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Simultaneous improvement in solvent permeability and deacidification of soybean oil by nanofiltration

L. Firman[1] · N. A. Ochoa[2] · J. Marchese[2] · C. Pagliero[1]

Abstract In this paper, soybean oil deacidification and hexane removal using laboratory scale solvent resistance nanofiltration membranes based technique is presented. Composite nanofiltration membranes made of different polymers poly(vinylideneflouride) (PVDF), polydimethyl-siloxane (SI), polycarbonate (PC), and glycerol were tested to remove the hexane and free fatty acid (FFA) from soybean oil/hexane miscella (oil feed solution 10, 25, and 35% w/w) at 20 bar of transmembrane pressure and 30 °C, in a dead-end filtration set up. All membranes tested showed low fouling phenomena and high stability in the presence of hexane throughout the membrane pre-treatment and permeation procedure. The PVDF-10SI-1PC membrane showed the best performance achieving a miscella permeability of $L_m = 6.8 \times 10^{-6}$ L (h m bar)$^{-1}$, oil and FFA sieving efficiency of $\beta_{(oil)} = 0.21$(80% of oil rejection) and $\beta_{FFA} = 2.43$ (27% of FFA removal), respectively, at oil feed concentration of 25%. Apart from these specific properties, the PVDF-10SI-1PC membrane presented excellent mechanical and chemical resistances and low reversible fouling. The results demonstrate that membrane technology can attain a high efficiency in the simultaneous solvent recovery and deacidification of oil/hexane miscella commonly processed in the soybean oil industry.

Keywords Soybean oil · Nanofiltration · Deacidification · Hexane recovery

Introduction

Vegetal oils can be extracted from industrial and edible oilseeds (soybean, palm, peanut, sunflower, etc.). Soybean oil is perhaps one of the world's widely known vegetable oils due to its intensive production, a wide variety of applications, and to its competitive price (Sipos and Szuhaj 2000). According to the estimates, the soybean production in 2014/15 was 317 MMT with United States of America (34.3%), Brazil (30%), and Argentina (18.5%) the major producers in the world (United States Department of Agriculture 2015). Most soybean production (75%) is destined for animal feed, 19% in soybean oil, 1–2% directly as food, and 4–5% as a waste product (peels and others). The 95–97% of oil production is utilized for edible purpose and the rest for non-edible uses (WWF 2014). Soybean oil has favorable characteristics compared to other vegetable oils, for example: possesses high levels of unsaturation, remains liquid in a wide temperature range, can be hydrogenated selectively to be mixed with liquid or semi-solid oils, and has natural antioxidants (tocopherols) which favor its stability (Sipos and Szuhaj 2000).

In the soybean oil extraction as performed today by the oilseed-crushing industry, usually involves solvent extraction with commercial hexane. In order to obtain the

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properties required for consumption, crude edible oils must be subjected to refining and treated to remove the hexane from miscella (oil–solvent mixture). Given that the conventional process of solvent recovery in edible oil refining involves a series of distillation columns, evaporators, stripping columns and condensers, the oil desolventizing requires about a 50% of the total energy consumption (Woerfel 1995). Chemical refining is the most common method used to produce a high quality product. This method involves several major steps in order to removal different detrimental contaminants as phospholipids (degumming); free fatty acids (FFA) (deacidification); phosphatides, pigments and soaps (bleaching); sterol, resins and volatiles (deodorization). The chemical process has disadvantages such as high energy consumption, oil thermal damage, high discharge of effluents, and oil loss (Koseoglu 1991). Particularly, during the deacidification process, large amounts of waste water are produced requiring expensive treatment. As a result, both capital and energy costs are high. One alternative is the FFA distillation method which improves the product quality, the elimination of soap stock, and effluent reduction; its disadvantage is that strict oil pretreatment is required (Subramanian et al. 2004). Another potential solution is the use of hybrid processes, i.e. the supercritical CO_2 process combined with membrane technology (Koseoglu 1991; Artz et al. 2005; Lai et al. 2008).

Membrane processes have gradually found a place in the industry since the late eighties, providing an alternative to the traditional processes of distillation, extraction, and evaporation. In the past two decades, solvent resistance nanofiltration membrane (SRNF) has received increased attention because it offers a large potential for energy saving in petrochemical, pharmaceutical, food and catalytic applications (de Morais-Coutinho et al. 2009; Schmidt and Lutze 2013). If solvent-resistant membranes with good permeation properties can be obtained, membrane technology may replace or be used in combination with conventional oil processes. Zwijnenberg et al. (1999) studied the separation of several oil/acetone mixtures (oils: sunflower, palm, rape seed) with two commercial SRNF (PEBAX and cellulose), achieving high oil retention and high both, acetone solvent recovery and FFA concentration in the permeate stream. The elimination of hexane from soybean oil/hexane miscella using ultrafiltration (UF) ceramic membranes was investigated by Wu and Lee (1999). Stafie et al. (2004) studied the permeation of sunflower oil/hexane mixture in polyacrylonitrile/polydimethylsiloxane composite membranes. Tres et al. (2009, 2014) examined several polymeric and ceramic commercial membranes for the separation of *n*-butane and *n*-hexane from refined soybean. A study on simultaneous degumming, dewaxing and decolorizing crude rice bran oil

using two commercial nonporous polymeric composite hydrophobic membranes was performed by Manjula and Subramanian (2009). Composite membranes of polydimethylsiloxane/poly(vinylideneflouride) (PDMS/PVDF) and Zeolite PDMS/PVDF were used in hexane recovery from soybean oil/hexane miscella (Cai et al. 2011). Darvishmanesh et al. (2011) studied four polymeric commercial NF membranes for the recovery of ethanol, isopropanol, acetone, cyclohexane and hexane solvents from their oil/solvent mixtures. Experimental results showed that the new generation of SRNF membranes has a superior performance compared to the previously used NF membranes. Hendrix et al. (2014) had improved significantly the retention of edible oil introducing free amines into the polyallylamine membrane structure.

