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Performance of Solvent-Pretreated Polyimide Nanofiltration Membranes for Separation of Dissolved Dyes from Toluene

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The major problem reported for commercially available membranes is their limited chemical stability in organic solvents. This article reports the influence of organic solvents with different polarity (methanol, acetone, acetic acid, toluene, and *n*-hexane) on the filtration performance of STARMEM membranes. These membranes are specified to be compatible with the solvents used. The pure toluene flux of these membranes and the rejection of azo dyes (Sudan Black and Rhodanile Blue) were measured before and after a week of exposure to one of the above-mentioned solvents. The results show that the structure of the membrane changed after pretreatment with polar solvents (methanol, acetone, acetic acid) and that the membrane performance shifts toward lower rejections with higher solvent flux. Nonpolar solvents do not change the polyimide membrane performances significantly. Contact angle measurements on new and solvent-treated membranes show that organic solvents change the hydrophobicity of polymeric membrane surfaces, leading to different toluene permeabilities before and after solvent treatment. Swelling measurements confirm the theory that a reorganization of the membrane material takes place, which leads to differences in porosity and changes in rejection. The study also shows that pretreatment of polyimide membranes with polar solvents increases the recovery of the membrane system when the solute size is large enough.

1. Introduction

Over the past decade, solvent-resistant nanofiltration (SRNF) was used as a separation process for product recovery in organic media.[1] SRNF is a promising energy-efficient and environmentally friendly unit process. Conventional polymeric membranes for water purification have a limited chemical resistance and cannot be applied for solvent separation. Solving the key problems (dissolution and disintegration of the membrane) throughout the membrane manufacturing process, researchers were successful in improving the stability of nanofiltration membranes and introduced a new generation of membranes that are stable in solvent media.[2] Every membrane system includes the arrangement of membrane module, pumping the feed from the tank through pipes, controls and monitoring, feed pretreatment, membrane pretreatment, and cleaning. Among all these aspects, membrane pretreatment attracted the least investigation. Membrane pretreatment is a part of the process design that has a strong influence on NF performance in aqueous and nonaqueous systems. General solvents used for membrane manufacture are glycerol, water, etc., which may remain in the membrane and affect the permeation of other solvents through the membrane. Therefore, membrane pretreatment is necessary to extract and exchange any residual solvents present in the membrane. Exchange of these residual solvents needs a suitable pretreatment method. Water is frequently used as a pretreatment solvent in aqueous NF. However, in SRNF, pretreatment should be carried out with suitable solvents. Unlike water, organic solvents can affect the membrane polymeric matrix. The following effects are reported in literature[3] for SRNF membranes: (i) changing the surface energy properties with no chemical effect on structure; (ii) swelling; (iii) slow dissolution of the membrane or disintegration of the membrane through the extensive swelling; and (iv) relaxation of polymer chains due to plasticization in organic solvents, resulting in swelling

with subsequent pore size reduction. These effects are related to the polymer type and manufacturing method (cross-linking) as well as the solvent's functional group(s). Most commercial SRNF membranes keep their separation performance in contact with nonaggressive solvents; however, they swell or disintegrate in more aggressive solvents. Van der Bruggen et al.[4] studied the effect of different organic solvents on the performance of commercially available nanofiltration membranes, which were specified to be compatible with the solvents used, in aqueous media. This study was carried out with the best available membranes at that time, which were mostly used in aqueous applications. However, membrane structures have been improved since then. Possible pretreatment methods include immersion in the pure solvent, gradual conditioning of membrane, and washing out of preserving solvents with pure solvent. These will be described below.

Pretreatment in Pure Solvent. In this method, applied by most researchers, the membrane is soaked in the test solution or test solvent prior to the experiment. Different pretreatment durations are reported in the literature. Han et al.[5] studied membrane rejections for several ionic liquids in methanol, toluene, and ethyl acetate with the STARMEM membranes. Experiments were conducted by preconditioning the membranes with pure methanol overnight to stabilize solvent fluxes before starting tests. Dijkstra et al.[6] studied the permeation of various mixtures of pentane−decane and pentane−dodecane through dense laboratory-made polydimethylsiloxane/polyacrylonitrile (PDMS/PAN) membranes. Their membranes were pretreated in the test solvents to be measured for at least 12 h. Silva and Livingston[7] examined fluxes and rejections of STARMEM122 for dissolved components in methanol. They soaked the membrane in lube oil, which is a preserving agent. Yang et al.[8] measured rejections and stability of different commercial NF membranes with aqueous and organic solution containing three different solutes with the same molecular weight. Van der Bruggen et al.[9] measured the rejection of 2′,2-methylenebis-(6-*tert*-butyl-4-methyl phenol) in water, ethanol, and *n*-hexane

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solution by hydrophilic and hydrophobic SRNF membranes. They applied pretreatment of the membranes by immersion for 24 h in the solvent used for flux measurements. They found that alterations in the membrane top layer structure change the hydrophobicity or hydrophilicity of the membranes. Ebert et al.[10] tested a laboratory-made PDMS membrane in a solution of polyethylene glycols dissolved in solvent mixtures containing ethanol and different amounts of alkanes (*n*-pentane, *n*-hexane, etc). Prior to the measurements, the membranes were soaked for 12 h in the respective solvent or solvent mixture. Separation of homogeneous catalysts from a synthetic postreaction solution was studied by Scarpello et al.[11] and Nadir et al.[12] They soaked the STARMEM122 and MPF50 membranes in toluene, which was the solvent used for reaction. Geens et al.[13] studied the effect of feed composition in binary mixtures of water−alcohol on permeability and rejection of dissolved solute. They pretreated the membranes by immersing them for over 20 h in the starting solvent of the measurement series, i.e., water for the water−methanol and water−ethanol series, and methanol for the methanol−ethanol series. Ribeiro et al.[14] used *n*-hexane as pretreatment solvent in the NF process for recovery of solvent from a mixture of soybean oil and *n*-hexane. Machado et al.[15] measured the permeability of different classes of solvent through the PDMS membranes. They washed the membrane in distilled water and then soaked it in ethanol for 24 h before use.

