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Macromolecular Nanotechnology – Short communication

Characteristics and performance of new nanoporous PEEKWC films

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Abstract

This rapid communication reports a summary of the key findings of preparation and characterization of new polymeric membranes for nanofiltration of organic compounds. A series of nanoporous asymmetric membranes of PEEKWC, a modified poly(etheretherketone) was prepared by means of the dry–wet phase inversion method. In particular, the type and concentration of internal non-solvent were varied in order to obtain membranes for nanofiltration. The optimization of these factors led to reproducible membranes, which were characterized for hydrophobicity, roughness, morphology, surface charge. The performance was studied by doing dead-end filtration experiments with aqueous solutions of uncharged and charged organic compounds. The new polymeric films exhibited interesting performance compared to commercial nanofiltration membranes in terms of retention and relative flux for positively charged organic compounds.

Keywords: Polyetheretherketone (PEEKWC); Dry–wet phase inversion; Nanoporous membranes; Nanofiltration; Membrane surface properties

1. Introduction

Membrane processes in general, and nanofiltration in particular are becoming more and more important in environmental technology. Nanofiltration (NF) membranes can remove multivalent ions as well as organic molecules with a molecular weight above 300 Da. Because of these properties, nanofiltration has proven to be a very effective method for the removal of organic compounds from aqueous solution, e.g., pesticides [1,2], dyes [3,4], NOM [5] in waste water treatment. The retention of organic compounds is influenced by different mechanisms. Several authors reported that molecular size is the most important factor determining retention in nanofiltration [6,7]. This parameter is not the only influencing the retention: polarity and charge of organic molecules are mentioned by Van der Bruggen et al. [6].

In this Short communication we reported on the preparation and characterization of new nanoporous polyetheretherketone (PEEKWC) membranes and the comparison of these membranes with NF commercial membranes in terms of characteristics and performance. PEEKWC is an amorphous modified poly(etheretherketone). As reported in our

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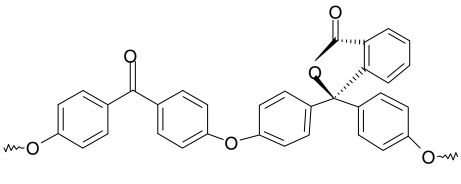
recent work [8], the dry phase inversion was a suitable method to prepare asymmetric gas separation membranes with a thin dense skin. In contrast to the traditionally used wet phase inversion, the dry casting technique does not need a coagulation bath since phase inversion is induced by the non-solvent present in the casting solution after it reaches a critical concentration upon the selective evaporation of the volatile solvent. In another early work [9], the preparation of PEEKWC asymmetric membranes by wet and dry–wet phase inversion was reported. In both cases, the phase inversion process involves a coagulation step in a non-solvent coagulation bath. As demonstrated by numerous studies [10–13] the coagulation conditions have a strong influence on the membrane properties. The coagulation rate determines the morphology of the bulk membrane (finger like or spongy) and the thickness of the skin layer [13]. In comparison with the dry-casting technique, the wet phase inversion has a higher potentiality because the exchange rate of the solvent and non-solvent can be easily controlled by the casting solution and coagulation bath composition. For a given casting system, an evaporation step prior to immersion in the coagulation solvent is often necessary to ensure the formation of a defect free skin layer in the dry–wet method. In this work, nanoporous PEEKWC asymmetric membranes for nanofiltration application, using dry–wet method were prepared and characterized. In the first part of the work, on the basis of our past results [9], the type of non-solvent added in the casting solution and its concentration were investigated to obtain membranes for nanofiltration application. The membrane performance concerned pure water flux and retention of charged and uncharged components. Characterization of the membrane surface properties, which are important to explain fouling phenomena, was also carried out.



Scheme 1. Structure of PEEKWC.

