J. of Supercritical Fluids 102 (2015) 115–122

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Cleaning of microfiltration membranes from industrial contaminants using "greener" alternatives in a continuous mode

Krzysztof Michałek[a,b], Jan Krzysztoforski[b], Marek Henczka[b], Manuel Nunes da Ponte[a], Ewa Bogel-Łukasik[a,*]

[a] LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
[b] Warsaw University of Technology, Faculty of Chemical and Process Engineering, Waryńskiego 1, 00-645 Warsaw, Poland

ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 14 April 2015
Accepted 15 April 2015
Available online 23 April 2015

Keywords:
Cleaning
Separation
Extraction
Supercritical carbon dioxide
"Greener" solvents

ABSTRACT

This work presents a sufficient cleaning of microfiltration membranes from industrial contaminants (oils) using supercritical fluids as alternative to industrial use of organic solvents used near their high boiling points. Supercritical carbon dioxide either as pure or with an insignificant addition of "greener" solvents such as ethyl alcohol or isopropyl alcohol were applied in this study. The cleaning process was investigated in a high pressure system with a continuous solvent flow and solvent recirculation. The effect of system pressure, temperature, solvent flow rate, solvent composition, cleaning time and type of the contaminant on cleaning efficiency was analysed. Powerful, "greener" solvents combined with CO_2 gave satisfactory results in removing oils from membranes allowing to increase the process rate and cleaning efficiency, as well as reduce energy consumption of the process.

1. Introduction

Commercial microporous membranes are widely used in medical as well as in industrial applications. One of the most popular manufacturing methods of these membranes is the Temperature Induced Phase Separation (TIPS), during which a porous polymer structure is produced, but filled with contaminants resulting from the phase separation. Contaminants, mainly oils, such as castor oil or soybean oil have to be removed before regular operation of the membrane. The current method of cleaning of membranes from oils requires organic solvents at high near their boiling point temperatures to be used [1]. This method of removing oils from membranes presents drawbacks, among which fire hazard, potentially negative effect on the natural environment and high costs due to expensive solvent regeneration are the most significant ones. Other negative effects include the interaction between the porous structure and the organic solvent, which can lead to membrane shrinkage and collapsing of the pores due to the presence of vapour–liquid interaction [2]. Supercritical carbon dioxide ($scCO_2$) has attracted great attention in recent years as an alternative solvent because of its greenness, lack of reactivity, good transport properties, zero surface tension, high diffusivity, and abundance as CO_2 is a major industrial waste. These properties provide opportunities for process intensification [3]. As it has been accurately pointed out by Jessop [4], several questions must be answered before deciding that a solvent is greener than other solvents. Low volatility is a highly desirable characteristic in a solvent, several solvents considered as "green" such as ethanol, ethyl acetate, and limonene are volatile yet at the same time are greener than other less volatile solvents [5]. For similar reason isopropyl alcohol was called to be an unusual, powerful, "green" solvent [6].

State of the art on supercritical carbon dioxide used in research focused on membrane technology indicates assessment of the changes of Reverse Osmosis membrane properties induced by $scCO_2$ [7] or its use for preparation of a porous membrane [8]. Moreover, it is known that supercritical carbon dioxide has the ability to solubilise various organic oils [9], including those used in the TIPS process, and that organic co-solvents can act as solubility enhancers.

$ScCO_2$ was reported to slightly decrease the Young's modulus and increases the filtration coefficient UFC of polypropylene microfiltration membranes [10]. The first results on membrane cleaning utilising supercritical CO_2 performed in a batch reactor, at $T = 40\,^{\circ}C$, $70\,^{\circ}C$ and $100\,^{\circ}C$ and $p = 18$ MPa [11] seemed to be promising. However, research demonstrated drawbacks such us execution of the process in a batch system not suitable for scaling up. This unique research suffers from lack of uniform hydrodynamic conditions, no effect of pressure studied, no solvent flow rate measured and

* Corresponding author. Tel.: +351 212948500ext.10941; fax: +351 212948550.
E-mail address: ewa.lukasik@fct.unl.pt (E. Bogel-Łukasik).

http://dx.doi.org/10.1016/j.supflu.2015.04.011
0896-8446/

Table 1
Properties of the membrane used in this study.

Parameter	Value
Type	Hollow fibre microfiltration membrane
Material	Polypropylene
Length	1300 mm
Outer diameter	2.7 mm
Inner diameter	1.8 mm
Thickness	0.45 mm
Porosity	70%
Range of pore size	0.4–0.8 μm
Mean pore size	0.45 μm
Standard deviation of pore size distribution	0.07 μm

inability to perform solvent recirculation. To overcome these drawbacks we propose alternative cleaning with supercritical carbon dioxide. For this reason, our work was designed to clean microfiltration membranes in a continuous mode (i.e. with continuous flow of the solvent through the extraction vessel, in which the membrane is placed, with solvent recirculation in the system), as preferable industrially and on screening "greener" solvent [5,6] addition to affect cleaning efficiency calculated as an extraction yield. The impact on other operational parameters such as solvent flow rate and process pressure on the process to overcome the drawbacks pointed out above were also aimed to be studied in this work.

