SINTEZA ŞI CARACTERIZAREA UNOR NOI MEMBRANE COMPOZITE HIBRIDE PE BAZĂ DE FOSFAZENĂ ORGANO-SUBSTITUITĂ ŞI REȚEA DE SiO_2

SYNTHESIS AND CHARACTERIZATION OF THE NEW HYBRID COMPOSITE MEMBRANES BASED ON THE ORGANO-SUBSTITUTED PHOSPHAZENE AND SiO_2 NETWORK

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În ultimii ani, o deosebită atenție s-a acordat preparării şi caracterizării materialelor hibride organo-anorganice de tipul fosfazenelor organo-substituite/rețea de SiO_2 în vederea obținerii de membrane compozite utilizate în procesele de separare selectivă. Prezența fosfazenelor în rețeaua de silice determină creşterea rezistenței acesteia iar rigiditatea compuşilor fosfazenici este mult îmbunătățită prin prezența rețelei de silice.

În această lucrare se prezintă prepararea a 9 membrane compozite (M0-M8) prin metoda tragerii din soluție. Soluțiile au fost obținute prin dizolvarea în N−metilpirolidonă a 12-22% suport polimeric (polisulfonă) şi a 0,1% fosfazenă organo−substituită/rețea de SiO_2. Fosfazena organo–substituită/rețea de SiO_2 a fost obținută printr-o reacție de tip sol–gel în cataliza acidă dintre tetraetoxisilan (TEOS) şi monomerul siloxanic. Monomerul siloxanic a fost sintetizat prin reacția de aminoliză dintre hexaclorociclotrifosfazenă ($N_3P_3Cl_6$) şi 3-(trimetoxisilil)-propilamină ($H_2N\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$). Membranele compozite astfel obținute au fost caracterizate prin spectroscopie în IR, microscopie electronică de baleaj (SEM) şi determinări gazometrice (diametrul mediu şi distribuția de pori).

In the last years a considerable attention has been paid to the preparation and characterization of the organic-inorganic hybrid materials like the organo-substituted phosphazene/SiO_2 network used in preparing the membranes intended to be used in the selective separation processes. In fact the phosphazene macromolecules within the silica matrix are known to improve the toughness of the ceramic network while the stiffness of the phosphazene phase being highly improved by the silica matrix.

In this paper the preparation of nine phosphazene based composite membranes (M0-M8) by making use of solution casting method is presented. The casting solutions were prepared from N−methylpyrrolidone (NMP), 0.1% organo-substituted phosphazene/SiO_2 matrix and 12-22% polymer support (polysulfone). The organo-substituted phosphazene/SiO_2 matrix was obtained by the acid catalyzed sol-gel reaction of tetraethoxysilane (TEOS) with siloxane monomer. The siloxane monomer was synthesized from hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and 3-(trimethoxysilyl)-propylamine ($H_2N\text{-}(CH_2)_3\text{-}Si(OCH_3)_3$). The resulting composite membranes were characterized by IR spectroscopy, SEM microscopy and gasometrical determination (medium diameter).

Keywords: *organo-substituted phosphazene/SiO_2 network, polysulfone membranes, SEM microscopy*

1. Introduction

For many years polysulfones have been the traditional polymer materials for the preparation of membranes used in microfiltration, ultrafiltration and gas separation processes [1-5].

The need for the preparation of more thermally, mechanically and chemically resistant polymers has led to the development of advanced materials, such as various types of organo - substituted phosphazene/SiO_2 networks [6, 7]. In fact the phosphazene macromolecules within the silica matrix are known to improve the toughness of the ceramic network while the stiffness of the phosphazene phase being highly improved by the silica matrix. [6, 8]. Promising results have been obtained starting from cyclo- and poly-organophosphazenes and oxides such as SiO_2, TiO_2, Al_3O_2 and ZrO_2 by sol-gel process [9-12].

The aim of this study is to obtain some new composite membranes (M0-M8) based on an organo-substituted phosphazene/SiO_2 network by making use of solution casting method. The casting solutions were prepared from N−methylpyrrolidone NMP, 0.1% organo-substituted phosphazene/SiO_2 network and

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12- 22% polymer support (polysulfone).

The organo-substituted phosphazene/SiO_2 network was obtained by the acid catalyzed sol-gel reaction of tetraethoxysilane (TEOS) with siloxane monomer **1**.

