A METHOD FOR THE USE OF ORGANIC SOLVENT NANOFILTRATION TO THE STUDY OF PLANT EXTRACTS

Xiaoping Wu¹, V. Koleva², E. Simeonov², G. Nedeva²

¹Membrane Extraction Technology Ltd, Unit 8 Wharfside, Rosemont Road, London, Wembley HA0 4PE, United Kingdom.
E-mail: xiaoping@membrane-extraction-technology.com

²University of Chemical Technology and Metallurgy 8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: koleva_velichka@abv.bg

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ABSTRACT

This paper describes a nanofiltration method for the separation and purification of extracts from natural products. The nanofiltration is based on a novel Organic Solvent Nanofiltration (OSN) membrane technology and a MET high-pressure cell. The intended material for the OSN is a natural plant extract of ethanol/water mixture. In this study, a method has been developed for using a MET cell operated in a dead-end nanofiltration model and cross-linked OSN membranes to investigate a natural plant extract for separation and purification purposes. The method consists of detailed steps for pre-treatment of plant extract, setting up membrane cell, conditioning OSN membrane, and determinations of the flux of extract liquid and the rejection rate of natural components in the extract. This method provides a base of using OSN for the scientific and technical studies of natural plant extracts, as well as other similar natural material extracts.

Keywords: nanofiltration, OSN membrane, solid-liquid extractions.

INTRODUCTION

Nanofiltration is a membrane-based and pressure-driven technique used for separation of molecules or other complex species with a molecular mass in the range of 200 - 1000 g/mol [1]. Recently nanofiltration has found numerous applications including solvent exchange, catalyst recovery and recycling, purification and concentration [2,3]. However, many OSN membranes tend to dissolve in many common solvents used for pharmaceutical, chemical and natural matter extractions. The application of the nanofiltration in many areas is limited. More recently, a novel cross-linked OSN membrane has been invented and developed [4, 5]. The developed membrane has shown remarkable stability in many common organic solvents. This development has opened the new opportunities for using the nanofiltration for separation and purification of natural product extracts, as many extraction processes organic solvents are involved. In our case, 70 % ethanol in water is used for the extraction of plant. Solid-liquid extraction from plants is used in pharmaceutical, food and chemical industries mainly to obtain a desired component or mixture of components from plants by dissolution with a suitable solvent. Nanofiltration processes have the potentials to be used to improve the efficiency and to reduce the operating cost in comparison with the traditional concentration and purification processes used in industry.
In a laboratory study, a membrane pressure cell and flat sheet membrane is generally employed to determine the flux of liquid passing through the membrane and rejection rates of different components in the extract. These data are fundamental to the evaluation of the OSN membranes, to the development of separation and purification processes of plant extract, and to carry out further investigations, as well as potential industrial scale applications. It is a highly important, from scientific and practical point of view, to develop a nanofiltration method for natural plant extracts.

**EXPERIMENTAL**

**Principle of the nanofiltration**

OSN membrane used in this study is a porous thin film made from polyimide polymer. The diameters of the porous holes in the membrane for passing liquid are estimated to be in the range of 0.5 to 1.0 nm. Under pressure, the membrane acts as a filter, which allow smaller molecules and solvent to pass through, but not large molecules. Fig. 1 shows the use of membrane to separate small molecules from large molecules.

**Organic solvent membrane**

Solvent-stable membrane (branded as Dura Mem™) used in this study was supplied from Membrane Extraction Technology Ltd in England. The membrane is made using polyimide polymer (Fig. 2). After cross-linking, the polymer film becomes stable in many common organic solvents.

**Nanofiltration apparatus**

**MET cell and pressure supply**

A MET cell, supplied by Membrane Extraction Technology Ltd. in England, is used for nanofiltration apparatus. The MET cell is a 316 stainless steel high-pressure stirred cell that is capable of performing a wide range of membrane separations. In this study, only dead-end filtration is used. The pressure for driving liquid passing membrane is obtained using a high-pressure gas of nitrogen from a gas cylinder. A laboratory magnetic stirrer plate is used to generate the stirring/mixing required in the cell to minimise concentration polariza-

![Fig. 1. An illustration of membrane separation of molecules with different sizes.](image)

![Fig. 2. Polymer used to make OSN membrane (Lenzing P84 polyimide 20 % I, 80 % II).](image)
tion effects. A general scheme of the set up of MET cell system is illustrated in Fig. 3.

**Extract and analytical techniques**

The extracts used in this study were produced by extracting geranium root using 70% (v/v) ethanol in water at 20°C. The size of geranium root was in the range of 0.2-1.2 mm. After the extraction, the extract was filtrated through a filtrate paper (model), and filtrate was stored in a dark bottle. For the longer-term storage, the filtrates were kept at 4°C. The analysis of the components in the extract, feed and permeate was performed by using KMnO₄ titration [6] and a UV method [7].