Our research group has been working in the area of membrane preparation and their applications in different vegetable oil treatment, among them, degumming of crude soybean oil/hexane mixture with UF membranes made from different polymeric material (PVDF), Polyethersulfone (PES), Polysulfone (PSf), Polyimide (PI) (Pagliero et al. 2001; Ochoa et al. 2001; Pagliero et al. 2004); recovery of hexane from sunflower oil/hexane miscella using composite membranes of PVDF/PDMS and PVDF/cellulose acetate (CA) (Pagliero et al. 2011); removal of free fatty acids (FFAs) and hexane recovery from soybean oil, combining liquid–liquid extraction (FFA separation) and NF membrane process (solvent recovery) (Fornasero et al. 2013). More recently, our group has established that SRNF made from PVDF as support and PDMS as active dense layer have high selectivity for hexane recovery and a reasonable selectivity for FFAs separation (Firman et al. 2013). Encouraged by the favorable results obtained with the composite membrane made with 12% of PDMS, high hexane flux and simultaneous FFA removal, the present study aims to improve the performance of this hydrophobic membrane. For that, the properties of the PDMS dense layer was modified incorporating two more hydrophilic compounds, polycarbonate (PC) and glycerol (GLY). PC is a well studied polymer that can contribute to decrease the hydrophobicity of PDMS. GLY is a hydrophilic compound that is usually used as plasticizer that allows separating the polymeric chains (Pasini Cabello et al. 2014). The efficacies of the new composite membranes are assessed for simultaneous hexane recovery and deacidification of soybean oil/hexane mixture.

Experimental

Soybean oil characteristics

The degummed crude soybean oil used to prepare synthetic miscella solution was provided by a local industry (OLCA

SAIC, Córdoba, Argentina). Soybean oil composition in weight according to the supplier was triglycerides 98.5%, FFA $0.9 \pm 0.2\%$, sterol 0.33%, tocopherols 0.18%, squalene 0.014%. The average molecular weight of triglycerides, MW = 862.7 g mol^{-1}, was calculated using major fatty acids composition (12% palmitic acid, MW 256.4; 3.3% stearic acid, MW 284.48; 17.7% oleic acid, MW 282; 56% linoleic acid, MW 280.45; 10% linolenic acid, MW 278.43); the average molecular weight of FFA was approximately of 280 g mol^{-1}. The oil concentration in the oil/hexane miscella samples for membrane separation tests was varied from 10 to 35% w/w.

The oil concentration was determined with an UV absorption spectrophotometer (Metrolab 330) at a wavelength of 458 nm (Wu and Lee 1999). Free fatty acid (FFA) concentration (as grams of oleic acid in 100 g of oil) was determined according to the AOCS Ca 5a-40 method using an automatic titrator (848 Titrino plus-Metrohm AG).

Composite SRNF preparation

Composite membranes were performed by covering the surface of an asymmetric membrane with a thin layer of polymeric material.

Asymmetric membrane support

The flat asymmetric membrane was prepared by the phase inversion process. Polymer solution, 23% w/w poly(vinylideneflouride) (PVDF) high viscosity (from Solvay, Belgium) in dimethylformamide (DMF) (Aldrich, Argentina), was cast onto a non-woven Viledon-2431 polymeric flat support (Carl Freudenberg, Germany), at 25 °C in air (45–50% relative humidity), by using a film extensor with a 400 μm knife gap. After 20 s of solvent evaporation, the nascent membrane was immersed in a bidistilled water coagulation bath (T = 25 °C) for 1 h and then stored in fresh water. The asymmetric PVDF membrane was dried at room temperature for 48 h before being used.

Composite membranes

Composite membranes were prepared by covering the surface of the dried asymmetric PVDF membrane with different solutions of poly-dimethylsiloxane (SI) (Siloc, Anaeróbicos S.A., Argentina), polycarbonate (PC) (from Lexan General Electric, MW = 34,577 g mol^{-1}, polydispersity = 1.46) and glycerol (GLY) (99.5% from Biopack, Argentina) in chloroform.

Given the positive results obtained with the composite membrane PVDF-12SI (Firman et al. 2013) our first formulation of the coating solution was performed with a 12% SI and 1% PC. The perm-selective performance of this PVDF-12SI-1PC membrane was lower than the PVDF-12SI one (similar oil rejection, lower FFA efficiency, and permeability 1.2 times lower). From this preliminary test it was proposed to prepare coating solutions starting with 10% SI and the total percentages of polymers (SI-PC or SI-GLY) in the solution should not be higher than 12%.

