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Impact of protein interactions and transmembrane pressure on physical properties of filter cakes formed during filtrations of skim milk

Tim Steinhauer[a*], Wolfgang Kühnl[a], Ulrich Kulozik[a]

[a] *Chair for Food Process Engineering and Dairy Technology, Technische Universität München, D-85354 Freising-Weihenstephan, Germany*

Abstract

Microfiltration (0.1 µm) was used to fractionate casein ($d_{50,3}$ = 180 nm) micelles from whey proteins (2-6 nm). The casein fraction forms a deposited layer on the membrane surface. Little is known about the structure of these layers and how transmembrane pressure affects their structure. In order to assess the properties, casein micelle deposits were characterized by dead-end microfiltrations. Casein micelle deposits of constant composition were formed following a standardized layer build up (permeate mass, pressure, pH). Then protein free milk serum was filtered through the deposit. Thus, the impact of compressive forces and protein-protein interactions on physical cake properties during constant solid height filtrations could be determined by stepwise variations of transmembrane pressure and pH without further deposition of proteins. It was found that the casein micelle deposits became more compactable, when their surface charge was lower. Specific cake properties were related to hydrophilic repulsion between casein micelles, whereas the influence of electrostatic interactions between micelles was negligible. The observed cake material properties obtained from dead-end filtrations provide valuable insights into deposit layer build-up and structure.

Results obtained for dead-end filtrations were used to describe cross-flow filtrations. For this purpose a new method was developed to assess the specific cake resistances by the evaluation of the kinetic of flux decrease due to deposit layer build-up at the start of filtrations. For the first time it could be shown that deposits consisting of casein micelles during cross-flow filtration were thin layers (1-3 µm), resulting in high specific resistances (up to $20 \cdot 10^{-15}$ m/kg). The specific cake resistance was pressure dependent and increased when the hydrophilic repulsion between casein micelles was reduced at a pH beyond the isoelectric point.

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Keywords: microfiltration; skim milk; colloidal interaction; cake properties; casein micelles

* Corresponding author. Tel.: +49-8161-71-2507; fax: +49-8161-71-4384.
E-mail address: tim.steinhauer@tum.de

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1. Introduction

Fouling is the major drawback in membrane (micro-) filtration of milk and other protein/particle containing solutions. The buildup of a deposit layer not only reduces the permeate throughput due to an additional filtration resistance, but also alters the separation characteristics of the system. Often the deposit layer can be considered as a secondary membrane, which dominates the fractionation process. Therefore, an understanding of the deposit layer structure - filtration performance relationship is a key factor in the optimization of membrane fractionation processes. The decisive properties of the deposit layer concerning filtration resistance and particle retention are layer thickness, porosity and compressibility. Apart from the hydrodynamic conditions in the membrane channel, colloidal substrate-membrane and protein-protein interactions determine the formation and the properties of a deposit layer.

For filtrations of model colloids such as latex spheres mathematical models were developed. The models describe deposit layer thickness and porosity as a function of the drag force of the filtrate flow compressing the filter cake and particle interaction forces. These forces can either be attractive or repulsive depending on the nature of the particles and the environmental conditions [1]. For complex protein solutions, such as milk, the modelling of the deposit layer properties is limited by an incomplete understanding of the colloidal interactions between the deposited proteins.

Milk consists of various protein fractions: casein micelles ($d_{50,3}$ = 180 nm, isoelectric point: pH 4.6) and several whey proteins with different molecular weights (d = 2-6 nm, isoelectric point: pH ~ 5). In an earlier work regarding the pH dependency of milk microfiltration flux during cross-flow filtration [2] we showed that casein micelle interaction in the pH range, where constant micelle sizes are observed (pH 5.9 - 6.8), can be described by a model which incorporates Van der Waals and electrostatic interactions as well as hydrophilic and hydrophobic Lewis Acid Base interactions. In addition to decreased electrostatic repulsion an acidification of milk from pH 6.8 to 5.9 leads to a strong reduction of hydrophilic repulsion between casein micelles while the micelle size remains the same [2]. Less repulsion between casein micelles in turn results in a flux drop. A basic problem in cross-flow filtration is that changes in colloidal interaction e.g. by varying the pH inevitably lead to simultaneous changes in the deposit layer porosity and the deposition probability and, thus, to a different layer composition. Therefore, from cross-flow experiments direct conclusions towards the impact of colloidal interactions on deposit layer porosity and compressibility cannot be drawn.

