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Effects of ultrasound on cross-flow ultrafiltration of skim milk: Characterization from macro-scale to nano-scale

Y. Jin [a,b], N. Hengl [a,b,*], S. Baup [a,b], F. Pignon [a,b,*], N. Gondrexon [a,b], M. Sztucki [c], G. Gésan-Guiziou [d,e], A. Magnin [a,b], M. Abyan [a,b], M. Karrouch [a,b], D. Blésès [a,b]

[a] Univ. Grenoble Alpes, LRP, F-38000 Grenoble, France
[b] CNRS, LRP, F-38000 Grenoble, France
[c] European Synchrotron Radiation Facility, BP220 38043 Grenoble Cedex 9, France
[d] INRA UMR1253 STLO Science et technologie du lait et de l'oeuf, 65 rue de Saint-Brieuc, 35042 Rennes Cedex, France
[e] AGROCAMPUS OUEST UMR1253 STLO Science et technologie du lait et de l'oeuf, 65 rue de Saint-Brieuc, 35042 Rennes Cedex, France

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ABSTRACT

This study investigates effects of ultrasound (US) on cross-flow ultrafiltration of skim milk by multi-scale characterization, using a custom designed "SAXS Cross-Flow US-coupled Filtration Cell". The study of flow properties of casein micelle suspensions shows an evolution of their rheological behavior from Newtonian to shear-thinning until the emergence of yield stress with the increase of concentration (from 27 g L^{-1} to 216 g L^{-1}). The concentration profiles during cross-flow filtration of skim milk have been revealed for the first time by real-time *in-situ* Small Angle X-ray Scattering (SAXS) measurement. Without any change of internal structure of casein micelles and membrane selectivity, the applied ultrasound (20 kHz, 2 W cm^{-2}) leads to a significant increase of permeate flux arising from a disruption of concentrated layer. Varying the US intensity from 0.6 W cm^{-2} to 2.9 W cm^{-2} does not affect the US enhancement factor, which however depends on the feed concentration. In fact, increase of feed concentration induces the formation of highly cohesive fouling layer during filtration that the applied US could hardly disrupt. Results also suggest that the preventive US application mode is promising since formation of the reversible fouling layer was strongly limited in this mode.

1. Introduction

In dairy industry concentration and fractionation processes of milk components are largely performed with membrane operations. Ultrafiltration is used to standardize the protein content of milk prior to the cheese manufacture. The bottleneck of skim milk ultrafiltration is the fouling phenomenon that affects the performance of the process and thus limits its productivity.

Different strategies have been adopted to control fouling. Some propose to increase the shear rate close to the membrane by simply increasing cross-flow velocity, by inserting spacers or turbulence promoters [1,2], or by using vibrating/rotating disk modules [3–5]. Instead of modifying the module, others suggest different procedures to remove fouling, such as backpulsing/backflushing (transmembrane pressure reversal) [6,7], or pulsating and reversing feed flows [8,9]. Gas bubbling [10–13] or scouring particles [14] are also proposed to reduce fouling. It is also reported that pressure loss along the membrane is responsible for the greater fouling in non-uniform crossflow processes, so uniform transmembrane pressure crossflow filtration system has been proposed to reduce fouling and cake build-up [15–17]. Though effective, these various strategies present drawbacks as well for skim milk filtration [18].

Ultrasound (US) was applied for the first time in 80s to enhance membrane process [19]. Since then, more and more investigations have been found in the literature reporting its effectiveness for membrane cleaning [20–22] and fouling control [22–24], thanks to different effects induced by its propagation, such as particles vibrations, cavitation and acoustic streaming [25]. However, membrane damage and material denaturation have been occasionally reported [26,27]. In fact, principal cause of these unfavorable consequences is the high ultrasonic intensity, often with close US transducer-membrane distance [28]. Otherwise, low US-intensity applications are promising for membrane process as far as we know, confirmed by majority of reports in the literature [20–25].

Since fouling is the major problem during milk filtration, ultrasonic assisted fouling control presents a great potential in this application. Several successful examples have already been found in literature. In immersing the cross-flow filtration cell in an ultrasonic water bath where the dissipated power is 20 W L^{-1},

* Corresponding authors at: CNRS, LRP, F-38000 Grenoble, France.
E-mail addresses: nicolas.hengl@ujf-grenoble.fr (N. Hengl), frederic.pignon@ujf-grenoble.fr (F. Pignon).

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Muthukumaran et al. [23,29] reported that ultrasound of low frequency (50 kHz) can be effective in enhancing both the production and cleaning cycles of whey ultrafiltration. Their results suggested that the application of ultrasound can lower the compressibility of protein deposit and increase the mass transfer coefficient within the concentration polarization layer. More recently, Mirzaie et al. [24] studied effects of various ultrasonic related parameters on flux enhancement in dead-end microfiltration of milk and obtained a flux enhancement factor of 490% by applying ultrasonic waves of 20 kHz and 31.57 W cm^{-2}. In addition, effect of ultrasound (20 kHz, 20 and 41 W) on the physical and functional properties of skim milk has been reported by Shanmugam et al. [30]. They found a slight denaturation of whey proteins (followed by their self-aggregation and aggregation with free caseins), but no change of milk viscosity caused by ultrasonication and no influence of acoustic cavitation on casein micelle structure. They suggested that the minor change to the milk imparted by US foresees its potential for optimizing this technique for industrial applications.

