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Negatively charged tangential flow ultrafiltration membranes for whey protein concentration

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ABSTRACT

This work examines the use of wide-pore negatively charged ultrafiltration membranes for whey protein concentration. The hypothesis is that by placing a negative charge on the surface of an ultrafiltration membrane, negatively charged proteins are rejected by electrostatic repulsion and not simply sized based sieving. This allows using wide-pore membranes that have a higher flux without suffering a loss in protein recovery. It was found that negatively charged 100 kDa ultrafiltration membranes had the same protein recovery as 10 kDa unmodified membranes used in the dairy industry, but offered a flux that was at least two-fold higher. The new membranes were used for a 40-fold concentration of whey with subsequent diafiltration to mimic the industrial process for making whey protein concentrate. Mass balance models of concentration and diafiltration were developed and each agreed well with the experimental results. The experimental methods and mathematical models developed in this work can be used to design, simulate and optimize different process flow sheets, and explore the effect of various operating conditions on the membrane processing of whey.

1. Introduction

Whey proteins are used for a variety of purposes. Their presence is ubiquitous as food ingredients; in snacks, infant formula, food for the elderly and for fitness enthusiasts. Specific whey proteins such as glycomacropeptide are also used in foods for people with medical conditions like phenylketonuria. Whey proteins are known to be among the most nutritionally complete proteins and each individual whey protein has unique health benefits. The uses and properties of whey proteins may be found elsewhere [1–4]. Sweet whey contains about 5% lactose, 1% non-protein nitrogen (NPN) and other small molecules like cheese color, minerals, and riboflavin (which imparts the yellow color to whey), 0.06–0.1% fat, and 0.6% protein. The remainder is water. Thus, on a dry basis, whey contains about 10–12% protein that individually range in molecular mass from 8.6 kDa to 150 kDa [1,3]. The purpose of whey protein concentration is to increase the protein-to-dry-solids content from about 12% to 80% by removing water and the other small molecules while retaining protein. This is accomplished using membrane ultrafiltration.

Industrial practice to produce whey protein concentrates (WPC) is to use ultrafiltration membranes that have a nominal molecular weight cut-off (MWCO) of 10 kDa or 20 kDa [5], to retain whey proteins and clear the lactose and small molecules. Because these membranes are tight, they offer the advantage of retaining most of the protein, thereby minimizing losses due to protein sieving. But, they have limitations. Tight membranes have a low hydraulic permeability or volumetric throughput for protein concentration. Using looser wide pore size membranes increases the hydraulic permeability, but at the expense of higher protein sieving losses. For example, Rektor and Vatai [6] found that only 75% of the protein was rejected using uncharged 100 kDa membranes for concentration of mozzarella cheese whey. This problem is described as the permeability-selectivity trade-off by Mehta and Zydney [7,8].

In addition to this trade-off, pore-blocking affects tight membranes wherein the protein molecules that are larger than the pore sit at the mouth of the pore and cause flux decline and fouling [9]. Furthermore, precipitation of calcium salts in the membrane pores may have occurred because of the absence of protein. The narrow pores of these membranes are filled with whey permeate that contains lactose, minerals and NPN and is devoid of protein. As described by Maubois, whey permeate devoid of protein is an unstable solution and this leads to precipitation of calcium salts in the pores above 20 °C. Precipitation does not occur in whey because the presence of the proteins provides a protective effect [10]. This pore precipitation phenomenon along with classical pore blocking adversely affects the performance characteristics of tight membranes during the ultrafiltration of whey.

The central hypothesis of the present work is that the permeability-selectivity trade-off and pore blocking can be overcome

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by use of wide pore charged ultrafiltration membranes. This idea is not entirely new as Mehta and Zydney pointed this out in 2005 and suggested that charged ultrafiltration membranes could help ameliorate this problem [7]. Much of the previous work using charged ultrafiltration membranes has used membranes in stirred cells not cross flow filtration membranes, worked with pure proteins in buffer not natural feed solutions such as whey, simply measured sieving coefficients not concentrated proteins, and not developed mass balance models of the process useful for design, scale-up and process optimization.

Other work on charged tangential flow ultrafiltration membranes focused on fractionation of proteins from mixtures of proteins, not protein concentration, including our previous work on charged membranes [11–14]. The present work is different than our previous work in that, in our previous work, positively charged membranes of 300 kDa were used to fractionate individual whey proteins like alpha-lactalbumin (ALA) and beta-lactoglobulin (BLG) at acidic pH values [11,12]. The membranes selectively permeated ALA and selectively retained BLG at pH 4.3. In the present work, negatively charged membranes of 300 kDa were used to completely retain all whey proteins at neutral pH values. The membranes retained ALA, BLG and glycomacropeptide (GMP) at pH 6.8. The present work stands in contradistinction to our previous work in that the membrane charge, pH, and purpose are essentially opposites.

