Membrane Processing for Dairy Ingredient Separation

Edited by
Kang Hu and James M. Dickson

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Kang Hu would like to dedicate this book to his family: Kate, Sarah, and Haiyan for the happiness and joy they bring to his life.

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Contents

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Kang Hu and James M. Dickson

Preface

According to the Food and Agriculture Organization of the United Nations, 2011, about 730 million tonnes of milk were produced annually from around 260 million dairy cows.[1] The vast majority of this production goes to feeding humans in various forms including raw milk, various processed milk products, and cheese. However, many valuable components exist within milk that are or can be produced industrially, such as lipids, proteins, minerals, and vitamins, by using various separation processes on milk and/or milk by-products. Membrane-based separation processes have proven to be effective in recovering these products and this book is concerned with such processes.

Dairy ingredients, such as lipids, proteins, peptides, lactose, and dairy minerals, provide a wide variety of potential for product development in the food, chemical, and pharmaceutical industries, due to the functional, nutritional, and biological characteristics, which are strongly influenced by the processes used for manufacturing. Among all dairy ingredient processes, separation processes are quite essential for fractionating ingredients from fluid milk. These processes could be as simple as just reducing pH to coagulate casein proteins or as complicated as isolating immunoglobulin G (IgG) by chromatography. Membrane separation processes have been applied in the dairy industry for many decades. One of the earliest applications was an ultrafiltration process to make soft cheese by Maubois, Macquot, and Vassal (1969) due to several advantages of ultrafiltration including increased yield and low energy consumption.[2] Compared to traditional membrane applications, such as water treatment and desalination, ingredient separation from fluid milk has particular challenges due to the high solid content and complicated composition of fluid milk, which increases the complexity of separation processes. With the continued development on membrane materials and membrane element configurations, almost all types of membrane processes have now been successfully applied in the dairy industry for solid concentration, ingredient separation, and waste recovery.

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[1] Food and Agriculture Organization of the United Nations (May 2012) *Food Outlook – Global Market Analysis*, pp. 8, 51–54.

[2] Cheryan, M. (1998) *Ultrafiltration and Microfiltration Handbook*, Technomic Publishing Company, Inc.

This book provides detailed information on the development of a variety of membrane separation technologies in dairy ingredient separation as they have evolved over the past decades. The approach in this book is to view membrane separation processes for dairy ingredient separation from a chemical engineer's point of view; that is, rather than just viewing a membrane as a tool to obtain the ingredients, the book also addresses questions of mathematical modeling, design, and optimization of the treatment systems. The text also presents in-depth knowledge of the mechanisms of each membrane separation process, as well as the membrane and module types applied in the dairy industry. Model equations are given to help the audience understand the processes and to help predict results (rejection, fractionation, and flux), and what factors are important for process control for these systems.

Microfiltration membranes, with relatively larger pore sizes (in the range of 0.1 to 10 μm) than other membrane processes, are typically used for dairy protein fractionation. In Chapter 1, the use of microfiltration processes for serum protein (or native whey protein) fractionation from skim milk is illustrated. Comparing this to traditional cheese-whey processes to obtain this protein ingredient, there are no changes in pH and ionic strength during the microfiltration process, resulting in less denaturation of the protein and more purity of the product streams, which then provides better functionalities of the ingredients.

Ultrafiltration is probably the most widely used membrane process in dairy ingredient manufacturing. Chapter 2 provides a comprehensive review of the current state of knowledge in using polymeric ultrafiltration membranes for separating dairy ingredients (with an emphasis on lactose recovery). The factors affecting lactose (also called milk sugar) separation/fractionation and the effects on yield are discussed in detail. The concept and principles of integrated membrane bioreactor to attain the functional dairy products are also presented. Finally, the future and challenges in separating milk sugar for a production of low-lactose milk and other value-added products are discussed. Chapter 3 focuses on the fouling occurring during ultrafiltration. In this chapter, the mechanism of ultrafiltration fouling and the factors affecting fouling are described, and certain fouling-control strategies are suggested. Chapter 4 proposes that placing a charge on the ultrafiltration membrane fundamentally changes separation mechanism, allowing fractionation of proteins with a similar size but different net charges. This chapter spells out the utility of charged ultrafiltration membranes for dairy protein fractionation, and also for traditional protein concentration applications where a significant flux increase is observed compared to uncharged ultrafiltration membranes.