Pretreatment through Gradual Conditioning of the Membrane. Tsui and Cheryan[16] applied a gradual solvent-exchange procedure to study the performance of NF membranes in ethanol solution. Membranes supplied in semidry or wet (with water) form were first washed to remove the preserving agent by filtration of deionized water. Chemicals in the membrane pores were flushed out by deionized water afterward. The membrane was then soaked in 10% (v/v) aqueous ethanol for one night. The membrane was then placed in the cell, and the flux of 10% ethanol was measured. Afterward, the membrane was pretreated in 20% ethanol overnight again, and the flux for 20% ethanol was measured. This procedure continued at 10% ethanol intervals until 100% ethanol was reached. They also used MPF-44 and MPF-60 membranes, which were available in 50% aqueous ethanol. These membranes were not exposed to water anymore. They found that the membrane performance is better when membranes were preconditioned by gradual solvent exchange. Bhanushali et al.[17] immersed PDMS-based (hydrophobic) membranes in distilled water for 30 min to eliminate manufacturing agents inside the membranes and then soaked them in isopropanol for 30 min in the case of a polar solvent (alcohol). For measuring the *n*-hexane flux, the membrane was then soaked in a mixture of 50−50 vol % isopropanol−*n*-hexane for 30 min followed by soaking in pure *n*-hexane for 30 min. Shukla and Cheryan[18] studied the effect of the pretreatment method on the performance of ultrafiltration (UF) membranes in a mixture of 30−70 vol % water−ethanol. They applied four different procedures: (i) gradual change from 0 to 70% ethanol similar to that in ref 16; (ii) direct change from 0 to 70% ethanol; (iii) direct exposure to 70% ethanol; and (iv) 100% ethanol to 70% ethanol. They claimed that gradual solvent exchange, i.e., gradual change from 0 to 70% ethanol, appears to be the most promising procedure for completely miscible solvents such as ethanol−water mixtures.

Washing out the Preserving Solvent with Pure Solvent. Koris and Vatai[19] screened the application of membranes in the oleochemical industry for degumming vegetable oil. First, they washed the membrane with distilled water for removing residual agents present in the membrane after the manufacturing

process (i.e., glycerol). After that, the properties of the membrane surface and the pores were changed to nonpolar by washing with pure solvent. Stafie et al.[20,21] studied *n*-hexane extraction from vegetable oil−hexane miscella with membranes. They flushed out the membrane preserving chemicals by pure *n*-hexane permeation. Then the hexane was replaced by an oil/hexane solution in filtrations device. Gibbins et al.[22] and Toh et al.[23] use the solvent of the filtration solution to flush out the membrane residue. The pure solvent filtration continued to reach the stable amount of flux. Han et al.[24] used MPF50 to extract phenol and toluene from water by membrane solvent-extraction technology. Decanol was used as the extractor solvent. For pretreatment, this solvent was recycled through one-half cell of the extraction module (the side with higher affinity toward the solvent) to fill membrane pores. Lencki et al and Williams[25] studied the effect of aqueous methanol, ethanol, and acetonitrile solutions on the flow resistance behavior of cellulose and polysulfone ultrafiltration membranes. They soaked the membranes overnight in the test solution and then rinsed thoroughly with water to remove all membrane preservatives. Whu et al.[26] applied SRNF to a methanol−pharmaceutical solution. They immersed the membranes in deionized water overnight to remove the preserving solution. The membrane then was pretreated by flushing it with ethanol. Sheth et al.[27] applied the same pretreatment procedure for extraction of methanol in solution containing a pharmaceutical component methanol. Darnoko[28] investigated the separation of carotenoids from methyl esters by DS7, MPF60, and MPF44 membranes. *n*-Hexane (which was not the test solvent) was used as the pretreatment liquid to wash out the residue from the membrane.

No Pretreatment. Tarleton et al.[29] did not apply any pretreatment to the laboratory-made PDMS membrane. They studied the PDMS separation performance for solutes dissolved in *n*-heptane, cyclohexane, and xylene. Vankelecom and co-workers[30,31] also did not report any pretreatment prior to the filtration experiment with commercial and laboratory-made PDMS membranes. Koike et al.[32] studied the separation of free fatty acids, phosphatides, sterols, tocopherols, pigments, etc. from vegetable oil by using a variety of nonporous SRNF membranes without any preconditioning.

The aim of this research is to study the effect of solvents with different polarity on the performance of the commercial polyimide membranes (STARMEM) for organic solvent filtration. STARMEM membranes are promising next-generation membranes with good performance for organic solvent filtration. By starting from a literature study of different membrane-pretreatment procedures applied to polymeric membranes in solvent separation, the effect of different classes of organic solvent on the separation performance of commercially available polyimide membranes (STARMEM) in toluene-solvent dye solutions will be investigated.

