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Transport properties of oleuropein through nanofiltration membranes

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A B S T R A C T

The present work investigates the effect of feed concentration and magnitudes of applied pressure of olive-extracted oleuropein on permeate flux and membrane transport properties through concentration polarization in a nanofiltration (NF) membrane. The filtration of oleuropein model solution by an NF membrane using different feed concentrations (0.3, 0.9, or 2.7 $kg\,m^{-3}$) enables the correlation of a transport model, comprised concentration polarization and osmotic pressure models, to membrane retention performance, evaluated using the Spiegler–Kedem model. Moreover, osmotic pressure was observed and interpreted using the van't Hoff equation at different levels of feed concentration and applied pressure. Transport parameters (reflection coefficient, water and oleuropein permeability, and mass transfer coefficient) were correlated with experiment values by developing a mathematical model that reflects the flux decline by increasing osmotic pressure.

Keywords: Nanofiltration; Concentration polarization; Osmotic pressure; Oleuropein; Flux decline

1. Introduction

Polyphenols are complex mixtures that have rich structural variety and a wide range of biological activities, as evidenced by their antioxidant and health-enhancing properties (Al-Azzawie and Alhamdani, 2006). Recent increasing interest has focused on olive polyphenol recovery, which correlates well with related physicochemical and biochemical processes adopted in recovering polyphenols from olive trees (Gutierrez-Rosales et al., 2012).

Oleuropein, which is an ester of hydroxytyrosol and elenolic acid glucoside (Fig. 1), has gained interest as a natural food antioxidant (Takaç and Karakaya, 2009). Oleuropein is the most abundant polyphenol in olive leaves (60–90 mg/g dry weight) (Le Tutour and Guedon, 1992; Servili et al., 1999). The health-promoting properties of oleuropein have been widely investigated (Al-Azzawie and Alhamdani, 2006; Ranalli et al., 2006; Sheu et al., 2004). Consequently, there has been much interest in developing new extraction and separation techniques to recover oleuropein from olive residue (Agalias et al., 2007; Garcia-Castello et al., 2010; Malik and Bradford, 2008).

Several techniques used individually or in combination have been adopted to recover olive polyphenols. These techniques are mainly extraction, centrifugation, and chromatographic procedures. In those processes, however, complexities result not only from their cost and operational characteristics, but also from the toxicity and flammability of the organic solvent that is required in large amounts (Takaç and Karakaya, 2009).

Nanofiltration (NF) is an advanced membrane separation process in the liquid phase. It uses membranes with pore sizes within nanometer range to meet industrial needs in the

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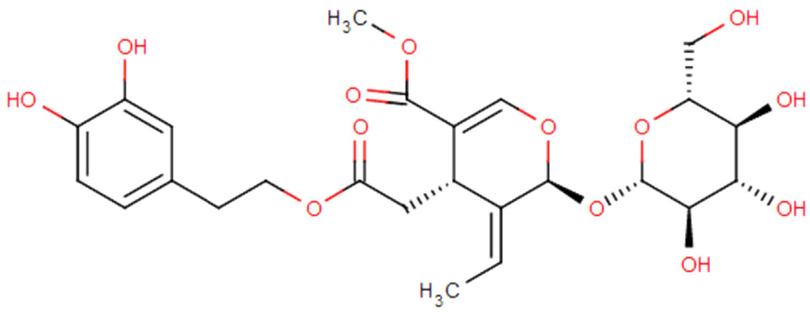

Oleuropein ($C_{25}H_{32}O_{13}$)

Fig. 1 – Chemical structure of oleuropein.

area of small molecules (<1 kDa) and ion separation (Saliha et al., 2009). Energy requirements are potentially much lower for NF than for conventional separation processes, leading to significant cost savings. Separation by NF membranes occurs primarily due to size exclusion and electrostatic interactions (i.e., the Donnan effect) (Yaroshchuk, 2008). For uncharged molecules, sieving or size exclusion is the major factor responsible for separation (Qi et al., 2011). However, the mechanism of solute transportation through NF membranes is not fully understood (Richards et al., 2011; Tang et al., 2011), and no efficient approach for accurately simulating membrane performance has been presented (Verliefde et al., 2009), due to the complex nature of the membrane surface and fouling species (Braghetta et al., 1997).

In this work, we studied the transport properties of oleuropein through NF membranes in order to clarify and identify the important factors that control the transport mechanism through an NF membrane. Aqueous oleuropein solution was selected as the model solution containing polyphenols. Performance flux and rejection of several commercial membranes were evaluated. This study provides a better understanding of the relationship between osmotic pressure and operating conditions. Also, we estimated values of flux decline after experimentally evaluating the flux decline caused by osmotic pressure and concentration polarization.

2. Materials and methods

2.1. *Reagents*

Oleuropein $C_{25}H_{32}O_{13}$ (molecular weight 540.5 g mol^{-1}, max. absorbance λ_{max} = 280 nm), a polyphenol, was provided by Extrasynthese Co., Ltd. (Genay, France), with 85% (w/w) oleuropein purity. The chemical structure of oleuropein is presented in Fig. 1. Milli-Q water was used for preparing different model solution concentrations (0.3, 0.9, or 2.7 kg m^{-3}).

2.2. *Flat sheet membranes*

To evaluate the separation of oleuropein using an NF membrane, the performance of several commercial membranes was evaluated, considering their permeate flux (J_v) and observed rejection (R_{obs}). Eleven types of flat-sheet NF membranes, whose specific properties are listed in Table 1, were tested.

2.3. *Membrane experiment procedure*

A flat-membrane test cell (Nitto Denko Co., Kusatsu, Japan) was operated in batch mode at room temperature (25 °C). The inner diameter of the cell was 7.0 cm with an effective membrane surface of 42.75 × 10^{-4} m^2. The experiment setup is schematically represented in Fig. 2. Experiments were conducted in a nitrogen atmosphere, and the operating pressure (0–40 bars) was controlled by adjusting the pressure regulator of the nitrogen cylinder. The membrane cell was placed on a magnetic stirrer and agitated (0–800 rpm) by a magnetic spin bar fitted inside the cell. The cell was loaded with a fixed quantity of feed solution. The permeated solution was collected through a port beneath the membrane support; the flux was recorded continuously using a personal computer interfaced with an electronic balance (model UX620H, Shimadzu, Japan).

To evaluate membrane performance, commercial NF membranes were tested with a model solution containing oleuropein 1 kg m^{-3}, until a volume reduction factor (VRF) of 1.4 (see Section 2.4), (here, permeate volume represents 1/3 of initial feed). A stirring rate of 500 rpm was used (for a laminar hydrodynamic state with a fixed mass transfer and reduced turbulent shear effect), and the applied pressure was 20 bar. The membrane with the highest rejection was selected for further study with different applied pressures and fixed stirring rates. A low VRF value (1.05) was applied to determine the effect of applied pressure on J_v and transport parameters in order to eliminate the effect of batch concentration created in this stirred cell. The concentration of oleuropein in retentate (C_{ret}) and permeate (C_p) was determined at each pressure level.

2.4. *Determination of permeate flux (J_v) and observed rejection (R_{obs})*

The filtration efficiency in separating oleuropein was evaluated using the observed rejection, which was calculated using the rejection formula in batch mode:

$$R_{obs} = \frac{\log(SCR)}{\log(VRF)} \tag{1}$$

where SCR is the solute concentration ratio, defined as the ratio of the final retentate concentration (kg m^{-3}) to the initial feed concentration (kg m^{-3}):

$$SCR = \frac{C_{ret,f}}{C_{ret,i}} \tag{2}$$