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A combined fouling model to describe the influence of the electrostatic environment on the cross-flow microfiltration of BSA

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ABSTRACT

In this paper, the influence of pH in the 3–9 interval and NaCl concentration up to 25 mM on the cross-flow microfiltration of BSA was studied. A tubular ceramic membrane with a mean pore size of 0.14 μm was employed. The evolution of permeate flow and BSA transmission with time was determined at 30 °C, a cross-flow velocity of 3.28 m/s and a transmembrane pressure of 100 kPa. The flow data were discussed by means of combination of two fouling mechanisms: complete and standard blocking when transmission of proteins occurred and complete blocking and cake formations otherwise. The effective radius of the protein and the electrostatic interactions protein–membrane explained the transmission protein values.

1. Introduction

Proteins purification and separation have been widely studied because of their important properties and applications in biotechnology and food industries. Membrane technology is one of the most important processes implemented due to their economical advantages, compared to other separation techniques, and the ease of scale-up.

From the first experiments, many authors have focused on the influence of chemical environment in the separation process. Consequently, there are a significant number of works which have studied the variation of flux, adsorption, fouling or transmission of proteins as a function of pH or ionic strength.

Fane et al. [1] discussed the ultrafiltration of BSA solutions with polyethersulfone membranes (20 and 30 kDa) over a range of pH values (2–10) and salt concentrations (0–0.2 M NaCl). A minimum flux was obtained at pH 5 in the absence of salts, but it was lowest in the presence of salt at pH 2, increasing with pH. The final flux was correlated with the adsorbed protein. Maximum adsorption occurred at the isoelectric point (≈pH 5) and was even greater with added salt.

Aimar et al. [2] studied the adsorption of BSA for pH values of 2.0, 4.7 and 7.2 and a concentration rate from 0.1 to 50 g/L with a 20 kDa polyacrylonitrile membrane. Adsorption isotherms correlated to Freundlich laws. The adsorbed protein increased when: (i) bulk protein increased, (ii) contact time increased and (iii) pH decreased, up to 10 g/L. For more concentrated solutions, the protein adsorbed was lowest at the isoelectric point. The presence of calcium ions increased the hydraulic resistance at pH values different from isoelectric point whereas an opposite effect was observed at iep.

Opong and Zydney [3] analyzed the filtration of BSA through ultrafiltration (30–1000 kDa) and microfiltration (0.16 μm) polyethersulfone membranes. The hydraulic permeability of protein deposit decreased with increasing filtration pressure, although variation with pressure was slow for time longer than 100 min. The permeability of the protein deposit was studied at different pH (2.0–7.4) and ionic strength (0–0.5 M NaCl) values, decreasing with increasing ionic strength and was maximum at the BSA isoelectric point.

Mochizuki and Zydney [4] employed a 0.16 μm polyethersulfone membrane to evaluate the variation of transmission of BSA with operating parameters. The flux decay was due to the formation of a protein deposit located on the surface of the membrane. The sieving coefficient also decreased along time, because of rejection of BSA by the protein deposit. The highest value was obtained at the isoelectric point of the protein. For values over and below this pH, the transmission obtained was lower and depended on the ionic strength and composition of the solution (Ca^{2+}, Na^{+}).

Palecek and Zydney [5] obtained data for hydraulic permeability of deposits formed during the microfiltration of BSA, lysozyme, ribonuclease A, hemoglobin, and immunoglobulins solutions (5 g/L and 69 kPa) through a 0.16 μm polyethersulfone membrane. The

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steady-state permeability for all proteins was minimum at its isoelectric point, and decreased when increase salt concentration at pH values above and below the p*I*. An increase in ionic strength resulted in a rise in flux followed by a relatively slow flux decline.

Oppenheim et al. [6] analyzed the internal surface coverage of BSA in 100 kDa polysulfone membranes at different pH values (5 and 7) and salt concentrations (0.05 and 0.15 M NaCl) up to 4 h of ultrafiltration. The results showed an important protein accumulation in the membrane after a short time of exposure. At pH 7, the protein was likely to be lodged in the ultrathin skin area of the membrane. However, at pH 5 and low ionic strength, BSA was lodged and adsorbed throughout all the membrane structure.

Herrero et al. [7] studied the flux decline of BSA solutions with 0.1 μm polycarbonate membranes at several pH values (4, 5, 6.8 and 8) and two ionic strengths (0 and 0.15 M NaCl). In all the cases membrane fouled in two steps: a rapid initial internal blocking dependent on operation parameters, followed by an external blocking with lower sensitivity of flux on operation conditions. For those pH values far from the isoelectric point fouling was especially low when no additives were presents (neutral pH and absence of salt).