2. Materials and methods

2.1. Preparation of the membranes

Chloroform, methanol (MeOH), 1-butanol (BuOH) were purchased from Carlo Erba Reagenti, Italy, and were used without purification; PEEK-WC was supplied by the Chanchung Institute of Applied Chemistry, Academia Sinica, and was used without purification. The chemical structure of PEEKWC is shown in Scheme 1. This polymer is a modified polyetheretherketone having a lactone group attached to the backbone. The presence of this functional group makes PEEKWC well suited for preparation of polymeric membranes by phase inversion techniques. In fact, the modified polymer is higher soluble in common organic solvents compared to the traditional PEEK preserving the good thermal and mechanical properties of this latter [14,15].

Asymmetric membranes were prepared by the dry–wet phase inversion technique. The polymer solution was cast on a glass plate by means of commercial knife (Braive instruments; gap 250 μm).

On the basis of our recent study, concerning different preparation conditions for asymmetric PEEKWC membranes [9] to tune the membrane nanoporous dimension, a series of membranes were prepared by wet casting of a 10 wt.% PEEKWC solution in chloroform. In order to avoid a too porous skin, the polymer concentration in the film-coagulant interface was increased by partial evaporation of the solvent using a fixed interval (30 s) between casting and coagulation.

Two alcohols were used: methanol as external (in the coagulation bath) and internal non-solvent; 1-

Table 1
PEEKWC 10wt% in $CHCl_3$, 30 sec evaporation time, external coagulant MeOH

Membrane	Internal non-solvent	Membrane thickness (μm)	ε, overall porosity	CO_2 permeance (m^3/m^2 hbar)	Tensile strength	
					E (N/mm^2)	ε break (%)
M1b	BuOH, 10 pHr	58	71	12.3	380.45 (± 2)	29.15
M2b	BuOH, 12 pHr	50	74	18.8	281.08 (± 3.2)	26.16
M2m	MeOH, 12 pHr	52	63	0.91	310.24 (± 2.5)	23.44
M3b	BuOH, 14 pHr	74	74	22.0	244.42 (± 3.0)	29.93

butanol only as internal non-solvent in casting solution (10–14 pHr). Membrane M2m was prepared using methanol either as internal and external non-solvent; membranes M1b-3b were obtained using 1-butanol as internal non-solvent (Table 1).

The films were coagulated in a coagulation bath containing methanol for at least 12 h and then were released from the glass plate with the aid of a few drops of water. The membranes were wet stored. For each set of process parameters, three identical membrane sheets were made and tested to obtain a mean value of the flux and the retention.

To have a reference commercial nanofiltration membranes were studied. It concerns the membranes N30F and NF-TFC 50 from Hoechst High Chem, Wiesbaden. In both these membranes, the top layer is composed of polyethersulphone.

2.2. Characterization

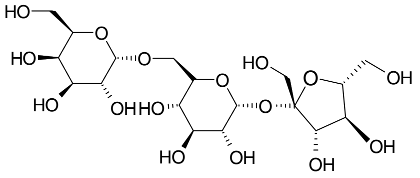
The morphology of the membranes was determined by scanning electron microscopy (SEM) (ESEM FEG QUANTA 200) at 0.2/30 KV. Sample specimens were freeze-fractured in liquid nitrogen to guarantee a sharp brittle fracture, and were successively sputter coated with a thin gold film prior to SEM observation. The thickness of each membrane was directly read from the SEM image of the cross-section and was also determined by a multiple-point measurement, using a digital micrometer (Karl-Mahr). The overall porosity ε of the membranes was calculated according to the equation:

$$\varepsilon = 100\% \times (1 - \text{density}_{\text{membrane}}/\text{density}_{\text{PEEKWC}}) \tag{1}$$

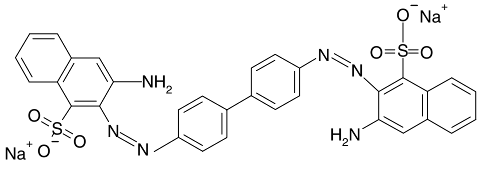
in which $\text{density}_{\text{PEEKWC}}$ was 1.29 g/ml and the density of the membrane was determined gravimetrically by weighing a sample of known area and thickness.

