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Changes in the physico-chemical characteristics of a protein solution in the presence of magnetic field and the consequences on the ultrafiltration performance



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ARTICLE INFO	A B S T R A C T
Keywords:	The use of magnetic field in protein solution (bovine serum albumin/BSA) was proposed as a strategy to improve
Ultrafiltration	the ultrafiltration (UF) performance. Permeation tests of BSA ($2.5 g L^{-1}$ and pH 6.5) through a 50 kDa hydro-
Magnetic field Protein Zeta potential Circular dichroism	philic polyethersulfone (PES) membrane were carried out in a tangential flow module. The magnetic induction
	effect (MI) on the feed solutions was studied by submitting the feed to the magnetic field (magnetic flux density 0.7 T and 1.4 T) for 0.5 h, 2 h and 12 h before permeation runs. Positive effects were observed in the permeate flux with flux increase up to 195% compared to control. Also, a reduction in the fouling resistance from 59%
	(control) to 18% and 16% using 2h of magnetic induction under 0.7 and 1.4 T, respectively, was noted. This
	behavior can be attributed to changes in structure and zeta potential of the BSA solution after magnetic field exposition, then increasing the repulsion between the membrane surface and the protein molecules.

1. Introduction

Membrane separation processes have found many industrial applications, due to the advantages when compared to conventional separation processes (Han et al., 2016). The mild process temperatures and use of low hydrostatic pressures are positive features that avoid physical and chemical changes in products, such as protein denaturation and loss of flavors, also reducing energy consumption (Luján-Facundo et al., 2015). The main limitations of this technology are the phenomena of concentration polarization and fouling, causing permeate flux reduction (Sadeghi et al., 2013).

Physical and chemical strategies have been developed to reduce fouling phenomena (Sadeghi et al., 2013). Even though chemical cleaning can be an efficient method, it may cause membrane and final product damage. The cleaning procedures and membrane replacement costs may vary from 20 to 30% (Mikhaylin and Bazinet, 2015). In this context, physical processes for fouling reduction, such as turbulencegenerator devices and use of magnetic or electric fields are advantageous, due to the molecule structure maintenance and no production of harmful waste for the environment (Liu et al., 2016; Mehrnia and Homayoonfal, 2016).

Fouling reduction in membranes can start from the development of

a simple pre-treatment method suitable for the feed solution, thereby reducing efforts and time spent in the cleaning of membranes (Mulder, 1996). The use of magnetic fields in the feed solution has been proposed as a promising alternative to reduce fouling on membrane processes (Gryta, 2011; Silva et al., 2015; Vedavyasan, 2001; Zin et al., 2016). This technology has drawn attention due to advantages such as low cost, simple operation and no damages to the environment (green technology) (Li et al., 2007).

Some studies report that magnetic field can interfere in the intermolecular interactions, in this manner, modifying solution properties such as viscosity and surface tension (Kobe et al., 2002; Madsen, 2007; Toledo et al., 2008). Furthermore, changes in the water conductivity were observed, due to the magnetic fields effects in the hydrated ion layer besides the changes in the hydrating water structure around the ions (Holysz et al., 2007; Szcześ et al., 2011). In saline solutions, numerous studies state that the effects of the magnetic field are generally on the increase in the amount of precipitate and in the precipitation rates (Alimi et al., 2009).

The application of a magnetic field has been shown as a potential technology for fouling reduction in ultrafiltration of model protein solutions. Vardanega et al. (2013) evaluated the effects of the magnetic field (0.4 T) during the permeation of bovine serum albumin (BSA)

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Received 14 February 2018; Received in revised form 8 August 2018; Accepted 13 August 2018 Available online 23 August 2018 0260-8774/ © 2018 Elsevier Ltd. All rights reserved. through an ultrafiltration (UF) membrane of 60 kDa. Zin et al. (2016) studied the influence of a magnetic field (0.7 T) in the UF of protein solutions (BSA, milk and milk whey). The best permeability recovery results were found for the magnetic induction of BSA solution at pH 4.0 and 6.5, reaching permeability recoveries of 81% and 82%, respectively, against 28% and 35% for control runs without the field.

