Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Food Engineering 78 (2007) 194–197
JOURNAL OF FOOD ENGINEERING
www.elsevier.com/locate/jfoodeng

Fouling of polymeric membranes during degumming of crude sunflower and soybean oil

Cecilia Pagliero [a], Miguel Mattea [a,*], Nelio Ochoa [b], José Marchese [b]

[a] Departamento de Tecnología Química, Universidad Nacional de Río Cuarto, CONICET, Ruta 36, Km 601, 5800 Río Cuarto, Córdoba, Argentina
[b] Universidad Nacional de San Luis-CONICET, Chacabuco y Pedernera, 5700 San Luis, Argentina

Received 6 June 2005; accepted 12 September 2005
Available online 2 November 2005

Abstract

Membrane separation is an optional technology to replace the conventional degumming step during the processing of vegetable oils. In this work, the performance of an asymmetric membrane of polyvinylidenfluoride (PVDF) during the degumming of a crude vegetable oil/hexane mixture was investigated. Samples of soybean and sunflower oil were treated and the effect of oil source on membrane fouling was evaluated.

The water and hexane membrane permeability were assessed by permeation experiments and their values were used to explain the membrane behavior. The degumming tests were performed in a stirred dead-end cell, at different temperatures and pressures.

Retention of phospholipids (selectivity) was greater than 95% in the whole range of studied conditions ($2\ \text{bar} < \Delta P < 6\ \text{bar}$; $30\ ^\circ\text{C} < T < 50\ ^\circ\text{C}$). The results showed that degumming of sunflower oil produced a higher membrane fouling than degumming of soybean oil.

Keywords: Membrane degumming; Vegetable oils; Fouling; PVDF

1. Introduction

Membrane separation is a very interesting technological alternative to the conventional method of degumming in the processing of crude vegetable oils. This technology allows the removal of phospholipids in early stages of the extraction process diminishing the fouling of distillation equipment. As membrane technology does not require the use of water or acid solutions, there is a lower generation of effluents. Also, it decreases the loss of neutral oil and reduces the energy cost associated to the process. In spite of these advantages, its application is currently reduced mainly due to the lack of stability of membranes in hexane—the solvent used in the extraction process.

Different research teams have applied membrane technology to perform the degumming of oil–hexane miscella (Alicieo, Mendes, Pereira, & Motta Lima, 2002; Kim, Kim, Lee, & Tak, 2002; Sen Gupta, 1977) as well as to that of crude oils without the addition of hexane (Subramanian & Nakajima, 1997; Subramanian et al., 2001). In this latter case the results are not of great interest due to the need of extreme operational conditions as a result of high oil viscosity and low permeability of assayed membranes. In previous works we have investigated the degumming of soybean oil–hexane miscella using ultrafiltration (UF) polymeric membranes (Ochoa, Pagliero, Marchese, & Mattea, 2001). These membranes were prepared from three polymeric materials: polyvinylidenfluoride (PVDF), polysulfone (PS) and polyethersulfone (PES). They were evaluated by permeation flux, phospholipids retention and membrane stability during degumming of soybean oil–hexane miscella. The results showed that PVDF in hexane is more stable than PS and PES. In other study (Pagliero, Ochoa, Marchese, & Mattea, 2001), a commercial membrane made of polyimide (PI) was compared with a

* Corresponding author. Tel./fax: +54 358 4676253.
E-mail address: mmattea@ing.unrc.edu.ar (M. Mattea).

0260-8774/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2005.09.015

PVDF membrane synthesized in our laboratory. The results showed that PVDF membrane was more effective than PI membrane to perform phospholipids separation from soybean oil–hexane miscella in the range of pressures and temperatures studied. Also, the PVDF membrane gave permeate fluxes up to three times higher than the PI one at the same operational conditions.

Since the PVDF appears as a promising material to make membranes for this type of application, the objective of this work was to evaluate the fouling that these membranes experience during the degumming of crude oil and hexane miscella. The membrane performance was evaluated by measuring the permeate flux with pure solvents (water and *n*-hexane) and miscella, phospholipid retention and permeate color.

2. Materials and methods

Membrane was synthesized from PVDF (Solvay and CIE), using PVP (Fluka) as pore former additive. The membrane was prepared by the phase inversion method (Kesting, 1985). The resulting membrane had a molecular weight cut-off (MWCO) of 6000 ± 800 Da and a mean pore radius of 27.2 ± 8.5 Å (Pagliero et al., 2001).

