1   Efficient degumming of crude canola oil using ultrafiltration
2   membranes and bio derived solvents

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Abstract

Vegetable oils derived from rapeseed and its genetic variant canola, are conventionally extracted from oilseeds by means of an organic solvent, typically hexane. Concerns regarding the toxicity of hexane have meant safer and more environmentally friendly solvents such as terpenes are becoming attractive. In this research, the degumming of canola oil/terpene mixtures using ultrafiltration is considered as a critical step in such an extraction process. Polysulfone (PSF) and polyethersulfone (PES) membranes were found to be ineffective in this application, as the oil appeared to cause swelling of the membrane structure. This meant that the original flux could not be restored after cleaning. Conversely, a ceramic membrane (MWCO 5 kDa) provided stable behaviour over several cycles of operation when cleaned with pure solvent at high cross velocity at 40 °C. This membrane showed high phospholipid retention ($95\pm 2\%$), although some oil was also retained ($16\pm 3\%$). Cymene emerged as the most attractive of the three terpenes tested, with higher permeate flux and phospholipid rejection than limonene or pinene.

Industrial Relevance: While hexane has been traditionally used for oilseed extraction, toxicity concerns are likely to restrict its industrial use in the future. This article provides information to engineers and food scientists on the use of terpenes as an alternative solvent. In particular, the potential for ultrafiltration to be used in degumming of canola oil/terpene mixture is assessed. Our research shows that polymeric membranes are unlikely to be useful at scale in this application, as they are not readily cleaned for reuse. Conversely, a ceramic membrane of 5 kDa pore size provides the necessary rejection of phospholipids. There is some oil retention, that might require a downstream recovery step. The best results were obtained with cymene, suggesting this is a good target for industrial use.

1. Introduction

In the processing of vegetable oil, the crude oil is extracted from oilseeds using an organic solvent. After solvent recovery using conventional evaporation, the crude vegetable oil is fed to a degumming step where phospholipids, often referred to as lecithin, are removed. Although the phospholipid content in most crude oils is no more than 3 wt%, their presence in the final product is undesirable, leading to an unpalatable, dark-coloured oil (García, Álvarez, Riera, Álvarez, & Coca, 2006; Gunstone, Harwood, & Dijkstra, 2007; Subramanian & Nakajima, 1997). In biodiesel, phospholipids can cause engine problems such as the clogging of parts or sooting (Ma & Hanna, 1999; Wibisono, Nugroho, & Chung, 2014).

In the conventional degumming process, water, salt solutions (NaCl, CaCl₂), or dilute acids (phosphoric acid, citric acid) are mixed with the crude oil with subsequent formation of hydratable gums. These gums can be separated from the oil by filtration, settling or centrifugation (de Souza, Cunha Petrus, Guaraldo Gonçalves, & Viotto, 2008; García et al., 2006; Gunstone et al., 2007; C. Pagliero, Ochoa, Marchese, & Mattea, 2001; Subramanian & Nakajima, 1997). Despite being efficient in the removal of phospholipids, this conventional degumming process consumes substantial amounts of water, chemicals and energy with subsequent production of large wastewater effluents and considerable oil losses. Other degumming processes such as enzymatic degumming, deep degumming and super-degumming have been developed to overcome the drawbacks of conventional degumming, however, they are expensive and/or complicated (de Souza et al., 2008; Vintilă, 2009).

Membrane separation technology represents a promising alternative to conventional degumming processes. This technology is characterised by lower energy consumption, mild operating temperature, decreased oil losses, no additional chemicals and elimination of wastewater effluent (Cheryan, 2005; Köseoglu & Engelgau, 1990). Unlike the triacylglycerols that are the main components in crude vegetable oil, phospholipids have a surfactant-like structure. In nonpolar solvents, they can form reverse micelles with an average molecular weight of 20 kDa or more (Gupta, 1977; Lin, Rhee, & Koseoglu, 1997). This large size facilitates the separation of phospholipids (hydratable and non-hydratable) from triacylglycerols (MW ≈900 Da) by ultrafiltration using appropriate membranes. Contrary to the traditional

degumming process, degumming by ultrafiltration is usually conducted upstream of the solvent recovery step, as the solution viscosity is much lower at this point in the process.

