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Experimental study of flux decline mechanisms in skim milk ultrafiltration

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Abstract

In this study, the flux decline during milk ultrafiltration was studied experimentally. Experiments were conducted for both milk and dextran to allow a comparison between foulant and non-foulant solutes. We measured concentrations in permeate during milk ultrafiltration experiments. Results show that considering dextran as non-foulant is an overstatement. The irregular shape of dextran makes it more difficult to clean compared to the spherical shape of milk micelle. The size of the micelles prevents them to enter the pores and to diffuse in the bulk feed, in this way the cake formation is favorized comparing to other fouling mechanism. Hermia models were used in a linear form to confirm the dominance of cake formation mechanism for milk fouling. Nevertheless, the close values of correlation factors suggest that cake formation mechanism depends on whey protein concentrations. It seems dominant for milk at 10 g/L but not for 5 g/L. Higher whey protein concentrations have stimulated the caking by increasing the compaction on the membrane.

Introduction

Since few decades, filtration membrane technologies are developed extensively. Microfiltration, ultrafiltration and reverse osmosis systems are largely used for many purposes such as desalination, water treatment and dairy industries. These systems are fairly attractive due to their facile use and low coast. Tangential ultrafiltration is used in dairy industry for transformation of raw milk into raffinate products as cheese, yogurt or skim milk (Leu et al., 2017; Luo et al., 2016; Méthot-Hains et al., 2016; Ng et al., 2018).

Dextran, comprising a family of neutral polysaccharides consisting of an α-(1→6) linked d-glucose main chain with varying proportions of linkages and branches, depending on the bacteria used, is an interesting starting material for chemical modification reactions for the design of new functional polymers with promising properties (Heinze et al., 2006). The dextran is currently employed for membrane characterisation (Zydney & Xenopoulos, 2007). Considering that it does not interact with most of the ultrafiltration membranes, it is generally used for control quality tests. Dextran does not produce fouling in appropriate conditions; local flux variations and system pressures influence it (René & Lalande, 1991; Zydney & Xenopoulos, 2007).

Since milk proteins are very different in size, it is plainly possible to separate them with size exclusion (Ng et al., 2017). Milk is composed of water, fat, proteins, lactose and salt (Aouanouk et al., 2017). Otherwise, a small amount of pigments, enzymes, vitamins and phospholipids can be found within the milk. There are two categories of milk proteins: caseins and the whey proteins (Ng et al., 2017). By ultrafiltration process, whey proteins are easier to extract from milk, by ultrafiltration, than caseins. Caseins form micelles (an aggregation of 10 to 100 times larger than original protein) and calcium present in milk contributes to bond these micelles to each other (Aouanouk et al., 2018).

However, the weak point of ultrafiltration in dairy production is that permeate flux decline over time that induces the necessity to replace the membrane. The loss of efficiency during ultrafiltration is due to concentration polarization and fouling. The molecules excluded by the membrane cannot return in the bulk feed because of their slow diffusivity thereby they accumulate at the surface and create an important concentration gradient involving a decrease in the permeate flow (Shi et al., 2014). In this manner, both feed flow and mass transfer influence the concentration profile (Field, 2010).

Fouling is initiated by the deposition of proteins and minerals, at the membrane surface. Casein micelles form a reversible fouling layer. However, whey proteins such as β-lactoglobulin and α-lactalbumin are adsorbed irreversibly at the membrane surface (Hanemaaijer et al., 1989; James et al., 2003; Marshall & Daufin, 1996; Tong et al., 1988). Fouling could occur in 4 forms: adsorption, pore blocking, deposition and gel/cake formation as represented in Fig. 1. These mechanisms are modeled in previous studies (Aryanti et al., 2016; Hermia, 1982).

Nowadays, many works were reported in this field but fouling mechanism and effect of many parameters such as proteins and minerals concentration are not completely understood. Hence, it is necessary to have a finer and accurate knowledge of this phenomenon in order to optimize milk ultrafiltration processes.

This work is an experimental contribution to enhance the understanding of the fouling phenomenon during milk ultrafiltration. A lab-scale ultrafiltration system is employed at constant temperature and transmembrane pressure and experiments are performed for both dextran and milk to allow a comparison between foulant and non-foulant solutes. The studied parameters are flux filtration and its protein concentration over time. Also, evolution of membrane resistance will be discussed. Finally, Hermia's model will be used to evaluate the dominant fouling mechanism.