Three different composite membranes were prepared according to the following composition: (1) 10% SI and 1% PC; (2) 10% SI and 2% PC; (3) 10% SI and 2% GLY. The SI-PC or SI-GLY solutions were cast onto the PVDF support surface (film extensor gap of 400 μm, T = 25 °C) and the chloroform was allowed to evaporate during 24 h. Next, the coated film was put into an oven at 60 °C for 4 h in order to assure the complete cross-linking of SI. The composite membranes were identified as PVDF-10SI-1PC, PVDF-10SI-2PC and PVDF-10SI-2GLY, respectively.

Filtration device

The permeation experiments were performed in a dead-end filtration setup described elsewhere (Firman et al. 2013). The effective transfer area of the membrane was A = 14.6×10^{-4} m^2. To minimize the fouling phenomena the feed solution was stirred with a magnetic bar (500 rpm) placed over the membrane surface. The trans-membrane pressure (Δp) was supplied by a nitrogen cylinder connected to the top of the cell.

Membrane characterization

Membrane morphology

The membrane morphology was analyzed using a scanning electron microscope (LEO 1450VP, Leo Electron Microscopy Ltd.). Membrane samples to be examined by SEM were obtained by soaked in isopropanol and then freeze-fractured in liquid nitrogen. Membrane samples were coated by sputtering a thin gold layer and then, SEM photographs of the cross-sections were taken.

Contact angle measurements

The hydrophobic character of the membranes was determined by measuring the water-membrane contact angle (θ) by the sessile-drop technique using a contact angle device (Micromeritics Instrument Corporation, Norcross, GA, USA). The procedure of contact angle measurements was described in elsewhere (Firman et al. 2013) and were evaluated from the following expression

$$\cos \theta = 1 - \sqrt{\frac{Bh^2}{\left(1 - \frac{Bh^2}{2}\right)}} \tag{1}$$

where B = ρg/2γ, being "g" the gravity acceleration (980 cm s^{-2}), "ρ" and "γ" the bi-distilled water density (0.9971 g cm^{-3}) and the interfacial tension of (71.97 erg cm^{-2}), and h the height of the liquid drop.

Molecular weight cut-off (MWCO)

Dyes Methylene Blue (MB) (MW = 374 g mol^{-1}, 99%) and Rose Bengal (RB) (MW = 1017gmol^{-1}, 99%) were used in the membrane MWCO estimation. MB was purchased, from Anedra S.A. (Argentina) and RB from Cicarelli Laboratories (Argentina). The MWCO of the composite membranes were estimated in the dead end setup described in "Filtration device" section. The membranes were pre-conditioned with pure solvents of decreasing polarities following the procedure given in "Pure hexane and oil/hexane miscella NF tests" section. Experiments were performed by triplicate at 20 bar of transmembrane pressure and T = 30 °C using 7.5 × 10^{-5} M Methylene Blue and 5.5 × 10^{-5} M Rose Bengal feed solutions in ethanol. Dye concentrations were determined by absorption spectrometry using UV–visible spectrophotometer (Metrolab 330) at 664 and 548 nm for Methylene Blue and Rose Bengal, respectively. The dye rejection values (%R_i) were evaluated from

$$\%R_i = \left(1 - \frac{C_{pi}}{C_{ri}}\right)x100 \tag{2}$$

where C_{pi} and C_{ri} are the solute i concentration in the permeate and retentate solutions respectively until the steady state flux was reached ($\approx$ 40 min).

Membrane solubility parameters

In the discussion of oil and FFA separation efficiency, the solubility parameters of the membranes (δ_M) were used. These parameters take into account the solute–solvent–membrane affinity and they were evaluated from the method of group contributions (Van Krevelen and te Nijenhuis 2009). In the δ_M evaluation the different polymer proportions (w_i) of the coating layers were used, according with the following expression

$$\delta_M = \delta_i w_i + \delta_{SI} w_{SI} \tag{3}$$

where δ_i and w_i are the solubility parameters and the mass fraction respectively of component i (i = PC or GLY), and δ_{SI} and w_{SI} are the solubility parameter and mass fraction of SI. The solubility parameters of pure components and coating layer of composite membranes are listed in Table 2.

Pure hexane and oil/hexane miscella NF tests

All membranes were pre-treated before the permeation experiments to minimize the effect of hexane on their structure. After the membranes were placed in the stainless steel dead-end filtration cell, they were flooded during 24 h with pure solvents of decreasing polarities; ethanol, iso-propanol and hexane (Ochoa et al. 2001). To gain a better idea of the stability and durability of the membranes in hexane, the structure of small membrane samples (2 cm × 2 cm) was observed visually after exposure to hexane during 48 h. No significant structural changes, such as crack-like openings on its surface and the swelling or shrinking of its structural matrix were observed for any of the membranes.