The aim of this study, therefore, was to investigate the impact of colloidal interactions between casein micelles on the deposit layer compressibility, porosity and specific resistance under dead-end filtration conditions were the layer composition is kept constant. The findings from these dead-end filtrations under experimental conditions were then applied to cross-flow microfiltrations of skim milk. Thus, an overall insight into the deposit layer structure during cross-flow microfiltrations can be derived and used to better understand the process for the fractionation of milk proteins.

2. Materials and Method

For the dead-end filtrations a casein solution was prepared by centrifugation of pasteurised skim milk at 70000 g for 1 hour. The casein micelles accumulated in the pellet and could be redissolved in protein free milk serum (milk ultrafiltration permeat) resulting in a whey protein free casein solution with identical casein concentration and micelle size distribution as was found in the original milk.

For the filtrations an Amicon dead-end filtration cell (AMICON 8050, Millipore, Billerica, USA) was used. Filtration temperature was kept constant at 20 °C during all dead-end-experiments. The filtration procedure consisted of two sequential dead-end filtration steps: At first, a deposit layer was formed by filtering 3 g of the casein solution through a fully retentive 0.025 µm nitrocellulose membrane (Millipore,

Cork, Island) at a transmembrane pressure of 4 bar (first filtration step). Then the filtration fluid was switched to protein free milk serum and the pressure was varied by a digital electronic pressure control unit (AL-PRESS, Bronkhorst, Ruurlo, NL) in the range of 0.08–4 bar (second filtration step). As during the filtration of milk serum no further deposition of casein micelles occurred, variations in deposit layer resistance with transmembrane pressure are only caused by changes in deposit layer porosity. The experiments were carried out at the native pH of milk (pH 6.8), at pH 6.2 and 5.9.

During the filtrations the flux was monitored by a balance. From the slope of the t/V – V relationship during the first filtration step the average specific resistance of the deposit layer α_{av} could be determined using equation (1) [3-5].

$$\frac{t}{V} = \frac{\eta \cdot \alpha_{av} \cdot C_{cas}}{2 \cdot \Delta p_{TM} \cdot A^2} V + \frac{\eta \cdot R_M}{A \cdot \Delta p_{TM}} \tag{1}$$

Here t is the filtration time, V the accumulated permeate volume, η the filtrate viscosity, C_{Cas} the feed casein micelle concentration, Δp_{TM} the transmembrane pressure, A the membrane area and R_M the membrane resistance.

Using equation (2) (Darcy's law) and the permeate volume throughput per membrane area (flux) at the end of the first filtration step the final solid high h of the deposit layer can be calculated.

$$\frac{dV}{dt \cdot A} = \frac{\Delta p_{TM}}{\eta \cdot (R_M + \alpha_{av} \cdot h)} \tag{2}$$

After switching the filtration fluid to milk serum no further casein micelles are deposited. Thus, h is constant during the second filtration step. Therefore, α_{av} can be calculated directly from the flux data as a function of transmembrane pressure. The modified Carman-Cozeny equation (3) for log-normal particle size distributions [6, 7] was used to calculate the mean deposit layer porosity ε_{av}:

$$\alpha_{av} = \frac{2 \cdot \left(\frac{\phi_S}{\phi_V} \right)^2 \cdot (1 - \varepsilon_{av})}{d^2 \cdot \varepsilon_{av}^{\ 4} \cdot e^{\left(4 \cdot \ln^2 \sigma_g\right)}} \tag{3}$$

For this purpose, d is the average geometric diameter of the casein micelle solution, σ_g is the geometric standard deviation and Φ_S/Φ_V is the surface-volume ratio.