Permeation studies of crude oil/hexane miscella were carried out in a stirred dead-end UF cell with a capacity of 400 ml and an effective area of 3.17×10^{-3} m^2. The membrane was supported by a sintered porous stainless steel disc. A magnetic stirrer was placed over the membrane surface to minimize the formation of a layer of higher concentration in the adjacent region. The transmembrane pressure (ΔP) for the permeation process was supplied by a nitrogen cylinder connected to the top of the cell. Hydraulic permeability ($L_{h,a}$) was calculated by Darcy's law measuring water flux through the membrane at different ΔP. The prepared membranes were pretreated by soaking them in a mixture of solvents of decreasing polarity with the object of minimizing hexane effect on the membrane structure, especially pore size. The cell was charged with pure hexane and solvent flux through the membrane was measured as a function of transmembrane pressure at different temperatures (20–50 °C). These results were used to evaluate membrane permeability to hexane ($L_{h,h}$).

Degumming experiments were carried out with mixtures of 25% (w/w) crude soybean or sunflower oil and hexane. In all the experiments the sample was constantly stirred at 750 rpm. Transmembrane pressure and operation temperature varied between 2 and 6 bars and 30–50 °C, respectively. The initial volume of miscella was 300 ml for all the experiments. The concentration of phospholipids in feed, permeate and retentate were assessed by measuring the phosphorous content in each sample following AOCS method Ca 12–55 (Firestone, 1989). The retention percentage, $\%R$, was defined as

$$\%R = (1 - C_p/C_f) \times 100, \quad (1)$$

where C_p and C_f are the concentration of phosphorus in permeate and feed, respectively. The color of feed and permeate was measured using a Lovibond Tintometer, model PFX190 (Lovibond Tintometer, UK). Sunflower oil had an initial wax content of 1200 ± 200 ppm as measured by a gravimetric method (Morrison, 1982).

All the experimental runs were carried out in duplicate. Differences between duplicates were less than ±8% in all cases. The mean values obtained are reported.

3. Results

Values of hydraulic permeability ($L_{h,a}$) and permeability to hexane ($L_{h,h}$) at different temperatures of operation are shown in Table 1.

The results indicate that permeability increases when the temperature rises. This effect is associated to the decrease of viscosity of assayed solvents (water and hexane) at different temperatures. However, the results show that permeability to hexane is lower than permeability to water although viscosity of hexane is lower than that of water in all the considered temperature range. This unusual behavior is attributed to membrane–solvent interactions that end up with membrane structural changes (such as swelling) and the development of surface forces adding to the viscous transport of solvent (Machado, Hasson, & Semiat, 1999).

In the purification of crude oil/hexane miscella using membranes, the limiting phenomenon is the fouling process due to the accumulation and deposition of some components of feed on the membrane surface or within the membrane pores. Typical experimental results of permeate flux, J_v, as a function of time of operation for degumming of oil/hexane miscella are shown in Figs. 1 and 2 for $\Delta P =$ 6 bar. In these figures, it can be observed a sharp decline at the beginning of the process followed by a smooth decrease of permeate flux.

Taking into account high retention of phospholipids (see Table 1) and presuming a size exclusion mechanism because of the large phospholipids agglomerate compared to the small membrane pore size (Iwama, 1987), this behavior is interpreted by a cake filtration model and represented by the following equation (Hermia, 1982):

$$\frac{t}{V^*} = \frac{k_c A^2}{2} V^* + \frac{1}{J_{vo}}, \quad (2)$$

where t is the permeate time [h], A is the effective area of membrane [m^2], V^* is the volume of accumulated permeate per unit of membrane area [l/m^2], k_c is the kinetic constant

Table 1
Comparison of hydraulic and hexane permeability at different temperatures

T (°C)	$L_{h,a}$ (l/m^2 hbar)	$L_{h,h}$ (l/m^2 hbar)
20	160.3	79.5
30	215.6	90.6
40	275.4	104.2
50	335.4	116.3

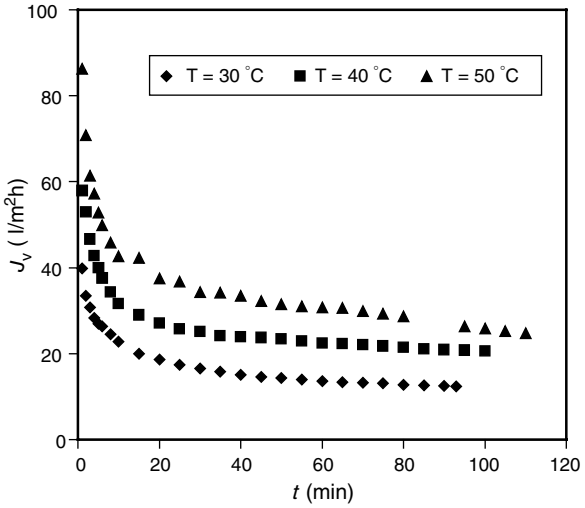

Fig. 1. Permeate flux during ultrafiltration of soybean oil + hexane miscella. $\Delta P = 6$ bar.

