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Pervaporation performance of unfilled and filled PDMS membranes and novel SBS membranes for the removal of toluene from diluted aqueous solutions

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ABSTRACT

In this study, the influence of downstream pressure on the pervaporative removal of toluene from water was investigated. An unfilled and CBV 3002-filled PDMS membranes were compared with novel dense and porous SBS membranes. Experiments were performed by varying the downstream pressure from 1 to 40 mbar. The effect of fillers incorporation into the polymeric network of PDMS-based membranes was also studied.

It was found that the performance factors of all examined membranes were dependent on downstream pressure. Both the water and toluene flux decreased with increasing downstream pressure, the former being more pronounced, resulting in increased membrane separation factors. Moreover, the partial fluxes of all examined membranes were linearly dependent on the vapor pressure difference between permeate and feed. From the analysis of the intrinsic membrane properties it was found that toluene sorption was enhanced at higher downstream pressures. This resulted in membrane swelling, and hence higher water permeability than expected; nevertheless increased the membrane selectivity.

Incorporation of the CBV 3002 fillers into the PDMS network enhanced both toluene removal rate and separation performance as well as intrinsic membrane properties. For the porous SBS membrane the highest toluene flux and permeability was obtained, but the lowest separation efficiency. The dense SBS membrane showed similar separation factors as the PDMS-based membranes, although a significantly higher toluene removal rate was observed.

1. Introduction

Volatile organic compounds (VOCs) are commonly encountered in industrial wastewaters. Among the most toxic VOCs are benzene, toluene, ethyl benzene and xylene (denoted as BTEX), which are widely known and used in for example paint and synthetic resin industries [1,2]. Because of environmental reasons, it is highly recommended to remove these harmful organics from wastewaters. Unfortunately, conventional separation techniques, such as distillation and liquid-liquid extraction can not be considered as an optimal solution in the removal of VOCs from water, due to the large volumes of the waste streams. Separation of VOCs from water is often performed by air stripping and adsorption with activated carbon [3,4]. Nevertheless, the high cost of activated carbon forced researchers to study the applicability of other economical and environmental friendly separation techniques. Hydrophobic pervaporation was found to be a very attractive alternative for conventional techniques, such as ozone addition/UV radiation [5,6] and reverse osmosis [7], in the VOCs removal from wastewaters, since no additives are required, and less energy is consumed rendering the operational cost relatively low [8–12].

As reported in literature, several membranes were successfully applied in the separation of VOCs/water mixtures. Since rubbery polymers exhibit a higher free volume than glassy polymers, the former show better diffusion characteristics and are thus more attractive in pervaporation applications [13]. However, high flux asymmetric membranes are difficult to manufacture due to the rubbery nature of this material. Therefore, composite membranes consisting of an ultra thin dense layer deposited on a porous support layer are applied in industry, allowing to achieve a high flux in combination with a high selectivity. Polydimethylsiloxane (PDMS) has been so far the most studied elastomeric polymer in hydrophobic pervaporation, among other materials proposed, such as polyoctylmethylsiloxane (POMS),

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polyether-block-polyamide (PEBA) and ethylene-propylene diene terpolymers (EPDM) [14–20].

Permeation of components during a pervaporation separation process takes place by sorption into the membrane combined with diffusion through the membrane. Therefore the membrane performance can be enhanced by either improving the selective sorption of a component or lowering the diffusion barrier or both [21]. It was found by several authors that this could be achieved by incorporating various types of fillers (i.e. silicalite, silicalite zeolite and carbon black) into the polymeric matrix, due to improved permeation characteristics as a consequence of the fillers [22–29].

Recently, a novel technique was proposed for preparation of an asymmetric membrane from the elastomeric styrene–butadiene–styrene block copolymer (SBS) material and the resulting membrane was tested for pervaporative removal of exemplary organics from water, as described in US Patent [30]. This invention could possibly entail a breakthrough in the development of high performance materials made of a single material. This idea was inspired by earlier work of Ganapathi-Desai and Sikdar [31], where SBS membranes showed promising results for 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE) removal.

In order to quantify the performance of membrane processes, partial permeate fluxes and separation factors, such as selectivity α and enrichment factor β, are taken into account. The permeate flux J_i of component i can be calculated on the basis of Eq. (1):

$$J_i = \frac{m_{i,p}}{S_m \cdot t}, \tag{1}$$

where $m_{i,p}$ *is* the absolute mass of component i in the permeate [g], S_m expresses the active membrane area [m^2] and t stands for the collection time [h]. In the case of low concentrations (ppm) of organic components in the feed, as it takes place for VOCs removal, the selectivity of a membrane is the most accurately described by the enrichment factor β, although the selectivity factor α can be also applied:

$$\alpha_{i,j} = \frac{(C_i/C_j)_p}{(C_i/C_j)_r}, \tag{2}$$

$$\beta_i = \frac{C_{i,p}}{C_{i,r}}, \tag{3}$$

where C represents the concentration of component i or j and subscripts p and r denote the permeate and retentate (feed for dead-end configuration) side, respectively. The overall membrane performance is determined by the combination of permeate flux and separation efficiency and is often expressed by the pervaporation separation index (PSI) which is defined as the product of total permeation rate and selectivity factor [32,33]:

$$\mathrm{PSI} = J_{tot} \cdot \alpha_{i,j} \tag{4}$$

As stated in the literature, several parameters influence the membrane performance. Among these, feed concentration, permeate pressure and temperature play an important part. Since the driving force for permeation of the components in pervaporation is the vapor pressure difference between retentate and permeate side, the partial permeate fluxes are expected to increase with decreasing downstream pressure.

