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Environmental fracture of polypropylene membranes used in membrane distillation process

Summary — The thermal and mechanical stability of different capillary polypropylene (PP) membranes used in the membrane distillation (MD) process were investigated. Membranes differed in storage time from the manufacturing (from 1 to 8 years). Small changes in polymers crystallinity, melting temperature (T_m) and crystallization temperature (T_c) were detected as the storage time of membranes increased. This can be assigned to the crystal growth in amorphous phase of PP. However, independently on the storage time the brand-new membranes were found to be flexible and elastic and capable to bending without fracture. The MD process was carried out either continuously or continuously/periodically. Distilled water and NaCl solutions were used as feeds in MD process. It was found that PP membranes are losing their flexibility and become brittle during long-term usage in MD modules, and as a consequence, they show susceptibility to cracking and fracture. These effects were more significant when NaCl solutions were used as feeds.

Key words: polypropylene, hydrophobic membrane, membrane distillation.

ŚRODOWISKOWE PĘKANIE MEMBRAN POLIPROPYLENOWYCH STOSOWANYCH W PROCESIE DESTYLACJI MEMBRANOWEJ

Streszczenie — W pracy przedstawiono wyniki badań stabilności mechanicznej i termicznej (rys. 3) kapilarnych membran polipropylenowych Accurel PP S6/2, które zastosowano w procesie destylacji membranowej (MD) (rys. 1 i 2). Badane membrany różniły się czasem przechowywania od momentu ich produkcji (od rocznych do ośmioletnich). Nowe membrany przed zastosowaniem w procesie MD były elastyczne i giętkie, co pozwalało je odkształcać bez zniszczenia. Stwierdzono, że wraz z czasem przechowywania membran zmienia się krystaliczność polimerów oraz ich temperatury topnienia (T_m) i temperatury krystalizacji (T_c) (rys. 4, tabela 1). Może to być związane ze wzrostem krystalitów w fazie amorficznej polipropylenu. Proces destylacji membranowej prowadzono w sposób ciągły lub ciągły/okresowy. Do zasilania instalacji MD zastosowano różne media (wodę destylowaną i roztwory NaCl). Stwierdzono, że podczas długotrwałej eksploatacji modułów MD zamontowane w nich membrany polipropylenowe tracą swoją pierwotną elastyczność, stają się sztywne i w efekcie są bardzo podatne na pękanie i zniszczenie (rys. 5). Zmiany właściwości polimerów były wyraźniejsze, gdy jako nadawę zastosowano roztwory NaCl (rys. 7, tabele 2 i 3). Częste zmiany temperatury membran kapilarnych spowodowały powstanie naprężeń termicznych, czego efektem było powstawanie szczelin na powierzchni membran (rys. 6).

Słowa kluczowe: polipropylen, membrany hydrofobowe, destylacja membranowa.

Microporous polypropylene (PP) membranes are commonly prepared by thermally induced phase separation (TIPS) process. In this process, strongly related to the temperature-dependent solubility of polymer, the polymer is dissolved in an appropriate solvent at elevated temperature, and when the temperature is decreased, at certain temperature, the polymer is no longer soluble and phase separation is induced. After removing the solvent, pores result giving the membrane its unique features [1—3]. The variation of the membrane morpho-

logy and the pore structure is possible by control of the thermodynamic conditions of the process (concentration of the polymer) and the kinetic ones (temperature, residence time and drawing-relaxation time). Microporous polypropylene membranes can be used for medical applications in dialyzers and oxygenators as well as in the industry, including waste-water treatment and water purification (in different membrane techniques) [1, 2].

One of the new membrane processes is membrane distillation (MD), applied successfully for water treatment and the concentration of the acid or salt solutions [3—5]. The most frequently studied and described case of MD is the direct contact membran distillation (DCMD), where the hot feed and cold distillate are in a direct contact with a hydrophobic porous membrane as it is shown in Figure 1. In this case membrane sepa-

