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Membrane Processing of *Echinacea purpurea* Herb Juice Extract

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An investigation was carried out to evaluate the feasibility of using an ultrafiltration membrane technique to concentrate polyphenolic acids in the juice of Echinacea herb plant materials. The processing was conducted using a commercially available ultrafiltration membrane of 5kD MWCO (Pellicon XL50, Millipore, U.S.A and Sartocon Micro, Sartorius, Germany). Initial trials with the Echinacea herb extracts obtained from an industrial extracts company in New Zealand, showed that the permeate flux was low with the undiluted feed, and only 10-20% increase in concentration was possible. Several dilutions of the feed were needed to achieve an enrichment of more than two times. The dilution also resulted in a significant increase in flux and percentage recovery of the desired components, e.g. polyphenolics. The processing was done with freshly squeezed juice of Echinacea herb plant material (tops and stalk) harvested from Rewa Herb, Rangitaiki, New Zealand. With this feed in undiluted form, the permeate flux was higher but the percentage recovery of the polyphenolics was lower.

Introduction

Echinacea is a native herb in both North America and Europe. The composition of the herbal extracts depends on the varieties and parts used for their preparations. The main components are alkamides, caffeic acid derivatives, cichoric acids, polysaccharides and glycoproteins [1]. The preparation from *Echinacea purpurea* is considered to be the most widely used herbal medicine for immunostimulant purposes [2, 3]. Due to the demand for "natural" components in foods and pharmaceutical

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preparations the importance of these compounds has increased significantly. The methods for separating and purifying the high-value components from the natural/synthetic sources are mainly based on adsorption and/or chromatography. Although these methods work well they are tedious, involve pre-treatment of the feed solution in addition to many batch-type steps (leading to additional costs in the processing). Moreover, some methods are not able to concentrate the solution and others produce secondary wastes. Therefore alternate methods are being evaluated for their effectiveness and efficiency in concentrating and separating these high-value compounds.

Membrane separation methods, especially ultrafiltration (UF), have the potential to overcome some of the disadvantages of the conventional processes. UF as a clarification method in fruit juice processing has been commercially successful and is considered attractive from the viewpoint of energy, environmental and processing benefits [3-6]. The availability of membranes with longer life, higher flux, resistance to organic solvents, pH and temperature, and better cleaning protocols have been the advantages for increased application of membrane processes in comparison with the conventional techniques [7-11]. Commercially available membranes, namely polyethersulphone and regenerated cellulose, were examined in order to evaluate their mass transfer performance (permeate flux and %recovery) for the concentration and separation of polyphenolic acids from various feed solutions.

Materials and Methods

Ethanol was purchased from Commodity Resources Ltd, New Zealand, and sodium hydroxide (NaOH), reagent grade from Scharlau Chemie, S.A. La Jota, Barcelona, Spain.

The feed solution from Rewa Herb was prepared by squeezing a known quantity of *Echinacea* plant materials and adding 20-40% ethanol to prevent degradation of the active component. The cleaning solution for the membrane was prepared by dissolving a known amount of sodium hydroxide in distilled water. A 0.1 M NaOH solution was used for this purpose.

The ultrafiltration membrane device was a Pellicon XL type from Millipore, USA. This is a composite, void-free regenerated cellulose membrane. The specifications of the device are listed in Table 1.

The filtration experiments were carried out in the membrane module by flushing the retentate channel with deionized water and pumping the feed through using a Masterflex L/S pump (compact drive type, Model 77200-12, USA). A schematic of the experimental set-up is shown in Figure 1. The operating pressures were measured by pressure gauges (Teltherm, New Zealand). The transmembrane pressure (TMP) was maintained by controlling exit flow and is defined by $[(P_{in} + P_{out})/2 - P_{permeate}]$, where P_{in} and P_{out} are the inlet and outlet pressures of the module and $P_{permeate}$ is the pressure of the permeate solution. The permeate samples were collected periodically and were not recycled back to the reservoir. The retentate samples were recycled back to the reservoir.