The siloxane monomer was synthesized from hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and 3-(trimethoxysilyl)-propylamine (H_2N-$(CH_2)_3$-$Si(OCH_3)_3$).

The composite membranes were characterized by IR spectroscopy, SEM microscopy and gasometrical determination (medium diameter).

2. Experimental

Equipment

- Vibrational spectra were recorded by means of a Bruker Equinox55 spectrophotometer in the wavenumber range of 400 – 4000 cm^{-1}.
- Elemental analyses were carried out on a Heraeus CHNO-Rapid apparatus.
- SEM analyses were performed on a HITACHI S2600N scaning electron microscope with EDAX, in primary electrons fascicle, on samples covered with a thin silver layer.
- Gazometric determinations of membrane permeabilities were performed based on the N_2 fluxes obtained by direct measurements at a given pressure. The determinations were performed on a Coulter II Porometer.

Synthesis of cyclophosphazene-siloxane precursor 1 (*N - (2,4 - bis(3 - (trimethoxysilyl) propylamino) -4,6,6-trichloro- 1,3,5,2,4,6 - triaza-triphosphinin-2-yl)-3-(trimethoxysilyl)propan-1-amine,* $N_3P_3Cl_3[NH(CH_2)_3Si(OCH_3)_3]_3$)

The synthesis of **1** was performed as described in the literature [13,14] by aminolysis reaction of hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) with 3-trimethoxysilylpropylamine in the presence of triethylamine.

To a solution of hexachloro-cyclotriphosphazene ($N_3P_3Cl_6$, 0.0028 mol) and triethylamine (5 ml, 0.0359 mol) in 50 ml of dry THF, 3-trimethoxysilylpropylamine (5 ml, 0.0172 mol, density = 1.027 g/mL) was added. The reaction mixture was stirred for 24h at 70°C. The reaction was monitored by TLC, using a CH_3Cl: MeOH (80:20 v/v, R_f=0.89) elution system. Triethylamine hydrochloride was removed by filtration; the solvent was evaporated in a rotary evaporator, resulting as a viscous oil. The resulting oil was mixed with diethyl ether and yield a white-yellow product (**1**) (η = 70 %).

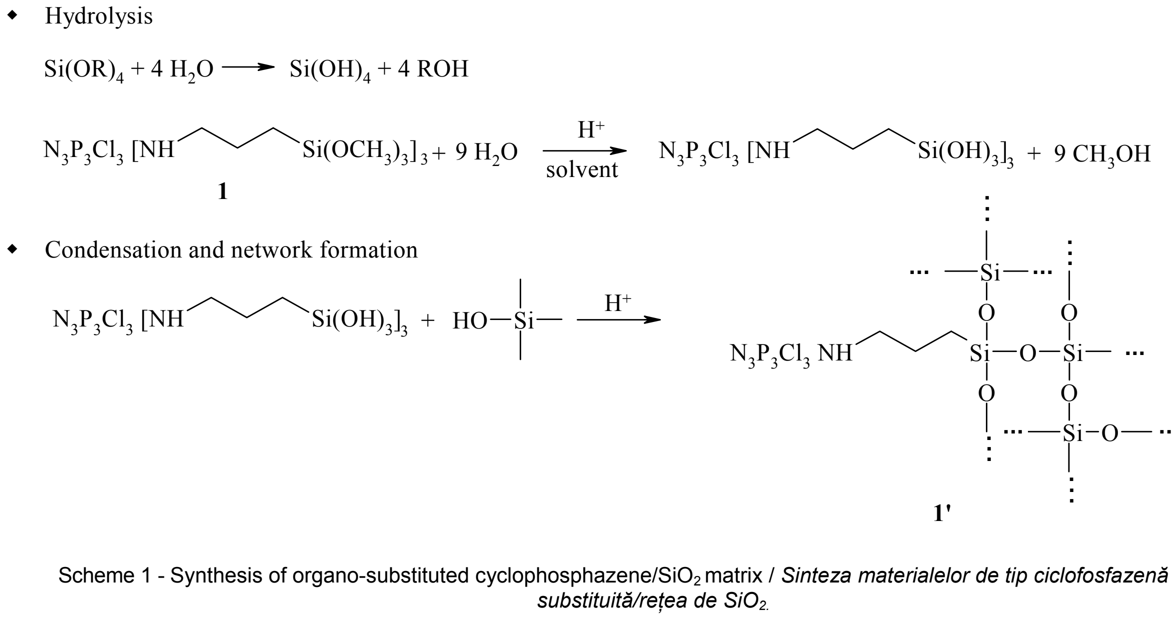
IR (cm^{-1}): ν_{NH}=3255.98 (w), $\nu_{CH3sym/CH3asym}$=2975.69–2932.45 (m-s), $\delta_{N\text{-}Hsec}$=1618.13, 1554.6 (m-w), δ_{CH3as}=1467.52(m), $\nu_{P=Nring}$= 1191.31 (m), $\nu_{Si\text{-}O\text{-}C}$=1090.8, 1031.5 (vs), $\nu_{P\text{-}N\text{-}Pring}$ = 913.37 (m).