2. Materials and Methods

Solvents and Solutes. Acetic acid, methanol, acetone, toluene, and *n*-hexane were selected in this study. These solvents belong to different chemical families, which gives the opportunity to monitor the effect of functional group on the membrane. All solvents were analytical grade (>99%) and were supplied by Across Organic (Across, Belgium). Sudan Black (456.54 g mol^{-1}) and Rhodanile Blue (778.38 g mol^{-1}) have been selected to study the solute rejection. Because of solubility constraints, low concentrations (∼10 mg/L) of these dyes in toluene were prepared. The reason for choosing toluene as the solvent of study is that STARMEM membranes are well-known

in toluene solution (based on the manufacturer data sheet). This can be taken as a reference for the membrane's performance. Solutes were purchased from Sigma-Aldrich (Germany). Because of the low solubility of Rhodanile Blue in nonpolar solvent, this dye was dissolved in 50 mL of ethanol first and then toluene was added to make the final solution.

Membranes. STARMEM122 and STARMEM240, an asymmetric SRNF membrane with a top layer of polyamides, were selected for the experiment. These membranes are known to have an excellent performance for SRNF separation. The nominal molecular weight cutoffs (MWCOs) are 220 and 400 g mol^{-1}, respectively (based on manufacturer data). Reported applications for these membranes include dewaxing of lube oil,[33] recycling of homogeneous catalysts,[11] and green chemical processing.[34]

Pretreatment Procedure. Residual solvents, which remain during membrane manufacturing, may affect the permeation of other solvents through the membrane. Glycerol and water are common solvents in membrane manufacturing[1] and should be washed out. The aim of paper is to investigate the effect of different solvents on the performance of SRNF membranes. This aim could be fulfilled only if the membrane were pretreated in pure solvent. The other discussed methods of pretreatment could not present a valuable understanding in this context. Membranes were cut in a circular shape with a diameter of 49 mm and then washed with water. The remaining water on the membrane surface was wiped off with a soft tissue. For every solvent, five sheets of each membrane were immersed in a glass bottle containing this solvent. The membranes were in the solvent for at least one week prior to the experiment to ensure fully equilibrated conditions.

Filtration Procedure. Retentions and permeabilities of membranes were determined using two parallel dead-end stirred cells (HP4750). A schematic of these filtration modules is presented elsewhere.[35] The effective membrane area is 14.6 cm^2. The solution inside the module was stirred by a Teflon-coated magnetic stirrer at 1200 rpm. The applied pressure was between 10 and 60 bar for pure toluene flux and 20 bar for rejection experiment. All experiments were carried out at ambient temperature. Pure toluene permeation was carried out prior to using dye−toluene solution. Filtrations were stopped when half of the volume of the feed solution had permeated. Graduated volumetric cylinders were used for measurement of the permeability. A Shimadzu UV-1601 double-beam spectrophotometer was used to analyze the concentration of dyes, which absorb light in the visible region. For each dye, the light spectrum was scanned to find the wavelength with the highest absorption peak ($\lambda_{Sudan\ black}$ = 575.5 nm and $\lambda_{Rhodanile\ Blue}$ = 614 nm). At this wavelength, calibration curves were made based on the law of Lambert−Beer, which assumes a linear relationship between the logarithm of the solute concentration and the absorbance.

Contact Angle Measurement. Contact angle measurements are used as a measure for the degree of hydrophilicity/hydrophobicity of the membranes. Theoretically, contact angles may vary from 0° to 180°. The higher the affinity between the solvent drop and the membrane surface, the smaller is the contact angle, resulting in a higher degree of surface wetting. In the case of water as solvent, hydrophilic surfaces show a small value for the contact angle, whereas hydrophobic surfaces show a large contact angle. Contact angle measurements were carried out with a Krüss DSA10 setup. For sessile drop fitting, the Young−Laplace fitting, theoretically being the most exact method for calculating contact angles, was used. Here, membranes were exposed to the different solvents for a week. Before
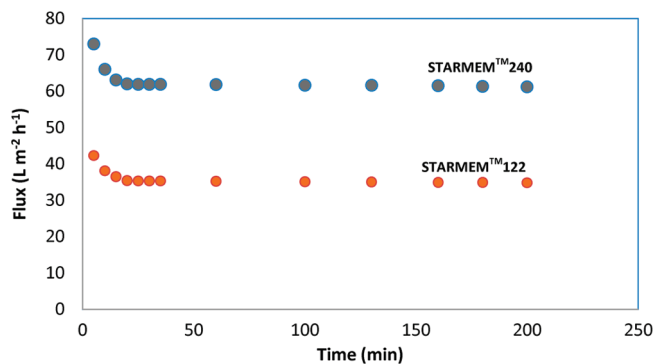

Figure 1. Flux of pure toluene through the membranes as a function of time (overall pressure was 30 bar and fluxes reach steady-state condition after 20 min).
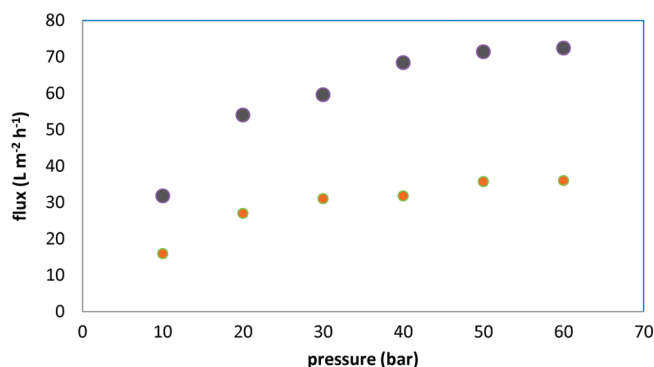

Figure 2. Nonlinear influence of pressure on flux for pure toluene (fluxes reach steady-state condition after 20 min).

contact angle measurement, samples were soaked in toluene for 2 h. It was assumed that solvent exchange occurs in the membrane prior to the experiment. Following this, the remaining solvent was wiped off by a very soft tissue.

