

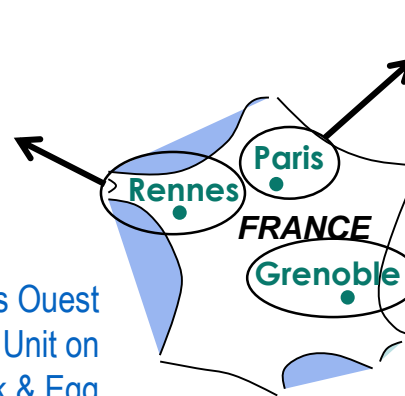
Structural organization of casein micelles concentrated layer during cross-flow ultrafiltration

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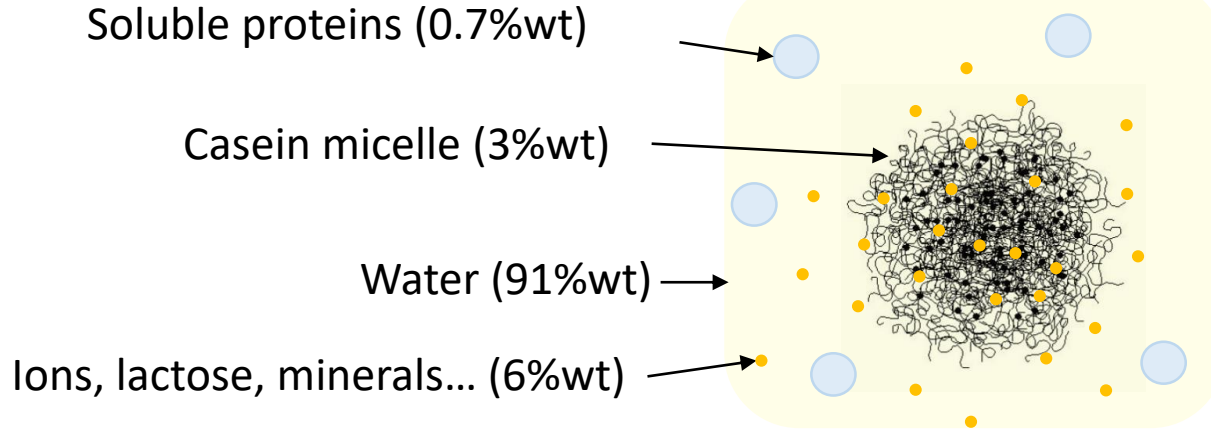
Laboratoire Rhéologie et Procédés



15 to 17 October 2018

Milk filtration

Skimmed milk:



Casein micelles are large globular aggregates of caseins with calcium phosphate, they are porous, deformable, compressible and dynamic particles (50-500nm)

Skimmed milk contains 26 g/L of casein micelles or 3%wt

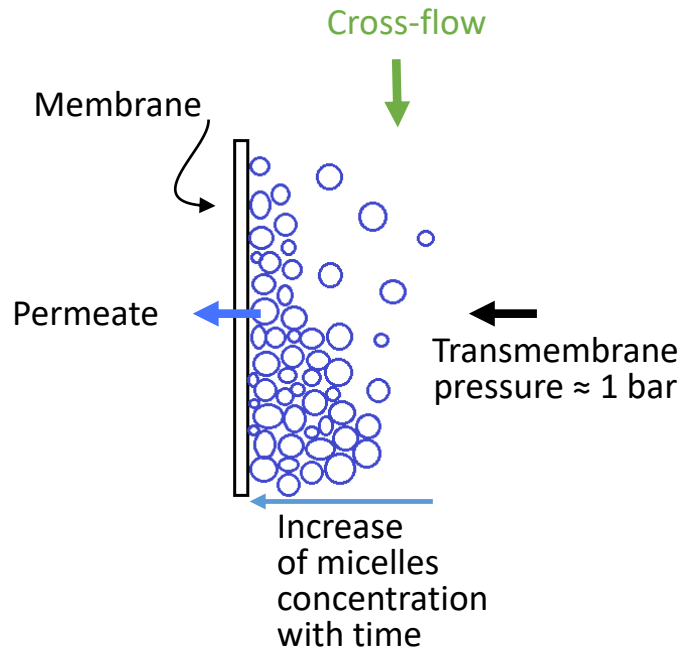
Micro- and ultrafiltration of skimmed milk are largely used in the dairy sector (≈ 40% of the membrane area installed in food sector)

ultrafiltration → proteins concentration (cheese manufacture, standardization)

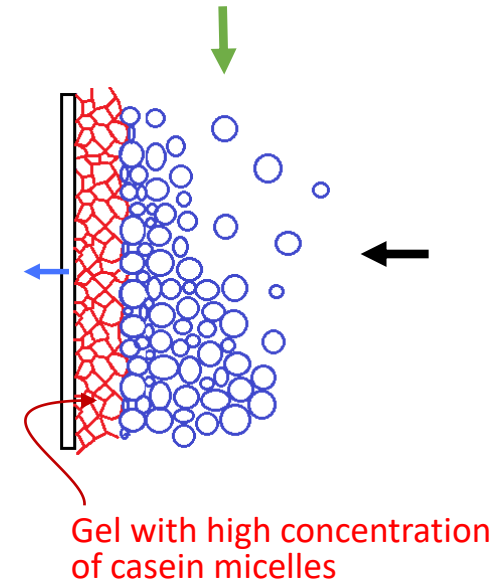
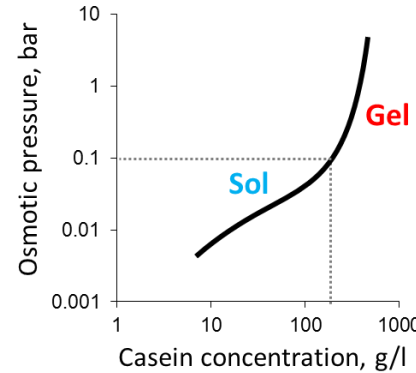
microfiltration → proteins fractionation (high added value ingredients)



Membrane fouling by casein micelles



Bouchoux et al., Biophys. J., 2009



Formation of fouling gel layer:

- limitation of the filtration performance

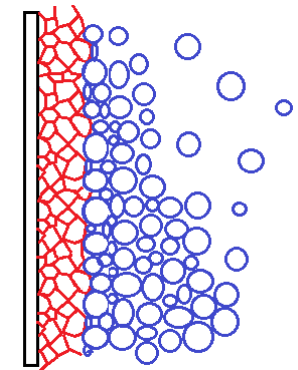
reduces permeate flux, decreases permeate quality (low transmission of soluble proteins)

- difficulties of cleaning operation

large consumption of water, detergents and energy...

Understand the structural organization and behaviour of concentrated casein micelles accumulated at the membrane surface during cross-flow ultrafiltration

- Analyse fouling layer development during filtration step and redispersion during pressure relaxation step
- Focus on the effect of temperature (12-45°C)



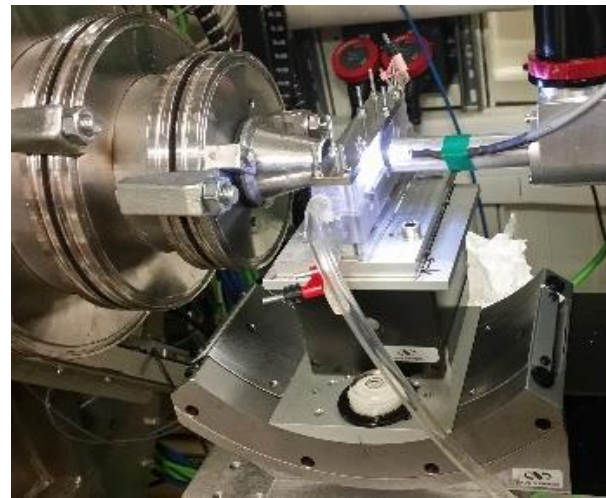
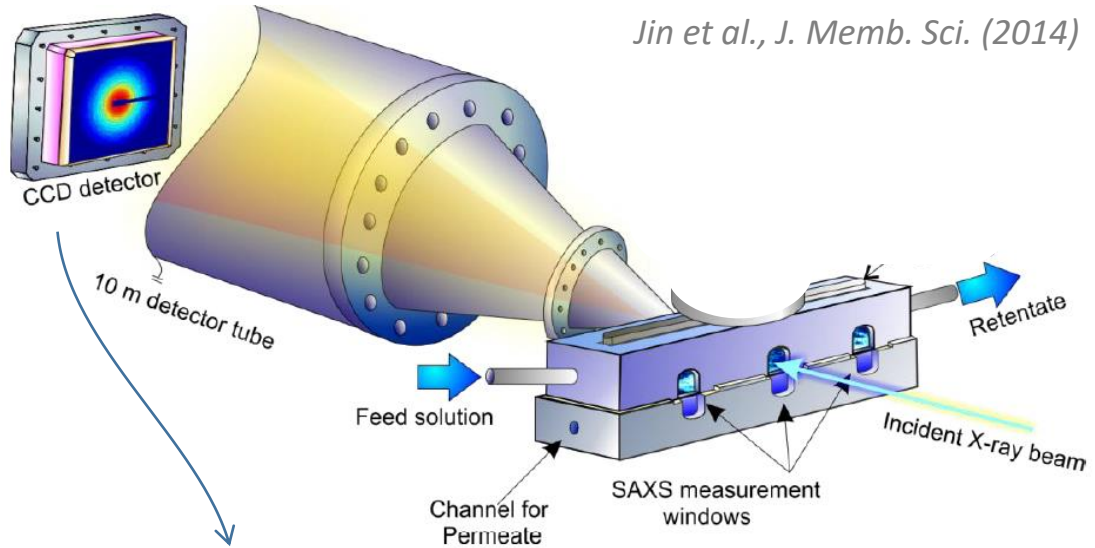
Organic spiral membranes
8-12°C