Nanofiltration is used in the dairy industry to remove sodium chloride from solutions. This can include the de-salting of milk protein concentrates, whey, or lactose solutions. The approach can also be used to recover important minerals, notably calcium and magnesium. Chapter 5 outlines the key features of such membrane systems, including the type of membranes usually employed and the mineral species of interest during these filtration processes.

In dairy ingredient manufacturing processes a large amount of water is consumed and this water ends up in waste streams with pollutants that must be further treated. In Chapter 6, reverse osmosis membrane processes are reviewed and discussed for the application to purifying dairy waste streams to produce a more concentrated waste stream and a clean permeate water stream for reuse. Such preconcentration before evaporating and drying saves energy consumption and reduces the residence time in heat environment, resulting in lower operation costs, and reduces denaturation of the milk proteins. The permeate water from reverse osmosis is almost “pure” water that can be reused for process diafiltration and system clean-in-place (CIP) cleaning; in CIP the permeate water is used to generate cleaning solutions for membrane systems and other processing equipment. Thus considerable advantages on cost saving and environmental sustainability are realized.

Besides the above widely used membrane processes, several unique and emerging membrane separation processes have also been applied for ingredient production. Chapter 7 deals with the current status of pervaporation membranes for dairy aroma concentration. The fundamentals of the pervaporation process for aroma extraction are presented and the membranes suitable for dairy aroma enrichment are documented. The various aspects related to the aroma recovery (e.g., the nature of aroma compounds, permselectivity of the membrane, and the interactions between the aroma compounds and the membrane materials) are discussed. Chapter 8 examines protein purification and analysis methods using membrane chromatography. This chapter discusses some of the more conventional applications such as purification and polishing of proteins before moving on to newer and lesser known applications such as analysis of protein aggregates and the use of membrane stacks as bioreactors for enzymatic and synthetic modification of proteins. Chapter 9 reviews electrodialysis that has recently been applied to separate efficiently certain dairy ingredients. The principles of conventional electrodialysis as well as mass transport phenomenon through ion-exchange membranes are first described. Then hybrid electrodialysis processes using bipolar and filtration membranes are highlighted. After that, recent results on conventional and advanced electrodialysis processes for the separation, purification, and fractionation of dairy ingredients from milk, whey, or milk by-products are presented.

This book should prove to be of value to anyone working in the development and design of membrane-based systems for recovery of products in the dairy industry. Overall, the contents of this book cover the majority of membrane separation processes used for dairy ingredient separation and product stream production. It includes membrane-based separation technologies that have been recently commercialized, which is of substantial interest to the dairy industry. As well the book includes some cutting-edge technologies that have been thoroughly researched and have a great potential to be commercialized in the near future. The target audience are those professionals, such as process and system design engineers and ingredient product developers. This contemporary information and experience-based knowledge will be of great use to those professionals in membrane and membrane processing industries, leading to greater potential for the commercialization of the membranes and the processes in dairy related industries described in this book.

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1 Microfiltration for casein and serum protein separation

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1.1 INTRODUCTION OF MICROFILTRATION

Microfiltration(MF), probably the oldest membrane separation technology, was developed between the First and the Second World Wars in Germany for the purpose of bacteria removal (Zsigmondy and Bachmann, 1922). Generally, MF membranes have a pore size ranging from 0.1 to 10 μm. This size range encompasses a wide variety of natural and industrial particles, such as colloids, bacteria, and red blood cells.

MF is a pressure-driven separation process, which is similar to other widely used membrane processes such as ultrafiltration, nanofiltration, and reverse osmosis. Compared to these processes, MF is typically operated at a relatively lower pressure and is mainly applied for larger particle separation and fractionation.

In this section, the principle of MF is introduced. This includes the introduction of MF membranes and processes, the mechanism of cross-flow MF, and membrane fouling.

1.1.1 Microfiltration membranes and processes

MF membranes can be synthesized from a wide variety of materials, normally categorized as either organic, such as polymers, or inorganic, such as ceramic materials. Polymeric materials can be hydrophobic, including polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF) and polypropylene (PP), or hydrophilic, including polycarbonate (PC) and poly(ethersulfone) (PES) (Mulder, 1996a). Ceramic membranes are typically made from alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2). During membrane fabrication, some hydrophobic materials can

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be surface-modified to become hydrophilic, as required by specific applications. Gekas and Hallstrom (1990) reviewed these materials and summarized both the advantages and disadvantages of them. They suggested that comparing the two materials, polymer membranes are generally less expensive and have a higher area/volume ratio than ceramic membranes. On the other hand, polymer membranes bind protein more readily and have a wider pore size distribution. Ceramic membranes have exceptional thermal and chemical resistance and a much longer membrane life.

