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Temperature dependent membrane fouling during filtration of whey and whey proteins

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ABSTRACT

Ultra- and microfiltrations are industrially applied for the concentration and fractionation of whey proteins. Thereby, either high (~50 °C) or low (<10 °C) processing temperatures can be selected to avoid microbial spoilage of the product. Filtration performance at the two temperature ranges was found to be significantly different. For this reason, this study focusses on the impact of temperature on membrane fouling during both ultra- and microfiltration of whey and whey protein suspensions. We found significantly different deposit layer structures at the two pore sizes investigated. During microfiltration (full whey protein permeation), membrane fouling due to adsorption processes was facilitated at temperatures ≤10 °C and >35 °C. For filtrations with fully retentive ultrafiltration membranes, an increase in processing temperature resulted in a decrease of specific fouling resistance, while deposit layer solid height increased. In cross-flow mode, fouling resistance was independent of temperature during acid whey microfiltration. A temperature increase during filtration of sweet whey resulted in a sharp increase of membrane fouling for temperatures above 40 °C. When increasing temperature, the stronger fouling reaction in neutral pH-range could be attributed to both, the acceleration of thiol/disulfide reaction speed and calcium based protein cross-linking.

1. Introduction

Ultrafiltration (UF) processes are applied for the concentration of whey, a byproduct of cheese making. By microfiltration (MF) of milk, casein micelles can be separated from whey proteins in native state in order to obtain a casein-free milk serum (also referred to as "ideal whey") [1–4]. Furthermore, by the MF of whey, a fractionation of native whey proteins and denatured whey protein aggregates can be carried out [5–9]. Membrane fractionation processes of whey and whey proteins are usually carried out at temperatures <15 °C or ≥50 °C in order to avoid microbial spoilage due to the thermophilic or mesophilic milk bacteria and cheese culture present in whey [10,11]. A disadvantage of a processing temperature ≥50 °C is the survival of thermoduric spoilage bacteria [11]. Independently from processing temperature it is generally agreed that whey proteins in general and, in particular the major whey protein β-lactoglobulin (β-Lg), are the main foulants during whey filtration processes [9,12–14]. In addition to whey proteins, some authors suppose that protein cross-linking by the formation of calcium-bridges or calcium phosphate precipitation are involved in membrane fouling [12,15–19].

Despite the fact that many studies deal with membrane fouling during the filtration of whey and whey proteins at different temperatures, within the majority of the studies only one temperature was investigated. For the minor whey protein bovine Serum Albumin (BSA) with low heat stability it is known that by a temperature increase, protein adsorption increases for pH above pI and that adsorption is not affected at pH below pI [20]. BSA denaturation leads to an impairment of operation and an enhancement of membrane fouling [21]. The membrane fouling mechanism for the major whey protein β-lactoglobulin (β-Lg) as a function of temperature was not described yet. For the complex substrate whey only two studies exist, dealing with the impact of temperature on whey filtration performance. Barukčić et al. [22] used ceramic multichannel membranes with pore sizes of 0.1, 0.5 and 0.8 μm at temperatures of 20, 40 and 50 °C for sweet whey microfiltration. The highest flux level observed was at a filtration temperature of 50 °C for all pore sizes investigated. Since fouling resistance, calcium permeation and whey protein permeation were given for only one of the two temperatures investigated, no further conclusions on the impact of temperature on deposit layer structures were drawn from the results presented. Muthukumaran et al. [23] studied the impact of temperature on sweet whey ultrafiltration flux and found a slight increase of flux (~5%)

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over a temperature range of 10–55 °C. They concluded that flux increase was due to viscosity decrease for higher temperatures. Taking into account the results presented by Barukčić et al. [22] according to which sweet whey permeate viscosity halved during a temperature increase of 20–50 °C, the conclusion drawn by Muthukumaran et al. [23] does not seem to be justified. Instead, it appears to be more meaningful that fouling resistance must have increased tremendously by temperature increase, which can be demonstrated by applying Eq. (1) using the data reported by both groups.

Temperature (ϑ) on the one hand affects filtration fluid viscosity. As can be derived from Eq. (1), flux (J) is inversely related to permeate viscosity (η). Hence, high filtration temperatures that are accompanied with low permeate viscosities are favorable for filtration performance. On the other hand, both particle morphology and properties have an impact on deposit layer structure and, thus, on deposit layer resistance [24,25]. One reason, accompanied with an alteration of particle morphology and properties, is thermally induced protein (un-)folding [26,27]. Hence, temperature has an indirect impact on deposit layer structure [28]. Dense deposit layer structures arise if either repulsive forces are low [29] or attractive van-der-Waals forces increase due to thermally induced exposure of the hydrophobic protein core to the environment [30,31]. In case of an increase in protein hydrophobicity, protein adsorption to solid surfaces, like membranes, is enhanced [30–32].