3. Results and Discussion

It is obvious that the structure of SRNF membranes should not change by the impact of different classes of organic solvents, so that their separation performance remains unchanged. Thus, the permeability and rejection of membranes should remain constant after exposure to organic solvents. Except for ceramic membranes, which have a rigid structure, network deformation may occur for all polymeric membranes. This may range from swelling to complete deterioration of the membrane structure. STARMEM membranes are well-known for their good performance in a solvent-separation process and are widely used by researchers.[7,23,36−49] The manufacturer's datasheet claims that these membranes are well designed for applications related to different solvent classes, specifically for treatment of toluene.[50] In a first step, to check the validity of our experimental data, the permeabilities of untreated membranes were measured in toluene. Figure 1 shows the permeability of two membranes as a function of time. There is a minor permeability drop in the first 20 min for both membranes; the permeabilites reach steady-state conditions afterward.

Measured permeabilities for STARMEM 240 are higher than indicated by the manufacturer (20 L m^2 h^{-1}). The lower applied pressure here (30 bar) compared to the pressure applied by the manufacturer (55 bar) may cause this higher permeability. To confirm this, the toluene fluxes are measured at different pressures for both membranes. Figure 2 shows the effect of pressure on the membrane flux. As can be seen, a nonlinearity
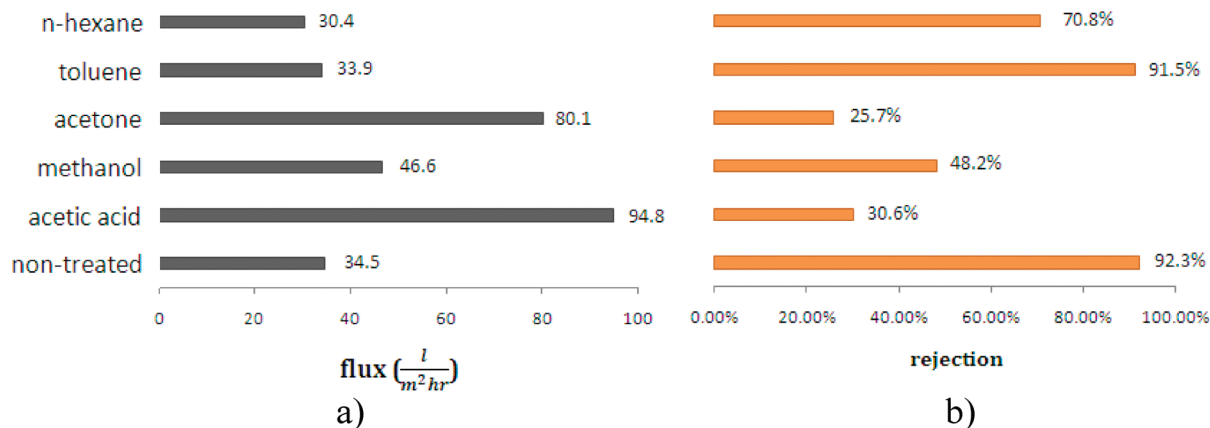
Figure 3. Effect of solvent treatment on STARMEM122 membranes performance: (a) flux of toluene (the numbers beside the lines indicate the amount of flux) and (b) rejection of Sudan Black (the numbers beside the lines indicate the amount of the rejection).
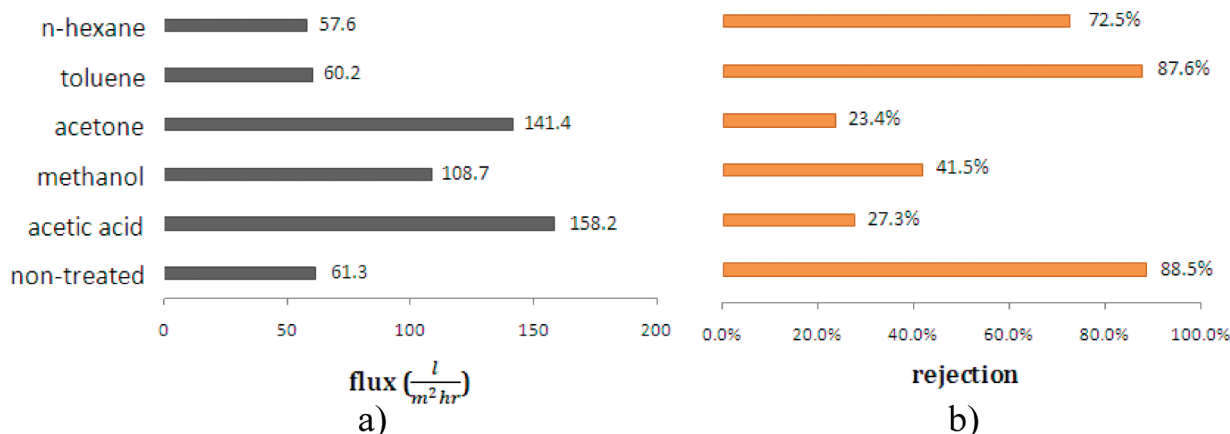