In dilute aqueous solutions, the organic and water flux can be expressed by an overall permeability according to the solution-diffusion model [34–37]:

$$J_i = \frac{Q_i^m}{l}(p_i^{sat}\gamma_i^{\infty}x_i - p_i) \tag{5}$$

$$J_w = \frac{Q_w^m}{l}(p_w^{sat} - p_w) \tag{6}$$

Here Q_i^m and Q_w^m are the intrinsic membrane permeabilities of component i and water respectively, l the membrane thickness, p_i^{sat} the saturated vapor pressure of component i, γ_i^{∞} the activity coefficient at infinite dilution, x_i the mass fraction in the retentate and p_i and p_w the partial pressures of organic and water in the permeate respectively.

The influence of the downstream pressure on the separation factors is however dependent on the relative volatility between the selective and non-selective permeating compounds. In the case of binary mixtures, it was proven that the permeate composition X_l' depends on the downstream pressure, as given by Eq. (7) [37,38]:

$$X_1' = \frac{p_1^* p_2^*}{p_2^* - p_1^*}\frac{1}{p_l} - \frac{p_1^*}{p_2^* - p_1^*}, \tag{7}$$

where 1 and 2 represent the fast and the slow permeating component respectively, X_l' expresses the mole fraction of component 1 in the permeate, p^* stands for the saturated vapor pressure at operational temperature and p_l is the downstream pressure. Derivation of this equation yields:

$$\frac{dX_1'}{dp} = \frac{p_1^* p_2^*}{p_1^* - p_2^*}\frac{1}{p_l^2} \tag{8}$$

In hydrophilic pervaporation, where water is the selective and less volatile component, the difference $p_1^* - p_2^*$ is negative, and therefore a permeate pressure as low as possible is applied, resulting in the highest components fluxes and highest separation factors. On the other hand, in the case of hydrophobic pervaporation, the organic compound is considered to be selective and more volatile. From Eq. (8) a better separation efficiency is thus expected as the permeate pressure is increased. Both partial fluxes will decrease due to a lower driving force, the effect however being more pronounced for water, as confirmed by several authors [39–41].

Although permeate fluxes, selectivity factor and enrichment factor are the most commonly used performance factors to characterize a membrane process, these quantities are heavily dependent on operation conditions and hence obscure the role of the actual driving force. These operation conditions can be decoupled from permeant-specific intrinsic membrane properties by the use of permeabilities and selectivities as suggested by Wijmans [42]. In this way, the contribution by nature of the membrane to the separation performance can be clarified and quantified as done by Verhoef et al. [43].

The permeability can be calculated from Eqs. (5) and (6), by multiplying the partial flux with the membrane thickness and dividing by the driving force. The membrane selectivity S is expressed as the ratio of permeabilities:

$$S_{i/w} = \frac{Q_i^m}{Q_w^m} \tag{9}$$

In this work, the influence of the downstream pressure on the performance factors in the pervaporative removal of toluene from water through unfilled and CBV 3002-filled PDMS-based membranes was examined and compared with dense and porous SBS membranes. In addition, the effect of fillers incorporation into the PDMS network on the membrane performance was investigated.

2. Materials and methods

2.1. Membrane preparation

In this research, laboratory-made unfilled (M1) and CBV 3002 filled (M2) PDMS/PI composite membranes, and dense (M3) and porous (M4) SBS membranes were examined. The synthesis of PDMS-based membranes is described below. The porous SBS membranes were obtained by applying phase inversion technique, while dense structure was obtained by means of solvent evaporation. The detailed preparation method of these novel materials is explained in the US Patent 2008/0114087 [30].

In order to obtain PDMS/PI composite membranes, a 15 wt.% polyimide (PI) support layer was firstly prepared as described by Gevers et al. [44]. After casting, the solvent was allowed to evaporate in open air for 30 s, to ensure formation of the skin layer with elevated polymer concentration. This prevents intrusion of PDMS into the support pores as confirmed by Vandezande et al. [45]. The resulting film was then immersed in a water bath at room temperature to form the final support layer. After immersion precipitation, membranes were cross-linked in paraxylenediamine/methanol mixture (1 g/10 ml) and further post-treatment was applied, as described elsewhere [46]. The obtained films were then wiped with tissue and dried in the oven at 60 °C for at least 1 h.

A PDMS (General Electrics, RTV 615A and B, prepolymer and cross-linker with a 10:1 ratio) solution in hexane was prepared by following the procedure described by Gevers et al. [44]. The concentration of all PDMS solutions was 10 wt.%.

The fillers used in this work were commercially available ZSM-5 zeolite fillers (CBV 3002) characterized by a particle size ranging from 1 to 1.5 μm and a Si/Al ratio of 240. Synthesis of filled PDMS membranes is fully described elsewhere [47]. The filler fraction was expressed in weight percent with the following equation:

$$\text{filler fraction} = \frac{\text{weight of fillers}}{(\text{weight of fillers}) + (\text{weight of polymer})} \tag{10}$$

The filler concentration in the membrane was 30 wt.%. As the final step, the PDMS/filler solutions were coated on the PI support in the same way as described above.

2.2. Membrane characterization

2.2.1. Contact angle measurements

Measurements of the contact angles allowed determining the hydrophobicity of the examined membranes. The standard procedure is to put a drop on the top layer of the membrane and to examine the contact angle with a special camera (sessile drop method). In this study, contact angles were measured with water, using a CAM 100 (KSV Instruments, LtD.).

2.2.2. Scanning Electron Microscopy (SEM)

To gain more insight in the membrane structure, cross-sections of all membranes were investigated by means of SEM. Prior to the analysis, membrane samples were broken under liquid nitrogen allowing the imagining of their cross-section. SEM-images were obtained with a Stereoscan 360 (Cambridge Instruments) at 20 kV.

3. Experimental

The dead-end pervaporation set-up is schematically presented in Fig. 1. During experiments, a constant vacuum was applied on the permeate side, by means of a RVS vacuum pump (Edwards High Vacuum International) to ensure a required driving force for permeation of components. Three different permeate pressures of 1, 15 and 40 mbar were applied in order to examine the influence of downstream pressure on the membrane performance. The active membrane area was 2.44 cm^2 for the porous SBS membrane and 8.81 cm^2 for the dense SBS membrane and PDMS-based membranes.

