



Characterization and performance of reverse osmosis and nanofiltration membranes submitted to subcritical and supercritical CO₂



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ABSTRACT

Behavior of nanofiltration (NF270 and NP030) and reverse osmosis (BW30 and ORAK) polymeric membranes in systems with dense CO₂ was evaluated. The influence of transmembrane pressure on the CO₂ permeate flux at subcritical and supercritical conditions was assessed and membrane characterization (FTIR-ATR, zeta potential, Hansen's solubility parameters) was performed. The results of CO₂ permeation suggest that selectivity of polymeric matrix depends, in great extent, on the interaction between solvent and polymer. This behavior corroborates with the presence of hysteresis phenomenon in permeability curves and solubility results. Also, zeta potential showed a decrease in the membrane point of zero charge (PZC) after pressurization/depressurization cycle, suggesting possible CO₂ sorption in the membrane polymer. Nevertheless, the oil retention for NP030 and ORAK membranes was up to 85% and no damage to the membrane structure was found. Both membranes presented potential for concentration of fatty acids under dense phase CO₂.

1. Introduction

Higher quality products with reduced energy consumption are required for food and chemical industry. To this end, alternative processes, based on membrane technology, for concentration and fractionation were developed. This technology is known to have the several advantages over traditional separation processes, such as simple scale up, low energy demand when compared with thermal process (distillation), and high efficiency in the separation and fractionation process. In most cases it generates a higher quality in the final product [1]. However, one of the major drawbacks of this technology is the permeability reduction during filtration, due to concentration polarization and fouling. Membrane technology can also be combined with other separation processes allowing greater flexibility for extraction and fractionation processes of natural compounds [2].

The study and use of separation processes with reverse osmosis (RO) and nanofiltration (NF) membranes in aqueous systems, as in concentration of functional compounds [3,4], milk and whey protein [5,6] are well established. In the last decades, the membrane use in non-aqueous systems has been considered promising for partially desolventizing or degumming of oil/solvent mixtures [7,9].

At the same time, many processes that use carbon dioxide (CO₂), as

supercritical technology, have been studied and developed for natural compounds extraction [10,11]. CO₂ is a nontoxic and environmentally friendly solvent if continuous recycle is performed, and has a tunable dissolving power, easily fitted by adjusting process temperature and pressure [12]. Supercritical CO₂ is reached when temperatures and pressures above its critical point (31 °C and 74 bar) are used. If temperature and pressure are below the critical point, CO₂ changes to a liquid and is referred to as subcritical. Coupling membrane processes with dense CO₂ can provide additional advantages, such as avoiding steps of intense depressurization and improvement of the separation of compounds by the combined effect of CO₂ and membrane selectivity [10,12].

However, the development of this technological breakthrough is linked to chemical stability and mechanical strength of the polymeric membranes. Particularly, tunable properties of CO₂ can cause potential changes in the polymeric structure, such as swelling, plasticization or even membrane material dissolution and consequent loss of morphological structure, affecting separation properties [13,14]. Specific membranes for separation of non-aqueous mixtures are still limited, and in-depth studies on the use of commercial polymeric membranes in presence of dense CO₂ are still quite restricted.

In previous work, permeate flux changes after exposure to dense

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CO₂ and preliminary membrane characterization were carried out [11], showing that the exposure to dense CO₂ can cause changes in chemical and morphological properties, which in some cases, could improve the filtration of non-aqueous feed streams. The behavior of permeate flux and membrane selectivity for NF and RO membranes with respect to the membrane compaction, i.e., permeate flux CO₂ at different transmembrane pressures, is still a gap to fill. Hence, the innovation of this study was the investigation of the behavior and performance of commercial membranes when used in hybrid system with supercritical technology. The effects of different conditions (subcritical and supercritical) and depressurization rates used in the process were evaluated by measuring CO₂ flux, oil retention and using different characterization analysis (zeta potential, FTIR and solvent solubility estimation in polymers) as indicators of performance and stability.

2. Materials and methods

2.1. Material specifications

Nanofiltration (NF270 Dow Filmtech – Edina, Minnesota, EUA, NP030 Microdyn – Wiesbaden, Hesse, Germany) and reverse osmosis (BW30, Dow Filmtech; ORAK, Osmonics – Trevose, Pennsylvania, USA) membranes were tested. The detailed characteristics of these membranes are described elsewhere [11]. Raw macauba oil was purchased from Cocal Special Oils Ltd. (Abaeté, Minas Gerais, Brazil). Commercial grade carbon dioxide (99.95%) was acquired from White Martins (São Paulo, São Paulo, Brazil).