Various techniques have been employed to fabricate microporous membranes for MF. For example, ceramic membranes could be prepared by sintering layers on supporting materials. Polymeric membranes, benefiting from current polymer processing technology, could be prepared by various methods including: melt stretching, track etching, phase inversion, and casting (Glimenius, 1985; Mulder, 1996b).

Depending upon the materials and techniques used to prepare the membranes, MF membrane pore structure varies significantly. Figure 1.1 illustrates some typical examples of membrane porous surface structures obtained with different fabrication methods and materials. From the images, membrane pores created by stretching (a) are not circular, but the manufacturing process is relatively simple. Pores created by track etching (b) are cylindrically shaped with uniform dimensions but with lower porosity, while pores created by phase inversion (c) have a much higher porosity (or pore density). For ceramic membranes, sintering results typically in a nodular structure (d).

The MF process is pressure-driven and generally is carried out in two modes: dead-end filtration or cross-flow filtration. As illustrated in Figure 1.2a, in the dead-end MF, an applied pressure pushes the feed stream toward the membrane perpendicularly. The solvent and some smaller particles permeate through the membrane due to the pressure difference across the membrane, but larger particles are retained and then accumulate and deposit on top of the membrane. As a consequence, a fouling layer is formed, resulting in a decrease in filtration permeate flux. As the fouling increases with time, the permeate flux decreases drastically. When the fouling is sufficiently large, no more permeate can be collected and the membrane needs to be replaced. Due to the nature of the process, dead-end MF is economically feasible only when applied to rather dilute and/or valuable solutions, since the fouled membranes are difficult to clean and are normally just discarded. Dead-end MF is typically conducted in batch mode and mostly applied on a laboratory scale, using cylindrical vessels such as syringes as the filtration cell.

In cross-flow MF (Figure 1.2b), the feed stream flows tangentially to the membrane surface on the feed side. Similar to the dead-end mode, the solvent and some small particles transport through the membrane and

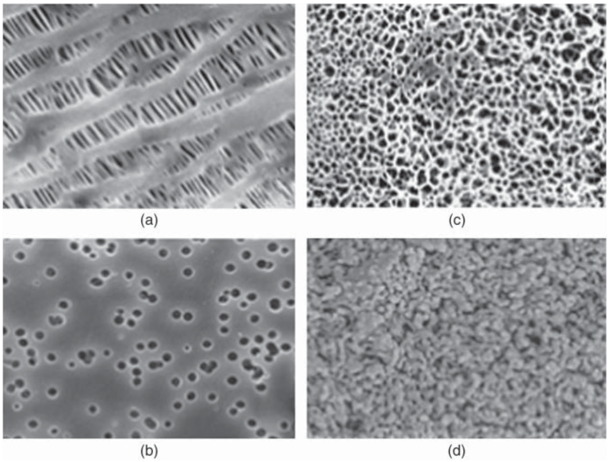


Figure 1.1 Microfiltration membrane surface images. (a) Polymeric membranes fabricated by melt-stretch (from Barbe, Hogan, and Johnson, 2000. Reproduced with permission of Elsevier). (b) Polymeric membranes fabricated by track-etching (Millipore Product Catalogue, 2013). (c): Polymeric membranes fabricated by phase inversion (Ying, Kang, and Neoh, 2002. Reproduced with permission of Elsevier). (d) Ceramic membranes fabricated by sintering (Zhang, Zhong, and Xing, 2013. Reproduced with permission of Elsevier).

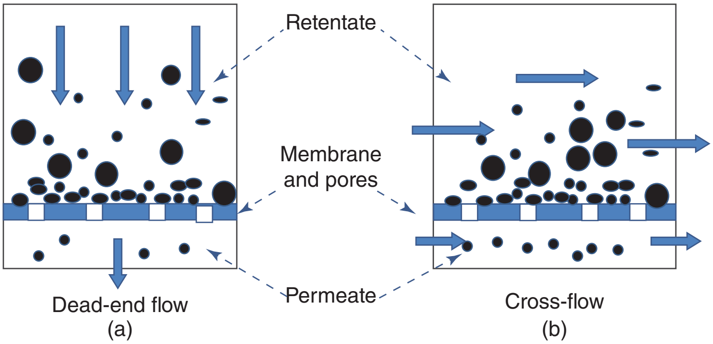


Figure 1.2 (a) Dead-end flow and (b) cross-flow MF.

are collected in the permeate side due to the pressure difference across the membrane. The remainder of the feed continuously flows along the membrane surface and is removed separately as a concentrated solution called the retentate.