M.W.=775.5 g/mol, **F.M.** $C_{18}H_{48}Cl_3N_6O_9P_3Si_3$, *Calcd*. C 27.86%, N 10.83 %, H 6.23 % *Found* C 27.74%, N 10.87 %, H 5.9 %.

Synthesis of organo-substituted cyclo-phosphazene/SiO₂ matrix. The organosubstituted phosphazene/SiO_2 matrix was obtained by acid-catalyzed reaction (HNO_3, pH=3) of tetraethoxysilane (TEOS, 8 mL, 0.038 mol) in 12.4 ml deionized water and cyclophosphazene-siloxane precursor (**1**) (0.001 mol) [13,14] (Scheme 1).

The sol was stirred in closed flask at room temperature until all fully solubilized components were dissolved and the organo-substituted phosphazene/SiO_2 network has resulted (t=48h).

Finally the resulting product, a transparent xerogel **1'** was dried (after drying the xerogel has shown no soluble fraction in most common solvents and water, proving the network formation)



Scheme 1 - Synthesis of organo-substituted cyclophosphazene/SiO_2 matrix / *Sinteza materialelor de tip ciclofosfazenă organo-substituită/rețea de SiO_2.*

and ground into a powder in order to be characterized and used in the membrane preparation.

IR (cm^{-1}): $\nu_{NH/OH}$ = 3257.83 (w-br), $\nu_{CH3sym/CH3asym}$= 2945.13–2891.11 (w-br), δ_{N-H} = 1630.93 (m), $\nu_{Si-O-Siasym}$=1053.07 (s-br), $\nu_{Si-O-Si}$=949.67 (m-br), $\nu_{Si-O-Si\ sym}$ = 784.95 (m), ν_{P-Cl} = 606 cm^{-1} (w).

Membrane preparation. Nine composite membranes (**M0-M8**) were prepared using a solution casting method from NMP, 0.1% organo-substituted phosphazene/SiO_2 matrix and 12-22% polymer support (polysulfone).

Casting solutions were obtained in borosilicate glass vials with polyester caps, and before use the solutions were filtered through a direct flow type module to remove any suspended particulate matter. Next, the polymer solutions were cast into a thin film of 0.2 mm/0.4mm on a glass plate using a doctor blade knife.

Distilled water was used as coagulation agent (coagulation bath temperature, 25ºC). In order to preserve the performance and structural characteristics of the membranes (Table 1), all the membranes were immersed into a glycerol conditioning bath (7 – 10 %wt).

3. Results and discussion

By phase-inversion process defect-free membranes based on organo-substituted phosphazene/SiO_2 network and polysulfones as polymer support were obtained. The casting was carried out by dissolving the organo-substituted cyclophosphazene/SiO_2 network in NMP because the most of the phosphazene materials did not show the structural integrity to form consistent durable sheets. Consequently they did not show the cohesive strenght to preserve their shapes when cast into films onto a supporting material.

The presence of phosphazene macromolecules in silica matrix should be able to improve the toughness of the ceramic network while the stiffness of the phosphazene phase should be largely improved by the silica network.

Polysulfone polymer was chosen as polymeric support because it has been shown to possess high solubility in N-methylpyrrolidone, excellent thermal stability up to 200°C and good adaptability to the preparation of dense microporous membranes.

NMP is used as a solvent because of its very good compatibility with polysulfone.

Scanning electron microscopy was used to analyze the morphology of the synthesized membranes (Fig. 1). It has revealed asymmetric structures (Fig.1c) consisting of two layers of different morphologies: a thin porous layer of cca. 40 – 50 μm and a dense cca. threefold thicker layer (120 - 150 μm). The two faces of the membranes are uniform with a "hill-valley" aspect, specific to the asymmetric composite membranes.

