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Fouling prevention of peptides from a tryptic whey hydrolysate during electromembrane processes by use of monovalent ion permselective membranes

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ABSTRACT

Peptide adsorption occurring on conventional anion- and cation-exchange membranes is one of the main technological locks in electrodialysis (ED) for hydrolysate demineralization. Hence, the peptide fouling of monovalent anion (MAP) and monovalent cation (MCP) permselective membranes was studied and compared to conventional membranes (AMX-SB and CMX-SB). It appeared that the main peptide sequences responsible for fouling were TPEVDDEALEKFDK, VAGTWY and VLVLDTDYK for both anionic membranes; and ALPMHIR and TKIPAVFK for both cationic membranes. However based on the MS-MS results, the fouling was about 97–100% lower for MAP than AMX-SB and 95–100% lower for MCP than CMX-SB. This was explained by the differences in charge sign distribution at the membrane surface. Consequently, monovalent membranes can represent a very interesting opportunity for treatment of hydrolysate solution in electrodialytic processes by practically eliminating peptide fouling. At our knowledge, it was the first time that such a demonstration was done.

1. Introduction

Whey protein hydrolysates (WPH) are excellent sources of bioactive peptides with functional properties such as antihypertive, antidiabetic or antibacterial activities [1,2]. Bioactive peptides must be separated from the total WPH into smaller fractions to be used in food applications. In other cases, the WPH should be desalinated for human consumption purposes. Fractionation and purification of WPH are achieved by using membrane technologies such as ultrafiltration, nanofiltration [3–5] or electrodialysis (ED) [6]. However, peptide fouling is one of the main drawback in the membrane industry. Membrane cleaning and replacement may cost 20–30% for the pressure-driven membrane processes and 40–50% for the ED process [7,8].

Recent studies showed that conventional food-grade anion-exchange membranes (AMX-SB) and/or cation-exchange membranes (CMX-SB) are exposed to fouling in presence of a WPH either in static [9,10] or in hydrodynamic conditions during an ED process [11]. Fouling was mainly due to a few peptides which could establish electrostatic interactions with the membranes, and that even with no current applied. The nature of the membrane interface is a predominant parameter in peptide fouling. Thereby, fouling may be different concerning membranes having particular interfaces and different characteristics. Many studies investigated the organic fouling resistance of membranes after surface modifications by grafting specific compounds for PES and PVDF [12–17] and for anion-exchange membranes [7,18] using model foulants. The monovalent ion permselective membranes are another category of ion-exchange membranes allowing the migration of their oppositely-charged monovalent ions through these last while retaining the polyvalent ions. The monovalent anion permselective (MAP) membranes are made of a resin including positive charges which is covered by a very thin and highly cross-linked negatively charged layer on its surface. Inversely, monovalent cation permselective (MCP) membranes are made of resin including negative charges coated with a thin positive charge layer [19,20]. Such layers on the membrane interface are able to separate ions with the same charge sign but different valences. The MAP are highly permeable only to monovalent anions like chloride ions whereas the MCP are highly permeable only to monovalent cations like sodium ions. With these particular layers on their interfaces, the MAP and MCP may have interesting resistance in peptide fouling. Nonetheless, there is no study dealing with the fouling of such membranes with model peptide solutions or complex peptide mixtures.

In this context, the aim of the present work was (1) to investigate the WPH fouling on MAP and MCP according to the pH, (2) to identify

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the characteristics and sequences of potential fouled peptide and (3) to compare that fouling in terms of quantity and peptide sequences with the conventional membranes from previous studies [9–11] carried-out with the same WPH and in the same static and ED conditions.

2. Materials and methods

2.1. Materials

Food grade Neosepta monovalent anion permselective membranes (MAP) and monovalent cation permselective membranes (MCP) were purchased from Astom (Tokyo, Japan). The HCl 1.0 N and NaOH 1.0 N were obtained from Fisher Scientific (Nepean, ON, Canada). NaCl and Na_2SO_4 were supplied by ACP Inc. (Montréal, QC, Canada). A BiPRO whey protein isolate (WPI), provided by Davisco Foods International (Eden Prairie, MN, USA) was used for the production of the whey protein hydrolysate (WPH). According to the manufacturer, the WPI composition was 92.7% of protein, 5.0% moisture and 2.3% salt (sodium, potassium, calcium, phosphorus and magnesium). Proteins in WPI consist of 68–75% β-lactoglobulin, 19–25% α-lactalbumin and 2–3% bovine serum albumin. The BiPRO WPI was hydrolyzed with pancreatic bovine trypsin (reference number: T9201) purchased from Sigma - Aldrich (St. Louis, MO, USA). Then, the hydrolysate was heated at 80 °C during 30 min in order to inactivate the enzyme and avoid further breakdown of peptides [21] and freeze-dried. The final WPH was composed of 89% peptides and 11% salt. Rhodamine B dye was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. ED cell configuration

A 500 mL solution of 0.5% (w/w) WPH supplemented with 0.4% (w/w) NaCl (final composition: 44.5% peptides and 45.5% salt) was demineralized by ED. The ED cell was a MicroFlow type cell from ElectroCell Systems AB (Täby, Sweden) using a Xantrex power supply (HPD 60-5, QC, Canada). Four MAP and five MCP membranes of surface area of 10 cm^2 were used. The compartments defined three closed loops containing the feed solution (0.5% WPH), the salt ion recovery (0.20 M NaCl) and the electrode-rinsing solution (0.14 M Na_2SO_4). Each closed loop was connected to an external plastic reservoir, allowing continuous recirculation for each compartment (Fig. 1). The current-tension curve of this system was determined according to the method of Cowan and Brown [22] and the limiting current was reached at 11 V.