Materials And Methods

Membrane

A Micro Kerasep KERMBMU1 ceramic membrane from Novasep was used for experiments. The membrane is alloyed by TiO_2, Al_2O_3 and ZrO_2. The active surface is 80 cm² and the manufacturer has identified that there is no affinity with dextran or milk proteins. The membrane characteristics are presented in Table 1.

Table 1
Membrane characteristics

MWCO (kDa)	pH	Temperature (°C°)	Pressure (bar)
15	1–14	0–85	1–4.4

Experimental design

The laboratory-scale filtration system used for experiments is a food ultrafiltration unit (UFA/1000). It is composed by a tank of 8L and an eccentric rotor pump PCM MOINEAU model M750C4 as shown in Fig. 2. Two manometers are placed at the inlet and the outlet of the membrane in order to determine the mean pressure of the membrane.

Three solutions were used as process feed for experiments: water with 5 g / L of dextran DT40 and skim milk containing respectively, 5 g / L and 10 g / L of whey protein. Operating parameters are 21°C for temperature and 2.7 bar for TMP. Note that a cleaning protocol was adopted before and after each experiment in order to minimize residual deposits.

A spectrophotometer was used for whey proteins dosage in permeate. The device is a Secocam UviLine 9400. The spectrophotometer was calibrated at 280 nm for the whey proteins dosage. Then, a standard slope of OD versus solution concentration was performed for each protein assay.

Fouling model

As previously discussed, four fouling mechanisms can appear in milk ultrafiltration. Hermia (1982) proposed mathematical models to describe these mechanisms, based on the following equation where *n* and *k* are constants, *V* the filtrate volume and *t* time.

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \qquad (1)$$

Each fouling mechanism is described by Eq. (1) with a particular value of n. Table 2 summarizes these models (Hermia, 1982; Nita, 2016) where J_0 is initial permeat flux and t the time filtration. K_c, K_i, K_p and K_f are constants of complete pore blocking, intermediate blocking, pore constriction and cake formation models, respectively.

In this way, the equation which will match better with the experimental data of flux as a function of time will indicate the dominant fouling mechanism during the experiment.

Table 2
Linearized fouling mechanisms models

Fouling mechanism	n	model	
Complete pore blocking	2	$\ln(J) = \ln(J_0) - K_c\, t$	(2)
Intermediate blocking	1	$\frac{J_0}{J} = 1 + K_i\, J_0\, t$	(3)
Pore constriction	1.5	$\sqrt{\frac{J_0}{J}} = 1 + \frac{K_p\, J_0\, t}{2}$	(4)
Cake formation	0	$\left(\frac{J_0}{J}\right)^2 = 1 + 2\, K_f\, J_0^2\, t$	(5)

Results And Discussion

The obtained results are presented in the following sections. Note that each experimental data is the average of at least three different measurements.

Irreversible fouling

The relationship between permeate flux, J, and transmembrane pressure, TMP, can be written as in Eq. (6) where R is the resistance.

$$J = \frac{TMP}{R} \qquad (6)$$

Only membrane resistance, R_m, is involved in the case of solvent (water) filtration. In the presence of solute, the resistance becomes $R = R_m + R_f$ where R_f is the additional resistance due to deposits which could be divided into reversible and irreversible resistance.

Figure 3 shows the variation of water flux vs. TMP for DT40 at 5g/L and milk at 5g/L and 10g/L respectively before (water filtration) and after ultrafiltration.

For DT40, the resistance of the membrane increased by 12.62%, which shows that an irreversible fouling occurred. Since there is no interaction between dextran and the ceramic membrane, the most probable assumption is that Dextran fouled partially or entirely the pores of the membrane. This is supported by the fact that dextran has a great capacity for solubilisation, a lack of ability to form gel and no chemical interaction with the membrane (McCurdy *et al.*, 1994).For milk at 5 g/L whey proteins concentration, the resistance of membrane increased by 7.6% (5% less than dextran) which was not expected. Since dextran is supposed to be non-foulant, it should be less strong than milk. This result can be explained by the size

of caseins micelles which are approximately twice of that dextran. Then, casein micelles don't penetrate pores of the membrane in contrast of dextran. Likewise, the particle size has a concrete effect. Dextran is a polymer with plenty of ramifications while micelles are more spherical (BeMiller, 2003). Then, dextran has a highest probability of narrowing pores.