Experiments were carried out with 500 ml of a toluene/water mixture containing 200–250 ppm of toluene. Constant stirring of the feed was applied in order to avoid concentration polarization. The temperature of the feed was kept constant at 25 °C.

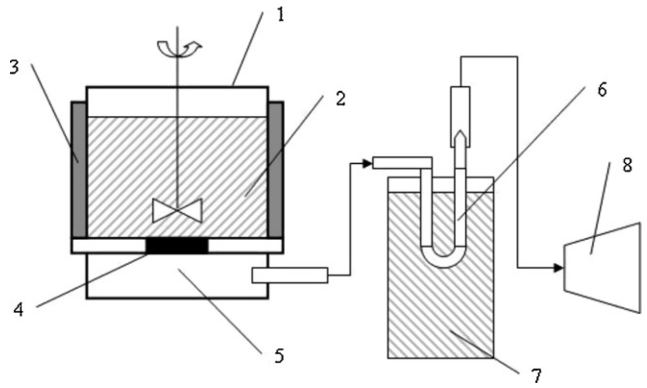

Fig. 1. Pervaporation process setup: (1) pervaporation cell; (2) feed/retentate; (3) recirculating water; (4) membrane; (5) permeate vapor; (6) cold trap; (7) liquid nitrogen; (8) vacuum pump.

Permeate was collected as a function of time in a cold trap immersed in liquid nitrogen and its mass determined every hour. Simultaneously a sample of the feed was taken and the toluene concentration was determined with UV spectrophotometer ($\lambda = 261.2$ nm [25]). According to the literature [3,20,25,26,48], the concentration of toluene in the permeate is expected to exceed the solubility limit by a factor of 100 up to 1000, due to a high hydrophobicity of this component. As a consequence, non-homogeneous samples are obtained, rendering UV analysis inaccurate; hence, sample dilution is required prior to analysis. However, due to the very volatile nature of toluene, this can lead to high experimental errors. It is therefore more accurate to calculate the permeate composition indirectly from the feed, by using a mass balance, since only permeation of components from feed to permeate occurs. The absolute amount of a toluene in the permeate can be thus calculated as its mass difference in the feed over a certain time period:

$$m_{tol_{p,t}} = m_{tol_{f,0}} - m_{tol_{f,t}}, \tag{11}$$

where m_{tol} is the absolute amount of toluene in the permeate (p) or in the feed (f) at the beginning (0) or at the end (t) of one cycle. The absolute mass of the toluene in the feed is calculated from the total mass and its composition. After determining the total permeate mass ($m_{tol,p}$) by weighing the cold trap, the toluene concentration in the permeate ($C_{tol,p}$) is calculated using Eq. (12):

$$C_{tol_p}\,[\text{ppm}] = \frac{m_{tol_p}}{m_{total_p}} \tag{12}$$

The total flux J (g m^{-2} h^{-1}) was calculated as the total amount of the solvent permeated per membrane area (m^2) per time (h). For quantitative comparison of the permeate fluxes through different membranes, the membrane thickness has to be taken into account, since the resistance to mass transfer is determined by the total membrane thickness. Moreover, the permeation rates are inversely proportional to membrane thickness [48]. Therefore all permeate fluxes were normalized to a thickness of 1 μm. Each experiment was repeated three times and results were averaged to minimize errors. Based on the relative error of each measurement method (permeate mass, membrane diameter, membrane thickness and UV analysis), the experimental error of the performance factors was estimated to be 8%.

4. Results and discussion

4.1. Membrane characterization

Table 1 presents the characteristics of the PDMS-based and SBS membranes used in this study. As can be seen, contact angles obtained with water showed similar values for all membranes used

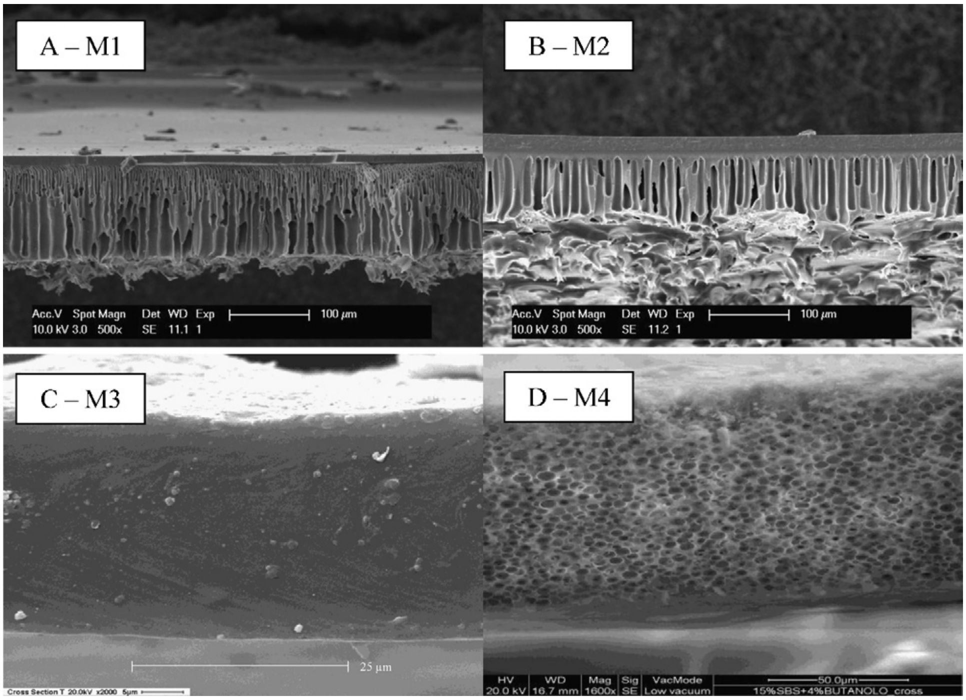

Fig. 2. Cross-sections of membranes used in the experiments taken by means of SEM (A—unfilled PDMS/PI (M1), B—PDMS/PI filled with CBV 3002 (M2), C—dense SBS (M3), D—porous SBS (M4)).