2.3. Protocol

In this study, the objective was to compare and to identify the peptide fouling of monovalent ions MAP and MCP membranes with previous results of conventional AMX-SB and CMX-SB membranes in the same static [9,10] and hydrodynamic [11] conditions and using the same model peptide solution (WPH). In static conditions, membranes were simply soaked in BiPRO WPH whereas in hydrodynamic conditions, membranes were stacked in an ED cell for demineralization.

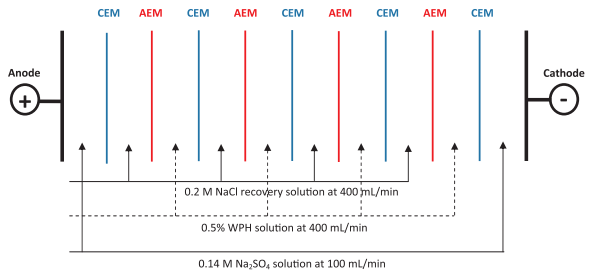

Fig. 1. Electrodialysis cell configuration for demineralization of the WPH solution.

2.3.1. Static conditions

Four virgin MAPs of 10 cm^2 were soaked overnight in 100 mL of a 0.5% (w/w) WPH solution after adjusting the initial pH of 8.2 at three different pH values (2, 6 and 10) in order to potentially promote the peptide-membrane interactions. Then, the membranes were rinsed with distilled water and half of them were analyzed. The second half was soaked in 20 mL of a 2.0% (w/w) NaCl desorption solution during three hours in order to remove potential peptides responsible for the fouling [23]. Afterwards, both membranes were rinsed and analyzed. The NaCl desorption solutions were recovered and freeze-dried for peptide identification by UPLC-QTOF. The same protocol was carried-out for MCP membranes. The peptide fractions previously obtained for AMX-SB [9] and CMX-SB [10] membranes were re-analyzed for peptide identification in the same conditions and with the same equipment as MAP and MCP to be able to compare the UPLC-QTOF results.

2.3.2. Hydrodynamic conditions

A 0.5% WPH solution was demineralized at pH 6 during 60 min at a voltage of 4.5 V (underlimiting current density) using an ED cell (Fig. 1) as in [11]. After ED treatments, MAPs and MCPs were recovered and half of them were soaked separately in 20 mL of 2.0% (w/w) NaCl in order to remove a potential peptide fouling. The NaCl desorption solutions were recovered and freeze-dried for peptide identification by UPLC-QTOF.

2.4. Analysis and chemicals

2.4.1. Nitrogen content of membranes

Membranes were analyzed in terms of nitrogen content using the Dumas method as described in [9]. Briefly, membrane samples were combusted at 950 °C with pure oxygen and the product of combustion (gases) containing nitrogen oxides was heated to 850 °C in a second furnace for complete oxidation and collected in a ballast tank. Helium was used as a carrier and nitrogen oxides were converted to molecular nitrogen and quantified.

2.4.2. Peptide concentration in NaCl desorption solutions

The peptide concentrations in the NaCl desorption solutions were determined using μBCA™ protein assay kit (Pierce Biotechnology Inc., Rockford, IL, USA). Assays were conducted as recommended by the manufacturer.

2.4.3. Peptide identification in freeze-dried NaCl desorption solutions

The freeze-dried NaCl desorption solutions were analyzed by UPLC-QTOF for peptide identification as described in [11]. Moreover, the freeze-dried NaCl desorption solutions of AMX-SB and CMX-SB in static conditions [9,10] were reanalyzed using this new UPLC-QTOF method in order to be comparable. Freezed-dried desorption solutions were dissolved with 1.5 mL of UPLC grade water to optimize peptide concentration for mass UPLC-MS analyses. RP-UPLC analyses were performed using a 1290 Infinity II UPLC (Agilent Technologies, Santa Clara, CA, USA). The equipment consisted of a binary pump (G7120A), a multisampler (G7167B), an in-line degasser and a variable wavelength detector (VWD G7114B) adjusted to 214 nm. Diluted peptides were filtered through 0.22 μm PVDF filter into a glass vial. The sample was loaded (5 μL) onto an Acquity UPLC CSH 130 1.7 μm C18 column (2.1 mm i.d. × 150 mm, Waters Corporation, Milford, MA, USA). The column was operated at a flow rate of 400 μL/min at 45 °C. The gradient consisted of solvent A (LC-MS grade water with 0.1% formic acid) and solvent B (LC-MS grade ACN with 0.1% formic acid) starting at 2% B and ramping to 35% B in 40 min, then ramping to 85% B to 40.50 min, holding until 42 min, then back to initial conditions until 45 min. A hybrid ion mobility quadrupole TOF mass spectrometer (6560 high definition mass spectrometry (IM-Q-TOF), Agilent, Santa Clara, USA) was used to identify and quantify the relative abundances of the tryptic peptides. All LC-MS/MS experiments were acquired using