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Evaluation of reverse osmosis and nanofiltration membranes performance in the permeation of organic solvents

Katia Rezzadori [a], Frederico Marques Penha [a], Mariane Carolina Proner [a], Guilherme Zin [a], José Carlos Cunha Petrus [a], Pedro Prádanos [b], Laura Palacio [b], Antonio Hernández [b], Marco Di Luccio [a],*

[a] Department of Chemical and Food Engineering, Federal University of Santa Catarina, 88040-970 Florianópolis, SC, Brazil
[b] SMAP, Surfaces and Porous Materials Group, Faculty of Science, University of Valladolid, P. Belén 7, 47011, Spain

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ABSTRACT

The aim of this study was to evaluate the influence of different solvents and time conditionings in the permeation of *n*-hexane and oil/*n*-hexane solutions through several reverse osmosis (ORAK – Osmonics, BW30 – Dow Filmtec) and nanofiltration (NF270 – Dow Filmtec, NP030 – Microdyn Nadir) polymeric membranes. The study of the influence of membrane conditioning on the *n*-hexane flux was carried out using different solvents (*n*-hexane, ethanol, *n*-propanol, *iso*-propanol and butanol) as pretreating agents in different time intervals. Membrane performance was tested by measuring *n*-hexane fluxes and rejections of dissolved castor oil. The conditioning with ethanol increased *n*-hexane fluxes in the polyamide membranes ORAK, NF270 and BW30, while the polyethersulfone membrane NP030 did not present any increase in permeability. An increase in contact angle after membrane conditioning was detected, as well as a reduction in free surface energy. This suggests that pretreatment steps alter the surface hydrophilic character. Salt rejections for all the membranes decreased after the pretreatments and permeation with *n*-hexane for 8 h. These rejections dropped from 87–99% to 72–77% for membranes NF270, NP030 and BW30; and from 99% to 88% for ORAK, which showed better stability to solvent exposure. For castor oil, the highest retention was 60% for reverse osmosis membrane ORAK. The results obtained in this work with commercial RO and NF membranes, normally used in aqueous solutions operations, indicate that most of these membranes do not present adequate stability towards non-aqueous solvents.

1. Introduction

On the last decade, the use of membrane technology in non-aqueous systems has been highlighted. The main applications include solvent recovery from micelles of vegetable oil/organic solvents; deacidification and clarification of vegetable oils [1–3] and separation of natural compounds from essential oils [4,5]. However, there are still few reports on the application of membranes in the separation of non-aqueous streams in industrial level. Even though there are some studies on the preparation of solvent resistant membranes, only few are commercially available, e.g. Borsig, PolyAn, Duramem®, Puramem® and SolSep®. Also, according to reports found in literature, commercial hydrophobic membranes have low permeate flux. Studies performed by Teixeira et al. [6], with hydrophobic commercial membrane Puramen®, demonstrated permeability of 0.23, 0.16, 0.0015 $L\,h^{-1}\,m^{-2}\,bar^{-1}$ for *n*-hexane, ethanol and oleic acid, respectively. Jimenez Solomon et al. [7] studied the permeate flux of nanofiltration Starmen™ and Puramem® of a feed solution comprising polystyrene oligomers dissolved in toluene, in operation conditions of 30 bar and 30 °C, and found fluxes between 18 and 114 $L\,h^{-1}\,m^{-2}$, respectively.

The major drawback for applying membrane technology in non-aqueous systems is the large range of interactions between the solvent and the membrane. These interactions can lead to phenomena as the swelling of the polymeric matrix, plasticisation or even the dissolution of membrane material and subsequent loss of morphological structure, causing changes in separation properties and/or mechanical resistance under pressure [8,9]. Extension of conventional steric and electrostatic separation mechanisms, typical of aqueous environments, to non-aqueous systems is complex, due to the significant differences in the structures and properties of the solvents [1,2]. Several authors have observed that membranes performance is

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* Corresponding author. Tel.: +55 48 3721 2529.
E-mail address: di.luccio@ufsc.br (M. Di Luccio).

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less predictable in the presence of organic solvents than in aqueous solutions [1,2,4–6], and the MMCO is an insufficient descriptor for the separation capability of the membrane in organic solvents. Compared to the aqueous membrane process, non-aqueous processes are categorised by the increase in the number of solute–solvent–membrane interactions, which play a determining role in the understanding of both solvent flux and solute rejection [6]. Therefore, studies in this field can promote benefits to edible oil industries, pharmaceutical products manufacturers and petrochemical industry, due to its low energy consumption and simplification of operational processes with organic solvents.