The medium pore diameters in the porous membrane layers vary with the polysulfone concentration; the mean pore diameters have shown a decrease with the increase in the polysulfone concentration (Fig. 1a).

Even at high magnification (15.000x – Fig.1b) the SEM images recorded for the dense membrane layers have revealed no visible pores meaning pore diameters less than 100nm.

IR spectroscopy. The **M0 – M8** membranes were characterized by ATR - FTIR spectroscopy in the 600-4500 cm^{-1} range, both for active layer (membrane/coagulation bath interface – Fig.2.) and porous layer (membrane/casting support interface – Fig.2.). The IR spectra have revealed the absorption bands of the polysulfone groups being in good agreement with standard polysulfone 1044cm^{-1} (SO_3H), 1106cm^{-1} (C-O), 1150cm^{-1} ($R(SO_2)$-R), 1241cm^{-1} (C-O), 1488cm^{-1} (aromatic bond), 2980-2859cm^{-1} (aliphatic CH3sym/CH3asym), 3020-3060cm^{-1} (aromatic CH) and 3362cm^{-1} (OH).

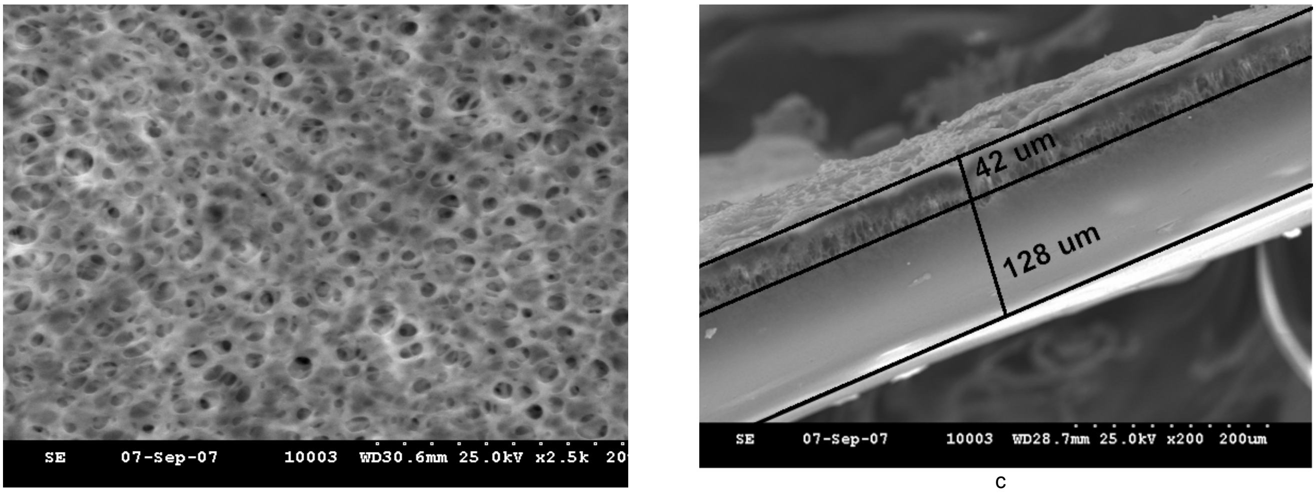
Because of the low polysulfone/organo-substituted cyclophosphazene/SiO_2 matrix ratio (0.1%), the changes revealed in the IR spectra of

Table 1

Membrane characteristics / Caracteristicile membranelor

Membrane *Membrana*	Polysulfone content *Conținut de polysulfonă* (%)	Content of organo–substituted phosphazene/SiO_2 matrix *Conținutul de fosfazenă organo-substituită/rețea de SiO_2*	Exposition time / *Timp de expunere* (sec.)	Coagulation time *Timpul de coagulare* (min.)	Doctor blade knife thickness *Grosimea trăgătorului* (mm)
M0	12	-	60	5	0.4
M1	12	0,1%	60	5	0.2
M2	12	0,1%	60	5	0.4
M3	15	-	60	5	0.4
M4	15	0,1%	60	5	0.2
M5	15	0,1%	60	5	0.4
M6	22	-	60	5	0.4
M7	22	0,1%	60	5	0.2
M8	22	0,1%	60	5	0.4