**RESULTS AND DISCUSSION**

It is the first time that OSN membrane is used for the study of natural plant extracts. Although a detailed operating procedure can be found in MET cell operating instruction, it is important to develop a general method for nanofiltration of extracts. The nanofiltration of our plant extract consists of steps shown in Fig. 4.

**Fig. 3.** Set up of MET cell system for nanofiltration.

**Fig. 4.** Steps of nanofiltration of the plant extract.
Step 1. Treatment of extracts

This step involves with the removal of the particles or suspensions in the plant extract to avoid or minimise the potential fouling of membrane.

Step 2. Pre-conditioning membrane

To use DuraMem™ membrane in many applications, particularly in pharmaceutical and food industries, it is necessary to understand and assess extractables and leachables and to perform pre-conditioning treatments to satisfy safety and regulatory requirements. In laboratory studies, pre-conditioning treatment of membrane (to remove conditioning reagent or other leachables) is usually required. However, the extent of the pre-conditioning treatment of membrane depends on the: (a) tolerance of impurity in the final products, (b) interference of analysis of other components. If the tolerance of impurities is low or the impurity has interference with other components, extended washing of the membrane sheet is required. The washing process involves in passing pure solvent through membrane under pressure. An example of pre-conditioning of DuraMem™ membrane using an organic solvent is given as a guide in Fig. 5.

When the tolerance of impurities in permeates is high, and the impurities from membrane have no interference with analysis, the pre-conditioning process can be shortened in laboratory experiment. In this study, permeate samples at different pre-conditioning stages were taken and analysed by using KMnO₄ titration. The results of titration are summarized in Table 1. It can be seen from the table that the titrated concentrations from pure solvent, permeates collected at different pre-conditioning stages are the same. It is concluded that the conditioning reagent from membrane has no interference to the analysis of components of the extract. Therefore, the amount of solvent used for washing membrane can be reduced to 200 ml.

Table 1. Analytical data for the comparison of pure extraction solvent and permeate from pre-conditioning membrane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent (Ethanol 70 % in water)</th>
<th>Permeate after 200 cm³ solvent passed through</th>
<th>Permeate after 550 cm³ solvent passed through</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration determined by KMnO₄ titration</td>
<td>0.62 kg/m³</td>
<td>0.62 kg/m³</td>
<td>0.62 kg/m³</td>
</tr>
</tbody>
</table>

(Note: 2 cm³ of liquid are used for each titration measurement)
Step 3. Addition of extract into MET cell  
The maximum amount of extract is 270 ml for the given MET cell in this study. The amount of extract left after nanofiltration is above 20 cm³. If the amount of extract is below this volume, the agitation becomes ineffective. This will result in concentration polarization in the nanofiltration process, and poor experimental results.

Step 4. Pressurisation & agitation  
Rapid applying or releasing pressure in MET cell may cause damage to membrane. It is essential to increase the pressure to MET cell slowly by adjusting regulator on the MET cell gas control unit or to reduce the pressure slowly by opening vent on the same gas control unit.

Step 5. Measurement of flux  
The flux is determined by measuring the volume of liquid permeated over given period of time.

Step 6. Sampling of permeate & retentate  
Before sampling, make sure the sampling point for permeate is clean to avoid any contamination.

Step 7. Analysis of concentrations  
The concentrations of extract components in permeate and retentate are determined using appropriate analytical techniques. In our case, KMnO₄ titration and UV are used for the analysis.

Step 8. Calculation of rejection rate [8]  
1. The concentrations of extract component i in permeate \((C_{\text{permeate, i}})\) and retentate \((C_{\text{retentate, i}})\) are determined by chosen analytical methods. The experimental rejection of solute i is calculated by the following equation:

\[
R_i(\%) = (1 - \frac{C_{\text{permeate, i}}}{C_{\text{retentate, i}}}) \times 100 .
\]

2. In the extract studied, the total organic concentration (as tannic acid, or phenolics, or flavonoids), is analysed. The concentrations of total organic concentration in permeate \((C_{\text{permeate, total}})\) and in retentate \((C_{\text{retentate, total}})\) are determined by KMnO₄ or UV method. The experimental rejection rate of total organics is calculated by the following equation:

\[
R_{\text{total}}(\%) = (1 - \frac{C_{\text{permeate, total}}}{C_{\text{retentate, total}}}) \times 100 .
\]

CONCLUSIONS  
A method and principle of work of nanofiltration installation for plants extract is presented. The main stages of the process are described – from treatment of extracts to calculation of rejection. The results obtained by defining of the work conditions show that the conditions of washing the membrane should be defined experimentally for each solid-liquid system.

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