2. Experimental

The model system used in this work consisted of microfiltration membranes contaminated with castor oil or soybean oil cleaned using an alternative solvent, supercritical carbon dioxide, either pure or with minor amounts of ethyl or isopropyl alcohol. Ethyl alcohol was selected as a model co-solvent, the most popular co-solvent used in supercritical fluid technologies. Selection of the isopropyl alcohol was directed by its use as primary solvent in a traditional method of membrane cleaning and promising contribution in increasing solubility of the contaminant in the supercritical fluid phase. It would be desirable, if the traditional primary solvent could be used as co-solvent and solubility enhancer in a novel technology, as it is already established in membrane processing and does not affect negatively the key properties of the membranes. When compared to other popular co-solvents used with supercritical carbon dioxide (such as acetone, acetonitrile, chloroform, hexane or benzene [12]), the two selected co-solvents may be regarded as "greener" co-solvents due to significantly lower toxicity and limited threat to the natural environment.

The microfiltration membranes were polypropylene membranes, ACCUREL hydrophobic capillary membranes, Type PP S6/2 used for microfiltration, manufactured by Membrana GmbH, Germany. The detailed information on the properties of the membrane is compiled in Table 1. The castor oil (CAS-No.: 8001-79-4) used in the experiments was purchased from Sigma–Aldrich. Soybean oil (CAS-No.: 8001-22-7) was kindly provided by Sovena, Portugal. Carbon dioxide (99.98% purity, CAS-No.: 124-38-9) was provided by Air Liquide. Ethyl alcohol (96% purity, CAS-No.: 64-17-5) was provided by FCT DQ Organic Chemistry Laboratory, isopropyl alcohol (Kosher Grade 99.7 purity, CAS-No.: 67-63-0) was purchased from Sigma–Aldrich.

The experimental system used in the investigation is shown in Fig. 1. Liquid carbon dioxide is supplied to the system from a tank V-1 equipped with a pressure indicator. CO_2 is pumped with a diaphragm pump P-1. In order to provide stable operation of the pump, CO_2 passes through a cooling bath E-1 upstream the diaphragm pump and is cooled down to ca. −10 °C. The mass flow of the $scCO_2$/"greener" solvent is measured using a mass flow metre

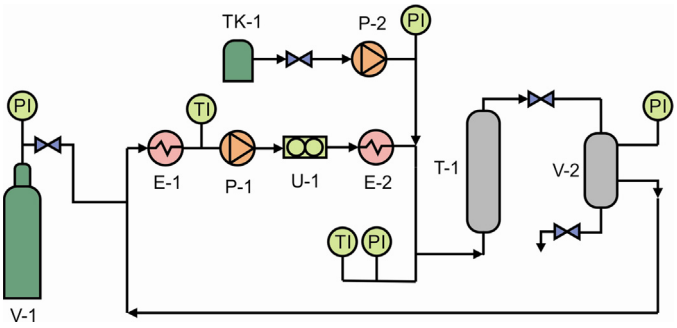

Fig. 1. Scheme of experimental system (V-1, tank with liquid CO_2; E-1, cooling bath; P-1, diaphragm pump; E-2, heating bath; T-1, extractor; V-2, separator; P-2, piston pump; U-1, mass flow metre; TK-1, tank with co-solvent; TI, temperature indicator; PI, pressure indicator).

U-1 (Rheonik RHM 01) and the flow rate is adjusted manually by means of a regulating screw at the pump. The solvent is pumped through the heating bath E-2 (consisting of two heat exchangers) in order to achieve the desired process temperature. If isopropyl alcohol or ethyl alcohol is used in an experiment, it is supplied from tank TK-1 using an additional piston pump P-2, Milton Roy 92014903. The solvent enters then the extractor vessel T-1, which is a cylinder with 1150 mm length and 6 mm internal diameter. The extractor is equipped with a heating jacket. Downstream of the extractor, the supercritical fluid containing the extract is depressurised to the pressure in the CO_2 tank (ca. 5 MPa) using a BPR valve (Tescom Europe, 26-1700). The extracted substances and "greener" solvent are separated from CO_2 in the separator V-2. The carbon dioxide is recycled and reused in the system.

Each membrane was cut in two equal pieces (ca. 650 mm each). Each piece was weighed and then put into a vessel containing castor oil or soybean for a sufficient time to fill the pores with the respective oil. The excess of oil at the outer surface of the membrane was removed mechanically. After this procedure, the membrane was weighed again and it was placed into the extractor. The system pressure was adjusted using the diaphragm pump and the BPR valve. The mass flow rate was set and the cleaning process was carried out for a defined process time. The co-solvent was supplied using the second pump. On completion of the cleaning process, the experimental system was depressurised, the membrane was removed from the extractor and weighed again. When ethyl or isopropyl alcohol was used, the membrane was stored for 24 h before the final weighing procedure in order to allow the co-solvent to evaporate. Each experiment was performed twice.

Cleaning efficiency was calculated as an extraction yield using the following equation:

$$\eta = \frac{\Delta m}{m} 100\% (\%),$$

where m is the initial amount of oil present in the membrane prior the cleaning process, and Δm is the amount of oil removed from the membrane pores during the cleaning process. Hence, extraction yield is defined as the percentage of oil removed by the cleaning process using $scCO_2$/"greener" solvent.

3. Results and discussion

The model system used in this work consisted of microfiltration membranes, contaminated with castor oil or soybean oil – typical solvents applied in the TIPS process. Supercritical carbon dioxide was used as solvent, either pure or with minor amounts of "greener" solvents (ethyl or isopropyl alcohol) in order to verify cleaning efficiency. The experimental system used in the