Degumming of crude vegetable oils using ultrafiltration has been reported in several studies, with authors testing both polymeric (Arora, Manjula, Krishna, & Subramanian, 2006; de Moura, Gonçalves, Petrus, & Viotto, 2005; García et al., 2006; Cecilia Pagliero, Mattea, Ochoa, & Marchese, 2007; Sehn, Gonçalves, & Ming, 2016) and ceramic (Basso, Gonçalves, Grimaldi, & Viotto, 2009; de Souza et al., 2008; Wibisono et al., 2014) membranes for this application. Lin et al. (Lin et al., 1997) studied the degumming of 25% cottonseed oil/hexane miscella using two different polymeric membranes with MWCO of 1000 and 15000 Da that achieved phospholipid rejection of 99.4% and 94.6%, respectively. (Subramanian & Nakajima, 1997) evaluated the performance of a silicon-based composite membrane in the degumming of undiluted crude soybean and rapeseed oil. The membrane showed phospholipid rejection of more than 96% but with a very low permeate flux of $0.22 \text{ kg m}^{-2} \text{ h}^{-1}$. Similar results were observed by Manjula and Subramanian in their recent work (Manjula & Subramanian, 2009). Koris et al. (Koris & Vatai, 2002) reported phospholipid rejections of 70-77% during the dry degumming of crude soybean and sunflower-seed oils using a polyethersulfone (PES) membrane with MWCO of 15 kDa. Upon the addition of water to the oil, the phospholipid rejection improved to 97%. Ochoa (Ochoa, Pagliero, Marchese, & Mattea, 2001) and his co-workers, studied the degumming of hexane-diluted crude soybean oil using PVDF, PES and PSF membranes and found the PVDF membrane was more stable with hexane, achieving more than 98% phospholipid rejection. De Souza et al. (de Souza et al., 2008) achieved phospholipid retention of 93.5% during the degumming of crude corn oil/hexane miscella using an alumina multichannel ceramic membrane with an average pore diameter of $0.05 \text{ }\mu\text{m}$. During the processing of crude canola oil with a tubular ceramic membrane ($\text{Al}_2\text{O}_3/\text{TiO}_2$ -pore size of $0.01 \text{ }\mu\text{m}$), Alicieo et al. (Alicieo, Mendes, Pereira, & Lima, 2002) reported phospholipid retention of up to 99% which corresponded to 4 mg kg^{-1} of residual phosphorus in the permeate stream.

In all reported studies, n-hexane, the typical solvent for extracting the crude oils from their oilseeds, was used to form the oil/solvent miscella. However, the increasing concerns regarding the toxicity of hexane have driven a need to find alternative solvents. Numerous studies have shown that bioderived terpenes such as limonene, cymene and pinene are highly

miscible with vegetable oils and offer a safer alternative (Aissou, Chemat-Djenni, Yara-Varón, Fabiano-Tixier, & Chemat, 2017; Dejoye Tanzi, Abert Vian, Ginies, Elmaataoui, & Chemat, 2012; Golmakani, Mendiola, Rezaei, & Ibáñez, 2014; Liu & Mamidipally, 2005; Mamidipally & Liu, 2004; Viro, Tomao, Ginies, & Chemat, 2008; Viro, Tomao, Ginies, Visinoni, & Chemat, 2008). The Hansen solubility parameters confirm that these terpenes can be considered excellent solvents for this application (Abdellah, Scholes, Freeman, Liu, & Kentish, 2018; Chemat & Vian, 2014). The limited supply of these solvents and higher price (approximately twice that of hexane) can restrict the large-scale utilisation of these solvents. However, taking into account the extra cost associated with environmental regulations, insurance and emission losses, utilisation of terpenes has been shown to be cost competitive with n-hexane (Mamidipally & Liu, 2004).

In our recent work, we investigated the performance of composite PDMS/PAN solvent resistant nanofiltration membranes for the recovery of these solvents from their binary mixture with canola oil (Abdellah, Liu, Scholes, Freeman, & Kentish, 2019; Abdellah et al., 2018). We concluded that organic solvent nanofiltration was a promising alternative to evaporation to recover these solvents from their oil mixtures. However, we did not assess the potential for membrane technology to be used in the degumming step with these novel solvents.

Membrane fouling is one of the main issues that has adverse effects on membrane performance. Membrane fouling occurs during operation due to the accumulation and deposition of foulant molecules onto the membrane surface or/and inside its pores (Gao et al., 2011). The foulant layer results in an additional mass transfer resistance with a subsequent decline in the membrane flux (Wang, Wang, & Fukushi, 2008). Membranes used for degumming of crude vegetable oils foul readily (de Moura et al., 2005; de Souza et al., 2008; García et al., 2006; Lin et al., 1997; Ochoa et al., 2001; C. Pagliero et al., 2001; Cecilia Pagliero et al., 2007; Sehn et al., 2016; Wibisono et al., 2014). However, only a few studies have reported protocols for membrane cleaning. In organic systems such as this, the use of acids or alkalis as commonly employed for cleaning in aqueous systems are not relevant. Instead, Basso et al. (Basso et al., 2009) used clean hexane solvent and found that the use of low transmembrane pressures (0.5 Bar) and high crossflow velocities (5 m/s) allowed the flux to be recovered after 85 minutes. Subramanian and Nakajima (Subramanian & Nakajima, 1997)

used ethanol to clean membranes exposed to crude rapeseed and soybean oils, but found that the membranes failed after two cleans due to this exposure.

