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Nanofiltration of glucose: Analysis of parameters and membrane characterization

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ABSTRACT

Membrane characterization and modeling of nanofiltration processes of uncharged solutes are of special interest for the food industry. In this work two commercial membranes, DK and DL, were used to concentrate glucose solutions. Membranes were characterized according hydrophobicity, thickness, porosity, and hydraulic permeability. The influence of pressure and concentration of glucose on the permeate flux and rejection were studied. Both membranes presented a great potential for the food industry due to their high rejection of glucose. The osmotic pressure model was combined with film theory and the real driven force was calculated taking into account the osmotic pressure and the concentration polarization. Both phenomena influenced the process (concentration polarization only in the most dilute solutions at low pressure) and the permeability for glucose solutions was similar to the hydraulic permeability. A mathematical model based on the Donnan-Steric Pore Model was used to determine the pore radius and the effective thickness of both membranes. As the concentration inside the pore (needed for the calculations) is difficult to measure experimentally, various alternatives were proposed. The average of the concentration at the interface and permeate best fitted the experimental data. The model was applied successfully; the maximum error was 8% within the range of concentrations (5–100 g/L) for the DL membrane and 5% for the DK membrane up to 50 g/L.

Keywords: Nanofiltration; Glucose; Osmotic pressure model; Concentration polarization; DSPM

1. Introduction

In the last years, significant progress has been made in the preparation and study of new polymeric and inorganic nanofiltration (NF) membranes. Many academic and industrial research projects in this area are also in progress (Drioli and Fontananova, 2004; Drioli et al., 2011; Strathmann, 1999). NF membranes have properties in between those of ultrafiltration and reverse osmosis membranes and exceptional stability at very low or high pH, very high temperatures or organic solvent media (Yacubowicz and Yacubowicz, 2005). The separation mechanism of these membranes involves steric and electrical (Donnan) effects. Because of this combination they are effective for the separation of small organic solutes and salts from a mixture. NF is currently used in water treatment, chemical and food processing industries, to concentrate, fractionate or purify aqueous solutions of organic solutes (Molecular Weight (MW): 100–500 g/mol), textile dyes, heavy metals, and mixtures of monovalent/multivalent solutions (Gao et al., 2014; Hinkova et al., 2002; Jiao et al., 2004; Luo and Wan, 2013; Ong et al., 2014; Zhu et al., 2014).

Different phenomena appear when sugar solutions, in contrast to pure water, are filtered. The concentration polarization and the raise of osmotic pressure are the causes for the flux declination observed in many applications due to increasing resistance to permeation and fouling susceptibility. To study these phenomena, the osmotic pressure model, combined with film theory, is generally used. It states that the permeate flux reduction is because the effective transmembrane pressure decreases. Furthermore, it is possible to define a real driving force which takes into account those phenomena (Cheng et al., 1998). The phenomenon of concentration polarization was also extensively studied and different correlations were developed (Bader and

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Table 1 – Properties of two commercial nanofiltration membranes: GE Desal_DK (DK) and GE Desal_DL (DL).

Property	DK	DL
Top layer	Aromatic polyamide	Aromatic polyamide
Support material	Polysulfone	Polysulfone
MWCO (Da)	300[a] (Zhao and Yuan, 2006)	490[a] (Jin et al., 2007)
Temperature resistance (°C)	90	90
pH resistance (at 20 °C)	2–11	2–11
$MgSO_4$ retention (%)	98	96

[a] According to Bargeman et al. (2005) the MWCO, reported by the manufacturers, of DK and DL membrane were 200 and 400 Da, respectively.

Veenstra, 1996; Gekas and Hallström, 1987; Geraldes and Afonso, 2007; van der Horst et al., 1995) involving different empirical expressions to predict the concentration polarization in membrane processes for different solutions, using experimental data. Using this method, Geraldes and Afonso (2006) predicted the concentration polarization for several geometries with 2D velocity fields and concentration distributions both in laminar and turbulent regimes. This correlation was applied in different works, where different NF membranes were studied and glucose, sucrose, and Na_2SO_4 solutions were used (Cavaco Morão et al., 2008; Rodrigues et al., 2010).

Since many monosaccharides are important ingredients in food and pharmaceutical industries and pure fractions of a specific monosaccharide are sometimes required, their purification and separation are under intense study. Among monosaccharides, glucose, the most frequently used sugar, is commercially available as dextrose, which is employed as an additive sweetener in popular beverages and processed foods. It is also a key ingredient in many commercial and medical products. Monosaccharide separations were traditionally performed by chromatographic methods and vacuum distillation (Feng et al., 2009; Sjöman et al., 2007). Currently, NF is a promising method since it requires lower energy consumption and maintenance costs in comparison with other alternatives (Feng et al., 2009).

