Separation and Purification Technology 132 (2014) 234–243

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Membrane performance and application of ultrafiltration and nanofiltration to ethanol/water extract of *Eucalyptus* bark

Paula C.R. Pinto *, Inês F. Mota, José M. Loureiro, Alírio E. Rodrigues

LSRE – Laboratory of Separation and Reaction Engineering – Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form 26 April 2014
Accepted 28 April 2014
Available online 9 May 2014

Keywords:
Ultrafiltration
Nanofiltration
Ethanolic solutions
Bark extract
Polyphenols
Carbohydrates

ABSTRACT

The aim of this work is to promote the enrichment of an ethanolic extract of *Eucalyptus globulus* bark in polyphenolic compounds relatively to other compounds such as carbohydrates. Several flat sheet membranes were tested with water and ethanol solutions (52% v/v and 80% v/v) assessing to permeability. Rejections to gallic and tannic acids and maltose were evaluated for nanofiltration membranes and for the ultrafiltration membrane of lower cut-off. The dependence of permeability and rejection relative to ethanol percentage is discussed giving new insights about the membrane performance towards ethanol/water solutions. Among the tested membranes, two ultrafiltration (JW 30,000 Da and PLEAIDE 5000 Da) and one nanofiltration (SolSep 90801) membranes were selected to the concentration process of an ethanolic extract of *Eucalyptus globulus* bark produced at previously optimized conditions. The performance of the three membranes was evaluated concerning polyphenolic compounds and carbohydrate composition. The volume reduction factor was 1.76. JW membrane revealed the lowest total decrease on permeability (53%) relative to the initial. All the three membranes showed selective retention of polyphenolic compounds, however JW promoted the highest enrichment of formaldehyde-condensable tannins (fcT) and proanthocyanidins (Pac) (17% and 28%, respectively). The final composition of the retentate (in % weight/dry weight) was: TPC 39%, fcT 46%, Pac 38%, GalT 3.2% and TC 15%. The detailed sugar analysis revealed that some arabinose- and rhamnose-containing oligo/polysaccharides are preferentially retained, while those with glucose and galacturonic acid moieties are transported through the membrane to permeate stream. Finally, cleaning performance of membranes was evaluated and 80–100% flux recoveries were attained.

1. Introduction

The development of biorefinery platforms is currently undergoing rapid expansion. Pulp and paper industries have a privileged position due to the availability of side-streams lignocellulosic materials usually classified as by-products, such as bark which is a disposal in mill site where the logs are debarked. This is the case of pulp plants in Portugal which produces about 124,000 tons of *Eucalyptus globulus* bark per medium size industrial unit. Bark is further integrated in the mill operation as energy source. The basic chemical composition of bark and wood is similar concerning the major macromolecular components: lignin, cellulose and hemicelluloses [1,2]. However, the extractive and inorganic content is usually higher in bark than in wood. This is one of the reasons why bark has not been used for pulp production. Among the undesired extractive fractions is the polyphenolic fraction. This is composed by simple phenolics such as gallic and ellagic acids, flavonoids, complex glycosides of phenolic compounds [3,4], hydrolysable tannins, and proanthocyanidins [5,6], often called condensed tannins. The awareness on these compounds is growing up due to their properties and biological activities with emerging applications on cosmetics, nutricosmetic and fortified foods or supplements industries turning it on high added-value additives or active principles [7,8].

In this perspective, *E. globulus* bark is a potential raw material to produce polyphenolic enriched extracts. In our previous work, the optimum conditions (time, temperature and ethanol %) for the extraction of polyphenolic compounds from *E. globulus* bark were reported. The extract produced at optimum conditions (OC extract) was obtained in ethanol/water solution (52/48, v/v) and it demonstrated important biological activity. The yield was 50 g of material per kg of bark with 1/3 of the extracted material being

* Corresponding author. Address: LSRE – Laboratory of Separation and Reaction Engineering, Faculty of Engineering, Chemical Engineering Department, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal. Tel.: +351 22 041 3606; fax: +351 22 508 1449.
E-mail address: ppinto@fe.up.pt (P.C.R. Pinto).

http://dx.doi.org/10.1016/j.seppur.2014.04.042
1383-5866/

Nomenclature

List of symbols

A	effective membrane area (m^2)
Ara	arabinose
C_p	concentration in the permeate ($g\ L^{-1}$)
C_r	concentration in the retentate ($g\ L^{-1}$)
Gal	galactose
GalA	galacturonic acid
GalT	gallotannins (% w/w)
Glc	glucose
fcT	formaldehyde-condensable tannins (% w/w)
J_p	volumetric flux through membrane ($L\ m^{-2}\ h^{-1}$)
L_p	membrane permeability coefficient ($L\ m^{-2}\ h^{-1}\ bar^{-1}$)
NF	nanofiltration
pH_{PZC}	point of zero charge
OC	optimum conditions
Pac	proanthocyanidins (% w/w)
Q_p	permeate flow rate ($L\ h^{-1}$)
Rha	rhamnose
Man	mannose
R_m	membrane resistance coefficient (m^{-1})
R_j	apparent solute rejection coefficient
SN	Stiasny number (% w/w)
TMP	transmembrane pressure (bar)
TPC	total phenolic compounds (% w/w)
TS	total non-volatile solids ($g\ L^{-1}$)
TC	total carbohydrates (% w/w)
UF	ultrafiltration
V_f	feed volume (L)
V_r	retentate volume (L)
VRF	volume reduction factor
Xyl	xylose