All curves can be fitted linearly and slope of each straight line present the total resistance of the membrane. Therefore, it is possible to deduce the resistance due to fouling for each solute as shown in Fig. 4. Data provided from this figure are represented in Table 3.

As for experiments conducted at 10 g/L of milk (Fig. 3 (c)), the slope is more considerable than above ones which generates a higher resistance (Fig. 4). This result confirms that concentration is a key factor in the fouling mechanism.

Table 3
Membrane resistance before and after filtration

	R (m^{-1})		
	Before	**After**	**Variation (%)**
5 g/L DT40	8.62×10^5	9.71×10^5	12.62
5 g/L Milk	9.71×10^5	10.4×10^5	7.63
10 g/L Milk	10.4×10^5	15×10^5	43.91

Flux decline and protein concentration

Figure (5) shows permeate flux variation over time for Dextran DT40 and milk at concentrations of 5 g/L and 10 g/L with TPM = 2.7 bar. First, it shows that the permeate flux of milk is clearly much lower than that of dextran. This could be related to the milk viscosity which is higher than that of dextran. The viscosity of Dextran is approximately equal to that of water.

Then, it seems that the flux reduction for dextran is negligible compared to that of milk. Over 40 minutes dextran flux is likely constant while an important decline occurs after 10 minutes of filtration with milk. This can be explained by high solubility of the dextran and its inability to form a gel (McCurdy *et al.*, 1994; Choe *et al.*, 1986). Also, the size of the micelles which are much larger than that of dextran. A low diffusivity of micelles could stimulate the concentration polarization which affects the transmembrane pressure and therefore induce a decrease in permeate flow.

Furthermore, if the filtration occurs in steady state at constant TMP, the increase of total membrane resistance, *R* in Eq. (2) is initially high, generating a consequent losses in permeate flux (Field, 2007), before reaching the flow establishment. It can be established that permeate flux decline occurs in two

steps. First, an important initial loss takes place. Then, the flow continues to decrease but with a less significant gradient.

The initial decline of permeate flux encountered in previous works (Ramachandra Rao, 2002). It is caused by concentration polarization. Afterwards, calcium precipitation increases fouling without altering the flow significantly.

Minerals, particularly calcium phosphate, are not a foulant agent in filtration process because of the pores are much larger than any mineral precipitation which could occur (Ng et al., 2017). But, they surely contribute to the phenomenon. Calcium phosphate acts as a hardener by dehydrating micelles and thus it creates an extra link between micelles which contribute to the compaction of the micelles layer (Hayes et al., 1974; Ramachandra Rao, 2002).

In order to study the relationship between flux decline and fouling, evolution of permeate flux and whey protein concentration in permeate were plotted in Fig. 6 for milk at 5 g/L (Fig. 6a) and 10 g/L (Fig. 6b).

For milk at 5 g/L, whey protein concentration increase in initial flux decline period (until 10 minutes). Mass transfer of proteins toward the membrane occurs, generating concentration polarization and high losses in permeate flux. Protein concentration value stay constant until around 30 min. Finally, a low decrease of concentration is observed while permeate flux decreases slowly. This is due to cake formation in the membrane (Large amounts of proteins are deposited at membrane surface) which prevents the mass transfer of proteins. So, the solution becomes more diluted. It can be concluded that the decrease of permeate flux is associated to the proteins concentration evolution (Ng et al., 2017).

As for milk at 10 g/L (Fig. 6b), the concentration values of proteins are higher than those of milk at 5 g/L because of mass transfer is greater. Note that initial period takes more time than for milk at 5 g/L. The difference is also observed in the second period where the concentration remains irregular for about 30 minutes before decreasing. This fluctuation can be explained by the fact that the concentration polarization is still involved beyond 20 minutes of filtration. It is therefore suggested to conduct an experiment that lasts more than 60 min to observe an evolution similar to that of milk at 5 g/L.

Fouling mechanism

Linearized Hermia formulas (Table 2) are used to determine the dominant milk fouling mechanism. Evolution of permeate flux was plotted over time according to Hermia equations (Eqs. 2–5). Figure 7 represents the plots for each eventual fouling mechanism. It is shown that, as expected, cake formation is the dominant fouling mechanism with a correlation factor of 0.9689 and 0.9649 for milk at 5 g/L and 10 g/L, respectively. Intermediate blocking, pore constriction and complete blocking, respectively, also contribute to the membrane fouling but less than cake formation. (Zeman Leos & Zydney, 2017) considers that the pore blocking is due to non-homogeneous size of the pores and to the proteins shape.