The gas permeance of the membranes for pure gases was determined at 25 °C and 1 bar of feed pressure. The procedure was based on the fixed volume pressure increase measurement on a permeability instrument constructed by GKSS, Germany. Details of the procedure and the equipment were described previously [8].

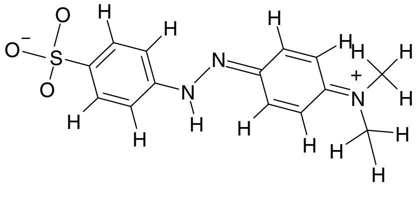
The roughness of the investigated membrane surfaces was evaluated by using Atomic Force Microscopy, Nanoscope III (Digital Instruments, VEECO Metrology Group) on a scan area of 1 μm × 1μm. Tapping Mode™ AFM operated by a scanning tip attached to the end of an oscillating cantilever across the sample surface. The cantilever was oscillated at or near its resonance frequency with amplitude ranging typically from 20 nm to 100 nm. Silicon probes with resonance frequency



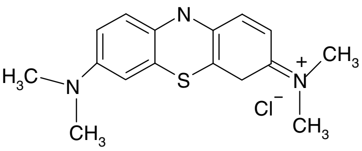
Raffinose,504g/mol



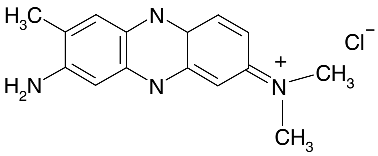
Congo red, 697 g/mol



Methyl Orange, 327 g/mol



Methylene blue, 320 g/mol



Neutral red, 289 g/mol

Fig. 1. Structure of the organic compounds used in this work.

200–400 kHz, nominal tip radius of curvature 5–10 nm and cantilever length 125 μm, were used. Surface roughness was estimated with respect to the mean absolute value difference, Ra, and the root mean squared difference Rq, between the actual surface height and that of the line dividing the surface of the investigated profile in two equal areas. Reported roughness values are the average of twenty measurements on different membrane samples. Specimen were analysed without any particular treatment.

Contact angle measurements were performed with a CAM 200 contact angle meter (KSV Instruments LTD, Helsinki, Finland). The sessile drop was formed by depositing the used test liquid from the above using an automatic microsyringe on the membrane surfaces.

2.3. Performance of the membranes

The performance of the membranes was tested in a dead-end set up operating at different pressures using compressed nitrogen. Flat sheet membranes with an effective membrane area of 38.5 cm^2 were employed. A PTFE-coated magnetic stirrer bar was employed at a stirring rate of 150 rpm, adjusted so that the depth of the vortex was no more than one third of the stirred solution level. Reverse stirring was also applied every 10 s to ensure that the feed solution was well mixed.

The temperature during the tests was equal to room temperature (293 K). To test a membrane the dead-end module was in a first step filled with distilled water and the pure water permeability was calculated according to formula (2).

$$\text{Water permeability} = \frac{\text{permeate volume(l)}}{\text{membrane area } (\text{m}^2) \text{ time (h) pressure (bar)}} \tag{2}$$

In a second step, the retentions of an uncharged component and negatively and positively charged components were studied. The performance of the self-made membranes was tested by filtrating a feed solution of uncharged and charged components during 2 h. To have a reference the same experiments were repeated for the commercial membranes.

The molecular structure of each organic component is shown in Fig. 1.

An aqueous feed solution was made with a concentration of 0.2 mmol/l for raffinose and 0.02 mmol/l for charged components. The retention was calculated with formula (3).

$$\text{Retention } (\%) = (1 - \text{Cp/Cf}) \times 100 \tag{3}$$

Where Cp and Cf are component concentration in the permeate and feed, respectively. An UV Shimadzu spectrophotometer was used to analyse the concentration of all charged components, the concentration of raffinose was determined using a colorimetric method [16].

To compare the flux decline between different membranes, relative flux (in %) were defined as the relation of the permeate flux to the pure water flux.

To evaluate the sorption on membrane, an aqueous feed solution was made with the same concentrations used in the nanofiltration experiments without pressurization. After >10 h, the compound concentration of the solution was measured and adsorption amount per unit area of the membrane was calculated.

