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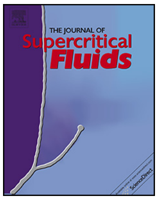

Performance of reverse osmosis and nanofiltration membranes in the fractionation and retention of patchouli essential oil

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ABSTRACT

Patchouli essential oil consists of over 24 different components. Patchoulol has been known for over a century as the most important component of this essential oil, being widely used in the perfumery and cosmetics industries. Recent research has demonstrated that another component of patchouli essential oil, α-bulnesene, has pharmaceutical properties, providing a decrease in thromboxane formation. In this study, three different membranes were evaluated in terms of their fractionation capability and retention of patchouli oil in supercritical media, aiming at the separation and concentration of the main oil components (patchoulol and α-bulnesene) and regeneration of CO_2. The membranes tested showed good resistance under the experimental conditions used, but did not show good fractionation and concentration of the patchouli oil components. The reverse osmosis membrane gave the highest oil retention (0.95) and lowest reduction in the permeate flux of the CO_2 in the presence of the essential oil.

1. Introduction

Patchouli oil is one of the important natural essential oils for the production of perfume and in medical applications [1–3]. It is obtained from the leaves of *Pogostemon cablin* (patchouli), a plant like many from the Lamiaceae family that accumulates large amounts of essential oil [4]. At present, patchouli oil is used in many fine fragrance products to provide a base and give lasting character, being one of the most valuable natural materials for the perfumery and cosmetic industries [4–6]. It is also listed as an approved substance for food flavoring by the FDA (Food and Drug Administration, USA) [7].

Patchouli oil contains bioactive compounds, which confer the plant anti-allergic and anti-bacterial activities on skin, as well as anti-oxidative and anti-inflammatory effects [8–12].

The color of patchouli essential oil is due mainly to the presence of substances commonly responsible for the color of oils of plant origin. These include chlorophyll (green) and the carotenoids (yellow and red).

The composition of patchouli oil is distinct, consisting of over 24 different sesquiterpenes, in which patchoulol is the major constituent and, due to its fixative characteristic, it regulates the oil aroma [3,4]. Also, α-bulnesene is an important compound present in the oil which, in recent research, showed a potent inhibitory effect on platelet aggregation, reducing the risk of cardiovascular diseases [13].

Traditionally, patchouli oil is obtained by steam distillation from *P. cablin* leaves. This procedure, performed at a high temperature, can cause the degradation of thermally labile compounds [13,14]. However, recent researches carried out by Donelian et al. [15] have demonstrated that extraction with supercritical CO_2 at 14 MPa and 40 °C provided a yield of 5.07%, while steam distillation yielded 1.50%. In relation to the quality of essential oil, represented mainly by the concentration of patchoulol, the supercritical extraction yielded 31.39% of patchoulol in the oil, while steam distillation obtained only 19.4% yield.

The use of supercritical CO_2 for separation has been described in numerous publications [16,17]. However, this approach requires a considerable amount of energy to recycle the solvent to its original thermodynamic state for further processing. To avoid this, some researchers have studied the association of membrane separation with supercritical fluid extraction process with the aim of retaining the essential oil and regenerating the fluid, reducing compression

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costs [18–21], and also, when possible, of fractionating some components of the natural products in order to obtain a concentrated fraction of the main oil component.

In order to isolate major compounds of patchouli oil, reports in published researches stand for the use of the host–guest inclusion method, using a host molecule to selectively recognize the guest molecule patchoulol, and of distillation combined with crystallization to isolate patchouli alcohol from patchouli oil [22,23]. For both of them the authors reported good separation results, recovering up to 40% of the patchouli alcohol. Su et al. [24] evaluated fractional distillation combined with crystallization as a method for the isolation of patchouli alcohol from patchouli oil, obtaining up to 52.9% of this compound.

Zhang et al. [25] used high performance centrifugal partition chromatography (HPLCPC) in a preparative scale to separate patchouli alcohol, using a two-phase solvent system. The purity achieved was more than 98%, but it has the disadvantage of requiring the use of organic solvents.

Sarmento et al. [18] evaluated the performance of three commercial reverse osmosis membranes: CG, AG and SG (*Osmonics*) in relation to the retention of lemongrass, orange and nutmeg essential oils at 12 MPa and 40 °C. The oil retention was studied as a function of the transmembrane pressure difference (ΔP) at values between 1.0 and 4.0 MPa and of the feed oil concentration (from 5 to 15% wt). The results demonstrated that the oil retention index was reduced with an increase in ΔP, and significant variations according to the feed oil concentration were not observed. The best results were obtained with the SG membrane and a ΔP value of 1.0 MPa, obtaining a retention index of up to 0.90 for all the essential oils tested, although these conditions gave the lowest CO_2 permeate fluxes, indicating the occurrence of fouling.