2.2. Experimental apparatus and operation procedure

The experimental runs were performed in a system that may be used in two different configurations, as described by Rezzadori et al. [11], to determine the effect of CO₂ on polymeric membranes. In one configuration only dense CO₂ enters the permeation cell, and this set-up was used for runs that involved pressurization and depressurization steps. In the second configuration, both CO₂ and oil mixture continuously enter the cell. The effective membrane filtration area was $2.624 \times 10^{-3} \text{ m}^2$. This configuration was used to concentrate fatty acids from macauba oil. Subcritical and supercritical conditions, 8 MPa/293.15 K and 13 MPa/313.15 K, respectively, were chosen based on a previous study by Rezzadori et al. [11].

2.2.1. Influence of transmembrane pressure (ΔP) on the dense CO₂ permeate flux

The tests of membrane compaction at increasing and decreasing transmembrane pressures were performed using both subcritical and supercritical conditions. After initial procedure, the retentate and permeate valves were adjusted to build up the desired transmembrane pressure (ΔP). A pressure gauge was used to check the ΔP between the feed and permeate streams. The membrane cell temperature was adjusted by a thermostatic bath connected to the cell's jacket and controlled by a temperature sensor (thermocouple). The ΔP ranged from 0 to 50 bar by 10 bar increments with 1 h of dwell time at each step. Then, the same procedure was followed by decreasing ΔP back to

0 bar. In each ΔP two measurements of CO₂ volumetric permeate flux were taken, using a flowmeter. This whole process was performed in duplicate using different membrane samples.

2.2.2. Macauba oil concentration

Macauba oil concentration was carried out according to Rezzadori et al. [11]. This operation mode included a HPLC pump (AcuFlow, Model Series III HPLC, Peterborough, Ontario, Canada) to displace the macauba oil to the membrane module. The feed flow rates of both streams were adjusted to reach the desired feed ratio of oil and CO₂ (1:1 v/v – 3 mL min^{-1}). The permeate flux was monitored for 60 min and permeate/retentate samples were collected periodically using micrometric valves. The macauba oil permeate flux was measured gravimetrically at time intervals by evaluation of the mass deposited in a collecting vial. This process was performed in duplicates using different membrane samples. Retention index (RI) was calculated according to Eq. (1)

$$RI(\%) = (1 - c_p/c_f) \times 100 \quad (1)$$

where C_p and C_f represent the total amount of oil/fatty acid collected at the corresponding processing time.

2.3. Membrane characterization

2.3.1. Zeta potential

Electrical charges on the surface of membranes was determined using with an electro kinetic analyzer (SurPASS, Anton Paar, Graz, Austria), using an adjustable-gap cell. The assays were accomplished ranging pH from 3.0 to 10.0. For each measurement, membrane samples of $20 \text{ mm} \times 10 \text{ mm}$ were attached onto the sample support using double-sided adhesive tape. The sample support was inserted into the adjustable-gap cell, such that two membrane samples were facing each other. The measurements were repeated at least twice for different membrane samples.

2.3.2. Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR)

New membranes and membranes submitted to different processing conditions were analyzed through infrared spectroscopy with the attenuated total reflection method (Perkin Elmer, Model Frontier, Waltham, Massachusetts, USA), from 4000 to 600 cm^{-1} .

2.3.3. Estimation of solvent solubility in polymers

The polymer/solvent interactions can be estimated based on their solubility parameters. The overall solubility parameter (Hansen solubility parameter), δ , can be considered as a function of the individual contributions related to dispersive forces (δ_d), polar interactions (δ_p – dipole-dipole forces) and hydrogen bonding (δ_h).

$$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5} \quad (2)$$

The Hansen solubility parameters are frequently used to predict a tendency concerning to the solubility of solvents in polymeric materials. Values used for the calculations are shown in Table 1. Solubility parameters (δ , δ_d , δ_p , δ_h) must match as closely as possible for a polymer

Table 1

Hansen solubility parameters for PES and polyamide and CO₂ in subcritical and supercritical conditions.

	δ_d	δ_p	δ_h	δ	V_m ($\text{cm}^3 \text{ mol}^{-1}$)	χ (dimensionless)	$\Delta\delta_{s,p}$ (dimensionless)
CO ₂ Subcritical	9.99	4.35	4.88	11.94	55.90	0.62	12.35
CO ₂ Supercritical	8.69	4.11	4.50	10.61	62.51	0.67	13.63
PES	19.6	10.8	9.2	24.2			
CO ₂ Subcritical	9.99	4.35	4.88	11.94	55.90	0.97	27.55
CO ₂ Supercritical	8.69	4.11	4.50	10.61	62.51	1.03	28.62
Polyamide	24.3	19.5	22.9	21.6			

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