3. Results and discussion

3.1. Preparation and characterization of membranes

In Fig. 2 SEM images of the prepared membranes are shown. In Table 1 some characteristics (thickness, overall porosity (ε), CO_2 permeance, tensile strength) are given.

Young's module *E* decreases in the series M1b-M3b in accordance to the presence of macrovoids along membrane cross-section (Fig. 2) and porosity. M2m in spite of its CO_2 permeance and overall porosity lower than the ones of M1b, has an E module of 310 N/mm^2. This is due to the morphology of the membrane (Fig. 3) characterized by a thin skin layer on elongated macrovoids across overall cross-section.

The membrane thicknesses are similar for M1b, M2b and M2m whereas M3b is thicker. The higher concentration of the large non-solvent 1-butanol in the casting solution hinders the entry of the small non-solvent methanol, determining a less compact membrane. The overall porosity is similar except for the membrane M2m. The use of the more volatile (MeOH) than BuOH as internal non-solvent, determines the formation of a less porous membrane: in fact, during the dry evaporation step before immersion, a part of this evaporates non-contributing to demixing in the coagulation bath. This fact is also confirmed by gas transport data

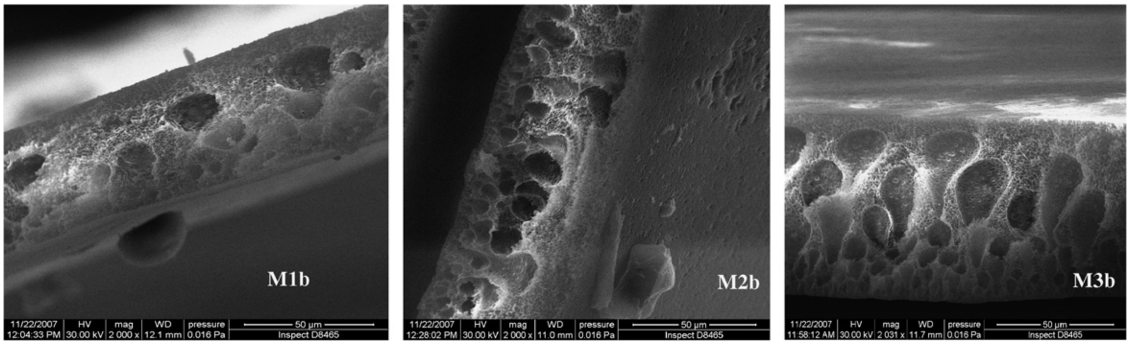


Fig. 2. SEM images of the membranes cross-sections, obtained by dry–wet phase inversion of a 10 wt.% PEEKWC solution in chloroform, using 1-butanol as internal coagulant (see Table 1).

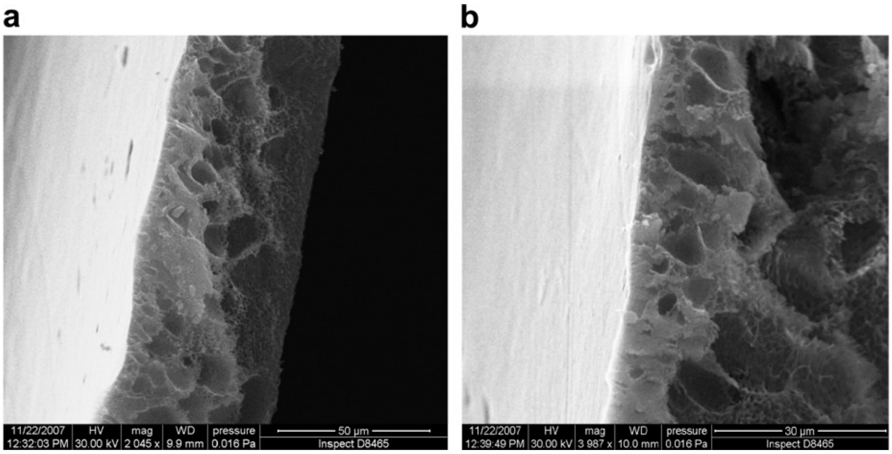


Fig. 3. Cross-section (a) and skin layer zoom (b) of membrane M2m prepared using methanol as internal coagulant (see Table 1).

