Journal of Membrane Science 493 (2015) 179–187

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Impact of biopolymer purification on the structural characteristics and transport performance of composite polysaccharide membranes for pervaporation

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ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form
23 June 2015
Accepted 4 July 2015
Available online 8 July 2015

Keywords:
Biopolymer
Dialysis
Dia-ultrafiltration
Polysaccharide membranes
Pervaporation

ABSTRACT

This study discusses the impact of biopolymer purification – by dialysis and by dia-ultrafiltration – on the properties and transport performance of composite polysaccharide membranes for pervaporation. The composite membranes prepared, using as active layer polysaccharides purified by these two methods, were compared in terms of structure, resistance to solvents, mechanical and transport properties.

Both composite membranes exhibited identical resistance to organic solvents, but presented significant differences in terms of swelling degree and transport selectivity. It was found that these differences may be caused by the shear stress imposed during purification by the dia-ultrafiltration method, which leads to a disintegration of polysaccharide aggregates. As a consequence denser membranes are obtained, due to smaller polysaccharide aggregates formed, which impact the transport selectivity.

Membranes prepared with polysaccharides purified by dia-ultrafiltration revealed to be the best choice for ethanol dehydration by pervaporation, since a water/ethanol selectivity of 143 for 10.0 wt% water in ethanol was achieved.

1. Introduction

Hydrophilic pervaporation is an attractive process for separation of close-boiling point mixtures, azeotropes and drying of solvents, due to its simplicity and low energy input as compared with traditional methods [1,2]. The highest challenge is the development of pervaporation membranes with good chemical resistance, mechanical stability and durability, exhibiting high selectivity and high permeation rate for the target solute [3]. Biopolymers based on natural polysaccharides extracted from plants, algae and animals, have received special attention due to their unique structures that translate into good selectivity and high permeation fluxes [4–6]. Additionally, microbial polysaccharides may present new or improved properties that make them competitive with other natural polysaccharides, as well as with synthetic polymers (e.g. polyvinyl alcohol (PVA)) [7].

The properties of microbial exopolysaccharides depend on the extraction, purification and drying methods; and the most appropriated processes must be selected for each case [7–9]. Microbial polysaccharides can be recovered from fermentation broths by chemical methods (e.g., using a cationic exchange resin (CER) or solvent precipitation), by physical extraction (by centrifugation, ultrasonication, microwave treatment or heating) or by a combination of both methods [9]. The most common technique used for polymer recovery is solvent precipitation with ethanol or acetone; however, this technique leads to polymers with low purity and high salt content. Additionally, solvent precipitation is a non-environmental friendly process, with low economic feasibility, due to high costs associated with the solvent and its disposal [9]. On the other hand, filtration techniques are recognized as good candidates for polymer recovery and purification at an industrial scale, since they can be easily operated and scaled-up [10]. Moreover, filtration techniques are regarded as more sustainable, due to their low energy and chemicals consumption requirements [11].

The main objective of this work is the development of highly selective composite polysaccharide membranes, comprising a microbial polysaccharide active layer supported on a polyethersulfone membrane for hydrophilic pervaporation processes. Composite membranes provide higher mechanical stability and higher fluxes when compared to homogeneous membranes due to their thinner top active layer [12,13]. The polysaccharide used in

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http://dx.doi.org/10.1016/j.memsci.2015.07.011
0376-7388/

this work is produced by a bacterial culture (*Enterobacter* strain A47) using glycerol, a by-product from biodiesel production, as carbon source [14]. This polysaccharide is composed by fucose, galactose and glucose, presents a high molecular weight (4.19×10^8–5.80×10^6 g/mol) and anionic character, due to the presence of acyl groups [15].

After biomass removal by centrifugation, the purification of the polysaccharide from the complex supernatant is presented and discussed in this work, using two different filtration approaches: dialysis in a static mode, which allows for polysaccharide purification by a purely diffusional transport, and dia-ultrafiltration involving the convective removal of contaminants (e.g. small peptides, sugars and salts) from the biomass free culture broth. These techniques were used in order to improve the functional properties of the polysaccharide and to remove impurities that interfere with the membrane-forming ability [16], as well as with their final structural, chemical and transport properties.

The purified polysaccharides obtained by the two processes were used to prepare membranes, which were characterized in terms of morphology, resistance to solvents and mechanical stability. Their transport properties were also evaluated for the dehydration of ethanol by pervaporation, since it is one of the most used industrial applications of pervaporation due to the increasing interest in bio-alcohols as alternative to fossil fuels [17].

In order to understand the different characteristics of the composite membranes obtained with the polysaccharide purified using dialysis and dia-ultrafiltration, the chemical composition, rheological properties and polymer particle size of those polysaccharide solutions were evaluated.