Our recent work has shown a great interest to apply US in filtration of colloidal suspensions: *in-situ* ultrasonication can lead to a significant increase of permeate flux without damaging the membrane structure [31]. Using a custom designed "SAXS Cross-Flow US-coupled Filtration Cell" in applying a lower US intensity (2 W cm^{-2} by input electric power), this permeate flux increase was confirmed for the filtration of Laponite dispersions (synthetic aqueous clay dispersion, consisting of nanometric platelets). Moreover, structural organization at nanometer length scale during filtration was revealed thanks to the real-time *in-situ* synchrotron radiation (Small Angle X-ray Scattering measurements, called SAXS), suggesting that the permeate flux increase results from the break-up of the concentrated layer [32].

Using this designed 'SAXS Cross-Flow US-coupled Filtration Cell', this study is devoted to enhance skim milk cross-flow ultrafiltration by applying *in-situ* ultrasonication and to characterize effects of ultrasound at multi-scales. Macroscopic results, presented by the permeate flux, will be combined with simultaneous observations of structure at nanometer length scale (mainly concentration profiles of casein micelles), revealed by SAXS measurements. As far as we know, it is the first time that evolution of concentration profiles over time during cross-flow filtration of skim milk is observed by *in-situ* measurement, needless to say that the employed cross-flow filtration itself is improved by applying a simultaneous ultrasonication.

2. Materials and methods

2.1. Sample preparation

Different suspensions were prepared in this study. The suspensions for filtration are skim milk suspensions. They were prepared from 'low heat' Bovine Skim Milk Powder containing soluble proteins and mineral salts in addition to casein micelles, the major protein of milk. This powder was provided by "UMR 1253 INRA Agrocampus Ouest, STLO Science et Technologie du Lait et de l'Œuf" Rennes, France [33]. To prevent the development of bacteria, sodium azide (0.2 g L^{-1}) was added to the suspension. The casein micelle content of standard skim milk suspension is about 27 g L^{-1} (26 g kg^{-1}). The equivalent mass of the 'low heat' powder (about 95.8 g) was dispersed in deionized water under steady stirring at a fixed temperature of 45 °C to obtain a 1 kg milk with a standard concentration in casein micelles. Mixing time was adapted according to the desired concentrations in order to produce homogeneous suspensions and sufficient hydration of casein micelles (30 min for standard concentration and until 2 h for concentrated suspensions). To simplify the interpretation of results, a relative concentration C/C_o was presented in this paper, where C is the casein micelle concentration of sample suspension and C_o corresponds to the casein micelle concentration of standard skim milk (27 g L^{-1}).

Other casein micelle suspensions were also used in the study of flow properties (Section 3.1). They were obtained by dissolution of a standard commercial "high protein content powder" (Promilk 852B, Ingrédia, 62, Arras, France) in aqueous phase. The same suspensions have already been used in precedent work [34]. The content of casein micelles in this powder is higher, about 75% (w/w), compared to that of "low heat" powder, about 26% (w/w). Therefore, the equivalent mass of powder is 35.2 g for 1 kg of suspension correspondent to the casein micelle concentration of standard skim milk. The preparation protocol is the same as that of "low heat" powder. In order to reveal the eventual difference of flow properties of casein micelle suspensions in different ionic equilibriums, three types of aqueous phase were exploited. The casein micelles were dispersed either in deionized water, in ultrafiltrate (UF) or microfiltrate (MF). The microfiltrate was obtained by microfiltration (0.1 μm) of skim milk. It contains some dissolved proteins, lactose and some minerals. The ultrafiltrate was acquired by ultrafiltration (8 kDa) of the obtained microfiltrate, it contains only lactose and minerals. The suspensions of casein micelles dispersed in MF could be considered as an equivalent of skim milk.

2.2. Rheometric, turbidity and pH measurements

The rheological behavior of casein micelle suspensions was studied with two stress-control rheometers (ARG2 and DHR3, TA INSTRUMENT, France). For the suspensions with relatively low concentration ($C < 175.5$ g L^{-1}), a titanium cone and plate geometry was used (diameter 60 mm, angle 1°). For the high concentrated suspensions ($C > 175.5$ g L^{-1}), a stainless steel cone-plate geometry was used (diameter 49 mm, angle 4°21′), whose surfaces were covered with sand-paper with a roughness of 200 μm in order to avoid sample slip at the geometry wall [35]. Measurements were carried out at a temperature of 25 ± 1 °C. The atmosphere around the sample was saturated with water to prevent evaporation during the measurement [35].

The pH of casein micelle suspensions was measured at 25 °C using a pH electrode connected to a pH meter (CRISON PH25, Spain). Turbidity of milk samples was measured using a turbidimeter (AL450T-IR, TURBIDIRECT, Germany) by transmission of LED light ($\lambda = 860$ nm) through a path, with an accuracy of ± 0.01 NTU. Turbidity of feed (NTU_{feed}) and permeate ($NTU_{permeate}$) was measured for each filtration run and the rejection rate of casein micelles ($TR_{caseins}$, %) can be calculated by:

$$TR_{caseins} = 1 - \frac{NTU_{permeate}}{NTU_{feed}} \times 100$$

2.3. SAXS Cross-Flow US-coupled Filtration

A "SAXS Cross-Flow US-coupled Filtration Cell" was previously developed to, on the one hand, apply ultrasonic waves close to the flat membrane by embedding in the feed compartment a thin titanium vibrating blade and on the other hand, to monitor *in-situ* the structure organization of the concentrated layer by SAXS [32]. This cell (Fig. 1a) is made of transparent polycarbonate and contains a flat polyethersulfone ultrafiltration membrane (PES 100 kD, PLEIADE®, ORELIS ENVIRONNEMENT, France). Placed above the flat membrane at a distance of 8 mm, this blade is connected to a sonotrode consisting of a piezoelectric transducer attached to a metal rod, which generates ultrasonic waves at a 20 kHz frequency and at an applied amplitude of 1.6 μm (SODEVA TDS, France). The input electric power stretches from 2 to 10 W,