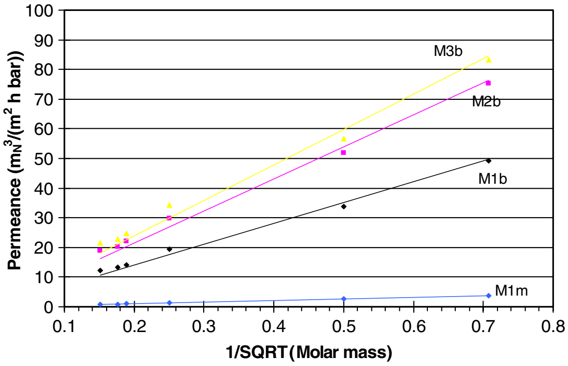


Fig. 4. Plot of the permeance against (molar mass of the permeation gas)-0.5 for the series of membrane M1b-M3b and M2m (Table 1).

(Table 1 and Fig. 4) M2m is the less permeable membrane compared to the other three membranes. Knudsen's type transport was observed for all the membranes (Fig. 4) and the slopes of the value permeance fitting are in the order M1m < M1b < M2b < M3b.

These results, observed for the gas permeance of membranes M1b-M3b, reflect the increasing demixing rate during the membrane formation [17,18]. Therefore, increasing the internal non-solvent concentration, a skin layer less dense, characterized by nanoporous, was formed.

The characterization of the membrane surface by means of AFM confirms this trend: M1b does not show pores (or they are of comparable dimensions to AFM tip radius) (Fig. 5a). In Fig. 5b, the presence of nanopores on M2b membrane is clear. A number of pores/µm^2 of 390 for this membrane is found. The relative pore size distributions with max on 15.63 nm and 52.4 nm for M2b and M3b, respectively, have been reported in Fig. 6.

This part of the work, concerning the preparation and characterization of the membranes, proves that

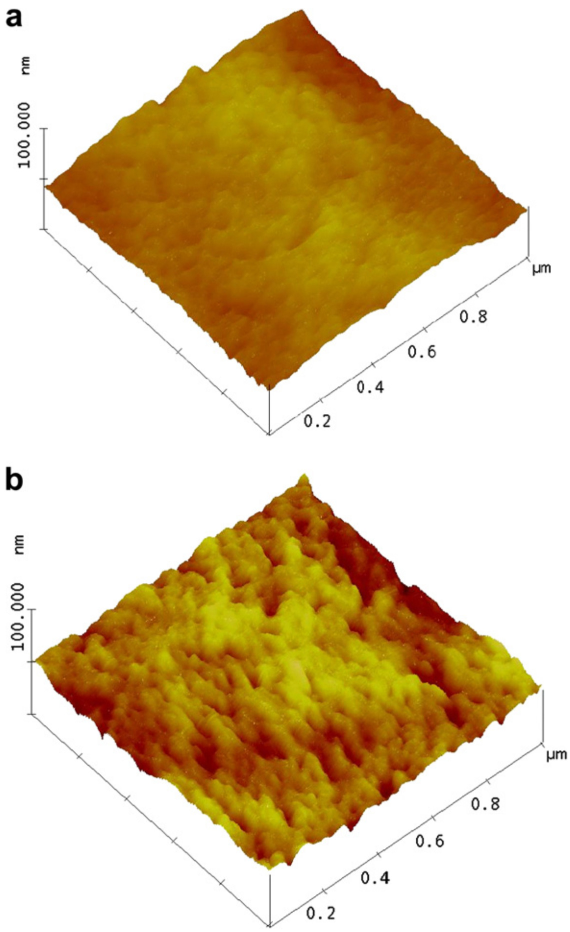


Fig. 5. AFM images of (a) M1b and (b) M2b.

varying the concentration of 1-butanol, added in the casting solution nanoporous (10–60 nm) membranes for nanofiltration applications can be prepared. In the same conditions, using a more volatile internal non-solvent (methanol), porous-dense membranes were obtained. Therefore, the concentration of non-solvent added and the type (methanol or butanol) constitute favourable preparation factors to obtain PEEKWC nanoporous membranes.