Also, since the particles are much larger than the pore size, pore blocking will occur first, then intermediate blocking will dominate, followed by cake formation / gel (Brião & Tavares, 2012).

Nevertheless, correlation factors obtained for milk at 5g/L are very close as seen in Table 4. This result suggests that all types of fouling mechanisms occurred at the same time without dominance unlike to milk at 10 g/L where higher concentrations accelerate the transition from pore blocking to cake formation by compacting more micelles at membrane surface.

Table 4
Correlation factor of linearized Hermia equations

Fouling mechanism	Correlation factor	
	Milk 5g/L	Milk 10 g/L
Cake	0.9689	0.9649
Intermediate blocking	0.9660	0.9595
Pore constriction	0.9642	0.9564
Complete blocking	0.9623	0.9530

Conclusions

In this work, experimental study on flux decline during milk ultrafiltration was conducted. Both milk and dextran solution were used, to compare foulant and non-foulant solutes, considering dextran as non-fouling solute.

Experiments results showed that using dextran, the membrane is fouled. The membrane resistance increased by 12.62 %. Taking into account that there is no possibility to form gel and no interaction between dextran and membrane material, fouling is due to the particle size which is greater than membrane pores.

As for milk, permeate flux decline occurs in two steps. A high and rapid initial drop is observed followed by a smaller decrease. The first period is mainly due to concentration polarization. As for the second period, fouling leads to lower flux decline. Also, increasing of milk proteins concentration increases flux decline. Total variation of membrane resistance achieved 7.63 % and 43.91 % for milk at 5 g/L and 10 g/L, respectively.

Measured whey protein concentration in permeate flux indicates an increase of concentration at the beginning of filtration. Next, a constant value is observed followed by a decrease of the concentration where permeate becomes diluted. It is also showed that these three phases are not observed for milk at 10 g/L of proteins, this is due to the concentration polarization that is not complete over the 60 minutes of the experiments.

These results suggest that the dominant fouling mechanism is cake formation, because of the size of micelles which prevents them to penetrate the pores and to diffuse in permeate. Also, Hermia's equations

confirmed the dominance of cake formation for milk fouling. Nevertheless, the close correlation factors suggest that cake dominance is less for milk 5g/L than 10g/L. The higher concentration stimulates cake formation by increasing the compaction on the membrane.

However, further studies are required to determine the exact mechanism and steps of milk fouling on membrane ultrafiltration, particularly at low protein concentrations, and the effect of minerals on this phenomenon.

Declarations

Conflict Interests: The authors have no competing interests to declare that are relevant to the content of this article.

Funding Declaration: The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial or non-financial interest in the subject matter or materials discussed in this manuscript.

Data Availability: All data generated during this study are included in this published article.

Author Contributions Statement: The participation of each author in this study is as follow:

Maxance Perron-Lacroix: Experiments, Analysis

Rafik Absi: Suppervision, Experiments, Writing, Analysis, Discussion

Saadi Amine Aouanouk: Writing, Analysis, Discussion

Abdelkader Mouheb: Suppervision, Discussion

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Figures

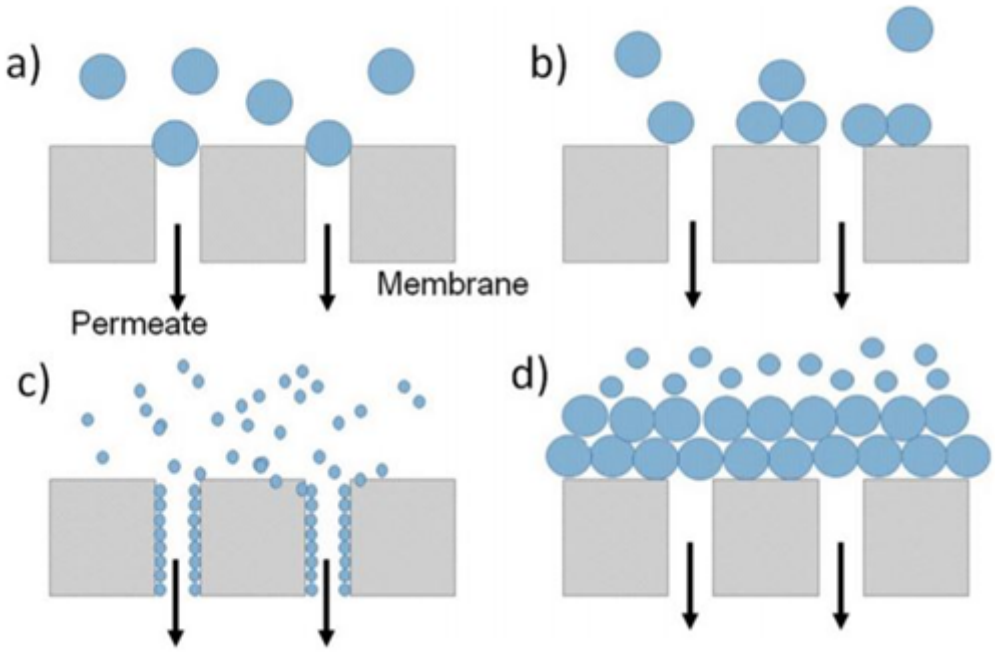


Figure 1

Schematic illustration of filtration fouling mechanisms: (a) complete blocking, (b) intermediate blocking, (c) internal pore blocking and (d) cake formation (Sousa et al., 2018).

