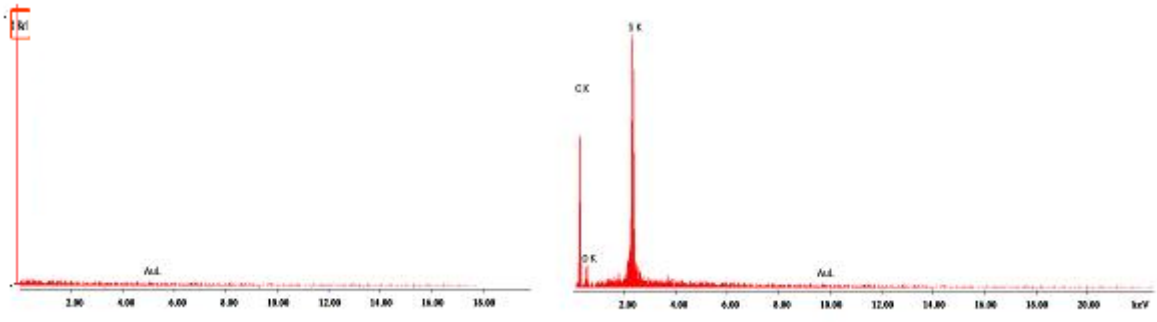


Fig. 4. The EDAX spectrum of capillary (PP) (a) and impregnated capillary (PP-SPEEK) fiber (b)

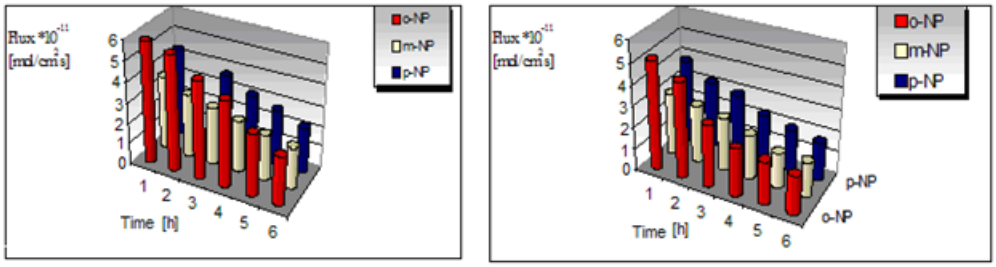


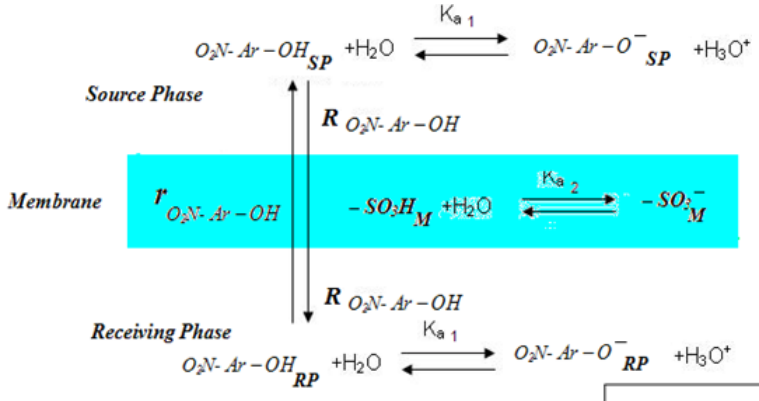
Fig. 5. Variation of nitrophenol flow through PP-SPEEK membranes to *p*H 5 of the source phase (a) and *p*H 7 of the source phase (b)

concentrated in m-nitrophenol, and the receptor phase in o- and p-nitrophenol.

To demonstrate the effect of nitrophenol acidity and their water solubility on PP-SPEEK membrane transfer, an experiment was conducted in which an equimolar mixture of mononitrophenol (NP) and 2, 4-dinitrophenol (2,4 DNP) was subjected pertraction under the aforementioned working conditions and at *p*H 5 of the source phase (fig. 6).

The results of the pertraction show that mononitrophenol is transferred much faster through the system, but both the mono and dinitrophenol flow decrease over time (fig. 6).

The data obtained in this case correlates with the much higher acidity and solubility of 2,4-dinitrophenol in the aqueous system which makes it more difficult to transfer through the membrane, so after 4-5 h of work the mononitrophenol concentration triples in phase receptors, while the concentration of 2,4-dinitrophenol doubles in the source phase.



Scheme 2. Specific balances and constants in the PP-SPEEK / nitrophenol membrane system

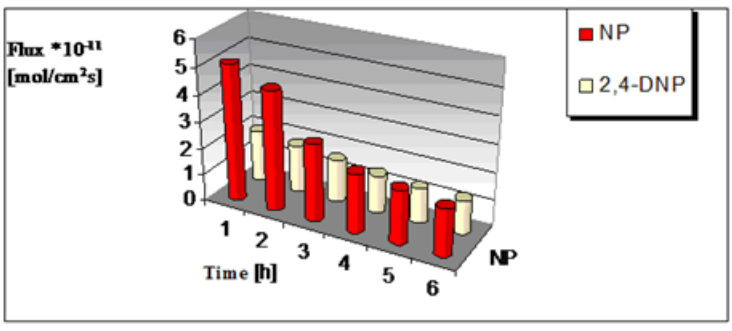


Fig. 6. Variation of nitrophenol flow through PP-SPEEK membranes to pH 5 of the source phase

Conclusions

The present paper outlines the results of the transfer of nitrophenols through a membrane system made of PPET impregnated with polyetheretherketone sulfonate (SPEEK).

The experiments were carried out in a PP-SPEEK capillary membrane module, with a useful size of 1 m^2. The determinations made by using a source phase at a flow rate of 4 L / min at a concentration of 5 mg / L of nitrophenols and *p*H 5 or *p*H 7, and the *p*H receiving phase of 12 and a flow rate of 0.3 L / min, revealed that:

- *o*- and *p*-nitrofenol are transferred much faster than m-nitrophenol (the flux is nearly double);
- the source phase of the system is concentrated in m-nitrophenol, and the receptor phase in *o*- and *p*-nitrophenols;
- the transfer data correlate with the higher water solubility of m-nitrophenol;
- mononitrophenols transfer much faster than dinitrophenol, but both the mono and dinitrophenol flow drops over time;
- after 4-5 h of work, the mononitrophenol concentration triples in the receiving phase, while the concentration of 2,4-dinitrophenol doubles in the source phase.

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