The present investigation aimed to determine the viability of membrane technology for the degumming of crude vegetable oil when terpenes are used in place of hexane as the solvent. This is accomplished by evaluating the performance of commercial ultrafiltration polymeric and ceramic membranes for the separation of phospholipids from crude canola oil diluted with d-limonene, p-cymene, α -pinene and n-hexane in a cross-flow membrane configuration. It should be noted that canola oil is very similar to rapeseed oil, but with less erucic acid in the fatty acid profile (<2%) ("Canola Council of Canada," 2019; *The Biology of Brassica napus L. (canola)*, 2008). In addition, membrane cleaning using different approaches was conducted to address membrane fouling.

2. Materials and methods

2.1. Materials

Food grade p-cymene, d-limonene and α -pinene were obtained from Sigma-Aldrich. n-hexane and absolute ethanol were obtained from ChemSupply. Polyethersulfone (TriSep) and polysulfone (GE Osmonics) ultrafiltration flat-sheet membranes with MWCO of 10 kDa and 90 kDa respectively were cut into coupons with a filtration area of 42 cm². A tubular ceramic membrane with MWCO of 5 kDa (Al₂O₃/ZrO₂) was purchased from Atech Innovations GmbH, Germany. Zirconia is negatively charged at neutral pH (Seshadri et al., 2003), with isoelectric points around 4.5 (Moritz, Benfer, Árki, & Tomandl, 2001) and has a contact angle with water of 40-80° (Kujawa, 2019; Lu, Zhang, Gutierrez, Ma, & Croué, 2016; Marchetti, Butté, & Livingston, 2012), indicative of a hydrophilic surface. The ceramic membrane had a channel diameter of 6 mm and length of 70 mm, which gave a filtration area of 13.2 cm². Crude canola oil samples were kindly provided by Windermere Oilseeds Pty. Ltd. Australia with an average phosphorus content of 280±10 mg kg⁻¹.

An enzyme cleaning kit consisting of an alkaline cleaner (Hi Flux Excel) and a four enzyme (lipase/protease/amylase/cellulase) buffered mixture (Hi Flux Enzyme Quatro) was kindly supplied by Jasol, Australia.

2.2. Filtration experiments

Filtration experiments of crude oil/solvent mixtures were carried out in a cross-flow membrane arrangement as reported in our earlier work (Abdellah et al., 2019, 2018). A Sterlitech-CF042 membrane cell was used for the polymeric membranes with a PTFE high foulant (65 mils, Sterlitech) feed side spacer placed on the feed side to minimise concentration polarisation. A stainless-steel housing obtained from Atech Innovations GmbH was used with the tubular ceramic membranes, where the feed was passed through the lumen side (**Figure 1**). In both cases, a variable speed diaphragm pump (Hydracell P200) was used to feed the crude oil/solvent mixture (1 kg) to the membrane unit, via a pulsation dampener and a coiled tube placed within a thermostatted water bath to control the temperature. A needle valve mounted on the retentate line was used to control the downstream pressure, measured by a silicone-filled pressure gauge (Floyd). The permeate was collected and weighed on a digital balance (Ohaus) connected to a PC to record the data using TWedge data acquisition software. After each 100 g of permeate had been collected it was returned to the feed tank to maintain constant feed concentration.

Figure 1. Schematic representation of the experimental setup used for the filtration experiments

Prior to use, all membranes were conditioned by permeating ethanol for 3 hrs followed by pure solvent overnight at 3 bar and 25 °C. The degumming experiments were conducted for

177 two hours immediately after the pure solvent filtration. All experiments were carried out at
178 constant pressure of 3 bar and cross-flow velocity of 32 cm s⁻¹. The permeate flux (kg m⁻²hr⁻¹)
179 was calculated as follows:

$$J_P = \frac{m_P}{t A} \quad (1)$$

180 where m_P is the permeate mass collected within time (t) and A is the membrane active area.

181 At the end of each experiment, a 50 g sample was taken from the permeate and the retentate
182 solution for analysis. The samples were placed in a vacuum oven at 120 °C for 4 hours to
183 remove the solvent. The phosphorus concentration in the residual oil samples was measured
184 by the standard molybdenum blue method (Ca 12-55) of AOCS (Society & Firestone, 1998)
185 The concentration of phospholipids in the oil was then estimated by multiplying the
186 phosphorous concentration by 25.9 (Fattori, Bulley, & Meisen, 1987). The phospholipid and
187 oil rejection (%R) were both calculated as follows:

$$\%R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \quad (2)$$

188 where C_P and C_F are the concentration of the phospholipid (or oil) in the permeate and the
189 feed solutions, respectively.