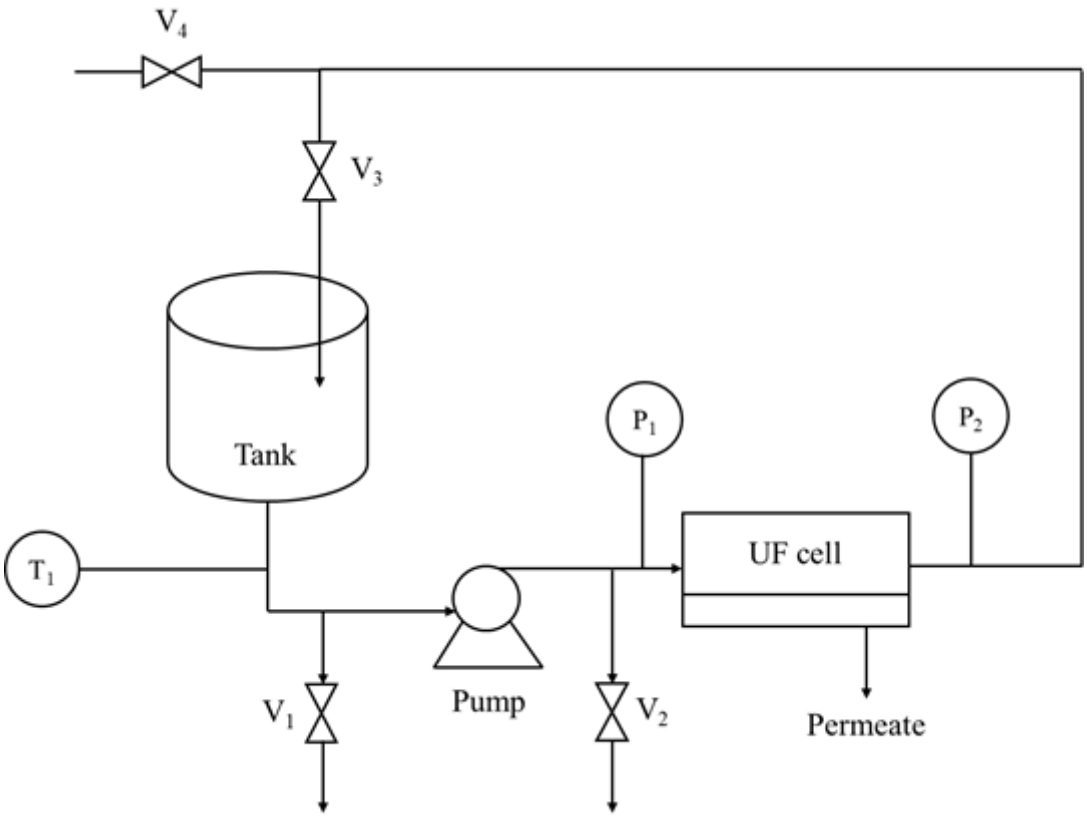


Figure 2

Laboratory-scale filtration system sketch

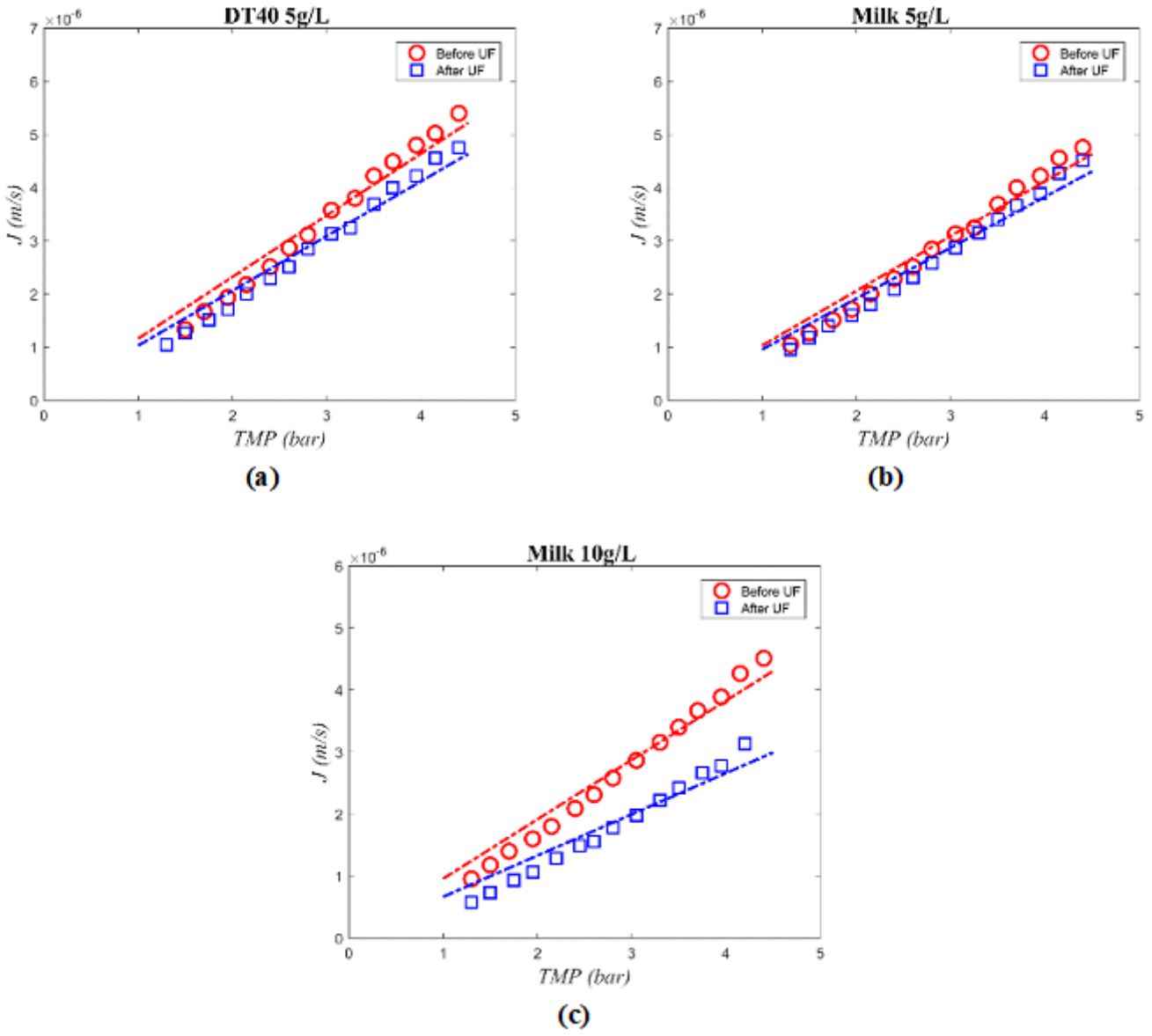


Figure 3

Variation of water flux vs. TMP for (a) dextran DT40, (b) milk at 5 g/L and (c) milk at 10 g/L