For the cross-flow experiments a small-scale filtration rig (SIMA-tec, Hürth, Germany) as described by Piry et al. [9] was used. The initial fouling process in terms of a fouling resistance could not be observed by simply recording the flux after putting on the feed circulation pump because thus the fouling process was overlapped by the pressure build up of the pump. Hence, starting from the previously presented dead-end filtration model [3-7] Furukawa et al. [8] developed a model which allows the calculation of a mean specific fouling resistance during cross-flow filtrations. This method is based on the linearization of the flux decline kinetics in the initial period of cross-flow filtrations due to a deposit layer formation on a clean membrane. The flux decline therefore can be linearized by using equation (4).

$$\frac{1}{\left(J^*\right)^2} \cdot ln \frac{J_0 \cdot \left(J - J^*\right)}{J \cdot \left(J_0 - J^*\right)} + \frac{1}{J^*} \cdot \left(\frac{1}{J} - \frac{1}{J_0} \right) = -\frac{\alpha_{CF} \cdot c_b}{R_M \cdot J_0} \cdot t = a \cdot t \tag{4}$$

To solve eq. (4) the initial flux value (J_0), the steady state flux (J^*), the membrane's resistance (R_M) and the concentration of the deposit layer forming particles (C_b) in the cross-flow bulk phase have to be determined experimentally. Due to the fact that the model of Furukawa et al. [8] is based on the deposit layer build up on a clean membrane an immediate switch from water to milk as filtration fluid would be required. This process is technically not possible because a mixed phase is formed, when two fluids meet. To allow the transfer of this model [8] to cross-flow filtrations of milk, a pressure step procedure was performed. The whole membrane was operated with milk below the critical flux at a transmembrane pressure of $\Delta p_{TM} = 0.22$ bar, and a linear relationship between flux and transmembrane pressure can be found in spite of cake formation [9, 10]. Since the filtration rig has a concentrate valve and a feed bypass valve transmembrane pressure can be regulated in a step function within less than a second while keeping the applied wall shear stress constant. Thus the whole membrane was transferred from membrane controlled state (below critical flux) to deposit layer controlled state (above critical flux). The transfer of the whole membrane across its whole length is essential, since Piry et al. [9] showed, that parts of the membrane at the membrane inlet can be in deposit layer controlled state while part at the membrane outlet remain in membrane controlled state due to the pressure drop along the membrane. The change of the membrane's state was supported by using a short (length: 295 mm) mono-channel (diameter: 6 mm) ceramic microfiltration membrane ($R_M = 1.82 \cdot 10^{12}$ m^{-1}, 0.1 µm, atech innovations GmbH, Gladbeck, Germany).

For the linearization of the initial flux decrease based on equation 4 [8], the total filtration resistance R_{tot} before the pressure step was used instead of the membrane resistance R_M. Starting from the total filtration resistance, the initial flux J_0 was calculated using Darcy's law entering the transmembrane pressure after the pressure step. Thus, the ln-transformation (left side of eq. 4) can be plotted over time (t). From the slope (a) the specific cross-flow fouling resistance (α_{CF}) based on the deposit layer's weight can be derived. Similar to the dead-end experiments a variation of transmembrane pressure results in a variation in the pressure drop through the deposit. Thereby it can be used for an investigation on the pressure dependency of the specific deposit layer resistance during cross-flow filtrations.

All experiments were carried out at a wall shear stress of 100 Pa and a process temperature of 20 ± 0.1 °C and two pH-values (pH 5.9 and 6.8). After each trial the membrane was cleaned in a two step basic/acidic cleaning procedure and conditioned alkali.