Pure solvent permeation

The hexane flux through the pre-treated membranes was determined in the dead-end filtration set-up. The unit was operated in batch mode by charging the reservoir cell with pure organic solvent, and solvent flux through the membrane was measured as a function of transmembrane pressure (Δp = 5–20 bar) at T = 30 °C. Permeate flux J_h (L h^{-1} m^{-2}) was determined by measuring the permeate solvent volume accumulated (ΔV) during the operation time (Δt) at the steady-state conditions and calculated from:

$$J = \frac{1}{A}\frac{\Delta V}{\Delta t} \tag{4}$$

Soybean oil/hexane miscella permeation

The cell reservoir of the filtration device was charged with 270 cm^3 of oil/solvent mixture and stirred at a constant speed of 500 rpm. The variable parameters analyzed in the oil-hexane separation performance experiments were: oil feed miscella concentrations of $C_{f(oil)}$ = 10, 25 and 35% w/w, transmembrane pressure Δp = 20 bar and operating temperature T = 30 °C. These experimental conditions were chosen according to the best performance on hexane recovery and FFA removal obtained in our previous work with the PVDF-SI membranes (Firman et al. 2013). Miscella Permeate flux J_m (L h^{-1} m^{-2}) was calculated from Eq. (4). The oil and FFA concentrations in the retentate and permeate were analyzed at the end of the permeation experiments (90 min). Membranes were reused after each permeation experiment. Each experiment was carried out in triplicate.

Results and discussion

SEM images

Cross section micrographs of composite membranes (Figs. 1a–c) show two well defined regions, a thicker macrostructure type finger like formed by the asymmetric PVDF membrane (support), and a thin dense selective layer produced by the coating material. The figures showed a clear boundary between the top layer and the PVDF support layer, and a good adhesion between coating layer and support surface. The coating layer thickness of membranes prepared with SI-PC increased from 7 to 12 μm as result of the higher amount of PC in the crosslinking solution (from 1 to 2% of PC). The membrane containing GLY shows a more regular dense layer without defects.

Membrane contact angles and MWCO

Table 1 shows the membrane contact angles and the colorant rejection factors with their standard deviation. The performance of the membranes depends on the chemical nature of the surface of the membrane and membrane–chemical interactions of solute–solvent, among other factors. A contact angle below 90° denotes hydrophilic character while a contact angle above 90° indicates material with hydrophobic characteristics. The values of contact angle for pure coating polymers indicated the semi hydrophilic character of the dense PC polymer ($\theta \approx 68$), and the hydrophobic character of the dense SI material ($\theta \approx 120$) due to van der Waals interactions (Darvishmanesh et al. 2010). It can be seen from Table 1 that all composite membranes have hydrophobic nature. As expected, the addition of PC or GLY to the SI phase causes a decrease of the hydrophobic character of the composite membrane regarding to the SI dense film. Although there is an adequate decrease in the hydrophobic characteristic with the increasing percentage of PC ($\theta = 116°$ and 112° for PC = 1 and 2%, respectively), these values are within the experimental error. The coating surface of PVDF-10SI-2GLY membrane showed the lower hydrophobic nature ($\theta \approx 111$) due to the presence of the GLY hydroxyl groups.

The RB rejection values obtained for PVDF-10SI-1PC ($R \approx 60\%$) indicate that this membrane has MWCO higher than 1 kDa. High rejection factor for RB ($R > 89\%$) with the PVDF-10SI-2GLY composite membrane was achieved. The MB retention was higher than RB having MB lower MW. It has been reported (Postel et al. 2013, Volkov et al. 2014) that dye rejection can be affected by solute-membrane interactions expressed in terms of solubility parameters. To analyze the effect of solute–membrane affinity on RB and MB rejections, the solute and the membrane solubility parameters (Table 2) were used. The absolute differences between the solubility parameters of membranes and dyes, $|\delta_M - \delta_{RB}| < |\delta_M - \delta_{MB}|$, indicated that RB has a higher membrane affinity than MB. Despite of the several membrane–dye factors that could affect the dye rejections (swelling, solubility, affinity, etc.) it could be assumed that the molecular weight cut-off of PVDF-10SI-2GLY membrane is near to 1000 Da. Unexpectedly, the PVDF-10SI-2PC membrane was practically impermeable to dye solutions, so it was not possible to determine the MWCO of this composite membrane.

Hexane permeation and membrane integrity

The permeability of pure hexane (L_h) or the intrinsic membrane resistance (R_M) values before and after the oil miscella permeation tests allows describing the membrane integrity. Solvent flux values (J_h) calculated from Eq. (4) were used to evaluate L_h or R_M from Darcy's law as follows

$$L_h = \frac{J_h}{\Delta p} = \frac{1}{\mu R_M} \tag{5}$$

where μ is solvent viscosity. Figure 2 shows the average flux of hexane at different transmembrane pressures and the hexane permeability values obtained from the slope of J_h versus Δp. Good concordance on the effect of pressure in the permeation of solvent according to Darcy's law can be observed, indicating that the solvent transport through the membranes was mainly due to convective mechanism. The linearity of hexane flux with applied pressure also point out that no compaction of the membrane occurs over the applied pressure range. The intrinsic membrane resistance can be evaluated from Eq. 5 by using the hexane viscosity at 30 °C ($\mu_h = 0.3$ cP).