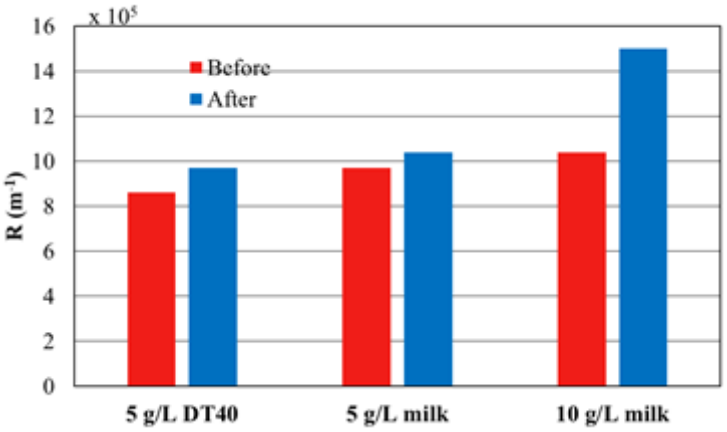


Figure 4

Membrane resistance before and after filtration for each solute

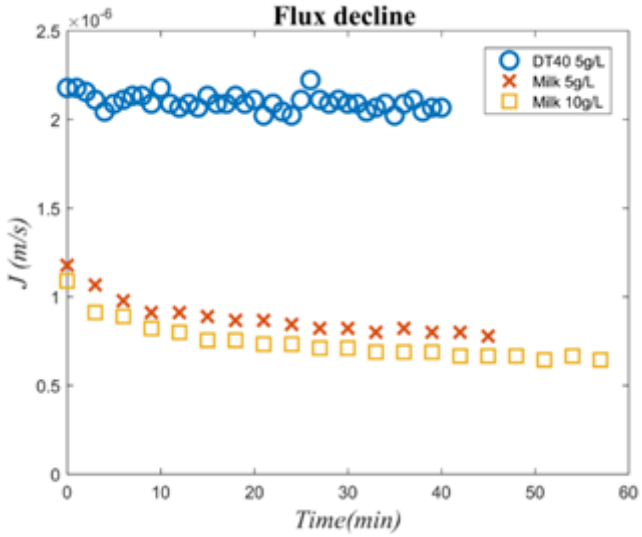


Figure 5

Flux profile over time for different solutes concentration

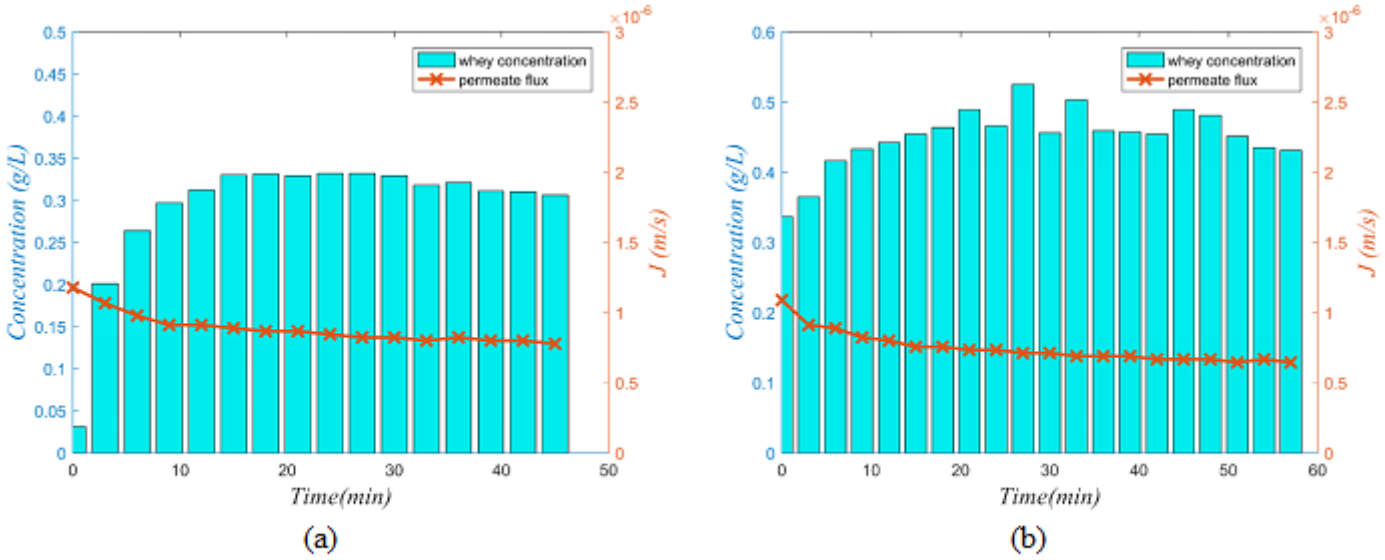


Figure 6

Variation of whey proteins concentration and flux permeate for milk at (a) 5 g/L and (b) 10 g/L