Figure 4. Effect of solvent treatment on STARMEM240 membrane performances: (a) flux of toluene (the numbers beside the lines indicate the amount of flux) and (b) rejection of Rhodanile Blue (the numbers beside the lines indicate the amount of the rejection).

between the flux and the applied pressure has been observed. The nonlinearity in solvent permeations by increasing the operation pressure was also observed previously for solvent filtration.[15,22,48,51]

Compaction of membranes usually takes place under high pressure. The following relation can be used to take this effect into account:[6]

$$ J_i = L_{p,i}^0 \, e^{(-\alpha_{p,i} \triangle p)} \triangle p $$

where $L_{p,i}^0$ is a permeability constant and $\alpha_{p,i}$ is an empirical pressure coefficient, which expresses a compression effect. Compaction may affect the effective thickness of the membrane. This would not relate to the physical thickness of the membrane (i.e., the top layer and all support layers), which is thought to decrease after compaction, but to the part that contributes to the membrane resistance and separation (the "effective" thickness). Because of the pressure, the top layer penetrates into the support pores so that the part of the membrane structure that contributes to the membrane resistance is now more than only the top layer; the sublayer also contributes to this. This is assumed to be the reason for the nonlinear behavior of fluxes observed in the case of toluene, for both membranes. The following equation can be used for the estimation of the membrane thickness:[6]

$$ \delta_M = \delta_M^0 \exp(\alpha_{p,i}) \triangle p $$

δ_M^0 is the membrane thickness under ambient pressure.

The rejections of nontreated membranes were also measured to compare with nominal values indicated by manufacturers (90% rejection). The nominal MWCO of STARMEM membranes was measured based on rejection of normal alkenes dissolved in toluene.[50] Rejection of Sudan Black (456.54 g mol^{-1}) was measured with STARMEM122 and Rhodanile Blue (778.38 g mol^{-1}) with STARMEM240. In both cases, solutes with molecular weight around twice the membrane MWCO have been chosen; therefore, higher rejections of these solutes were expected (more than the values indicated by manufacturers). The rejections of these two solutes, given in Figures 3 and 4 for nontreated membranes, are lower than the expected values. It is clear that the type of solute may change the nominal MWCO of the SRNF membranes.[8,52]

The values for permeability and rejection of solutes mentioned above for untreated membranes were used as reference to compare with rejection experiments for solvent-treated membranes. The effect of solvent treatment on the performance of STARMEM122 and STARMEM240 membranes is given in Figures 3 and 4. As shown, fluxes of toluene significantly changed when the STARMEM membranes were treated with different solvents (Figures 3a and 4a). The acetic acid-pretreated membranes had a toluene flux as high as 94.8 L m^{-2} h^{-1} for STARMEM122 and 158.2 L m^{-2} h^{-1} for STARMEM240 (Figures 3a and 4a), which is >2.5 times higher than the flux of nontreated membranes. Similar to acetic acid, acetone-treated membranes also had a high toluene flux (80.1 L m^{-2} h^{-1} for STARMEM122 and 141.4 L m^{-2} h^{-1} for STARMEM240).
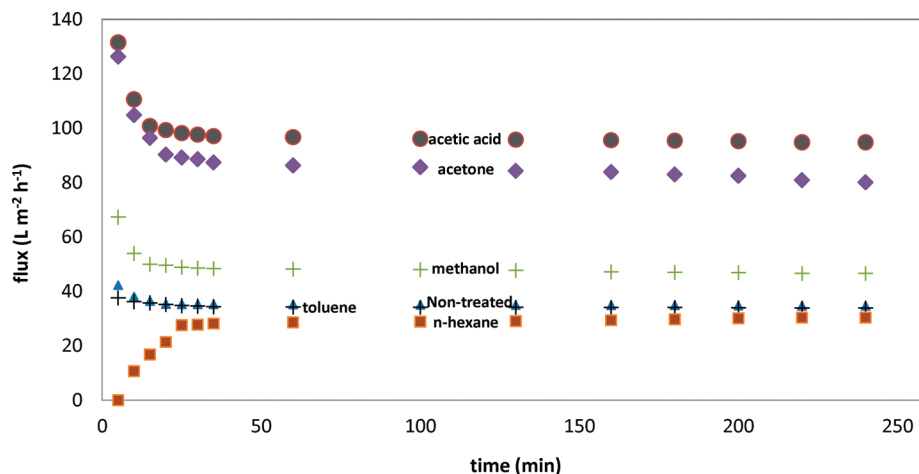
Figure 5. Comparison between flux of toluene through solvent-treated STARMEM122 membrane and nontreated STARMEM122 membrane versus time.
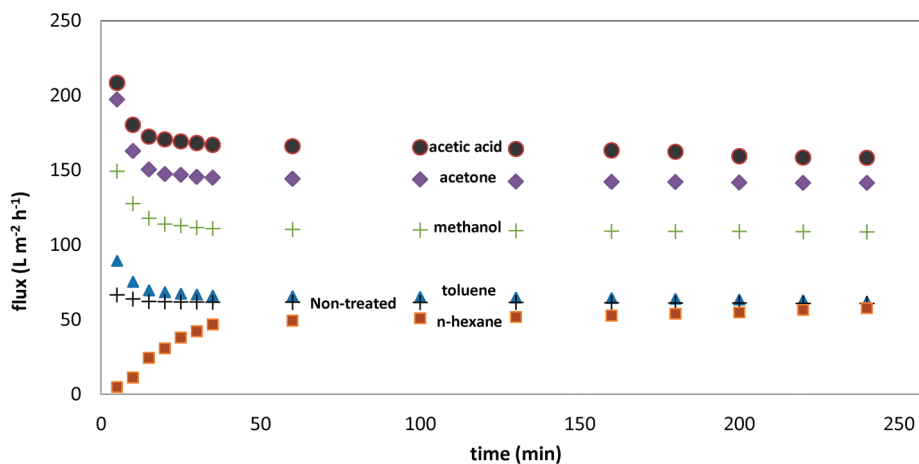