Table 1. *Specifications of the UF modules.*

Specifications	***Pellicon XL50 (5kD)***	***Sartocon Micro (5kD)***	***Sartocon Slice (1kD)***
Material	*Regenerated cellulose*	*Polyethersulphone*	*Polyethersulphone*
pH compatibility	2 - 12	1 - 14	1 - 14
Maximum pressure (psi)	80	30	30
Maximum temperature (^0C)	45	50	50
Membrane area (m^2)	0.005	0.005	0.100

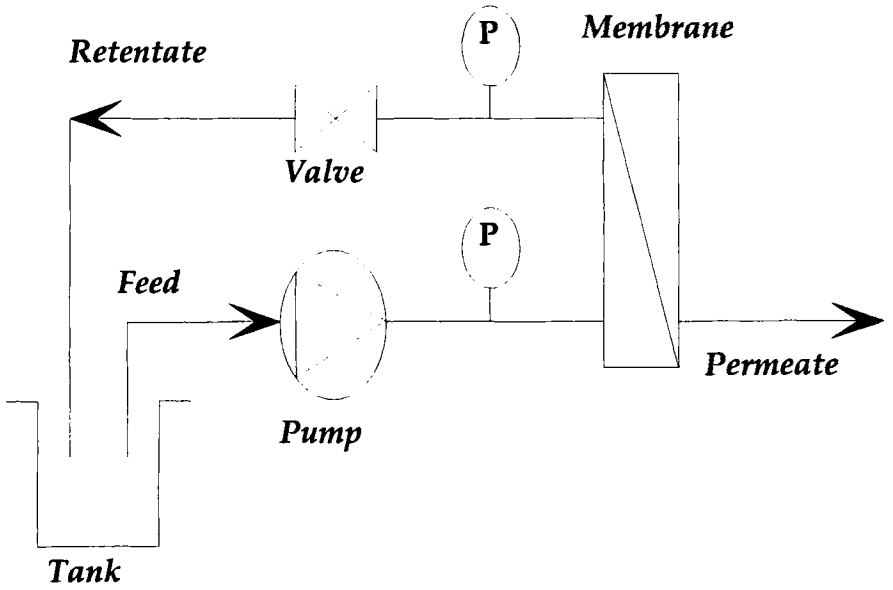

Figure 1. *Schematic of the UF process.*

The feed, retentate and permeate samples were analyzed for concentrations of the polyphenolics by measuring the UV absorbance over a wavelength of 200-700 nm, using a Diode Assay Spectrophotometer (Hewlett Packard, Model 8452A, Germany). Analysis of the samples was also performed using a HPLC method reported in [12] at the Crop and Food Research, Dunedin, New Zealand. The method uses a Phenomenex Prodigy column (5 mm, 100 Å, 4.6 x 250 mm) in conjunction with a Phenomenex security guard cartridge (4 x 2 mm). The column temperature was 35^{0}C. The mobile phases were water (containing 0.1% phosphoric acid, solvent A) and acetronitrile (Solvent B) in the following gradient system: initial 10% B; linear gradient to 22% B in 13 minutes; then to 40% B in 1 minute; hold at 40% B for 0.5 minutes; recycle to initial conditions in 0.5 minutes; and hold for 5 minutes. The flow rate was 1.5 ml/min and the detection was at 330 nm.

Performance Parameters

The performance parameters considered in the process were the permeate flux, the concentration factor and recovery (%). The average permeate flux (J) is the filtration rate per unit membrane area; the concentration factor of the phenolic acids (E_R) is the ratio of the concentration of the acids in the retentate (C_R, mg/L) compared to that in the initial feed (C_F, mg/L); and recovery (%) is defined as the fraction of total solutes recovered in the permeate.

The following equations were used to calculate the average solute flux (L/m^2/hr), concentration factor and percentage recovery (%):

$$J_s = V_p / t / A \tag{1}$$

$$E_R = \frac{C_R}{C_F} \tag{2}$$

$$R(\%) = \left(\frac{V_P C_P}{V_F C_F} \right) \times 100 \tag{3}$$

where V_P is the permeate volume (L); t is time (hr); A is the membrane area (m^2); and V_F and Vp are the volumes of the initial feed and permeate, respectively.