On analyzing the separation process with membranes for the regeneration of CO_2, using D-limonene as the solute, Carlson et al. [19] also found that the SG membrane, made of polyamide, gave the highest retention index, above 0.80 for an experimental period of 3 h. However, after the first 120 min, the permeate flux fell to zero, demonstrating that the high retention index was followed by an irreversible clogging of the membrane. However, it was verified that on alternating the feeding between CO_2 + D-limoneno and pure CO_2, it was possible to achieve a retention index of over 0.94, but with low fluxes of CO_2.

Hsu and Tan [26] used a reverse osmosis membrane made of polyamine (FilmTec FT-30) to remove ethanol from a mixture with water. Using $scCO_2$ under pressure and temperature conditions slightly above the critical values the authors verified that the retention index of ethanol increased from 0.20 to 0.70, due to the formation of clusters of ethanol and CO_2. Sarmento [27] analyzed the behavior of different models of commercial nanofiltration and reverse osmosis membranes in relation to the retention and fractionation of polyphenol extracted from cocoa extract under supercritical conditions. The experiments were carried out at 12 MPa and 40 °C, and the results showed that the nanofiltration membrane models DL, HL and NF gave the highest permeabilities with a retention index for polyphenol of over 0.90 when a ΔP value of 1.0 MPa was applied. In relation to the fractionation of polyphenol, only the HL membrane showed a separation capacity, promoting a fraction in the permeate with no oligomers in the range between heptamers and decamers.

Two nanofiltration membranes, TN and T, were investigated by Sarrade et al. [28] in the fractionation of triglycerides originated from fish oil and the purification of β-carotene from either carrot oils or carrot seeds. The experiments were carried out at 31 MPa, 40 °C and with a ΔP value of 3 MPa, and the results showed that the TN membrane allowed a significant concentration of important triglycerides with a high molar mass (over 52 carbons) in the retentate and short-chain fatty acids in the permeate. In relation to the purification of β-carotene, the T membrane allowed a 2.4-fold increase in the concentration of the pigment in the permeate stream.

Therefore, the objective of this study was to evaluate the performance of three different commercial membranes in the separation of patchouli essential oil using supercritical CO_2, in order to promote the regeneration and recirculation of CO_2 with a lower minimum pressure during the supercritical extraction, reducing the energy requirement for the solvent recompression [27]. The membranes were also assessed in relation to their capacity for the fractionation of patchouli oil, aiming at the separation and concentration of patchoulol with fixative properties, and α-bulnesene with pharmacological properties.

2. Experimental

2.1. Patchouli essential oil and membranes

Patchouli essential oil was obtained by extraction with $scCO_2$ at 10 MPa and 32 °C. The pressure and temperature chosen were the best conditions identified by Donelian [29] under which to perform the patchouli essential oil extraction with $scCO_2$. For the extraction, patchouli leaves were collected from "Colônia Penal Agrícola" (Palhoça, SC, Brazil). The extraction procedure is described in Donelian et al. [15].

Three different kinds of commercial membrane supplied by Dow Filmtec (USA) were studied. The membranes are described below:

- Commercial membranes (maximum operation temperature: 45 °C):
  - Nanofiltration membrane – model NF-90 – Thin polyamide film.
  - Nanofiltration membrane – model NF – Thin polypiperazine amide film.
  - Reverse osmosis membrane – model BW-30 – Thin polyamide film.

2.2. Equipment

In this study, a membrane unit was designed and built from a supercritical extraction unit developed at the Laboratory of Separation and Reaction Engineering (LSRE). The equipment is schematically represented in Fig. 1.

The experimental unit was constructed in stainless steel and designed to work up to 20 MPa. However, there is a security valve (V_S) regulated to lead the CO_2 stream to the purge line if the pressure exceeds 19 MPa. The cylinder (1) supplies liquid CO_2 (99.8% purity, Praxair, Portugal) to the surge tank (5). The pressurization of the system was accomplished through a high pressure pump (3) (Model MCPV 71, Haskel, USA) and the CO_2 stream was cooled before entering the pump (3) in order to prevent cavitation inside the pump.

The separation unit comprised two cells (6 and 7) constructed of stainless steel with a unit volume of 30 cm^3 and arranged in series. The membrane to be tested was positioned in one cell (7), while the other cell (6) contained patchouli essential oil. The essential oil was placed together with glass beads to provide resistance in order to avoid a large quantity of oil from moving directly to the surface of the membrane. The membrane was placed over a perforated metal support, and the cells were sealed with poly(tetrafluorethylene) rings. The filtration area of the membrane was 3.14 cm^2 and a cross flow regime was used during the experiments.

The feed pressure in the cell was controlled through a downstream control valve (VR) (Model APR66, Veriflo, Parker Hannifin Corporation, USA) which allowed the pressure in the surge tank

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