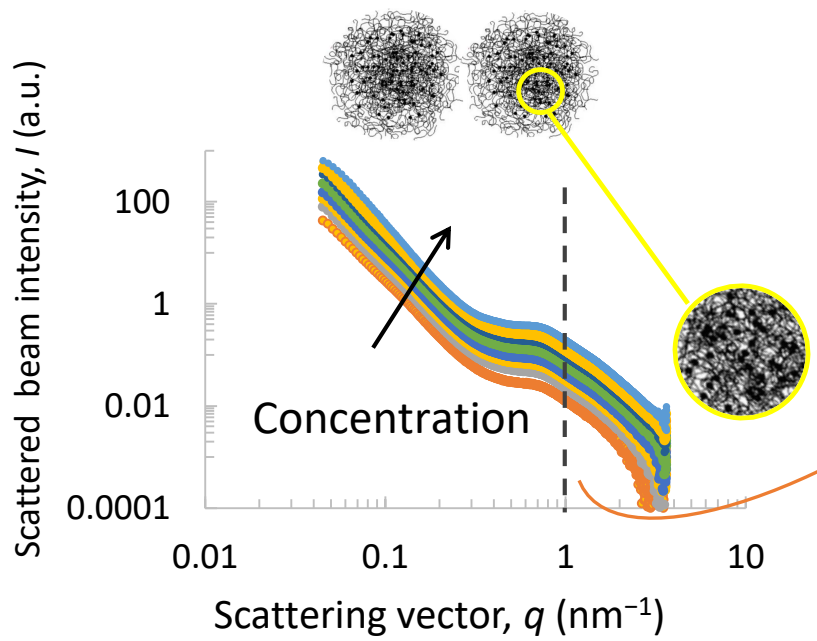
Mineral membranes
50-53°C

In-situ SAXS cross-flow filtration

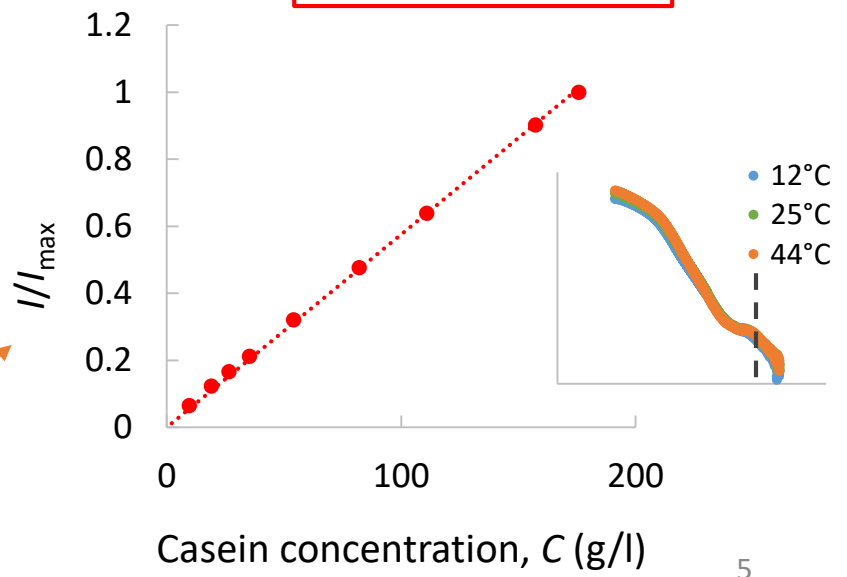
Jin et al., J. Memb. Sci. (2014)



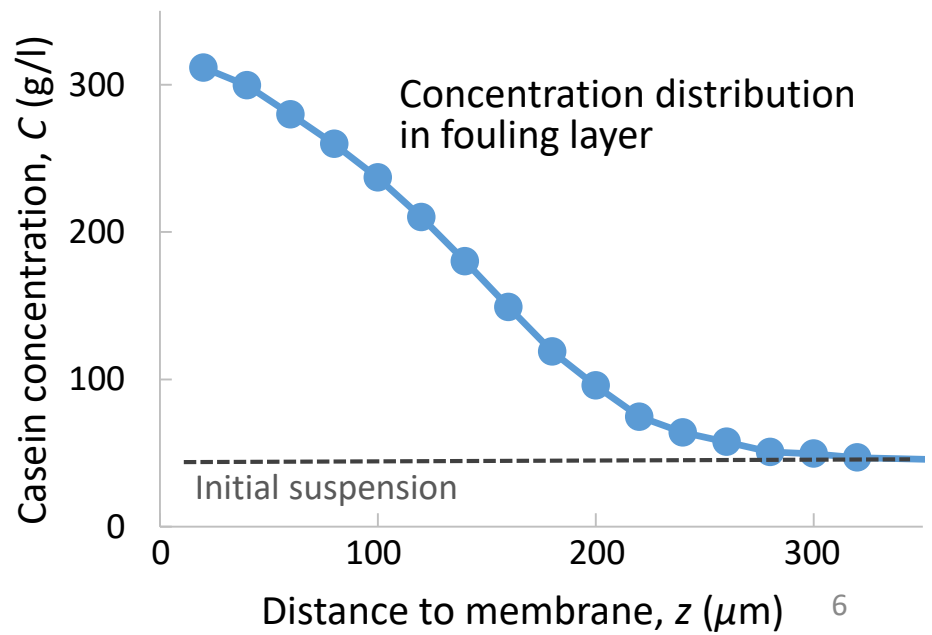
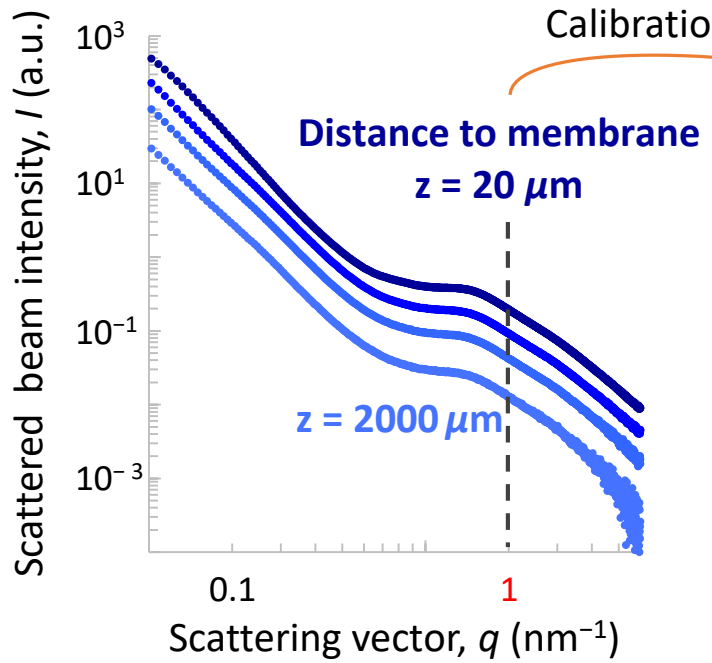
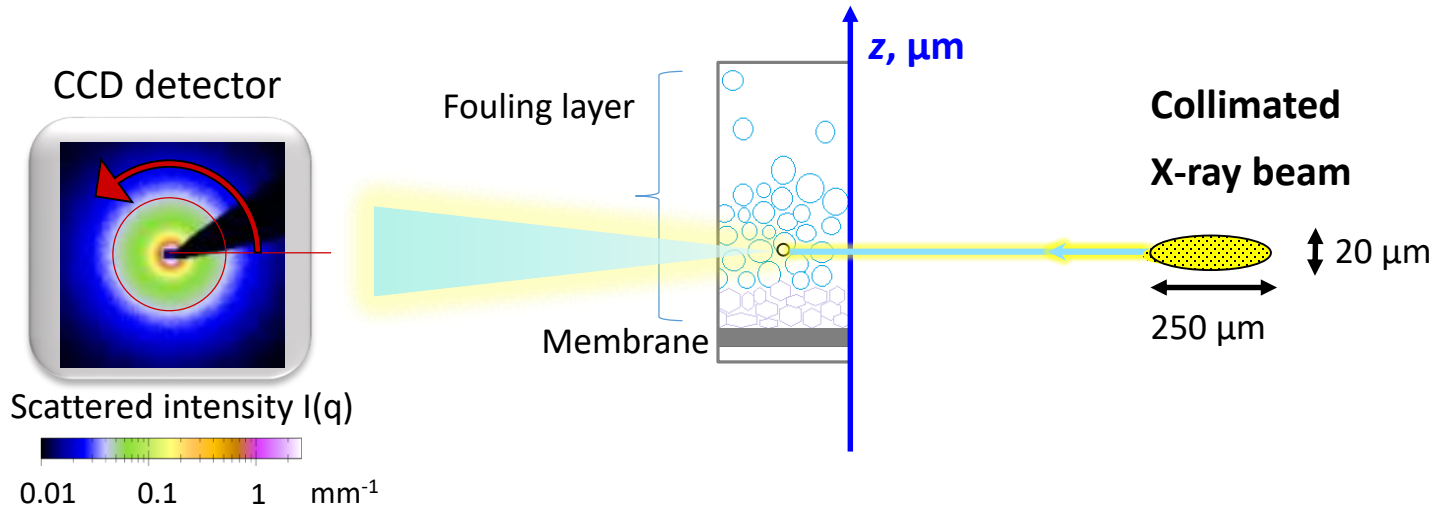
Typical SAXS «spectra» of casein micelles suspension