190 2.3. Membrane cleaning

191 Cleaning of the membrane was conducted by a forward washing method. At the end of each
192 filtration experiment, the crude canola oil/solvent mixture was drained from the system. The
193 system was then rinsed using fresh hexane to remove any residual oil. After that, pure hexane
194 was loaded in the feed tank and was circulated through the system at a very high cross
195 velocity of 165 cm s⁻¹ and temperature of 40 °C for 1 hour. The high cross velocity can detach
196 deposited foulants on the membrane surface while the high temperature can enhance their
197 diffusion into the cleaning solvent. Hexane was used for cleaning, in place of the relevant
198 terpene solvent, due to the high cost of these solvents when purchased at laboratory scale.
199 Since hexane and terpenes have similar solvation power (Dejoye Tanzi, Abert Vian, & Chemat,

200 2013; Dejoye Tanzi et al., 2012; Liu & Mamidipally, 2005; Mamidipally & Liu, 2004; Virost,
201 Tomao, Ginies, & Chemat, 2008), we expect that using terpenes to clean the membrane would
202 provide comparable results. Residual hexane in the system was removed after cleaning and
203 draining by purging with air for around 10 min.

204 As an alternative approach, enzyme cleaning was trialled. After draining the oil/solvent
205 solution, HI Flux Excel solution of 0.4% (v/v) was circulated through the system at 50 °C for 10
206 min. The system was then washed with water before 0.2 % (v/v) HI Flux Enzyme Quatro was
207 circulated for 20 min at 50 °C. The pH of the solution was adjusted between 9-10 as
208 recommended by the supplier. The system was then flushed with water for 10 minutes
209 followed by recirculation of the HI Flux Excel solution again at 60 °C. At the end, the system
210 was flushed with water to remove any residual chemicals. Ethanol was then circulated
211 through the system to remove any residual water inside the system and avoid emulsion
212 formation. The system was rinsed again with pure hexane and the flux of pure solvent was
213 measured and compared with that of the fresh membrane flux to determine the efficiency of
214 cleaning.

215 Teneo VS^{TM} (ThermoFisher SCIENTIFIC) scanning electron microscopy was used to study the
216 morphology and monitor any structural changes of the membranes. Prior to imaging,
217 polymeric membrane samples were snapped in liquid nitrogen and mounted on an aluminium
218 stub with two-sided tape and sputtered with a thin gold film. Before analysis, all membranes
219 samples were dried under vacuum at 25 °C overnight.

220 3. Results and discussion

221 3.1. Polymeric membranes performance

222 The absolute flux of any of the pure solvents (hexane, limonene, cymene and pinene) through
223 different polymeric membrane coupons was highly variable, as is often observed with the
224 pure water flux in comparable ultrafiltration experiments in aqueous systems. This variability
225 is usually attributed to the variability in membrane thickness, porosity and pore size
226 distribution of the membrane coupons. More consistent results could be obtained when this
227 pure solvent flux was normalised to that of pure ethanol at 3 bar and 25 °C (see

Supplementary Information Table S1). While the membranes appeared to provide stable flux in these pure solvents, the flux declined continuously in an oil solvent mixture (see Figure 2 as an example, with others in Supplementary Information Figures S1 to S6). This flux decline is usually attributed to either membrane fouling or concentration polarisation. The pure solvent flux after oil processing remained low, indicating that these effects were not caused by concentration polarisation. More importantly, the pure solvent flux could not be recovered during cleaning, regardless of whether physical cleaning with hexane, or enzymatic cleaning was used. Indeed in some cases, the membrane flux even deteriorated after cleaning.

Figure 2. Permeate flux normalised to that of pure ethanol at 3 bar and 25 °C as a function of time through fresh PSF membranes of cymene/oil solutions

While other authors attribute this loss of flux to membrane fouling, cross-sectional SEM images of both the PES and PSF membranes before and after the filtration process suggest that the loss of performance over time may also be due to swelling of the membrane structure by penetration of either the solvent or the oil (Figure 3 and Figure 4). It can be seen that after the degumming experiment a dense swollen layer has formed on the surface of the PSF membrane that infiltrates about 3 µm down the top layer (Figure 3B, indicated by arrow). Similarly, there is evidence of swelling of the structure of the PES membrane (Figure 4B) as indicated by a loss of definition in the image. These changes would appear likely to have a

significant impact on the flux. Conversely, there was no evidence of accumulation of a fouling cake on the membrane surface.

Figure 3. Cross-sectional SEM images of polysulfone (PSF) membrane A) before and B) after the degumming process

Figure 4. Cross-sectional SEM images of polyethersulfone (PES) membrane A) before and B) after the degumming process