Figure 6. Comparison between flux of toluene through solvent-treated STARMEM240 membrane and nontreated STARMEM240 membrane versus time.

Treating the membranes with methanol increases the toluene flux moderately. *n*-Hexane- and toluene-treated membranes have approximately the same fluxes (~30 L m^{-2} h^{-1} for STARMEM122 and 60 L m^{-2} h^{-1} for STARMEM240), which is comparable to the nontreated membrane. The reversibility of the membrane pretreatment has been investigated for both membranes. The experiment was run until steady-state conditions were achieved. Fluxes of all solvent-treated membranes changed significantly, except for the toluene-treated membrane. Any explanation for this phenomenon could be based on the following: first, the surface energy of the membrane changes in contact with the solvent; second, the membrane internal matrix swells, which changes the membrane's performance. Figures 5 and 6 show the flux of toluene through solvent-treated membranes as well as nontreated membranes as a function of time. As illustrated, the flux reached a steady-state condition after the first hour. Only in the case of toluene-treated membrane is the flux similar to that for nontreated membrane. This indicates that solvent pretreatment is an irreversible phenomenon. Depending on the solvent, during solvent treatment the polymeric matrix structure may change. This polymeric matrix reorganizes again another time when a filtration experiment is run with toluene. The reason for flux decreasing in the first 30 min of the filtration experiment could be this structure reformation. In the case of toluene-treated membranes, the flux reaches the final value faster than for nontreated membranes. This was expected, since the membrane and solvent reached the equilibrium condition already when the

membrane was placed in the toluene container. The rejections of Sudan Black and Rhodanile Blue were also measured. Sudan Black, with a molecular weight of 456.54 g mol^{-1}, is 2 times above the nominal MWCO of the STARMEM122 (220 Da), while Rhodanile Blue (778.38 g mol^{-1}) is almost twice the MWCO for STARMEM240. The rejections of these azo dyes through the solvent-treated membrane are given in Figures 3b and 4b. The highest rejections were observed for the nontreated and toluene-treated membrane (>90% for STARMEM122 and >87% for STARMEM240. Around 70% rejection of dyes was achieved in both cases for *n*-hexane-treated membranes. Acetone-treated membranes had the lowest rejection, while acetic acid-treated membranes show a performance similar to acetone. Rejections improved slightly for methanol-treated membranes. Figures 3 and 4 show that the rejections of Sudan Black and Rhodanile Blue are related to the toluene flux. Lower rejections were found for the treated membranes, which have higher fluxes. This shows that the membrane pore size increases in contact with the treatment solvents. The STARMEM membranes are asymmetric solvent-resistant nanofiltration membranes with an active layer of polyimide and are thought to be porous.[22] Thus, the rejection capability of these membranes decreases when solvent permeability increases.

The acetic acid-treated membranes had a higher flux compared to the acetone-treated membranes, but rejections were lower than for the acetone-treated membranes. The flux of methanol-treated membranes is lower than acetic acid- and

acetone-treated membranes. Rejection values for methanol-treated membranes are also higher compared to those solvent-treated membrane. This indicates that methanol increased the membrane pore size moderately. It is obvious that toluene did not change the membrane structure since the membranes (toluene-treated and nontreated) kept their separation performance. A fairly good rejection was achieved with n-hexane-treated membranes, which showed the lowest permeability of the solvent-treated membranes. Results from filtration experiments for this membrane were in contrast with the other membranes (Figures 5 and 6). The flux of toluene increased whene final equilibrated value was reached, whereas for the other membranes the flux dropped to the end values. In addition, there was no flux at the start of the permeation experiment, which shows that n-hexane changes the membranes properties differently than the other solvents. Toluene changes the membrane structure again with increasing the flux.