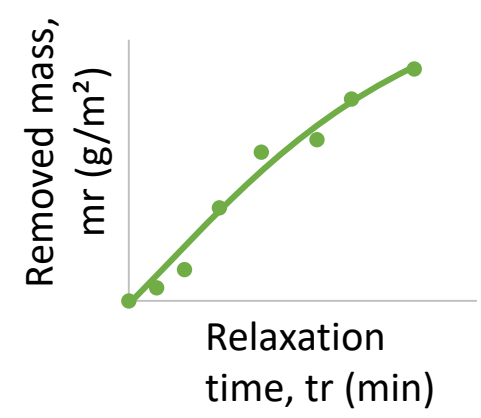
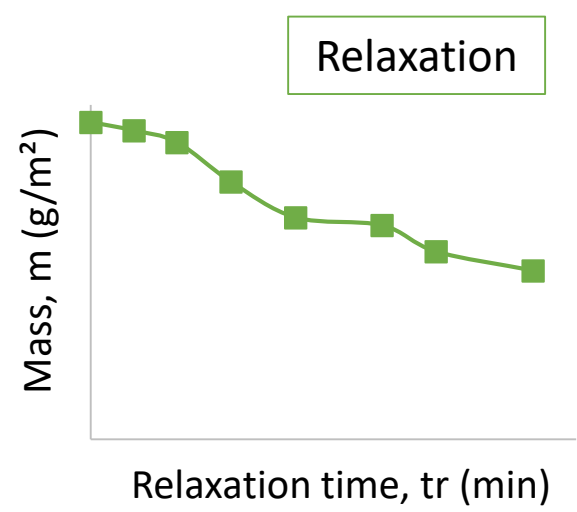
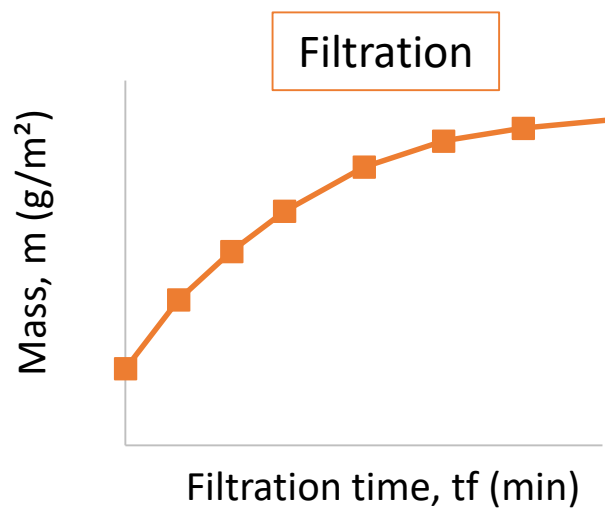
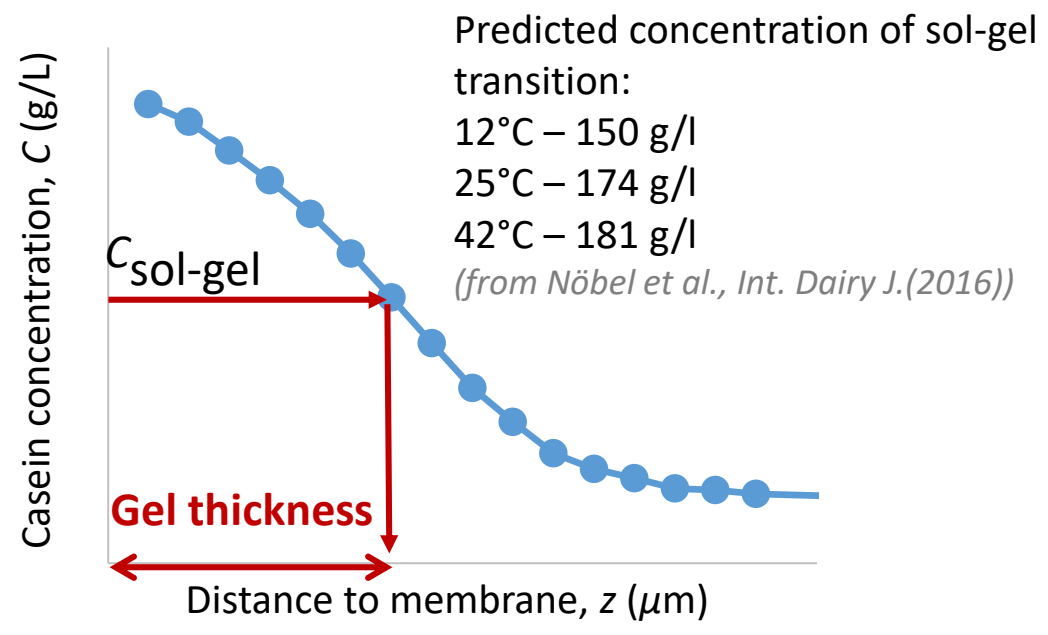
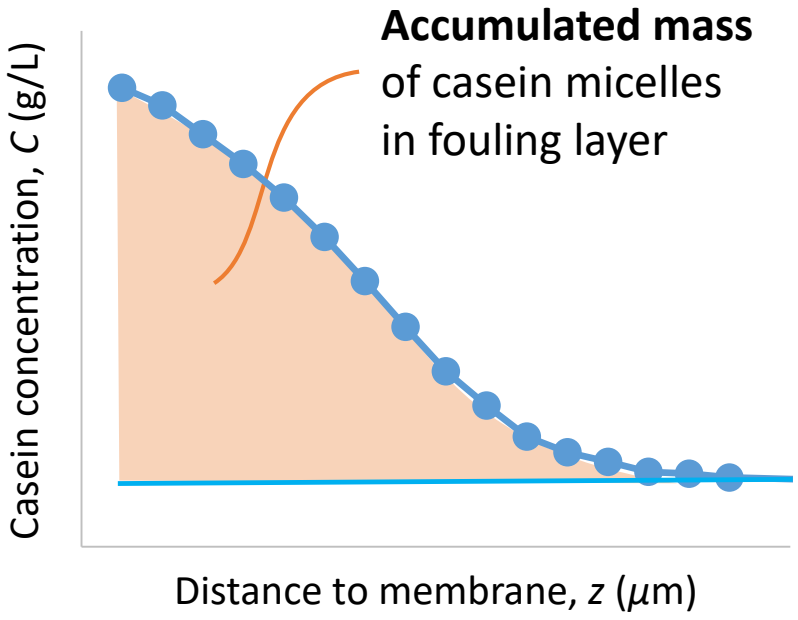
Calibration curve