To confirm whether this membrane swelling was caused by the oil, or the solvent, membrane samples were soaked in both solutions individually for a 24 hrs period. No changes in membrane structure were observed after immersion in any of the solvents, but significant changes in morphology were seen when the membranes were soaked in oil (**Figure 5A** and **Figure 6A**). While some of these changes may be an artefact of the imaging process in the presence of the oil, they suggest that it was the crude canola oil that was the cause of the changes in membrane structure observed in **Figure 3B**. This is consistent with the results of (de Souza Araki, de Moraes Coutinho, Gonçalves, & Viotto, 2010), who show that PES membranes are stable in solvents such as hexane, with no visual change in membrane

morphology when observed with SEM. The changes may have been caused by the triacylglycerols in the oil, the phospholipids or indeed any other impurity. It was interesting to note that while hexane was ineffective in recovering the membrane flux when applied to the membrane in a cleaning procedure, the SEM images shown in **Figure 5** and **Figure 6** indicate that the swelling was reversed after a soak of one hour in a stirred container (**Figure 5B** and **Figure 6B**). This suggests that in the forward washing cleaning process, the hexane is unable to penetrate sufficiently into the membrane pores to remove the trapped oil, whereas this is possible in a full soak. However, the results suggest that, contrary to the findings of other workers (de Moura et al., 2005; García et al., 2006), neither PES nor PSF membranes are viable for this application, particularly as it is impractical to perform full soak cleaning in an industrial environment.

Figure 5. Cross-sectional SEM images of the polysulfone (PSF) membrane A) after soaking in oil for 24 hrs and B) after soaking in hexane for 1 hr, after the 24 hrs soak in oil.

Figure 6. Cross-sectional SEM images of the polyethersulfone (PES) membrane A) after soaking in oil for 24 hrs and B) after soaking in hexane for 1 hr, after the 24 hrs soak in oil.

3.2. Ceramic membrane performance

3.2.1 Flux Results

The pure solvent flux through the 5 kDa ceramic membrane is presented in **Figure 7**. As expected, the solvent flux increased linearly with the transmembrane pressure. For all membrane types, hexane showed the highest flux followed by cymene, limonene and pinene which is the same order of increasing solvent viscosity (Abdellah et al., 2019, 2018). The pure solvent flux increased with increasing the temperature as shown in **Figure 7** which is explained by the decrease in solvent viscosity.

Figure 7. Pure solvent flux as a function of transmembrane pressure through the 5 kDa ceramic membrane at A) 25 °C and B) 40 °C. Error bars represent $\pm$ one standard deviation.

Similar to the trend observed with the pure solvents, higher permeate fluxes were observed with hexane than for cymene, limonene and pinene solutions when oil/solvent mixtures were tested (**Figure 8**). For the same oil/solvent solution, the permeate flux decreased with increasing the oil concentration which is explained by the increase in solution viscosity.

While there was minimal flux decline observed over time for the ceramic membrane (**Figure 9**), there was a significant decline in the pure solvent flux when measured after oil processing (**Figure 10**), indicative of some membrane fouling. Membrane fouling occurs due to the presence of phospholipid molecules that can agglomerate and deposit within the membrane pores and on the membrane surface. Accordingly, membrane cleaning was conducted to

remove the fouling layer and recover the membrane performance. Forward washing with hexane was very effective to restore the pure solvent flux to its initial value (see **Figure 10**). As noted above, in industrial practice, the relevant terpene would be used for this cleaning step, to avoid the toxicity of hexane.

Figure 8. Permeate flux of crude oil/solvent solutions through the 5 KDa ceramic membrane. Error bars represent $\pm$ one standard deviation.

Figure 9. Permeate flux as a function of time through the 5 kDa ceramic membrane for cymene/oil solutions.

Figure 10. Pure solvent flux recorded at 3 Bar and 25°C for the fresh ceramic membrane; and after each of two cycles of oil processing and hexane cleaning. Error bars represent $\pm$ one standard deviation.

3.2.2 Retention of Phospholipids and Oil

For the 5 kDa ceramic membrane, the average phospholipid retention was $95 \pm 2\%$ with an average phosphorus content in the permeate of $13 \pm 6 \text{ mg kg}^{-1}$ (**Figure 11**). The phosphorus concentration was slightly lower for the 30 wt% oil solutions than 10 wt%, suggesting this is a better target oil concentration for the degumming operation. Within experimental error, no significant variation in phospholipid retention is observed with increasing the temperature from 25 °C to 40 °C. The lowest phosphorus concentrations are detected for the hexane and cymene solvents, which possibly relates to the lower value of the hydrogen bond Hansen parameter, δ_h (**Table 1**), which is indicative of lower polarity (Hansen, 2007). These reduced Hansen values probably reflect the lack of double bonds in these structures. The greater lipophilicity may mean that these solvents are less likely to interact with the phosphate head of the phospholipid and thus solubilise this molecule. However, the residual phosphorus content in all permeate streams complies with the specifications for commercial degumming in which the residual phosphorus in the processed oil should be less than 30 mg kg^{-1} (Daun, Eskin, & Hickling, 2015).

Figure 11. The percentage phospholipid retention and the corresponding phosphorus content in the permeate for the 5 kDa ceramic membrane. Error bars represent $\pm$ one standard deviation.