Jones and O'Melia [8] evaluated the adsorption of BSA and humic acid onto a 30 kDa regenerated cellulose ultrafiltration membrane. They calculated adsorption isotherms and rate of adsorption by measuring adsorbed mass as a function of time. Experiments were carried out at differing conditions of pH, ionic strength and bulk feed concentration. For both compounds, adsorption was higher at lower pH values and adsorption decreased as pH increased. The increase in salt concentration reduced electrostatic repulsion between like-charged material (increasing adsorption), and decreased electrostatic attraction between oppositely charged material (decreasing adsorption). They analyzed these interaction using two models, and concluded that an adequate control of electrostatic interactions could reduce adsorption onto the membrane, and consequently, long-term membrane fouling. The same authors [9] calculated reversible and irreversible fouling resistances, to study the effect of convective flow and electrostatic interactions on fouling behaviour. They filtered BSA and humic acid, varying conditions of pH and ionic strength, through 30–100 kDa cellulose membranes. Convective forces increased the amount of material accumulated near the membrane, but electrostatic forces were stronger, affecting reversible and irreversible resistances. These resistances were higher at the isoelectric point of the membrane, and decreased at higher pH values. On the other hand, humic acid adsorption decreased when pH was increased from 4.7 to 10.

Persson et al. [10] investigated the transmission of BSA through two MF membranes (nylon, 0.2 μm and polyethersulfone, 0.16 μm). The transmission was highest for the polyethersulfone membrane, and was affected by the pH. At pH 5 the transmission was 100% (almost constant during the entire experiment), and much lower at pH values of 3 and 7 (even 40%). However, an increase in the ionic strength resulted in an increase of the transmission for both MF membranes (at pH 3 and 7). This involved that protein–filter cake and protein–membrane electrostatic interactions affected the transmission. The increase in transmission near its iep (pH 5) was due to the lack of electrostatic repulsion. High ionic strength shields charged proteins from each others and from the membrane and the filter cake by the ions in the solution, acting as though they were uncharged, increasing the transmission of BSA.

Mehta and Zydney [11] observed the effect of membrane charge density on hydraulic permeability and protein transport during ultrafiltration. Using a series of charge-modified cellulose membranes, the membrane charge was evaluated from streaming potential measurements. Protein transmission decreased by a factor of 100 as the membrane potential increased from 0.3 to 6.6 mV. The protein sieving data were discussed according to a partitioning model, while the hydraulic permeability data were related to a model accounting for the effects of counter-electroosmosis.

More recently, Bowen and Williams [12] have performed a study on the quantitative predictive modelling of protein ultrafiltration processes. According to colloidal interactions and hydrodynamics, particle–particle interactions may be calculated using a cell-model description of electrostatic interactions coupled with quantification of London–van der Waals forces and the entropic pressure. The predictive calculations may be used in a number of different ways, depending on the level of knowledge of the colloidal properties available.

The aim of this work was to evaluate the electrostatic interactions in the microfiltration of a model protein through a ceramic membrane. To this aim, the effects of pH and salt concentration on the evolution of permeate flow and transmission on the cross-flow filtration of BSA were investigated. The results obtained were discussed according a combined fouling model and the effective protein size.

2. Experimental

2.1. Materials and experimental rig

BSA (molecular weight 69 kDa) was obtained from Sigma (USA). Ceramic membrane employed was Céram Inside 25 (pore radius 0.14 μm) from Tami Industries (France). This mineral membrane was tubular and consisted of a support made of a mixture of aluminium/titanium/zirconium oxides with an active layer of zirconium oxide. The membrane length was 25 cm and its hydraulic diameter 3.6 mm, giving a total surface area of 93.8 cm^2.

The experimental rig (Fig. 1) included the membrane housing, a variable frequency vane pump (Cole Parmer, USA), a flow meter (Badge Meter, Germany) and an analytical balance (Mettler Toledo, Switzerland), two pressure gauges located before and after the membrane and pH and temperature probes.

2.2. Determination of the pzc

The method described by Mullet et al. [13] was employed to determine the point of zero charge of the membrane, which corresponds to zero surface charge density, i.e., to equivalent amounts of negative and positive charges developed by proton equilibria.

The pzc of this membrane was calculated in a previous work [14] and was about 6.9. At initial pH values below the pzc, the hydroxyl groups at the surface of the membrane (MOH) become protonated and so positively charged (MOH^+). On the other hand, at initial pH values above the pzc, the hydroxyl groups become deprotonated and therefore negatively charged (MO^-).

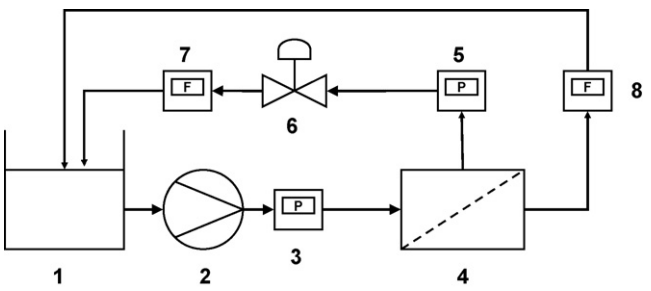

Fig. 1. Drawing of the experimental system: (1) feed tank, (2) recirculation pump, (3) manometer, (4) membrane module, (5) manometer, (6) back-pressure valve, (7) flowmeter, and (8) flowmeter.