Results and Discussion

The experimental conditions of the ultrafiltration runs are listed in Table 2. A feed volume of 360 ml of undiluted solution can be treated in a processing time of 7-8 hours. For diluted solutions, higher feed volumes (550-650 ml) can be used. The feed solutions were prepared from (i) freshly squeezed tops and stalk and it was used without dilution (but with 22% ethanol as preservative), and (ii) *Echinacea* extract samples obtained from Extracts NZ Ltd., Nelson. The performance parameters for the processing of various *Echinacea* herb solutions through Pellicon XL50 (5kD) membranes are presented in Table 3.

Table 2. *Experimental conditions for the Echinacea processing.*

Process conditions	***Pellicon XL50 (5kD)***	***Sartocon Micro, (5kD)***	***Sartocon Slice, (1kD)***
Transmembrane pressure (TMP in psi)	27	25	19.2
Initial feed solution (ml)	360	260	180
Water permeability at TMP 15 psi ($L/h.m^2.psi$)	1.0	0.8	1.0
Tangential flow (L/h)	2.6	1.1	0.4
Temperature (^{0} C)	18	18	18

Table 3. *Recovery of polyphenolics with Pellicon XL50 (MWCO 5kD).*

Feed material	***Average flux ($L/m^2.h$)***	***Recovery in permeate (%)***	***Concentration factor E_R (-)***
Fresh Echinacea sample from Rewa Herb, undiluted (1:1)	10.5	56.0	1.1
Echinacea sample from NZ Extracts, undiluted (1:1)	5.6	64.2	1.1
Echinacea sample from NZ Extracts, diluted (1:2)	14.4	77.2	1.6
Echinacea sample from NZ Extracts, diluted (1:5)	18.6	86.7	2.4

A comparison is made between the processing of the samples in terms of the permeate flux and percentage recovery of the polyphenolics. For the undiluted sample, the flux was higher for the freshly prepared sample possibly because of the smaller concentration of the polyphenolics in this sample. The solute permeation through the membrane was greater and the concentration increase in the retentate was low, only about 10%. From the HPLC analysis it was determined that the samples from Rewa Herb actually contained low levels of the desired solute, the cichoric acid, and high levels of the other acids.

The results of the experiments with the other sample (prepared sample from the industry as mentioned in (ii) above) are presented for undiluted and two diluted preparations. It is shown that the solute flux and the percentage in permeate increased significantly by diluting the feed. At a dilution ratio of 1:5, about three times increase in permeate flux was obtained. The concentration increase in the retentate was about 2.4 times and the percentage in permeate was about 87% of the initial feed. This permeate solution will need further treatment for concentrating polyphenolics and separating more water from it. Finally the results are compared in Table 4 when a five-times diluted feed is processed with a Pellicon XL50 (5 kD) as well as a Sartocon slice (1kD). The latter device offered much lower flux without any significant benefit in the recovery and concentration of the polyphenolics.

Therefore, ultrafiltration is demonstrated as a potential processing step in order to produce a concentrated fraction of polyphenolics from the herb extract. Membrane modules of regenerated cellulose (Pellicon XL50) have been shown to offer superior performance.

Table 4. *Recovery of polyphenolics from a diluted feed (diluted five times the initial feed) and at a TMP of 1.5 bar (22.1 psi) using Pellicon XL50 (5 kD) and Sartocon slice (1 kD).*

Membrane module	***Average flux*** ***($L/m^2.h$)***	***Recovery in permeate (%)***	***Concentration factor*** ***E_R (-)***
Sartocon slice (1 kD)	0.1	71.2*	1.4*
Pellicon XL50 (5 kD)	18.6	86.7	2.4

* *Recovery and concentration factors were in the retentate samples.*

Conclusions

This study has shown that UF processing is able to separate the major components (polyphenolic acids) from *Echinacea* herb extract juice. The MWCO of the membrane has a significant effect on the permeation rate of the product. The performance of the membrane is improved when using juice that is diluted. The favourable operating conditions include a transmembrane pressure of 40-50 psi, and a dilution factor of 1:5.

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