3.2. Performance of the membranes

Table 2 summarizes some characteristics such as water permeability and surface properties as contact angle and roughness for the PEEKWC membranes. In particular, the evaluation of the roughness was important to understand the interaction between the tested components and the membrane surfaces [19–22]. The characteristics of two commercial polyethersulphone membranes (N30F and NF TFC 50) are also reported for reference. In general, the pure water permeability for commercial nanofiltration membranes ranges between 1.5 and 15 l/m^2/h/bar. Therefore, on the basis of the water permeabilities of the self-made membranes (Table 2), their performance corresponded with the performance known for commercial nanofiltration membranes. This confirms that the preparation factors selected (type of internal non-solvent and its concentration in the casting solution) are favourable to obtain nanoporous membranes for nanofiltration applications.

NF TFC 50 and N30F have the most hydrophobic surfaces due to the larger contact angle compared to the self-made PEEKWC membranes. This difference is primarily due to different polymer material constituting the membranes. However, it is interesting to observe the different contact angle values between M1 b (69.5°) and the other three membranes M2b, M2m and M3b, that have similar contact angle (≈60°). This result could be caused by the difference in surface pore size and porosity [23] or surface roughness [24] as for ultrafiltration membranes (UF). In particular, Ulbricht et al. [25] observed that with increasing pore size of UF mem-

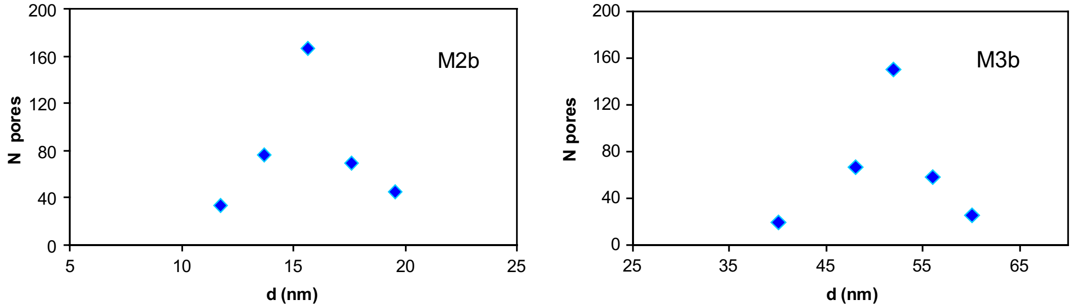


Fig. 6. Pore size distribution of M2b (left) and M3b (right) membranes.

Table 2
Characteristics of the self-made membranes and commercial nanofiltration membranes

Membrane		M1b	M2b	M2m	M3b	NF-TFC 50	N30F
Water permeability (l/m^2 hbar)		1.32 (±0.20)	3.7 (±0.28)	0.24 (±0.1)	7.9 (±0.4)	1.15 (±0.19)	3.8 (±0.8)
Contact angle (°)		69.5 (±2.6)	59.4 (±3.5)	57.9 (±3.0)	62.7 (±2.0)	84.6 (±3.1)	72.7 (±2.5)
Roughness (nm)	Rq	2.05 (±0.22)	2.27 (±0.39)	3.50 (± 0.28)	2.00 (±0.20)	5.52 (±0.46)	4.08 (±0.8)
	Ra	1.6 (±0.19)	1.76 (±0.30)	2.72 (±0.26)	1.58 (±0.14)	4.34 (±0.33)	3.05 (±0.6)

branes from the same material and manufacturing process, the contact angle values decreased due to higher porosity. Membranes of the series M1b-M3b have a comparable roughness factor Rq (≈2.0 nm) and the difference observed in contact angle confirm the relation between surface porosity and contact angle: M1b is the less porous surface membrane compared to M2b and M3b membranes and has the larger contact angle. In apparent contradiction, membrane M2m characterized by the lowest surface porosity has the more hydrophilic surface: in this case a correction for the different roughness factor (Rq = 3.50 nm) is necessary [24].