Solvent-resistant membranes are known as membranes that keep their initial polymeric network arrangement and do not lose their structure and dissolve in contact with organic solvents. However, most polymeric membranes do not follow this definition and change their structure in most solvents. The STARMEM membranes have a quite acceptable performance for most of the common organic solvents. These membranes, which are solvent resistant and not visually damaged by the solvents while there is a change in their separation performance, may be referred to as semistable membranes.[4] A semi-solvent-stable membrane can be defined as a membrane keeping its mechanical strength, while its flux and rejection change because of interactions with organic solvents. To understand the solvent effect on membrane structure, a clear distinction should be made between polymeric materials, which have been used for membrane manufacturing. Van der Bruggen et al.[4] exposed the commercial hydrophobic MPF50 membrane to different solvents. This membrane showed a significant increase of the water flux upon exposure to ethanol and ethyl acetate. Because of the hydrophobic character of the membrane top-layer polymer (polydimethylsiloxane), the original fluxes were very small, although after contact with ethanol and ethyl acetate, it seems that the membrane became more hydrophilic. The polymeric network can be reorganized in contact with solvent. Roudman and DiGiano (2000) and Bridge et al. (2002) claimed that the hydrophilic groups in polymeric structure tend to form small "clusters" so that the membrane becomes locally hydrophilic, corresponding to the Flory–Huggins solution theory for polymer.[53] Although for MPF50 solvents affect the structure significantly by increasing the flux, the pore size does not change because only a small fraction of available hydrophilic groups is obtained. The effect of chain reorganization is more pronounced for semihydrophilic membranes such as STARMEM membranes, which are made from polyimide. The fraction of hydrophilic groups is obviously larger in polyimide compared to polydimethylsiloxane. These clusters develop into larger groups. In addition, because of this, chain reorganization could affect the pore sizes. In this case, rearrangement of the network may result in larger pores. Parallel to this, the membrane surface energy would be changed in contact with solvents. Geens et al.[3] studied the influence of solvent on membranes by measuring the surface contact angle and determining the weight difference between wet and dry membrane samples. They confirmed that solvents change the hydrophilicity of polymeric membrane surfaces, leading to different membrane performances. They also mentioned that swelling measurements show that reorganization of the membrane material takes place, which may lead to

Table 1. Contact Angles (With Standard Deviation) of Water on Nontreated and Solvent-Treated Membranes Soaked in Toluene

	contact angle of water on STARMEM122	contact angle of water on STARMEM240
nontreated membrane	55.1 ± 3.7	93.3 ± 4.3
acetic acid-treated membrane	68.7 ± 4.2	66.9 ± 3.4
acetone-treated membrane	62.4 ± 3.1	71.3 ± 4.1
methanol-treated membrane	65.1 ± 5.6	68.5 ± 5.1
toluene-treated membrane	71.1 ± 2.4	82.5 ± 2.6
n-hexane-treated membrane	70.3 ± 2.3	79.3 ± 3.3

Table 2. Contact Angles (With Standard Deviation) of Water on Nontreated and Solvent-Treated Membranes without Soaking in Toluene

	contact angle of water on STARMEM122	contact angle of water on STARMEM240
acetic acid-treated membrane	47.3 ± 3.6	36.2 ± 2.7
acetone-treated membrane	35.6 ± 2.8	43.4 ± 2.3
methanol-treated membrane	40.7 ± 5.2	37.6 ± 4.7
n-hexane-treated membrane	59.3 ± 2.8	77.6 ± 4.1

differences in porosity and changes in rejection. To confirm this hypothesis for STARMEM membranes, the contact angle (membrane−water) of both new and solvent-treated membranes was determined. Table 1 summarizes the results of the contact angle measurements.

Moderate contact angles for nontreated samples of STARMEM122 indicate that this membrane consists of both a hydrophilic and a hydrophobic part in the membrane polymeric matrix. STARMEM240 has a higher contact angle. Contact angles of the solvent-treated membranes are different from those of the nontreated membranes. These differences are solvent dependent. Solvent pretreatment increases hydrophobicity of STARMEM122, while hydrophobicity of STARMEM240 decreases. Total contact angels are lower for STARMEM122. For both membranes, toluene-treated membranes have higher contact angles compared to the other solvent-treated membranes. For STARMEM122, acetone-treated membranes had a lower contact angle, whereas the acetic acid-treated membrane has a lower hydrophobicity (large contact angle) for STARMEM240. In both cases, polar solvent-treated membranes have a lower hydrophobicity compared to apolar solvent-treated membranes. However, there is a slight difference between the contact angles of the solvent-treated membranes. Because of the initial fraction of hydrophilic and hydrophobic groups in a polyimide membrane, reorganization through solvent treatment may affect the overall hydrophilicity. After filtration with toluene, the surface hydrophilicity and the membrane structure change again. To prove this hypothesis, contact angles of solvent-treated membranes were measured again. After solvent treatment, the membranes were not soaked in toluene. The results are given in Table 2. The results for nontreated membranes and toluene-treated membranes were similar (not presented here).

For both types of membranes, solvent treatment decreases the surface hydrophobicity, except for STARMEM122, for which n-hexane increased the membrane surface hydrophobicity. In the case of STARMEM240, polar solvent decreased the hydrophobicity of the membrane dramatically. However, soaking the membrane in toluene increased the hydrophobicity in both cases. The membrane structure and hydrophilicity reform two times through the solvent-treatment procedure (Figure 7).

As a result of this reformation, the toluene flux will be different before and after exposure to the different solvents, with different effects in either surface tension or pore size. This was found indeed for polar solvents (acetone, acetic acid, and methanol), for which the difference between toluene fluxes both before and after the
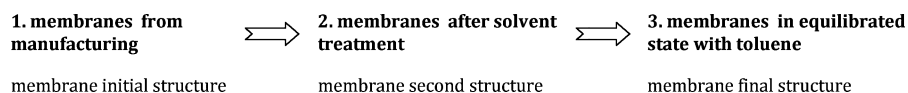
1. membranes from manufacturing ⟹ 2. membranes after solvent treatment ⟹ 3. membranes in equilibrated state with toluene

membrane initial structure   membrane second structure   membrane final structure

Figure 7. Reformation procedure in membrane structure during the pretreatment.

