Mechanisms controlling retention during ultrafiltration of charged saccharides: Molecular conformation and electrostatic forces

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ABSTRACT

Separation of different biomass components in solution, including charged saccharides, is one of the key challenges in biorefining of plant biomass. Ultrafiltration is one of the potential processes that could cope with such separation. Electrostatic interactions between solute molecules and between solute molecules and membrane material are amongst the key factors determining the separation efficiency during ultrafiltration of charged saccharides. Our hypothesis is that the manipulation of pH in addition to the classic pressure control should enhance the ultrafiltration performance for charged saccharides in terms of permeate flux and observed retention of the target molecules. Series of batch ultrafiltrations with carboxymethyl-cellulose (CMC) showed that an increase of transmembrane pressure (from 2 to 4 bars) resulted in higher permeate fluxes and lower observed retentions. These results were explained by the cake-layer model. An increase of pH from 2.0 to 7.4 caused an increase in flux and we propose that this effect was due to a conformation change in the CMC molecules from an entangled, globular shape to a more linear one in response to repulsion amongst the negative charges on the molecules at higher pH. The results obtained in this work demonstrate that it is possible to control the observed retention of charged saccharides during ultrafiltration by manipulating pH and transmembrane pressure. Therefore, beyond operational conditions, specific molecular mechanisms must be taken into account when it comes to optimizing ultrafiltration of such species.

1. Introduction

Efficient separation of different solubilized biomass components, including various poly- and oligosaccharides, is a key prerequisite for the development of a range of product streams of specified purities from biomass. Highly concentrated solutions of charged saccharides are e.g., required for the synthesis of biopolymer complexes used for encapsulation and delivery of functional food ingredients [1]. Efficient ultrafiltration to obtain concentrated solutions requires high solute retentions and high permeate fluxes, but both requirements are usually impeded by severe concentration polarization and fouling. There is, however, a lack of knowledge about the significance of the molecular conformation and interactions between the solute and the membrane material on fouling formation during filtration of charged saccharides, since most of the literature related to filtration of charged compounds has focused on proteins. The present study was undertaken to obtain a clearer picture of the significance of some key operational parameters for ultrafiltration of charged poly- and oligosaccharides with the objective of identifying the mechanisms controlling the separation efficiency of charged saccharides. Carboxy-methyl-cellulose (CMC) was selected as a model compound to study the behavior of charged saccharides during ultrafiltration, because it has a linear structure (it has a backbone structure made of β-$(1 \rightarrow 4)$-bonded D-glucopyranose units), is water soluble, is available commercially at different, relatively well-defined molecular weights, has a high viscosity even at low concentrations, and the charge density can be easily regulated by pH (isoelectric point, IP: 4.7). CMC is produced via reaction of cellulose alkali and monochloroacetate of sodium. When dissolved in water, the molecule dissociates into sodium ions and a polymer anion, so CMC becomes a polyelectrolyte. The ions in solution interact through electrostatic forces, which are responsible for some of its most interesting properties e.g., high viscosity. Such properties make CMC a prominent additive for food industry, where it is currently widely used as a stabilizer, binder and thickener [2,3].

As for membrane filtration, the characteristics of CMC allow us studying three phenomena with particular relevance in relation to filtration of charged saccharides, particularly in terms of concentration polarization and fouling:

(a) *Molecular conformation*: depending on the charge density of the molecule, the CMC molecules can adopt a linear configuration – due to the repulsion of the negative charges at high

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pH – or a more globular configuration when the density of negative charges is lower i.e., at lower pH [4,5]. It is expected that the geometrical configuration has an impact in the concentration polarization and retention of the molecule during filtration [6].

(b) *Intermolecular electrostatic forces*: repulsion of negative charges amongst the soluble or solubilized molecules (i.e., the solute) will influence the nature of the cake typically formed on the membrane surface when performing filtrations in a dead-end mode. The compactness of the cake will in turn influence the permeate flux and the separation performance [7].

(c) *Solute–membrane interactions*: i.e., interactions between the CMC molecules and the membrane material. Previous studies have indicated that the electrostatic forces induced by the changes of the charge on the CMC molecules in response to pH can modify the affinity between the charged molecule and the membrane [8,9]. The zeta potential of polyethersulfone membranes has been shown to be influenced by the pH of the solution [10]; such a change in zeta-potential may affect the extent of the interaction between charged solutes (e.g., charged saccharide molecules) which in turn may change the molecular retention dramatically.