SAXS analysis of fouling layer



Quantification of fouling layer



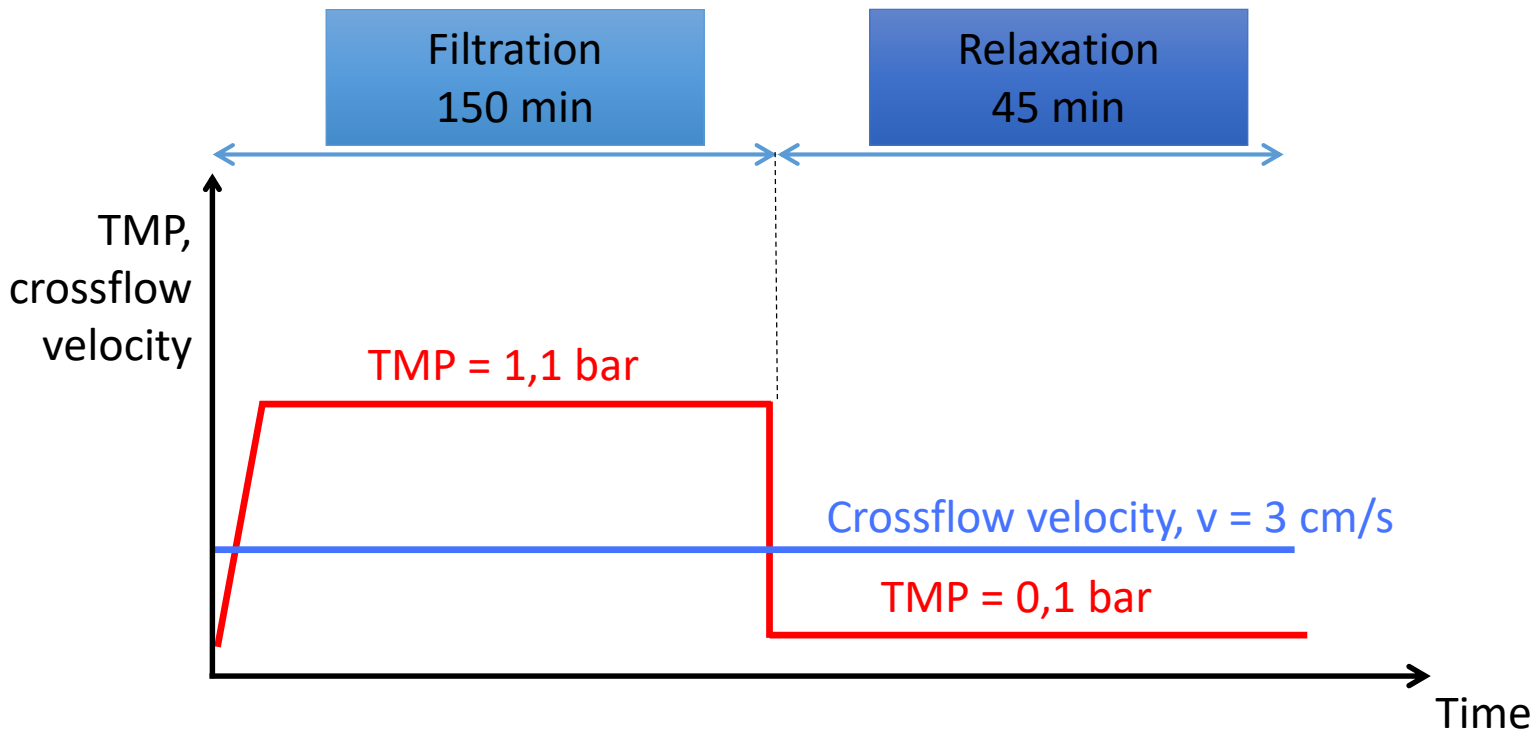
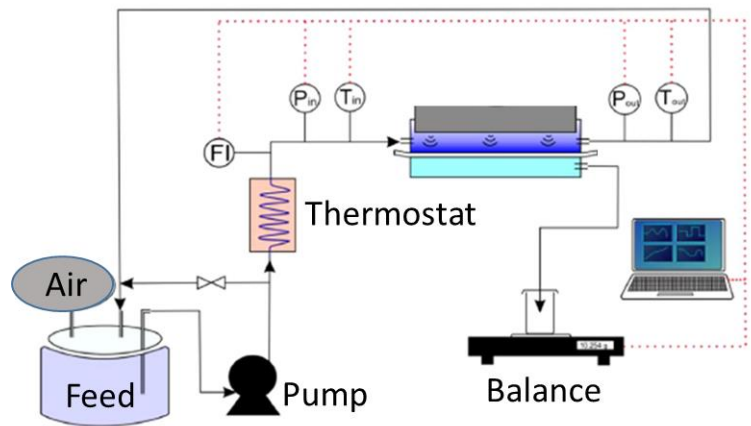
Filtration protocol

Suspension: 50 g/L of casein micelles in milk ultrafiltrate

Membrane: Polyethersulfone 100 kDa (Orelis, France)

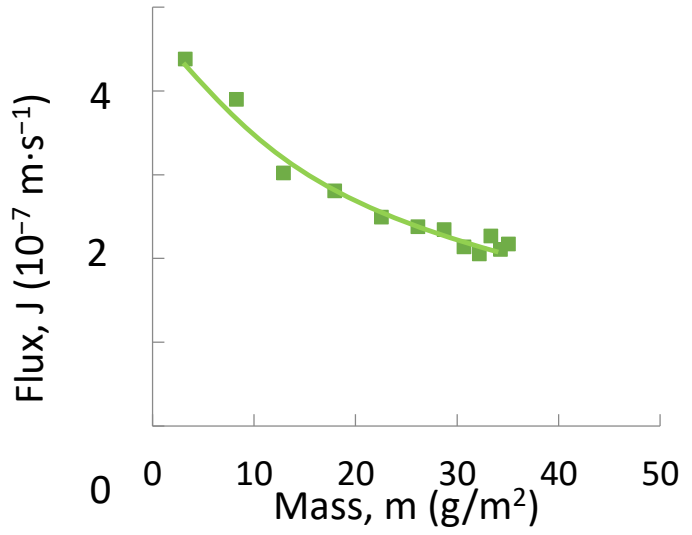
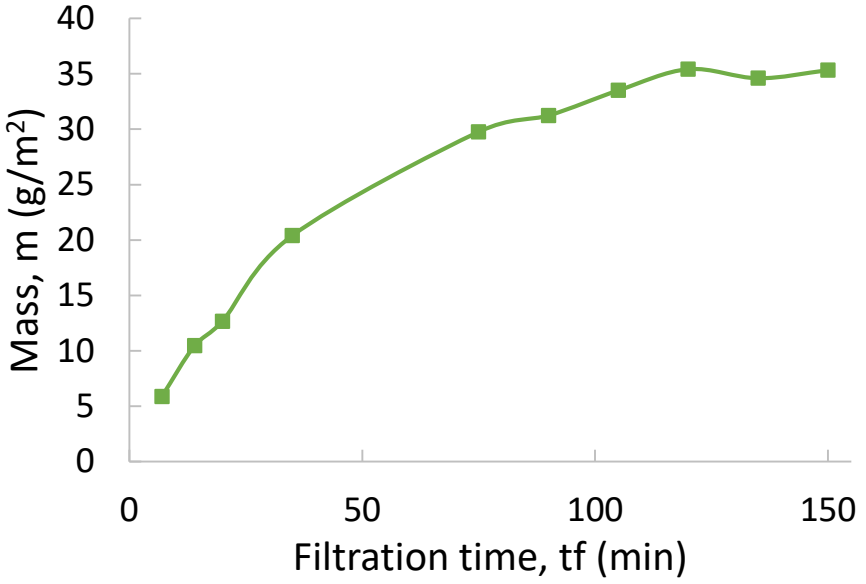
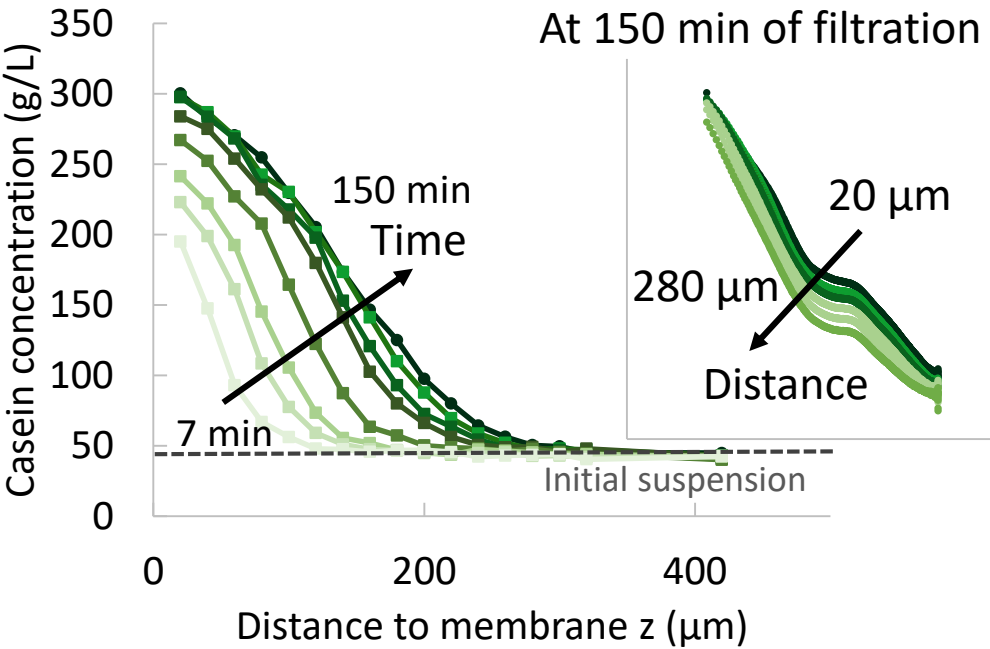
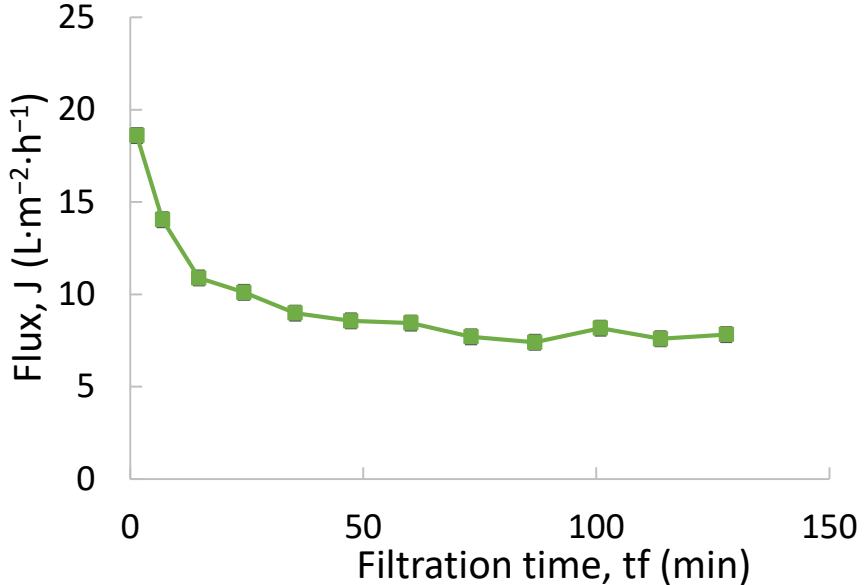
Filtration cycle: 2 steps