in this work (~116°), indicating their high hydrophobicity degree. The nearly identical hydrophobicity allowed for a good comparison of the performance of membranes made from these materials. As mentioned before, the total membrane thickness is determining the magnitude of the permeation rate through the membrane. Nevertheless, in the case of composite membranes, the resistance to mass transfer is almost completely determined by the dense top layer [48]. As a consequence, only the selective layer thickness was thus used for flux normalization. The dense layer thicknesses are relatively large compared to commercial composite membranes [3,25]. It is therefore expected that absolute fluxes of membranes M1, M2 and M3 will be relatively low. Finally, incorporation of the CBV 3002 fillers into the PDMS network led to an almost doubling of the top layer thickness, which is also visible by comparing cross section of the membrane, as presented in Fig. 2.

The composite structure of the PDMS/PI membranes (Fig. 2A and B) is clearly visible, showing a 'finger-like' porous layer on which a thin dense PDMS layer is deposited. In Fig. 2C a smooth surface is shown, indicating a completely dense structure (M3), while Fig. 2D presents a sponge-like porous structure of M4.

4.2. Pervaporative toluene removal from water

The decrease in toluene feed concentration for the examined membranes at downstream pressures of 1, 15 and 40 mbar respectively and temperature of 25 °C is presented is Figs. 3–5.

Table 1
Characteristics of PDMS-based and SBS membranes used in the experiments.

Membrane	Composition	Contact angle [°]	Thickness [μm]	
			Total	Top layer
M1	PDMS/PI	114	91.9	12.5
M2	CBV 3002 filled PDMS/PI	116	94.5	20.5
M3	Dense SBS	115	34	–
M4	Porous SBS	119	63	–

As can be seen from Figs. 3–5, the decrease in toluene feed concentration for membranes M1, M2 and M3 is almost identical, and more pronounced in comparison to M4. The difference between M1, M2 and M3 on the one hand and M4 on the other hand can be explained by the magnitude of the membrane area used for the

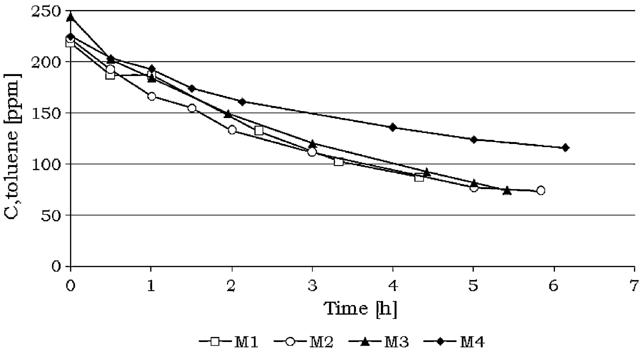

Fig. 3. Toluene feed concentration as a function of time for M1, M2, M3 and M4; temperature: 25 °C; permeate pressure: 1 mbar.

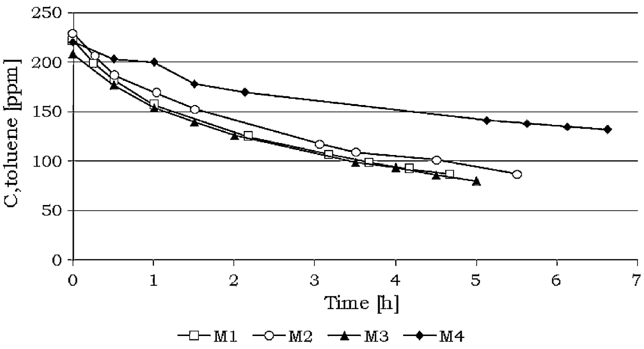

Fig. 4. Toluene feed concentration as a function of time for M1, M2, M3 and M4; temperature: 25 °C; permeate pressure: 15 mbar.

Table 2
Permeate fluxes, selectivity factor and enrichment factor of the examined membranes; temperature: 25 °C; toluene feed concentration: 150 ppm; downstream pressures: 1, 15 and 40 mbar.

Membrane	Downstream Pressure (mbar)	Flux [g m^{-2} h^{-1}]			Selectivity factor (α)	Enrichment factor (β)
		Total	Toluene	Water		
M1	1	670	220	450	3283	2200
	15	470	190	280	4680	2750
	40	270	160	110	9921	3988
M2	1	720	330	390	5676	3066
	15	530	300	230	8523	3741
	40	350	260	90	18967	4933
M3	1	1250	570	680	5650	3058
	15	1070	560	510	7196	3461
	40	840	540	300	11879	4270
M4	1	9950	1170	8780	885	781
	15	5250	1000	4250	1571	1272
	40	1550	600	950	4238	2591

experiments. Over a 5-h time period, the decrease in toluene feed concentration was observed to be ~65% for M1, M2 and M3 and ~45% for M4 at downstream pressure of 1 mbar. The toluene concentration decline in time reduced with increasing downstream pressure to ~50% for M1, M2 and M3 and to ~33% for M4 at a downstream pressure of 40 mbar. From this, it can be concluded that the downstream pressure plays an important part in the pervaporative removal of toluene as discussed in detail in following sections.

4.3. *Influence of the downstream pressure on the performance factors*

4.3.1. *Total and partial flux*

The effect of the downstream pressure on the total and partial fluxes for the membranes used in this work is presented in presented in Table 2.

From the data shown in Table 2, a decrease in permeate fluxes with increasing downstream is observed for all membranes. These observations are a consequence of an increasing vapor pressure of different compounds in the permeate and hence, a decrease in the vapor pressure differences with the feed. Linear correlation factors (R^2) of all fluxes of the examined membranes were above 0.9, indicating a linear dependency of the permeate fluxes on the downstream pressure.