The objective of the present work was thus to obtain a better understanding of the significance of some key separation process parameters i.e., pressure and pH, on the retention and flux during concentration of charged saccharides, using CMC as a model, and secondly, to identify the mechanisms behind the influence of these variables on the separation performance.

2. Materials and methods

2.1. Chemicals

90 kDa Sodium carboxy-methyl-cellulose (CMC), and HCl were from Sigma Aldrich (St. Louis, MO, USA).

2.2. Experimental setup

Ultrafiltration experiments were performed in a 100 mL Amicon dead-end ultrafiltration cell (Model 8050, Millipore Corporation, Billerica, MA, USA) connected to dried atmospheric air through a valve and a pressure regulator. A 100 kDa polyethersulfone membrane (Millipore Corporation) was placed at the bottom of the cell (water permeability = 1.5 ± 0.1 L/m^2 h bar). The volume of the feed solution was 100 mL in each experiment. To measure the flux, the permeate was collected during time recording in a 100 mL glass container placed on a digital scale next to the ultrafiltration cell. Stirring was provided by a magnetic stirrer, and the stirring rate was set at 400 rpm. The initial concentration of CMC in the feed solution was 40 g/L. To evaluate the effect of pressure, three experiments at three different pressures (2, 3, and 4 bars) were performed. The specifications of the experimental setup did not allow the use of pressures higher than 4.5 bars. However, increases of pressure beyond 3 bars did not result in an increase of permeate flux through the membrane. In the experiments where pressure was varied, the pH was 7.4 (natural pH of the CMC solution). To evaluate the effect of pH, pH was set at three different values by using HCl: 7.4 – which is the natural pH of a CMC solution – 4.7 – which is the isoelectric point of CMC – and 2.0. In the experiments in which pH was varied, the pressure was kept at 3 bars.

2.3. Membrane cleaning and water permeability

After each experiment, the membrane was cleaned by passing 400 mL of distilled water through the membrane in the reverse mode at 2 bars and 400 rpm. The membrane was maintained in 20% ethanol/distilled water overnight. Membrane permeability was evaluated before each experiment. A new membrane was used if the variation of water permeability was higher than ±5%.

2.4. Determination of resistance due to fouling

The permeate flux, J (g/m^2 s), equalling the specific mass transfer rate over the membrane, was determined at different filtration times intervals:

$$J = \frac{\Delta m_p}{A_m \Delta t} \tag{1}$$

where Δm_p is the difference of weight in a time interval (g), A_m is the membrane area (m^2) and Δt is the time interval between two measurements (s). In order to determine the total flux resistance (R_{tot}), Eq. (1) was equalled to:

$$J = \frac{\Delta V}{\Delta t} = \frac{\Delta P}{\mu R_{tot}} \tag{2}$$

where V is the volume (m^3), ΔP is the transmembrane pressure (bar), and μ the dynamic viscosity (poise).

The resistance to flux due to fouling (R_F) was calculated as follows:

$$R_F = R_{tot} - R_{membrane} \tag{3}$$

where $R_{membrane}$ is the resistance due to the membrane, which can be determined considering the water permeability. The shape of the curve R_F versus time was used to confirm the type of fouling internal or external in each of the experiments [11].

2.5. Viscosity measurements

The concentration of CMC in the permeate was determined through viscosity measurements. 5 mL of CMC solution were placed in the test chamber of a Haake Mars Modular Advanced Rheometer System (Germany), connected to a Haake Universal Temperature Controller, in order to make the measurements at a constant temperature of 25 °C. First, a calibration curve was obtained from CMC solutions at known concentrations (data not shown). Values of concentration were then obtained from the measured values of viscosity. No differences in viscosity were detected for same-concentration solutions at the different pHs used in the study, probably due to the low concentration of the solutions.

2.6. Reproducibility

All experiments were performed, at least, in duplicate. The values shown in the figures are the average of the duplicates. The experimental error was expressed as an average coefficient of variation, which is the average, in percent, of the sum of the standard deviations, each calculated as a percentage of the average of each of the individual points, corresponding to an experiment. The average coefficient of variation was lower than 10% in all cases.