On the retentate side, similar to the dead-end mode, the retained particles accumulate at the membrane surface forming a fouling layer, resulting in a decrease of permeate flux over time. However, a shearing effect, induced by the tangential flow of feed, limits the build-up and the growth of the fouling layer. Thus, during cross-flow MF, after an initial rapid formation, the growth of the layer slows down or even stops. At this point, the accumulation of particles becomes equivalent to the amount of particles lifted back to the bulk stream by cross-flow. The hydraulic resistance generated by the fouling layer becomes relatively constant and the permeate flux becomes stable. Under such conditions, cross-flow MF can operate continuously at a steady-state filtration flow for a long operating time, which substantially improves the separation performance and broadens the industrial application.

1.1.2 Cross-flow MF mechanisms

In MF, the separation mechanism is primarily size exclusion or the so-called “sieve effect.” Particles smaller than the pore size may pass through the membrane but particles larger than the pore size are rejected. A great number of parameters influence this separation performance, including the cross-flow velocity, applied pressure, physical and chemical properties of the membranes and particles, interactions between particles and particles, and interactions between particles and membrane materials. Considering all these parameters, many mathematical models have been developed to describe the transport mechanisms of cross-flow MF. All these models have their limitations owing to the fact that the phenomena occurring on the membrane surface and interface are far from clear, especially when various types of particles are present in the feed solution, adding to the complexity. However, utilizing these models can improve understanding of the process and provide guidance on the process design of such operations.

Earlier attempts to modeling cross-flow MF started with the concentration polarization model, since concentration polarization affects membrane performance for almost all types of membrane separations. As illustrated in Figure 1.3, during MF the particles are rejected by the membrane and then accumulate near the membrane surface. Thus, the concentration of particle i at the membrane surface ($C_{i,m}^{B}$) is always higher than that in the bulk solution (C_i^B). This phenomenon, just outside the membrane surface, is called "concentration polarization". The formed polarized layer (boundary layer), with thickness z, on the membrane feed side has some undesirable effects on the membrane separation. The higher concentration of particles at the membrane surface can cause increased fouling (binding of particles to the membrane surface). In addition, the concentration polarization invariably leads to reduced flux since the layer has a relatively large resistance to permeation (Zeman and Zydney, 1996) and can cause either increased rejection or decreased rejection as the fouled layer can be more restricting to solute permeation (hence increasing rejection) and the higher concentration in the boundary layer translates into a higher concentration in the permeate layer (hence decreasing rejection).

On the retentate side, the concentration build-up on the membrane surface generates a diffusive flow back of the particles from the membrane to the

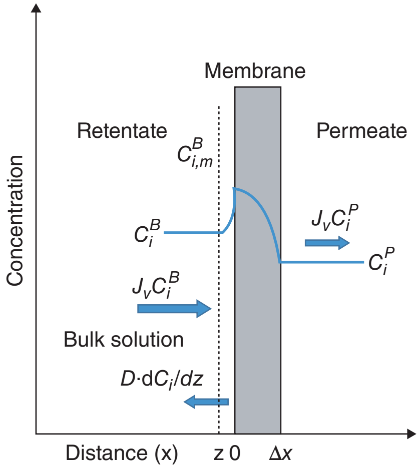


Figure 1.3 Concentration polarization effects of a microfiltration membrane with particle concentration profiles.

bulk of the feed solution. After a period of time, a steady state is achieved and the flow of particles i to the membrane surface ($J_V C_i^B$) is balanced by the particle flow through the membrane ($J_V C_i^P$) plus the diffusive flow from the membrane surface back to the bulk ($D\,\mathrm{d}C_i/\mathrm{d}z$). The mass balance is given by

$$J_V\, C_i^P = J_V\, C_i^B + D\frac{\mathrm{d}C_i}{\mathrm{d}z} \tag{1.1}$$

where J_V is the volumetric permeate flux, D is the diffusion coefficient of particles in the solution, C_i^P is the permeate concentration, and $\mathrm{d}C_i/\mathrm{d}z$ is the concentration gradient through the boundary layer. The apparent membrane rejection of species i is defined as

$$R = \left(1 - \frac{C_i^P}{C_i^B}\right) \tag{1.2}$$

Integration of Equation (1.1) gives (Kimura and Sourirajan, 1967)