As it was mentioned in "Pure hexane and oil/hexane miscella NF tests" section, membranes were reused after each miscella permeation experiment. In order to reach the initial membrane solvent flux, the used membranes were cleaned in situ according to the following protocol: the membrane was rinse stirred for 1 h with pure isopropanol, and then the isopropanol was replaced by pure hexane and stirred for 1 h. Finally, the permeation cell was filled with hexane and allowed to permeate during 40 min at a pressure of 20 bar and a temperature of 30 °C. Subsequent to each cleaning procedure, the pure hexane permeability of the membrane (L_h) was determined according with the procedure given in "Pure hexane and oil/hexane miscella NF tests"

Fig. 1 Cross section SEM images of composite membranes: **a** PVDF-10SI-1PC, **b** PVDF-10SI-2PC, **c** PVDF-10SI-2GLY
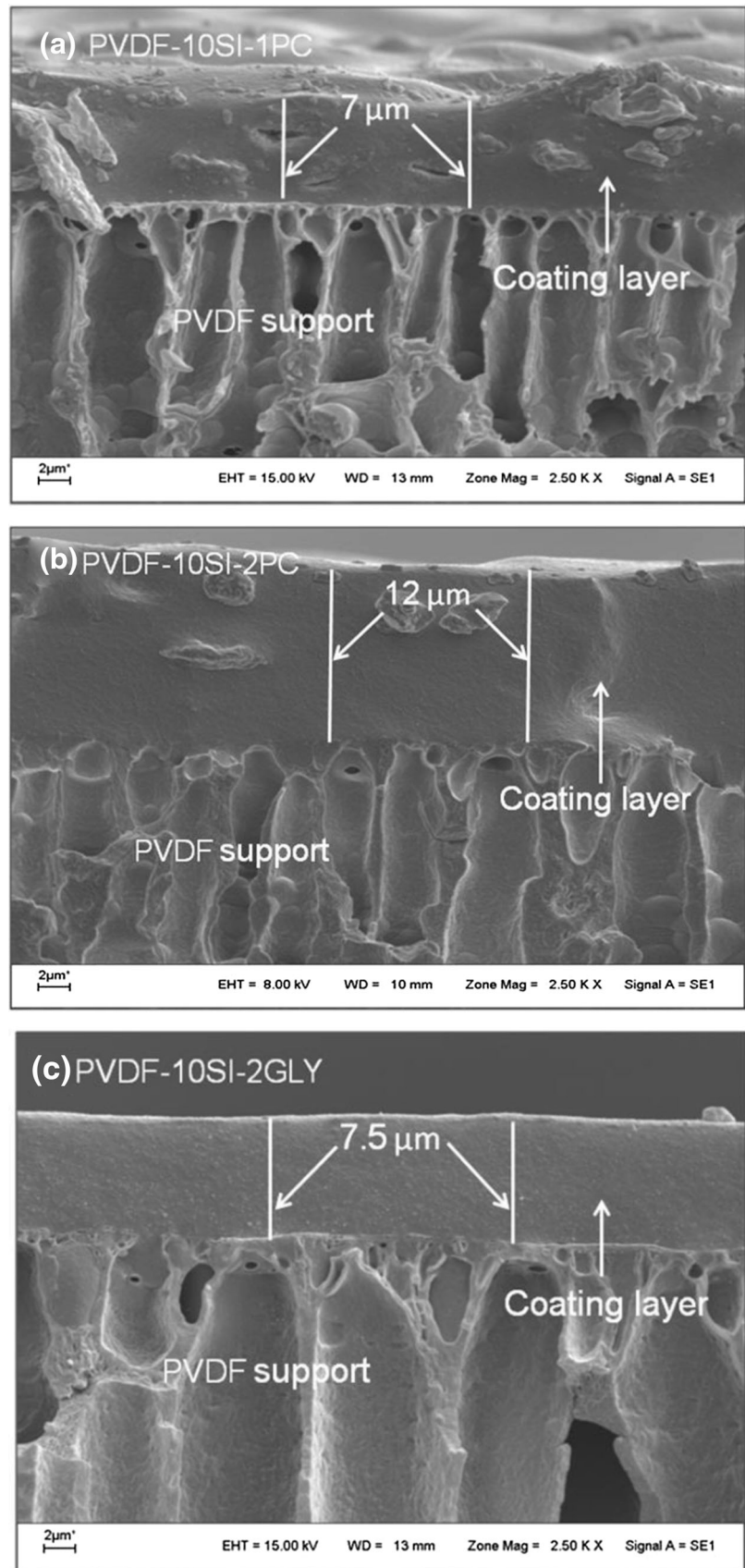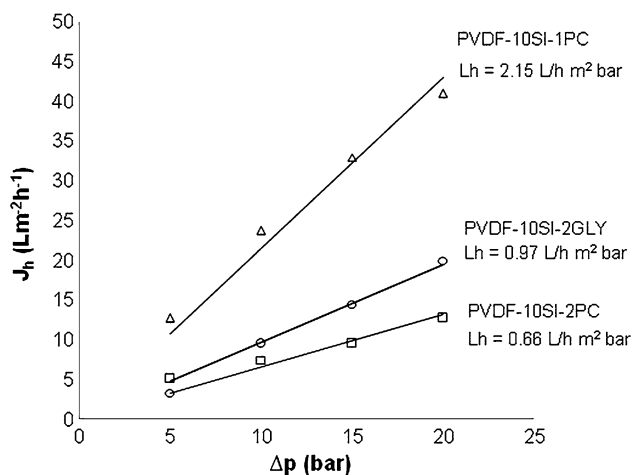
Table 1 Contact angles, colorant rejections, and molecular weight cut-off