Temperature: 12, 25 or 42°C



Filtration kinetics

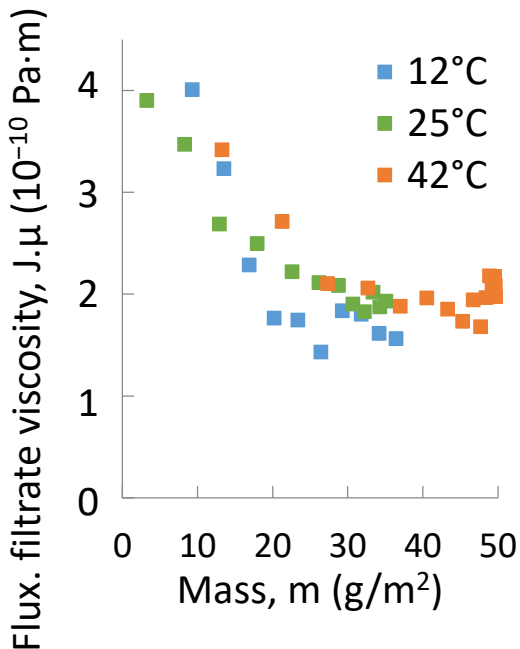
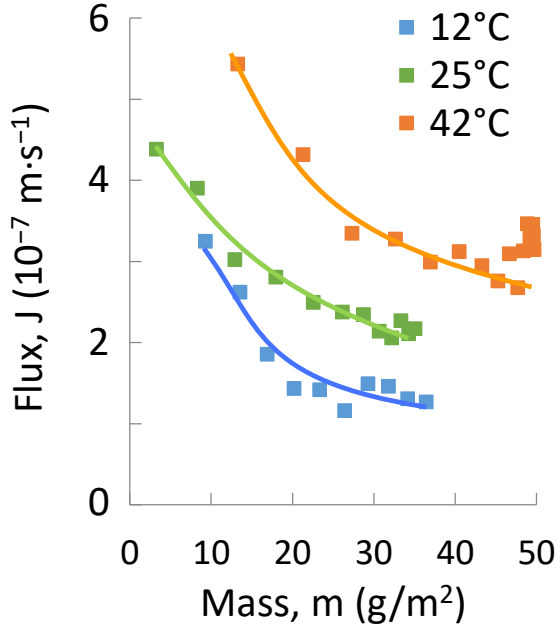
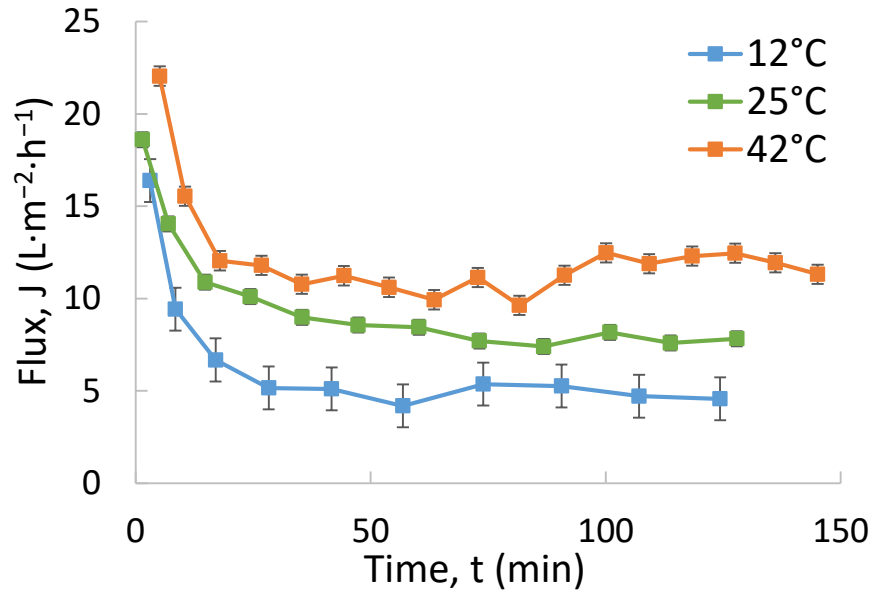
25°C
 TMP = 1.1 bar
 v = 3cm/s



Flux decrease over time linked to casein micelles accumulation

Impact of temperature on filtration kinetics

TMP = 1.1 bar
v = 3cm/s



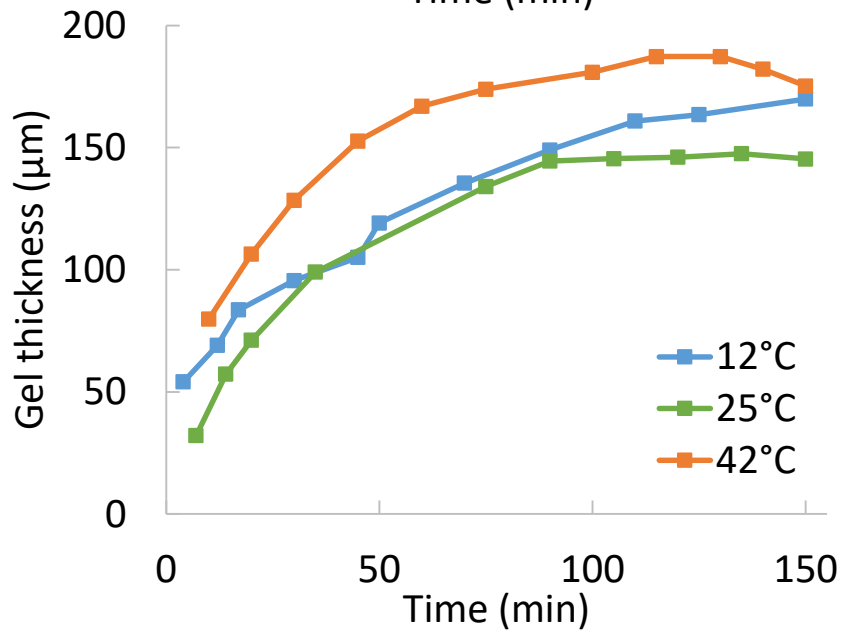
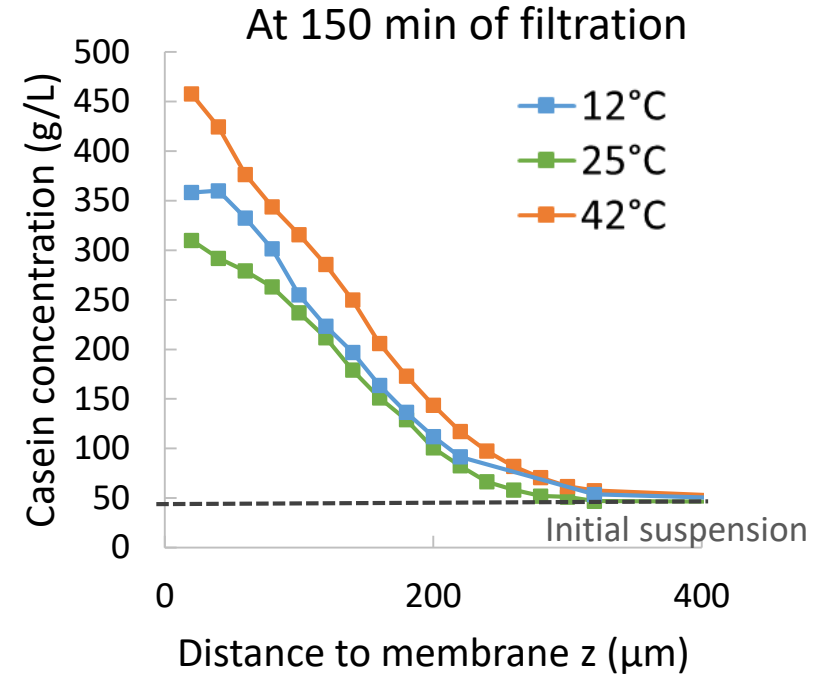
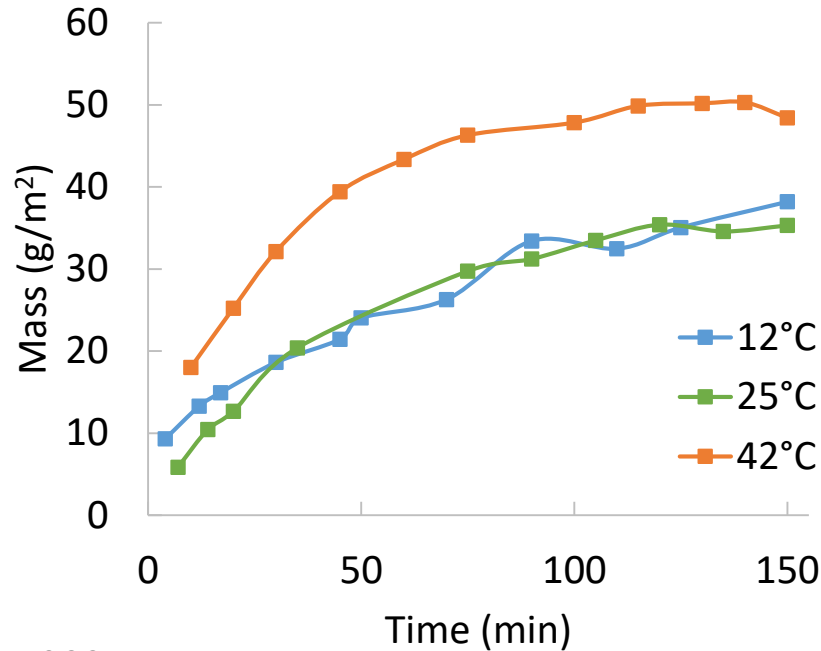
Darcy's law:

$$J \times \mu = \frac{TMP}{R_m + R_f}$$

Flux is higher under higher temperature due to a lower filtrate viscosity

Impact of temperature on casein micelles accumulation

$TMP = 1.1 \text{ bar}$
 $v = 3 \text{ cm/s}$



At 42°C, accumulation is faster and more pronounced: gel is more concentrated and thicker than at 12 or 25°C