Furthermore, the influence of the vapor pressure difference between feed and permeate of water and toluene on the partial fluxes was investigated. This is shown on Figs. 6 and 7. From these figures it can be seen that both toluene and water fluxes are almost completely linearly dependent on the vapor pressure difference. Ghoreyshi et al. [51] studied the mass transport of different organics through PDMS membranes and also observed a linear relationship between the component flux and the overall driving force, which is in agreement with our findings.

Moreover, it was found that the decrease in partial fluxes was more pronounced for the water flux in comparison to the toluene flux. A plot of the relative proportions of the partial fluxes at different downstream pressure highlights this (Fig. 8). As can be seen, all membranes show similar behavior with increasing downstream pressure, nevertheless the highest increase in the toluene-over-water flux ratio was found for M4 (~5 times in the pressure range from 1 to 40 mbar), in comparison to the PDMS-based M1 and M2 membranes and dense SBS membrane M3 (respectively 3.0, 3.3 and 2.1 in the same downstream pressure range).

From above considerations, the conclusion can be drawn that by increasing the downstream pressure from 1 to 40 mbar, water permeation through examined membranes is more inhibited, resulting

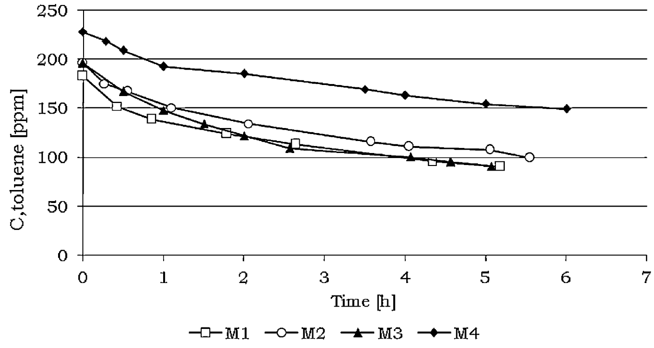

Fig. 5. Toluene feed concentration as a function of time for M1, M2, M3 and M4; temperature: 25 °C; permeate pressure: 40 mbar.

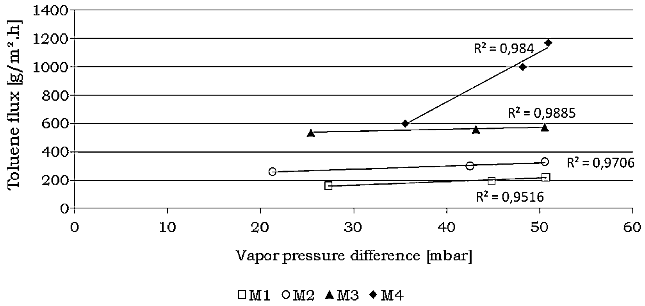

Fig. 6. Dependency of the vapor pressure difference on the toluene flux; temperature: 25 °C; toluene feed concentration: 150 ppm.

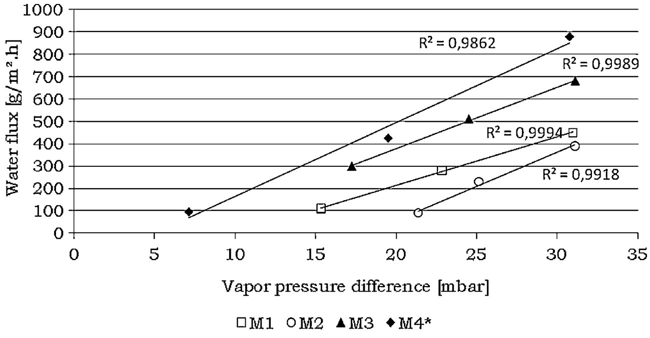

Fig. 7. Dependency of the vapor pressure difference on the water flux; temperature: 25 °C; toluene feed concentration: 150 ppm.

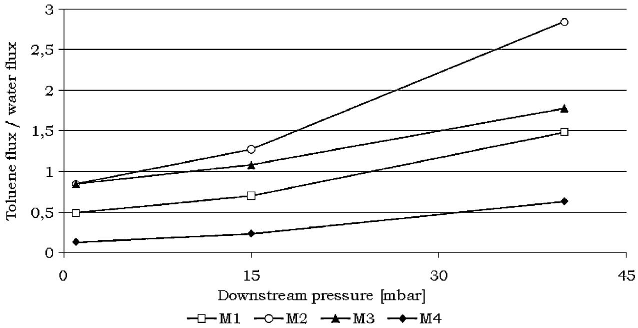

Fig. 8. Dependency of the downstream pressure on the partial fluxes of M1, M2, M3 and M4; temperature: 25 °C; toluene feed concentration: 150 ppm.

in higher toluene concentration in the permeate, as demonstrated in Fig. 9. The highest increase in permeate composition was found for M4 (3.3 times) followed by M1, M2 and M3 (respectively 1.8, 1.6 and 1.4).

Chang et al. [41] observed a similar effect and explained it by the relative volatility between the two components. According to the authors, increasing the permeate pressure, leads to an increase in desorption resistance of all components at the permeate side. This increase, however, is more pronounced for the less volatile component, resulting in a higher decrease in water flux in comparison to the organic flux and hence a more concentrated permeate.

Similar results were observed by Wu et al. [39] for removal of 1,1,1- trichloroethane (TCA) from water through asymmetric polyvinylidene fluoride (PVDF) hollow fiber membranes. Here a more pronounced decrease in water flux compared to the organic flux was also observed when the downstream pressure was increased from 27 to 133 mbar. The observations found in their work correspond well to the behavior of the asymmetric SBS membrane. Lau et al. [40] observed a linear dependency of permeate fluxes vs. downstream pressure in the pressure range from 7 to 20 mbar in the case of toluene removal from water using oligosilylstyrene–polydimethylsiloxane membranes, which is in agreement with our findings.