Table 1. Hansen Solubility Parameters of the solvents used in the current study (Filly *et al.*, 2014; Hansen, 2007)

Properties	n-hexane	d-limonene	α-pinene	p-cymene
Chemical structure				
Hansen Solubility Parameters (MPa ^{1/2})				
Dispersion δ_d	14.9	17	16.7	18.5
Polar, δ_p	0	1.3	2.2	2.6
Hydrogen, δ_h	0	2	4.9	1.9
Total, δ_t	14.9	17.2	17.5	18.8

Another important factor that should be considered is the percentage oil retention. As mentioned earlier, the objective of the degumming process is the separation of the phosphatides from the oil, accordingly, the percentage oil rejection should be minimised (García et al., 2006). The oil retention observed for the 5 kDa ceramic membrane was an average of $16\pm3\%$, which is a considerable loss of oil feedstock (**Figure 12**). This oil is possibly retained within the core of the phospholipid micelles, making it difficult to remove. Further processing would be required to recover the loss, possibly through diafiltration (Cheryan, 2005). The oil loss is not often reported in other papers, but (Cheryan, 2005) indicates that 97% of the oil can be recovered with very high rejection of phospholipids when tubular polyimide membranes are used with hexane in this application.

The percentage oil rejection falls at 30 wt% oil relative to 10 wt% oil, particularly for cymene. However, this effect arises partly from the higher feed concentration of oil for the 30 wt% case (see **Equation 2**). In fact, for all experiments, the oil flux in $\text{kg m}^{-2} \text{h}^{-1}$ increases when the concentration is increased from 10 to 30 wt%. However, the increase is less than threefold that of the solvent flux and hence the net rejection falls.

It is notable that the oil retention is lowest for the cymene solvent. Terpenes have been shown to be able to disrupt the membrane bilayers present in the phospholipid miscella, if they are lipophilic in nature (Beretta, Artali, Facino, & Gelmini, 2011; Kalemba & Kunicka, 2003). Cymene has the highest value of the Hansen solubility parameter for dispersion forces (δ_d , see **Table 1**), due to its fully aromatic structure (Hansen, 2007) and as discussed above, shares a low value of the parameter for hydrogen bonding with hexane. Our previous work has shown that of the three terpenes, it has the smallest binary Flory Huggins interaction parameter with the canola oil, indicating the strongest affinity to oil (Abdellah, Liu, Scholes, Freeman, & Kentish, 2019). This lipophilicity may mean it can penetrate the miscella more easily, displacing oil and allowing this to then permeate the membrane.

Figure 12. The percentage oil retention by the 5 kDa ceramic membrane. Error bars represent $\pm$ one standard deviation.

4. Conclusions

In this work, green solvents known as terpenes were used as an alternative to n-hexane in the degumming of crude canola oil using commercial ultrafiltration polymeric and ceramic membranes. The polymeric membranes proved unsuitable, as swelling of the active layer made the membranes impossible to clean. Conversely, washing with hexane was effective in cleaning the ceramic membrane and recovering its initial performance. While hexane was used in this work as a cheaper alternative for this cleaning step, in industrial practice the relevant green solvent would be used. The 5 kDa ceramic membrane showed stable performance with an average phospholipid retention of $95 \pm 2\%$, which corresponds to a residual phosphorus level less than 30 mg kg^{-1} , as required in a conventional degumming process. However, the oil retention was too high at $16 \pm 3\%$ for a commercial process to be viable without further treatment of the retentate. Finally, the cymene solvent gave the highest permeate fluxes of the three terpene solvents tested as well as high phospholipid retention and thus appeared as the best choice for use in this application.

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References

- Abdellah, M. H., Liu, L., Scholes, C. A., Freeman, B. D., & Kentish, S. E. (2019). Organic solvent nanofiltration of binary vegetable oil/terpene mixtures: Experiments and modelling. *Journal of Membrane Science*, 573, 694–703.
- Abdellah, M. H., Scholes, C. A., Freeman, B. D., Liu, L., & Kentish, S. E. (2018). Transport of terpenes through composite PDMS/PAN solvent resistant nanofiltration membranes. *Separation and Purification Technology*, 207, 470–476.
- Aissou, M., Chemat-Djenni, Z., Yara-Varón, E., Fabiano-Tixier, A.-S., & Chemat, F. (2017). Limonene as an agro-chemical building block for the synthesis and extraction of bioactive compounds. *Comptes Rendus Chimie*, 20(4), 346–358.
- Alicio, T. V. R., Mendes, E. S., Pereira, N. C., & Lima, O. C. M. (2002). Membrane ultrafiltration of crude soybean oil. *Desalination*, 148(1), 99–102.
- Arora, S., Manjula, S., Krishna, A. G. G., & Subramanian, R. (2006). Membrane processing of crude palm oil. *Desalination*, 191(1), 454–466.
- Basso, R. C., Gonçalves, L. A. G., Grimaldi, R., & Viotto, L. A. (2009). Degumming and production of soy lecithin, and the cleaning of a ceramic membrane used in the ultrafiltration and diafiltration of crude soybean oil. *Journal of Membrane Science*, 330(1–2), 127–134.