On the other hand, systematic studies about the magnetic field effects in the protein solutions physico-chemical characteristics are still quite limited, encouraging the present study. Therefore, analytical techniques as circular dichroism and zeta potential can provide essential information for understanding the changes caused by the magnetic field on BSA solution and membrane, and thus give some insights on mechanisms responsible for the observed effects. Such information can be correlated with the membrane performance (flux and solute rejection), selectivity and transport resistances. These factors are critical in optimizing the performance of membranes and designing novel strategies for fouling reduction.

Due to lack of information about possible changes that can occur during the BSA solution pretreatment and permeation with magnetic fields, this work aims to evaluate the magnetic field effects (flux density and induction time) in the BSA solutions and to verify their influence in polymeric membrane fouling.

2. Material and methods

2.1. Membrane

An ultrafiltration membrane with molar mass cut-off (MMCO) of 50 kDa (Microdyn-Nadir GmbH, Germany), made of polyethersulfone, was used in all assays. According to the manufacturer, this membrane can operate at temperatures up to 95 $^{\circ}$ C and pH ranging from 0 to 14. A new sample of the membrane was used for each set of experimental runs.

2.2. Magnetic field

Two magnetic flux densities, 0.7 and 1.4 T, were tested. The magnetic flux density of 1.4 T was generated using a Halbach array consisting of an arrangement of permanent neodymium-iron-boron (Nd₂Fe₁₄B) magnets, with a 1 cm gap. The arrangement design is rectangular with dimensions $180 \times 120 \times 113$ mm (length, height, width). The magnetic flux density of 0.7 T was generated by two neodymium-iron-boron (Nd₂Fe₁₄B) permanent magnets with dimensions of $50 \times 50 \times 25$ mm, placed facing each other with a 1 cm spacing. The experimental set-up for each case is depicted in Fig. 1. A magnetic

transducer was used to measure the magnetic flux density (model TMAG-1T, Globalmag Ltda, Brazil).

2.3. Experimental apparatus

A tangential ultrafiltration (UF) unit with total recycle was used to perform the permeation assays. The unit consists in a feed tank with a capacity of 500 mL, a positive displacement pump (Micropump, cat.75211-15, USA), and a permeation module made of stainless steel with dimensions of $120 \times 90 \times 10$ mm and an effective filtration area of 2.9×10^{-3} m². The system is provided with a pressure gauge (Fiedler Ltda, Brazil) with capacity from 0 to 4 bar, a backpressure valve (SS4BK, Swagelok, USA) and a flow meter (Blaster Controles Ltda., Brazil). In the magnetic induction assays, permanent magnets were positioned perpendicularly to a flow cell, with the same dimensions as the permeation module (Fig. 1).

2.4. Protein solution and reagents

Bovine serum albumin (BSA) (Sigma-Aldrich, A2153, purity > 96%, Mw = 66 kDa) was used as a model protein in all assays. The protein solution was prepared with ultrapure water. Phosphoric acid (H₃PO₄) was used to adjust the protein solution pH to 6.5. In all assays, the concentration of the BSA solution was set at 2.5 g L⁻¹. The chemical cleaning procedure employed solutions of phosphoric acid (H₃PO₄), sodium hydroxide (NaOH) and sodium phosphate buffer at pH 7.0 and concentration 0.01 mol L⁻¹ (Vetec Ltda, Brazil).

2.5. Experimental procedure

BSA ultrafiltration was carried out in a tangential flow cell, in batch mode with full recycle of permeate at ambient temperature (25 °C \pm 2 °C), at constant pressure of 2 bar, feed flow rate of 0.3 L min⁻¹ and 25 °C, based on previous experience of the group. Permeate flux was determined at each 15 min for BSA solutions. At the end of protein UF, the physical cleaning procedure was performed by circulating 5 L of ultrapure water (flow rate 0.6 L min⁻¹), then circulating a NaOH solution at pH 10.0, followed by a HCl solution at pH 4.0, with a subsequent recirculation of sodium phosphate buffer at pH 7.0 for 30 min. Before each cleaning procedure, the recovery of hydraulic permeability was measured by water permeation at different transmembrane pressures and then compared with the new membrane permeability.



Prior to permeation run, the BSA solution was exposed to the

Fig. 1. (a) Schematic diagram of experimental apparatus, (b) side view of the tangential flow cell under a magnetic field 0.7 T.

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