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Mechanisms of flux decline in skim milk ultrafiltration: A review

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ABSTRACT

Skim milk ultrafiltration (UF), used for milk protein concentration, is one of the most important unit operations in dairy processing. However UF performance is severely reduced by flux decline resulting from concentration polarisation (CP) and fouling, the mechanisms of which are still not fully understood for the complex colloidal fluid of skim milk. In this review, we analyse published observations of CP and fouling of relevance to skim milk UF to examine the underlying mechanisms. Current approaches for modelling the flux decline caused by CP and fouling are reviewed. Focussed discussion is given to the current state of understanding of CP and fouling in relation to the physicochemical properties of skim milk and the effectiveness of chemical cleaning. This review identifies the roles of various milk components in CP and fouling behaviour and offers insights into the mechanisms that govern flux decline.

1. Introduction

Skim milk ultrafiltration (UF) is a key unit operation in dairy processing in which milk proteins are concentrated through the removal of lactose, salts, peptides and other solutes, and water. UF exploits size differences in the milk components to preferentially concentrate the proteins, which cannot be achieved by evaporation alone, allowing more flexible control over product composition. In addition, filtration is considerably less energy-intensive [1,2], and avoids prolonged heat exposure, allowing the functional properties and sensory qualities of milk to be well preserved [3]. It is used extensively in the production of cheese [2,4–7] and milk protein concentrates (MPC) [5–9], and also for protein standardisation [5–8,10].

Skim milk UF is particularly susceptible to poor operational efficiency [8] due to flux decline resulting from concentration polarisation (CP) and fouling. CP is the accumulation of retained particles at the membrane surface, while fouling occurs due to adsorption or deposition of colloidal particles on the membrane surface and in the membrane pores [2,11]. CP and fouling contribute resistance to permeation flow, and can be responsible for severe reductions in flux and changes in rejection properties, ultimately resulting in lower throughput and altered product quality. The CP layer is a direct result of flux and is usually reversible in the sense that it will quickly diffuse if flux across the membrane is halted. However, severe CP can also result in the formation of a gel layer formed through particle-particle interactions and such a layer dissipates slowly, if at all, when the flux is halted. From an operational perspective CP is unavoidable but it can be minimised by improving particle convection away from the membrane [2,12,13]. On the other hand, fouling is irreversible (upon cessation of flux), and its removal requires back washing or often even chemical cleaning. This interrupts operation, lowers productivity, consumes large amounts of water and chemicals, and reduces membrane life [2].

The optimisation of skim milk UF (both operation and cleaning) requires an understanding of the mechanisms of flux decline in relation to the physicochemical properties of skim milk, however this is still not fully understood despite the widespread use of skim milk UF for over 30 years. In recent years substantial progress has been made in understanding milk chemistry, and separately, the physics of CP and membrane fouling by proteins. In addition significant advances have been made in the development of mathematical models to describe filtration behaviour, in particular via computational fluid dynamics (CFD). However, this whole body of work has yet to be brought

Abbreviations: AAS, atomic absorption spectroscopy; ATR-FTIR, attenuated total reflection Fourier transform infrared spectroscopy; BSA, bovine serum albumin; CCP, colloidal calcium phosphate; CFD, computational fluid dynamics; CFV, cross-flow velocity; CIP, cleaning-in-place; CM, casein micelle; CN, casein; CP, concentration polarisation; DF, diafiltration; EDTA, ethylenediaminetetraacetic acid; EDX, energy dispersive X-ray; GISAXS, grazing incidence small-angle X-ray scattering; IEP, isoelectric point; MF, microfiltration; MPC, milk protein concentrate; MWCO, molecular weight cutoff; NPC, native phosphocaseinate; PAN, polyacrylonitrile; PEG, polyethylene glycol; PES, polyethersulfone; PSf, polysulfone; PVDF, polyvinylidene difluoride; SAXS, small-angle X-ray scattering; SEM, scanning electron microscopy; SMUF, simulated milk ultrafiltrate; TMP, transmembrane pressure; TN, total nitrogen; UHT, ultra-high temperature; UF, ultrafiltration; VRR, volume reduction ratio (or volume concentration factor, VCF); WP, whey proteins; WPI, whey protein isolate

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together in the context of skim milk UF and relatively few studies have been made specifically investigating CP and fouling mechanisms in skim milk UF. Past reviews on skim milk UF or dairy filtration have mostly focused on applications and avenues for product development, and very little has been dedicated to the discussion of CP and fouling in relation to the physicochemical properties of skim milk.

In this review we bring together results from recent studies of CP, membrane fouling, and filtration modelling with existing knowledge to extend our understanding of the fundamental mechanisms of flux decline in relation to the physicochemical properties of skim milk. Aspects of membrane cleaning and processing factors affecting flux decline are also discussed. Through the analysis of the available literature, we hope to derive new insights that will allow further optimisation of skim milk UF.

2. The skim milk system

Some knowledge of milk chemistry is necessary for discussing how flux decline behaviour can be affected by changes in milk properties. This section provides an overview of the major milk proteins, mineral equilibria, and casein micelle structure and interactions with the surrounding milk serum.