The purpose of the present research was to examine flux enhancement for whey protein concentration using wide-pore size negatively charged, tangential flow ultrafiltration membranes and study their performance characteristics for a 40-fold concentration and diafiltration process for producing whey protein concentrate (WPC). The principle of the research was that because the major whey proteins have an average isoelectric point (pI) of 4.6, then the proteins have a net negative charge at the neutral pH of whey, and should be electrostatically rejected by a wide-pore size negatively charged membrane. Because of the wider pores (higher permeability), the membrane should allow operation at a higher flux. Mass balance models were developed for concentration and diafiltration that utilize only sieving coefficients measured under conditions of total recycle. Experimental observations were compared to mass balance model calculations for validation. It was found that the permeability-selectivity trade-off rule of thumb could be broken using charged ultrafiltration membranes for a 40X concentration and diafiltration process. Thus, charged ultrafiltration membranes were found to be an attractive option to dairy and bioprocessing based on the results of this work. The experimental methods and mass balance models developed in this work should be useful for others who concentrate proteins by ultrafiltration and diafiltration using charged and also uncharged membranes.

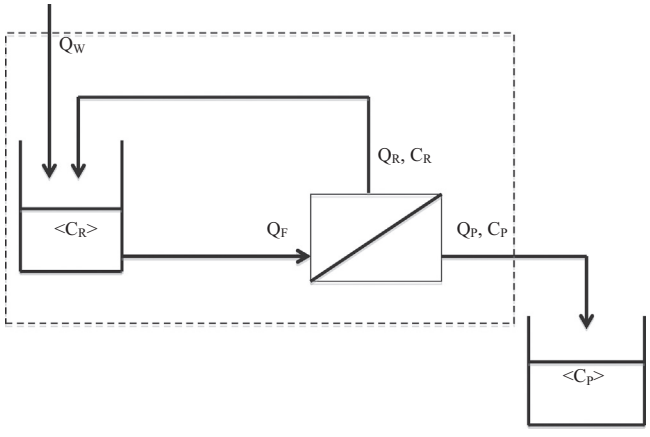

Fig. 1. Schematic of a single-stage ultrafiltration system with constant volume diafiltration.

2. Theory

2.1. Mass balance model for ultrafiltration and constant volume diafiltration

Membranes are used for concentration of proteins (ultrafiltration) and for small-molecule clearance (ultrafiltration/diafiltration). In both cases, it is desired to retain the proteins by the membrane while clearing the small molecules and water. Protein transmission is characterized by the observed sieving coefficient, $S_o = C_P/C_R$, where C_P and C_R are the instantaneous concentrations of protein in the permeate and retentate of the membrane, respectively. In our previous work, it was shown that sieving coefficients measured under conditions of total recycle (without concentration) can be used to accurately predict the performance of a multistage membrane system with concentration [11].

A single-stage ultrafiltration/diafiltration system is shown in Fig. 1. Feed solution of volume V_F and protein concentration C_F is placed into a supply reservoir at time zero. Let V_R be the retentate volume at any time t. It is assumed that the densities of the streams entering and leaving the membrane are the same and constant. Permeate is drawn from the membrane at a constant flow rate Q_P and protein solution fed to the membrane at a constant flow rate Q_F. In case of concentration without diafiltration, the flow-rate of water entering is set as $Q_W = 0$.

Doing ultrafiltration without diafiltration, the final mixing-cup retentate concentration $\langle C_R \rangle$ is given by the following equation [11]:

$$\ln \frac{\langle C_R \rangle}{C_F} = \left(1 - \widehat{S_O}\right) \ln VCF, \tag{1}$$

where the volume concentration factor $VCF = V_F/V_R$, and the lumped sieving coefficient is [11]

$$\widehat{S_O} = \frac{S_O}{1 - \hat{Q}(1 - S_O)} = \frac{C_P}{\langle C_R \rangle}. \tag{2}$$

The dimensionless flow rate $\hat{Q}$ is defined as

$$\hat{Q} = \frac{Q_P}{Q_F}. \tag{3}$$

As shown previously [11], the average "mixing-cup" concentration of protein in the permeate $\langle C_P \rangle$ is obtained by mass-balance

$$\langle C_P \rangle (VCF - 1) = C_F VCF - \langle C_R \rangle. \tag{4}$$

In a constant volume diafiltration operation, water for diafiltration is added continuously to the feed tank such that $Q_W = Q_P$, and the volume of the solution in the feed tank (V_F) is held constant. The dimensionless ratio for water addition is the number of diafiltration volumes, N_D

$$N_D = \frac{Q_P t}{V_F}. \tag{5}$$

In the system shown in Fig. 1, the initial charge to the supply reservoir is feed solution of volume V_F and protein concentration C_F. Note that if ultrafiltration is followed by diafiltration (UF/DF), then V_F for diafiltration is the same as V_R after ultrafiltration, and C_F for diafiltration is the same as $\langle C_R \rangle$ after ultrafiltration. The permeate flow rate during ultrafiltration and diafiltration (Q_P) need not be the same. Writing a mass balance on protein around the system boundary shown in Fig. 1

$$-Q_P C_P = V_F \frac{d\langle C_R \rangle}{dt} \tag{6}$$