$$J_V = k\ \ln\left(\frac{C_{i,m}^B - C_i^P}{C_i^B - C_i^P}\right) \tag{1.3}$$

where k is the mass transfer coefficient in the concentration polarization layer. For turbulent flow, a semi-empirical relationship for the mass transfer coefficient in pipes and channels has been described as (for example, from Mulder, 1996c)

$$Sh = \frac{k\, d_h}{D} = a\, Re^b Sc^c \tag{1.4}$$

where Sh, Re, and Sc are the Sherwood, Reynolds and Schmidt numbers, respectively, d_h is the hydraulic diameter of the membrane flow channel, and a, b, and c are constants that have to be determined by experiment. From Equation (1.4), the mass transfer coefficient k is a function of the feed flow velocity that is in turn related to the Reynolds number, the feed solution physical properties are represented by the Schmidt number, and the particle diffusion coefficient and the membrane module shape and dimensions are related by the Sherwood number.

In an ideal system, assuming no membrane fouling, the Hagen–Poiseuille equation is generally believed to be the best way to describe the fluid transport through microporous membranes, where the membrane pores are modeled as cylindrical channels. This equation can be written as one form that is broadly used in membrane processing (Nakao and Kimura, 1981):

$$J_V = \frac{r_P^2\, \Delta P}{8\mu \left({}^{\Delta x}/_{A_K}\right)} \tag{1.5}$$

where r_p is the capillary pore radius of the membrane, μ is the viscosity of the solution at the operating temperature, ΔP is the transmembrane pressure (TMP), which is the pressure difference across the membrane, and $\Delta x/A_K$ is the ratio of the membrane effective thickness to the membrane porosity. Using the Hagen–Poiseuille equation, the permeate flux can be simply related to the membrane structure and the operating conditions, such as pressure and temperature. From Equation (1.5), permeate flux is proportional to TMP, pore size, porosity, and indirectly to temperature, as a temperature increase reduces the viscosity. Conversely, the permeate flux is inversely proportional to the membrane effective thickness that generates a hydraulic resistance to the fluid flux. In the real world, however, flux does not conform exactly to the model, owing to other factors such as the nature of the membrane–particle interactions and particularly due to fouling.

In this concentration polarization model, the particle convective flux toward the membrane is balanced by Brownian back-diffusion, as illustrated in Equation (1.1) and Figure (1.3). In addition, for cross-flow MF, shear stress, induced by high-speed cross-flow, has an effect on lifting particles away from the layer, increasing particle back-diffusion to the bulk solution. Thus, several modifications integrate these effects by using different approaches to obtain the diffusion coefficient (Ripperger and Altmann, 2002). For example, Zydney and Colton (1986) assumed that the shear-induced particle diffusion was the predominant transport mechanism at cross-flow MF and the diffusion coefficient could be expressed as $D = 0.03\ r^2\tau$, where r is the particle radius and τ is the wall shear rate. Agashichev (2006) proposed a model that could analyze the effect of shear stress on the degree of concentration polarization and enabled calculation of the concentration profile where shear-dependent behavior took place.

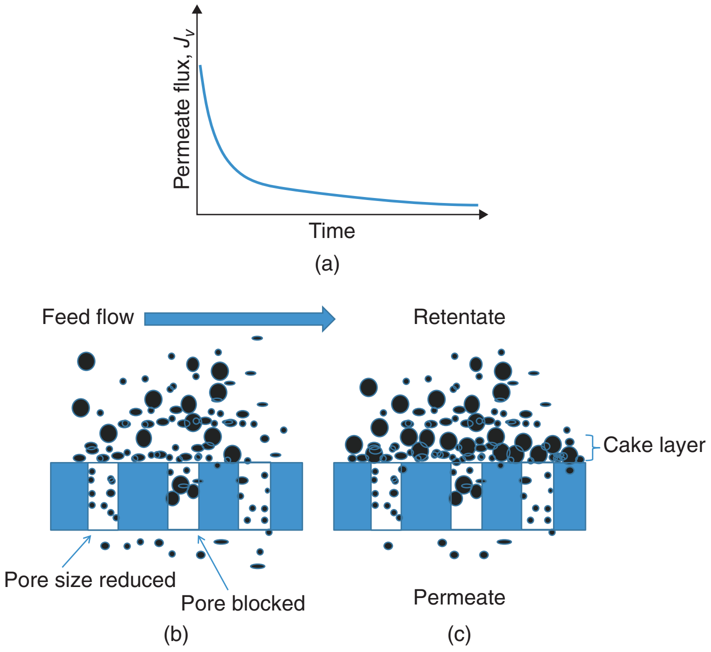
Overall, it is difficult to develop a model sufficient enough for all types of cross-flow MF applications, since the ideal condition can never be achieved and the understanding on what occurs on the membrane surface or the fouling mechanism is far from complete (Gekas and Hallstrom, 1990). Thus, some assumptions have to be made, such as the adsorption of particles on the membrane surface. These assumptions simplify calculations but increase the discrepancy between models and experimental results.