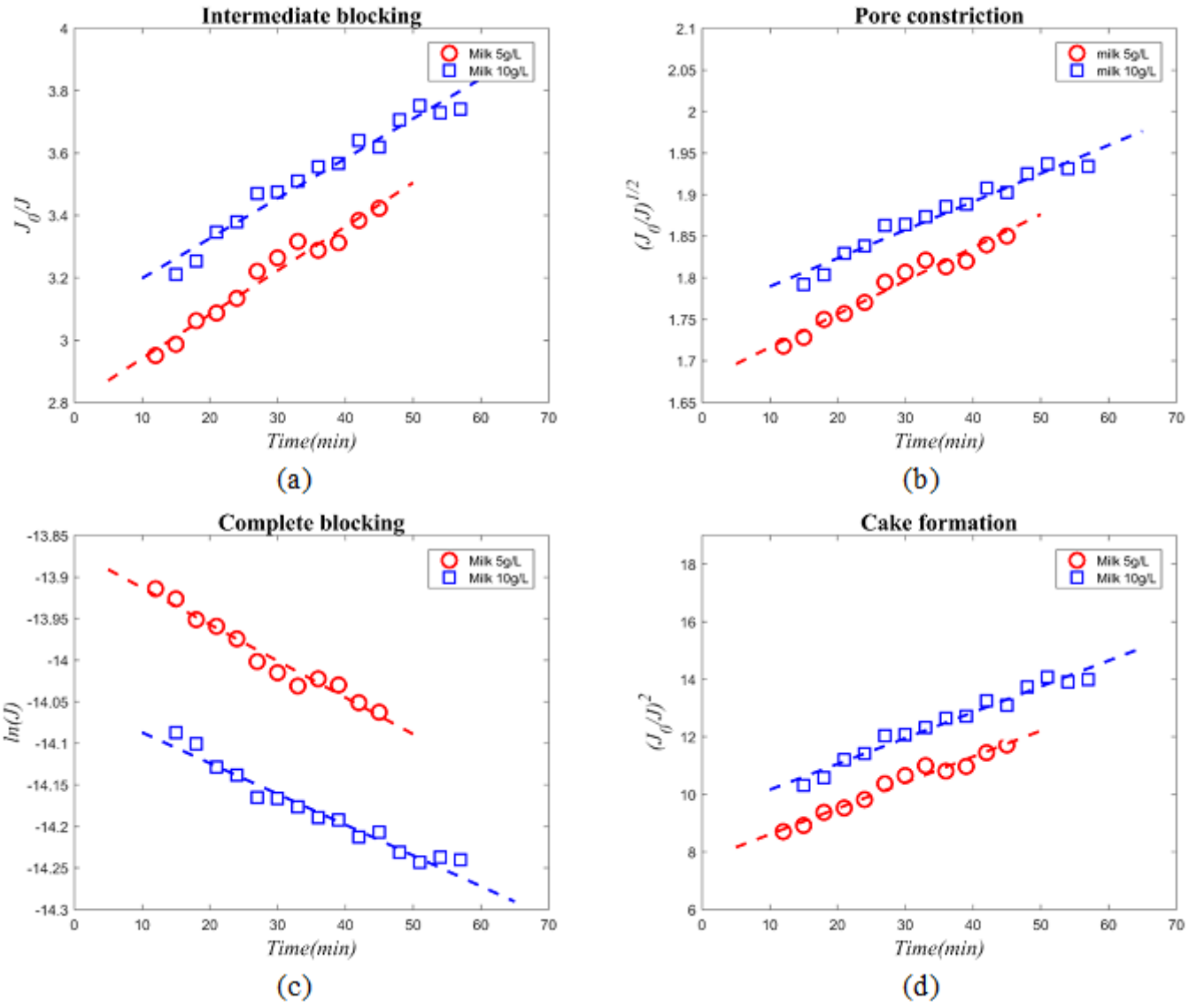


Figure 7

Permeate flux predicted by (a): intermediate blocking model; (b): Pore constriction model; (c): complete blocking model and (d) Cake formation model.