M0, M3, M6 – membranes used as controls / membrane utilizate ca referințe



a

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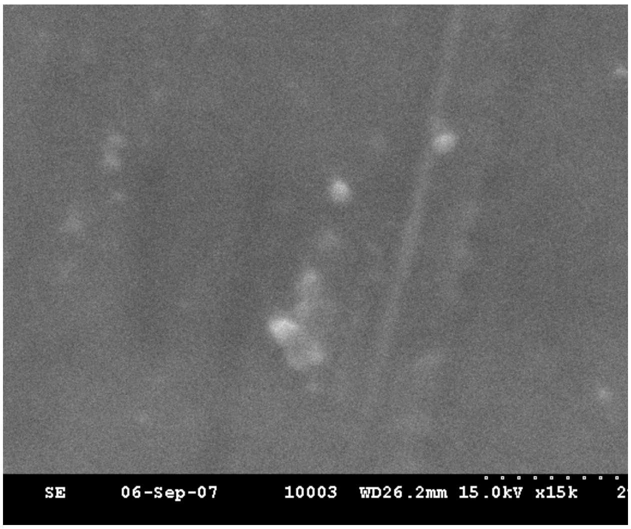

b

Fig. 1 - Characteristic SEM images of the synthesized membranes / *Imagini SEM caracteristice membranelor obținute*

a) Characteristic SEM image of M4 membrane at the membrane/casting support (porous layer) interface / *Imagini SEM caracteristice membranei M4 la interfața membrană/support de tragere (strat poros).*
b) Characteristic SEM image of M4 membrane at the membrane/coagulation bath (dense layer) interface / *Imagini SEM caracteristice membranei M4 la interfața membrană/baie de coagulare (strat dens).*
c) Characteristic SEM image of the M4 membrane cross section / *Imagini SEM caracteristice membranei M4 în secțiune transversal.*

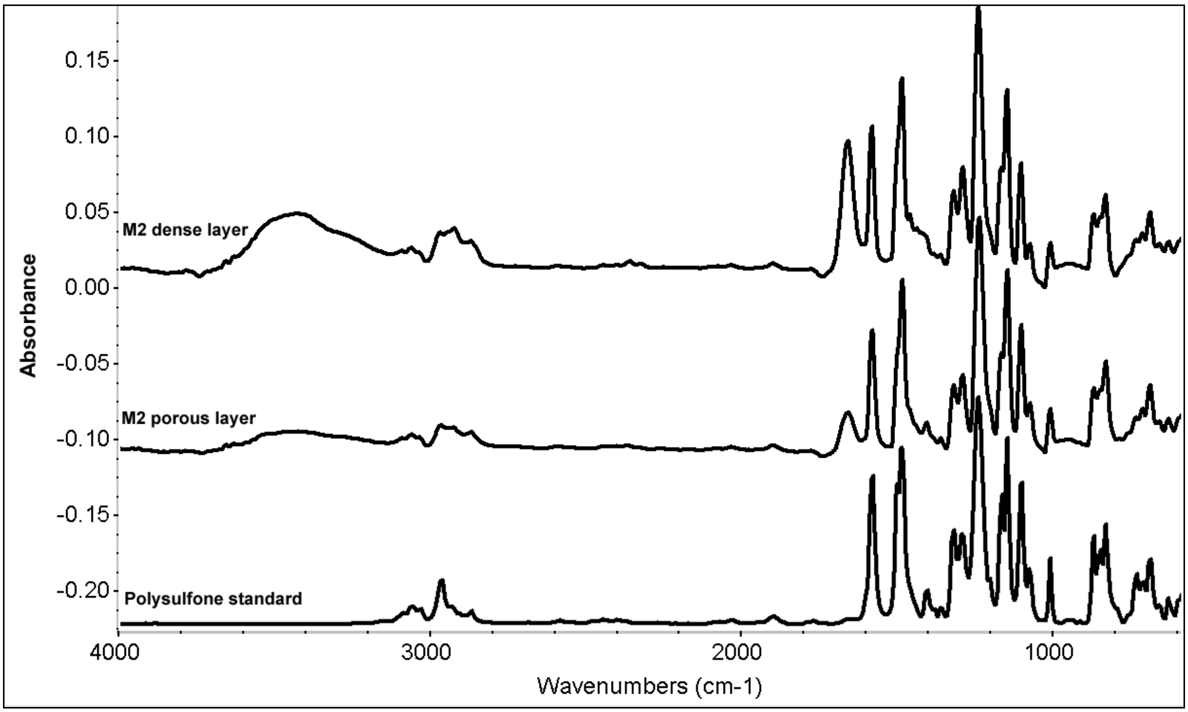

Fig. 2 - Infrared spectra of the M2 membrane recorded on both surfaces and polysulfone / *Spectrele IR înregistrate pe ambele fețe ale membranei M2 cât şi pe polisulfonă.*

