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EFFECTS OF HYPOCHLORITE TREATMENT ON TRANSPORT-SEPARATION PROPERTIES OF POLYSULFONE CAPILLARY MEMBRANES

Key words

Polysulfone membranes, hypochlorite, treatment, permeability.

Abstract

Different types of polysulfone capillary membranes supplemented with porophores were obtained. The membranes were treated with sodium hypochlorite using the flowing method. The membrane ultrafiltration and retention was evaluated for chosen markers before and after treatment. Ultrafiltration increase and retention decrease for polyethylene glycols were observed, and there was not a difference in bovine albumin retention for post-treatment membranes. Hypochlorites caused porophores removal from the membrane structure resulting in opening the pore passages and increasing permeability without increasing pore size.

Introduction

Polymeric membranes parameters are not always useful for specific applications. Therefore, there is a need to modify the membranes by changing

their structure, permeability, and separation properties in a specific way for a given application. The structure, chemical composition, and spinning process parameters of membranes have considerable influence on separation properties.

Hydrophobicity is a major defect found in polysulfone membranes that causes membrane fouling. Therefore, in order to reduce fouling [1, 2], hydrophilic porophor polymers like polyvinylpyrrolidones (PVP), or polyethylene glycols (PEG) are added to the membranes. PVP and PEG cause an increase in membrane porosity and hydrophilicity, but in some cases permeability reduction and retention increase as well. It is a result of the remaining particles of PVP or PEG molecules inside the membrane structure. Thus, developing a method of effective removal of porophores from the membrane will have a significant influence on membrane permeability.

The membranes treatment with sodium hypochlorite (NaOCl) effectively removes PVP from their structure. Wienk et al investigated the influence of NaOCl treatment for polysulfone (PSf) membrane including PVP (K90). Elongating treatment time causes an increase in permeability, but retention of bovine serum albumin (BSA) remained constant [1, 3]. Hypochlorites cause PVP removal from the membrane structure without it changing as result of opening the pyrrolidone ring or cutting PVP chain, which reduces their molecular mass and makes elution easier.

Qin et al investigated the influence of NaOCl treatment for cellulose acetate and PSf membrane parameters [2]. The authors suggested that treatment not only removed PVP but also caused a porosity increase and enlarging of pore size, while permeability increased and retention coefficient decreased. A similar investigation was conducted for other membranes: polyethersulfone/PVP [4], polyacrylonitrile/PVP [5], and PSf/PVP. The observations were quite different as compared to Wienk's results who suggested that NaOCl treatment did not change the membrane pore structure [1].

These modifications were applied for flat membranes in the treatment using a static method through soaking membranes in hypochlorite solution. In our work, we found that, for PSf capillary membrane modification, the flowing method of treatment is more effective.

1. Experimental

1.1. Materials

Polysulfone [PSf] Udel 1700 NT LCD from Dow Corning m.w.70 kD, N, N-dimethylformamide [DMF] from POCH, N-methyl-pyrrolidon [NMP] from Sigma – Aldrich, dimethylacetamide [DMA] from Sigma-Aldrich, polyvinylpyrrolidones [PVP] from Sigma-Aldrich, m.w.10 kD, 55 kD and 360 kD, inulin from Sigma-Aldrich, m.w. 5 kD, polyethylene glycols [PEG] from

Fluka, m.w. 15 kD and 35 kD, bovine serum albumin [BSA] from Fluka, m.w. 67 kD.

1.2. Capillary membranes' fabrication

Polysulfone (PSf) was selected as the material for capillary membrane fabrication. Polyvinylpyrrolidone (PVP) or polyethylene glycol (PEG) was added to the solution as a porophore in order to aid the formation of a porous structure. Polymers were dried overnight under vacuum at 100°C before dope preparation. N, N-dimethylformamide (DMF), N-methyl-pyrrolidon (NMP), and dimethylacetamide (DMA) were used as the solvents for polymeric materials. DMF, DMA, and NMP were dried with a molecular sieve before being used. The polymer (PSf), porophore (PVP or PEG) and solvent were mixed in a flask and stirred at room temperature until the polymer and porophore dissolved completely.

The membranes were obtained by the dry/wet-spinning, phase-inversion technique through the extrusion of a polymer solution employing a spinneret.