1.1.3 Fouling in cross-flow microfiltration membrane operations

The major technical hurdle that limits the applications of MF is membrane fouling. Once substantial fouling occurs, the permeate flux declines drastically and the particle rejection increases, resulting in undesired separation results. Then the operation needs to stop for cleaning, which typically consumes time and generates waste streams. Thus, membrane fouling increases the complexity of the process operation, changes the product quality, and adds production downtime and cost.

Membrane fouling is influenced by a variety of factors, as presented in Figure 1.4. These factors include membrane internal pore-blocking, membrane surface cake layer formation and growth, and concentration polarization. To illustrate the fouling phenomenon, a typical permeate flux versus time curve of cross-flow MF is presented in Figure 1.4a. On a commercial scale, cross-flow MF operation is generally started by processing with water and then replacing the water with the feed stream. At time zero, the permeate flux is basically at the highest value. As the feed stream is introduced to the system, a drastic decrease in permeate flux is observed. This usually takes place within minutes. Following this, the permeate flux decreases continuously but more slowly than before. Finally, the permeate flux stabilizes at a steady-state value.

The drastic decline of permeate flux when the feed solution is first replaced with water is due to the rapid blocking of membrane pores (Song, 1998). As illustrated in Figure 1.4b, once the particles are trapped inside



(a)

(b)

(c)

Figure 1.4 (a) Cross-flow microfiltration permeate flux decreases with time due to membrane fouling. Membrane fouling caused by pore plugging and cake layer formation: (b) initial deposition of particles and concentration polarization followed by (c) cake layer formation.

the membrane, the effective number of membrane pores and the pore size are reduced. The permeate flux decreases immediately due to the reduction of r_P and A_K, as indicated by Equation (1.5). Pore-blocking is a typical phenomenon for porous membranes, especially for microporous membranes used for MF. This phenomenon is influenced by both membrane–particle interactions and by the shape and size of the particles compared to the pore size. Thus fouling is much more significant when the particles and the pores are similar in both shape and size (Belfort, Davis, and Zydney, 1994).

Following the rapid decline, the permeate flux decreases exponentially, due to the formation and the growth of the cake layer. As presented in Figure 1.4c, particles retained by the membrane due to the sieve effect and the particle–membrane adsorption accumulate and deposit on the membrane surface and create the cake layer. This layer creates a hydraulic resistance to permeate flux and particle transport. However, the cake layer resistance can be minimized in a commercial process by employing a higher flow velocity and/or lower feed concentration. In other words, mass transfer can be improved by a higher Reynolds number, as indicated in Equation (1.4).

After the exponential decrease, the permeate flux keeps decreasing but the rate starts to level off as the cake layer approaches a constant thickness. When the cake layer “thickness” stabilizes a steady-state flux is obtained.

Development of an overall theory of cake layer formation is difficult because of the many factors that impact on the layer formation and growth. These factors include operation conditions and the interactions between membrane and particles and between particles and particles. For example, if the membrane material is hydrophobic, then hydrophobic particles are readily adsorbed. At a certain pH and ionic strength, some particles may also coagulate on the membrane surface and form a gel layer.

Overall, it is the particles in the feed that cause the fouling. Thus, the permeate flux, reflecting the convective flow of the solution (including particles) from bulk toward the membrane, is the critical factor that controls the fouling. Field et al. (1995) proposed a critical-flux hypothesis; if the initial permeate flux is less than a certain value, a constant filtration rate is achieved since the slow growth of the fouling could be diminished by exerting a cross-flow velocity that lifts the particles back to the bulk. Brans et al. (2004) proposed that in membrane filtrations, such as milk MF or ultrafiltration, the permeate flux did not always increase linearly with TMP, as given by Equation (1.5), due to the fouling. Three regimes could be distinguished with a different flux dependency on TMP (Figure 1.5).

In the filtration zone I, the permeate flux is low with only slight fouling. The flux increases linearly with the TMP, as expected from Equation (1.5). As the permeate flux increases, more particles are carried toward the membrane, but the growth of the cake layer is limited by the cross-flow shear