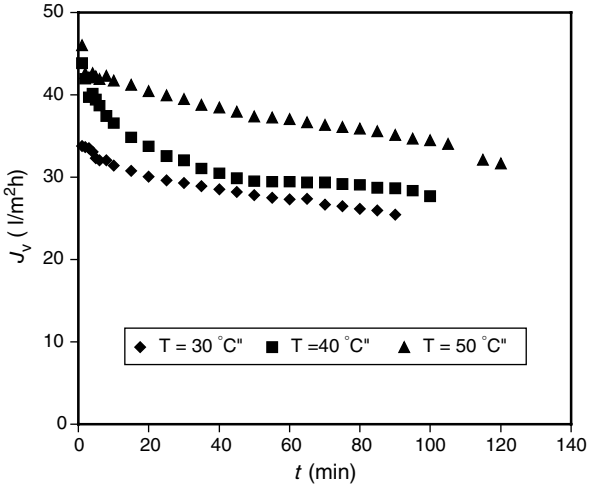

Fig. 2. Permeate flux during ultrafiltration of sunflower oil + hexane miscella. $\Delta P = 6$ bar.

of the model [h/l^2] and J_{vo} is the initial flux of permeate that would be produced by the membrane and the first layers of deposited cake [l/m^{2}h]. The parameters of the model obtained when fitting the experimental data with Eq. (2) are detailed in Table 2.

Other filtration models (Ochoa et al., 2001) were checked with the experimental data but the fitting was not as good as that obtained with the cake model verifying it is the main fouling mechanism. The results clearly indicate that an increase of temperature leads to a decrease of the kinetic constant, i.e. there is a lower fouling. This effect is due to a decrease of the solution viscosity and to an increase of phospholipids diffusivity (Kim et al., 2002). An increase in transmembrane pressure results in an increase of k_c as a consequence of a higher concentration of phospholipids in the zone near the membrane. Values of J_{vo} correspond to values of permeate flux once the first layers of the cake have been formed. These values are noticeably lower than those of pure solvent flux and in general, they tend to decrease when k_c increases. Comparing the fouling of both oils, it can be observed that, at low temperatures, sunflower oil produces higher fouling than soybean oil. This is attributed to the waxes present in sunflower oil which may increase the deposited layer on the membrane surface as well as to occlude internal pores.

Table 3 shows the results of color and phosphorus content in permeate and retention coefficient calculated from Eq. (1).

Table 2
k_c and J_{vo} for the operational conditions used in this work

ΔP (bar)	T (°C)	k_c (h/l^2)		J_{vo} (l/m^{2}h)	
		Soybean	Sunflower	Soybean	Sunflower
2	30	44.4	93.5	17.7	27.7
	40	36.0	36.6	25.1	38.5
	50	15.9	27.7	34.2	46.1
4	30	45.2	113.8	28.5	29.9
	40	31.2	68.3	28.5	28.1
	50	21.7	27.5	34.6	80
6	30	47.8	290.6	33.4	18.9
	40	34.2	78.8	36.0	28.4
	50	17.9	59.3	42.2	42.9

Table 3
Content of phosphorus, retention coefficients and color in permeate during degumming of (soybean/sunflower oil)/hexane miscella

T (°C)	ΔP (bar)	Phosphorus[a] (ppm)		%R		Color[b]	
		Soybean	Sunflower	Soybean	Sunflower	Soybean	Sunflower
30	2	10.0	5.1	99.2	98.6	0.5R 65Y	0.3R 5Y
	4	1.6	0	99.9	100	0.4R 65Y	0.3R 6Y
	6	6.7	0	99.5	100	0.2R 65Y	0.2R 5Y
40	2	2.0	0	99.8	100	0.5R 65Y	0.3R 6Y
	4	3.7	15.6	99.7	95.7	0.4R 65Y	0.3R 6Y
	6	3.9	0	99.7	100	0.3R 65Y	0.2R 5Y
50	2	2.7	0.9	99.8	99.8	0.6R 65Y	0.3R 6Y
	4	12.0	9.9	99.1	97.5	0.4R 65R	0.3R 6Y
	6	5.9	0	99.5	100	0.4R 65Y	0.3R 5Y

[a] Initial phosphorous content—Soybean oil: 1297 ppm; sunflower oil: 367 ppm.
[b] Initial color—Soybean oil + hexane miscella: 1.7R 65Y ; sunflower oil + hexane miscella: 2.9R 18Y (R: Red; Y: Yellow).