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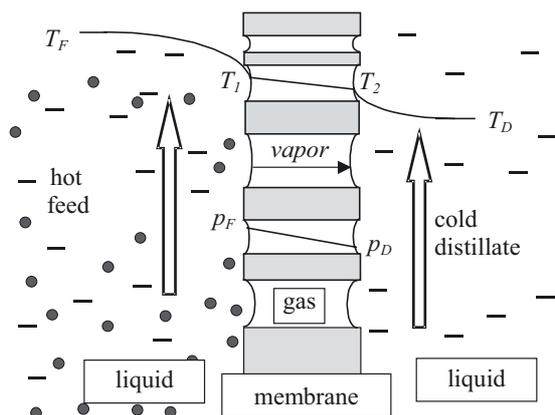


Fig. 1. Principles of direct contact membrane distillation (DCMD); T_1 , T_2 , T_F , T_D — temperatures at both sides of the membrane, and temperatures of feed and distillate, respectively; p_F , p_D — water vapor partial pressure at the feed and distillate sides, respectively

rates the two aqueous solutions which differ in the temperature and composition. The volatile components of the feed, most often water, evaporate at the interface feed/membrane. These components then diffuse through the air filling up the membrane pores and condensate in the cold distillate stream. The driving force for the mass transfer is a vapor pressure difference ($p_F - p_D$) occurring at both sides of the membrane, which depends on both the temperature (T_1 , T_2) and the composition of solutions in the layers adjacent to the membrane.

Membrane for MD must not be wetted by aqueous solutions and even at elevated temperatures it is necessary for the membranes to retain sufficient strength. A number of polymers, such as polyolefines (e.g. PP) and fluoropolymers: poly(vinylidene fluoride) (PVDF) and polytetrafluoroethylene (PTFE), have necessary hydrophobic properties. The commercial membranes produced for microfiltration have been already used in MD process [3—6]. Among them, the Celgard PP membranes with rendered porosity *via* stretching process and Accurel PP membranes produced by a thermal phase-separation process are used as materials of high porosity and narrow pore size distribution [3, 4, 7].

The polypropylene Accurel PP membranes are resistant to aqueous salt solutions, diluted inorganic acids as well as concentrated caustic solutions, but are not resistant to hypochlorite solutions. Aromatic and aliphatic hydrocarbons with low boiling points such as petrol ether, benzene, and carbon tetrachloride diffuse into the polymers and will cause swelling and decreasing mechanical strength [8].

As it was already demonstrated [9], the Accurel PP S6/2 membranes investigated after 3 years of the direct contact membrane distillation applied for production of the demineralized water showed both good thermal stability and separation characteristics. It was also found

that water (permeate from reverse osmosis process) did not cause the wetting of the used membranes despite a long-term membrane module exploitation.

In spite of those positive observations, a serious concern appears when mechanical stability of PP membranes used for long-term distillation process is considered. In this paper, we report on environmental fracture of PP membranes after long-term MD.

EXPERIMENTAL

Materials

Hydrophobic capillary polypropylene membranes (Accurel PP S6/2, Membrana GmbH, Germany), with outside/inside diameter equal to $d_{out}/d_{in} = 2.6 \text{ mm}/1.8 \text{ mm}$, were used in the studies. The capillary membranes have the pore size with the maximum and nominal diameter of $0.55 \mu\text{m}$ and $0.22 \mu\text{m}$, respectively, and the porosity of 72% (manufacturer's data). Membranes manufactured 1, 4 and 8 years prior to presented investigations were used (marked P1, P4 and P8, respectively). The membranes were stored in an air atmosphere, but without light deposition.

Methods

Polypropylene membranes were working in MD process at different conditions since we were interested in mechanical strength of membranes, which in turn depended on thermal and chemical degradation of the polymer. The membrane resistance experiments were performed using two testing protocols:

- membrane distillation with distilled water or the solution of 250 g NaCl/dm^3 used as a feed;
- membranes soaked for two months in the thermostated (347 K) baths (distilled water and solutions of 200 or 300 g NaCl/dm^3).