Beretta, G., Artali, R., Facino, R. M., & Gelmini, F. (2011). An analytical and theoretical approach for
 the profiling of the antioxidant activity of essential oils: the case of *Rosmarinus officinalis* L.
Journal of Pharmaceutical and Biomedical Analysis, 55(5), 1255–1264.

Canola Council of Canada. (2019). Retrieved October 11, 2019, from <https://www.canolacouncil.org/>

Chemat, F., & Vian, M. A. (Eds.). (2014). *Alternative Solvents for Natural Products Extraction*. Berlin,
 Heidelberg: Springer.

Cheryan, M. (2005). Membrane technology in the vegetable oil industry. *Membrane Technology*,
 2005(2), 5–7.

Daun, J. K., Eskin, M. N. A., & Hickling, D. (2015). *Canola: Chemistry, Production, Processing, and
 Utilization*. USA: American Oil Chemists' Society.

de Moura, J. M. L. N., Gonçalves, L. A. G., Petrus, J. C. C., & Viotto, L. A. (2005). Degumming of
 vegetable oil by microporous membrane. *Journal of Food Engineering*, 70(4), 473–478.

de Souza Araki, M., de Moraes Coutinho, C., Gonçalves, L. A. G., & Viotto, L. A. (2010). Solvent
 permeability in commercial ultrafiltration polymeric membranes and evaluation of the
 structural and chemical stability towards hexane. *Separation and Purification Technology*,
 71(1), 13–21.

de Souza, M. P., Cunha Petrus, J. C., Guaraldo Gonçalves, L. A., & Viotto, L. A. (2008). Degumming of
 corn oil/hexane miscella using a ceramic membrane. *Journal of Food Engineering*, 86(4),
 557–564.

Dejoye Tanzi, C., Abert Vian, M., & Chemat, F. (2013). New procedure for extraction of algal lipids
 from wet biomass: a green clean and scalable process. *Bioresource Technology*, 134, 271–
 275.

Dejoye Tanzi, C., Abert Vian, M., Ginies, C., Elmaataoui, M., & Chemat, F. (2012). Terpenes as Green
 Solvents for Extraction of Oil from Microalgae. *Molecules*, 17(7), 8196–8205.

426 Fattori, M., Bulley, N. R., & Meisen, A. (1987). Fatty acid and phosphorus content of canola seed
 427 extracts obtained with supercritical carbon dioxide. *Journal of Agricultural and Food*
 428 *Chemistry*, 35(5), 739–743.

429 Filly, A., Fabiano-Tixier, A.-S., Lemasson, Y., Roy, C., Fernandez, X., & Chemat, F. (2014). Extraction of
 430 aroma compounds in blackcurrant buds by alternative solvents: Theoretical and
 431 experimental solubility study. *Comptes Rendus Chimie*, 17(12), 1268–1275.

432 Gao, W., Liang, H., Ma, J., Han, M., Chen, Z., Han, Z., & Li, G. (2011). Membrane fouling control in
 433 ultrafiltration technology for drinking water production: A review. *Desalination*, 272(1), 1–8.

434 García, A., Álvarez, S., Riera, F., Álvarez, R., & Coca, J. (2006). Sunflower oil miscella degumming with
 435 polyethersulfone membranes: Effect of process conditions and MWCO on fluxes and
 436 rejections. *Journal of Food Engineering*, 74(4), 516–522.

437 Golmakani, M.-T., Mendiola, J. A., Rezaei, K., & Ibáñez, E. (2014). Pressurized limonene as an
 438 alternative bio-solvent for the extraction of lipids from marine microorganisms. *The Journal*
 439 *of Supercritical Fluids*, 92, 1–7.

440 Gunstone, F. D., Harwood, J. L., & Dijkstra, A. J. (2007). *The Lipid Handbook*, (3rd ed.). CRC Press.

441 Gupta, A. K. S. (1977). *United States Patent No. US4062882A*.

442 Hansen, C. M. (2007). *Hansen Solubility Parameters: A User's Handbook, Second Edition*. New York:
 443 CRC Press.

444 Kalembe, D., & Kunicka, A. (2003). Antibacterial and antifungal properties of essential oils. *Current*
 445 *Medicinal Chemistry*, 10(10), 813–829.

446 Koris, A., & Vatai, G. (2002). Dry degumming of vegetable oils by membrane filtration. *Desalination*,
 447 148(1), 149–153.

448 Köseoglu, S. S., & Engalgau, D. E. (1990). Membrane applications and research in the edible oil
 449 industry: An assessment. *Journal of the American Oil Chemists' Society*, 67(4), 239–249.

450 Kujawa, J. (2019). From nanoscale modification to separation - The role of substrate and modifiers in
 451 the transport properties of ceramic membranes in membrane distillation. *Journal of*
 452 *Membrane Science*, 580, 296–306.