Greek letters

μ	dynamic viscosity of water/solvent ($kg\ m^{-1}\ s^{-1}$)

of phenolic nature (assessed by Folin–Ciocalteu method for quantification of total phenolic compounds) [1]. Envisaging the fractionation and the increase of the polyphenolic fraction as the next step in the valorization process, membrane processing of OC extract was carried out. Based on its principle, membranes processing should lead to a fractionation of the polyphenolics and other components in the extract according to their molecular weight, hydrodynamic volume (size and shape of the hydrated/solvated molecule) and solvent–solute–membrane interactions. However, the adsorption and the build-up of a gel layer may act as a secondary membrane, changing both solute retention and permeate flux rate [9]. Moreover, the performance of a system strongly depends on the feed characteristics, operating conditions, membrane, and system configuration.

Membrane separations have been applied to fractionate and purify polyphenolic rich streams from several biomass resources as recently reviewed [10]. Olive mill wastewaters [11–14], extracts of grape seeds [15] and grape pomace [16,17] are the main examples of liquid streams derived from industrial activity processed by ultrafiltration (UF) and/or nanofiltration (NF) for polyphenols recovery. Concerning woody bark extracts, only one study for tannins recovery by UF was found [18]. Moreover, most of the studies in literature deal with aqueous solutions/extracts and just a few report real streams of organic solvent or binary mixture, namely ethanol/water [19–21].

In this work, seven commercial membranes were characterized and the impact of solvent composition on membrane performance was evaluated. Gallic acid (170 g mol^{-1}), tannic acid (1701 g mol^{-1}) were used as models for phenolic compounds, and maltose (342 g mol^{-1}) as model for carbohydrates, to test the NF membranes and the UF membrane of lower cut-off. The OC extract was submitted to UF and NF in concentration mode. The goal was to evaluate the performance of membrane processing in the polyphenol enrichment of the *E. globulus* extract. For this, the flux declines were evaluated and the compositions of retentates and permeates were assessed considering total non-volatile solids (TS), total phenolic compounds (TPC), formaldehyde-condensable tannins (fcT) quantified as Stiasny number (SN), proanthocyanidins (Pac), gallotannins (GalT), and sugar composition allowing the quantification of total carbohydrates (TC).

2. Experimental

2.1. Equipment, membranes and conditioning

Benchtop studies were conducted using a membrane cell system Sepa CF II Med/High Foulant System (GE Osmonics, USA) with an effective area of 0.014 m^2 plus a flow meter, a diaphragm pump Hydra-Cell, model M-3/G-13, (Wanner Engineering, Inc.) with a frequency inverter (MC07, Movitrac®B, SEW Eurodrive), and a manual hydraulic pump (P19, SPX Corporation, USA). The NF/UF unit withstands a maximum operating pressure of 69 bar, and a maximum operating temperature of 177 °C. The temperature of the feed was assured by a Lauda thermostatic bath (Ecoline Staredition Re 206) and a coil immersed on the feed tank. The feed temperature was checked by an electronic contact thermometer (VT-5 S40, VWR).

The UF and NF flat sheet membranes studied are listed in Table 1. Aqueous solutions of ethanol (Panreac) were prepared on a volume/volume basis using deionized water. All membranes were preconditioned according to the protocol recommended in the literature [22]. Prior to use, the membranes were first rinsed with water and soaked overnight. Afterwards, the membranes were soaked with ethanol solutions starting with 10% (v/v) ethanol and then with increments of 10–20% ethanol until 52% or 80% (v/v) ethanol, depending of the programed assays. For the experiences with water, membranes were simply soaked with water for three times and left overnight. The SolSep membranes were directly washed and conditioned in the working solvent as recommended by the fabricant. Before operation, each membrane was prepared by compressing it into the module by means of system hydraulic pressure (about 10–15 bar more than the operating pressure in the experiments), using water or ethanol/water solutions at a transmembrane pressure (TMP) of 1 bar for about 30 min to remove material from the pores. Then, using fresh solution, the membranes were submitted to compaction with a TMP 1–2 bar higher than the operating pressure in the experiments. The permeate flux was measured and usually the time to ensure the steady state was 1 h.

Ultra-pure water and analytical grade reagents were used for membrane characterization.