3. Discussion

3.1. Dead-end filtrations

Fig. 1 (a) shows the mean specific resistance of the casein micelle deposit layer at pH 6.8, 6.2 and 5.9 as a function of transmembrane pressure. An increase in transmembrane pressure results in higher specific resistances. At low transmembrane pressures ($\Delta p_{TM} < 0.5$ bar) the pressure dependency (slope of the curve) was highest and identical for pH 6.8 and 5.9. At $\Delta p_{TM} > 0.5$ bar the specific resistance at pH 5.9 showed a stronger pressure dependency than the resistance at the native pH of milk.

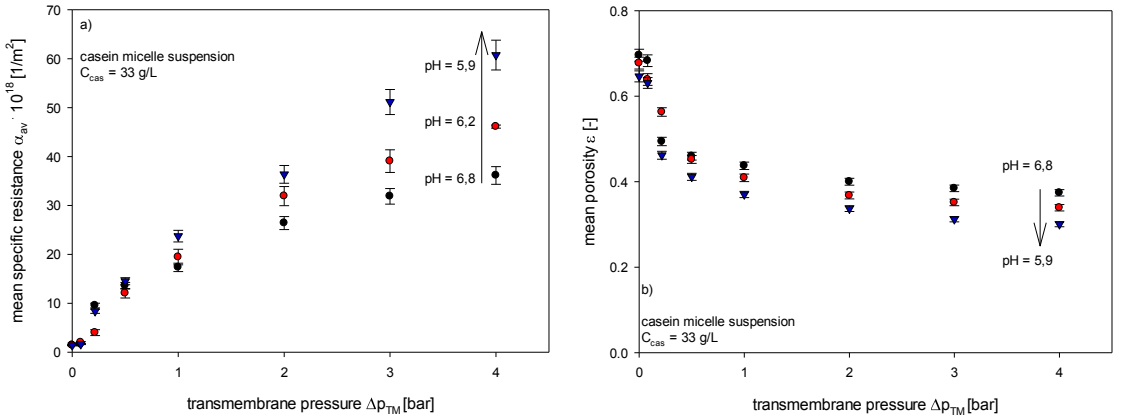

Figure 1. (a) Mean specific resistance α_{av} and; (b) mean porosity ε of a casein micelle deposit layer as a function of transmembrane pressure and pH

From the specific resistance the mean porosity of the deposit layer can be calculated using equation (3). Results are depicted in fig. 1 (b). The porosity values were ~ 0.63 at the lowest pressure (0.08 bar) for both pH values. An increase in transmembrane pressure leaded to a compaction of the deposit layer, resulting in a mean porosity of 0.30 for pH 5.9 and 0.35 for pH 6.8 at Δp_{TM} = 4 bar.

Decreasing the pH from 6.8 to 5.9 leaded to a 50% reduction of the repulsive interaction energy between casein micelles. But repulsive energies are still measurable [2]. Interestingly, the reduction of the repulsive interaction energy does not change the porosity of the deposit layer below a transmembrane pressure of 0.5 bar in spite of the strong pressure dependency of the porosity at low values, see fig. 1 (b).

These results show that casein micelle deposits are highly compressible and that a minimal pressure exists below which the particle separation distance is not significantly reduced when micelle repulsion is decreased. Above the critical pressure a reduction of micelle repulsion increases the compressibility of the deposit layer.

3.2. Cross-flow filtrations

By using the newly modified method for the determination of the mean specific resistance during cross-flow filtrations of milk a study was carried out, which allows an evaluation of the mean specific fouling resistance as a function of pressure and colloidal interactions between casein micelles in the deposit. Due to the extremely fast flux decline, when milk was used as a filtration fluid, milk was diluted by protein free milk serum (10 kDa UF-permeate).