An interesting observation is that the highest flux variations were observed for the porous membrane, and were less pronounced when the selective, dense layer of M1, M2 and M3 (respectively 12.5, 20.5 and 34 μm) increased. For example, in the downstream pressure range from 1 to 40 mbar, the total flux decreases were −81%, −60%, −51% and −33%, for M4, M1, M2 and M3 respectively. This indicates a higher dependency on the downstream pressure of the permeate fluxes for a more porous membrane.

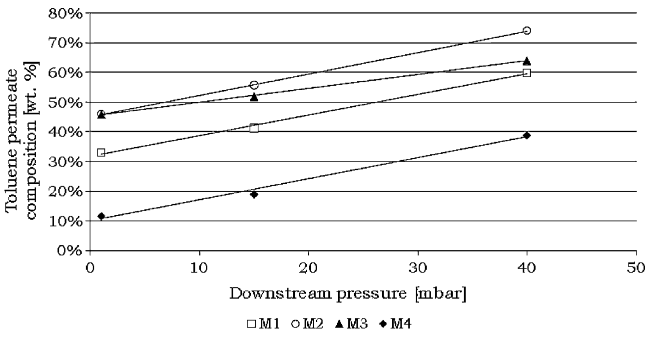

Fig. 9. Toluene permeate composition as a function of the downstream pressure; temperature: 25 °C; toluene feed concentration: 150 ppm.

Table 3

Permeabilities and membrane selectivities of the examined membranes; temperature: 25 °C; toluene feed concentration: 150 ppm; downstream pressures: 1, 15 and 40 mbar.

Membrane	Downstream pressure (mbar)	Permeance [kg m^{-2} h^{-1} bar^{-1}]		Selectivity $S_{i/w}$
		Toluene	Water	
M1	1	43.67	145.28	0.301
	15	47.24	122.65	0.385
	40	58.63	71.67	0.818
M2	1	65.30	125.39	0.521
	15	70.59	91.50	0.771
	40	122.20	42.14	2.900
M3	1	113.71	218.61	0.520
	15	129.81	208.20	0.623
	40	211.41	174.15	1.214
M4	1	229.98	2854.09	0.081
	15	207.75	2179.22	0.095
	40	168.98	1332.56	0.127

4.3.2. *Selectivity factor and enrichment factor*

From the analysis of the permeate fluxes, it is expected that the separation efficiency, expressed by the selectivity factor α and separation factor β, will increase with increasing downstream pressure. This is a consequence of a more pronounced decrease of the water flux in comparison to the toluene flux and hence a more concentrated toluene permeate. The effect of the downstream pressure on the separation factors α and β is also shown in Table 2.

From the data presented in Table 2, a clear increase in separation efficiency with increasing permeate pressure was observed for all examined membranes. Moreover, a linear increase with increasing downstream pressure was found for the enrichment factor β. This could also be seen from Fig. 9 since the enrichment factor is calculated by Eq. (3).

Similar observations were found by Lau et al. [40] and Chang et al. [41], namely a clear increase of the membrane selectivity caused by an increase of the downstream pressure in the pervaporative separation of organics/water mixtures. Moreover, a linear dependency of the enrichment factor with the downstream pressure was found, which is in agreement with our findings.

Since the highest decrease in the water flux in comparison to toluene flux was found for the porous M4 membrane within the examined pressure range (as discussed above), also the highest increase in separation factors was observed for this membrane ($\beta_{1\text{mbar}} = 780$; $\beta_{40\text{mbar}} = 2600$). As for the permeate fluxes, the increase in separation factors was less pronounced for the composite PDMS-based membranes (M1 and M2), and dense SBS membrane (M3) due to the more dense structure. Based on the above considerations, the conclusion can be drawn that permeate fluxes and separation factors of porous membranes are more dependent on the downstream pressure and less dependent for a denser membrane.

4.3.3. *Permeability and membrane selectivity*

To gain more insight in permeant-specific intrinsic membrane properties, permeabilities and membranes selectivities were calculated as presented in Table 3.

From the data shown in Table 3, and clear decrease in water permeability with increasing downstream pressure is observed for all examined membranes, together with a significant increase in toluene permeability, except for M4 where a decrease in toluene permeability was observed. The highest increase was found to be M2 (+87%), followed by M3 (+86%) and M1 (34%) in the concentration range from 1 to 40 mbar. The toluene permeability of M1, M2 and M3 exhibit a completely opposite behavior than the toluene

Table 4
Pervaporation separation index (PSI) of the examined membranes; temperature: 25 °C; toluene feed concentration: 150 ppm; downstream pressures: 1, 15 and 40 mbar.

Downstream pressure	Membrane	PSI/10000
1 mbar	M1	220
	M2	409
	M3	706
	M4	881
15 mbar	M1	220
	M2	452
	M3	770
	M4	825
40 mbar	M1	268
	M2	664
	M3	998
	M4	657

fluxes upon changing the vapor pressure. An explanation of this can be provided with the help of the solution-diffusion model, which states that permeability a combination of solubility and diffusivity is. When the downstream pressure decreases, diffusion will slow down due to a lower driving force. The effect on sorption of components is less clear. Greenlaw et al. [52] studied the effect of the downstream pressure of hexane permeability through a rubbery membrane. The authors observed an increased hexane permeability, which was explained by an increased concentration, and hence sorption, into the membrane. Moreover, the authors stated that this behavior was typically for membranes that are swollen significantly by the permeant. Thus, for M1, M2 and M3, the increase in toluene sorption is more than counterbalanced by the lower diffusivity. On the contrary, for the porous SBS membrane (M4), the decrease in diffusivity is the dominant factor, which can be attributed to the membrane's structure. The decrease in water permeability with increasing downstream pressure was also observed to be smaller than the decreases in water flux. This can now be explained by membrane swelling due to higher toluene sorption, resulting in a more open membrane structure and hence higher water diffusivity than expected. The highest decrease was found for M2 (−66%), followed by M4 (−53%), M1 (−51%) and M3 (−20%).