The polymeric dope solution was extruded by syringe pumps through the spinneret. The bore fluid (pure water) was supplied towards the spinneret via ambient gas pressure. The nascent capillary membrane passed through an air gap (the distance between the spinneret and the coagulation bath; distance varying from 5 to 10 cm) and was drawn into coagulation baths and transported over rollers. The coagulant was pure water in the first bath and tap water in the two other ones. A take-up wheel was used to collect the capillaries. The spinning process was conducted at room temperature. Membranes were cut into small pieces and placed in the clean water bath for about four days for residual solvent extraction. After washing, the membranes were stabilized in a glycerine solution (10% water solution) for one day. The remaining glycerine in the pores increased hydrophilicity of the membranes. Next, the capillaries were air-dried at ambient temperature.

The capillary membrane modules were prepared by putting twenty pieces of capillaries of a 6-cm effective length into a polypropylene module (25 cm² area). Both ends of the modules were sealed with an epoxy resin. Finally, membranes were ready for further tests and study.

1.3. Membrane characterization

1.3.1. Permeability measurements

Hydraulic permeability of the capillaries was determined as a volume of the solution passed through the membrane walls during ten minutes with stable transmembrane pressure. Ultrafiltration coefficient (UFC) was calculated according to the following formula:

$$UFC = \frac{v}{t \times a \times p} \quad (1)$$

where: v – volume of the solution [cm³], t – time of measurement [min.],
 a – nominal capillaries area in module [cm²], p – transmembrane pressure [hPa].

1.3.2. Retention measurements

The separation characteristics of a membrane determine the retention coefficient. Inulin (5 kD), polyethylene glycols [PEG] (15 and 35 kD), and bovine serum albumin [BSA] (67 kD) were successively used for the measurement of the retention coefficient of each capillary module. The membrane retention R (%) is defined as follows:

$$R = \{1 - (C_P / C_F)\} \cdot 100\% \quad (2)$$

where: R – retention coefficient, C_P – concentration of marker in the permeate [g/dm³], C_F – concentration of marker in the feed [g/dm³].

The concentrations of markers were measured by a UV-spectrophotometer (HITACHI U-3010).

2. Results and discussion

2.1. Membranes measurements

Four sorts of PSf membranes were produced using different composition solutions (described in Section 2.2). PVP of 55 kD and PEG of 35 kD were applied to a PSf 1 membrane. PVP of 10 kD and of 55 kD were applied to PSf 2 and PSf 3 membranes. PVP of 55 and of 360 kD were applied to a PSf 4 membrane. The compositions of membrane solutions are shown in Table 1.

Table 1. Composition of membrane solutions

Membrane	Solvent	Content of polymer in solvent [%]	Porophor	Weight composition [polymer/porophor I/porophor II]
PSf 1	NMP	16.0	PVP (55 kD) PEG (35 kD)	1.0/0.4/0.4
PSf 2	DMF	16.0	PVP (10 kD) PVP (55 kD)	1.0/0.3/0.3
PSf 3	DMF	16.0	PVP (10 kD) PVP (55 kD)	1.0/0.3/0.3
PSf 4	DMA	15.8	PVP (55 kD) PVP (360 kD)	1.0/0.3/0.3

Membranes were treated with 15% NaOCl water solution using the flowing method. The NaOCl solution of 250 cm³ volume was passed through the capillary module. The solution was passed inside the capillaries and flowed through the capillary walls to the outside module at 0.5 MPa transmembrane pressure. After membrane treatment, pure water was flushed in both directions through the membrane walls in order to remove residual hypochlorite.

2.2. Membranes hydraulic permeability

The hydraulic permeabilities of the membranes were measured (accordingly to the Formula 1) before and after the treatment with NaOCl. The observed values are shown in Table 2. Post-treatment membranes are indicated in italic.

Table 2. Coefficient of hydraulic permeability for membranes before and after treatment with NaOCl

Membrane	PSf 1	PSf 2	PSf 3	PSf 4
UFC [initial]	14 ± 0.1	19 ± 0.2	10 ± 0.1	13 ± 0.1
<i>UFC</i> <i>[after NaOCl]</i>	<i>19 ± 0.2</i>	<i>24 ± 0.3</i>	<i>15 ± 0.2</i>	<i>18 ± 0.2</i>
% increase UFC	36	26	50	39

The coefficients of hydraulic permeability for all post-treatment membranes increase from 26% for the PSf 2 membrane to 50% for the PSf 3 membrane.

2.3. Elementary analysis and wetting angle of membranes

Elementary analysis and the wetting angle of membrane measurements were performed to justify the membrane permeability increase after NaOCl treatment. Elementary analysis of PSf 1 and PSf 3 membranes was performed using a CHNS analyser. Results are shown in Table 3 for membranes before and after treatment with NaOCl solution.