Membrane	θ	R (%)		MWCO (Da)
		MB	RB	
PVDF-10SI-1PC	116.0 ± 2.1	86.4 ± 4.6	60.0 ± 4.3	>1000
PVDF-10SI-2PC	112.0 ± 1.8	–	–	–
PVDF-10SI-2GLY	111.2 ± 2.3	95.7 ± 5.3	89.4 ± 3.5	~ 1000
SI (dense)[a]	120.3 ± 3.6	–	–	–
PC (dense)[a]	68.2 ± 1.5	–	–	–

[a] From Firman et al. 2013

Table 2 Solubility parameters and absolute solubility differences of components and membranes

Component	δ_c (MPa$^{1/2}$)	Membrane	δ_M (MPa$^{1/2}$)	$|\delta_M - \delta_H|$ (MPa$^{1/2}$)	$|\delta_M - \delta_{FFA}|$ (MPa$^{1/2}$)	$|\delta_M - \delta_o|$ (MPa$^{1/2}$)
Glycerol (GLY)	33.52	PVDF-10SI-1PC	15.57	0.64	2.33	3.34
Rose Bengal (RB)	21.30	PVDF-10SI-2PC	15.99	1.06	1.91	2.92
Metilen Blue (MB)	23.78	PVDF-10SI-2GLY	18.24	3.31	0.34	0.67
Soybean Oil (o)	18.91					
Free acid (FFA)	17.90					
Hexane (H)	14.93					
Silicone (SI)	15.11					
Policarbonate (PC)	20.27					

Fig. 2 Hexane permeate flux (J_h) with transmembrane pressure (Δp)

section. According to the oil miscella permeation tests (each oil feed concentration in triplicate), every membrane was subjected at least to nine cycles of cleaning. Following the cleaning procedure, all the membranes recovered 96–99% of their original hexane permeability. Moreover, a remarkable reproduction of oil rejections and FFA sieving efficiencies (within the experimental error ±6–10%) was verified after each cleaning procedure the membrane. These results clearly showed the membranes integrity was not affected by the hexane and oil permeation experiments, indicating there were not damage, degradation and chemical changes in the membrane structures.

Soybean oil/hexane miscella permeation

All permeation trials were carried out in triplicate and mean values of miscella permeate flux (J_m) with time determined by Eq. (4) were reported in Fig. 3. All the membranes showed similar miscella flux behavior. There is a moderate drop in permeate flux (around 10–15%) through the composite membranes during the first 20 min. This smooth decrease in the initial flow can be attributed to the oil primary adsorption and concentration polarization effects. Then, after 20 min of operational time, there is a very soft decline of the permeate flux which can be attributed to the increase in the feed concentration with the operational time (dead-end filtration set-up), and to several more or less independent but generally coexisting fouling phenomena (reversible pore blocking, gel layer formation, etc.). The average permeate flux values between t = 60 min and t = 90 min, J*, were used as reference fluxes to evaluate the membrane permselectivity performance. Table 3 summarises the average values of J* for the synthesized composite membranes obtained using different feed oil concentrations at Δp = 20 bar and T = 30 °C. From these values it is clear that the miscella permeability decrease when the feed oil concentration increases. A higher miscella concentration in the feed implies an augment in the quantity of dissolved solutes, increasing the
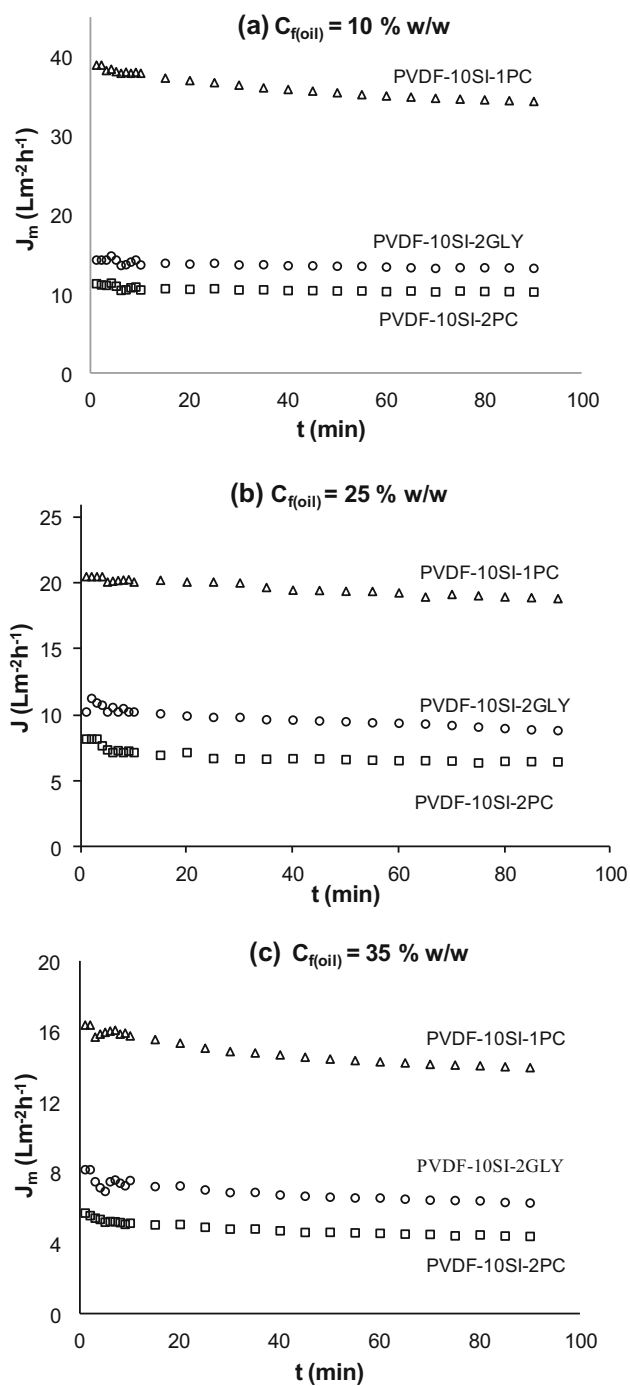
Fig. 3 Miscella permeate flux (J_m) with operational time ($\Delta p = 20$ bar, $T = 30$ °C): **a** $C_{foil} = 10\%$, **b** $C_{foil} = 25\%$, **c** $C_{foil} = 35\%$