The laboratory MD equipment is presented in Figure 2. The membrane modules without housing were used. The testing membranes were arranged as a parallel bun-

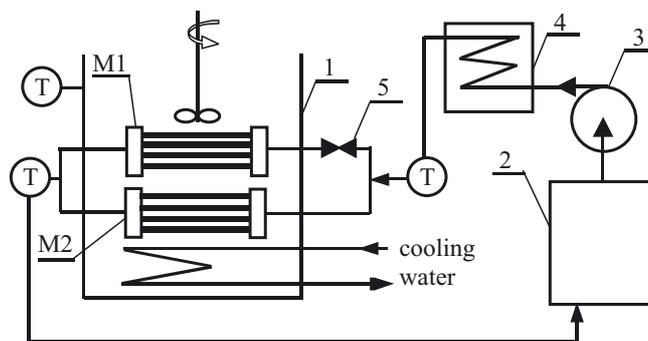


Fig. 2. Scheme of experimental equipment for MD: 1 — distillate tank, 2 — feed tank, 3 — pump, 4 — heat exchanger, 5 — valve, T — thermometer, M1 and M2 — membrane modules

dle of capillaries. The modules were assembled in the MD installation in a horizontal position. Installation was operating 5—6 h a day. The feed flow was inside the capillaries, whereas the distillate (demineralized water) flow through the inter-capillary space. The distillate temperature amounted to 295 K, and was kept constant during the MD process. The inlet and outlet temperature of the feed was 350 and 340 K, respectively.

The MD process was carried out continuously or continuously/periodically. In the last case, the modules M1 and M2 were equipped with the same type of membranes (P1, P4 or P8). During periodic investigation, the valve 5 (Fig. 2) was closed and opened every 10 min. This operation caused temperature changes within module M1 from 295 K to 350 K six times per hour. An assumption was taken into account, that polymers can undergo crazing in response to thermal shock, *i.e.* when the component undergoes large cyclic temperature variations.

Brand-new Accurel PP membranes are flexible. Stiffness of polymeric membranes was systematically investigated by simple test: a membrane was removed from a module and fixed from one side, while from the other side the capillary membrane was bended until to angle equal 90°. In this way, the breaking angle was evaluated during experiments.

The measurements of characteristic polymer temperatures [glass transition temperature (T_g) and melting temperature (T_m)] can be very useful indicators for evaluating the extent of degradation of polymer [10, 11]. Thermal properties of used polypropylene membranes were evaluated by differential scanning calorimetry (DSC). Measurements were made with use of Q1000 TA Instruments apparatus, at heating-cooling rate of 10 deg/min.

Changes of the crystallinity of the membrane materials were evaluated using X-ray diffractometer HZG-4 (Germany) equipped with $\text{Co}\alpha$ cathode.

Scanning electron microscopy (SEM) was used to evaluate membrane's morphology. Jeol JSM 6100 SEM operated at accelerated voltage of 20 kV was used. The samples were sputter coated with gold and palladium.

The studies by Fourier transform infrared spectroscopy (FT-IR) using a FT/IR-430 apparatus (Jasco) coupled with Harrick equipment for diffuse reflectance spectroscopy technique (DRS) have been carried out in order to determine the composition of the membrane materials.

RESULTS AND DISCUSSION

Polypropylene is classified as non degradable material, therefore to determine the long-term stability and performance, we used membranes which were manufactured from 1 to 8 years before the experiment. The DSC scans of investigated membranes showed small differences in thermograms when phase transitions of polypropylene were recorded during first heating run (Fi-

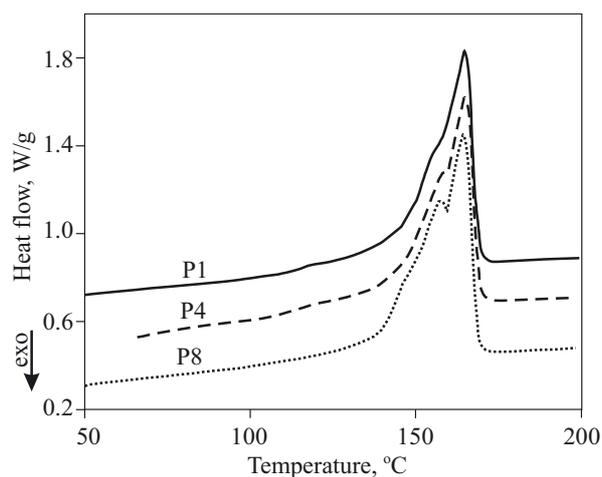


Fig. 3. DSC scans (first heating curves) obtained for brand-new Accurel PP membranes with different storage time: P1 — 1 year, P4 — 4 year, P8 — 8 year

gure 3). However, these small changes in amorphous regions of material can be responsible for decreased impact properties of the polymer. The mechanical properties of semicrystalline polymers like PP are significantly influenced by their crystalline structure. During polymer storage, the secondary crystallization can occur, and as a result, the decrease in the amorphous layer thickness is observed [10]. Partial degradation of polymer can also occur under interaction with surrounding environment (*e.g.* oxidation). The complete description of thermal characteristics of P1, P4 and P8 membranes are presented in Table 1.