The speed of the deposit formation could thus be reduced. As shown in fig. 2, a dilution did not lead to a significant change in deposit build up and thus resulted in an equivalent specific fouling resistance. A dilution of 1:5 (milk: UF-permeate) gave the required speed reduction for gaining a sufficient amount of data points (>>10) for the ln-linearization (4). Hence, this concentration was used for all experiments to keep the casein concentration as close to the native concentration as possible. Fig. 2 shows, that an increase in the pressure drop through the deposit layer increased the mean specific resistance for the filtration of milk at native pH 6.8 as well as for a lower pH 5.9. During filtrations at reduced pH, the pressure dependency was significantly higher. For a better visualization, trend lines based on e-functions are used in the diagram.

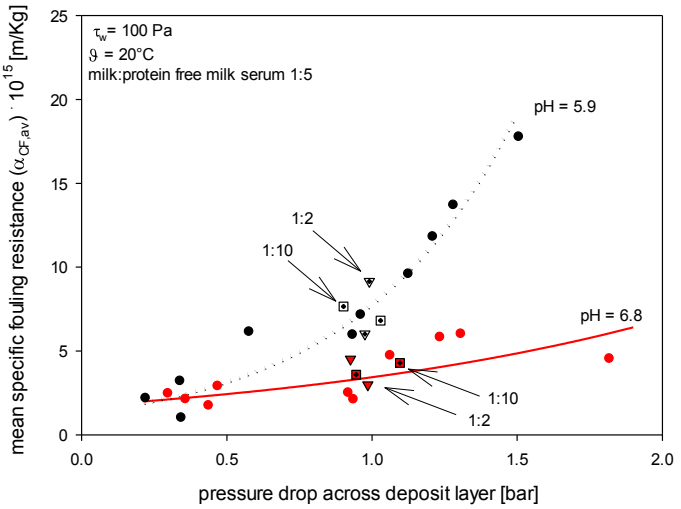

Figure 2. Mean specific fouling resistance α_{CF} during cross-flow microfiltration of diluted skim milk as a function of the pressure drop through deposit layer (20°C)

For cross-flow filtrations a pressure increase not solely leads to a compression of the deposit, but also to an altered composition of the deposit layer. Steps towards higher transmembrane pressures resulted in increased initial flux values (J_0). Thus the particle size cut-off shifted to larger particle diameters due to the increased convective transport. Increased transmembrane pressures, therefore, resulted in deposits of higher polydispersity. This should result in a reduced specific fouling resistance for a constant porosity with regard to equation (3). Since small micelles can move through cavities in the deposit, certain cavities can be filled up by small casein micelles. As a consequence the porosity decreases and the mean specific resistance increases [11].

The porosity impacts equation (3) reciprocal by the fourth power. Hence, pressure dependency of the mean specific resistance during cross-flow filtrations is very likely due to a change in the polydispersity of the casein micelle deposit. This effect must be enhanced by a compaction of the micelle deposit as similarly found during model dead-end filtrations.

An acidification of milk and, thus, reduction of the repulsion between casein micelles must lead to an increase in compressibility similar to the results for the dead-end filtration of pure casein solution. Additionally, a reduced repulsion between casein micelles facilitates their deposition. Thus, the polydispersity of the deposition increases due to the higher probability of deposition and the deposit becomes more compact for higher transmembrane pressures.

4. Conclusions

During dead-end microfiltrations of pure casein solutions highly compactable deposits were formed. The compressibility of the deposit strongly depended on the hydrophilic repulsion between the deposited casein micelles. At reduced repulsion for pH-values closer to the casein's isoelectric point the compressibility is most pronounced. In addition a critical transmembrane pressure of $\Delta p_{TM} = 0.5$ was found below which the compressibility increases strongly for all pH-values.

For cross-flow filtrations of skim milk a specific fouling resistance based on the deposit weight was determined and investigated with regard to its dependency on transmembrane pressure and colloidal

interactions between casein micelles. The mean specific resistance during cross-flow filtrations was found to be strongly dependent on transmembrane pressure. This pressure dependency is due to a change in the polydispersity of the casein micelle deposit. Similar to the findings for dead-end microfiltrations, the pressure dependency of the specific resistance was increased at reduced repulsion between the casein micelles (pH 5.9).

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