The PSf 1 membrane consisted of 0.47% mass nitrogen, and the PSf 3 membrane consisted of 0.30% mass nitrogen before treatment. Nitrogen content decreased below 0.1% mass for both membranes after treatment. Nitrogen was present only in PVP, and none was found in PSF and PES. The absence of nitrogen in the membranes after treatment proved that PVP was removed completely from the membrane structure. The chemical mechanism of the removal of PVP with the aid of NaOCl is not explained precisely in the literature. Most probably, hypochlorites caused the cutting of PVP chains reducing its chain length and making the removal easy [1].

Table 3. Elementary analysis of membranes

Membrane	% mass N	% mass S	% mass C	% mass H
PSf 1 before treatment	0.49	6.73	69.08	5.28
	0.45	6.68	68.85	5.32
PSf 1 after treatment	< 0.1	7.51	72.30	4.88
	< 0.1	7.63	72.64	4.92
PSf 3 before treatment	0.30	6.92	70.90	5.19
	0.31	6.95	70.84	5.16
PSf 3 after treatment	< 0.1	7.40	72.58	5.10
	< 0.1	7.54	72.16	5.08

Wetting angles were measured in order to investigate whether the treatment changed membrane hydrophilicity. For that purpose, two sorts of flat membranes were studied (having the same constitution as PSf 1 and PSf 3) and their wetting angles were measured before and after treatment. The results are shown in Table 4.

Membrane wetting angles before and after treatment did not change; therefore, the hydrophilicity of the membrane's surface remained unchanged. Applied treatment did not caused the forming of polar groups in the membrane structure. Additionally, removal of hydrophilic PVP did not increase the membrane hydrophobicity. Hypochlorite treatment of PSf membranes did not change their chemical structure character.

Table 4. Wetting angle for membranes

Membrane	Wetting angle before treatment	Wetting angle after treatment
PSf 1	56° ± 1	54° ± 1
PSf 2	55° ± 1	55° ± 1

2.4. Retention coefficients and molecular weight cut-off

The membrane retention coefficients before and after NaOCl treatment were measured for markers: inulin, PEG 15, PEG 35 and BSA. The method of measurement is described in Section 2.3.3. Retention coefficient values for different markers and molecular weights are shown in Figures 1–4.