Table 1. Thermal transitions of P1, P4 and P8 samples of brand-new Accurel PP membrane

Sample	I run (heating)			Cooling (crystallization)		II run (heating)	
	T_m °C	T_{m2} °C	ΔH_m J/g	T_c °C	ΔH_c J/g	T_m^{II} °C	ΔH_m^{II} J/g
P1	165.2	—	87.4	117.2	86.7	162.5	86.6
P4	164.7	— ^{a)}	90.5	118.1	87.6	161.8	88.9
P8	164.3	157.1	95.6	118.2	88.8	161.2	90.6

T_m , T_c — melting and crystallization temperatures; ΔH_m , ΔH_c — melting and crystallization enthalpy.

^{a)} Formation of a second melting peak on the lower-temperature shoulder of the main transition was observed.

The results presented in Table 1 indicate small decrease in melting temperature (T_m) and simultaneous increase in melting enthalpy (ΔH_m), with increasing storage time of the sample (from P1 to P8). During the manufacturing process of PP membranes — final stage — polymer melt is quenched and thus, an initial crystallization occurs. As a consequence, small and numerous crystals are formed except the amorphous phase formation. We

can speculate, that during a long storage of PP membranes, a slow process changing primary PP membrane structure can occur (secondary crystallization). DSC analysis shows depression of the melting point due to the formation of oligomeric fraction of polypropylene in membrane material. Moreover, increase in ΔH_m values indicated that the crystallinity of the polymer also increased during the storage of membranes. Formation of secondary peak (T_{m2}) was observed for polymers stored for several years. This secondary, lower temperature melting endotherm peaks arise due to crystal growth in the amorphous phase and a corresponding reorganization in the higher melting crystal structure [10].

In spite of differences in the storage time these membranes did not differ by eye inspection. The used Accurel PP S6/2 membrane samples were flexible and elastic, and can be bent without fracture. SEM investigations of several membrane samples did also not reveal significant differences in their morphology. Surface morphology presented in Figure 4 was characteristic for all samples tested. Thus, it can be concluded that morphology of P1, P4 and P8 membrane samples was independent on the storage time.

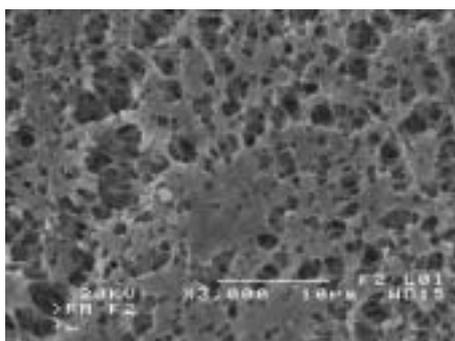


Fig. 4. SEM image of internal surface of Accurel PP S6/2 capillary membrane (sample P4)

Accurel PP membranes manufactured for microfiltration processes are stable up to 4 years according manufacturer's data (storage in nitrogen atmosphere). However, in the MD process, the operation conditions are different because membrane pores are filled in with an air and temperature is much higher. In this situation, thermal oxidation of PP membranes may occur. In order to evaluate such possibility, PP membranes were placed in water and saline solutions (not saturated) at 347 K for two months. After storage time, membranes became more brittle. Simple bending test showed that only membranes immersed in water can be bent up to 90° without any damage. For the rest of samples, visible and permanent deformations of membrane walls were observed. DSC phase transitions for P4 membrane samples soaked in different solutions are collected in Table 2. The obtained results confirmed that thermal oxidation of crystalline polymers led to the appearance of low tem-

perature melting peaks. The main melting peaks are generally also shifted to lower temperatures. Another important change that accompanies thermal oxidation is a reduction of the area under the melting (melting enthalpy), as well as the crystallization peaks (crystallization enthalpy) [10]. These results show that saline solutions significantly change the PP membrane properties. Polypropylene is hydrophobic material, however, it has relatively high surface energy (29 mN/m) what resulted in partial surface wetting of Accurel PP membranes after two weeks of MD process [4, 12]. Probably, the wet surface enables salt penetration into the polymeric material structure. The presence of salt apparently stiffens molecule, prevents disentanglement and ultimately leads to chain scission. This decreases polymer's toughness [10]. The membrane resistance to salt solutions is a vital problem since main applications of MD are separation of brackish water and brines [3—6, 13—15].