solvent treatment was >35% for STARMEM122 and 77% for STARMEM240. Moreover, deviations were found in both directions, i.e., an increase of the flux as well as a decrease of the rejection (pore size increases). The surprising results for membranes with *n*-hexane are possibly related to different clustering formation on the membrane. As mentioned for polar solvents, hydrophilic groups form clusters, while for apolar solvents this is caused by hydrophobic groups. There is no correlation between solvent properties and the effect on the toluene flux. This is not surprising, because the screening of the effect of nanofiltration experiments themselves should be carried out with a related solvent, not toluene. Complexity arises for understanding the changes in toluene flux, because these changes are a result of interactions between the solvents and the membrane material as well as interactions between toluene and the membrane, which both are largely unknown. Rejection of dyes is generally a result of size exclusion and depends on pore size and pore size distribution in the membrane top layer.[54] Rejection could change due to the contact with organic solvent, which results in a change in pore size or pore size distribution. Clustering of hydrophilic groups obviously increases the pore size of the STARMEM membranes, so that dye rejections as a result were lower after treatment with polar solvents. The effect of clustering is smaller in the case of nonpolar solvents, because it seems that the solvent (*n*-hexane) had less effect on the membrane. Solvent-resistant membranes have less changes in the polymeric matrix of the top layer, so the membrane performance is slightly affected by organic solvents. In this view, STARMEM membranes should be denoted as "semisolvent resistant", with reformation of the structure and clustering of hydrophobic/hydrophilic groups. More aggressive solvents such as aprotic solvent have a stronger effect, resulting in a complete dissolution or decomposition of the membranes.[55] The pores in the membranes may remain unchanged in contact with polar solvents if the fraction of hydrophilic groups were small; the chain reorganizations are more significant for the membrane with more hydrophilic groups. The pore size does not change significantly in case of *n*-hexane because the amount of toluene permeating through the membrane is approximately same with a nontreated membrane, but a slightly smaller amount of dye molecules is retained. When the pore size increases significantly, a decrease of rejections would be found. Membrane−solvent interactions may happen instantly or slowly. The rate at which these interactions may take place was not studied, although it might play a role in filtration performance. In this study, it was assumed that the steady-state condition was achieved after 1 week.

The goal of every membrane filtration system is to reach a high flux while separation is acceptable. Acetic acid-, acetone-, and methanol-treated STARMEM membranes reached high fluxes although they had lost their nominal separation performance. However, there is a possibility to use these membrane for separation of bigger components in filtration solution. In this way, the separation performance of solvent-treated STARMEM122 for a solution containing toluene and Rhodanile Blue has been tested. The molecular weight of Rhodanile Blue is ~4 times above the MWCO of the membrane. Figure 8 shows the rejection value of this dye for the STARMEM122 solvent-treated membrane.
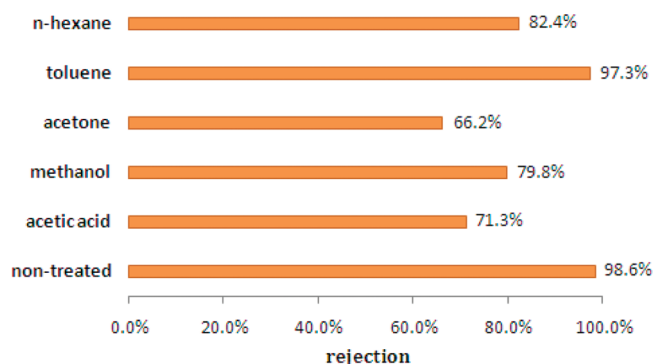

Figure 8. Rejection of Rhodanile Blue in toluene by using pretreated STARMEM122 by different solvent. (The numbers beside the lines indicate the amount of the rejection.)

As illustrated in Figure 8, for larger solutes, solvent-treated STARMEM122 membrane shows better performances. It was mentioned already that the rejection in NF membranes is in general based on size-exclusion phenomena and depends on pore size. The STARMEM122 membrane was found to have a larger pore size after treatment with the polar solvents (acetone, methanol, and acetic acids), which results in lower rejection. Increasing the solute size could compensate for this weakness. When solvent treatment is insignificant for small solutes, it would be practical to do solvent treatment prior to filtration to increase the flux, while the solute sizes are larger than the membrane pore size after solvent treatment.

4. Conclusions

Solvent pretreatment of the STARMEM membranes may have an effect on solvent permeation and separation of the membrane in toluene and dye. STARMEM membranes thought to be solvent stable showed visible changes after 1 week of exposure to organic solvents, and the characteristics of these membranes changed after exposure to the organic solvents except toluene. Acetone, acetic acid, and methanol change the membrane structure more, which indicates that membranes have a high interaction with these solvents. On the basis of the achieved results, membranes should be denoted as "semisolvent-resistant NF membranes", in view of the fact that they had lost their initial properties. Thus, this implies that manufacturer guidelines are to be followed strictly; stability in other solvents is not guaranteed. Polyimide-based SRNF membranea are considered to go through a polymeric network chain reformation in contact with the polar solvent, resulting in larger pores or increasing the free volume in the structure and correspondingly lower rejections of dissolved components (toluene fluxes remain approximately unchanged for apolar solvent). However, further verification with atomistic techniques such as transmission electronic microscopy (TEM) or atomic force microscopy (AFM) is required along with solvent-treatment experiments in which the contact duration can be examined (kinetics of the interactions). Eventually, it was found that membrane pretreatment could be a promising procedure in membrane filtration by increasing the flux, if only the solute size was large enough to keep the rejection high.

Acknowledgment

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