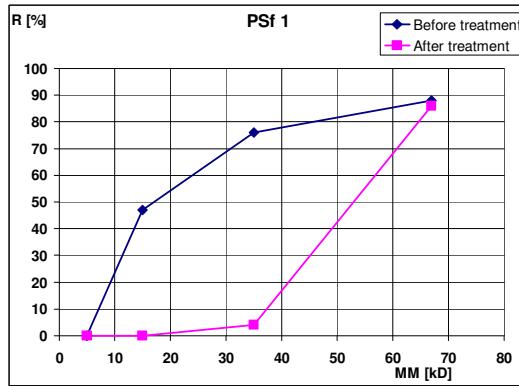


Fig. 1. Retention coefficient values for different markers for PSf 1 membrane

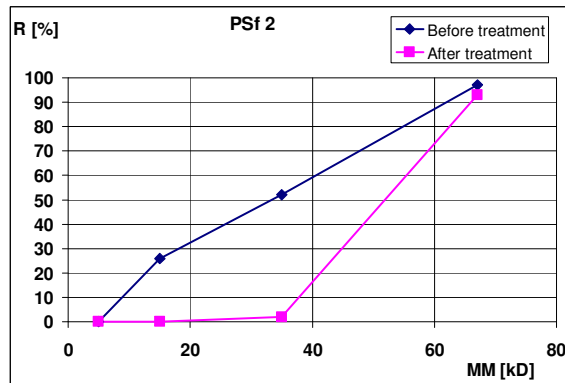


Fig. 2. Retention coefficient values for different markers for PSf 2 membrane

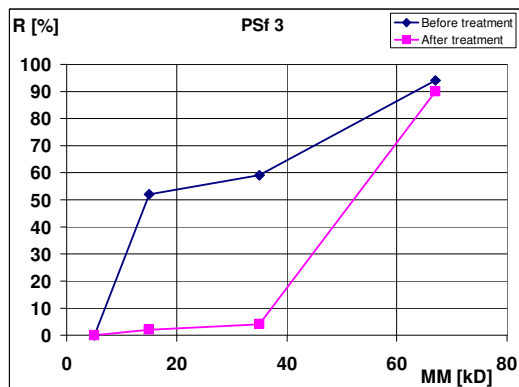


Fig. 3. Retention coefficient values for different markers for PSf 3 membrane

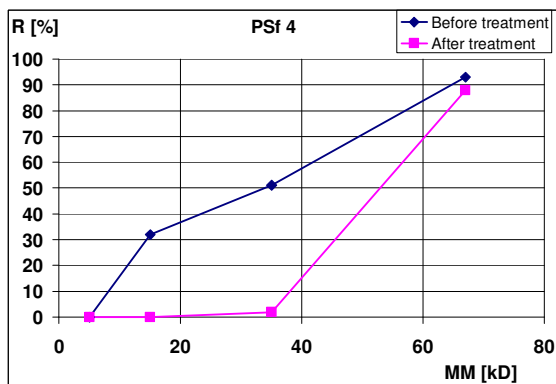


Fig. 4. Retention coefficient values for different markers for PSf 4 membrane

Table 5. Retention coefficients and molecular weight cut-off

Membrane	R [%]				MWCO [kD]
	Inulin	PEG 15	PEG 35	BSA 67	
PSf 1	0	47	76	88	77
<i>PSf 1</i>	0	0	4	86	-
PSf 2	0	26	52	97	62
<i>PSf 2</i>	0	0	2	93	-
PSf 3	0	52	59	94	64
<i>PSf 3</i>	0	2	4	90	-
PSf 4	0	32	51	93	65
<i>PSf 4</i>	0	0	2	88	-

Retention coefficients values and molecular weight cut-off (MWCO) for 1–4 PSf membranes are shown in Table 5. Post-treatment membranes are indicated in italics.

All membranes transmitted inulin completely before treatment. Retention values of the membranes before treatment for PEG 15 kD were ranging from 26% to 52%, while for PEG 35 kD were ranging from 51% to 76%. Retention values of the membranes before treatment for BSA were ranging from 88% to 97%. Molecular weight cut-off values were ranging from 62 to 77 kD for all membranes.

Retention values of membranes for inulin were reduced to nil, while for PEG 15 and PEG 35 retention values were reduced from 2–4% to nil for all membranes after treatment. BSA retention values decreased several percentages for all membranes after treatment. It means that membrane became completely

permeable for PEG 15 and PEG 35 after treatment. The PEG's molecules sizes was smaller, while the BSA's molecule sizes was larger than the membranes' pore sizes, which is why the PEG's molecules completely passed and the BSA's molecules were stopped by these membranes.

Porophores residue removal caused the opening of the pores of membranes and facilitated the passage of PEG molecules. The hypochlorite treatment did not change the membrane structure and did not increase membrane pore sizes, but it resulted in the passage of PEG molecules as result of removing porophores.

Conclusions

The PSf membranes treatment with a sodium hypochlorite solution using the flowing method caused nearly complete removal of porophores, like PVP, from their structure. The absence of nitrogen in the treated membranes, demonstrated in elementary analysis, proved the removal of PVP. Removing porophores from the membrane structure resulted in opening passages and pores inside the membrane, which caused an evident permeability increase in comparison to the untreated membrane. The unchanged wetting angles before and after membrane treatment indicated that the membranes hydrophilicity remained unchanged. Removal of hydrophilic PVP did not cause a hydrophobicity increase; however, opening the new passages and pores caused a permeability increase.

Porophores removal did not change the membrane separation features significantly. The MWCO of treated membranes did not decrease and remained on the average of 60 kD; therefore, the BSA and other molecules of higher than 60 kD molecular weight did not pass through the membrane walls. The retention coefficient values of treated membranes obtained for molecules of the sizes smaller than 60 kD (like PVP) were considerably lower than for untreated membranes because of greater number of passages and pores opened in the wall. It brings us to the conclusion that the membranes' structure, pores size, and their shape remained the same after the treatment process.

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Wpływ obróbki podchlorynem polisulfonowych membran kapilarnych na ich właściwości transportowe i selektywność

Słowa kluczowe

Membrany polisulfonowe, podchloryn, obróbka, przepuszczalność.

Streszczenie

Obróbce poddano różne typy kapilarnych membran polisulfonowych zawierających porofory. Membrany traktowano podchlorynem sodu metodą przepływową. Filtrowalność oraz retencję membran ultrafiltracyjnych przed i po obróbce oceniano za pomocą wybranych markerów. Membrany poddane obróbce charakteryzowały się wyższą filtrowalnością i niższą retencją dla glikolu polietylenowego przy niezmienionej retencji albuminy bydlęcej. Obróbka podchlorynem sodu spowodowała zmniejszenie ogólnej porowatości membran ultrafiltracyjnych i jednocześnie zwiększenie udziału porów otwartych, dzięki czemu wzrosła przepuszczalność membrany bez wzrostu rozmiarów porów.