From the analysis toluene and water permeabilities, one can forecast an important influence of the downstream pressure on the membrane selectivity. All membrane selectivities increase significantly with increasing downstream pressure, the increase being most pronounced in the range from 15 to 40 mbar. Consistent with the data of permeabilities, the highest increase was found for M2 (5.6 times) and lowest for M4 (1.6 times) when the downstream pressure was increased from 1 to 40 mbar.

4.4. Membrane comparison

In Tables 2 and 3 the membrane performance parameters are compared for all examined membranes, measured at 25 °C, a feed toluene concentration of 150 ppm and downstream pressures of 1, 15 and 40 mbar, respectively. In Table 4, the pervaporation separation index (PSI) of the membranes as defined by Eq. (4) is presented.

Comparison of the filled to the unfilled PDMS-based membrane showed a clear increase in toluene removal rate combined with a slightly smaller water flux, and hence resulting in higher separation factors when fillers were incorporated into the PDMS network. The mean toluene flux increase was 57%, where the enrichment factor increased by 33%. This resulted in a clear increase in pervaporation separation index (113% as mean value for the three downstream pressures). The conclusion can thus be drawn that incorporation of the CBV 3002 fillers increased the overall membrane performance significantly.

Panek et al. [25] obtained higher total and partial fluxes when carbon black was introduced into the PEBA membranes for the removal of a 200 ppm toluene-solution from water at 25 °C. The authors explained it by the formation of empty cavities, during the membrane synthesis. Moreover, the increase in water flux was more pronounced than the increase in toluene flux, resulting in lower separation efficiency for the filled membrane, which is in contrast to our findings. On the other hand, when carbon black was incorporated into PDMS membranes, the water flux decreased drastically, compared to the unfilled membrane. The toluene flux was unaffected by the fillers, resulting in a clear increase in separation factors. These effects were explained by the similar hydrophobic character of the filler and toluene. Vankelecom et al. [49] also studied ZSM-5 filled and unfilled PDMS membranes for the pervaporative removal of ethanol from an ethanol/water mixture containing 6 wt.% of alcohol at 35 °C. In contrast to our results, the authors observed a decrease in the total and partial fluxes for the filled PDMS membranes in comparison to pure PDMS, which was explained by the cross-linking action of the zeolites in PDMS network. Similar observations to this were found by Peng et al. [50] for the removal of benzene from water using carbon molecular sieve (CMS)-filled PDMS membranes. The increased separation performance for the filled membrane was explained by the favorable absorption properties of CMS towards benzene molecules.

Te Hennepe et al. [21] studied the influence of silicalite content in PDMS membranes for the removal of methanol, ethanol and 1-propanol from water at 22.5 °C. The authors found a clear increase in separation factors with increasing silicalite content, which was more pronounced as the alcohol size increased. The total permeate fluxes also increased with increasing silicalite content, but in contrast to the separation factor, the effect was more pronounced as the alcohol size decreased. This was explained on the one hand by a stronger adsorption capacity for the longer alcohols of silicalite and hence enhanced solubility into the membrane. On the other hand, due to the very strong the interaction between 1-propanol and pore system, water was totally excluded from the zeolite pores, resulting in a decreasing water flux with increasing silicalite content.

From the above considerations it is clear that the effects on incorporation of fillers are strongly dependent on the interactions between solvent molecules, the polymer itself and the fillers used. Compatibility between fillers and polymer and a good dispersion of the fillers into the polymer matrix are crucial factors. Therefore carefully established selection criteria must be taken into account in developing proper filled membranes for a given separation.

In terms of intrinsic membrane performance parameters, resulted the incorporation of fillers in an increase in toluene permeability, together with a decrease in water permeability and hence increased membrane selectivity. These changes were the highest at 40 mbar, namely +108%, −41% and +254% for toluene permeability, water permeability and membrane selectivity respectively. Baker et al. [53] investigated the effect of dispersing 60 wt.% ZSM-5 zeolite fillers in a silicone rubber matrix for the removal of ethanol from water. The authors observed an increase in ethanol permeability and decrease in water permeability upon incorporating of fillers in the membrane, which is in agreements with our findings. The author explained this, by an increased permeability of toluene in the zeolite pores compared to the silicone polymer matrix. Simultaneously, water can not permeate through the zeolite particles, resulting in a more tortuous path and hence lower permeability.

The results obtained in our study indicate that incorporation of the CBV 3002 fillers into the PDMS network enhanced toluene permeation significantly and prohibited water permeation. This could be explained by the highly hydrophobic nature of these fillers and hence higher affinity for toluene and lower for water, resulting in increased adsorption for toluene and decreased adsorption for water, when compared to the unfilled PDMS membrane. Due to the

Table 5
Comparison of membranes used for the pervaporative removal of toluene from water; feed temperature: 25 °C; downstream pressure: 1 mbar.

Membrane	SLT [μm]	Total flux [g/m^2 h]	Ethanol flux [g/m^2 h]	Water flux [g/m^2 h]	Enrichment Factor	Reference
PDMS/PAN[a]	3	2130	18	2112	85	[22]
PDMS/PAN + CB[a]	3	900	18	882	200	[22]
PDMS	400	2600	2000	600	8000	[22]
PDMS + CB	266	3458	1224	2234	6000	[22]
PEBA	75	1613	345	1268	1900	[22]
PEBA + CB	75	2475	420	2055	1800	[22]
PDMS[a]	8	2509	139	2370	280	[17]
POMS[a]	9	1156	151	1006	720	[17]
PEBA	75	2222	990	1232	800	[23]
PEBA + CB	75	3638	1211	2427	600	[23]
PDMS/PI	12.5	670	220	450	2200	This study
PDMS/PI + CBV 3002	20.5	720	330	390	3066	This study
SBS dense	34	1250	570	680	3058	This study
SBS porous	63	9950	1170	8780	871	This study

[a] Commercial membranes (SLT: selective layer thickness, PAN: polyacrylicnitrile, CB: carbon black).

higher adsorption of toluene into the zeolite pores, water molecules are forced to diffuse through a more tortuous path, explaining the decrease in water flux and permeability. Since permeation takes place as a combination of sorption into the membrane and diffusion through the membrane [21], incorporation of CBV 3002 fillers results in an overall better membrane performance.