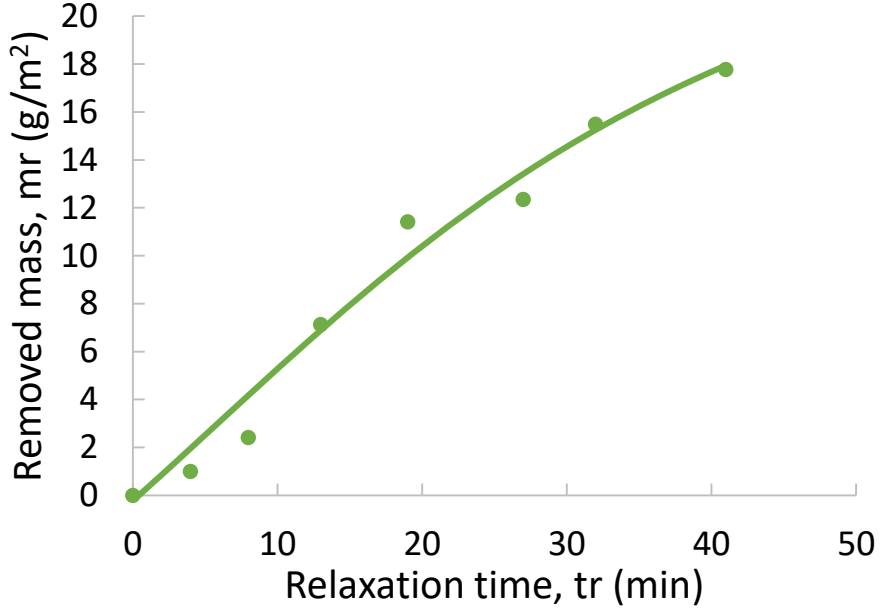
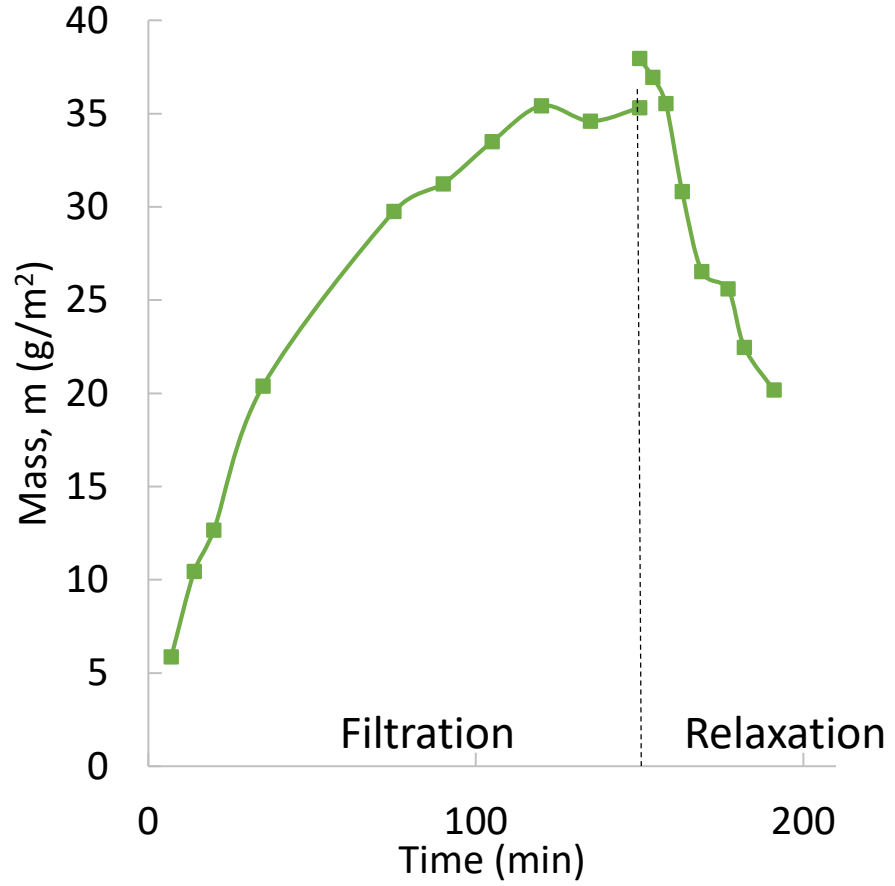
Temperature impacts filtration performances:

At 42°C:

- Flux is high
- Because of a lower filtrate viscosity
- And a high accumulation of casein micelles
- Concentration of casein micelles at membrane surface is high
- Gel thickness is high

Pressure relaxation

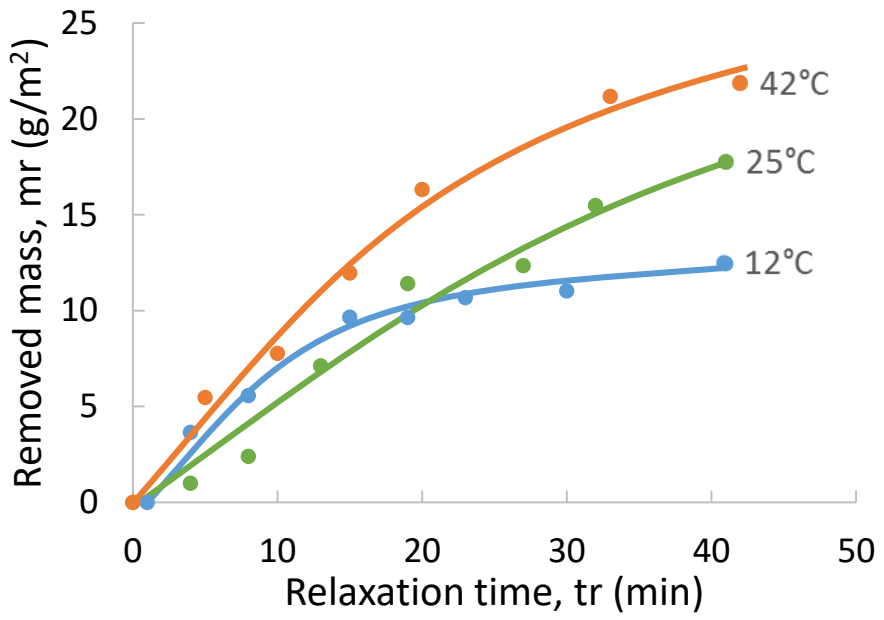
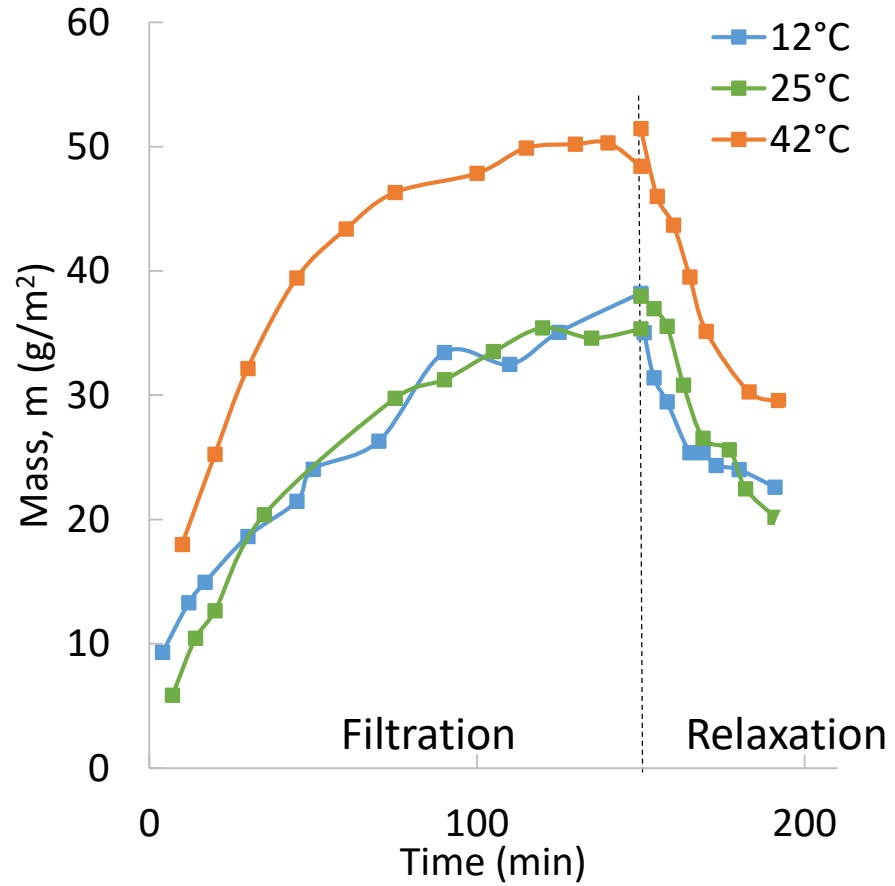
25°C
TMP = 0.1 bar
 $v = 3\text{cm/s}$