The above described background clearly shows that there is hardly any knowledge on the impact of processing temperature on the arising deposit layer structures and the mechanism of deposit layer formation gained by systematic investigation. In consequence, knowledge on the impact of processing temperature on membrane fouling during filtration of whey and whey proteins is strongly limited. Therefore, this study focusses on the impact of temperature on whey filtration performance and the related fouling resistance.

For this reason, in a first step the impact of temperature on microfiltration membrane fouling of highly purified β-Lg suspensions suspended in protein free milk serum (PFMS) was investigated at a lab-scale in dead-end mode. In a second step, the approach was transferred to the temperature dependent filtration of native sweet and acid whey in a lab scale cross-flow unit. The comparison of dead-end versus crossflow mode should shed light on the deposit layer structure as affected by flow conditions.

2. Experimental

2.1. Preparation of β-lactoglobulin suspensions and whey protein isolate suspensions

According to a method published by Toro-Sierra et al. [33], β-Lg was isolated from whey protein isolate (WPI 895, Fonterra, New Zealand, Lot. No. CT 08). Thus, highly purified β-Lg (> 98% native protein content) powder was obtained. Stock solutions were prepared by dissolving 2.5 g of WPI powder or 2.5 g of β-Lg powder in 97.5 g of protein-free milk serum (PFMS). PFMS was produced from raw skim milk using UF (MWCO 10 kDa, GR81PE 6338/30, DSS Silkeborg AS, Silkeborg, Denmark, Material: PES). Filtrations for PFMS production were carried out at 10 °C to avoid calcium phosphate precipitation [34]. Stock solutions were preserved from microbial spoilage using 0.02% (w/w) sodium azide (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and a storage temperature of 4 °C. Additionally, samples were pre-filtered for the removal of insoluble particles (0.2 μm, Merck KGaA, Darmstadt, Germany). After pre-filtration, suspensions were adjusted to a total whey protein concentration of 2.2% (w/w) based on quantitative RP-HPLC analysis as described by Voswinkel and Kulozik [35]. For thermodynamic equilibration, samples were prepared one week prior to filtration.

Table 1
Mean composition of sweet and acid whey (± represents standard deviation of mean data from duplicate experiments).

	Content [% w/w]	
Ingredient	**Sweet whey**[a]	**Acid whey**[a]
Protein	0.54 ± 0.02	0.59 ± 0.01
Lactose	3.40 ± 0.09	4.0 ± 0.08
Lactate	0.04 ± 0.00	0.9 ± 0.01
Calcium	0.03 ± 0.00	0.1 ± 0.09

[a] Values as originally presented by Steinhauer et al. [9] for similar whey types.

2.2. Sweet whey and acid whey

Raw sweet whey from Edam cheese production with pH 6.4–6.5 as well as separated acid whey from cottage cheese production with pH 4.5 were obtained from local dairies. Remaining cheese curd in the whey was removed using a disc separator (z=8000 g; GEA Westfalia Separator Group GmbH, Oelde, Germany). A detailed composition of the whey types is given in Table 1, as also reported earlier by Steinhauer et al. [9].

2.3. Filtration rigs and membranes

For lab-scale filtrations of isolated β-Lg suspensions and WPI suspensions, a dead-end rig (AMICON 8050, Merck-Millipore, Billerica, USA) was used and equipped with MF membrane discs (Pall Supor PES, nominal pore size: 0.1 μm, Pall Corporation, Port Washington, USA) or with UF membranes fully retentive to whey proteins (Pall Omega PES, MWCO 30 kDa, Pall Corporation, Port Washington, USA). Transmembrane pressure was adjusted to $0.2 \cdot 10^5$ Pa during MF and $4.0 \cdot 10^5$ Pa during UF by a pressure control unit (AL-PRESS, Bronkhorst, Ruurlo, NL). For pressurization nitrogen gas was used.

For temperature regulation, the dead-end cell was connected to a water bath by a flexible insulated silicon hose. The temperature was kept constant during filtration, the precision of temperature regulation was ± 0.5 °C.

For a separate evaluation of both overlapping effects of temperature, i.e. viscosity change and deposit structure related deposit resistance (R_c) on flux, the Shirato–Darcy equation (Eq. (1)) can be used

$$J = \frac{TMP}{\eta(\vartheta) \cdot (R_{Mem} + R_c(\vartheta))} \tag{1}$$

with transmembrane pressure TMP, membrane resistance R_{Mem} and temperature dependent fouling resistance R_c.

For dead-end filtrations, with known amount of particles deposited on the membrane per permeate volume, a specific fouling resistance (α_{av}) can be derived. Fouling resistance and specific fouling resistance are interconnected by deposit layer solid height (w) as follows:

$$R_c = \int_0^w \alpha_{av}(\vartheta) \cdot dw. \tag{2}$$

This specific fouling resistance allows a characterization of membrane fouling independently from filtration time.

For determination of the specific fouling resistance α_{av} based on cumulated permeate volume V_{cum}, an established linearization