For the successful implementation of a NF process it is necessary to obtain information about the separation efficiency and the capacity of the membrane. This is traditionally done by trial and error, although this approach is time consuming and expensive. Several models have been or are being developed for this purpose (Bowen et al., 1997; Bowen and Mukhtar, 1996; Garba et al., 1999; Hagmeyer and Gimbel, 1998; Straatsma et al., 2002; van der Horst et al., 1995). The Donnan-Steric Pore Model (DSPM) proposed by Bowen and Mohammad (1998) successfully predicted NF performance and is currently one of the most used models (Bowen and Welfoot, 2002; Santafé-Moros et al., 2008). However, one of the main disadvantages of the DSPM model is that physicochemical properties must be calculated. Thus, it is necessary to make different assumptions and analyze which are the most appropriate.

In this work we performed the nanofiltration of glucose solutions as the simplest model for juice. The aims were (i) to evaluate the filtration process, (ii) to analyze the osmotic pressure and concentration polarization phenomena using the pressure osmotic model and an empirical correlation for concentration polarization, (iii) to calculate the parameters involved in the DSPM model, and (iv) to characterize the membranes using the proposed model.

2. Materials and methods

2.1. Membrane characterization

Two commercial NF membranes, GE Desal_DK (DK) and GE Desal_DL (DL), with different Molecular Weight Cut-Off (MWCO) values, were used (Table 1). These membranes are thin-film membrane of hydrophilic character. The water used in the NF set-up and for the preparation of the solutions was distilled with an electrical conductivity less than 0.4 μS/cm. Glucose was of pro-analysis grade and delivered from Sigma–Aldrich.

Characterization of membranes included determination of the water contact angle, porosity and thickness. The water contact angle was measured at room temperature using a Standard Goniometer with DRO Pimage Standard (model 200-00, Ramé-Hart Instrument Co.). The porosity plays an important role with regard to permeation and separation (Chen et al., 2004) and was determined according to Chakrabarty et al. (2008). The membrane thickness was measured using and electronic micrometer screw Flower. The cross-sectional morphology of membranes was examined using Scanning Electron Microscopy (SEM) with a JEOL equipment (model JSM-6480 LV). The samples were fractured in liquid nitrogen and sputter-coated with gold.

2.2. Nanofiltration set-up and membrane permeability

A small scale filtering apparatus (Fig. 1), with total recirculation of both permeate and retentate, was used. A circular cell made of stainless steel with radial flux and an effective membrane area of 40 cm^2 held the NF membrane. The feed tank had a capacity of 50 L, and the liquid was pumped with a piston pump to the filtration unit at a flow rate of 400 L/h. All experiments were performed at 50 °C.

The membranes were flushed with distilled water at atmospheric pressure. The pressure was increased to 30 bar and the membranes were treated at high pressure for 2 h. Next, in order to calculate the membrane permeability, the pure water fluxes were measured at different operating pressures between 4 and 30 bar. The hydraulic permeability of the membrane was determined by the slope of the straight line obtained by plotting the permeate flux of water versus the driving force (ΔP, bar).

2.3. Filtration of glucose solutions

Different concentrations of glucose solutions were filtered: 5, 10, 50, and 100 g/L. The corresponding viscosities were 1.012, 1.024, 1.136, and 1.308 cp, respectively. The solution pH was adjusted to 6.00 with the addition of a few milliliters of concentrated nitric acid (65% w/w). Filtration was performed at 4, 8, 12, 24, and 28 bar and 50 °C, a temperature chosen to obtain low viscosities in the feed solutions that was considered reasonably safe according to membrane and glucose stabilities (Sjöman et al., 2007). Concentration and pH of glucose solutions were measured with a Maselli refractometer, model LR-01, and with a pHmeter Altronix, model TPX1. After each filtration, the membrane module was cleaned in two steps. The first one was performed recirculating distilled water for 30 min through the membrane module at a water flow rate of 600 L/h and a pressure of 10 bar, in order to remove the reversible polarized layer. In the second step, the membrane module was cleaned using the following solutions: an acetic acid solution (pH = 4.0, used an acidic cleaning agent) and a NaOH solution (pH = 9.0, used as basic cleaning agent). Cleaning solutions were recirculated in the NF system for 45 min at 50 °C at a flow rate of 600 L/h and a pressure of 10 bar. At the end of each cleaning procedure the membrane module was rinsed with distilled water for 20 min, at room temperature and pressure. It is important to remark that for the second cleaning step the basic agent followed the acidic one as this