Table 2

Membranes characterization from the point of view of permeability, permeation and mean pore diameter

Caracterizarea membranelor din punct de vedere al permeabilității, permeației şi a diametrului mediu al porilor

Membrane *Membrana*	Permeability *Permeabilitatea* m/s.kPa	Permeation *Permeația* m^2/s.kPa	Knudsen permeability factor *Factorul Knudsen de permeabilitate* m^2/s	Medium pore diameters *Diametrul mediu al porilor* nm
M3	2.65×10^{-6}	2.30×10^{-2}	3.31×10^{-7}	26.3
M4	1.28×10^{-6}	5.10×10^{-3}	1.91×10^{-7}	2.82
M5	2.78×10^{-6}	1.30×10^{-2}	2.31×10^{-7}	24.5
M6	6.78×10^{-8}	3.71×10^{-4}	1.16×10^{-9}	15.0
M7	5.76×10^{-8}	3.10×10^{-4}	8.26×10^{-9}	0.798
M8	1.76×10^{-5}	7.70×10^{-2}	1.94×10^{-6}	13.5

the both faces of the **M0-M8** membranes are a consequence of the presence of water but not the presence of organo-substituted cyclophosphazene/SiO_2 network. There is a higher level of water in the dense layer than in the porous layer due to the narrower pores enabling a limited water evaporation.

Gasometrical determinations. The medium pore diameters, the permeation and the permeability of the membranes were measured by direct determination of the gas flow through the membranes based on three characteristics (thickness, porosity and surface pores distribution) at a known pressure (0-10 barr).

Based on the obtained data the permeation was determined, and the gas flow and Poissuille-Knudsen flow versus pressure drop were plotted. The gas permeability through the membranes (l/cm^2.min) was determined by measuring the slope of the flux versus pressure curve.

The medium pore diameters in membranes were calculated based on the slope of the Poiseuille-Knudsen curve versus pressure drop. The obtained data are given in Table 2.

The table reveals that M8 membrane has shown the highest permeability while the M6 and M7 membranes have shown the lowest permeabilities, the M8 membrane permeability being about 250-300 times greater than the M7 and M6 membrane permeabilities, respectively, because of the membrane thicknesses and morphologies (see for instance mean diameters). For the membranes of the same thickness, M6 and M8, the permeability changes have resulted from the presence of organo-substituted cyclophosphazene/SiO_2 network.

The membrane permeations have shown the same variation as permeabilities.

The medium pore diameters, obtained by gasometrical determination is the medium open pore diameters in the dense layer with both the dense layer surface and while the porous layer surface or. As result from the Table 2 data the medium pores size variation are not related with permeation and permeability. The pores size are related both with the polysulfone level used for synthesis and doctor blade thickness. The smallest pore diameters were found in the thinner membranes.

4. Conclusions

By phase-inversion process some defect-free membranes were obtained by making use of an organo-substituted phosphazene/SiO_2 network and polysulfone polymer support. Composite membranes have shown asymmetric structures consisting of two layers; a porous layer of cca. 40-50 µm in thickness and a dense layer of cca. 120-150 µm in thickness. The medium pore diameters were of cca. 0.5 - 2 µm in the porous layer (as obtained by SEM) and less than cca. 25 nm in the dense layer (as obtained by gasometrical determination). The dense layer is uniform with a “hill-valley” aspect, specific to the asymmetric composite membranes.

In conclusion, the M8 membrane has shown the highest permeability, meaning that the presence of organo-substituted cyclophosphazene/SiO_2 matrix in the membrane structure, polysulfone concentration and membrane thickness have had a decisive influence on the permeability.

We have in view to prepare different membranes with different porosities to be tested in different applications such as separation processes and drug delivery.

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MANIFESTĂRI ŞTIINŢIFICE / SCIENTIFIC EVENTS

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