Table 2. Thermal transitions of Accurel PP membrane (P4) soaked for two months in different solutions at 347 K; symbols' meaning is the same as in Table 1

Solutions	I run (heating)			Cooling (crystallization)		II run (heating)	
	T_m °C	T_{m2} °C	ΔH_m J/g	T_c °C	ΔH_c J/g	T_m^{II} °C	ΔH_m^{II} J/g
initial	164.7	— ^{a)}	90.5	118.3	87.6	161.9	88.9
water	164.3	— ^{a)}	84.1	115.7	82.1	160.9	81.6
200 g NaCl/dm ³	163.4	156.7	85.7	115.8	85.3	160.2	84.4
300 g NaCl/dm ³	162.8	155.1	69.3	116.4	65.8	159.8	63.6

Table 3. Temperature transitions of P4 and P8 membrane during continuous or periodic MD process operation for different periods of time; symbols' meaning is the same as in Table 1

Samples/ MD process duration, h	I run (heating)			Cooling (crystallization)		II run (heating)	
	T_m °C	T_{m2} °C	ΔH_m J/g	T_c °C	ΔH_c J/g	T_m^{II} °C	ΔH_m^{II} J/g
Continuous MD; feed: distilled water							
P1/50	164.3	— ^{a)}	84.13	115.8	—	160.9	81.64
P8/37	165.7	156.6	84.2	117.6	84.4	162.1	83.6
P8/1400	164.5	154.3	85.6	116.2	83.1	161.2	81.7
Continuous MD; feed: 250 g NaCl/dm ³							
P8/140	164.2	156.8	83.3	117.9	88.0	159.4	86.1
P8/180	162.7	153.5 157.6	82.9	118.5	89.5	157.9	84.8
Periodic MD; feed: 250 g NaCl/dm ³							
P8/81	164.4	159.2	84.9	118.7	85.6	160.2	84.2
P8/171	163.8	157.1	72.3	118.3	90.2	158.3	87.1

During the MD process, temperature gradient is observed (Fig. 1), what can lead to occurrence of internal

stresses and can be additional factor affecting degradation. To assess membranes stability during MD process, P8 membranes were examined after exposure to distilled water at 350 K. The obtained DSC results are summarized in Table 3 (continuous MD). Polymers, which were used in modules operating for 37 h, showed slightly altered crystallization temperature (T_c). For membrane sample from module working for 1400 h. T_c decrease from 118.2 °C (Table 1) to 116.2 °C (Table 3) was found. As a consequence of this decrease, changes of crystallization enthalpy (ΔH_c) are also observed. T_m^{II} remains unchanged, however melting enthalpy in second heating (ΔH_m^{II}) decreases with increasing exposure time to hot water (the lowest value was observed for sample P8 treated for 1400 h). All materials become more rigid after such treatment, but showed no sign of damage. Similar pattern of changes was observed for P4 material, exploited for 50 h.

Having changed a feed from distilled water to NaCl solution (250 g/dm³), we noticed that MD module with P8 membrane operating at continuous conditions for 180 h showed double T_{m2} peak during first heating and unchanged T_c in contrast to experiments with distilled water (Table 3). ΔH_c was also unchanged. Melting temperature and enthalpy decreased with increasing exposure time. We also observed, that membranes became brittle and were susceptible to fracture after removing them from the module, as showed in Figure 5. This confirmed previous observations, that the presence of NaCl in the feed accelerated negative changes (degradation) in membrane performance.