Skim milk is a complex colloidal suspension of proteins in an aqueous solution of lactose and minerals, and some minor components including residual milk fat globules. Milk proteins make up 3.5 wt% of milk, of which 80% are casein (CN), defined as proteins insoluble at pH 4.6 and 20 °C, while the remaining 20% are whey proteins (WP) (Table 1). Caseins are comprised of α_{s1}-CN, α_{s2}-CN, β-CN and κ-CN, in approximate proportions of 38%, 10%, 35% and 12% respectively [14]. They generally have high phosphoserine content which can interact with the calcium phosphate in milk (except κ-CN), and proline content which limits their ability to fold into secondary (α-helices and β-sheets) and tertiary structures. Consequently, caseins generally have an open structure, and the majority of them are present in milk as casein micelles (CMs) (see Section 2.2).

Whey proteins are comprised of about 60% β-lactoglobulin (β-LG), 20% α-lactoglobulin (α-LA), 10% bovine serum albumin (BSA) and 10% immunoglobulins (Ig). Other proteins such as lactoferrin, peptides, hormones and enzymes are also present in skim milk in minor amounts. Unlike caseins, whey proteins generally have tertiary and quaternary structures, which as discussed later, can influence CP and fouling behaviour in skim milk. Under physiological conditions of milk, β-LG exists as dimers held together by hydrophobic interactions (Lewis-acid-base interactions), but also exhibits different aggregation states depending on the pH. It is also known to dissociate into monomers and undergo reversible conformational changes (Tanford transition) between 40 and 55 °C [14]. α-LA is a compact globular protein that has a very strong affinity for binding calcium (association constant, K_a at 25 °C ~3×10^8 M^{-1} [15]), which is important for its structure and stability [14]. BSA is a large elongated molecule with high disulphide content.

2.1. Mineral equilibria

Milk contains a large variety of salts, principally sodium, potassium, calcium, magnesium, phosphate, chloride, sulphate, carbonate and citrate [17]. These salts are not fully dissolved nor fully ionised in the milk serum [4] – dissolved salts are present in the aqueous serum phase as free ions or associated with proteins, lactose and other salts; undissolved salts are associated with CMs. In addition, α-LA and lactoferrin contain ion binding sites that specifically bind calcium and iron respectively.

Of major importance is calcium phosphate, which is sparingly soluble (solubility of $CaHPO_4$ in milk=~1.8 mmol/L; $Ca_3(PO_4)_2$=~0.06 mmol/L) [4] and is present in milk at supersaturated concentrations. It is thermodynamically unstable but natural precipitation is prevented by complex associations of calcium with other salts and milk components. About two-thirds of the calcium is undissolved and incorporated into CMs along with half of the inorganic phosphate and other undissolved salts, collectively referred to as colloidal calcium phosphate (CCP). The remaining calcium is present in the serum as ionic calcium or complexed with free soluble caseins, other salts (e.g. citrate), proteins [18,19], and also lactose [20]. All these fractions exist in a dynamic and complex equilibrium influenced by temperature, concentration and pH [21–23]. Stabilisation of calcium phosphate is provided by the presence of CMs, however the partitioning of calcium and phosphate between serum and CMs is also responsible for many of the alterations to CM properties reported in literature (see below).

2.2. Casein micelles

At native pH and room temperature, about 95% caseins are associated as colloidal assemblies of micelles. CMs are comprised of all the casein fractions in milk, and the caseins make up approximately 93% of the total dry matter of the CM. The remaining 7% is CCP, which is present in the form of nanoclusters. CMs are also highly voluminous, occupying about 4.4 mL/g casein at 25 °C, and are considerably hydrated (3.7 g_{water}/g_{casein}) [24]. In addition, CMs are highly polydisperse, with sizes ranging from about 50–300 nm in diameter. On a volumetric basis, the average diameter of CM is about 150–200 nm [25].

The exact structure of the CM has not been unequivocally elucidated. A number of models have been developed over the decades that attempt to describe the CM structure and the interactions of its components with the serum. These models have been continuously refined, and has been discussed in a number of reviews [25–31]. For the purpose of this review, knowledge of the precise CM structure is not crucial. Rather, the key attributes of CMs that must be accounted for in any proposed mechanistic or mathematical model of skim milk UF are described below.

It is generally accepted that almost all κ-CN is present on the micelle exterior, inferred by the higher κ-CN content in smaller CMs compared to larger CMs [32–34], but the κ-CN is not evenly distributed on the CM surface [27]. Long hydrophilic sections of the κ-CN protein extend into the serum, giving rise to a so-called 'hairy layer'. This ~7 nm thick layer provides steric stabilisation for CMs [4,14]. Meanwhile, the CM interior is considered to be a network of α- and β-CN linked to nanoclusters of calcium phosphate of about 2–3 nm in diameter [30,35,36]. Both CCP content and hydrophobic interactions are necessary for micellar integrity [31]. This is indicated by observations of micellar disintegration upon sufficient removal of calcium [37–39], or if surfactants or urea are added [14]. The voluminous and hydrated nature of CMs also suggests that the interior is fairly porous. This is supported by recent permeability measurements of CM dispersions by Bouchoux et al. [40] that were found to fit better to hard sphere models by considering the CMs to be 8.8 nm particles, whereas large deviations were seen when an average CM size of 100 nm was

Table 1
Major proteins in skim milk [16].

Protein	Concentration in skim milk (g/L)	Molecular weight (kDa)
Caseins		
α_{s1}-CN	12–15	23.6
α_{s2}-CN	3–4	25.2
β-CN	9–11	24.0
κ-CN	2–4	19.0
Whey proteins		
β-LG	2–4	18.3
α-LA	0.6–1.7	14.2
BSA	0.4	66.4
Ig	0.4	150–1000