The results show that the reduction of red color was significant (higher than 70%). In soybean miscella, yellow color did not decrease but in sunflower, the decrease was important. This fact come out as an advantage of the degumming process with membranes since there is less need of bleaching which results in a lower loss of oil. In Table 3 it can be seen that in all the cases, $\%R$ was higher than 95% at all pressure and temperature used, validating high selectivity of the PVDF synthesized membrane.

4. Conclusions

The results indicate the PVDF-based membranes can be used to perform the degumming of vegetable oils effectively. The assayed membrane yielded phospholipids retention values higher than 95% in the range of studied conditions. It also came out from the tests that fouling is an important phenomenon leading to a flux reduction that can reach up to 50% in the case of soybean oil degumming. Increasing the temperature of the process produces a notably decrease of fouling. This decrease was much pronounced in the case of sunflower due to the increase of solubility of waxes present in this oil which led to k_c values from 93.5 h/l^2 ($T = 30$ °C) to 27 h/l^2 ($T = 40$ °C) at $\Delta P = 2$ bars. Transmembrane pressure increases membrane fouling for both oils.

Besides fouling, results show that red color reduction was significant (higher than 70%). Although yellow color did not decrease in soybean miscella, in sunflower the decrease was important.

Acknowledgements

The authors thank National Agency of Scientific and Technological Research for its support to this work (Project PICT 09-09818).

References

Alicieo, T. V. R., Mendes, E. S., Pereira, N. C., & Motta Lima, O. C. (2002). Membrane ultrafiltration of crude soybean oil. *Desalination, 148*, 99–102.

Firestone, D. (1989). Official methods and recommended practices of the American Oil Chemists' Society, Method Ca12–55 (5th ed.). AOCS Press Champaign.

Hermia, J. (1982). Constant pressure blocking filtration law: application to power law non-Newtonian fluids. *Transaction of the Institution of Chemical Engineers, 60*, 183–186.

Iwama, A. (1987). New process for purifying soybean oil by membrane separation and economical evaluation of the process. *Proceeding of the World Conference on Biotechnology for the Fats and Oils Industry*. Am. Oil Chem. Soc., pp. 244–248.

Kesting, R. E. (1985). *Synthetic polymeric membranes* (2nd ed.). New York: John Wiley & Son Inc., pp. 224–226.

Kim, I. C., Kim, J. H., Lee, K. H., & Tak, T. M. (2002). Phospholipid separation degumming from crude vegetable oil by polyimide ultrafiltration membrane. *Journal of Membrane Science, 205*, 113–123.

Machado, D. R., Hasson, D., & Semiat, R. (1999). Effect of solvent properties on permeate flow through nanofiltration membranes. Part I: investigation of parameters affecting solvent flux. *Journal of Membrane Science, 163*(1), 93–102.

Morrison, W. C. (1982). Rapid determination of wax in sunflower seed oil. *Journal of the American Oil Chemists' Society, 59*, 284–285.

Ochoa, N., Pagliero, C., Marchese, J., & Mattea, M. (2001). Ultrafiltration of vegetable oils. Degumming by polymeric membranes. *Separation and Purification Technology, 22–23*, 417–422.

Pagliero, C., Ochoa, N., Marchese, J., & Mattea, M. (2001). Degumming of crude soybean oil by ultrafiltration using polymeric membranes. *Journal of the American Oil Chemists' Society, 78*(8), 973–976.

Sen Gupta, A. K. (1977). Process for refining crude oils by filtration, US Patent 4062882.

Subramanian, R., & Nakajima, N. (1997). Membrane degumming of crude soybean and rapeseed oils. *Journal of the American Oil Chemists' Society, 74*(8), 971–975.

Subramanian, R., Raghavarao, K., Nabetani, H., Nakajima, M., Kimura, T., & Maekawa, T. (2001). Differential permeation of oil constituents in nonporous dense polymeric membranes. *Journal of Membrane Science, 187*, 57–69.