At a downstream pressure of 1 mbar, it was found that the porous SBS membrane (M4) was characterized by a double toluene removal rate in comparison to dense SBS membrane (M3) but the enrichment factor of M3 was 4 times higher. Due to the much higher permeate flux in comparison to M3, the PSI value of M4 was 25% higher. At 40 mbar downstream pressure, the toluene flux obtained through M4 was only 11% higher than M3, while the enrichment factor of M3 was 1.6 times higher. This resulted in a PSI value for M3 which was more than 50% higher than M4. Although higher toluene removal rates were observed for M4, was the mean PSI of M3 higher and hence the overall membrane performance. The intrinsic membrane properties exhibited the same behavior, namely a similar or slightly higher toluene permeability for M4, but a more than 6 times higher membrane selectivity for M3.

In comparison to the PDMS-based membranes, all permeate fluxes obtained for M3 were found to be higher at all downstream pressures. Toluene fluxes through M3 at 1 mbar were 2.6 and 1.7 times higher than for M1 and M2 respectively. These values increased only slightly when compared at 40 mbar (3.4 and 2.1 times high than for M1 and M2 respectively for). Water fluxes through M3 at 1 mbar were found to be 1.7 and 1.5 times higher than for M1 and M2 respectively. The change from 1 to 40 mbar was however more significant than for the toluene flux, namely a 2.7 and 3.3 higher water flux for M3, if compared to M1 and M2 respectively. This obviously influenced the separation efficiency of the membranes considered. In comparison to M1, the enrichment factor of M3 was 40% higher at 1 mbar and decreased to a slightly higher value of 7% at 40 mbar. Despite equal separation performance factors obtained for M2 and M3 membranes at the downstream pressure of 1 mbar, the enrichment factor of M2 was 20% higher than for M3, when the pressure increased to 40 mbar. The PSI of M3 was 220% and 73% higher is compared to M1 and M2 respectively at 1 mbar downstream pressure. This value increased at a downstream pressure of 40 mbar when compared to M1 (270% higher) but decreased to 50% for M2, due to the very high toluene concentration in the permeate and hence selectivity factor. Toluene and water permeabilities were also higher for M3, when compared to M1 and M2. The intrinsic membrane selectivity of M2 and M3 were comparable at 1 and 15 mbar and higher than observed for M1. At 40 mbar however, M2 exhibited a membrane selectivity which was 2.4 times higher than found for M3. Nevertheless, the conclusion can be drawn that the dense SBS membrane showed a superior membrane performance at all permeate pressures, due to its much higher toluene removal rate, despite the more pronounced increase in separation efficiency obtained for the PDMS-based membranes.

Results presented in this work are in contrast with data obtained by Sikdar et al. for pervaporative removal of 1,1,1-trichloroethane (TCA) from water, as presented in the US Patent [30]. The authors observed separation factors of the porous SBS membrane exceeding those of commercially available PDMS membranes by a factor of 2 to 3. In this research all separations factors of the porous SBS membranes (M4) are smaller than the ones obtained for PDMS membranes, however the toluene removal rate is much higher. At a downstream pressure of 40 mbar, the toluene flux of M4 was 3.8 and 2.3 times higher than M1 and M2 respectively, while the enrichment factor of M1 and M2 was 1.5 and 1.9 times higher than M4. Despite lower separation factors, the PSI of M4 was 300% and 215% higher compared to M1 and M2 respectively at a downstream pressure of 1 mbar, while at 40 mbar the PSI of M4 was 145% higher than M1 and similar to M2. Thus, the overall membrane performance was better for the porous SBS membrane (M4) than for PDMS-based membranes M1 and M2. The intrinsic membrane properties of M4 were worse than M1 and M2, which is due to porous nature of the membrane and hence poor separation quality if compared to dense membranes. From this, it is clear that the nature of the permeants and its interactions with the membrane material are fundamental for the separation behavior of the membrane.

Finally, the obtained results for the removal of toluene from water can be compared to literature as presented in Table 5. This comparison was done at an operation temperature of 25 °C and permeate pressure of 1 mbar. As can be seen from this table, the obtained values of the examined membranes are of the same order of magnitude with previous reported data in literature.

5. Conclusions

The aim of this research was to investigate the influence of the downstream pressure on the performance factors in the case of pervaporative toluene removal from water. Both unfilled (M1) and filled (M2) PDMS-based membranes were compared with a dense (M3) and a porous (M4) SBS membrane.

For all membranes a decrease in permeate fluxes with increasing downstream pressure was observed, which was a consequence of increased desorption resistance at the permeate side. Due to the more volatile character of toluene, toluene permeation was less inhibited than water permeation resulting in a more significant water flux decrease with increasing downstream pressure and hence higher separation factors. This was confirmed by the analysis of permeabilities and explained by an increased sorption of toluene in the membrane at higher downstream pressures, which resulted in a better intrinsic membrane performance. Partial fluxes were observed to be linearly dependent with the vapor pressure difference between permeate and feed as predicted by the solution-diffusion model.

Incorporation of CBV 3002 fillers into the PDMS network increased the toluene removal rate, toluene permeability and retained water permeation, resulting in a better separation performance. The highest permeation rates and permeabilities were found for porous SBS membranes, nevertheless the separation factor and selectivity obtained were the lowest. Dense SBS membrane exhibited the best overall results, due to a high separation factor and high toluene removal rate, proving to be a good alternative for PDMS-based membranes.

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