2. Material and methods

2.1. Materials

Genipin supplied by Comercial Rafer S.L. (Spain) was used as crosslinking agent in the preparation of polysaccharide membranes. The polyethersulfone (PES) membranes with a nominal pore size of 0.45 μm and positive charge from Gelman Sciences SB-6407 (USA) were used as support in the preparation of the composite membranes. Ethanol (99.9%) was purchased from VWR International – Material de Laboratório, Lda (Portugal). Ethyl acetate (99.9%) was purchased from Panreac Química SA (Spain). Dichloromethane (99.9%) and toluene (99.9%) were obtained from Fluka Riedel-deHaën (Germany) and Sigma-Aldrich Chemie GmbH (Germany), respectively. Tetrahydrofuran (THF) (99.8%) was obtained from E. Merck (Germany). Acetone (99.8%) was purchased from Valente e Ribeiro Lda. (Portugal). The sodium hydroxide used to adjust the pH was acquired from Eka (Sweden). Albumin used for calibration of Lowry method was purchased from Merck (USA).

The membranes utilized for dialysis and dia-ultrafiltration were provided, respectively, from Thermo Fisher Scientific (USA), model SnakeSkin® Pleated; and GE Healthcare (USA), model UFP-500-6A.

2.2. Methods

2.2.1. Extraction and purification of polysaccharides

The protocol used for extraction of extracellular microbial polysaccharides from the fermentation broths involved the following steps: dilution with deionised water (1:4 v/v) to reduce the viscosity; heat treatment during 1 h at 70 °C in order to inactivate the bacterial cells and enzymes [18], followed by cell removal by centrifugation. The supernatant containing the polysaccharide was then further purified by dialysis or by dia-ultrafiltration for removal of low molecular weight compounds (e.g. small peptides, salts, glycerol and sugars). The polysaccharide was then obtained by freeze drying the purified supernatant.

The cell free supernatant was purified by dialysis using a 10 kDa dialysis tubing (SnakeSkin® Pleated, Thermo Fisher Scientific, USA) against 5 L of distilled water during 2 days (replaced each day).

In parallel, the cell free supernatant was also purified by dia-ultrafiltration for removal of low molecular weight compounds from the fermentation broth, allowing for their faster removal, when compared with the dialysis process. Dia-ultrafiltration was performed in a tangential flow filtration mode using polyethersulfone hollow fiber membranes with a molecular weight cut-off (MWCO) of 500 kDa. This hollow fiber membrane module had an area of 0.28 m^2 and presented a water permeability of 260 ± 50 l/h bar m^2. The diluted polysaccharide supernatant was pumped from the feed tank to the lumen of the hollow fiber membranes. The permeate stream was collected in the shell side and the retentate stream was recirculated to the feed tank. This process was performed with constant addition of distilled water to the supernatant container in order to maintain the feed volume constant, facilitating solute permeation by reduction of concentration polarization effects and membrane fouling. This procedure was carried out at room temperature (23 °C) and at a constant transmembrane pressure (TMP) of 0.4 ± 0.1 bar.

Each run was performed with 3 L of the polysaccharide fermentation broth. During dia-ultrafiltration, samples of retentate and permeate were collected every 20 min, in order to monitor the retentate conductivity and protein content. When the conductivity reached a value below 200 μS/cm (identified as the value below which the removal of impurities becomes irrelevant), the treated supernatant was concentrated 3 times in the same membrane system, in order to facilitate the freeze drying process of the polysaccharide.

2.2.2. Membrane preparation

The membrane forming solutions were obtained by dissolution of 1.5% w/v of the dried polysaccharide, purified either by dialysis or by dia-ultrafiltration, in distilled water during 12 h. Then, 1% w/v of Genipin was added to the aqueous solution and stirred during 1 h, followed by a pH adjustment to 11 using a sodium hydroxide solution (NaOH). Genipin was added in order to promote the crosslinking of the polysaccharide matrix.

The composite membranes were prepared by casting successive layers of the membrane forming solution on a polyethersulfone (PES) porous support (17.35 cm^2). Each layer had an amount of 2 g of polymer solution. The first layer was allowed to dry for 24 h at 30 °C, before adding the second layer, which was dried in the same conditions.

In addition, homogeneous membranes were also prepared by casting the membrane forming solution in a Petri dish and drying at 30 °C during 24 h. These homogeneous membranes were used in order to provide information relative to the dense active layer of the composite membranes (which are identical in structure and chemistry).

2.2.3. Characterization of the active layer of the composite membranes

2.2.3.1. Hydrophilic character. The hydrophilic character of the membranes was determined from the water contact angles of the homogeneous membrane surfaces. The water contact angles were measured at room temperature (23 °C) using a goniometer (KSV Instruments LTD, CAM 100, Finland) with the software KSV CAM 100.

The contact angle values determined correspond to the average of four measurements performed in different regions of the membrane surfaces.