In this communication, our main aim was to obtain new nanoporous membranes for the separation of organic molecules. For this purpose, we selected membranes M2b and M3b characterized by higher water permeability (Table 2) compared to M1b and M2m membranes. For a first screening of the two selected membranes (M2b, M3b), congo red was used (negatively charged component) (Fig. 1): retentions of 100% and 74%, respectively, were found. Therefore, we selected the membrane with the higher retention to congo red, i.e., M2b membrane. The performance of M2b, in terms of retention and relative flux with the other charged and uncharged substances smaller than congo red (M_w 697 g/mol), was compared to the ones of commercial membranes N30F and NF TFC 50.

Retentions and relative fluxes for both the self-made and the commercial membranes are shown in Table 3.

3.3. Evaluation of retention

A difference in retention of M2b membrane depending on the charge of the component was observed. When the component carried a positive charge, the retention was 100% even for small components like methylene blue (M_w 320 g/mol) and neutral red (M_w 289 g/mol).

Strong repulsion forces between the positively charged membrane M2b and the positively charged components can explain this phenomenon: the charge effect played a fundamental role in the retention in respect to sieving mechanism. This fact is confirmed by the retention values for negatively charged components. Retention of methyl orange (M_w 327 g/mol) was of 64%. The retention of 100% for Congo Red (M_w 697 g/mol) can be explained on the basis of its larger dimension. In general from data in Table 3a, it is evident that the retention of commercial polysulphone membranes is lower than the one of M2b.

Table 3
Retention (a) and relative flux (b) of charged and uncharged components after 2 h of filtration

	M2b	NF TFC 50	N30F
(a)			
Congo red	100	60	99
Methylene blue	100	95	38
Methyl orange	64	31	66
Neutral red	100	68	77
Raffinose	41	73	71
(b)			
Congo red	79	60	48
Methylene blue	82	90	54
Methyl orange	72	77	89
Neutral red	92	52	55
Raffinose	31	79	75

In particular with NF TFC 50 membrane, Congo red was retained for 60% whereas, for smaller positively charged molecules as neutral red and methylene blue retentions of 68% and 95%, respectively, were observed. The retention of methyl orange characterized by a size similar to methylene blue was of 31%.

As reported by the manufacturer, the commercial membranes tested in this work are made of polysulphone negatively charged and the retentions found are in strident contrast with this fact. The contradiction can be explained on the basis of adsorption data (Table 4). The small negatively charged methyl orange is more adsorbed (9.7 mmol/m^2) by NF TFC 50 than neutral red (6.9 mmol/m^2) and methylene blue (4.86 mmol/m^2). This means that the

Table 4
Adsorption (mmol/m^2) of charged and uncharged compounds on the PEEKWC and the commercial membranes

	M2b	NF TFC 50	N30F
Congo red	0.76	0	4.2
Methylene blue	0	4.9	20
Methyl orange	9.7	9.5	18
Neutral red	0	6.9	20.3
Raffinose	1.2	3.0	30

membrane became saturated resulting in a breakthrough effect [26] and hence in a lower retention of this component. Adsorption phenomenon on membrane N30F could also explain the unusual retention of two positively charged components methylene blue (33%) and neutral red (77%): both are more adsorbed than the other components but with contrasting effects. With the larger methylene blue a breakthrough effect is responsible for the lower retention, whereas neutral red molecules were stuck in the pores, resulting in a decreased mass transfer.

Raffinose (uncharged component) has the lowest retention which is due to the absence of charge interactions between the component and the membrane surface. Sieving mechanism cannot explain the different retentions observed for M2b, N30F and NF TFC 50. On the basis of AFM analysis N30F has a pore size of 58.60 nm whereas pores of 27.20 nm are observed on NF TFC 50 surface.

