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Assessment of solvent resistant nanofiltration membranes for valorization of deodorizer distillates

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ABSTRACT

The valorization of deodorizer distillates from the oil refining industry requires a stable membrane suitable to separate steryl esters (bioactive compounds with high molecular weight (MW), 650 < MW < 800 g/mol) from pesticides (150 < MW < 400 g/mol), whose content is restricted by the actual legislation. This work aims at identifying a suitable solvent and a solvent resistant nanofiltration (SRNF) membrane to be used in a diananofiltration process for the removal of pesticides.

Hexane, ethanol and oleic acid were investigated as potential solvents. The role of solvent–membrane interactions was found to be important in the permeability of the membrane, supported by a strong relationship with the swelling/solvent viscosity ratio. Selected membranes were compared in a dead-end filtration mode, which allowed for identifying the membrane(s) that showed the best compromise between permeability and discrimination between the target compounds. The membranes with the best performance were GMT-oNF2 from Borsig/GMT, PuraMemS600 from Evonik and 030306F from Solsep. The performance of the process was enhanced while operating in a cross-flow mode, being further improved after optimization of the concentration of deodorizer distillate and of the processing solutions and the transmembrane pressure.

The membranes identified in this work proved to be suitable for valorization of deodorizer distillates, presenting high rejections of steryl esters (> 96%) and significant low rejection of pesticides (< 65%), under optimised conditions.

1. Introduction

The production of natural bioactive extracts from agro-industrial by-products for pharmaceutical, food and cosmetic industries has grown significantly in the last few years due to the increasing consumer interest for products with a positive impact in health [1]. Deodorizer distillates are a by-product of the refining edible oil industry and have a special interest as a source of bioactive compounds (2–20% w/w), such as sterols and tocopherols [2]. However, deodorizer distillates cannot be used directly as an additive without a previous purification step mainly due to their high content in pesticides. Maximum residue levels (MRLs) in vegetable oils for human consumption are not specifically set, but it is recommended to be lower than the established for seeds (0.05 ppm for the main lipophilic pesticides) [3]. The concentration in deodorizer distillates can be 800–1000 times higher than the actually allowed values [4,5]. Therefore, their use as a food additive depends on a quantitative removal of pesticides, which, however, remains challenging.

Methods for the recovery of sterols based on molecular weight (MW) difference showed to be labor intensive, time consuming, energetically intensive and inefficient in terms of mass recovery. These methods used include crystallization, supercritical carbon dioxide extraction and molecular distillation [6]. It has been previously shown that steryl esters can be produced by enzymatic esterification of fatty acids and sterols from deodorizer distillates under optimised operating conditions [7]. The use of steryl esters as a food additive has been intensified mainly after their approval by the European Food Safety Authority (EFSA) as compounds with anti-cholesterol activity [8]. Moreover, there are studies indicating that sterols in the esterified form are more bioactive than their free form [9] and present a higher solubility in oil phase, making easier their incorporation in fat-based products. Therefore, the production of steryl esters is advantageous and, on the other hand, their high molecular weight (700–800 g/mol) facilitates their recovery and separation from pesticides (150–400 g/mol).

Membrane technology is considered as a technology environmentally clean which enables the purification and concentration of natural extracts, without requiring high process temperatures, which typically negatively affect the valuable compounds in natural

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extracts. Diananofiltration is a membrane-based technique used for the removal of contaminants (such as pesticides) from value-added streams. This method consists in continuously feeding fresh solvent at the same rate as permeate is recovered, where valuable compounds are retained by the membrane, while contaminants are washed-out in the permeate. Therefore, the structural stability of the membrane in the selected solvent is a necessary condition for assuring a successful process. Commercial solvent resistant membranes are available from mid-1990s, however, the number of membrane producers is still limited [10], being Evonik [11], GMT [12] and Solsep [13] the most important. Polyimide (PI) crosslinked with PDMS and polyacrylonitrile (PAN) are examples of materials used to prepare such membranes due to their satisfactory resistance to solvents.

SRNF membranes are mostly used in pharmaceutical industry applications, such as purification of active pharmaceutical ingredients (API) [14,15], catalyst recycling [16], continuous solvent exchange [17], and solvent recycling [18]. Even though, the only reported application of such technology in large scale is the solvent recovery from lube oil dewaxing (MAX-DEWAX™) [19]. The use of SRNF in the oil refining industry has been discussed in the literature, mostly in the scope of solvent recycling and oil recovery [20–25]. This work proposes the investigation of a different perspective, through the use of SRNF in diananofiltration mode for valorization of by-products, producing extracts that are enriched in bioactive compounds and free of contaminants. Therefore, our work aims at determining the performance of commercial solvent-resistant nanofiltration (SRNF) membranes in the valorization of deodorizer distillates by the removal of pesticides and simultaneous recovery of steryl esters.