Relaxation step allows to remove a part of accumulated casein micelles without using chemical products
But, relaxation time is same order of magnitude with accumulation time

Impact of temperature on pressure relaxation

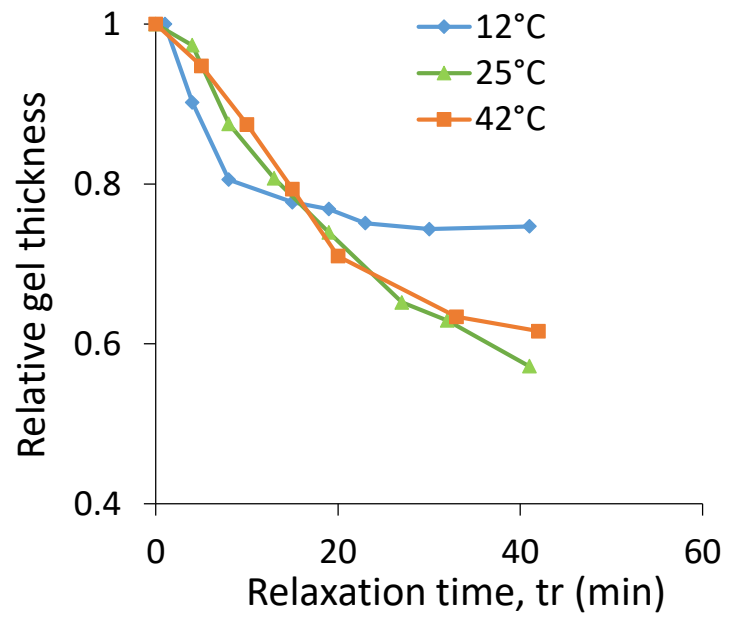
TMP = 0.1 bar
 $v = 3\text{cm/s}$



Removed mass rises with temperature:
likely due to the lower viscosity of accumulated casein micelles layers at high temperature

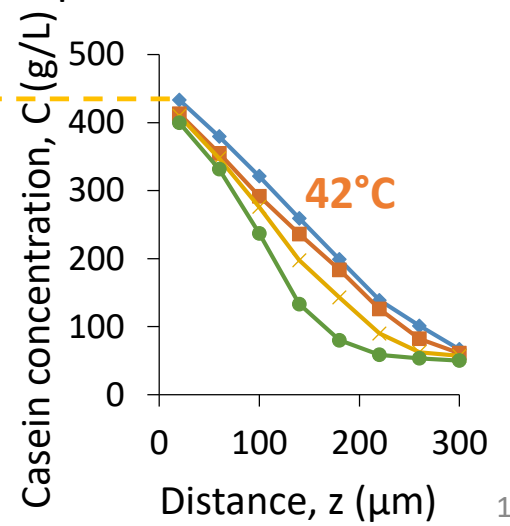
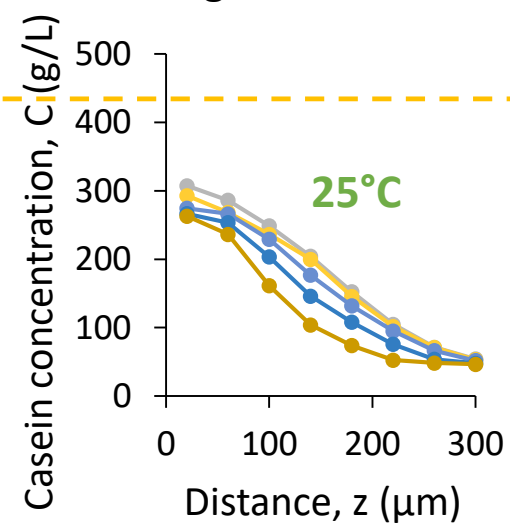
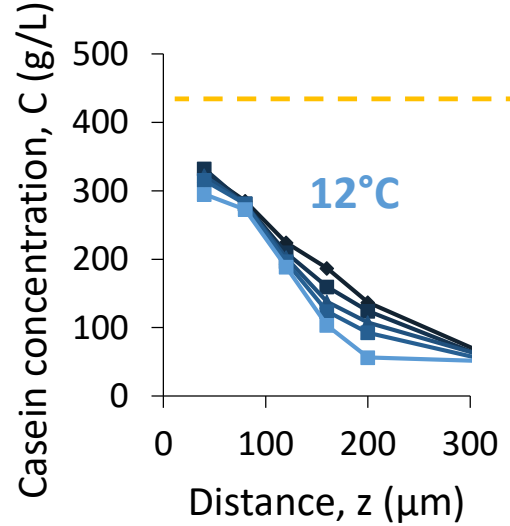
Impact of temperature on gel relaxation

TMP = 0.1 bar
 $v = 3\text{cm/s}$



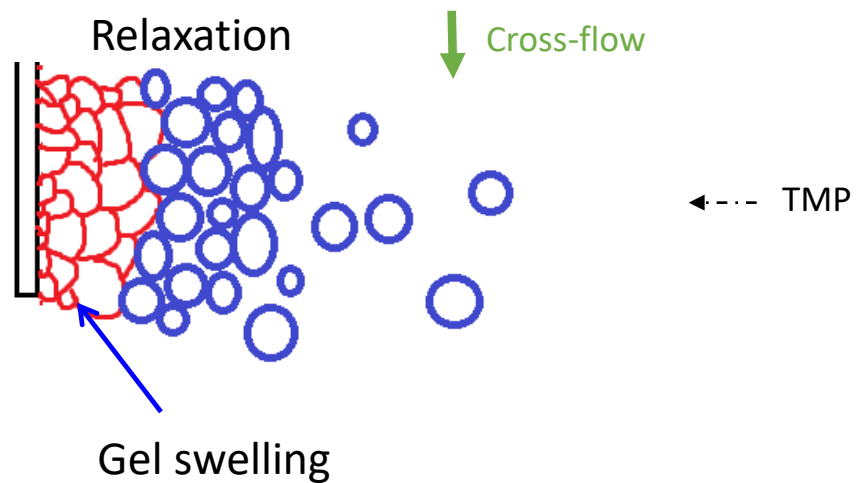
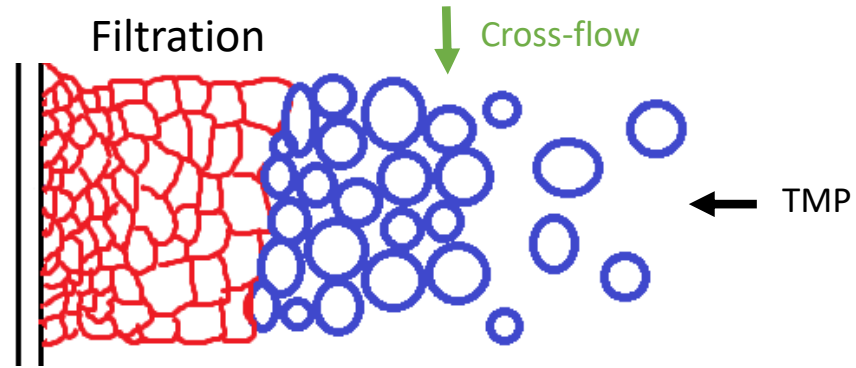
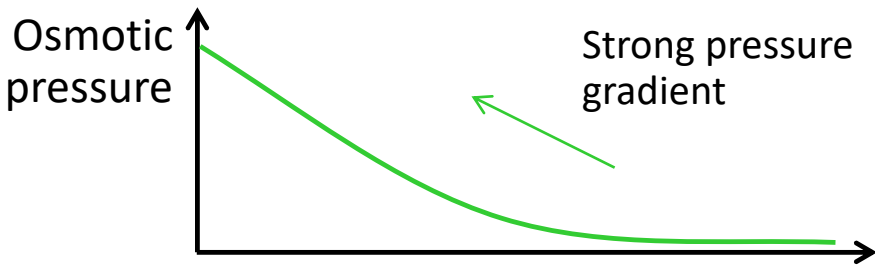
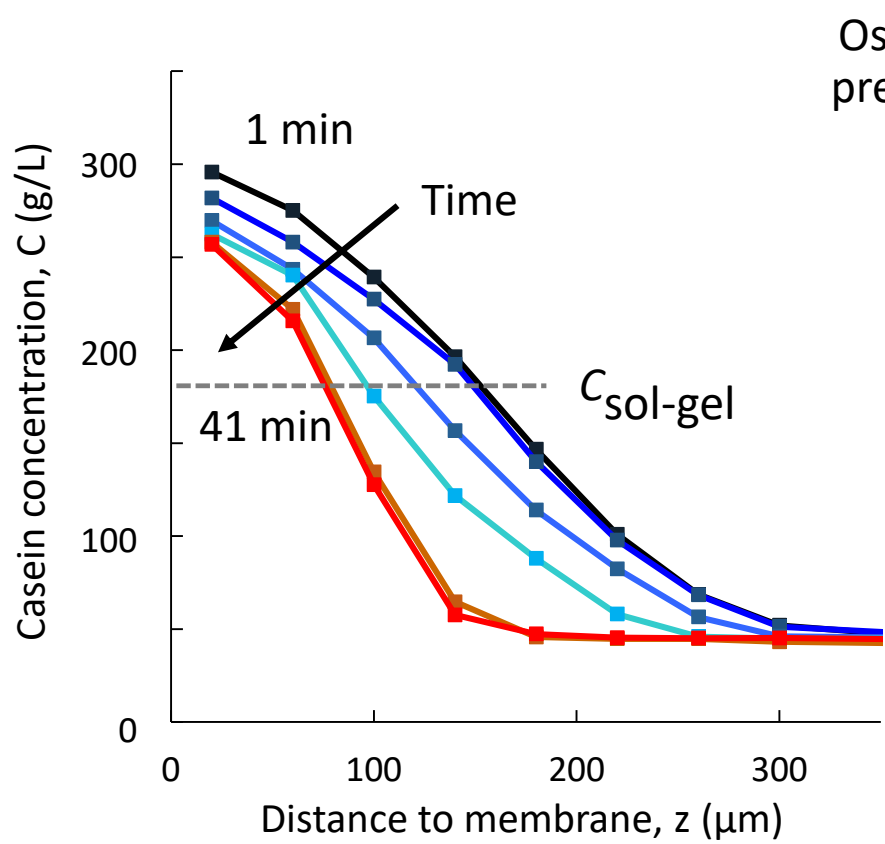
At 12 °C, gel removal seems limited even if the concentration is not the higher
Gel is more cohesive at 12°C