prompt fouling (primary adsorption) and concentration polarization effects, decreasing the membrane permeability. This effect and the increasing viscosity of the miscella leads to a reduction in J* permeate flux as oil concentration increases.

The PVDF-10SI-1PC membrane showed higher J* than the PVDF-10SI-2PC and PVDF-10SI-2GLY. This could in

part be explained considering the lowest thickness of coating layer (Fig. 1) and to the highest hydrophobic nature (Table 1) of the PVDF-10SI-1PC membrane. In this study, the flux resistance of the PVDF membrane support is the same for all the synthesized membranes (23% of PVDF and identical experimental conditions of synthesis), thus the coating layer thickness of the composite membrane (ℓ) play an important role in the permeation flux. Hence, for comparing membranes with different coating thicknesses, the permeability is usually defined as follows:

$$L_m = \frac{J * \ell}{\Delta p} \tag{6}$$

where L_m is the miscella permeability expresed as L (h m bar)$^{-1}$. The L_m values evaluated from Eq. (6) were included in Table 3. From this table it can be observed that the PVDF-10SI-1PC membrane performs better, with L_m values between 2.41 and 1.65 times higher than L_m values of the others synthesized composite membranes. This behavior results from a little change in membrane hydrophobicity modifying the interactions among membrane/solute or membrane/solvent. A high solvent permeability can be addressed to a high interaction between membrane and hexane, interpreted by a close difference between membrane/hexane solubility parameters ($\Delta\delta = |\delta_M - \delta_H|$) (Table 2). As expected, there was an adequate correlation between the increasing L_m values (Table 3) with the decreasing $|\delta_M - \delta_H|$) values.

In order to determine the SRNF membrane performances on FFA separation, the separation efficiency or sieving efficiency, β_i, was used. This factor is defined as:

$$\beta_i = \frac{C_{pi}}{C_{ri}} = 1 - R_i \tag{7}$$

where C_{pi} and C_{ri} are the solute i concentration in the permeate and retentate respectively. The sieving efficiency factor is related to the solute molecular weight and to the affinity between the solvent–solute. If the β factor is higher than one, the solute will preferably permeate through the membrane; if it is lower than one it would preferentially be retained by the membrane. The permeate concentrations ($C_{p(oil)}$, $C_{p(FFA)}$), and sieving efficiencies ($\beta_{(oil)}$, $\beta_{(FFA)}$) of oil and FFA are given in Table 3. The retentate concentration of oil ($C_{r(oil)}$) and FFA ($C_{r(FFA)}$), can be deduced from Eq. (7).

Although the oil rejection values of the SRNF membranes showed some differences ($R_{oil} \approx 0.82 - 0.80$), these were within the experimental error (6–10%), so the average R_{oil} can nearly be considered the same for the entire synthesized membranes ($R_{oil} \approx 0.8$, $\beta_{oil} \approx 0.2$). Interesting sieving efficiency values were achieved with the lab tailor-made SRNF composite membranes ($\beta_{(FFA)} > 1.85$), indicating that hexane was a better solvent

Table 3 Permeate flux, permeability and sieving efficiency at different feed oil concentration ($\Delta p = 20$ bar, T = 30 °C)

Membrane	$C_{f(oil)}$ (%w/w)	J^* (Lm^{-2} h^{-1})	$\ell \times 10^6$ (m)	$L_m \times 10^6$ L (h m bar)$^{-1}$	$C_{p(oil)}$ (%w/w)	$C_{p(FFA)}$ (%w/w)	β_{oil}	β_{FFA}
PVDF-10SI-1PC	10	35.1 ± 2.6		12.3 ± 0.9	2.62	1.59	0.21	2.17
	25	19.3 ± 1.5	7.0 ± 0.8	6.8 ± 0.5	5.59	1.60	0.21	2.43
	35	14.3 ± 0.6		5.0 ± 0.4	9.51	1.63	0.25	2.35
PVDF-10SI-2PC	10	10.4 ± 0.7		6.2 ± 0.5	2.53	1.19	0.19	1.95
	25	6.8 ± 0.6	12 ± 0.9	4.1 ± 0.3	5.32	1.22	0.20	1.91
	35	4.6 ± 0.5		2.8 ± 0.2	8.67	1.25	0.23	2.04
PVDF-10SI-2GLY	10	13.5 ± 0.5		5.1 ± 0.4	2.01	1.09	0.18	1.85
	25	9.4 ± 0.6	7.5 ± 0.5	3.5 ± 0.2	4.74	1.14	0.18	2.19
	35	6.6 ± 0.5		2.5 ± 0.2	8.31	1.23	0.23	1.99