Recent researches suggest that the polymeric membrane pretreatment, through their immersion in an organic solvent, is fundamental for membrane performance in non-aqueous systems. The pretreatment may differ according to the membrane material nature and the solvent used in the process. Several pretreatment solvents and pretreatment times have been proposed for different polymeric membranes. Firman et al. [10] used different nanofiltration membranes (polymeric tailor made membranes – asymmetric, composite and dense; and commercial membranes–SOLESP®). All membranes were immersed for 24 h with pure solvents of decreasing polarities (ethanol, *iso*propanol and *n*-hexane). Darvishmanesh et al. [11] used nanofiltration and reverse osmosis commercial membranes (made of polyamide (PA), polyethersulfone (PES) and sulfonated polyethersulfone) and pretreatment in ethanol for at least 24 h. Darvishmanesh et al. [12] used immersion treatments in various organic solvents for one week before permeation in nanofiltration membranes produced with PA. Van der Bruggen et al. [13] also reported on their work with NF membranes, treatments of 24 h by immersion in ethanol and *n*-hexane. All the authors noted improvements in the permeate flux after the pretreatment. According to these studies, membrane conditioning can prevent pore collapse during permeation of non-polar solvents [13–15] and enable the solvent to reach all membrane pores, increasing the permeate flux [16]. Moreover, conditioning would also change polarity characteristics of the membranes, which are mainly hydrophilic, increasing its permeability to the organic solvents.

Nonetheless, to the best of our knowledge, membrane pretreatment were studied only in terms of solvent immersion and more information about the time exposure or solvent type, as well as the changes in the membrane structure are poorly reported. In this context, the present work aims to evaluate the influence of different solvent and time conditionings in the permeation of *n*-hexane through commercial reverse osmosis and nanofiltration polymeric membranes, assessing the surface hydrophilicity and structural changes caused by solvent permeation.

2. Material and methods

2.1. Material specifications

Four commercial membranes were studied, two nanofiltration (NF) and two reverse osmosis (RO). The main characteristics of each membrane, according to manufacturer description, are shown in Table 1.

Solvents used in conditioning and in permeate fluxes determining, as well as some of their characteristics are shown in Table 2. All solvents are analytical grade (> 99%, Vetec, Brazil).

2.2. Permeation of *n*-hexane and water

2.2.1. Experimental apparatus

The assays were conducted in a dead-end filtration cell, 120 mL volumetric capacity, coupled with a manometer (0.1–4 MPa). Transmembrane pressure was obtained by nitrogen (99.99%, White Martins, Brazil) pressurisation of the headspace of the permeation cell. The effective membrane filtration area was $2.624 \cdot 10^{-3}$ m^2.

The solvent permeability tests were performed at room temperature. Permeate was collected through an on-off ball valve (Swagelok, model SS-42GS4) located at the basis of the cell, in a graduated cylinder compatible with the permeate flux. To avoid solvent evaporation, the cylinder was immersed in an ice bath.

2.2.2. Membrane conditioning

Membranes were immersed in distilled water for 24 h, replacing the water each 4 h, to remove possible manufacturing residues that could affect solvent permeation through the membranes (1st step). This step was carried out with all membranes tested.

The conditioning procedure was performed by the immersion of the membranes in a homologous series of alcohols, with different chain lengths (methanol, ethanol, *n*-propanol, *iso*-propanol and butanol). Pretreatment started with the immersion of the membrane in one of the alcohols for 2, 8, 12 or 24 h in a closed recipient, thereafter, membrane was subsequently immersed in *n*-hexane for 2 h before the permeation assay with *n*-hexane. Conditioning tests using only *n*-hexane were performed (4 h) too. Each pretreatment was performed with a new flat sheet membrane.

n-Hexane fluxes of each membrane, before and after conditioning, were assessed according to the following procedure: filtration cell was loaded with 120 mL of *n*-hexane; membrane compaction was performed for 30 min at the highest pressure (3.5 MPa) to be tested, then, the fluxes were collected with progressive reduction of pressure (3.5; 3.0; 2.5; 2.0; 1.5; 1.0; 0.5 MPa). The permeation cell was continuously stirred (400 rpm) to minimise concentration polarisation. The assays were performed at 293.15 ± 274.15 K and in duplicates.

2.2.3. *n*-hexane resistance and membrane integrity

After washing with water, as described in Section 2.2.2, without any conditioning, membranes were immersed in ethanol for 30 min, after which, its hydraulic permeability was measured. Then, another immersion in ethanol for 30 min was performed and thereafter, *n*-hexane permeation started. This short pretreatment was necessary to enable the comparison between the water and *n*-hexane permeability in the same membrane sample. Since *n*-hexane is immiscible in water, it is not possible to measure water flux after *n*-hexane permeation, without the solvent exchange procedure. These assays were performed at 1.5 MPa for NF membranes and 2.0 MPa for RO membranes. *n*-hexane flux through the membranes was assessed during 8 h.

Integrity assays were performed after the *n*-hexane resistance tests to verify possible changes in the membranes. After completion of the resistance test, as described above, the membrane was removed from the permeation cell and immersed in ethanol for 30 min. Then, the membrane was placed in the cell, and water permeability was measured. Membrane integrity was also verified by measuring salt rejection in water before any pretreatment (new membrane), after pretreatments and after membranes were permeated with hexane for 8 h. Saline solutions and operating conditions used for determining of rejections were in accordance with manufacturer's details for each membrane (Table 3). The assays were carried out at room temperature (293.15 ± 2 K).

The experiments performed in this work were summarised in Fig. 1 to provide better understanding.

2.3. Membrane characterisation

2.3.1. Contact angle and surface free energy

These properties were characterised by static contact angle measurements, which were carried out by the sessile drop method using a goniometer (FTA 200, Virginia, USA). Contact angle was