This work addresses the identification of the most adequate solvent to be used for diananofiltration purposes (oleic acid, hexane and ethanol were assessed). The main criteria to select the most adequate solvent and membrane are the membrane permeability in the target solvents and their discrimination capacity between the target compounds, specifically steryl esters and pesticides. Finally, the most adequate membrane and the solvent system are assessed in their performance in a crossflow operation, with the objective of preparing the scale-up of the process.

2. Materials and methods

2.1. Material

2.1.1. Esterified deodorizer distillate

A sunflower deodorizer distillate obtained from Lesieur (France) was characterized in our laboratory (its composition is presented in more detail in a previous work [7]) and enriched in steryl esters by an enzymatic esterification between sterols and free fatty acids (FFA). The reaction was carried out under previously established optimised conditions [7].

The esterified deodorizer distillate used in this study is rich in acylglycerides (50%) and free fatty acids (29.5%). It also contains bioactive compounds, such as sterols (0.4%), steryl esters (8.5%), tocopherols (2.3%) and squalene (1.6%). Other compounds comprise hydrocarbons, aldehydes, ketones, pesticides, herbicides and oxidized products from breakdown of tocopherols and free phytosterols. High concentrations of pesticides were detected, namely, 20 ppm of pirimiphos-methyl, 9.7 ppm of chlorpyriphos-methyl and 1.6 ppm of chlorpyriphos.

2.1.2. Chemicals

Analytical-grade hexane, ethanol and isopropanol were obtained from VWR (Germany). A technical grade of chloroform (99%) for GC analysis and oleic acid food-grade with an acid value of 196.0–204 mg KOH/g were purchased from Sigma Aldrich (Belgium).

The derivatizing and silylation agent, N,O-bis (trimethylsilyl) trifluracetamide (BSTFA) containing 1% of trimethylchlorosilane (TCMS) solution (from Fluka) and pyridine respectively was both obtained from Sigma (France).

All analytical-grade standard substances, squalene (99.3% purity), stigmasterol (97% purity), β-sitosterol (99% purity), campesterol (99% purity), cholesteryl stearate (96% purity), monoglyceride olein ($>99\%$ purity), diglyceride olein (99.7% purity) and triglyceride olein (99.6% purity) were purchased from Sigma (Saint Quentin, France). A tocopherol kit consisting of α-, β-, γ- and δ-tocopherols was obtained from Merck ($>95\%$ purity).

The internal standard heptadecanyl stearate (HDS) was prepared by condensation of heptadecanol and stearoyl chloride, both obtained from Aldrich (Bornem, Belgium), as described by Verleyen et al. [26].

2.1.3. Membranes

Five commercial SRNF membranes from different manufactures were selected to be used in this work, namely the 030303, 030306F and 070706 from Solsep (The Netherlands), PuraMem600 from Evonik (U.K.) and GMT-oNF2 from GMT Membrantechnik (Germany). Table 1 compiles the most relevant information of each membrane provided by the respective manufacturer.

2.2. Experimental setup

2.2.1. Dead-end

Experiments in a dead-end operating mode were performed in a stainless steel METcell test cell, supplied by Membrane Extraction Technology (MET, UK). The feed reservoir has a total volume of 250 cm^3 and the agitation is promoted by a cross head magnetic bar, providing the adequate fluid dynamic conditions. The pressure applied through the membrane (circular sheet with an effective area of 51.4 cm^2) was regulated by a pre-assembled gas unit. The permeate

Table 1
Properties of the selected membranes provided by the respective manufacturer.

Membrane	Manufacturer	T_{max} (°C)	P_{max} (bar)	Separation	Active layer
030306	Solsep	150	40	R(99%) ~ 1000 Da (in ethanol)	PDMS[a]
030306F		120	40	R(85%) ~ 1000 (in ethanol)	PDMS[b]
070706				Not available	
PuramemS600	Evonik	50	60	R(90%) = 600 Da (in toluene)	PDMS[c]
GMT-oNF2	GMT	60	35	R(93%) = 327 Da (in 2-propanol)	PDMS[c]

[a] Van der Bruggen et al. [27,10].
[b] 030306 based-membrane accordingly the manufacturer.
[c] According to the specifications provided by the manufacturer.