for FFA solutes than oil components. In this case, the FFA tends to remain in the hexane phase, leading to a FFA coupled transport when hexane is transferred through the membrane, increasing the concentration of FFA in the permeate side. Furthermore, the absolute solubility difference (Table 2) between membrane and FFA solubility parameters ($\delta_M - \delta_{FFA}|$) was lower than that of the membrane and oil ($|\delta_M - \delta_o|$) for all prepared membranes, indicating a higher interaction between the membrane material and the FFA component. Another factor that also promote the transport and selectivity for FFA is the solute molecular size since oil molecules (>900 Da) are about 3 times larger than FFA chains (<300 Da). The best efficiency of FFA extraction was accomplished by the PVDF-10SI-1PC membrane achieving β_{FFA} values of 2.17, 2.43, and 2.35, and L_m values of 12.3, 6.8 and 5.0 ($\times 10^{-6}$ L (h m bar)$^{-1}$), for feed oil concentration of 10, 25, and 35% respectively. The performance of PVDF-10SI-1PC membrane related to oil retention was lower compared with those of Stafie et al. (2004) (87–90%) and Cai et al. (2011) (96%), however the permeate fluxes of PVDF-10SI-1PC were 6.0–2.7 times and 4.8 times higher than PDMS/PAN and Zeolite PDMS/PVDF membranes, respectively. Relatively lows, both the oil rejections and miscella permeation fluxes were obtained by Tres et al. (2014) in their separation of soybean oil/*n*-hexane mixtures using UF Zircon S700-01446 (5 kDa) and UF Zircon S700-0144 (10 kDa) commercial ceramic membranes. Considering an average miscella density of 0.7–0.73 kg L^{-1}, the permeate flux ranged between 1.55 and 6.61 Lm^{-2} h^{-1} (5 kDa) and 1.85 and 11.6 Lm^{-2} h^{-1} (10 kDa), and the oil rejections varied between 8.0 and 40% (5 kDa) and 9.3 and 32.6% (10 kDa), within the investigated conditions (Δp of 3–5 bar; oil/solvent mass ratios of 1:1 and 1:3).

Even if there are several works related with the solvent recovery from oil/hexane miscella, only a few works provide complete datasets on the simultaneous solvent recovery and deacidification by using membranes. Ribeiro et al. (2006) in their solvent recovery from soybean oil/hexane miscella by SEPA GH polymeric commercial membrane, very low permeation of FFA through the membrane was observed. The lowest content of FFA compounds (9.59%) was obtained with the highest working pressure (27 bar) and 35 °C, with good permeate flux (30.0 Lm^{-2} h^{-1}), achieving an oil rejection of $R_{oil} = 36.6\%$.

As it was mentioned in the introduction section, good oil rejection and FFA performance were obtained in our previous work (Firman et al. 2013) with PVDF-12SI nanofiltration membrane. In this study, a similar oil rejection ($R_{oil} = 0.8$, at $C_{f(oil)} = 25\%$, T = 30 °C, and $\Delta p = 20$ bar), was achieved by the PVDF-12SI membrane, however the miscella permeability (2.5 × 10^{-6} L (h m bar)$^{-1}$) and the FFA efficiency ($\beta_{FFA} = 1.85$) were lower than those of the PVDF-10SI-1PC ($L_m = 6.8 \times 10^{-6}$ L (h m bar)$^{-1}$, $\beta_{FFA} = 2.43$) at the same experimental conditions. In this operational conditions, the FFA concentration in the retentate fraction of the oil (solvent-free basis) was $C_{r(FFA)} = 0.66\%$ (Eq. 7). Considering that the initial FFA concentration in the feed solution was $C_{f(FFA)} = 0.9$ the FFA reduction in the retentate at the end of permeation test was around 27%.

Conclusion

The synthesized nanofiltration membranes were able to reduce the hexane content in the feed oil/hexane miscella solution along with removal of FFA. Besides effective deacidification and hexane removal, the SRNFs showed high hexane permeability and very low fouling phenomena, which are some of the technical limitations in the membrane technology application. Experimental results showed that the composite membrane made with 1% of PC (PVDF-

10SI-1PC) provided the best efficiency for soybean oil deacidification and hexane recovery, combining high miscella permeability ($L_m = 6.8 \times 10^{-6}$ L (h m bar)$^{-1}$), high oil rejection ($R_{oil} \approx 80\%$), and high FFA sieving efficiency ($\beta_{FFA} = 2.43$) achieving an FFA reduction in the retentate solution of about 27%. These results were related to interactions between membrane, solute and solvent.

As it is well known, the membrane cost and performance are essential since the membrane acts as the key separator and contributes to total equipment cost (investment cost). Thus, the above results indicate that the PVDF-10SI-1PC membrane showed the best economic benefit (higher both, permeate flux and FFA efficiency, and similar oil rejection) compared to the synthesized PVDF-12SI and the Solsep conventional membranes (Firman et al. 2013).

It can be concluded that membrane manufacture with adequate solubility parameters can improve the performance on the simultaneous removing of FFA and hexane, from crude soybean oil.

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