453 Lin, L., Rhee, K. C., & Koseoglu, S. S. (1997). Bench-scale membrane degumming of crude vegetable
 454 oil: Process optimization. *Journal of Membrane Science*, 134(1), 101–108.

455 Liu, S. X., & Mamidipally, P. K. (2005). Quality Comparison of Rice Bran Oil Extracted with d-
 456 Limonene and Hexane. *Cereal Chemistry*, 82(2), 209–215.

457 Lu, D., Zhang, T., Gutierrez, L., Ma, J., & Croué, J.-P. (2016). Influence of Surface Properties of
 458 Filtration-Layer Metal Oxide on Ceramic Membrane Fouling during Ultrafiltration of
 459 Oil/Water Emulsion. *Environmental Science & Technology*, 50(9), 4668–4674.

460 Ma, F., & Hanna, M. A. (1999). Biodiesel production: a review. *Bioresource Technology*, 70(1), 1–15.

461 Mamidipally, P. K., & Liu, S. X. (2004). First approach on rice bran oil extraction using limonene.
 462 *European Journal of Lipid Science and Technology*, 106(2), 122–125.

463 Manjula, S., & Subramanian, R. (2009). Simultaneous degumming, dewaxing and decolorizing crude
 464 rice bran oil using nonporous membranes. *Separation and Purification Technology*, 66(2),
 465 223–228.

466 Marchetti, P., Butté, A., & Livingston, A. G. (2012). An improved phenomenological model for
 467 prediction of solvent permeation through ceramic NF and UF membranes. *Journal of*
 468 *Membrane Science*, 415–416, 444–458.

469 Moritz, T., Benfer, S., Árki, P., & Tomandl, G. (2001). Influence of the surface charge on the permeate
 470 flux in the dead-end filtration with ceramic membranes. *Separation and Purification*
 471 *Technology*, 25(1), 501–508.

472 Ochoa, N., Pagliero, C., Marchese, J., & Mattea, M. (2001). Ultrafiltration of vegetable oils:
 473 Degumming by polymeric membranes. *Separation and Purification Technology*, 22–23, 417–
 474 422.

475 Pagliero, C., Ochoa, N., Marchese, J., & Mattea, M. (2001). Degumming of crude soybean oil by
 476 ultrafiltration using polymeric membranes. *Journal of the American Oil Chemists' Society*,
 477 78(8), 793–796.

478 Pagliero, Cecilia, Mattea, M., Ochoa, N., & Marchese, J. (2007). Fouling of polymeric membranes
 479 during degumming of crude sunflower and soybean oil. *Journal of Food Engineering*, 78(1),
 480 194–197.

481 Sehn, G. a. R., Gonçalves, L. a. G., & Ming, C. C. (2016). Ultrafiltration-based degumming of crude rice
 482 bran oil using a polymer membrane. *Grasas y Aceites*, 67(1), 120(1-8).

483 Seshadri, K. S., Selvaraj, M., Kesavamoorthy, R., Srinivasan, M. P., Varatharajan, K., Lal, K. B., &
 484 Krishnasamy, V. (2003). Estimation and Comparison of Pore Charge on Titania and Zirconia
 485 Membranes Prepared by Sol-Gel Route Using Zeta Potential Measurement. *Journal of Sol-Gel*
 486 *Science and Technology*, 28(3), 327–333.

487 Society, A. O. C., & Firestone, D. (1998). *Official Methods and Recommended Practices of the AOCS*.
 488 American Oil Chemists' Society.

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

491 *The Biology of Brassica napus L. (canola)*. (2008, February). Office of the Gene Technology Regulator,
 492 Department of Health and Aging, Australian Government.

493 Vintilă, I. (2009). THE PHYSICAL-CHEMICAL MECHANISM OF THE EDIBLE OILS DEEP REFINING.
 494 *Scientific Study & Research: Chemistry & Chemical Engineering, Biotechnology, Food*
 495 *Industry*, 2, 179–183.

496 Viot, M., Tomao, V., Ginies, C., & Chemat, F. (2008). Total Lipid Extraction of Food Using d-Limonene
 497 as an Alternative to n-Hexane. *Chromatographia*, 68(3–4), 311–313.

498 Viot, M., Tomao, V., Ginies, C., Visinoni, F., & Chemat, F. (2008). Green procedure with a green
 499 solvent for fats and oils' determination: Microwave-integrated Soxhlet using limonene

500 followed by microwave Clevenger distillation. *Journal of Chromatography A*, 1196–1197,
501 147–152.

502 Wang, L., Wang, X., & Fukushi, K. (2008). Effects of operational conditions on ultrafiltration
503 membrane fouling. *Desalination*, 229(1), 181–191.

504 Wibisono, Y., Nugroho, W. A., & Chung, T.-W. (2014). Dry Degumming of Corn-oil for Biodiesel Using
505 a Tubular Ceramic Membrane. *Procedia Chemistry*, 9, 210–219.

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