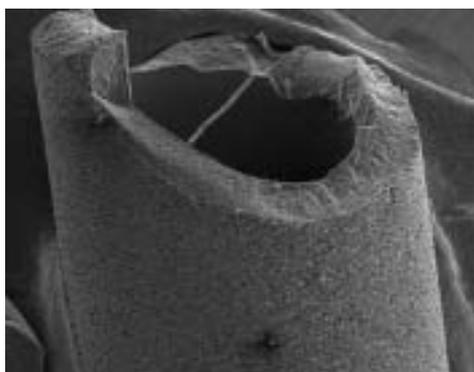


Fig. 5. Fracture surface of P8 membrane broken after 160 h MD process of concentrated NaCl solution

During periodical MD investigations, the membranes were heated to 350 K and after 10 min cooled down to 295 K, and after next 10 min again heated to 350 K. In other words, the MD process was started three times per hour. This caused relaxation of residual stresses and allowed some loss of molecular orientation. High residual stresses in the form of surface tensile stress are generally responsible for premature partial failure. The crazes or cracks will appear in areas where high tensile stress is



Fig. 6. SEM image of the fracture surface of crack in the membrane wall observed in the samples after 171 h periodic MD process of NaCl solutions

concentrated [10]. The SEM image presented in Figure 6 confirmed that cracks were found on the membrane surface, which temperature was changed over 1000 times. The results of DSC analysis of P8 membrane samples are presented in Table 3. Analysis of thermal transitions during second heating indicated significant decrease in ΔH_m^{II} for membrane operating for 81 and 171 h, what can indicate decreased polymer crystallinity. Melting temperatures are also diminished as compared to the neat membrane (Table 1) while T_c remains unchanged.

FT-IR investigations of membrane samples of different storage time showed almost identical spectra (spectra not presented here). Some little differences were observed only for membranes subjected to severe damage during the experiment (membranes showed in Figs. 5 and 6). The bands which can be used to determine the crystallinity of PP appeared at 1166, 998 and 840 cm⁻¹ [10]. In our experiments, significant changes were found only at 1166 cm⁻¹. In a region 1550–1750 cm⁻¹, an additional broad peak was observed or intensity of existing peaks was enhanced. This region is characteristic for C=O bonds. This can confirm that degradation of polymer *via* oxidation processing can occur.

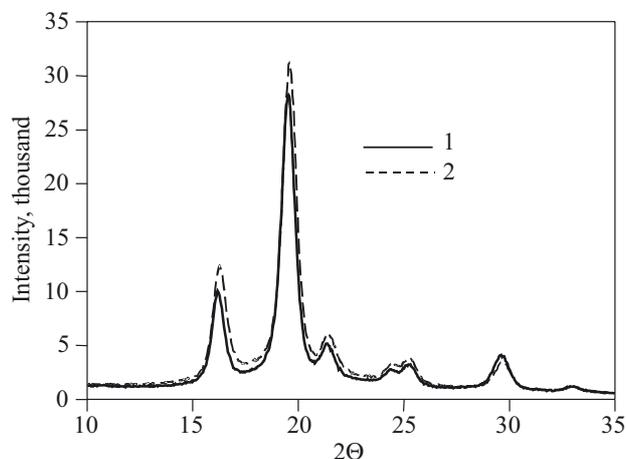


Fig. 7. Comparison of XRD analyses results obtained for new Accurel PP membrane (1) and membrane used in MD process (P8) with NaCl solutions (2)

The changes of crystallinity of polymer material were investigated using a Simens diffractometer, recording the wide angle scatter in the region of $10^\circ \leq 2\Theta \leq 80^\circ$. The crystallinity level was determined from the peak areas in the region of $10^\circ \leq 2\Theta \leq 30^\circ$ [14]. The results obtained for brand-new Accurell PP S6/2 membrane and this membrane after 180 h MD process of NaCl solution were presented in Figure 7. There is no formation of a new crystalline phase, therefore both diffractograms look alike. Small change in peaks intensity can be observed, what can indicate the increase in crystallinity of PP membrane during MD process.

CONCLUSIONS

We observed that slow degradation of PP membranes occurred during storage of the material. Despite of those structural changes, the brand-new membrane properties (*e.g.*, porosity, flexibility) were not affected by the type of investigated membranes (even for 8 year old membranes).

Polypropylene membranes used in distillation process are losing their flexibility, become brittle, and as a consequence, they show susceptibility to cracking and fracture during long-term usage in MD modules.

The conditions of MD process (at elevated temperature, presence of air) were affecting changes of crystallinity of PP membranes (increase in crystallinity) and decreasing molecular weight of polymer. Small changes of these parameters significantly reduce membrane's performance.

The presence of solutes (NaCl) in the feed accelerated intensity of the membrane degradation. Similarly nega-

tive effects were obtained by changes of material temperature with high frequency.

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