To study the influence of adsorption on retention, the permeate concentration was measured in time and the corresponding apparent retentions were calculated. Fig. 7a shows the apparent retention as a function of time during the first 2 h of filtration for raffinose.

For N30F and NF TFC 50, a breakthrough effect could be noticed: retention decreased strongly during 90 min and then reached a stable value. This breakthrough effect was more evident for N30F, as expected, on the basis of the retention of raffinose (Table 3a). For membrane M2b, the retention of raffinose cannot be influenced by adsorption because it is not found (Table 4): the increase of retention results from pore blocking [27].

3.4. Evaluation of the relative flux

Table 3b shows the relative fluxes after 2 h of filtration for different feed solutions. The relative flux is a measure for the degree of fouling: a small relative flux corresponds with a lot of fouling. The fouling degree of the three membranes for all feed solutions is different.

Congo red and neutral red have lower relative flux for commercial membranes with relation to M2b. In fact, these compounds are less or not at all adsorbed on this membrane (Table 4). In this case, roughness is the key physical parameters to explain this phenomenon: M2b is the smoother and less hydrophobic membrane. According to Vrijenhoek et al. [22] fouling can be correlated with the surface roughness of nanofiltration membranes. It was demonstrated through use of AFM analysis that particles preferentially accumulate in the valleys of rough membranes, leading to "valley clogging" and causing more severe flux decline than in smooth membranes.

However, methyl orange and raffinose have smaller relative fluxes for M2b compared to N30F and NF TFC 50. For methyl orange, due to adsorption on membrane surface, a breakthrough effect was responsible for relative fluxes higher than M2b (Table 3b). As reported before, for M2b the retention of raffinose cannot be influenced by adsorption on the membrane, but by pore blocking.

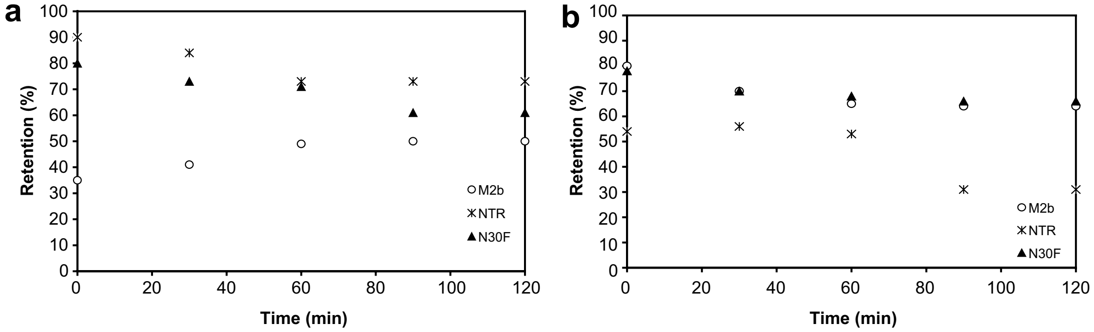


Fig. 7. Retention as function of time for (a) raffinose and (b) methyl orange.

4. Conclusions

New nanoporous PEEKWC with pore ranging from 5 to 60 nm were obtained using the dry–wet phase inversion technique. It was proven that for their preparation the type of internal non-solvent and its concentration in the casting solution are important factors. In particular, the study of the performance of membrane M2b showed a good agreement between retentions and AFM characterization. Retentions and relative fluxes depend on the charge and size of the tested compounds. The retention of small positively charged molecules (methylene blue and neutral red) was remarkably high, which was explained by the less adsorption (avoiding breakthrough effect) and by the positive surface charge of the membrane. The degree of fouling depends on the interactions between the component and the membrane. In general, it was not a severe problem for the charged components in the order neutral red < methylene blue < congo red < methyl orange. In fact, the relative fluxes range from 72% to 92%. With raffinose a severe fouling was observed for membrane M2b (relative flux of 31%) with relation to the commercial membranes N30F (75%) and NF TFC 50 (79%).

To conclude, the results obtained, in terms of retention and relative flux, make the new nanoporous self-made PEEKWC membranes very interesting when filtrating aqueous solution of charged components.

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