Concentration profiles during relaxation at different temperatures



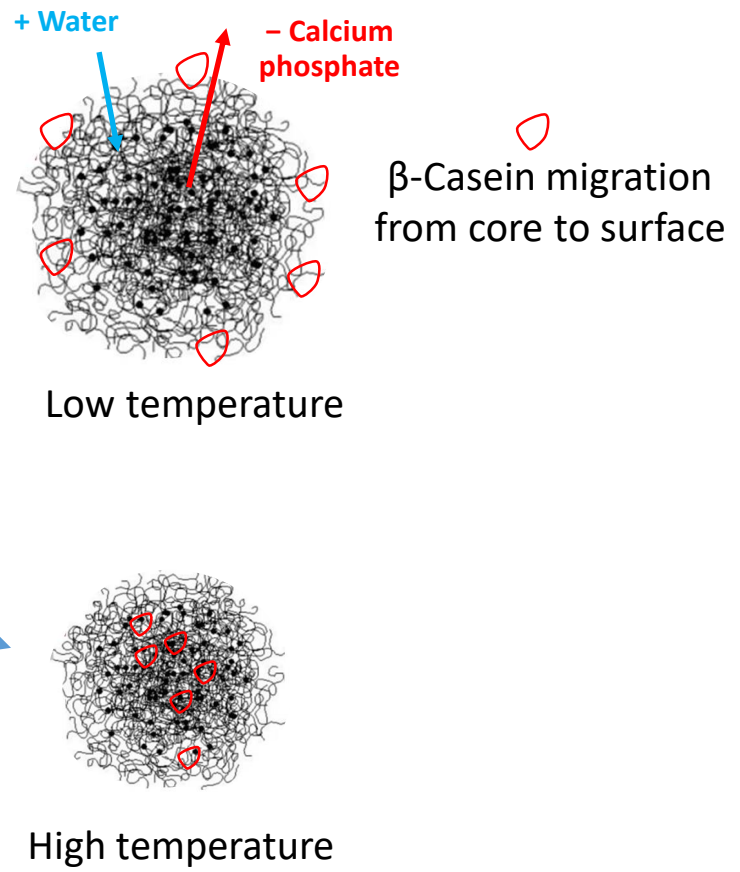
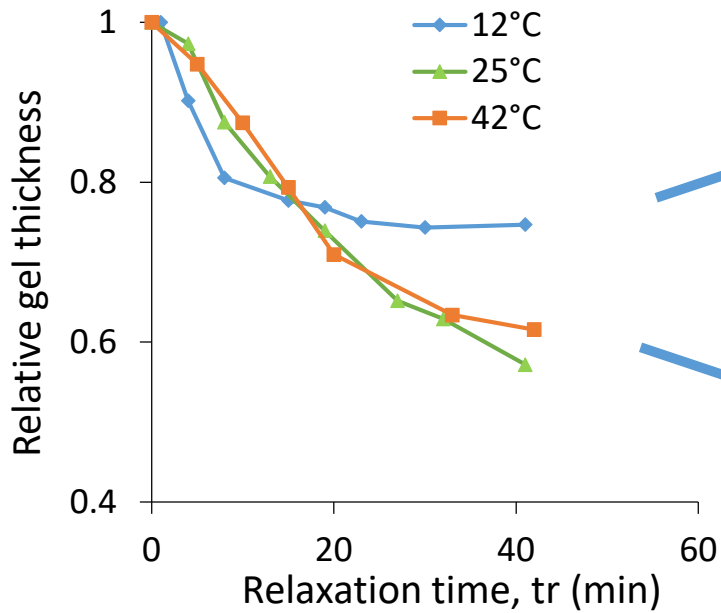
Pressure relaxation: gel swelling

25°C
 TMP = 0.1 bar
 v = 3cm/s



Accumulation of casein micelles is removed via gel swelling and re-dispersion of swelled part

Pressure relaxation: impact of temperature

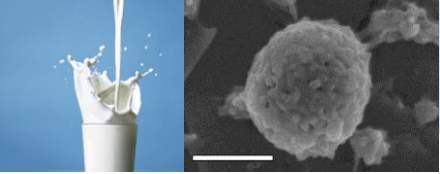


Cohesion of gel (repulsive gel or attractive gel) depends on temperature

- In-situ SAXS cross-flow filtration allowed analysis of casein micelles fouling layer with an unique resolution of 20 μ m during filtration step and relaxation step
- During filtration of casein micelles, temperature has a significative effect on filtration performances:
 - Increasing temperature implies:
 - flux decrease because filtrate viscosity decrease
 - casein micelles accumulation at membrane surface
 - But during pressure relaxation, an easily removal of casein micelles and a gel that is less cohesive

Future work:

- 1) rheological characterization of gels at different temperatures
- 2) local strength force of fouling layer at different temperatures



Thank you for your attention!



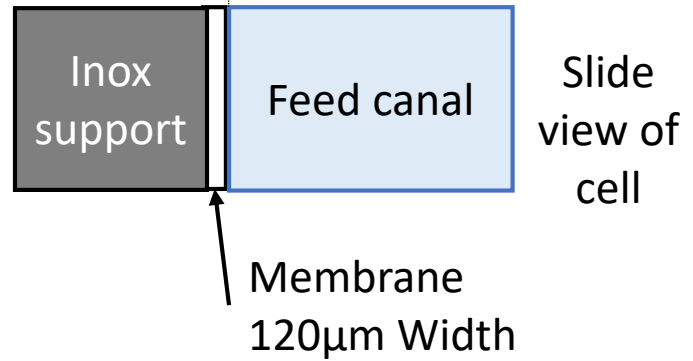
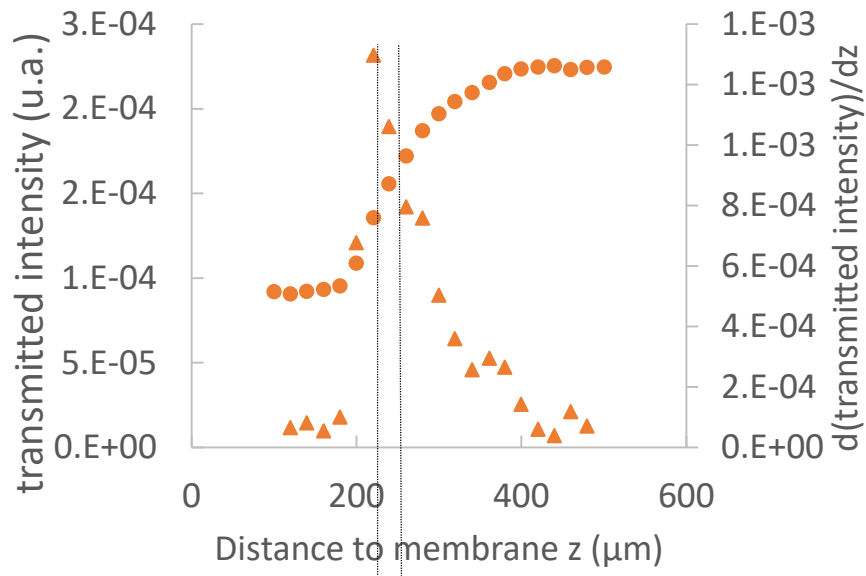
Laboratoire Rhéologie
et Procédés

Mohamed KARROUCH



Michael Sztucki

1) Zero membrane placement



2) Calibration in static

